A STUDY OF SOME RANEY NICKEL CATALYZED REACTIONS.

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by

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CONTENTS

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SUMMARY

This study of the mechanisms and synthetic applications of organic reactions with Raney nickel catalysts has been divided into three sections; the investigation of the cleavage of Group IVb-organo compounds with Raney nickel, the examination of the alkylation of amines catalyzed by Raney nickel, and the synthesis of several 2,2'-bipyridyl derivatives.

Twelve phenyl derivatives of silicon have been cleaved by treatment with several Raney nickel catalysts to give mixtures of benzene and cyclohexane and small quantities of by-products including biphenyl and tetracyclohexylsilane. Tetraphenylstannane, tetraphenylgermane, triphenylgermanol, and tetracyclohexylplumbane were similarly cleaved, while alkyl derivatives of silicon and tin were found to be stable under the conditions used. Phenylsubstituted siloxanes and silanols were less readily split than those silanes without oxygen functions. A mechanism for the cleavage of organosilicon bonds has been proposed, involving chemisorption of the silicon atom by accepting electrons into its empty 3*d* orbitals, expulsion of a phenyl anion, and hydrogenolysis of the remaining groups. This mechanism has been discussed with respect to other Group IVb-organo derivatives.

The reactions of aniline and cyclohexylamine with Raney nickel giving *N*-cyclohexylaniline and other related secondary amines has been studied. These reactions have been extended to α-naphthylamine, the toluidines, and compounds with two nitrogen atoms, including 3-aminopyridine, 3-aminopiperidine, 1,2-diaminocyclohexane, and the phenylene diamines. The reactions have been shown to be a useful synthetic pathway to N-alkylarylamines. The reaction pathways and mechanisms of these reactions are discussed with respect to the types of adsorptions possible between nitrogen and Raney nickel. The results of previous workers has been correlated by these conclusions.

Eighteen new 4-substituted 2,2'-bipyridyls and 2,2'-bipyridyl-1-oxides have been synthesized from 2,2'-bipyridyl by a synthetic route through 4-nitro-2,2'-bipyridyl-1-oxide.

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STATEMENT

The work described in this thesis incorporates no material previously submitted for any degree in any University, and to the best of my knowledge and belief contains no material previously published or written by another person except where due reference is made in the text.

Keith Oliver Wade.
December, 1966.

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INTRODUCTION

Catalysis is one of the fundamental processes of organic chemistry, and indeed it may be considered that nearly all reactions involve some kind of catalytic effect. Chemical catalysts, both homogeneous and heterogeneous, are defined as species which by forming an intermediate complex with a compound undergoing reaction lower the activation energy for the reaction and consequently increase the reaction rate. Perhaps the most intriguing of these are the solid heterogeneous metal catalysts, for the nature of their surface properties and their mode of action is probably the least understood of all catalysts.

Among the most widely known of these metal catalysts is Raney nickel, first developed in 1927 by Murray Raney[1] by leaching aluminium from a nickel-aluminium alloy with concentrated sodium, hydroxide solution. The resulting nickel was in a highly active finely divided form incorporating a considerable quantity of the hydrogen derived from the action of sodium hydroxide on aluminium. Adkins and his co-workers[2,4,5] were responsible for a considerable development of this catalyst.

By variations of the digestive and washing procedures, the hydrogen content of Raney nickel was increased, making the catalyst more active towards hydrogenation reactions. The first modification was termed by Adkins as W-1 Raney nickel[2] and the second which was made by Mozingo[2] as W-2 Raney nickel. Subsequent catalysts developed by Adkins and associated workers were named W-3, W-4,[4] and W-5, W-6, and W-7[5] in order of increasing activity. More recently, degassed catalysts such as W-7J Raney nickel developed by Sasse[6] have been investigated and found to have quite specific properties. The preparation of W-7J catalysts involve the heating of W-7 Raney nickel under reduced pressure at temperatures usually between 100 and 200°, thus removing a considerable portion of hydrogen. The reactions on this catalyst will be considered in more detail later.

This large variation in the hydrogen content of Raney nickel makes it perhaps the most versatile of all metal catalysts.[7] Besides a great number of hydrogenation and hydrogenolysis reactions, Raney nickel has been used for a variety of other reactions which have been amply reviewed by other workers.[8] However, despite a prolific flow of work published on the reactions of Raney nickel catalysis, comparatively little is known of its structure.

Raney[9] first suggested that the catalyst is a mixture of nickel hydrides including NiH_2. Later Freidlin and Ziminova[10] proposed that the hydrogen is partly adsorbed on the nickel surface and the rest dissolved in the bulk nickel. Smith, Chadwell and Kirslis[7] showed that the activity of Raney nickel is directly proportional to the hydrogen content, and concluded that the gas was held to the nickel in some unspecified metastable state and was released as hydrogen atoms. However, no theoretical or practical evidence was produced for these postulates, and it was not until 1959 when Kokes and Emmett[11,12] published results of a thorough physical investigation, that any real insight into the nature of the catalyst was obtained.

Kokes and Emmett calculated from density measurements that W-6 Raney nickel contains approximately 30% lattice defects in its crystal structure. Assuming that each lattice vacancy retains one hydrogen atom, a hydrogen content of 70 ml/g of catalyst may be estimated, a figure which is close to the measured value of 72-81 ml/g.

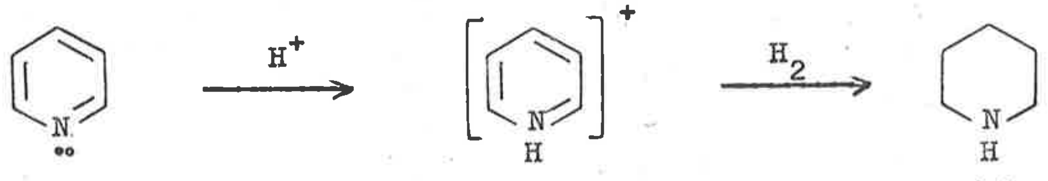
Magnetic measurements[11] showed that W-6 Raney nickel has a low magnetic susceptibility which rises proportionally as the catalyst is degassed. From this evidence, Kokes and Emmett concluded that the last two electrons in the d band of nickel must be used in bonding to hydrogen atoms, and are released on removal of hydrogen. Differential thermal analysis, X-ray diffraction, and surface area studies also rule out the possibility of the hydrogen being physically adsorbed or in solution with nickel.

In conclusion, Kokes and Emmett suggested that Raney nickel is a substitutional alloy of hydrogen and nickel, in which approximately 30% of the lattice sites in the face-centred cubic crystal structure have a hydrogen atom replacing a nickel atom. The hydrogen is held by covalent bonding through the d band electrons of nickel. This hydrogen may be removed by degassing at high temperatures, leaving the nickel lattice structure mostly unchanged and presumably held in place by the small quantities of residual alumina in the catalyst. These lattice vacancies may also be reoccupied at high temperatures and pressure by hydrogen or some other organic molecule which can bond (or chemisorb) to the nickel in a similar manner.

Little is known of the exact nature of this bonding or chemisorption of organic compounds to metal catalysts, and partly because of this, much is still unknown about mechanisms of metal catalysis. In order to learn more about these mechanisms, several authors have studied the poisoning of metal catalysts with various agents.

Maxted[13] studied systematically the poisoning of the Group VIII metal catalysts, nickel, palladium, and platinum. He defined a poison as a compound which by forming strong chemical bonds to the metal and remaining in this bound state for a greater proportion of the reaction time, reduced the number of catalytic sites available for reaction, and divided these into three groups.[14]

(a) Organic derivatives of Groups V, VI, and VII which act as poisons by chemisorption <u>via</u> a lone-pair of electrons. Maxted has shown that "protection" of these lone-pair electrons by protonation or oxidation greatly reduces the toxic effect, as in the hydrogenation of pyridine (1) <u>via</u> the pyridinium ion (1a) to piperidine (2).



(1) toxic

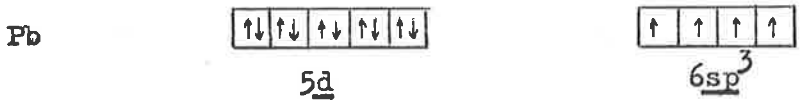
(1a) non-toxic

(2)

Maxted did not observe any poisoning through oxygen lone-pairs, but this has since been reported[15] although it occurs to a lesser degree.

This poisoning by means of hetero-atoms is very important as the basis of a large series of catalytic reactions commonly known as hydrogenolysis. The best known example of these is the desulphurization reaction which has been explored and applied in considerable detail over the past twenty years.[16,17,18]

(b) Derivatives of metals in which all five orbitals of a d shell immediately preceding the s and p valency shells are nearly or completely filled may poison metal catalysts.[19] Poisoning by such compounds is claimed to involve donation of a pair of electrons from the d shell of the poison to the catalyst. Tetramethylplumbane, for example, has the electronic configuration -



Maxted suggested that it is chemisorbed to a vacant orbital in the catalyst by donation of two electrons from the penultimate 5d shell of lead.

(c) Compounds which can be chemisorbed by bonding through the π-electron cloud of a multiple bond may also act as poisons. In many cases this leads to hydrogenation of the multiple bond.

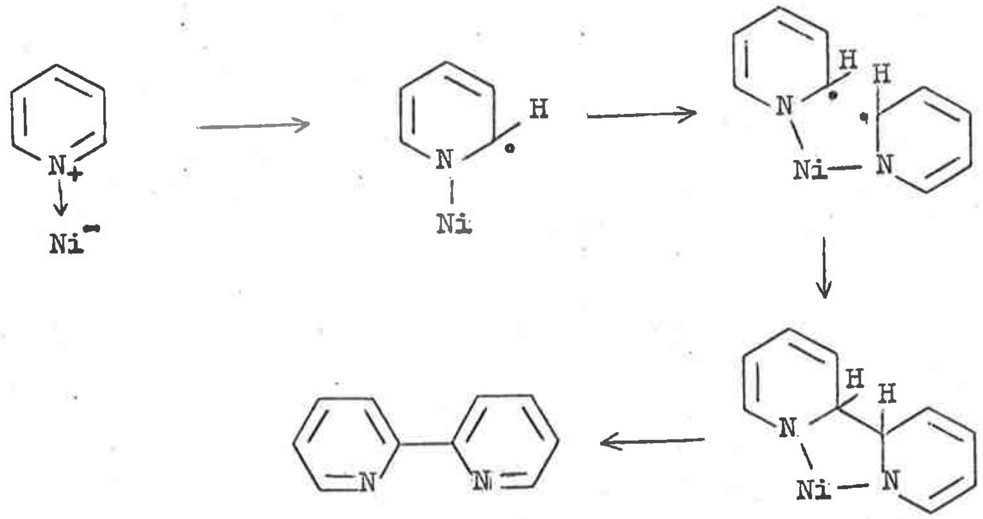
The strength of chemisorption bonds has been estimated for many different systems by measurement of heat of adsorption,[20,21] and it is the strength of this bond which determines the ultimate path of the reaction.[22] While adsorbed to the catalyst, the reacting species undergoes further reaction such as rearrangement or addition of hydrogen, followed by desorption of the product.

Badger and Sasse[23] have applied Maxted's theories to the formation of 2,2'-bipyridyl (3) from pyridine over W-7J Raney nickel. They postulated a mechanism involving the chemisorption of pyridine by donation of the nitrogen lone-pair to nickel followed by addition of hydrogen to the nitrogen atom, forming a radical with a free valence in the α-position. When two of these species come close enough, they combine, and on desorption and dehydrogenation give 2,2'-bipyridyl.

In the view of Kokes and Emmett's work,[11] however, Maxted's theory becomes inadequate. The assumption that the original bonding to the catalyst is by donation of a lone-pair of electrons from the nitrogen atom means that the mechanism involves the addition of a hydrogen radical before dimerization and dehydrogenation can occur.[23] It has been observed that the action of degassed Raney nickel on pyridine gives far better yields of 2,2'-bipyridyl than an undegassed W-7 Raney nickel, and calculations from Kokes and Emmett's work[11] show that not enough hydrogen exists in degassed catalysts for this mechanism to operate.

To postulate a mechanism then, it appears necessary to involve a donation of electrons from the metal to the substrate which subsequently does not require the addition of hydrogen (Scheme 1).[24]

This may explain why degassed catalysts which already have more vacant sites per unit cell for adsorption, give better yields of biaryl



(3)

Scheme 1.

than hydrogen rich catalysts.[24]

The idea that electrons can be donated from the catalyst to nitrogen is not without further analogy. Wahba and Kemball[25] have studied the heats of adsorption of ammonia to the surface of tungsten, iron, and nickel. These authors have proposed a mechanism which involves electrons from the metal in the chemisorption bond.

$$\begin{matrix} H - \underset{\circ\circ}{NH}_2 \\ M - M \end{matrix} \longrightarrow \begin{matrix} H \\ | \\ M \end{matrix} + \begin{matrix} \overset{\circ\circ}{NH}_2 \\ | \\ M \end{matrix}$$

The transient participation of the lone-pair on the nitrogen is supported by the fact that the protonated species, NH_4^+ is found to be non-toxic (i.e. not adsorbed) to catalysts.[26]

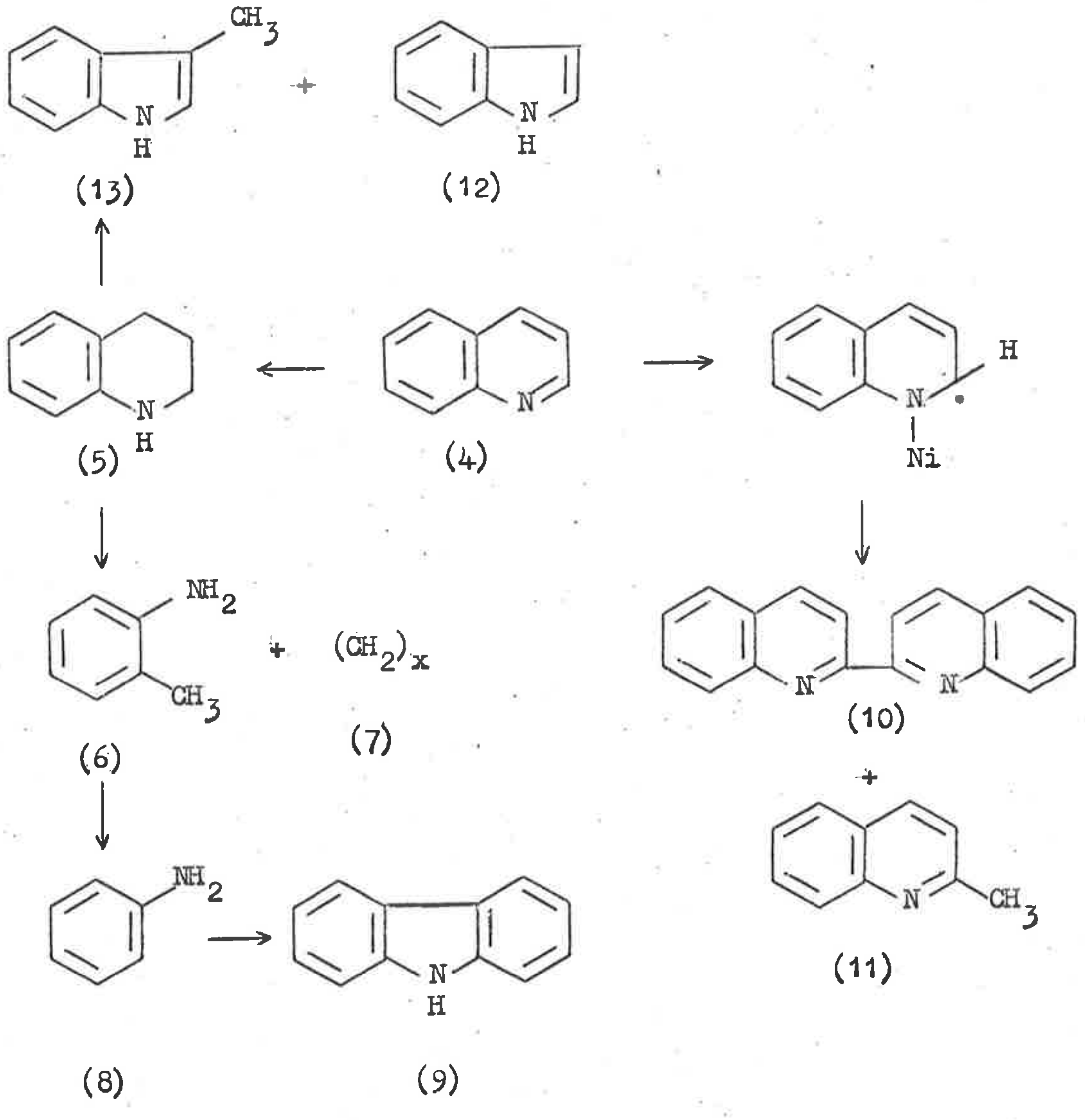
How the metallic electrons of the d band actually participate in bonding to the adsorbate is open to debate. It is well known that catalytic activity of metals is confined to the transition series which have incompletely filled d shells. The most active metals towards catalysis, for example, are nickel, palladium, and platinum with 8d electrons in their valency shell. However, the mechanism of chemisorption cannot be explained entirely by considering only donation of these d level electrons to the bond.

To understand the nature of these bonds, it is necessary to first consider some aspects of the theory of solid state. Isolated metal atoms have their d electrons in separate discrete energy levels which, on formation of crystal structures, broaden out to a d band of electrons with a wide range in energy states. Pauling[27] has postulated that these electrons of the d band in crystals may be of three types: bonding (in the form of dsp hybrids), atomic (or non-bonding) and metallic (associated with conductivity). Since the first of these are already bound up in metal-metal linkages, it is very unlikely that these are used in chemisorption, for such a bond would cause a break-up of the catalyst's crystal structure. Consequently, either the atomic or metallic electrons must be used in bonding. Magnetic and conductivity data of catalysts with adsorbed hydrogen, nitrogen, and oxygen both indicate that it is the atomic (non-bonding) d orbital electrons which are involved in chemisorption.[28]

If the highest occupied level of the metal lies above the highest occupied level of the adsorbate, then an exothermic exchange of electrons from the catalyst to the adsorbate is possible. However, it has also been shown that in the above cases of adsorption, surface dipoles are almost non-existent,[29] precluding the possibility of dative bonding and suggesting very strongly a covalent chemisorption.

Hence, it is the energy levels of the bonding electrons in the adsorbate which determine the degree of dative bonding, and this ultimately controls the path of the reaction. Caution is needed in applying this theory, however, as the above conclusions have been drawn from the study of adsorbed gases on metals, but similar electronic principles might be expected to apply to reactions in solution.

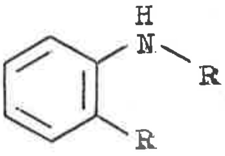
In an extension of the work on the formation of 2,2'-bipyridyl from pyridine, Sasse[30] has investigated the reactions of quinoline (4) over degassed Raney nickel. The reactions were found to be somewhat different, giving, besides a much smaller yield of the analogous 2,2'-biaryl (10), a series of eight other compounds (Scheme 2). The formation of these products may be explained by considering the chemisorption of the two compounds, 1,2,3,4-tetrahydroquinoline (5) and quinoline (4) onto the nickel.[30] The formation of 2,2'-biquinolyl (10) was very likely to be identical to the formation of 2,2'-bipyridyl from pyridine, the lower yields caused by steric factors.[23] The α-methylation giving 2-methylquinoline (11) has been studied by Meyerly and Weinberg,[31] and it may be assumed that a similar mechanism will operate here. This α-methylation



Scheme 2.

of nitrogen heterocyclic compounds has been known for some time.[31,32,33] Formation of the other products, in particular, indole (12), 3-methylindole (13) and carbazole (9) have been investigated closely by Jackson,[34] who studied the reactions of 1,2,3,4-tetrahydroquinoline over W-7J Raney nickel.

In their study of the formation of indole, Jackson and Sasse[35] have investigated the reactions of several N-alkyl-o-alkylanilines with W-7J Raney nickel, in which the possible products from cleavage of the 1-2(14), 2-3(15), and 3-4(16) bonds of tetrahydroquinoline were included.



(14); R = H, R' = nPr

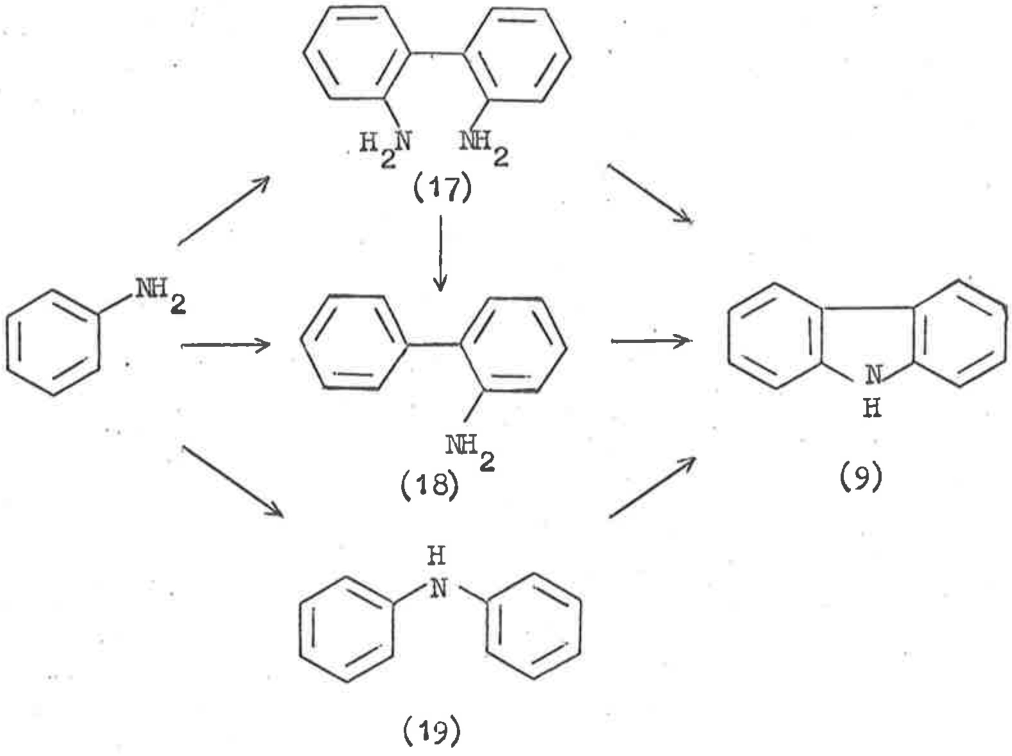
(15); R = Me, R' = Et

(16); R = Et, R' = Me

Although none fitted exactly the results obtained from the quinoline reaction with regard to indole formation, these authors concluded that N-methyl-o-ethylaniline (15) fitted the results obtained from quinoline better than the others, and proposed that tetrahydroquinoline is cleaved preferentially at the 2-3 bond. This confirmed the earlier work of Padoa[36,37] who studied the hydrogenolysis of quinoline and 1,2,3,4-tetrahydroquinoline (5) over reduced nickel catalysts at 260-280°. Padoa concluded that tetrahydroquinoline cleaved through the 2-3 bond and recyclized to give 3-methylindole (13). However, his work on quinoline in which he claimed to obtain 2-methylindole has been questioned,[30,35] and he has apparently obtained a mixture of 3-methylindole and indole, as obtained by Sasse.[30]

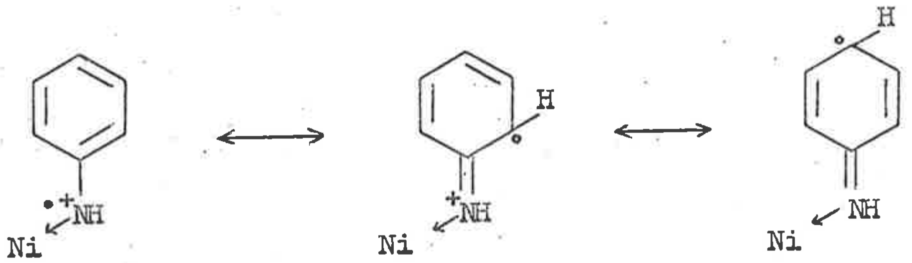
Jackson[34] has also studied the reaction of tetrahydroquinoline (5) over W-7J Raney nickel, and similarly has obtained a proportionally larger yield of 3-methylindole besides a number of hydrogenated products, 2,2'-biquinolyl and other products as reported from quinoline. He proposed that N-methyl-o-ethylaniline (15), formed by cleavage of tetrahydroquinoline, may recyclize to 3-methylindole (13), or undergo stepwise degradation of the side-chains to give polymethylene (7) and other amines. No N-methyl products were isolated, but o-ethylaniline could cyclize to indole (12), and both o-toluidine (6) and aniline (8) were detected in small yields.

Jackson and Sasse[38] obtained evidence for at least four pathways for the formation of carbazole (9) from aniline with Raney nickel catalysts (Scheme 3). All three intermediates, 2,2'-diaminobiphenyl



Scheme 3.

(17), 2-aminobiphenyl (18), and diphenylamine (19) were isolated from the reaction of aniline with W-7J Raney nickel, and all were found to give carbazole in various yields under similar conditions.[38,39] The cyclodehydrogenation of diphenylamine to carbazole has been known for some time, and has been shown to occur catalytically,[40], pyrolytically,[41,42] and photochemically.[43,44,45] The proposed mechanism for the cyclization of diphenylamine and for the formation of 2,2'-diaminobiphenyl (17) is essentially the same, involving the adsorbed species (20) and (21).[38]



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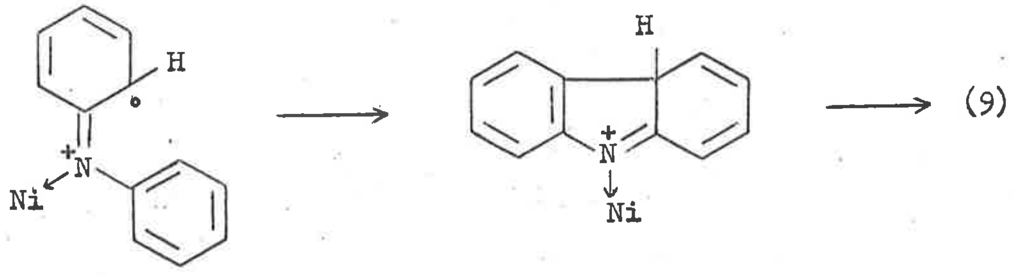


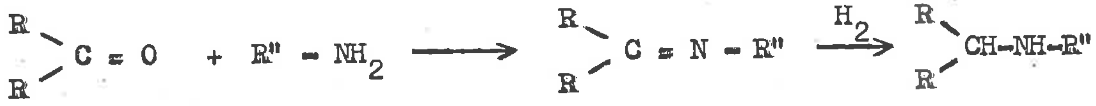
(21)

The latter route to carbazole is especially interesting, since it first involved the formation of N-cyclohexylaniline (28b) which is dehydrogenated to diphenylamine. Jackson[34] has reported 70% yield of N-cyclohexylaniline from the reaction of aniline with cyclohexylamine (26) in the presence of W-7J Raney nickel, although this figure was based only on the cyclohexylamine, and the overall yield was in fact 22%. Nevertheless, this product shows remarkable stability to Raney nickel and indicates that this reaction may be a suitable synthetic pathway to this and related compounds.

There are three main catalytic methods of preparing secondary amines from primary amines.[46] Firstly, amines may be alkylated by alcohols in excellent yields as shown by Adkins and Cramer.[47]

$$R\text{-}OH \quad + \quad R'\text{-}NH_2 \longrightarrow R\text{-}NH\text{-}R' \quad + \quad H_2O$$

This reaction has been adopted successfully and is used commonly as a synthetic method for preparing secondary and tertiary amines.[48,49,50] The second method for catalytic alkylation of amines is with ketones or aldehydes, which probably proceeds via the imine intermediate.[51]



$$R_2C=O \;+\; R''\text{-}NH_2 \longrightarrow R_2C=N\text{-}R'' \xrightarrow{H_2} R_2CH\text{-}NH\text{-}R''$$

This has also been used extensively in recent synthetic work.[52,53].

The third method, alkylation of amines with amines, which is applicable to this series has received much less attention than the first two. This reaction was first noticed by Ipatiew[54] in 1908. He found that hydrogenation of aniline with nickel oxide catalysts gave, besides cyclohexylamine (26), 10% yields of dicyclohexylamine (28a) and N-cyclohexylamine (28b). Rosenmund and Jordan[55], and Kindler[56] found that benzylamine (22) and α-phenylethylamine could both be converted to the corresponding secondary amines and ammonia with palladium catalysts, but cyclohexylamine and aniline showed little reaction under similar conditions. Similarly, in the catalytic hydrogenation of phenylcyanide (22), it was noticed that good yields of dibenzylamine (25) were obtained.[57] VonBraun[58] has suggested a mechanism for this reaction involving attack of the imine intermediate (23) on the amine (24) (Scheme 4).

$$\underset{(22)}{C_6H_5.CN} \xrightarrow{H_2} \underset{(23)}{C_6H_5.CH{=}NH} \xrightarrow{H_2} \underset{(24)}{C_6H_5.CH_2{-}NH_2} \xrightarrow[(23)]{-NH_3} C_6H_5.CH_2{-}N{=}CH.C_6H_5$$

$$\xrightarrow{H_2} \underset{(25)}{C_6H_5.CH_2{-}NH{-}CH_2.C_6H_5}$$

Scheme 4.

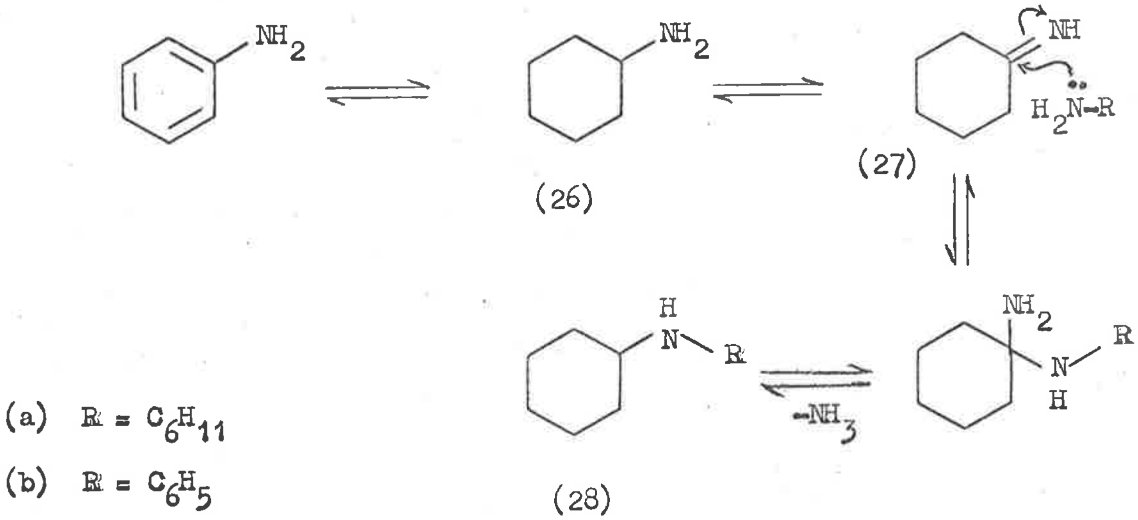
Winans and Adkins[46] have presented an argument to confirm this mechanism.

Consequently, since amines have been shown to dehydrogenate to imines on Raney nickel and other metal catalysts,[59,60] it is not surprising that recently Kindler and Mathies[61,62] have proposed a similar mechanism for the formation of several aliphatic secondary amines over Raney nickel.

The formation of dicyclohexylamine (28a), N-cyclohexylaniline (28b) and diphenylamine (19) from aniline has been known since 1908.[54] Debus and Jungers[63] in 1953 were the first authors to publish an extensive study of the hydrogenation of aniline. They showed that short reaction times and low temperatures favoured the formation of cyclohexylamine and dicyclohexylamine, while more vigorous conditions yielded greater quantities of N-cyclohexylaniline. They established also that if water is present in the reaction mixture, good yields of cyclohexanone and cyclohexanol were obtained. Other workers[64] have utilized this reaction in the preparation of dicyclohexylamine. From these results, Debus and Jungers conclude that the reaction proceeds by hydrogenation of aniline to cyclohexylamine followed by dimerization to dicyclohexylamine and dehydrogenation to N-cyclohexylaniline (Scheme 5; R = C_6H_{11}). The isolation of cyclohexanone in reactions in the presence of water indicate the formation of cyclohexylidenimine (27) which is readily hydrolyzed to the ketone in situ.[65]

Greenfield[66] has reviewed most of the work concerned with the formation of dicyclohexylamine by hydrogenation of aniline, showing that all steps in the reaction are reversible. He attempted to increase the yields of cyclohexylamine in the hydrogenation with metal catalysts by adding ammonia or ammonium hydroxide, thus reversing the dimerization reaction, but was unsuccessful because of poisoning of the catalyst. However, he made no mention of the formation of N-cyclohexylaniline from dicyclohexylamine.

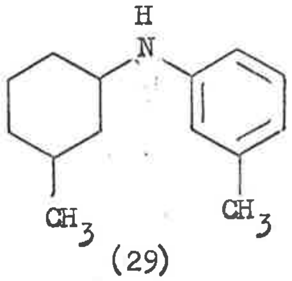
Jackson and Sasse,[38] on the other hand, have proposed that N-cyclohexylaniline is formed by attack of aniline on cyclohexylidenimine without the formation of dicyclohexylamine intermediate (Scheme 5; R = C_6H_5). They also isolated cyclohexanone, confirming the identity of the imine intermediate.



Scheme 5.

They base their argument on the fact that aniline, when refluxed with W-7J Raney nickel at 180°, gave N-cyclohexylaniline (28b) as the main product, and no dicyclohexylamine was detected. Even when cyclohexylamine was added to the reaction of aniline with W-7J Raney nickel, no dicyclohexylamine was detected, and a 90% conversion of cyclohexylamine to N-cyclohexylaniline was reported. These authors also showed that diphenylamine and carbazole which also formed in the reaction were not converted to N-cyclohexylaniline.[38]

Köhncke and Hanisch[67] have apparently applied this reaction to the preparation of N-cyclohexylaniline, N-(3-methylcyclohexyl)-m-toluidine (29) and N-(2-methylcyclohexyl)-o-toluidine (30), but give very scant detail on both materials and methods.



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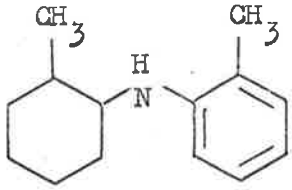


(30)

Part of this thesis is devoted to the investigation of the reactions of aniline and its derivatives over Raney nickel with the object to learn more about mechanisms involved, and to develop a synthetic pathway to partly saturated secondary amines related to N-cyclohexylaniline.

During their work, Jackson and Sasse[68] have studied also the toxicities of the phenyl derivatives of Group V, VI, and VII elements towards Raney nickel, and the tendencies of these compounds to undergo hydrogenolysis. In this work they have shown that the poisoning coefficient, as measured by the retardation of hydrogenation of trans-crotonic acid, increases down each Group of the periodic table. Also it was found that Group VI had the greatest toxic effect, followed by Groups VII, and V in that order. These results have their limitations since the phenyl derivatives were hydrogenolyzed during hydrogenation and the variation in stabilities of the phenyl-hetero-atom bonds may be responsible for the observed trends.

Nevertheless, with the exception that oxygen was found to be toxic, this work is compatible with the theories of Maxted[13] who studied the poisoning of platinum catalysts. It is surprising to note, however, that in the same series of experiments,[34,69] Jackson and Sasse found tetraphenylsilane to have a poisoning coefficient towards Raney nickel in the same order as chloro- and bromobenzene, both of which hydrogenolyze very readily to benzene and hydrogen halide. Sasse[70] has also shown on a spectroscopic scale in ethanol that tetraphenylsilane is cleaved to benzene, and in boiling toluene over W-7 Raney nickel, triphenylsilanol was formed in small yields as a by-product.

Although there are a number of references in the literature to the hydrogenation of organosilicon compounds,[71,72,73] the hydrogenolysis of the silane function appear not to have been reported previously. Other Group IVb organic compounds of tin and lead have been shown to undergo hydrogenolysis on metal catalysts.[74,75,76] Spialter, Buell and Harris[77] have attempted to hydrogenate all the Group IVb phenyl derivatives with a nickel catalyst in order to compare their abilities to hydrogenate. Tetraphenylsilane was the only derivative which could be hydrogenated, the others being recovered in yields ranging from 0-79%. Also they found that tetraphenyl-germane, -stannane, and -plumbane, and triphenylsilane all poisoned the catalyst to varying degrees during the hydrogenation of tetraphenylsilane to tetracyclohexylsilane. They suggested that poisoning occurs by coordination of the nickel through the central atom of these compounds. Initial steric hindrance in tetraphenylsilane prevents it from poisoning the catalyst, and hydrogenation proceeds with this compound. Triphenylsilane, which is less sterically hindered did show some poisoning properties toward the catalyst.

It is interesting to note that these workers also found silane derivatives to poison catalysts as, according to Maxted,[13] it should be impossible for silicon to coordinate with metal catalysts. As explained earlier, Maxted has classified all poisons into three groups, the Group IVb derivatives falling into the second. These compounds coordinate by donating electrons from their penultimate _d_ shell to empty _d_ orbitals of the catalyst. Silane derivatives, however, have the electronic configuration -

$$\mathrm{Si}\quad 1s^2\quad 2s^2\quad 2p^6\qquad \underset{3\underline{sp}^3}{\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow}}$$

and have no filled _d_ shells which could possibly combine with the _d_ oribtals of nickel in chemisorption. Maxted proposed that higher elements in Group IVb should poison catalysts by donation of inner _d_ orbital electrons such as in the case of tetramethylplumbane mentioned earlier. As silicon cannot do this, a completely new explanation for silane adsorption must be found.

Spialter, Buell and Harris[77] have tentatively suggested, without supporting evidence, that poisoning may occur by donation of electrons to the empty 3_d_ orbital of silicon.

Some of the work in this thesis aims at accounting for this apparent anomalous behaviour of the Group IVb organics. Also, since many of these organosilicon compounds are extremely stable,[78] a new method of cleaving silicon-carbon bonds could be of considerable synthetic value in organo-metallic chemistry.

CHAPTER I

Hydrogenolysis of Group IVb - organo compounds.

DISCUSSION

It has been shown that cleavage of silicon-carbon bonds is comparatively difficult.[78] Silicon-aryl bonds are the most readily cleaved, but this nearly always involves either electrophilic[79] or nucleophilic[80] attack on the aromatic ring and usually requires activating groups in the aromatic system. The difficulty of homolytic cleavage of organo-silicon bonds may be illustrated fairly accurately by the average bond energy of Si-C bonds (76 Kcal/mole) which is only slightly less than C-C bond energy (83 kcal/mole).[81] This fact is borne out by the stability of tetraphenylsilane to pyrolysis, which may be distilled unchanged at 430°/760 mm, appreciable thermal decomposition not occurring until 500-600°.[81,82] Hence it is surprising that tetraphenylsilane may be cleaved under such mild conditions at temperatures as low as 80-100° in a few hours over Raney nickel as was described in the Introduction.

The first problem in the investigation of this reaction was the choice of a suitable solvent. Previous hydrogenolyses had been carried out in methanol,[68] but this was unsuitable because of the poor solubility of silane derivatives in this solvent, and Sasse[70] had shown that ethanol was suitable only for reactions on a spectroscopic scale. Toluene, although a better solvent, is cleaved over Raney nickel to give benzene and cyclohexane,[70] and is therefore unsuitable if yields of these products from the reaction are to be measured. Ethers are much better solvents for these compounds, and as dioxan has a reasonably high boiling point

(101.5°), and does not react appreciably over Raney nickel catalysts at atmospheric pressure below 210°,[3] it was chosen for this series.

Since W-7, W-5, and W-1 Raney nickel had to be freed of water before use, these catalysts were washed with solvent. To lessen the expense of washing with dioxan, methanol was used initially to remove most of the water, and this removed with dioxan, the final reaction mixture having about 5 vol.-% methanol in dioxan.

The method by which these reactions were carried out was essentially similar to that used previously,[68] with the following modifications. By refluxing the reaction mixture on a distillation column, the products (usually benzene and cyclohexane) could be removed conveniently from the reaction site by distillation, and the path of the reaction followed by the boiling point of the distillate. The small quantities of methanol present in the solvent were therefore useful in that it formed an azeotrope with benzene and cyclohexane, and thus removed most of the products before the distillate boiling point reached 65°. This was usually achieved in about two hours, after which the temperature at the top of the column rose at a steady rate to 101°, and the reaction was stopped after about four hours.

Yields of benzene and cyclohexane were determined by gas chromatography, or if the solutions were too wet, the concentration of benzene was determined by its ultraviolet absorption, and the ratio cyclohexane-benzene determined by gas chromatography, from which were calculated the yields. The accuracy of this procedure was demonstrated by blank runs in which benzene, instead of the silane, was added to the catalyst, and 98% of the starting material was accounted for.

Preliminary experiments had shown that 0.06 moles of tetraphenylsilane with W-7 Raney nickel from 125 g of 1:1 nickel-aluminium alloy gave 45% yield of benzene and cyclohexane, while 0.018 moles of silane to the same quantity of catalyst yielded about 60-70% hydrocarbon mixture. Except for a few experiments, this latter ratio of silane catalyst was used throughout this series. Most experiments were carried out in refluxing dioxan (at approximately 100^{o}). Nevertheless, several silicon-phenyl derivatives were found to cleave, though much more slowly, at room temperature.

Tetraphenylsilane or the various phenylchlorosilanes were prepared from silicon tetrachloride and the required quantity of phenyl lithium according to the method of Gilman and Clark.[83] For example, addition of three moles of phenyllithium to one mole of silicon tetrachloride gave triphenylchlorosilane, which on treatment with methylmagnesium iodide gave triphenylmethylsilane. Hydrolysis of triphenylchlorosilane with a weak base gave triphenylsilanol which, with formic acid, gave hexaphenyldisiloxane. The other phenylmethylsilanes, silanols, and siloxanes were similarly synthesized.

Tetra(p-tolyl)silane was prepared by treatment of p-tolyllithium with silicon tetrachloride. This was oxidized with chromium-trioxide to tetra(p-carboxyphenyl)silane by a method similar to that of Gilman, Brannen and Ingham.[84]

TABLE I

The action of W-7 and related Raney nickel catalysts on organosilanes : % Yields.

Compounds	Main Products			Starting Material	Other Products
	Aromatic	Aliphatic	Total		
Ph_4Si	19	47	66		$(C_6H_{11})_4Si$ (a)
Ph_4Si (b)	33	48	81		
Ph_4Si (c)	54	24	78		
Ph_4Si (d)	12	60	72		
Ph_4Si (e)	3	< 1	< 4	96	
Ph_3SiMe	51	12	63	17	
Ph_2SiMe_2	26	34	60	20	$(C_6H_{11})_4Si$, 1 ; Siloxanes (a)
$PhSiMe_3$	24	43	67	32	$(C_6H_{11})_4Si$, 1 ; $Me_3Si(C_6H_{11})$ (g) ; Methane (a) ; Siloxanes (a).
(*p*-$MeC_6H_4)_4Si$	38	25	63	30	
(*p*-COOH $C_6H_4)_4$ Si (f)	*ca.* 25	*ca.* 25	50		
Ph_3SiOH	23	22	45	22	
$Ph_2Si(OH)_2$	40	6	46		
Ph_3SiOEt	24	15	39		Ethanol, 5.
$Ph_3SiOSiPh_3$	2	12	14	45	
$Ph_3SiOSiPh_3$(d)	10	32	42		

TABLE I (Contd.)

Compounds	Main Products			Starting Material	Other Products
	Aromatic	Aliphatic	Total		
$(Me_2PhSi)_2O$(d)	16	32	48		
$(Ph_2SiO)_3$	1	6	7		
$(C_6H_{11})_4Si$	none	none	-	92	
$(C_6H_{11})SiMe_3$	none	none	-		
$(C_6H_{13})_3Si\ _2O$	none	none	-	87	
Benzene	63	35	98	-	
Methanol	-	-			Methane(a)

(a) Detected in infrared spectra.

(b) W-5 Raney nickel catalyst.

(c) W-1 Raney nickel catalyst.

(d) Reaction carried out with exclusion of methanol.

(e) Raney cobalt catalyst.

(f) Reaction carried out in aqueous $NaHCO_3$ solution.

(g) Detected by gas chromatography.

Both tetracyclohexylsilane and cyclohexyltrimethylsilane were prepared by hydrogenation of tetraphenyl- and phenyltrimethyl-silane respectively. The method of Kanazashi and Takakusa[85] was modified for the use of W-7 Raney nickel, giving slightly better yields of hydrogenated products. Attempts to prepare the previously unknown tetracyclohexylgermane from tetraphenylgermane by the same procedure failed.

The results of a series of organosilanes treated with W-7 Raney nickel in dioxan is shown in Table I. Blank spaces indicate that the particular yield was not measured.

In this series of experiments, difficulties were experienced in the reproducibility of the yields of benzene and cyclohexane, and variations of up to 10% were common. In most cases, an average of at least two experiments were recorded to minimize this error. It is not known what caused these variations.

In the cleavage of tetraphenylsilane to benzene and cyclohexane, it was considered that steric effects may exert some control on the reaction,[77] since the relief of steric crowding of the four phenyl groups by expulsion of a benzene molecule would supply a driving force for the initiation of the reaction. Consequently, the compounds triphenylmethylsilane, diphenyldimethylsilane, and phenyltrimethylsilane, all having less steric crowding of the substiuent groups, were tested. Inspection of Table I shows that within experimental error, these compounds all gave yields of benzene and cyclohexane comparable to that from tetraphenylsilane, from which may be concluded that relief of steric crowding has little or no control over the reaction.

Similarly, electronic effects on this cleavage were examined by treating tetra-(p-tolyl)silane and tetra-(p-carboxyphenyl)silane with W-7 Raney nickel. Tetra-(p-tolyl)silane gave toluene and methylcyclohexane in similar yields to tetraphenylsilane. The yields of benzoic and cyclohexanoic acids from tetra-(p-carboxyphenyl)silane were lower by about 10%, but it is not clear whether this is significant, as the reaction had to be carried out in aqueous sodium bicarbonate solution rather than in dioxan-methanol. It is unfortunate that other electron-withdrawing substituents which could be used in place of the carboxylic acid group would interact independently with the catalyst. However, it may be concluded that electron-withdrawing or donating substituents on the phenyl rings have comparatively little effect on the reaction yields.

Significantly lower yields (approximately 40%) of benzene and cyclohexane were obtained however, from triphenylsilanol, diphenylsilanediol and triphenylethoxysilane. The siloxanes were found to be the most stable compounds with Raney nickel. Hexaphenyldisiloxane gave 14% yield of benzene and cyclohexane, while hexaphenylcyclotrisiloxane gave only 7% under standard conditions. Hence, all compounds with oxygen functions were found to give less yields of benzene and cyclohexane than other silanes.

Several reactions were carried out with catalysts which had been washed only in dioxan and therefore contained no methanol. In every case, the yields were considerably increased, suggesting that methanol might exert a distinct poisoning effect on the catalyst. Tetraphenylsilane yielded 72% benzene and cyclohexane, while hexaphenyldisiloxane and sym-diphenyltetramethyldisiloxane gave yields between 40% and 50%.

Tetracyclohexylsilane was treated with W-7 Raney nickel to determine whether alkyl groups could be removed by this procedure. This compound was found to be stable, and was recovered almost quantitatively from the catalyst. As this unreactivity may have been caused by the considerable steric hindrance of the four cyclohexyl groups, cyclohexyltrimethylsilane was also tested and found to be similarly stable under the same conditions. It can then be concluded that at least one phenyl substituent is necessary before fission of any silicon-carbon bonds will occur.

It was shown that alkyl groups could be cleaved from silicon if phenyl groups are also present, since methane was detected from phenyltrimethylsilane. Methanol alone reacts over Raney nickel to give methane but in much smaller yields under these conditions. Unfortunately, these gaseous products were mixed with about four to five litres of hydrogen from the catalyst, and yields could not be measured directly.

Perhaps the most unusual result was the formation of tetracyclohexylsilane in the reactions of phenyltrimethylsilane and diphenyldimethylsilane. Analysis by gas chromatography of the liquid residues from these reactions indicated a number of other components in small yields including cyclohexyltrimethylsilane. Although the other compounds were not checked by standards, their retention times indicate that they may include dicyclohexyldimethylsilane and tricyclohexylmethylsilane. The infrared spectra of these liquid residues also showed broad strong bands at 1,100-1,000 cm^{-1} characteristic of siloxanes, and at 3,600-3,400 cm^{-1}

characteristic of silanols.[86] These saturated silanes and hydroxysiloxanes were the only by-products detected in any of these hydrogenolyses.

Triphenylethoxysilane gave ethanol in about 5% yield, but this need not be formed exclusively by catalysis, as attack by hydroxide on alkoxysilanes is known to cause hydrolysis.[87,88]

Because of the basicity of W-7 Raney nickel,[5] a neutral W-5 Raney nickel catalyst was employed to test whether this alkalinity contributed to the cleavage of these compounds. Although W-5 catalysts contain less hydrogen, it was found that the yields of benzene and cyclohexane were increased. Similarly with a W-1 catalyst, which has a smaller hydrogen content than W-5, the yields of hydrocarbons from tetraphenylsilane were better than for W-7 Raney nickel. These results indicate that a hydrogen rich catalyst is not necessary for good yields in this reaction and, in fact, excess hydrogen may hinder the cleavage.

These results prompted experiments with degassed Raney nickel, and as expected, the yields were even higher than for W-1 and W-5 catalysts. The results of the action of degassed Raney nickel on several organosilanes is shown in Table II.

Once again, the labilities of tetraphenylsilane, tetra-(p-tolyl)-silane and phenylmethylsilanes were approximately the same, and also gave best yields of benzene and cyclohexane. As with W-7 Raney nickel, triphenylsilanol and sym-diphenyltetramethyldisiloxane gave lower yields, but in this case were over 60%. From this it may be concluded that the

TABLE II

The action of degassed Raney nickel on some organosilanes : % Yields.

Compound	Main Product			Starting Materials	Other Products
	Aromatic	Aliphatic	Total		
Ph_4Si	78	13	91	5	biphenyl, 3 ; $(C_6H_{11})_4Si$, 1.
Ph_4Si (b)	32	5	37		
Ph_3SiMe (b)	50	16	66		
Ph_2SiMe_2	65	25	90		biphenyl, 3 ; Siloxanes (a).
Ph_2SiMe_2 (b)	50	11	61		
$PhSiMe_3$	64	27	91	5	biphenyl, 3 ; $(PhMe_2Si)_2O$; Methane, 87.
$PhSiMe_3$ (b)	35	22	57		
$(p\text{-}MeC_6H_4)_4Si$	77	13	90	3	
Ph_3SiOH	55	11	66		biphenyl, 1 ; siloxanes (a).
$(PhMe_2Si)_2O$	45	20	65	20	biphenyl, 1 ; siloxanes (a).
Benzene	75	22	97		

(a) Detected in infrared spectra.

(b) Methanol (*ca.* 20 ml) added to reaction mixture.

only difference between degassed and W-7 catalysts is in the efficiency of hydrogenolysis.

In earlier experiments with degassed catalysts, methanol (approximately 5 vol %) was added to the dioxan before commencing the reaction so as to simulate conditions used with W-7 catalysts and to help distil the products. In these cases, a very marked decrease in yields was observed. Tetraphenylsilane showed a drop in yields of benzene and cyclohexane from 91% to 37%, while diphenyldimethylsilane and phenyltrimethylsilane showed a decrease in yields of about 30%. This reduction in yields must presumably be caused by poisoning of the catalyst with methanol. This is unusual since alcohols have been used extensively as solvents for many catalytic reactions.[16,17,18,68] However, Meyerly and Weinberg[31] have shown that primary aliphatic alcohols react with nickel catalysts to form the next lower homologous alcohol. They postulate this to occur by dehydrogenation to the aldehyde followed by elimination of carbon monoxide which may be hydrogenated to methane. They have shown that methanol gives both methane and carbon dioxide over a nickel catalyst. Reinecke and Kray[49] have postulated similar reactions on Raney nickel.

The catalysts from all reactions with degassed Raney nickel except with tetra-(p-tolyl)silane were extracted exhaustively with benzene in a Soxhlet apparatus. In every case examined, biphenyl was isolated in yields of up to 3%. This is reminiscent of the formation of dimeric products from desulphurization and dehalogenation with degassed Raney nickel, and may indicate a similar mechanism.[89] Tetraphenylsilane gave small yields of tetracyclohexylsilane, but it was not detected among by-products formed from phenylmethylsilanes as with W-7 catalysts. As observed with the residues obtained earlier, the infrared spectra of these residues indicated the presence of hydroxysiloxanes. _sym_-Diphenyltetramethyldisiloxane in the residue from phenyltrimethylsilane was recognized by its retention time with gas chromatography.

Since negligible quantities of hydrogen were evolved from reactions over degassed catalysts, the yield of methane could be measured accurately. This was achieved by replacing the air in the apparatus with carbon dioxide, and throughout the reaction, a slow stream of this gas was passed through the apparatus. All gases issuing from the condenser were passed through a cold trap and collected in a gas burette over concentrated potassium hydroxide solution which dissolved the carbon dioxide. The remaining gas was identified, by its infrared spectrum, as methane contaminated with traces of water and carbon dioxide. Phenyltrimethylsilane gave 87% yield of methane compared to 91% yield of benzene and cyclohexane.

Tetraphenylsilane, triphenylmethylsilane, and tetra-(_p_-tolyl)-silane and diphenylsilanediol were found to react at room temperature over W-7 or degassed catalysts to give corresponding hydrocarbons as shown in Table III. In every case, the yields of benzene and cyclohexane after 48 hours were less than for reactions at 100°, and starting materials were recovered in greater quantities. However, even though the reaction is much slower at room temperature, this still indicates that

TABLE III

The action of Raney nickel on some organosilanes at room temperature : % Yields.

Compound	Catalyst	Main Products			Starting Material
		Aromatic	Aliphatic	Total	
Ph_4Si	W-7	35	2	37	60
Ph_4Si	W-7J	21	1	23	68
Ph_3SiMe	W-7	55	6	61	31
$(p\text{-}MeC_6H_4)_4Si$	W-7	(a)	(a)	ca. 12	84
$Ph_2Si(OH)_2$	W-7	16	2	18	80

(a) These yields were not determined accurately.

the conditions for cleavage of silicon-carbon bonds with Raney nickel may be very mild.

To test the effect of the electronic structure of the central atom in this reaction, a comparison was made of cyclohexyl and phenyl derivatives of all the Group IVb elements. These results are listed in Table IV.

Tetraphenylmethane was found to be unaffected by degassed Raney nickel. Triphenylcarbinol showed no carbon-carbon bond cleavage but only underwent hydrogenolysis through the oxygen atom to give triphenylmethane.[90] Hence, carbon analogues were found to be unreactive to Raney nickel under these conditions.

TABLE IV

The action of Raney nickel on Group IVb-organo compounds : % Yields.

Compound	Catalyst	Main Product		
		Aromatic	Aliphatic	Total
Ph_3COH(a)	W-7	none	none	-
Ph_4C	W-7J	none	none	-
Ph_4Si	W-7	19	47	66
Ph_4Si	W-7J	78	13	91
$(C_6H_{11})_4Si$	W-7	none	none	-
Ph_3GeOH	W-7J	76	21	97
Ph_4Ge	W-7J	81	16	97
Ph_4Sn	W-7	49	41	90
$(C_6H_{11})_4Sn$ (b)	W-7J	none	none	-
$(C_6H_{11})_4Pb$	W-7J	-	91	91

(a) Triphenylmethane, 90%.

(b) Starting material recovered, 97%.

Tetraphenylgermane, triphenylgermanol, and tetraphenyltin were cleaved very readily giving yields of over 90% of benzene and cyclohexane, even with W-7 catalysts. Tetracyclohexylstannane was found to be stable to degassed catalysts and was recovered unchanged. Tetracyclohexylplumbane, however, gave a 91% yield of cyclohexane with degassed Raney nickel, but this may be anomalous to this series, as Krause[91] has reported that this lead compound was unstable, and decomposed readily on standing. The lead-carbon bond would therefore be expected to be unstable towards homolytic cleavage, for example, by hydrogen atoms.

Hence, with the exclusion of lead, these results indicate that all the Group IVb compounds except those of carbon show the same hydrogenolytic properties with Raney nickel. If phenyl substituents are present, then the organometallic bonds may be cleaved quite readily, with the ease of reaction increasing down the Group.

In order to propose a mechanism for these reactions, it is necessary to first understand how the reactants are adsorbed onto the catalyst. In the case of tetraphenylsilane, two possibilities must be considered; chemisorption through the π-electron system of the phenyl rings, or chemisorption through the silicon atom. Evidence for the former of these two suggestions is lacking, while the latter proposal would involve a completely new mechanistic approach.

If chemisorption did occur through the phenyl rings causing cleavage of the silicon-carbon bonds, then a great deal of desorption would be by hydrogen attack giving large yields of cyclohexane compared with benzene, which was not observed. Comparison of Tables I, II and III show that an increase in the hydrogen content of the catalyst, or an increase in reaction temperature both favour the formation of cyclohexane. On the other hand, reactions in which the catalyst was partially poisoned with methanol showed a greater proportion of benzene in the products. These trends indicate that cyclohexane was formed by the hydrogenation of benzene, and benzene must therefore be the primary product from cleavage.

Strong evidence against cleavage by adsorption through phenyl rings come from the observation that both tetraphenylmethane and triphenylcarbinol showed no hydrogenolysis of phenyl groups under equivalent conditions. Thus chemisorption of the aromatic system must lead only to hydrogenation and not hydrogenolysis.

Support for a mechanism involving chemisorption by direct nickel-silicon bonding comes from the findings of Jackson and Sasse[69] (mentioned in Introduction). They showed that the poisoning coefficient of tetraphenylsilane was much greater than, for example, triphenylamine[68] although on steric and electronic effects the latter would be expected to adsorb more strongly through the phenyl rings. The fact that tetraphenylsilane chemisorbs more strongly than triphenylamine to Raney nickel shows that adsorption must be through more than the π-electron system of the phenyl ring. The only other possible mechanism for chemisorption of tetraphenylsilane is through the silicon atom.

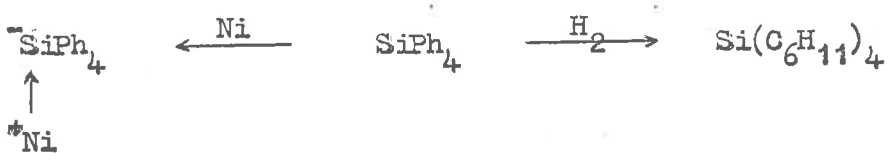
As silicon and carbon both have the same outer electronic configuration, the non-reactivity of the carbon analogues makes the postulation of a mechanism for the chemisorption of tetraphenylsilane rather difficult. However, the availability of the empty 3*d* orbitals of silicon makes the properties of organosilicon compounds substantially different from those of carbon compounds, and the completely different results obtained with carbon and silicon compounds indicate that these must be used in initial chemisorption of silanes to Raney nickel.

The atomic properties of silicon compounds have been described in reasonable detail elsewhere,[92,93] but they may be briefly summarized by considering the effect of the five outer d orbitals on the valence shell of silanes. Normally silicon compounds are considered to exist in an sp^3 hybridized state, and hence like carbon are tetravalent.[94] However, if the substituent groups are electronegative enough to induce a positive charge on the silicon atom, the outer d orbitals will contract. In many cases, this is sufficient to alter the energy and spatial properties of the d orbitals so as to allow them to mix with s and p oribtals of the valence shell, and form hybrids of the three shells.[93]

Because only two of the five d orbitals of silicon are of π-symmetry relative to the tetrahedral σ-bonds, only these two may participate in extra bonding. They may associate by forming sp^3d or sp^3d^2 hybrids in one of two ways. Firstly by accepting electron pairs from other molecules or atoms, or secondly by accepting electrons from π-orbitals of substituent species.[93] This latter example of $(p \rightarrow d)$ π-bonding is known as back coordination, and has been shown to occur in many silicon compounds where a substituent has electron pairs (such as oxygen, the halogens or nitrogen) or π-orbital electrons (as in phenyl rings) which may coordinate with the silicon atom. The first is illustrated by numerous examples of penta- and hexavalent silicon compounds which have been investigated recently.[95,96]

Consequently it is quite reasonable to suggest that the silicon atom will accept a pair of electrons into the d orbitals from the catalyst in chemisorption of tetraphenylsilane to Raney nickel, forming a pentavalent intermediary complex. This complex will have considerable d character in the valence shell. This postulate is in contrast to Maxted's theory which proposes that chemisorption of all poisons to transition metal catalysts is by donation of electrons from the substrate to the catalyst.[13]

Even though the silicon atom may adsorb quite strongly to the catalyst, this still does not preclude the possibility of chemisorption of the phenyl rings during the same reaction. In fact, it is envisaged that two reactions must occur simultaneously, one involving chemisorption of the phenyl ring leading to hydrogenation, and the other through the silicon atom leading to hydrogenolysis (Scheme 6).

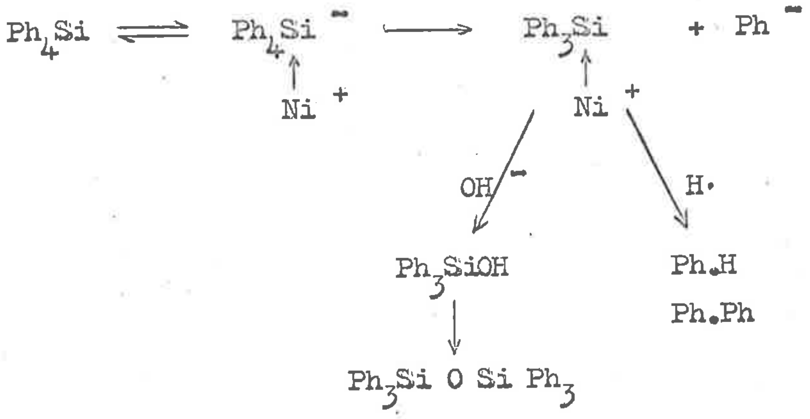


$$\underset{\overset{\uparrow}{{}^{+}\mathrm{Ni}}}{{}^{-}\mathrm{SiPh_4}} \xleftarrow{\mathrm{Ni}} \mathrm{SiPh_4} \xrightarrow{\mathrm{H_2}} \mathrm{Si(C_6H_{11})_4}$$

Scheme 6.

The hydrogenation has been shown to proceed smoothly under a large pressure of hydrogen,[71,85] which would be expected on the basis of LeChatelier's principle,[97] since there is a large decrease in the number of moles of reactants. The cleavage reaction, on the other hand, would be expected to dominate at atmospheric pressure, since there is little driving force for the hydrogenation.

The coordinately bound adsorbed species thus formed would be expected to be very unstable and react by two methods. Firstly, it may desorb from the catalyst and regenerate the silane, or secondly, it may eject a phenyl anion leaving a trisubstituted silyl species covalently bound to the catalyst. In the case of tetraphenylsilane, loss of a phenyl anion leaves a triphenylsilyl group linked with nickel (Scheme 7). Subsequent cleavage of the remaining phenyl groups would proceed by attack of hydrogen as proposed in desulphurization mechanisms.[16,17,18,89] Products from this hydrogenolysis include bezene and biphenyl, which were also formed during desulphurization of phenyl derivatives of sulphur.



Scheme 7.

Cleavage of the nickel-silicon bond by hydrogen, after ejection of the first phenyl group, would give triphenylsilane. This was not detected in any by-products indicating that the strength of this bond is greater than that of the silicon-phenyl bonds of the adsorbed species. However, attack by hydroxyl ions would give triphenylsilanol, which was isolated by Sasse[69] using toluene as a solvent. The presence of mixtures of silanols and siloxanes is indicated by the infrared spectra of the residues of reactions carried out in dioxan. This could arise by subsequent hydrogenolysis of the O-H bond with Raney nickel to give various siloxanes, according to the stage at which the silicon-nickel bond was cleaved. The smaller yields of these products in reactions carried out in dioxan may be explained by the solvation of hydroxyl ions with the more polar solvent, hence retarding attack by these ions.

From this postulated mechanism, it may be explained why a phenyl substituent is necessary for any cleavage to occur. Firstly, the phenyl substituent will act as an electron-attracting group (or "Electron well") on approach of the nickel to silicon, thus creating a slight positive charge on the silicon atom. This causes contraction of the _d_ shells of silicon as described earlier and enables a nickel-silicon bond to form more readily. Secondly, once the phenyl substituted silane is adsorbed, it could quite conceivably eject a phenyl anion which has its negative charge stabilized somewhat by conjugation. This conjugation lowers the activation energy for this crucial step in the reaction. A compound such as tetracyclohexylsilane, on the other hand, would have great difficulty in chemisorption since there is no induced charge on the silicon atom, and even if this barrier was overcome, the ejection of a cyclohexyl anion is extremely unlikely. Aliphatic carbanions cannot be stabilized by delocalization of the negative charge, and hence a very high energy of activation would be required before ejection of these species is possible. Consequently aliphatic substituted silanes, if chemisorbed at all, would very quickly desorb again, giving starting materials.

Phenyltrimethylsilane gives the best illustration of the complete reaction mechanism. Chemisorption to the nickel and subsequent expulsion of a phenyl anion would leave trimethylsilyl-nickel complex, which when attacked by hydrogen on the silicon-methyl bonds yield the observed methane. Alternatively, methane could be liberated by attack of phenyl groups on the intermediary complex, giving a phenyl substituted adsorbed species. By a series of these disproportionation reactions similar to that described by Nelson, Angelotti, and Weyenberg[98] it would be possible to build up a series of compounds such as tetraphenylsilane, triphenylmethylsilane, and diphenyldimethylsilane. Tetraphenylsilane, after desorption, could be hydrogenated on the large excess of catalyst and hydrogen to give tetracyclohexylsilane which was isolated in small yields from both phenyltrimethylsilane and diphenyldimethylsilane. The other intermediary by-products, although not isolated, have been shown by gas chromatography to possibly exist.

In all previously postulated mechanisms quoted in the literature, there are no cases in which compounds are claimed to be chemisorbed by accepting a pair of electrons from a metal catalyst. Maxted[13] claims poisoning and chemisorption occur by donation of electron pairs from substrate to the catalyst, a view which has been widely accepted. There are a few examples where nickel is presumed to donate single electrons to the adsorbate[24] as mentioned in the Introduction. However, apart from the work by Spialter, Buell and Harris,[77] interaction of organosilanes with metal catalysts has never been reported.

Spialter, Buell, and Harris[77] briefly mention the poisoning of nickel catalysts with triphenylsilane, but claim that tetraphenylsilane has little or no poisoning effect. They have tentatively suggested that a new mechanism must operate, perhaps involving coordination through the "empty" d orbitals of silicon, but they elaborate no further.

However, it is noticed that in all cases where electron donation from the catalyst is proposed, that reactions are much more efficient with degassed catalysts. This is probably because there are more reaction sites available for chemisorption on removal of hydrogen, and the hydrogen content of the catalyst is not critical for the reaction to proceed.[24]

The dependence of hydrogen in this reaction is illustrated by the very low yields obtained from Raney cobalt catalyzed reactions. Raney cobalt is known to retain very little hydrogen.[99,100] It is not likely that the activation energy for this reaction is too high for Raney cobalt to operate efficiently, but the basis for this catalyst's unreactivity is more likely to be the lack of hydrogen available for hydrogenolysis.

W-7J Raney nickel, although having lost a considerable portion of its hydrogen, still has enough to give good yields of hydrocarbons by hydrogen attack. Rough calculations from the work of Kokes and Emmett[11] as illustrated by Sasse and Whittle[24] indicate that W-7J Raney nickel degassed at 100° would retain approximately 42 cc of hydrogen/g of catalyst. In these reactions where about 62.5 g of catalyst was used, this could supply 0.12 moles of hydrogen. Assuming that four moles of hydrogen would be ultimately used in the hydrogenolysis of one mole of tetraphenylsilane, this corresponds to 0.072 moles of hydrogen required for complete cleavage on the scale at which these experiments were carried out. Hence, these reactions over degassed catalysts were carried out with approximately 50% excess of hydrogen, enabling good yields of benzene and cyclohexane to form.

It is interesting to note that in the reaction over W-7 Raney nickel with 0.06 moles of tetraphenylsilane (which required 0.24 moles of hydrogen for complete cleavage), only 45% yield of hydrocarbons was obtained. This corresponds to 0.11 moles of hydrogen used in hydrogenolysis. Assuming that the W-7 Raney nickel loses as much hydrogen at the reaction temperature of 100° as W-7J when degassed at 100°, this constitutes all the hydrogen available for hydrogenolysis. However, although these figures agree reasonably with the observed results, this argument is complicated by other factors such as poisoning of the catalyst by solvents and hydrogenation of benzene to cyclohexane, both of which consume hydrogen. Consequently, an excess of hydrogen is desirable in the reaction, and in fact gives very good yields of the required products.

It was noticed that silanes with oxygen functions such as silanols, silanediols, and siloxanes, gave markedly lower yields of benzene and cyclohexane than those silanes without oxygen substituents. This is unusual, as it would be expected from the postulated mechanism that the electronegative oxygen would be a far better leaving group than a phenyl anion, and hence an increase in yields would be expected from these compounds.

One possible explanation is suggested by the observation that methanol considerably poisoned the catalyst during these experiments.[31,101] Consequently, it may be envisaged that the oxygen atoms bound to silicon may similarly interact with the catalyst, and competition for reaction sites between oxygen and silicon atoms would reduce the efficiency of the reaction. However, as discussed earlier, the oxygen-silicon bond is considerably different from carbon-oxygen bonds, due to back coordination of lone-pairs of electrons from oxygen to silicon. This would make chemisorption of silanols and siloxanes through oxygen much less likely, and therefore this method of reaction retardation may be of small importance. This is exemplified by the failure of Rushton[73] and previous workers[102] to cleave aryloxysilanes with Raney nickel.

Once again, the answer to this question may lie in the nature of the organo-silicon bond. Silicon-oxygen-silicon bonds have been shown to have a bond angle of approximately 140-150° which is consistent with a hybridization of the oxygen atom between sp and sp^2.[103,104] This would place the oxygen lone-pair electrons in p orbitals, which may then overlap with the silicon d orbitals in back coordination.[105] The silicon oxygen bond would then be expected to be much shorter, and the force constants much higher, than would be expected for simple σ-bonds, and this has been reported.[105] The observed bond angles (in most cases of 140-150°) suggest that both lone-pairs of oxygen occupy p orbitals, and hence, both may coordinate with the two available d orbitals of silicon (see earlier discussion). This would then considerably reduce the availability of the d orbitals of silicon for chemisorption to Raney nickel, and so reduce the yields of benzene and cyclohexane in these reactions.

The evidence for back coordination in phenyl derivatives is much more obscure. It has been suggested from acid dissociation constants and base strengths of silyl-substituted aromatic acids and bases, that the π-orbitals of the aromatic system might conjugate with the d orbitals of silicon.[106,107] However, the ultraviolet spectra of trimethylsilylbenzene and t-butylbenzene were found to be very similar,[108] suggesting on the other hand that no conjugation will occur. The most exhaustive work on this system, dealing with the Hammet σ-constants,[109,116] indicates that the silyl group may both donate and withdraw electrons from an attached aromatic ring, depending upon the environment. Hence, on the approach of nickel catalysts to the phenyl-substituted silicon atom, donation of electrons from the catalyst to the d orbitals of silicon would facilitate withdrawal of back coordinated electrons to the phenyl ring. This would weaken the silicon-carbon bond even further, making ejection of a phenyl anion more likely.

The results shown in Table IV also provide discussion for this mechanism. According to Maxted,[13] germanium, tin, and lead compounds should all undergo chemisorption by donation to the catalyst of electron pairs from the penultimate 3d, 4d, and 5d orbitals respectively. However, it is significant that tetracyclohexylstannane showed no detectable cleavage under these conditions. According to Maxted's theories, there is no reason why this compound should be stable to catalysts. Tetracyclohexylplumbane was cleaved under these conditions to give good yields of cyclohexane.

On present scanty knowledge of the physical data of the organic derivatives of germanium and tin, it is difficult to assert which mechanism will operate. Bonds between carbon to other Group IVb elements become weaker as the stability of the divalent state increases down the Group.[111,112] However, there is still evidence from the dissociation constants of p-substituted aromatic acids to show the possibility of π-bonding between trimethylgermyl, trimethylstannyl, and trimethylplumbyl groups with benzene rings.[112] This would suggest that the outer "empty" d orbitals of these elements could still be used in chemisorption to catalysts. The existence of many five coordinated stannyl compounds also supports this evidence.[113,114]

In contrast to this, it has been shown that tetraphenylplumbane, tetraphenylstannane, and related compounds may be decomposed to benzene and the parent metal by the action of hydrogen under high temperature and pressure, both with and without the aid of metal catalysts.[75,76,115,116] Gershbein and Ipatieff[74] have also shown that alkyl substituted tin compounds may be cleaved by hydrogen, though higher temperatures are necessary on moving up the group and for alkyl compounds. No work appears to have been carried out on germanium compounds.

In conclusion, it is apparent that the ease of cleavage of Group IVb-organo bonds with hydrogen increases down the group, and also that phenyl derivatives are removed more readily than alkyl. This is consistent with the results shown in Table IV. The compounds of carbon and silicon, and possibly germanium are considerably stable as cleavage of these compounds by hydrogen without catalysts has never been reported. Aryl-silicon compounds may be cleaved by the mechanism described. Compounds of elements below silicon are apparently cleaved by hydrogen with increasing ease down the group, as well as by catalysis as described for silicon. As lead compounds are the most easily cleaved, tetracyclohexylplumbane gave good yields of cyclohexane by hydrogen attack only. Tetracyclohexylstannane, and alkyl derivatives of compounds above tin were stable probably because the temperature and pressure were not high enough. The phenyl derivatives of germanium and tin could possibly have been cleaved by both mechanisms.

***

EXPERIMENTAL

1. General

Gas chromatographic analyses were carried out either with a Griffen George V.P.C. apparatus Mk. II with a 6ft. x 0.25 in column packed with Embacel (coated with 10% tricresyl phosphate) and a 3ft. x 0.25 in. column packed with crushed fire brick (40-60 mesh; coated with 30% Dow Corning High Vacuum Silicone grease) in series, or with a Perkin-Elmer model 800 Gas Chromatograph equipped either with a 12ft. x 0.125 in column packed with Chromosorb W (coated with 30% succinate polyester of butane diol) or with a 12ft. x 0.25 in. column of Chromosorb W (coated with 20% Ucon oil 0.1 LB-550-X).

Ultraviolet spectra were measured with a Perkin-Elmer model 137 UV spectrophotometer.

Infrared spectra were determined either with a Perkin-Elmer Infracord 137 or with a Perkin-Elmer 237 spectrophotometer.

Analyses were carried out by the Australian Microanalytical Service, Melbourne.

2. Solvents

Commercial dioxan was purified by refluxing with hydrochloric acid and drying with potassium hydroxide according to the method of Vogel,[117] and distilled through a jacketed fractionating column (2 x 60 cm. packed with single turn glass helices and equipped with a variable take-off total condensation head; reflux ratio 1:4), collecting the fraction b.p. 101°, (found to be homogeneous by gas chromatography). Methanol was purified by distillation from sodium hydroxide.[68]

3. Catalysts

W-1,[2] W-5,[5] and W-7[5] Raney nickel catalysts were prepared from nickel-aluminium alloy (1:1; B.D.H.) according to the literature methods.

The preparation of degassed Raney nickel was slightly modified from the published method for W-7J Raney nickel.[6] The mixture resulting from the dissolution of the alloy was kept in a boiling water-bath for one hour, during which time the volume was kept at approximately 750 ml by adding water. The water-bath was then allowed to cool to room temperature while the flask containing the catalyst was immersed. After ten hours, the catalyst was washed by decantation with ten 500 ml portions of water, and the catalyst transferred with a small amount of water into the apparatus described, which was then immersed in a cold water-bath. The catalyst was then kept at 40° at 15-25 mm until all water had been evaporated. Towards the end of this process, the pressure in the apparatus rose for a short time. Finally, the temperature of the water-bath was raised to 100° and kept at this temperature for 3 hours.

Raney Cobalt was prepared from cobalt-aluminium alloy (1:1; Fluka) by the method used for the preparation of W-7 Raney nickel.

4. General Reaction Conditions

(i) Hydrogenolyses with W-7, W-5, and W-1 Raney nickel and Raney cobalt catalysts.

- W-7 Raney nickel (prepared from 125 g of alloy) was freed of water by washing first with methanol (4 x 150 ml) and then with dioxan (3 x 150 ml). It was then transferred with dioxan to a flask which carried a jacketed fractionating column as described for the purification of dioxan. The condenser of this column was linked to the atmosphere by way of a trap cooled with solid carbon dioxide. The starting material (0.018 moles except where otherwise stated) was added to the catalyst, the total volume made up to about 250 ml. by adding dioxan, and this mixture heated under reflux. After one hour, the following fractions were collected (reflux ratio 1:10) : (a) b.p. up to 65°; (b) b.p. 65-101°; and (c) b.p. 101°. These fractions were analyzed qualitatively and quantitatively by gas chromatography using suitable standard mixtures for calibration. In experiments with phenyl derivatives, fraction (a) contained methanol and the bulk of benzene and cyclohexane. Fraction (b) was combined with the condensate from the cold trap; this mixture consisted of dioxan, water, and small quantities of benzene and cyclohexane. Fraction (c) was dioxan. Details of the analysis of products other than benzene and cyclohexane are given below. After heating for four hours, the reaction was stopped, the catalyst filtered off and washed with hot dioxan (3 x 50 ml). In some experiments, the combined filtrate and washings were freed of dioxan and the residue examined for starting material and further products as described below.

(ii) *Hydrogenolyses with degassed Raney nickel.* - After cooling the degassed Raney nickel (from 125 g of alloy) under vacuum, dioxan (200 ml) was added while the connections to the pump were closed. After the catalyst was thoroughly wetted with dioxan, the starting material (0.018 moles except where otherwise stated) and dioxan (to make the total volume up to approximately 250 ml) was added. The mixture was then refluxed and distilled as above, except that all materials boiling below 101° were collected in one fraction. These mixtures were too wet for accurate analysis by gas chromatography described in (i). Instead, the concentration of benzene was determined by ultraviolet absorption, and the ratio benzene-cyclohexane was determined with a gas chromatograph equipped with a flame ionization detector. The residues were worked up as described in (i).

In some experiments, methanol (10 ml) was added to the reaction mixture before refluxing was commenced. In these cases, the fractionation was as described in (i).

(iii) Hydrogenolyses at room temperature. - The suspension of catalyst in a dioxan solution of the starting material (total volume approximately 400 ml) was stirred at room temperature in a sealed apparatus which was connected to the atmosphere by a trap cooled with solid carbon dioxide. After 48 hours, the catalyst was filtered off and washed with cold dioxan (3 x 50 ml). The filtrate and washings were combined with the condensate in the cold trap, and analyzed by distillation as described under (i).

5. Other Hydrogenolyses.

(i) Tetra-(p-tolyl)silane - When tetra-(p-tolyl)silane was treated with W-7 Raney nickel in dioxan containing methanol, all methylcyclohexane and part of the toluene distilled over together with methanol and dioxan. This mixture was analyzed quantitatively by gas chromatography. The residue of the distillation was freed of the catalyst and the filtrate distilled at 100 mm pressure, leaving a solid which was mainly starting material. The toluene in the second distillate was estimated by its ultraviolet absorption.

In the experiments with W-7J Raney nickel catalysts in the absence of methanol, water (12 ml) was added after two hours of heating. All the methylcyclohexane distilled below 101°, together with water, dioxan and toluene. The yield of toluene was determined spectroscopically, and the ratio toluene-methylcyclohexane was determined by gas chromatography. The catalyst was then filtered off and washed with boiling benzene. The filtrate and washings were then distilled and the toluene estimated by gas chromatography.

(ii) Tetra-(p-carboxyphenyl)silane. - To a solution of this silane (0.018 moles) in aqueous sodium bicarbonate solution (5%; 150 ml) was added W-7 Raney nickel (from 125 g of alloy) which had been washed only with water. The mixture was refluxed for four hours while being stirred. The hot mixture was then filtered, and the catalyst washed with hot aqueous sodium bicarbonate solution. The combined filtrate and washings were acidified with concentrated hydrochloric acid, and the white precipitate collected. The aqueous filtrate was continuously extracted with ether, and this extract evaporated leaving a white residue. Both solids were extracted with warm water to yield a mixture of cyclohexanoic and benzoic acids (4.5 g) identified by paper chromatography.[118]

(iii) Triphenylcarbinol. - The carbinol (0.018 moles) was hydrogenolyzed with W-7 Raney nickel in dioxan as described in 4(i). Distillation yielded only methanol and dioxan. Recovery of the residue gave a thick oil which crystallized from petroleum ether (b.p. 30-40°) as colourless prisms of triphenylmethane (4.2 g), m.p. 91° (lit.[119] 92°C).

6. Isolation of by-products.

(i) By-products from reactions of W-7 Raney nickel with triphenylmethylsilane and diphenyldimethylsilane. - The residue from these reactions was recovered as an oil (*ca.* 1 g) which on distillation failed to separate into pure components. Gas chromatography showed that the residue obtained from dimethyldiphenylsilane contained at least eleven components; one of these (approximately 30% by area) had the retention time of the starting material. The residue of this distillation (0.04 g) was recrystallized from hexane to give colourless prisms (0.025 g), m.p. 276-280°. Admixture with tetracyclohexylsilane gave a m.p. 278°, and the infrared spectra of the two samples were superimposable.

The residue from the experiment with phenyltrimethylsilane (ca. 1 g) was similarly examined. Eight volatile components were detected by gas chromatography, starting material (40%) and cyclohexyltrimethylsilane (30%) were characterized by their retention times only. Tetracyclohexylsilane (0.015 g), m.p. 278° was identified by its infrared spectrum.

(ii) By-products from experiments with degassed Raney nickel. - In several experiments with degassed Raney nickel which had been carried out in the absence of methanol, the spent catalysts were exhaustively extracted with benzene in a Soxhlet apparatus. The crude products were chromatographed on silicic acid using petroleum ether (b.p. 60-80°) and benzene as eluants.

Phenyltrimethylsilane (catalyst extracts from two experiments were combined) gave starting material (0.1 g) (identified by its infrared spectrum); biphenyl (0.085 g) (direct comparison), and diphenyltetramethyldisiloxane (0.15 g) (infrared spectrum).

Catalyst extracts from two experiments with dimethyldiphenylsilane were combined and similarly worked up to give biphenyl (0.14 g), and fractions showing strong absorption at 900, 1020-1120, 1257, 1450, 3400 and 3800 cm^{-1}.

Triphenylsilanol (two experiments) gave biphenyl (0.11 g) and brown mixtures which could not be separated by the above procedures.

The residue of two experiments with diphenyltetramethyldisiloxane gave starting material (2.0 g) and biphenyl (0.075 g).

Tetraphenylsilane (one experiment) gave biphenyl (0.185 g), tetracyclohexylsilane (0.019 g) (infrared spectrum), starting material (0.047 g) and unidentified yellow matter.

(iii) Methane from phenyltrimethylsilane. - Phenyltrimethylsilane (2.70 g) was treated with W-7J Raney nickel in boiling dioxan in the absence of methanol while a slow stream of carbon dioxide was passed through the apparatus. The gas flowing from the cold trap was collected in a gas burette filled with 40% aqueous potassium hydroxide solution. The evolution of gas ceased after six hours refluxing. The gas (1100 ml at 15°/740 mm) was identified as methane containing traces of water and carbon dioxide (infrared spectrum). The approximate yield of methane was therefore 1015 ml at S.T.P. (84%).

Fate of the silicon. - After having been used in the hydrogenolysis of tetraphenylsilane, W-7 Raney nickel catalyst was dissolved in dilute hydrochloric acid. The resulting mixture was filtered to give a dark-brown residue (1.1 g). Continuous extraction with benzene gave a brown solid (0.72 g), which on chromatography (silicic acid) gave, besides tetraphenylsilane, yellow and brown oily fractions which were not identified. The benzene-insoluble matter was further extracted with ethanol and pyridine, but only trace amounts of organic extracts were obtained. The residue (0.34 g) was analyzed by X-ray fluorescence by Dr. K. Norrish and found to consist of silicon dioxide (47%), nickel (25%), aluminium, and other elements. This accounts for approximately

50% of silicon introduced as tetraphenylsilane.

7. Starting Materials.

The following compounds were commercial samples which were used without purification: silicon tetrachloride (B.D.H.), methyltrichlorosilane (Fluka, purum), dimethyldichlorosilane (Fluka, purum), sym-diphenyltetramethylsiloxane (Fluka, purum), triphenylmethane (Fluka, purum), germanium tetrachloride (Fluka, purum), tin tetrachloride (B.D.H.) and lead dichloride (B.D.H.).

The following compounds were prepared via the corresponding organo-lithium reagents[83] and purified by standard procedures: tetraphenylsilane, m.p. 235-236° (lit.[82] m.p. 236.5-237°); tetra-(p-tolyl)-silane, m.p. 231° (lit.[120,121,122] m.p. vary between 223° and 255.5°); methyltriphenylsilane, m.p. 67-68° (lit.[123] m.p. 68.5-69°); dimethyldiphenylsilane, b.p. 145°/20 mm (lit.[124] b.p. 176-178°/45 mm); and trimethylphenylsilane, b.p. 82°/22 mm (lit.[125] b.p. 171.5°/745 mm). Tetraphenylmethane, m.p. 283-284° (lit.[126] m.p. 284.5-285.5°) was prepared from triphenylmethane;[126] germanium tetrachloride and phenylmagnesium bromide gave tetraphenylgermane, m.p. 226° (lit.[127] m.p. 225-226°), and triphenylgermanol, m.p. 134° (lit.[128] m.p. 134.2°); cyclohexylmagnesium bromide with tin tetrachloride gave tetracyclohexylstannane, m.p. 253° (lit.[129] m.p. 248°) and with lead dichloride gave tetracyclohexylplumbane, m.p. 140-160° d. (lit.[91] m.p. 130-160° d.).

(i) Triphenylsilanol. - A solution of chlorotriphenylsilane (10 g) in acetone (100 ml) was added slowly with stirring to an aqueous solution of sodium bicarbonate (200 ml ; 5%). After ten minutes the product was filtered off and crystallized from light petroleum, (b.p. 60-80°), to give colourless needles of triphenylsilanol (95%), m.p. 153° (lit.[130,131] m.p. 155°; 150.5 - 151.5°).

(ii) Ethoxytriphenylsilane. - Triphenylsilanol (5 g) and ethanol (150 ml) were refluxed for four hours. The crude product, which was precipitated on removal of part of the solvent, was crystallized from ethanol to give colourless prisms of ethoxytriphenylsilane (65%), m.p. 63-64° (lit.[132] m.p. 63°).

(iii) Hexaphenyldisiloxane. - This compound was prepared by the method of Gilman and Oita.[133] As experimental details are not available the following procedure was used: triphenylsilanol (10 g) was refluxed with formic acid (150 ml, 98-100%) for 24 hours. The crude product which separated on cooling was recrystallized from acetic acid to give colourless plates of hexphenyldisiloxane (64%), m.p. 221-222° (lit.[134] m.p. 224-224.5°).

(iv) Diphenylsilanediol. - The method of Dilthey and Eduardoff[130] was modified as follows: an ethereal solution of phenylmagnesium bromide (3 moles) and silicon tetrachloride (1 mole) was refluxed for eight hours. The resulting mixture was then carefully reacted with excess sodium bicarbonate solution (5%). The product was extracted with ether and crystallized from light petroleum (b.p. 60-80°), to give colourless needles of diphenylsilanediol (54%), m.p. 148° (lit.[131,135, 136] m.p. vary between 118° and 148°).

(v) Hexaphenylcyclotrisiloxane. - This was prepared in 70% yield from diphenylsilanediol by the method described for the preparation of hexphenyldisiloxane. Hexaphenylcyclotrisiloxane crystallized from acetic acid in colourless plates, m.p. 188-188.5° (lit.[136] m.p. 190°). (Found: C, 73.0; H, 5.3; Si, 14.7. Calc. for $C_{36}H_{30}O_3Si_3$: C, 72.7; H, 5.1; Si, 14.2%).

(vi) Tetra-(p-carboxyphenyl)silane. - This compound has been described by Wu and Yu.[137] As this reference was not available the following procedure was developed: Finely powdered tetra-(p-tolyl)silane (1 g) was suspended in a mixture of glacial acetic acid (200 ml, A.R.) acetic anhydride (60 ml, A.R.) with sulphuric acid (6 ml. 92%). The flask containing the mixture was immersed in a large water-bath the temperature of which was kept at 30 ± 1°. Chromium trioxide (20 g, A.R.) was added during 60 minutes while the mixture was being stirred. After the addition was completed stirring was continued for one hour at 30°. The mixture was then poured onto crushed ice (500 g) and stirred until the ice had melted. The yellow precipitate was collected and washed with ice-water. The crude product was dissolved in aqueous sodium bicarbonate solution, freed of insoluble matter, and reprecipitated with hydrochloric acid. The precipitate was recrystallized from dioxan to give colourless plates of tetra-(*p*-carboxyphenyl)silane (69%), m.p. 400° (lit.[137] m.p. 300°). (Found: C, 65.2; H, 4.2; Si, 5.6. Calc. for $C_{28}H_{20}O_8Si$: C, 65.6; H, 3.9; Si, 5.5%).

(vii) Tetracyclohexylsilane. - The method of Kanazashi and Takakusa[85] was modified as follows: a solution of tetraphenylsilane (10 g) in methylcyclohexane (500 ml ; free of cyclohexane) was hydrogenated in the presence of W-7 Raney nickel (*ca.* 5 g) at 100° and 1500 lb/in^2 of hydrogen for 12 hours while being magnetically stirred. The residue left after removal of the catalyst and solvent was crystallized from hexane to give colourless triclinic prisms of tetracyclohexylsilane (73%), m.p. 283-284° (lit.[85] m.p. 279-281°). (Found: C, 80.0; H, 12.2. Calc. for $C_{24}H_{44}Si$: C, 80.0; H, 12.3%).

(viii) Cyclohexyltrimethylsilane. - A solution of trimethylphenylsilane (3 g) in methylcyclohexane (30 ml) was hydrogenated in the presence of W-7 Raney nickel (2 g) at 100° and 1800 lb/in^2 of hydrogen for 12 hours. After removal of the catalyst, the filtrate was freed of methylcyclohexane and lower boiling materials using a spinning-bond column. The residue was redistilled to give cyclohexyltrimethylsilane (71%), b.p. 67-69°/20 mm (lit.[85] b.p. 67-69°/25 mm). The infrared spectrum of this product was identical with that published by Kanazashi and Takakusa.[85]

(ix) Hexa(*n*-hexyl)disiloxane. - *n*-Hexyllithium (0.25 moles) was treated with silicon tetrachloride (0.06 mole) in ether. After eight hours, the mixture was worked up to give hexa(*n*-hexyl)disiloxane, b.p. 160-162°/0.7 mm (lit.[138] b.p. 223-225°/4.5 mm) in 41% yield. The infrared spectrum showed a broad intense band at 1100-1010 cm^{-1} characteristic of siloxane linkages.[86] Other strong peaks occurred at 1100-1200 and 1420-1460 cm^{-1}.

CHAPTER II

The Action of Raney nickel on aniline and related compounds.

Aniline has been shown[38,54,63,66] to form cyclohexylamine, ammonia, dicyclohexylamine, N-cyclohexylaniline, diphenylamine, and carbazole by the action of metal catalysts and hydrogen (see Introduction). The first aim in the exploration of this reaction was to determine the conditions which gave rise to best yields of these products. This was done by two methods. Aniline, cyclohexylamine, and a mixture of the two, were systematically subjected to both W-7 and degassed Raney nickel in a series of six experiments, and the yields of all products determined in each case. During some of these reactions, small samples were taken from the reaction at various intervals, and these were investigated by gas chromatographic analysis to determine any variations in concentration with reaction time of each individual product.

Reaction conditions were similar to those used by Jackson and Sasse.[38] The amine (approximately 1 mole) was added to the catalyst (from 125 g of alloy), and the mixture refluxed for 50 hours without solvent. The reaction temperatures consequently varied considerably from one reaction to another and even during the same reaction the reflux temperature gradually rose. With the exception of this one variable, the reactions and product analysis (carried out by gas chromatography) were all identical with one another.

The results (Table V) showed some significant trends. In all cases with both W-7 and degassed Raney nickel, no cyclohexylamine was detected in the final product analysis. From this it is assumed that

TABLE V.

Reactions of aniline and related compounds with Raney nickel catalysts : % Yields [(c)]

Compounds	Catalyst	Aniline	Dicyclohexylamine	*N*-cyclohexylaniline	Diphenylamine	Carbazole	Other Products
Aniline	W-7	47	trace	16			NH_3,(20); *o*-toluidine (2.0)
	W-7J	60	-	11	1.4	0.6	*o*-toluidine, (1.7); indole (trace)
Cyclohexylamine	W-7	4.5	2.9	40			NH_3, (53).
	W-7J	3	1.0	45	0.5	1.4	NH_3, (56).
Aniline + cyclohexylamine (a)	W-7	8	trace	47			*o*-toluidine (trace)
	W-7J(b)	trace	trace	64	-	-	-
N-cyclohexylaniline	W-7J	trace	trace	71	1.0	1.2	

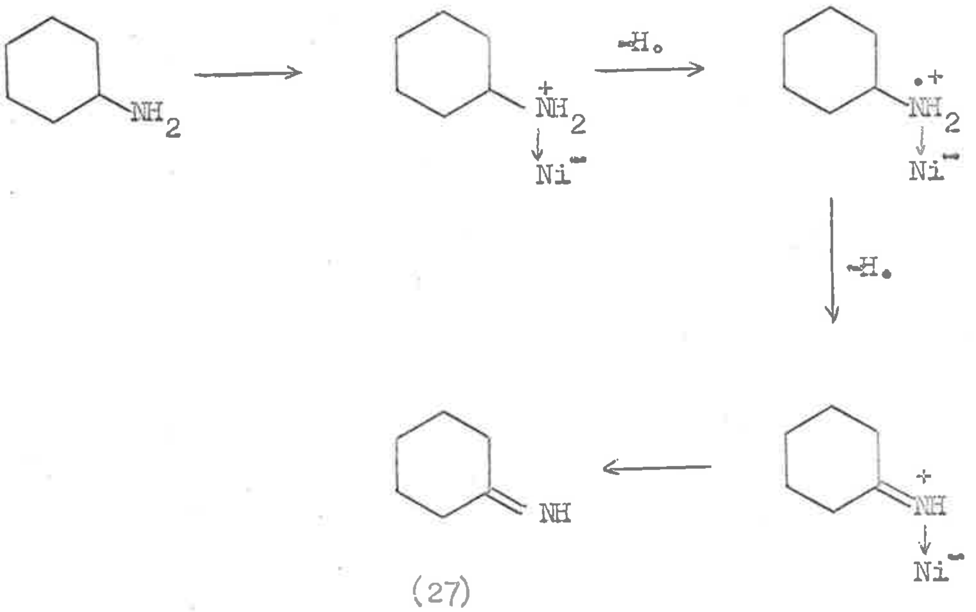
(a) Equimolar quantities

(b) Reaction carried out in xylene

(c) "Trace" means detected by gas chromatography (< 1%)

cyclohexylamine (formed during the reaction or added as starting material) is unstable under these conditions. As cyclohexylamine is the main product which aniline could be expected to form by hydrogenation, it presumably will be one of the initial products of the reaction, and investigation of its reaction path was essential.

Cyclohexylamine may undergo one of two reactions; dehydrogenation to aniline, or partial dehydrogenation to cyclohexylidene imine (27). This ketimine intermediate has never been isolated, but by analogy with other reactions of nitrogen compounds with Raney nickel, it could quite reasonably be expected to form, (Scheme 8).

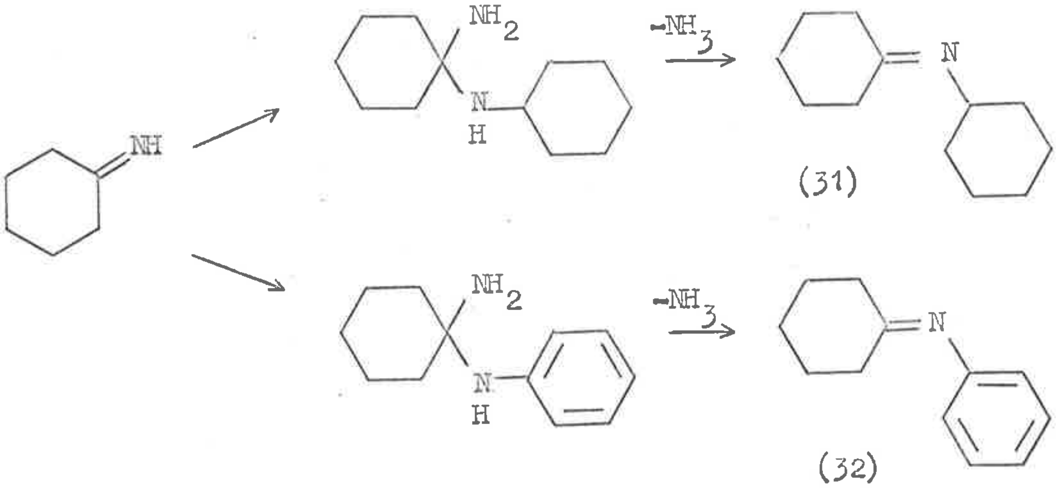


(27)

Scheme 8.

This ketimine would be expected to be very reactive, and even if it does not undergo further reaction, would hydrolyze under the work-up conditions to cyclohexanone,[65] which was detected in small yields by Jackson.[34] Also, Debus and Jungers,[63] who added water to the reaction (facilitating hydrolysis of any imine groups), isolated considerable quantities of cyclohexanone and cyclohexanol (formed by hydrogenation of cyclohexanone). Consequently, it seems likely that cyclohexylidene imine is the main intermediate in the reaction of cyclohexylamine with catalysts.

Imines have been shown to undergo addition to primary amines in exactly the same way as they add to water to form ketones.[65] Hence, cyclohexylidene imine may either add to an amine, hydrogenate to cyclohexylamine, or dehydrogenate to aniline. If it adds to a primary amine, there are two possibilities; addition to aniline or to cyclohexylamine, (Scheme 9).



Scheme 9.

According to Debus and Jungers,[63] the reaction path proceeds via addition of cyclohexylamine to give N-cyclohexylidene cyclohexylamine (31) which was not isolated, but quickly hydrogenated to dicyclohexylamine as the first product. Jackson and Sasse[38] on the other hand, postulate that either aniline addition is more important than cyclohexylamine addition, giving N-cyclohexylidene aniline (32) which was not isolated but hydrogenated to N-cyclohexylaniline (28b), or that the intermediate (31) was dehydrogenated immediately to N-cyclohexylaniline as the main product in this reaction, rather than dicyclohexylamine.[34]

As it has been shown that stronger bases add preferentially to imines,[65] it would be expected that cyclohexylamine would be favoured to the weaker base, aniline. However, this is complicated by a further factor in the availability of each of these primary amines. Consequently, it would be expected that both reaction paths should operate, the predominance of either determined by the relative concentration of aniline or cyclohexylamine in the reaction mixture.

Inspection of Table V shows that aniline with both W-7 and W-7J Raney nickel gave no more than trace amounts of dicyclohexylamine. This indicates that under these reaction conditions, dicyclohexylamine is either not formed, or if it is, would be efficiently dehydrogenated to N-cyclohexylaniline. Aniline with W-7 Raney nickel gave better yields of N-cyclohexylaniline (the main product) than with degassed catalysts, from which a larger proportion of starting material was recovered. It is assumed that this is caused by the hydrogen rich W-7 catalyst hydrogenating more aniline than the W-7J catalyst, giving greater quantities of cyclohexylamine during the reaction. Cyclohexylamine is converted to the imine, and as there would be a much larger concentration of aniline than cyclohexylamine present, the imine would be converted to (32) and hence to N-cyclohexylaniline as reported by Jackson and Sasse.[38]

Added support for this theory of imine addition comes from the reactions of cyclohexylamine with Raney nickel. In this case, cyclohexylamine on conversion to cyclohexylidene imine would react preferentially with cyclohexylamine rather than aniline since the former would be expected to be in large excess, and is a stronger base. These conditions would probably approximate more closely to those of Debus and Jungers,[63] and would explain why they isolated dicyclohexylamine as the main product. Aniline formed by dehydrogenation of cyclohexylamine was isolated in yields of only 3 to 4%, indicating that the concentration of this compound during the reaction is insignificant. Dicyclohexylamine was isolated in this case, but only in yields of 1 to 2%. Dicyclohexylamine which would be expected to form first, must be rapidly dehydrogenated to N-cyclohexylaniline (as described by Debus and Jungers[63]) which was obtained in yields over 40%.

Best yields of N-cyclohexylaniline were obtained when an equimolar mixture of cyclohexylamine and aniline was treated with Raney nickel. In this case, it may be envisaged that attack may occur by both aniline and cyclohexylamine on the imine. Preference for the first of these is indicated by the detection of only trace quantities of dicyclohexylamine. A possible explanation for this fact is that cyclohexylamine is consumed rapidly by the catalyst, leaving aniline in a greater concentration.

In the reaction of cyclohexylamine and aniline with degassed Raney nickel, aniline dissolved in xylene was added to the catalyst first. While the mixture refluxed, cyclohexylamine was slowly added. By this means, there could never be a large concentration of cyclohexylamine in the mixture, as it would be converted to the imine on addition to the catalyst, and rapidly taken up by aniline to form N-cyclohexylaniline. This method gave the best yields of N-cyclohexylaniline (64%), and was adapted to the preparation of a wide range of N-alkylarylamines.

Basic volatile material from the reaction was collected by passing gaseous products through hydrochloric acid solution. The yield was determined by titration of the resulting solution with sodium hydroxide solution. As no other volatile bases other than ammonia were expected from these reactions, this titration was taken as a measure of the ammonia yield. Although the gaseous products were not examined in any detail, it is felt that the assumption should be reasonably accurate. The observed values corresponded closely to those expected from deamination and formation of the secondary amines.

In summary, it appears that in the reaction of aniline over Raney nickel, the first step is hydrogenation to cyclohexylamine, which is dehydrogenated to cyclohexylidene imine. This then adds to either aniline or cyclohexylamine, depending on their relative concentrations, to form either dicyclohexylamine or N-cyclohexylaniline. Dicyclohexylamine is readily dehydrogenated to N-cyclohexylaniline.

These conclusions are confirmed by the analysis of the samples taken during the reaction. The reaction of aniline with W-7 Raney nickel is illustrated in Figure 1. Aniline is used up in the first ten hours of the reaction, but after this, the catalyst has presumably exhausted most of its hydrogen, and the hydrogenation ceases. In approximately the same period, N-cyclohexylaniline is formed at a similar rate, but little dicyclohexylamine is formed. This indicates that most cyclohexylidene imine adds to aniline and is hydrogenated to N-cyclohexylaniline as postulated earlier. Small quantities (ca. 3%) add to cyclohexylamine and are hydrogenated to dicyclohexylamine, which is then mostly dehydrogenated to N-cyclohexylaniline throughout the reaction. The other products from the reaction are benzene, cyclohexane, and o-toluidine, none of which have been reported before.

The reaction of cyclohexylamine with W-7 Raney nickel (Figure 2) is considerably different from that of aniline. In this case, all cyclohexylamine is used up rapidly, and simultaneously the concentration of dicyclohexylamine builds up to a maximum after eight hours. This is then slowly converted at a steady rate to N-cyclohexylaniline throughout the rest of the reaction, which is essentially completed after 40 hours. Very small quantities of aniline are formed, but the yields of cyclohexane and benzene were considerably increased compared to those in the reaction of aniline.

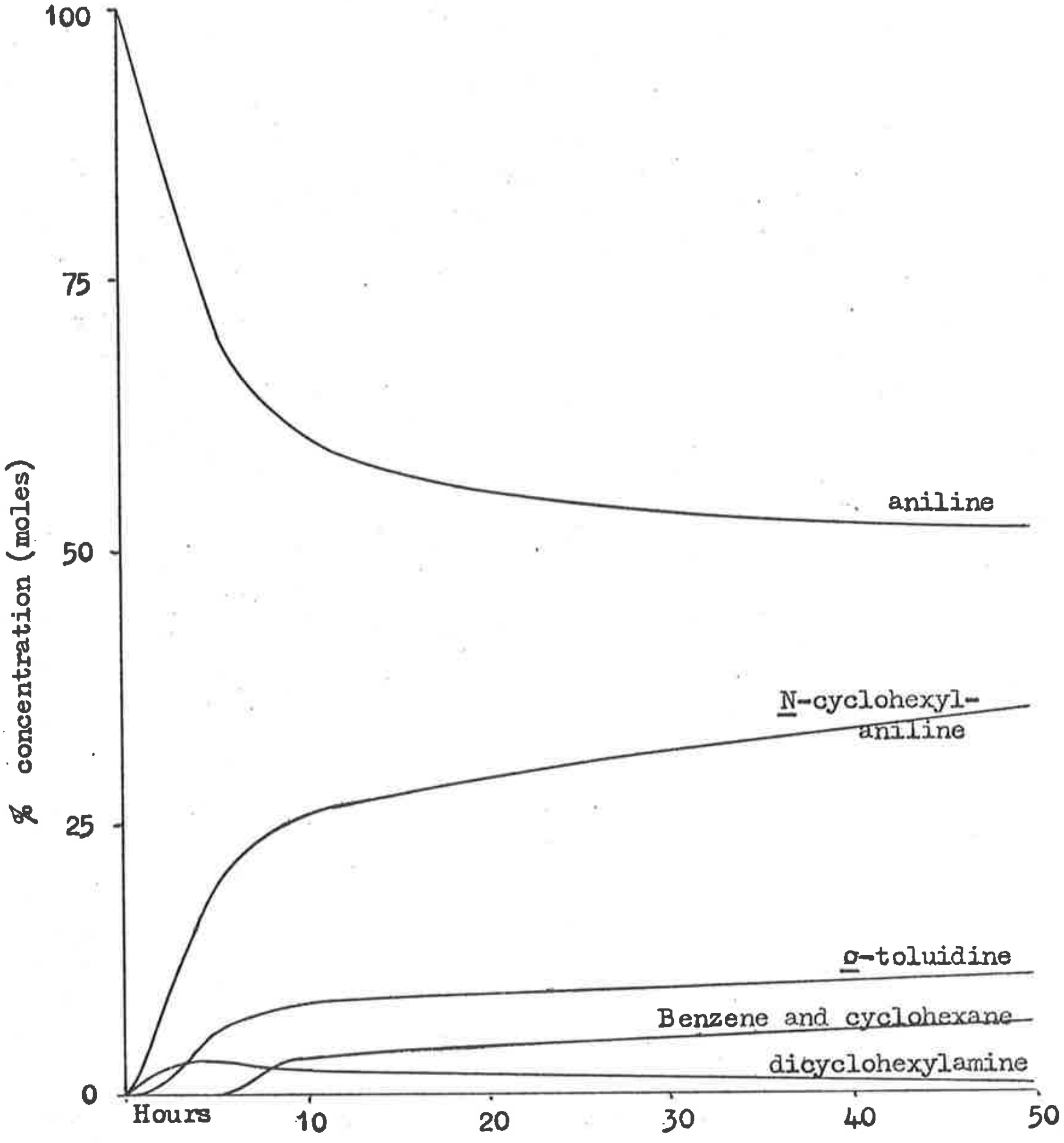


Figure 1 - Reaction of aniline with W-7 Raney nickel.

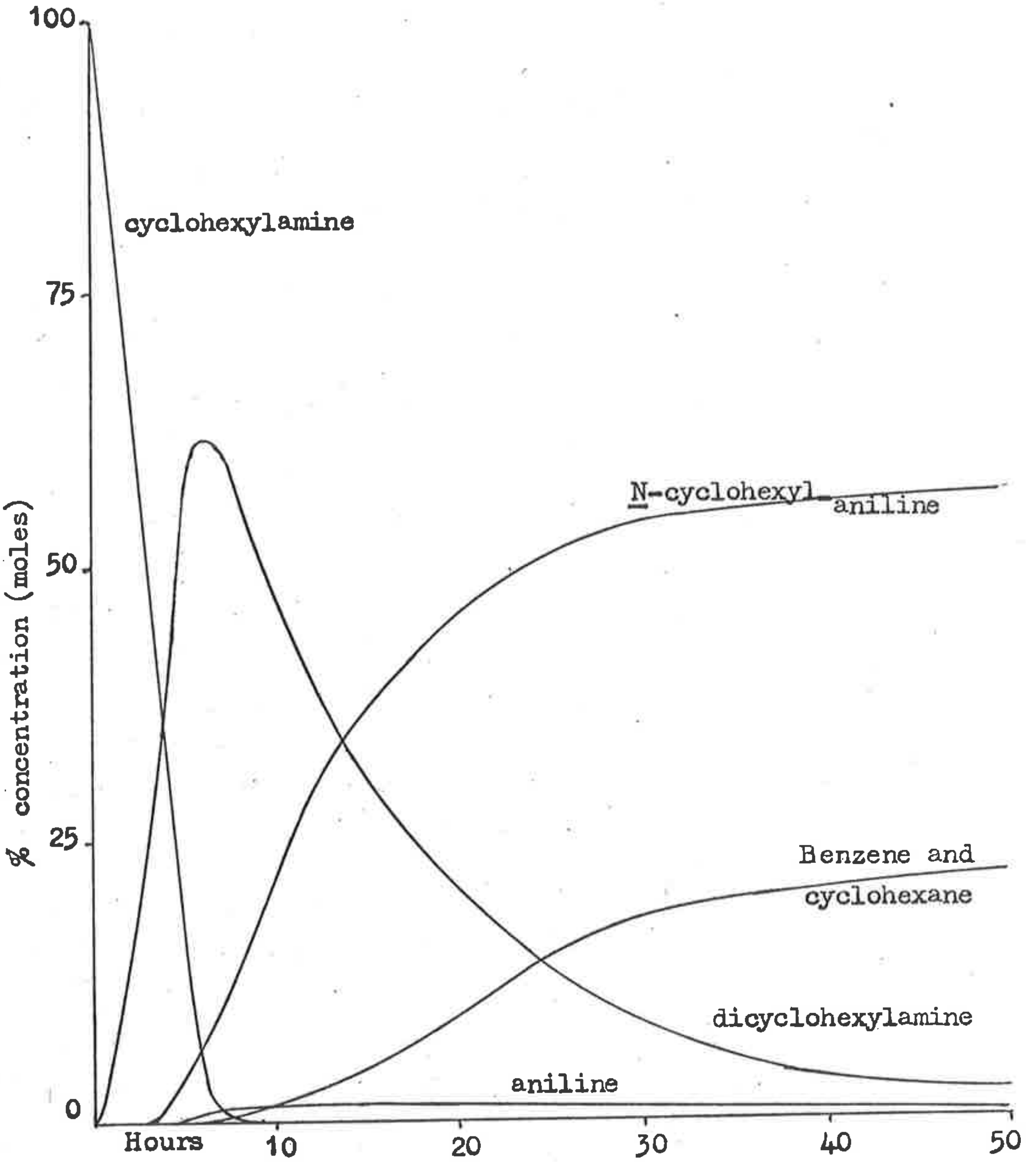
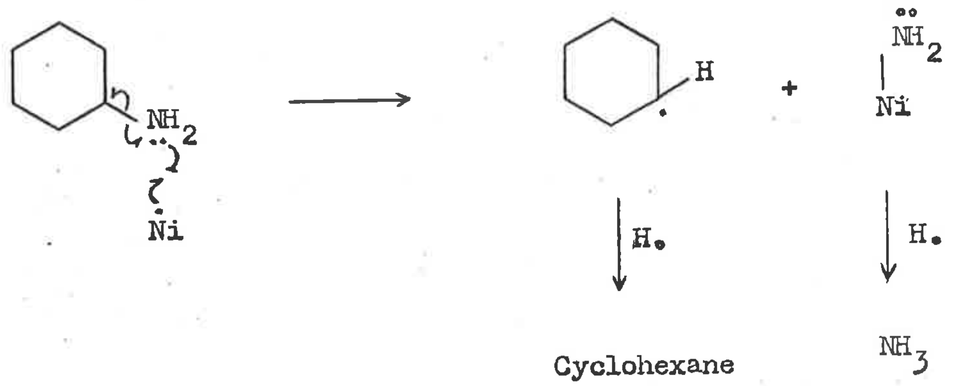


Figure 2 - Reaction of cyclohexylamine with W-7 Raney nickel.

By analogy with previously postulated mechanism, (see Introduction pp.6-8 and ref. 25), the deamination of these primary aliphatic amines could be by electron donation from the catalyst as shown in Scheme 10.



Scheme 10.

This mechanism is in contrast to that for dehydrogenation of cyclohexylamine (Scheme 8) which is postulated to proceed via lone-pair donation from nitrogen to the nickel. As explained in the Introduction (see p.9), it is possibly the energy levels of the lone-pairs on the hetero-atom which determine the type of chemisorption, and hence the reaction path. In aromatic amines such as aniline, it appears that most chemisorption occurs by donation of the nitrogen lone-pair to the nickel, (e.g. as shown by α-methylation and 2,2'-diaminobiphenyl formation[38]). With cyclohexylamine, it must be assumed that the lone-pair on the nitrogen is at as intermediary level in which either type of chemisorption may occur. This discussion is very speculative however, and an obvious method to give a clearer picture of these mechanisms would be to study these reactions with the aid of electron spin resonance spectra.[176]

This deamination of cyclohexylamine has the effect of reducing the yields of N-cyclohexylaniline quite appreciably in the reaction as compared with the yield from the reaction of a mixture of aniline and cyclohexylamine with Raney nickel. However, with cyclohexylamine, no other by-products formed, and this simplified purification of the main product.

Analysis of the reaction of a mixture of cyclohexylamine and aniline with W-7 Raney nickel, (Figure 3) shows it to be a modification of the first two. All the cyclohexylamine was used up in about six to eight hours. The amount of dicyclohexylamine formed was less than half that in the cyclohexylamine reaction (Figure 2), and once again was steadily dehydrogenated to N-cyclohexylaniline. Most aniline was used up, either in addition to cyclohexylidene imine as shown by the large rapid rise in N-cyclohexylaniline concentration, or in hydrogenation to cyclohexylamine. o-Toluidine was also formed as before, and was used up during the reaction in a similar way to aniline.

The formation of o-toluidine was noticed only in reactions with aniline and not with cyclohexylamine. It could possibly be formed by a mechanism similar to that postulated for the formation of

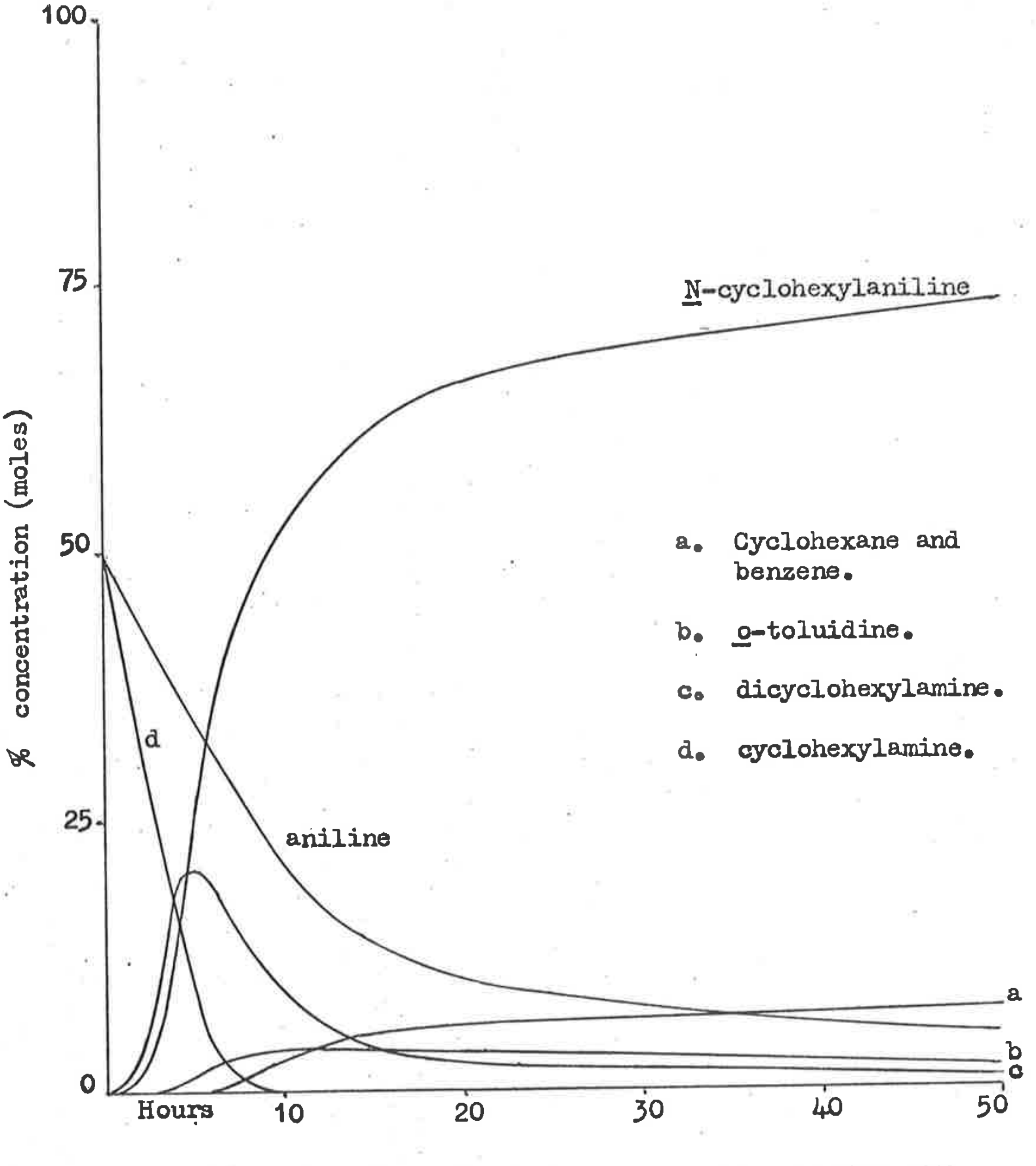
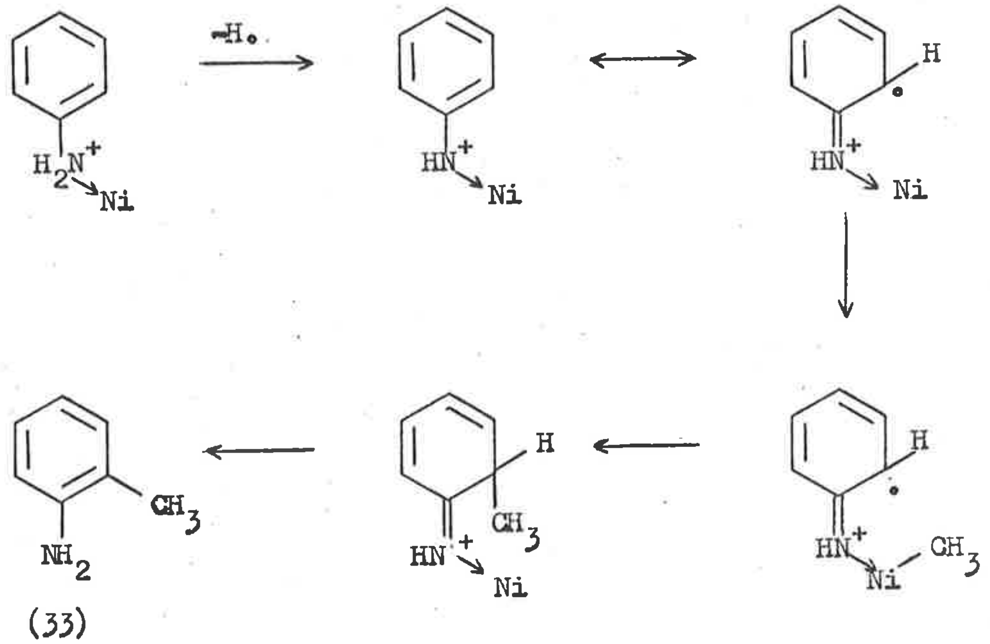


Figure 3 - Reaction of aniline and cyclohexylamine with W-7 Raney nickel.

carbazole from *N*-cyclohexylaniline[38] (Scheme 11). The source of the

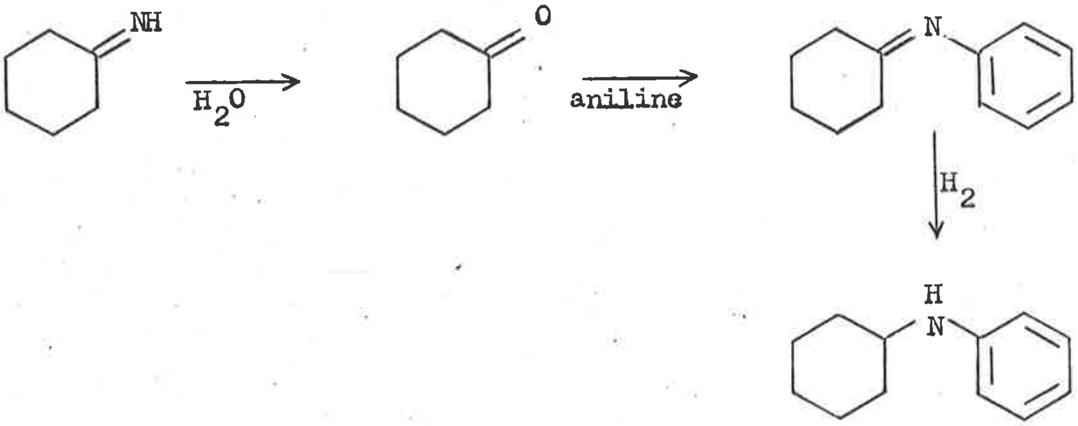


Scheme 11.

methyl group is obscure. It may be formed from cyclohexylidene imine which could hydrolyze and hydrogenate to cyclohexanol. Alcohols have been shown to give carbon monoxide on nickel catalysts, and this carbon monoxide is adsorbed strongly to the metal and converted to potential methyl groups.[31,33,101] Nevertheless, this reaction path appears rather involved compared with the efficiency of α-methylation, and further investigation could possibly reveal another pathway.

A related problem is the formation of indole in the reaction of aniline with W-7J Raney nickel, though in very small yields. The indole precursor is probably *o*-toluidine, which could be methylated to _o_-ethylaniline and then cyclized to indole.[35] Alternatively, it could have been a breakdown product of carbazole, but Padoa[139] has indicated that 1,2-diethylindole is the main product from this reaction, and indole is therefore an unlikely product.

These reactions also show that the secondary amines are formed by attack of amines on the imine. It has been suggested, though not generally accepted, that the imine intermediate may hydrolyze to a ketone. This could then condense with an amine forming an anil which could hydrogenate to the secondary amine.[46] (Scheme 12).



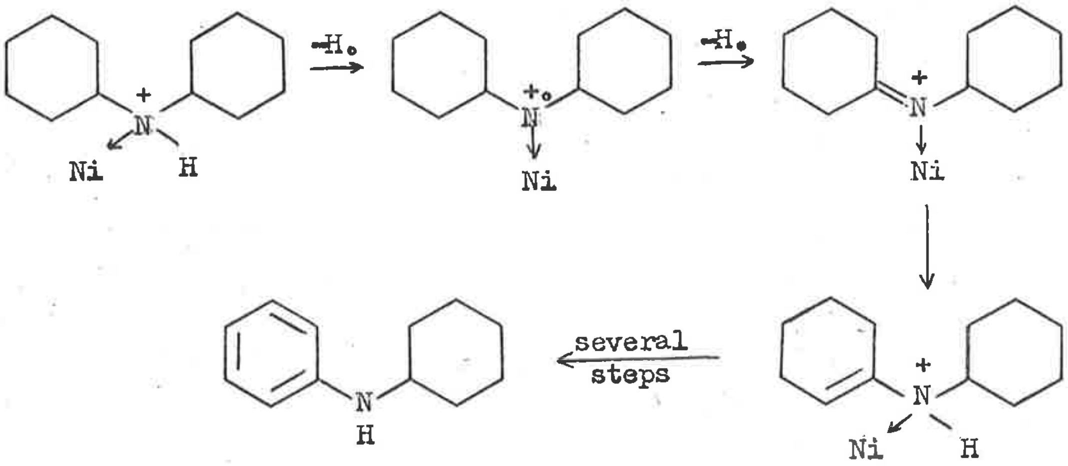
Scheme 12.

The graphs (Figures 1-3) all indicate that as cyclohexylamine is consumed in the reaction, the only compounds to form are dicyclohexylamine or _N_-cyclohexylaniline. Cyclohexanone was not detected as a reaction intermediate, but was obtained in small quantities in the reaction residues. This indicates that the greater majority of ketimine adds directly to amines during these reactions.

A certain amount of caution is needed in interpreting these results however, as the graphs (Figures 1-4) were plotted by analysis of the supernatent liquid from the reactions. Consequently, this takes no account of adsorbed species on the catalyst surface, and therefore some discrepancies may arise. This would explain why cyclohexylidene imine was not detected by this means, as after desorption it would be reactive, condensing with a primary amine before gas chromatographic analysis could be carried out. Nevertheless, this method does show the path of formation of the main products reasonably accurately.

Having shown that N-cyclohexylaniline may be formed by two paths, the question remains as to why it should be so stable over Raney nickel. Good yields of dicyclohexylamine would be expected from the reaction of cyclohexylamine with W-7 Raney nickel if heating is stopped after eight hours, but for longer periods it is almost quantitatively dehydrogenated to N-cyclohexylaniline. On the other hand, N-cyclohexylaniline undergoes very little dehydrogenation to diphenylamine and carbazole even with degassed catalysts as shown in Table V. The answer to this question probably lies in a discovery of Debus and Jungers,[63] who found that hydrogenation of a mixture of aniline and benzene resulted in good yields of cyclohexylamine, but the benzene was almost untouched. This shows that a great proportion of adsorption, even in hydrogenation of the π-electron system, is initiated by the basic nitrogen atom. For example, it may be envisaged that dicyclohexylamine is initially chemisorbed to the nickel by donation of an electron pair

(Scheme 13).



Scheme 13.

Once having formed a double bond in the alicyclic ring, chemisorption and dehydrogenation should occur much more readily through this π-electron system. If the availability of the nitrogen lone-pair is a measure of the ease of chemisorption of these compounds, then the basicities should indicate roughly their reactivity towards dehydrogenation. The dissociation constant for dicyclohexylamine is apparently unknown, but would be expected to be similar to N-methylcyclohexylamine which has a pKa 11.04.[140] This is a far stronger base than N-cyclohexylaniline with a pKa 5.6,[141] which in turn is stronger than diphenylamine which has a pKa 0.77.[142] These low basicities could explain why N-cyclohexylaniline is only slowly dehydrogenated to diphenylamine, and this is equally slowly converted to carbazole[38] (see Table V). According to this basicity hypothesis, the formation of carbazole should occur less readily than dehydrogenation of N-cyclohexylaniline. However, this latter reaction requires two steps and the elimination of six hydrogen atoms, making it slow as the cyclodehydrogenation of diphenylamine which requires only the removal of two hydrogens.

In an attempt to extend this series of reactions, the three toluidines were similarly treated with degassed Raney nickel, (Tables VI, VII, and VIII). In every case, the yields of the various dimethyl-substituted N-cyclohexylanilines were lower than for N-cyclohexylaniline from aniline. The recovery of unchanged toluidine was also greater than for aniline.

The reaction of m-toluidine (38) and its derivatives were examined, in some detail (Table VI), and as p-toluidine was assumed to show similar behaviour, was only examined briefly (Table VII). m-Toluidine with degassed Raney nickel gave only 3% yield of the main product, N-(3-methylcyclohexyl)-m-toluidine (29), and 77% recovery of starting material. Apart from the isolation of small quantities of polymethylene, and that no 3,3'-dimethyldiphenylamine (34) was separated, the reaction was similar to that of aniline. It is assumedthat the slight overall decrease in activity must be due to increased steric interaction of the methyl group slowing the hydrogenation of toluidine to 3-methylcyclohexylamine (39).

The much smaller yields of carbazole derivatives may also be explained by steric hindrance. The methyl groups of N-(3-methylcyclohexyl)-m-toluidine (29) could prevent the alicyclic ring from "sitting"

TABLE VI

Reaction of *m*-toluidine and related compounds with degassed Raney nickel : % Yields.

Compound	*m*-toluidine	2,5-dimethylaniline	*N*-cyclohexyl-*m*-toluidine	*N*-(3-methylcyclohexyl)-aniline	*N*-(3-methylcyclohexyl)-*m*-toluidine	Other Products
m-toluidine	77	4	-	-	5.5	$(CH_2)_x$, (0.04 g); 3-methylcyclohexanone, (0.4); mixture of carbazoles (0.12 g).
m-toluidine + 3-methylcyclohexylamine (a)	14	2.1	-	-	53	$(CH_2)_x$, (0.05g); mixture of carbazoles.
3-methylcyclohexylamine	trace	-	-	-	68	aniline, (trace).
m-toluidine + cyclohexylamine (a)(b)	13	5	28	trace	trace	aniline, (7); dicyclohexylamine, (2.5); *N*-cyclohexylaniline, (16).
aniline + 3-methylcyclohexylamine (a)(b)	1.0	-	-	71	trace	aniline, (1.0); *N*-cyclohexylaniline, (trace).

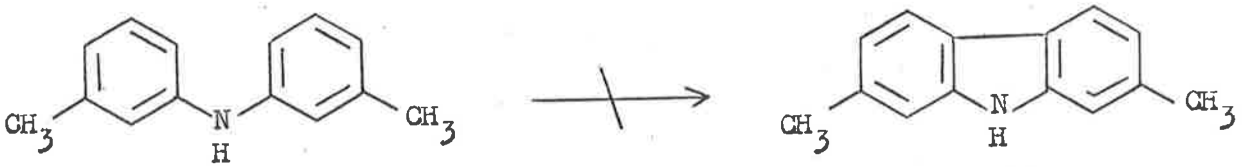
(a) Equimolar quantities.

(b) Reaction carried out in xylene.

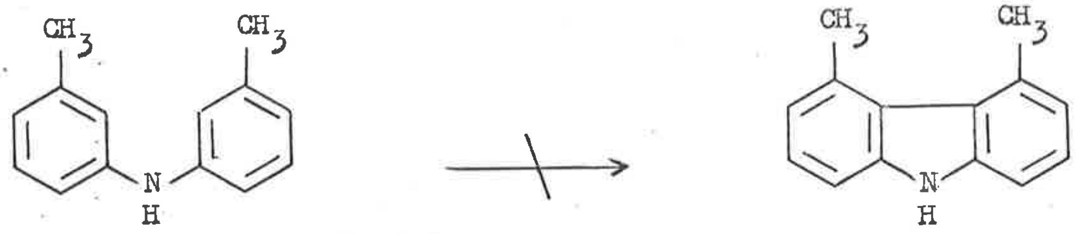
flat on the catalyst surface, considerably interfering with the hydrogenation. With very small quantities of 3,3'-dimethyldiphenylamine formed, the main route to carbazole is stifled.

The carbazole mixture which was isolated was shown to be carbazole (29%) and one other compound which was isolated by preparation thin-layer chromatography, and could not be separated into any other components by gas chromatography. This compound gave the correct analysis and had the required molecular weight (mass-spectrum) for dimethylcarbazole. The n.m.r. spectrum showed two methyl absorptions separated by about 2.5 c.p.s. The aromatic absorption was not analyzed. Hence, it may be assumed that the compound is either 2,5-dimethylcarbazole (35), or a mixture of the various possible isomers; 2,7-dimethylcarbazole (36), 2,5-dimethylcarbazole (35), and 4,5-dimethylcarbazole (37). 2,7-Dimethylcarbazole is the only previously reported example,[39] which has a melting point of 283° compared to 229-230° for the isolated sample. Assuming that the dimethylcarbazole isolated was formed from 3,3'-dimethyldiphenylamine (34), Catalin models suggest that steric clash between the two methyl groups would rule out 4,5-dimethylcarbazole (37). Also the 2,7-dimethyl derivative (36) on forming would show a slight steric clash of the methyl groups with the catalyst surface. As these catalytic reactions have been shown to be sensitive to steric factors,[23,30] it is proposed that the structure of this carbazole derivative is 2,5-dimethylcarbazole (35).

(34) (35)

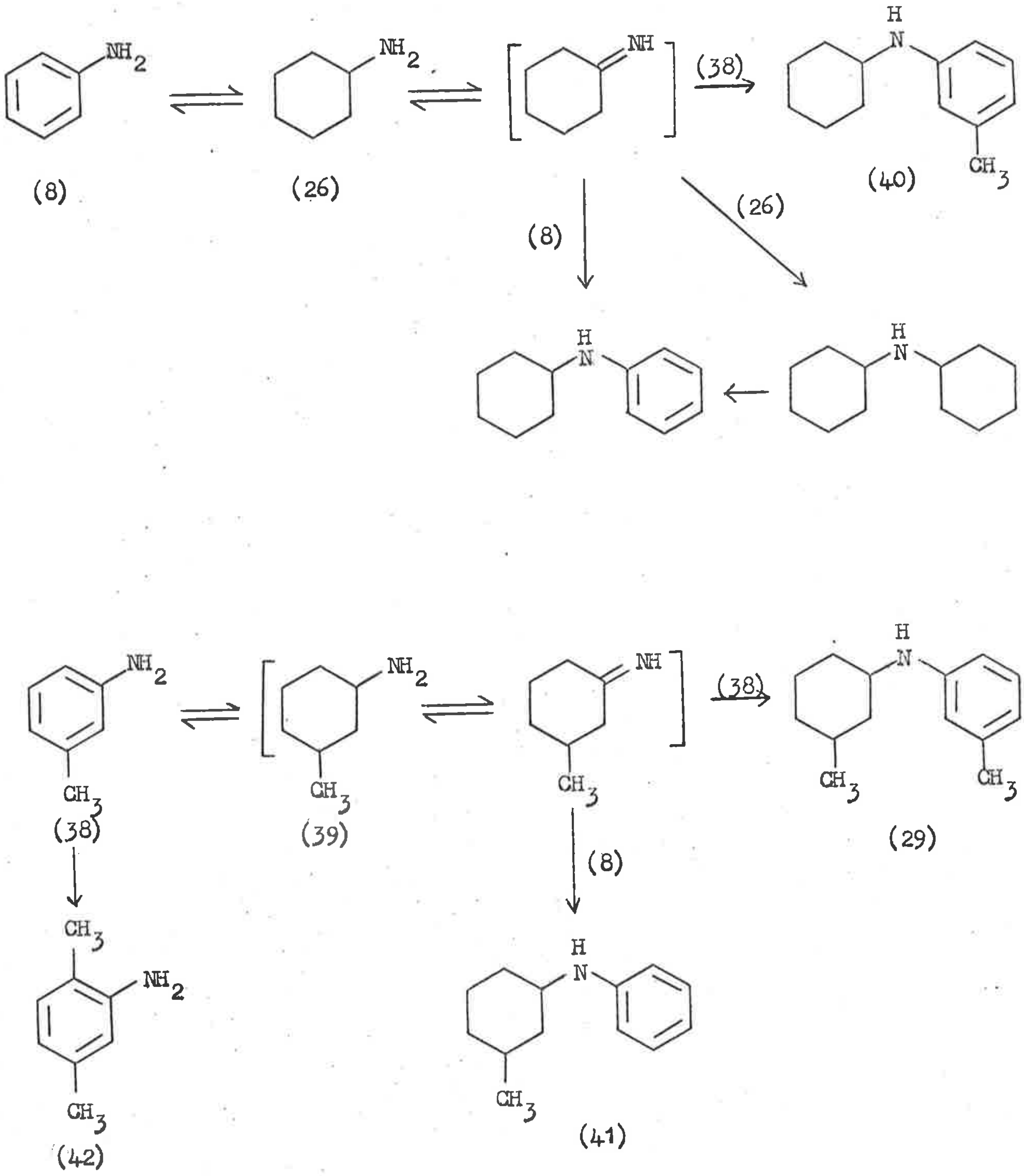


(34) (36)



(34) (37)

By analogy with the reactions with aniline mixed with cyclohexylamine, m-toluidine and 3-methylcyclohexylamine with W-7J Raney nickel gave the predicted result, proving a good synthetic pathway to N-(3-methylcyclohexyl)-m-toluidine (29). In this series, two other mixed experiments were carried out, both applicable to synthetic routes. 3-Methylcyclohexylamine was added to aniline while treated with degassed catalyst in xylene solvent as described earlier, and gave 71% yield of N-(3-methylcyclohexyl)aniline (41). Similarly, m-toluidine was refluxed in xylene with W-7J Raney nickel and cyclohexylamine added, resulting in 28% yield of N-cyclohexyl-m-toluidine (40) as the main product. This reaction was followed by gas chromatography as before (Figure 4), showing the formation of eight products (Scheme 14).



Scheme 14.

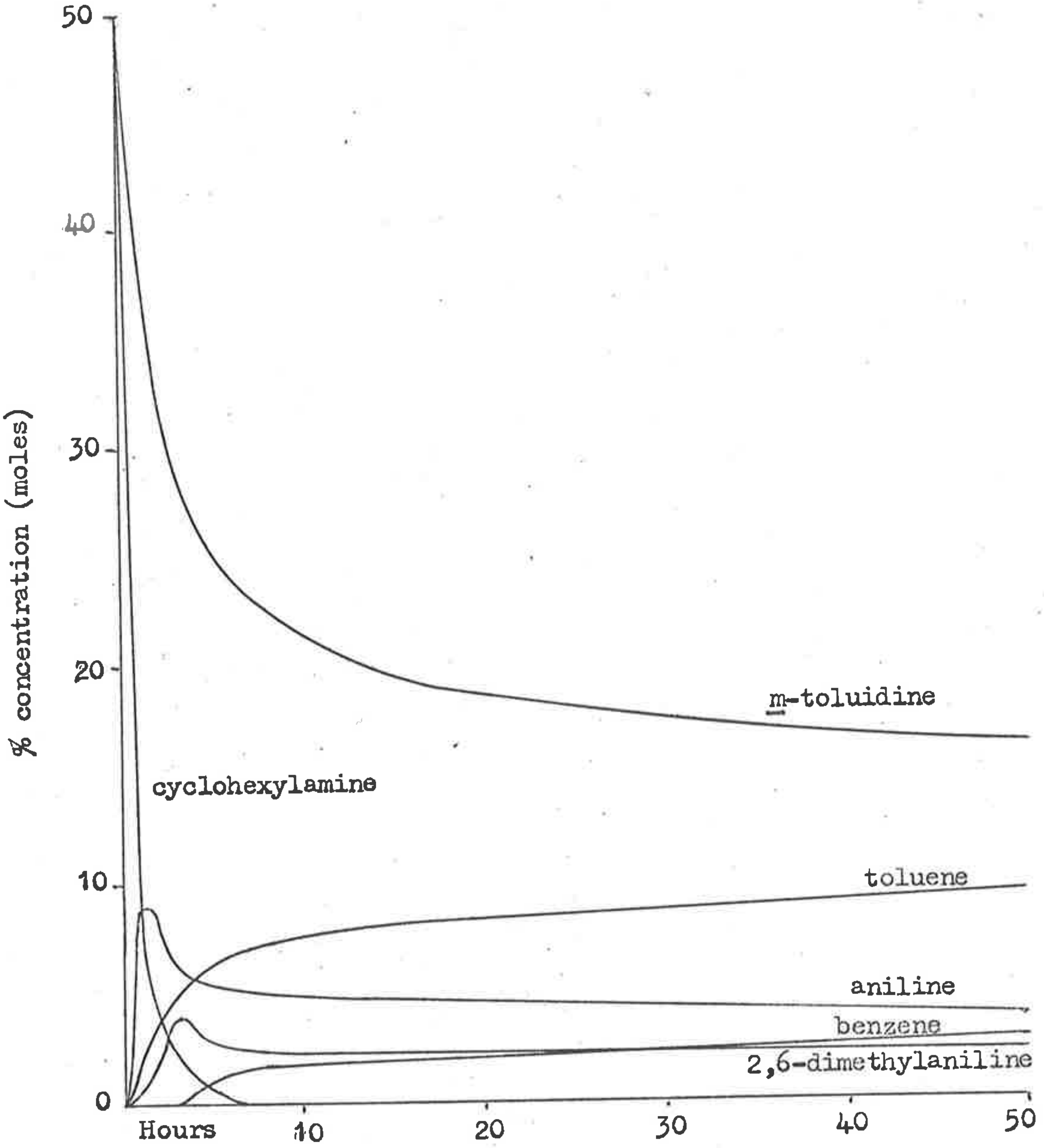


Figure 4 - Reaction of m-toluidine and cyclohexylamine with W-7J Raney nickel.

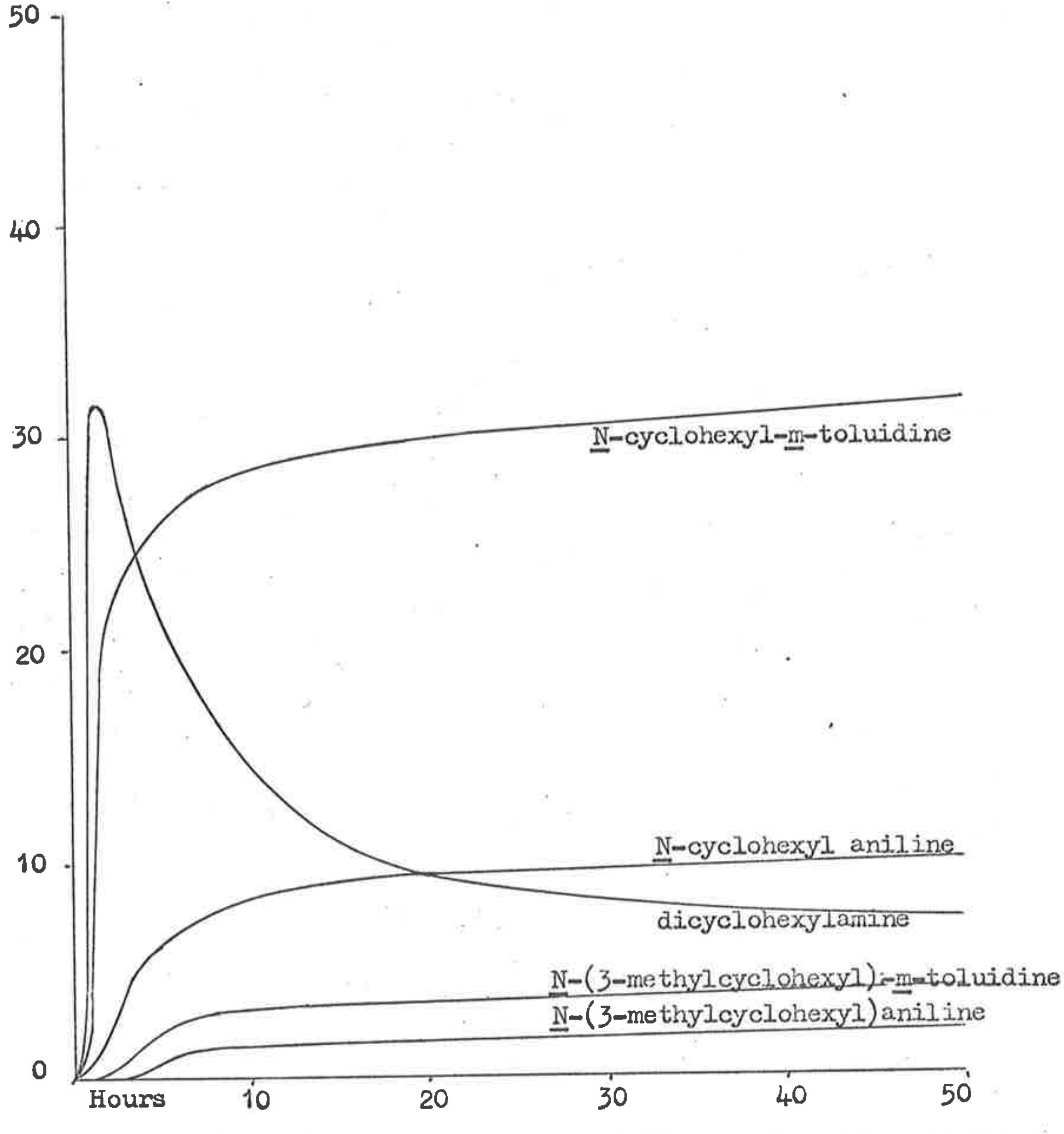


Figure 4 (contd) - Reaction of m-toluidine and cyclohexylamine with W-7J Raney nickel.

The formation of 2,5-dimethylaniline (42) is presumably analogous to the formation of o-toluidine from aniline.

Jackson[34] has reported the reaction of p-toluidine (43) over W-7J Raney nickel, but only detected the formation of benzene, toluene, polymethylene, and a white solid (0.03 g) with the same melting point as 3,6-dimethylcarbazole.

TABLE VII.

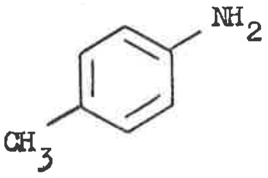
Reaction of p-toluidine and related compounds with degassed Raney nickel: % Yields.

Compound	p-toluidine	N-4-methyl-cyclohexyl)-p-toluidine	Other Products
p-toluidine	61	10	$(CH_2)_x$, (0.02 g); 4-methylcyclohexanone, (0.05) ; 4,4'-dimethyldiphenylamine, (0.03); mixture of carbazoles, (0.14 g)
p-toluidine + 4-methylcyclohexylamine (a) (b)	2.5	64	-

(a) Equimolar quantities

(b) Reaction carried out in xylene.

On repeating this experiment (Table VII), in addition to these compounds, N-(4-methylcyclohexyl)-p-toluidine (44), 4,4'-dimethyldiphenylamine, 4-methylcyclohexanone and carbazole were isolated. The carbazole obtained was mixed with what appeared to be 3,6-dimethylcarbazole, but this was not isolated or positively identified.



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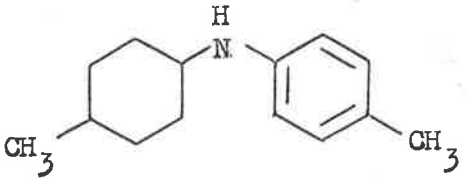


(44)

N-(4-methylcyclohexyl)-p-toluidine (44) was prepared in 71% yield by treating p-toluidine in xylene over degassed catalyst with 4-methylcyclohexylamine.

The reactions of o-toluidine (33) were found to be anomalous (Table VIII). Analogous reactions to the toluidine series were limited by steric factors as the methyl group apparently interfered with chemisorption of the nitrogen atom as well as the phenyl ring. This is indicated by a large proportion of de-methylated products. o-Toluidine with degassed Raney nickel gave: aniline (2.5%), N-cyclohexylaniline (10%), polymethylene (0.119 g), carbazole (0.02%), and N-cyclohexyl-o-toluidine (46) (5.5%), all products of demethylation. However, methylation was also observed in the isolation of 2,6-dimethylaniline (45) and indole (12), and by the detection of 3-methylindole (13) by thin-layer chromatography. Identification of 2-methylcyclohexanone once again

TABLE VIII

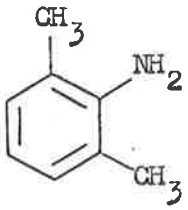
Reactions of *o*-toluidine and related compounds with degassed Raney nickel : % Yields.

Compound	Aniline	*o*-toluidine	2,6-dimethylaniline	*N*-cyclohexylaniline	*N*-cyclohexyl-*o*-toluidine	Other Products
o-toluidine	2.5	63	4.4	10	5.5	$(CH_2)_x$, (0.119 g); indole, (1.6); 3-methylindole, (trace); 2-methylcyclohexanone, (0.6 g); carbazole, (0.02).
o-toluidine + 2-methylcyclohexylamine (a)	2.3	21	8.5	31	25	
o-toluidine + cyclohexylamine (a)(b)	1.1	7.5	3.8	50	12.5	

(a) Equimolar quantities.

(b) Reaction carried out in xylene.

supports the postulate of a ketimine intermediate.



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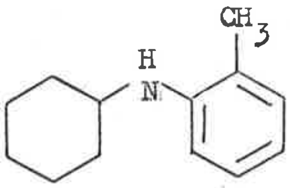

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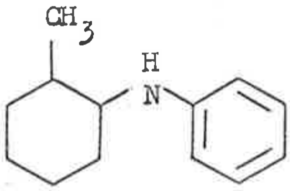


(47)

The reaction of a mixture of *o*-toluidine and 2-methylcyclohexylamine was seriously hindered. Instead of obtaining large yields of *N*-(2-methylcyclohexyl)-*o*-toluidine (30) as reported by Köhncke and Hanisch,[67] this product could not be isolated but may have been formed in small yields ($< 5\%$) as gas chromatographic analysis showed at least two unidentified peaks. The main products were *N*-cyclohexylaniline and *N*-cyclohexyl-*o*-toluidine (46). *N*-(3-methylcyclohexyl)aniline (47) also could not be isolated, but may have been formed in small yields.

Similarly, *o*-toluidine with cyclohexylamine gave a large yield of *N*-cyclohexylamine and a smaller yield of *N*-cyclohexyl-*o*-toluidine (46).

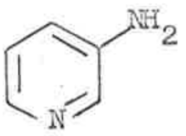
It is assumed that this demethylation is the reverse reaction of α-methylation which was observed with aromatic amines. The demethylation is favoured with *o*-toluidine probably because the methyl group is readily accessible to the catalyst on adsorption of the nitrogen atom, and also because it supplies relief to steric strain in this adsorbed state. For example, *o*-toluidine may be demethylated to aniline, which hydrogenates to cyclohexylamine more readily than *o*-toluidine would give 2-methylcyclohexylamine. Consequently, there would be a greater concentration of cyclohexylidene imine than the 2-methyl derivative resulting in the formation of N-cyclohexyl-o-toluidine and N-cyclohexylaniline as the major products.

Nevertheless, considerable methylation also takes place both on the aromatic ring to give 2,6-dimethylaniline (45) and on the side chain, eventually leading to indole and 3-methylindole. Once again, the origin of these methyl groups is abscure, but as the yields of these methylated products are greater than that observed with aniline, then the source of some of these may have resulted from demethylation of o-toluidine.

α-Naphthylamine would be expected to show similar steric factors effecting the nitrogen atom as o-toluidine. On treating α-naphthylamine with degassed Raney nickel under similar conditions, no secondary amines were isolated, and the only detectable reaction was a 10% deamination. This lends support to the postulation of steric hindrance in the o-toluidine reactions.

To gain a greater insight into the reactions of different nitrogen functions over Raney nickel, 3-aminopyridine (48) and 3-aminopiperidine (51) were treated with degassed catalysts. The first of these has been reported by Whittle[143] who obtained small quantities of a yellow solid which analyzed for diaminobipyridyl. However, no structure was proposed.

If 3-aminopyridine behaved in the same way as other 3-substituted pyridines over Raney nickel,[144] the expected product would be 5,5'-diamino-2,2'-bipyridyl (49). However, if chemisorption occurred through one amine nitrogen and one ring nitrogen, or through both amine nitrogens, the formation of diaminopyridine (by a mechanism similar to that proposed for the formation of 2,2'-diaminobiphenyl[38]) would result in the formation of 3,3'-diamino-2,2'-bipyridyl (50).



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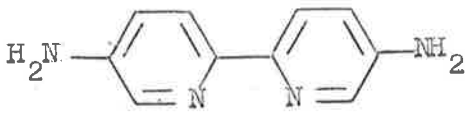

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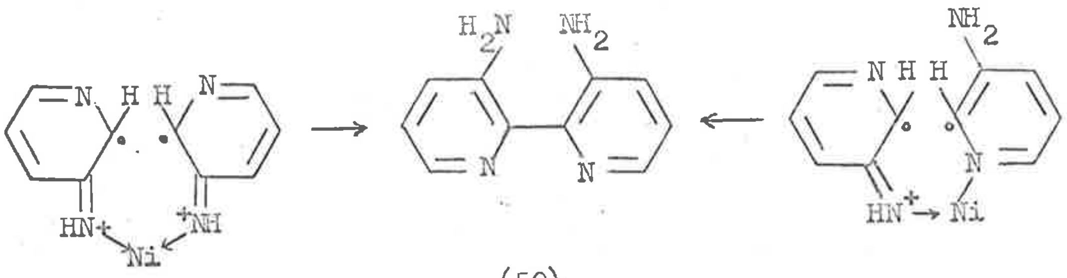


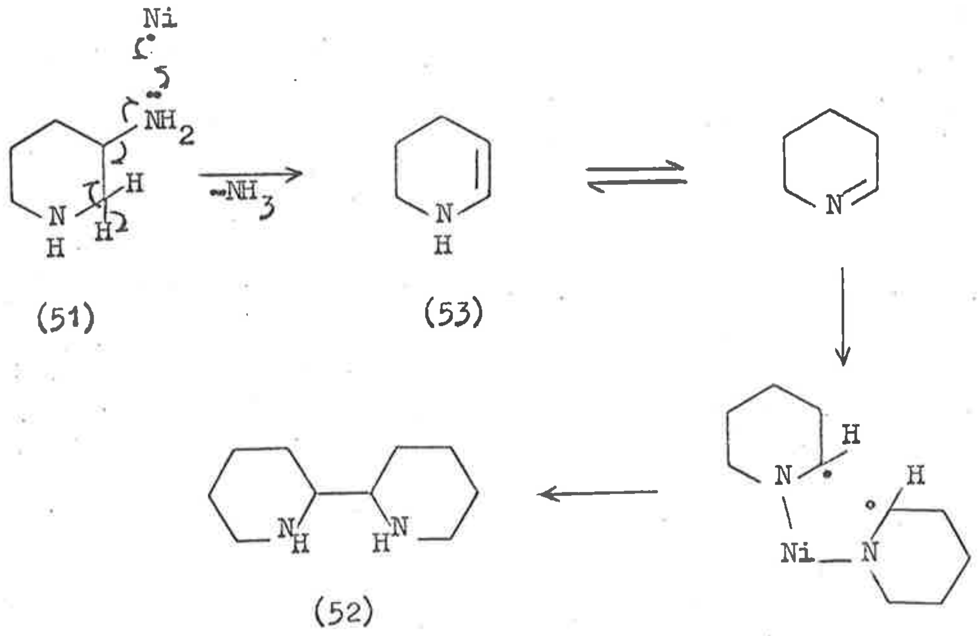
(50)

On repeating this experiment, a similar compound (with the same melting point) was obtained, which gave a distinctive red colouration with ferrous sulphate. This test is characteristic of 2,2'-bipyridyl nucleus, and rules out the other possible bipyridyl isomers. The n.m.r. spectrum shows an α-proton (τ 2.04) with at least one ortho coupling of 6 c.p.s. which favours structure (50). Also the N-H absorption in the n.m.r. spectrum is low (τ 3.87) compared with for example, 2-aminopyridine (τ 5.25).[145] This could be due to deshielding by the adjacent aromatic ring, or by hydrogen bonding of the amine protons with the heterocyclic nitrogen atoms, both of which could only occur with 3,3'-diamino-2,2'-bipyridyl (50).

3-Aminopiperidine, (51) on treatment with degassed Raney nickel, gave 40% yield of 2,2'-bipiperidyl (52). The formation of this product was quite unique and has no immediate analogies. Piperidine has been shown to undergo ring contraction,[146] N-alkylation,[146,147] dehydrogenation,[147] and N-substitution with alcohols,[50] under the influence of Raney nickel and similar catalysts. Reaction conditions with 3-aminopiperidine may have been too vigorous to observe these products, as only intractable tars were obtained other than 2,2'-bipiperidyl (52).

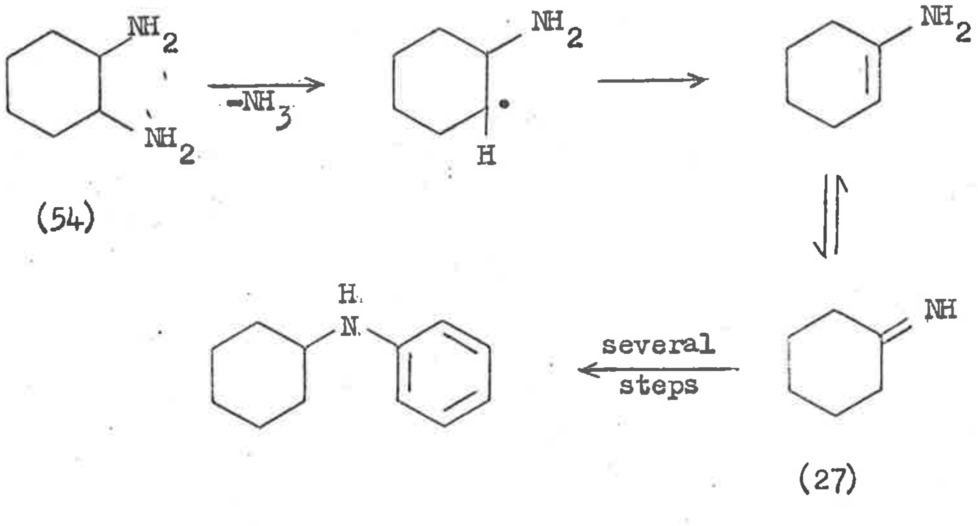
The formation of 2,2'-bipiperidyl may be explained by postulating initial adsorption through the primaty amine group leading to deamination. Assuming that this is followed by elimination of hydrogen to give tetrahydropyridine (53), this could isomerize and form 2,2'-bipiperidyl by a mechanism very similar to that proposed for the formation of 2,2'-bipyridyl[24] (Scheme 15).

An analogous compound to 3-aminopiperidine is 1,2-diaminocyclohexane (54). In both cases, the two nitrogen atoms are separated



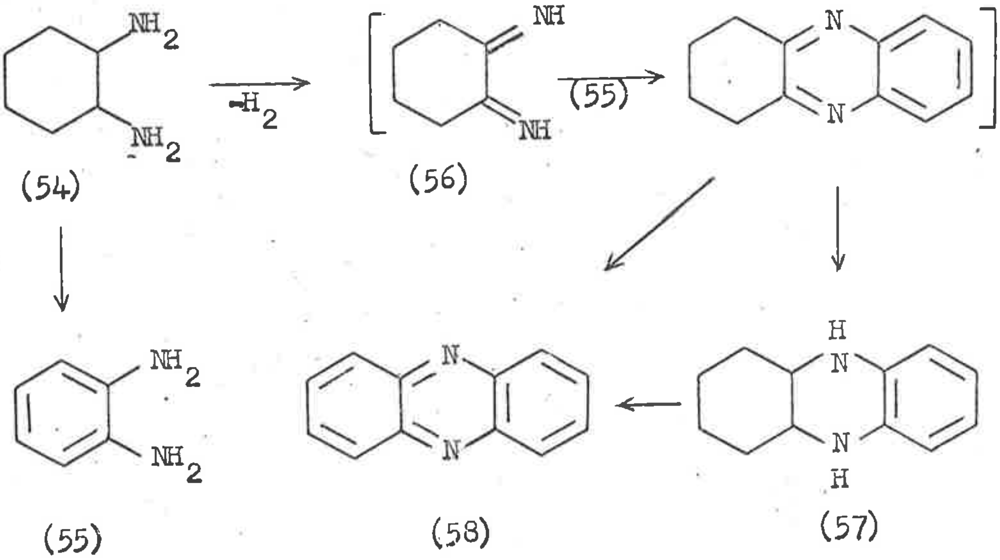
Scheme 15.

by two aliphatic carbon atoms, and hence a similar reaction should be expected. In this case, deamination would lead to cyclohexylidene imine (27) (Scheme 16).



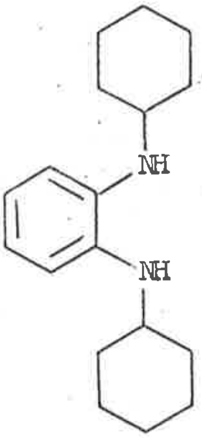
Scheme 16.

On investigation of the reaction of 1,2-diaminocyclohexane with degassed Raney nickel, N-cyclohexylaniline was the main product isolated in 30% yield. Other products formed were o-phenylenediamine (55), trans-1,2,3,4,4a,5,10,10a-octahydrophenazine (57), and phenazine (58). Octahydrophenazine was probably formed by attack of o-phenylenediamine on the diimine (56), perhaps in several steps, then followed by hydrogenation. The formation of the trans-isomer is consistent with the findings of Clemo and McIlwain[148] who showed that basic conditions for the hydrogenation led to the trans-isomer. Phenazine could form by dehydrogenation of octahydrophenazine[148,156] (Scheme 17).

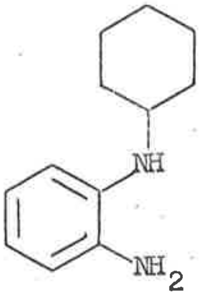


Scheme 17.

o-Phenylenediamine (55) was treated with cyclohexylamine and Raney nickel in an attempt to prepare N,N'-dicyclohexyl-o-phenylenediamine (59). However, in this case there were no products related to o-phenylenediamine. Aniline (16%), o-toluidine (12%), dicyclohexylamine (14%), N-cyclohexylaniline (47%), diphenylamine (1.6%), carbazole (0.5%) and starting material (4%) were the only products isolated from the reaction.

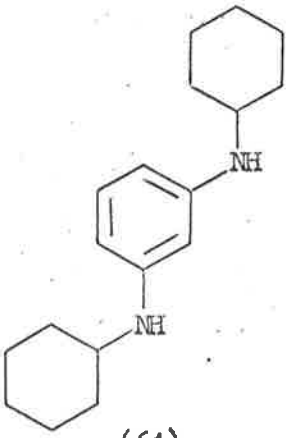


(59)

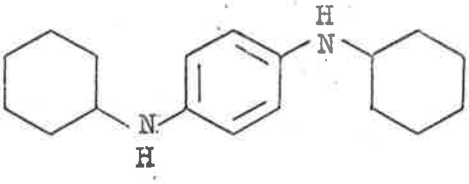


(60)

Once again it appears that the crowding of the ortho-substituents is too great to permit reactions on Raney nickel. After hydrogenation of o-phenylenediamine to diaminocyclohexane, deamination may occur as in Scheme 16. However, if N-cyclohexyl-o-phenylenediamine (60) did form, it is possible that the large bulk of the cyclohexyl group would facilitate elimination of the free amine function (thus easing steric strain) by deamination as described earlier. N,N'-dicyclohexyl-o-phenylenediamine (59) has never been recorded in the literature.



(61)



(62)

Similar preparations were carried out with *p*- and *m*-phenylenediamines with cyclohexylamine. In each case, yields of 25% *N*,*N*'-dicyclohexyl-*m*-phenylenediamine (61) and 30% of *N*,*N*'-dicyclohexyl-*p*-phenylenediamine (62) were obtained.

EXPERIMENTAL

1. General.

Gas chromatographic analyses were carried out with a Perkin-Elmer model 800 Gas Chromatograph equipped with either a 6ft. x 0.125 in. column packed with Gas Chrom-22 (80-100 mesh coated with 15% Silicone grease) or a 3ft. x 0.125 in. column of Chromosorb-W (80-100 mesh coated with 15% Apiezon L grease). Preparative gas chromatographic separations were carried out with an Aerograph Autoprep Model A700 fitted with a 5ft. x 0.375 in. column packed with Chromosorb-W (60-80 mesh coated with 30% SE-30 silicone grease). Compounds identified by gas chromatography were characterized by retention times with authentic samples as internal standards on both the silicone and Apiezon columns.

Nuclear magnetic resonance (n.m.r.) spectra were determined with either a Varian DP.60 spectrometer calibrated relative to tetramethylsilane using side-band technique, or with a modified Varian DA.60-IL spectrometer with field frequency lock calibration. Chemical shifts are given as τ values; solvents were carbon tetrachloride, deuterated chloroform or acetone/carbon tetrachloride (40:60).

Mass spectra were measured with a Hitachi Perkin-Elmer RMU-6D single focusing mass spectrometer using a 75V ionization potential.

Infrared spectra were measured with a Perkin-Elmer Infracord 337 or 237 spectrophotometer. Ultraviolet spectra were determined with a Perkin-Elmer 137 U.V. spectrophotometer.

Separations involving column chromatography were carried out on Mallinckrodt silicic acid or Spence alumina with an adsorbent-adsorbate ratio of 50:1 using hexane, benzene and ether as eluants. Thin-layer chromatography was carried out on silicic acid plates (0.03 cm thick) or preparative plates (0.24 cm thick).

Analyses were performed by the Australian Microanalytical Service, Melbourne.

2. Materials.

The following compounds were commercial samples purified by distillation: aniline, b.p. 82-83°/15 mm; cyclohexylamine, b.p. 133-134°; *o*-toluidine, b.p. 94-95°/15 mm; *m*-toluidine, b.p. 93-94°/15 mm. The following were commercial samples which were used without purification: 2,6-dimethylaniline (Fluka, purum), *p*-toluidine (B.D.H.), *o*-phenylene diamine (B.D.H.), *m*-phenylene diamine (B.D.H.), *p*-phenylene diamine (B.D.H.), and diphenylamine (Fluka, purum). α-Naphthylamine (B.D.H.) was recrystallized from aqueous ethanol, m.p. 49-50°. 3-Aminopyridine, m.p. 63° (lit.[152] m.p. 63-64°) was prepared from nicotinamide.[152]

2-Methylcyclohexylamine, b.p. 60-63°/30 mm (lit.[149] b.p. 153.5-154.5°), 3-methylcyclohexylamine, b.p. 61°/30 mm (lit.[149] 152.7-153.4°), and 4-methylcyclohexylamine, b.p. 65°/38 mm (lit.[149] b.p. 153.3-153.7°) were prepared from the corresponding toluidine acetate by high pressure hydrogenation over W-7 Raney nickel, and subsequent hydrolysis in 70% sulphuric acid of the methylcyclohexylamine acetate.

1,2-Diaminocyclohexane, b.p. 80°/15 mm (lit.[150] b.p. 183-185°/720 mm) and 3-aminopiperidine, b.p. 82°/15 mm (lit.[151] b.p. 7-71°/10 mm) were similarly prepared from o-phenylenediamine and 3-aminopyridine respectively.

2,5-Dimethylaniline, b.p. 112°/15 mm (lit.[153] b.p. 215°) was prepared from p-xylene by the method of Nölting and Forel.[153]

Xylene solvent, b.p. 137-140°, and benzene were freed from sulphur compounds and purified by distillation from Raney nickel.

W-7 and degassed Raney nickel were prepared as described in Chapter I.

3. General Reaction Conditions.

(i) With W-7 Raney nickel. - The catalyst (from 125 g of 1:1 nickel-aluminium alloy) was freed from water by washing (by decantation) with methanol (6 x 250 ml), and the amines then added. The remaining methanol was removed by distillation through a fractionating column as described in Chapter I, and the mixture refluxed for 50 hours. In some experiments, all gases issuing from the condenser were passed through 1N hydrochloric acid solution (500 ml) to dissolve any basic volatile material given off. The yield of these compounds (assumed to be mostly ammonia) was determined by back-titration of this solution with 1N sodium hydroxide solution. After completion of the refluxing period, the solution was filtered through a glass sinter (porosity 4), and the catalyst washed with hot methanol (250 ml) and hot benzene (250 ml). Filtrate and washings were combined, the solvents removed, and the liquid residue distilled through a Claisen distillation apparatus at approximately 15 mm pressure. Analysis of the distillates were carried out by gas chromatography. The residues from the distillations were further investigated by column chromatography.

(ii) With degassed Raney nickel. - After cooling the catalyst (from 125 g of alloy) and closing the apparatus' connections to the water pumps, the amines were added (thoroughly wetting the nickel) before admitting air to the apparatus. The mixture was then refluxed for 50 hours. In some experiments, small samples (ca. 1 ml) were taken from the reaction mixture at two hourly intervals for the first 12 hours, and then at 24, 26, and 48 hours. These samples were investigated by gas chromatography using suitable standard mixtures for calibration.

The reactions were analyzed for products as described in 3(i).

(iii) With degassed Raney nickel in xylene. - The catalyst (from 62.5 g of alloy) was cooled, and sulphure-free xylene (50 ml) added while the water pump connections were closed. The catalyst was covered with solvent and the apparatus opened to the atmosphere. The aromatic amine was added to the mixture and refluxed while the aliphatic amine was added dropwise over a period of 1.5 hours. The mixture was then refluxed for 30 hours.

Filtration and distillation of the products was carried out as described in 3(i).

4. Specific Reactions.

(i) Aniline.

(a) With W-7 Raney nickel. - Aniline (93 g) was treated with W-7 Raney nickel as described. Distillation of the reaction products gave aniline, b.p. 80-85°/21 mm (43 g) and N-cyclohexylaniline, b.p. 155-160°/21 mm (13 g) showing traces of dicyclohexylamine, leaving a dark brown oily residue (6 g) which was not further investigated. Back titration of the hydrochloric acid solution indicated 0.20 moles of ammonia had been liberated.

(b) With degassed Raney nickel. - Aniline (100 g) was treated with degassed Raney nickel as described. Distillation of reaction products gave (a) aniline, b.p. 80-82°/15 mm (54 g), (b) an oil, b.p. 82-140°/15 mm (8.6 g), and (c) N-cyclohexylaniline, b.p. 145°/15 mm (9.5 g). Fraction (b) was a mixture of aniline (65%) o-toluidine (30%), and traces of N-cyclohexylaniline. The dark solid residue (5.8 g) from this distillation was separated into basic (3.1 g) and neutral (2.7 g) fractions with 5% aqueous hydrochloric acid/ether. The basic residue contained N-cyclohexylaniline (1 g), and tarry intractable material. The neutral fraction was chromatographed on alumina to give diphenylamine (1.26 g), m.p. and mixed m.p., 54° and carbazole (0.57 g), m.p. and mixed m.p., 245°. The catalyst after filtration was extracted exhaustively in a Soxhlet apparatus with benzene, which on evaporation left a brown residue (0.25 g). No pure components were isolated after chromatography on alumina, but thin-layer chromatography showed compounds with R_f values corresponding to diphenylamine, indole, and carbazole. The presence of indole was also indicated by a deep red colouration with p-dimethylaminobenzaldehyde.[6]

(ii) Cyclohexylamine.

(a) With W-7 Raney nickel. - Cyclohexylamine (99 g) was refluxed over W-7 Raney nickel for 50 hours. The solution was filtered as before, and on distillation gave (a) an oil b.p. 90-120°/21 mm (7 g), and (b) N-cyclohexylaniline, b.p. 156-158°/21 mm (35 g). Fraction (a) was shown by gas chromatography to be aniline (62%) and dicyclohexylamine. The light brown residue (2 g) from this distillation was not investigated further. Titration of the hydrochloric acid solution indicated 0.53 moles of ammonia was given off.

(b) With degassed Raney nickel. - Cyclohexylamine (99 g) was refluxed with degassed Raney nickel for 50 hours as described. Filtration and distillation of the crude reaction mixture gave (a) a colourless oil, b.p. 110-150°/19 mm (12.5 g), (b) N-cyclohexylaniline, b.p. 155°/19 mm (30 g) and a brown solid residue (3.8 g). Fraction (a) contained aniline (20%), dicyclohexylamine (7%), and N-cyclohexylaniline, all identified by gas chromatography. The ammonia collected was equivalent to 0.56 moles. The residue from the distillation was separated into basic (1.0 g) and neutral (2.5 g) fractions. The neutral residue was chromatographed on silicic acid and gave diphenylamine (0.4 g), m.p. and mixed m.p. 54°

and carbazole (1.2 g), m.p. and mixed m.p. 243-245°. The basic residue contained only N-cyclohexylaniline and tars.

(iii) Aniline and Cyclohexylamine.

(a) With W-7 Raney nickel. - A mixture of aniline (56 g, 0.5 moles) and cyclohexylamine (59.5 g, 0.5 moles) was refluxed over W-7 Raney nickel for 50 hours. Filtration and distillation of the resulting mixture gave (a) an oil b.p., 90-115°/19 mm (8 g) which was shown by gas chromatography to be aniline (ca. 95%) with traces of o-toluidine and dicyclohexylamine, and (b) N-cyclohexylaniline, b.p., 155-160°/19 mm (41 g). The dark brown solid residue (6 g) was not further investigated.

(b) With degassed Raney nickel. - Cyclohexylamine (12.5 g, 0.125 moles) was added dropwise over a period of 1.5 hours to a refluxing solution of aniline (12.0 g, 0.125 moles) in sulphure-free xylene over degassed Raney nickel (prepared from 62.5 g of alloy). The solution was refluxed for 30 hours and products recovered as before. Distillation gave (a) an oil b.p.80-100°/15 mm (0.5 g) which was shown by gas chromatography to be a mixture of xylene, aniline and dicyclohexylamine, and (b) N-cyclohexylaniline, b.p. 100°/1.2 mm (13.5 g). The residue (0.3 g) was chromatographed on alumina, but no pure products were isolated.

(iv) N-cyclohexylaniline with degassed Raney nickel. - N-cyclohexylaniline (100 g) was refluxed with degassed Raney nickel for 50 hours and the products recovered as described. Distillation gave (a) N-cyclohexylaniline b.p. 140-150°/16 mm (70.7 g) which was shown by gas chromatography to be contaminated by traces ($<5\%$ by area) of aniline, dicyclohexylamine and five other minor components, and (b) a light yellow solid residue (3.5 g) which was separated into basic (1.0 g) and neutral (2.2 g) fractions. Chromatography of the neutral residue on alumina gave diphenylamine (1.0 g), m.p. and mixed m.p., 54° and carbazole (1.1 g), m.p. and mixed m.p. 244°. The basic fraction was starting material.

(v) α-Naphthylamine with degassed Raney nickel. - α-Naphthylamine (71.5 g) was added to the catalyst (prepared from 62.5 g of alloy) with sulphur-free benzene (25 mls). The benzene was distilled from the reaction mixture which was then refluxed for 50 hours. Recovery of the reaction mixture was as before, and distillation gave (a) a white solid, (6.5 g), sublimed at 50-100°/0.8 mm identified by ultraviolet absorption and gas chromatography as naphthalene, m.p. 77-80°, and (b) α-naphthylamine (50.2 g), b.p. 116-118°/0.8 mm. The black solid residue (7.0 g) was chromatographed on alumina, but gave only further starting material (4 g) and highly coloured polymeric material.

(vi) o-Toluidine with degassed Raney nickel. - o-Toluidine (150 g) was treated with catalyst as previously described. Distillation of the crude reaction mixture gave (a) o-toluidine (56.3 g), b.p. 95-102°/25 mm which was shown by gas chromatography to contain aniline (5%) and traces of 2,6-dimethylaniline, and (b) an oil, b.p. 102-166°/25 mm, (23 g) shown by gas chromatography to be a mixture of o-toluidine (80%), 2,6-dimethylaniline (15%) and N-cyclohexylaniline, and (c) an oil b.p. 166-170°/25 mm (20 g) shown to be a mixture of N-cyclohexylaniline (60%), N-cyclohexyl-o-toluidine (35%) and traces of two other compounds with longer retention times. The black tarry residue (13.3 g) was divided into basic (5.9 g) and neutral (7.1 g) fractions with 5% hydrochloric acid solution/ether. Chromatography of the neutral residue on silicic acid gave, on elution with hexane, (a) polymethylene, m.p. 47-49° (0.119 g), (b) a brown solid, m.p. 35-40° (0.93 g) shown by thin-layer chromatography and colouration with p-dimethylaminobenzaldehyde[6] to be a mixture of indole and 3-methylindole, (c) indole, m.p. and mixed m.p. 52°C (1.88 g). Elution with benzene gave (d) a white solid, m.p. 190-200° (0.10 g) and (e) a dark red oil (1.08 g), the infrared spectrum showing a carbonyl stretching frequency of 1715 cm^{-1}. The oil (e) was characterized as 2-methylcyclohexanone by its 2,4-dinitrophenylhydrazone derivative, m.p. and mixed m.p. 136°. The white solid (d) had an n.m.r. spectrum very similar to carbazole with a small singlet ($<$ 1 proton) at 7.45. Gas chromatography indicated a mixture consisting mostly of carbazole (ca. 86%) and at least one other component. Fractional recrystallization failed to yield any pure compounds.

(vii) o-Toluidine and 2-methylcyclohexylamine with degassed Raney nickel. - A mixture of 2-methylcyclohexylamine (40 g) and o-toluidine (37.5 g) was refluxed for 50 hours over the catalyst.

Filtration and distillation as before gave (a) an oil b.p. 105-115°/15 mm (10 g), (b) an oil b.p. 60-100°/2.0 mm (15 g), and (c) a yellow oil b.p. 110-120°/2.0 mm (35 g). Gas chromatographic analysis of these fractions showed (a) was o-toluidine (80%), aniline (15%) and 2,6-dimethylaniline. Fraction (b) was o-toluidine (50%) and 2,6-dimethylaniline (45%) with traces of two other components, while (c) was N-cyclohexylaniline (55%) and N-cyclohexyl-o-toluidine (40%) with small quantities (ca 5%) of two other components with longer retention times.

(viii) o-Toluidine and cyclohexylamine with degassed Raney nickel. - o-Toluidine (53 g, 0.5 mole) and cyclohexylamine (49.5 g, 0.5 mole) were refluxed over the catalyst for 50 hours. The crude products were filtered and distilled to give (a) an oil b.p. 80-100°/15 mm (5 g), (b) an oil b.p. 100-160°/15 mm (20 g) and (c) an oil b.p. 100-120°/2.0 mm (45 g). The oil (a) was shown by gas chromatography to be o-toluidine (80%) and aniline. Fraction (b) was a mixture of o-toluidine (20%), 2,6-dimethylaniline (23%), N-cyclohexylaniline (57%) with traces of dicyclohexylamine. Fraction (c) was N-cyclohexylaniline (73%), and N-cyclohexyl-o-toluidine, purified by distillation through an 8 in. Vigreux column, b.p. 110°/0.9 mm (lit.[157] 230°/50 mm), (Found: C, 82.8; H, 9.8; N, 8.0. Calc. for $C_{13}H_{19}N$: C, 82.5; H, 10.1; N, 7.4%). The n.m.r. spectra showed a methyl absorption at 7.98 (singlet).

(ix) m-Toluidine with degassed Raney nickel. - m-Toluidine (110 g) was refluxed with degassed Raney nickel for 50 hours as previously described, and the reaction products filtered. Distillation gave (a) m-toluidine b.p. 98-100°/20 mm (80 g), (b) an oil b.p., 100-145°/15 mm (12 g) shown by gas chromatography to consist of m-toluidine (35%), 2,5-dimethylaniline (45%) and N-(3-methylcyclohexyl)-m-toluidine, and (c) N-(3-methylcyclohexyl)-m-toluidine b.p., 120°/0.9 mm (3 g). The thick black tarry residue (7.1 g) was divided into basic (4.5 g) and neutral (2.0 g) fractions. The neutral residue was chromatographed on alumina which gave polymethylene (0.04 g) m.p. 48°, and 3-methylcyclohexanone (0.4 g) identified as its 2,4-dinitrophenylhydrazone derivative, m.p. and mixed m.p., 155° on elution with hexane. Eluting with 20% ether/hexane gave a white solid (0.12 g) which was crystallized from hexane, m.p. 210-220°. Thin-layer chromatography and gas chromatography showed this to be a mixture of carbazole and at least one other component.

(x) m-Toluidine and 3-methylcyclohexylamine with degassed Raney nickel. - A mixture of 3-methylcyclohexylamine (25 g) and m-toluidine (22 g) was added to degassed Raney nickel (from 62.5 g of alloy), and refluxed for 50 hours. Filtration and distillation as before gave (a) an oil b.p., 100-145°/16 mm (7.0 g) and (b) N-(3-methylcyclohexyl)-m-toluidine b.p. 115-120°/0.8 mm (22 g). The fraction (a) was shown by gas chromatography to consist of m-toluidine (85%), 2,5-dimethylaniline and traces of two other components. Fraction (b) was purified by distillation through an 8 in. Vigreux column to give pure N-(3-methylcyclohexyl)-m-toluidine b.p. 130-131°/2.2 mm. (Found: C, 82.6; H, 10.3; N, 6.9. $C_{14}H_{21}N$ requires: C, 82.7; H, 10.4; N, 6.9%). The n.m.r. spectrum

(CCl_4) showed aliphatic methyl absorption at 9.08 (doublet, J = 6 c/s) and an aromatic methyl at 7.78 (singlet).

The light brown solid residue was chromatographed on alumina to give (a) a yellow oil (1.18 g) and (b) a white solid (0.28 g), m.p. 220-230°. The yellow oil (a) was separated into basic (0.58 g) and neutral (0.54 g) fractions. The neutral fraction was rechromatographed on silicic acid to yield polymethylene m.p. 49-50° (0.05 g) and a clear oil (0.4 g) which could not be crystallized, and having an ultraviolet absorption similar to diphenylamine. The white solid (b) was shown by gas chromatography to be a mixture of a carbazole (29%) and at least one other component. The second component was separated from carbazole by preparative thin-layer chromatography and crystallized from hexane as colourless plates of dimethylcarbazole, m.p. 228-229° (Found: C, 85.4; H, 6.5; N, 7.2. $C_{14}H_{13}N$ requires: C, 86.1; H, 6.7; N, 7.2%). The mass spectrum had a molecular ion and base peak at m/e 195, which lost two successive methyl groups (56% and 10% of base peak). The n.m.r. spectrum ($CDCl_3$) showed aromatic methyl absorption at 7.53 and 7.57 (6 protons) and in acetone/carbon tetrachloride showed aromatic proton absorption from 1.95-3.13 (3 protons).

(xi) 3-Methylcyclohexylamine with degassed Raney nickel. - 3-Methylcyclohexylamine (22 g) was refluxed in methylcyclohexane (25 ml) over degassed Raney nickel (from 62.5 g of alloy) for 50 hours and the catalyst then removed as before. Distillation gave (a) an oil b.p. 170-180°/14 mm (2.4 g) and (b) N-(3-methylcyclohexyl)-m-toluidine, b.p. 190-195°/14 mm

(12.5 g). The oil (a) was shown by gas chromatography to be N-(3-methylcyclohexyl)-m-toluidine (ca. 50%), traces of m-toluidine and aniline, and a compound (ca. 50%) with a retention time very similar to dicyclohexylamine. The dark residue (0.4 g) could not be separated into any pure components.

(xii) m-Toluidine and cyclohexylamine with degassed Raney nickel. - A mixture of m-toluidine (53 g, 0.5 moles) and cyclohexylamine (49.5 g, 0.5 moles) was refluxed over the catalyst as before. Small samples (ca. 1ml) were taken at various intervals during the reaction, and were investigated by gas chromatography. Products were filtered and distilled as previously described which gave (a) an oil b.p. 90-130°/15 mm (14 g), (b) an oil b.p. 80-100°/1.8 mm (15 g) and (c) a yellow oil b.p. 100-120°/1.8 mm (40 g). Gas chromatography showed that fraction (a) was aniline and m-toluidine (53%) and fraction (b) was m-toluidine (45%), 2,5-dimethylaniline (40%) and dicyclohexylamine (15%) with traces of aniline. Fraction (c) contained N-cyclohexylaniline (35%) and N-cyclohexyl-m-toluidine (65%) with traces of N-(3-methylcyclohexyl)aniline and N-(3-methylcyclohexyl)-m-toluidine. Distillation of (c) through an 8 in. Vigreux column separated pure N-cyclohexyl-m-toluidine as a colourless oil b.p. 105°/0.3 mm (lit.[157] b.p. 200°/30 mm) (Found: C, 82.5; H, 9.8; N, 8.2. Calc. for $C_{13}H_{15}N$: C, 82.5; H, 10.1; N, 7.4%). The n.m.r. spectrum showed an aromatic methyl absorption at 7.82 (singlet).

(xiii) Aniline and 3-methylcyclohexylamine with degassed Raney nickel in xylene. - Aniline (12.0 g, 0.13 mole) dissolved in sulphur-free xylene (40 ml) was refluxed over degassed Raney nickel (from 62.5 g of alloy) and 3-methylcyclohexylamine (15 g, 0.13 mole) added slowly as previously described. The mixture was refluxed for 50 hours and the catalyst then removed by filtration. Distillation of the crude reaction mixture gave (a) an oil b.p. 50-100°/1.5 mm (1.1 g) shown by gas chromatography to be N-(3-methylcyclohexyl)aniline (50%), aniline (25%) and m-toluidine, and (b) N-(3-methylcyclohexyl)aniline, b.p. 119-121°/1.5 mm (19.5 g) with traces of N-cyclohexylaniline and N-(3-methylcyclohexyl)-m-toluidine. N-(3-methylcyclohexyl)aniline was purified by distillation of fraction (b) through an 8 in. Vigreux column to give a colourless oil, b.p. 119°/1.5 mm (Found: C, 82.0; H, 9.7; N, 8.0. $C_{13}H_{19}N$ requires: C, 82.5; H, 10.1; N, 7.4%). The n.m.r. spectrum showed a methyl absorption at 9.09 (doublet, J = 5.5 c/s).

(xiv) p-Toluidine with degassed Raney nickel. - p-Toluidine (170 g) was warmed and added as a liquid to the catalyst. The mixture was refluxed for 50 hours and filtered as before, and on distilling gave (a) p-toluidine, b.p. 100-140°/26 mm (104 g) contaminated with traces of two other components, (b) a light yellow oil b.p. 140-190°/26 mm (30 g) containing N-(4-methylcyclohexyl)-p-toluidine (ca. 50%) and three other compounds. The dark red liquid residue (11.2 g) was divided into basic (6.9 g) and neutral (3.4 g) fractions. Chromatography of the neutral residue on alumina gave (a) polymethylene m.p., 47-49° (0.02 g), (b) 4-methylcyclohexanone (0.08 g) characterized by its 2,4-dinitrophenylhydrazone m.p. and mixed m.p. 134°, (c) 4,4'-dimethyldiphenylamine (0.04 g) crystallized from aqueous ethanol, m.p. 78-79° (lit.[154] 79°), and (d) a white solid (0.14 g) m.p. 200-205°. Gas chromatographic analysis of the solid (d) showed it to be carbazole (25%) and at least one other component. The basic residue was not investigated.

(xv) *p-Toluidine and 4-methylcyclohexylamine with degassed Raney nickel in xylene.* - 4-Methylcyclohexylamine (15 g, 0.13 moles) was added over a period of 1.5 hours to a refluxing solution of *p*-toluidine (145 g) in sulphure-free xylene (50 ml) over degassed Raney nickel (from 62.5 g of alloy). The solution was filtered and distilled as described to give (a) an oil b.p. 90-150°/16 mm (1.4 g) containing *p*-toluidine (*ca.* 50%) and two other components, and (b) *N*-(4-methylcyclohexyl)-*p*-toluidine (17.6 g), b.p. 120-126°/12 mm which was purified by chromatography on 200 g of alumina and recrystallized from aqueous ethanol (1:5) to give colourless plates m.p. 50-51°[158] (Found: C, 82.7; H, 10.3; N, 6.7. $C_{14}H_{21}N$ requires: C, 82.7; H, 10.4; N, 6.9%). The n.m.r. spectrum showed absorption due to an aliphatic methyl group at 9.10 (doublet, J = 5.1 cps) and an aromatic methyl group at 7.80 (singlet).

The black solid residue (0.5 g) was not investigated.

(xvi) *3-Aminopyridine with degassed Raney nickel.* - 3-Aminopyridine (40 g) dissolved in sulphure-free benzene (50 ml) was added to degassed

Raney nickel (from 62.5 g of alloy), the benzene evaporated, and the remainder refluxed for 60 hours. The mixture was filtered as previously described, and on distillation gave pyridine b.p. 50-60°/45 mm (1.0 g) and starting material b.p., 140-150°/28 mm (30 g). The dark brown residue (3 g) was chromatographed on silicic acid and gave a light yellow solid when eluted with 20% ether/benzene. Crystallization from petroleum ether (b.p. 60-80°) gave yellow needles (0.025 g) m.p. 131-132° (lit.[143] m.p. 132.5-133.5°). The n.m.r. spectrum showed absorption for four protons (N-H) at 3.87 (broad), four aromatic protons at 3.00 (doublet, J = 3 cps) and two aromatic protons at 2.04 (triplet, J = 3 cps).

(xvii) <u>3-Aminopiperidine with degassed Raney nickel in methylcyclohexane.</u> - 3-Aminopiperidine (23 g) was added to a mixture of methylcyclohexane (45 ml) and degassed Raney nickel (from 62.5 g of alloy), and then refluxed for 50 hours. This was filtered as before and the solvents evaporated leaving a dark tarry mass. Extraction of this with ether, evaporation of the ether, and distillation of the residue gave (a) 3-aminopiperidine b.p. 80°/14 mm (0.4 g) and (b) a yellow oil b.p., 176-178°/14 mm (9.4 g). The black residual tar (8.1 g) was chromatographed on alumina but no pure compounds were isolated. The yellow oil (b) was purified by distillation to give 2,2'-bipiperidyl b.p., 180-180.5°/16 mm (lit.[155] b.p. 259°). The mass spectrum showed a molecular ion at m/e 168 (7%) and an (m-1) peak (50%). (Found: C, 70.7; H, 12.2; N, 17.3. Calc. for $C_{10}H_{20}N_2$: C, 71.4; H, 12.0; N, 16.7%).

(xviii) 1,2-Diaminocyclohexane with degassed Raney nickel in xylene. - 1,2-Diaminocyclohexane (10 g) dissolved in sulphur-free xylene (50 ml) was added to degassed Raney nickel (from 62.5 g of alloy) and refluxed for 50 hours. Recovery of the products as before and evaporation of the solvents left a dark purple solid (7.5 g) which was chromatographed on alumina. Elution with hexane gave N-cyclohexylaniline (2.3 g) identified by its infrared absorption and gas chromatography. Ether/hexane eluants gave phenazine (1.8 g) recrystallized from hexane as apricot yellow needles, m.p. and mixed m.p. 172°, and trans-1,2,3,4,4a,5,10,10a-octahydrophenazine (0.5 g), crystallized from hexane as colourless needles, m.p. 155° (lit.[156] 156°). (Found: C, 76.4; H, 8.4; N, 14.7. Calc. for $C_{12}H_{16}N_2$: C, 76.5; H, 8.6; N, 14.9%). The mass spectrum showed a molecular ion at m/e 188 (80%). o-Phenylenediamine (0.29 g) was eluted with ethanol/hexane.

(xix) o-Phenylenediamine and cyclohexylamine with degassed Raney nickel in xylene. - o-Phenylenediamine (21 g, 0.2 mole) in sulphur-free xylene (50 ml) was refluxed over degassed Raney nickel (from 62.5 g of alloy) and cyclohexylamine (33 g, 0.33 mole) added over a period of one hour. After 50 hours refluxing, the solution was filtered and distilled as previously described, giving aniline, b.p. 80-85°/15 mm (7.9 g), o-toluidine 85-135°/15 mm (6.5 g), dicyclohexylamine b.p. 135-140°/15 mm (6.9 g), and N-cyclohexylaniline b.p. 150-151°/15 mm (21.5 g), all characterized by gas chromatography and infrared spectra. The black solid residue (3.8 g) was chromatographed on alumina which yielded diphenylamine (0.68 g) m.p. and mixed m.p. 54°, carbazole (0.21 g) m.p. and mixed m.p. 243-244°, and _o_-phenylenediamine (2.4 g).

(xx) _m-Phenylenediamine and cyclohexylamine with degassed Raney nickel in xylene_. - _m_-Phenylenediamine (21 g) was treated with degassed Raney nickel and cyclohexylamine (33 g) in sulphure-free xylene as in part (xix). Chromatography of the crude filtered reaction mixture on alumina gave cyclohexanone (0.25 g), characterized by its 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 162°, and _N_-cyclohexylaniline (9.1 g) characterized by its infrared absorption and gas chromatography, both eluted with hexane. Ether/hexane (1:10) eluted a dark thick tar (16 g) which was distilled and gave (a) _N_-cyclohexylaniline, b.p. 50°/0.6 mm (1.5 g) and (b) a viscous yellow oil b.p. 156-158°/1.0 mm (10.2 g). The black residue (4.1 g) was not investigated further. The yellow oil (b) decomposed to a black solid before analysis could be obtained. The n.m.r. spectrum (CCl_4) showed a broad absorption for 20 aliphatic protons at 7.82-9.2, a broad peak (four protons) at 6.77, and three aromatic protons absorbed at 4.13-4.35 (multiplet) and one aromatic proton at 3.26 (triplet, J = 7.5 cps). The infrared spectrum (CCl_4) showed peaks at 3380, 3040, 2930, 2860, 1610, and 1600 cm^{-1}. The ultraviolet absorption was similar to _m_-phenylenediamine, but bathochromically shifted by 5 mu.

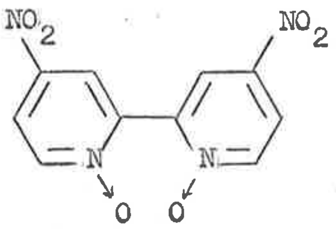
(xxi) p-Phenylenediamine and cyclohexylamine with degassed Raney nickel in Xylene. - Cyclohexylamine (33 g) was added to refluxing p-phenylenediamine (21 g) in sulphur-free xylene over degassed Raney nickel as in part (xix). After 50 hours the catalyst was removed, and distillation of the resulting mixture gave (a) aniline b.p. 80-85°/16 mm (4 g), (b) a mixture b.p. 110-150°/16 mm (10.2 g) of N-cyclohexylaniline (20%), and dicyclohexylamine, (c) N-cyclohexylaniline, b.p. 99-102°/1.0 mm (7.1 g), (d) p-phenylenediamine, sublimed 110-150°/1.0 mm (0.4 g), (e) a yellow oil b.p. 160-165°/1.0 mm (4.5 g) and a black liquid residue (8 g). The black residue was shown by thin-layer chromatography to consist mainly of the oil (d). Redistillation of this oil gave N,N'-dicyclohexyl-p-phenylenediamine as a pale yellow oil, b.p. 164-165°/0.9 mm, (lit.[159] m.p. 55°) which on standing at room temperature for two hours turned dark red, and was black after one day. The n.m.r. spectrum of the freshly distilled sample showed absorption for four aromatic protons at 3.64 (doublet, $J = 2.5$ cps), a broad peak at 7.05 (four protons), and a broad absorption from 7.75-9.17 for 20 aliphatic protons. The mass spectrum showed a molecular peak at m/e 272 (0.2% of base peak).

CHAPTER III

Synthesis of monosubstituted 2,2'-bipyridyls.

Until the introduction in 1956 of Raney nickel as a catalyst for the dimerization of pyridine to 2,2'-bipyridyl,[6] the preparation of this compound and its derivatives was a laborious procedure usually involving the Ullmann reaction of halo-pyridines with copper catalysts.[160,161] With degassed Raney nickel, pyridine couples exclusively in the α-position, giving a relatively simple pathway to large quantities of bipyridyl, greatly facilitating further work on this system. Subsequently, this reaction was adapted very successfully to the synthesis of symmetrically disubstituted 2,2'-bipyridyls.[144]

This reaction was limited by the fact that substituents which react with the catalyst could not be incorporated, and those with electron attracting properties gave much lower yields of the required dimer.[143] Haginawa,[162] and concurrently Maerker and Case,[163] developed a method of preparing 2,2'-bipyridyl-1,1'-dioxide from 2,2'-bipyridyl, which gave, on nitration, 4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (63), and hence the route to a large number of disubstituted 2,2'-bipyridyls. Recently, Case and Lesser[164] have applied this same sequence of reactions to the preparation of 4,4'-disubstituted-2,2'-biquinolyls.



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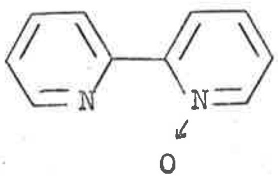

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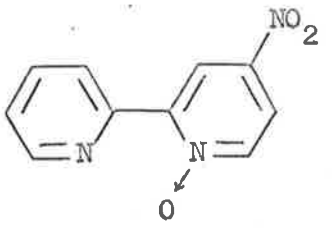
However, a much greater problem remained in that unsymmetrical or mono-substituted bipyridyls could not be synthesized successfully from bipyridyl. Burstall,[165] in 1938, showed that bromination of 2,2'-bipyridyl at 500° gave a mixture of 6-bromo- and 6,6'-dibromo-2,2'-bipyridyl in poor yields. Phenyllithium was also found to substitute in the 6-position to give 6-phenyl-2,2'-bipyridyl,[166] and 4-methyl-2,2'-bipyridyl was reported by Cislak,[167] using sodio-pyridine and a quaternary salt of γ-picoline-1-oxide, but no yields or methods were described. The only other examples of mono-substituted 2,2'-bipyridyls have been reported by Leont'ev, Stroshchenko, Mangutova and Dadykov[168] who measured the electronic absorption spectra of 4-cyano- and 4-carboxy-2,2'-bipyridyl, but made no mention of their source.

Hence, the isolation of 4-nitro-2,2'-bipyridyl-1-oxide (65) by Sasse[70] was of great importance as the first major break-through in the preparation of 4-substituted 2,2'-bipyridyls. Bipyridyl-1-oxide (64) had been reported before by Murase,[169] as a by-product from the preparation of 2,2'-bipyridyl-1,1'-dioxide, but he ignored the mono-oxide, apparently not realizing its potential, and developed conditions for a greater yield of the dioxide. Sasse oxidized 2,2'-bipyridyl at 50° with hydrogen peroxide in acetic acid, and using a method similar to that of den Hertog and Combie,[170] removed the excess acids and directly nitrated the crude mixture of bipyridyl-N-oxides with fuming nitric acid and sulphuric acid.

This project had, as its aim, the synthesis of a variety of previously unknown 4-substituted 2,2-bipyridyls and their N-oxides, in order that their infrared and ultraviolet spectra and their pKa values could be measured.

The maximum yield (21%) of 4-nitro-2,2'-bipyridyl-1-oxide (65) was obtained with the oxidation procedure at 50° for 12 hours, followed by nitration as described above. By-products include a 10% yield of 4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (63), 34% yield of 4-nitro-2,2'-bipyridyl-1,1'-dioxide (66), and a 7% recovery of starting material.



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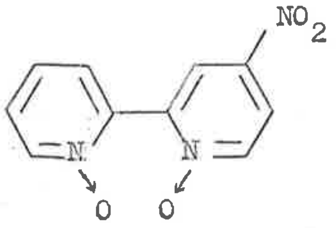

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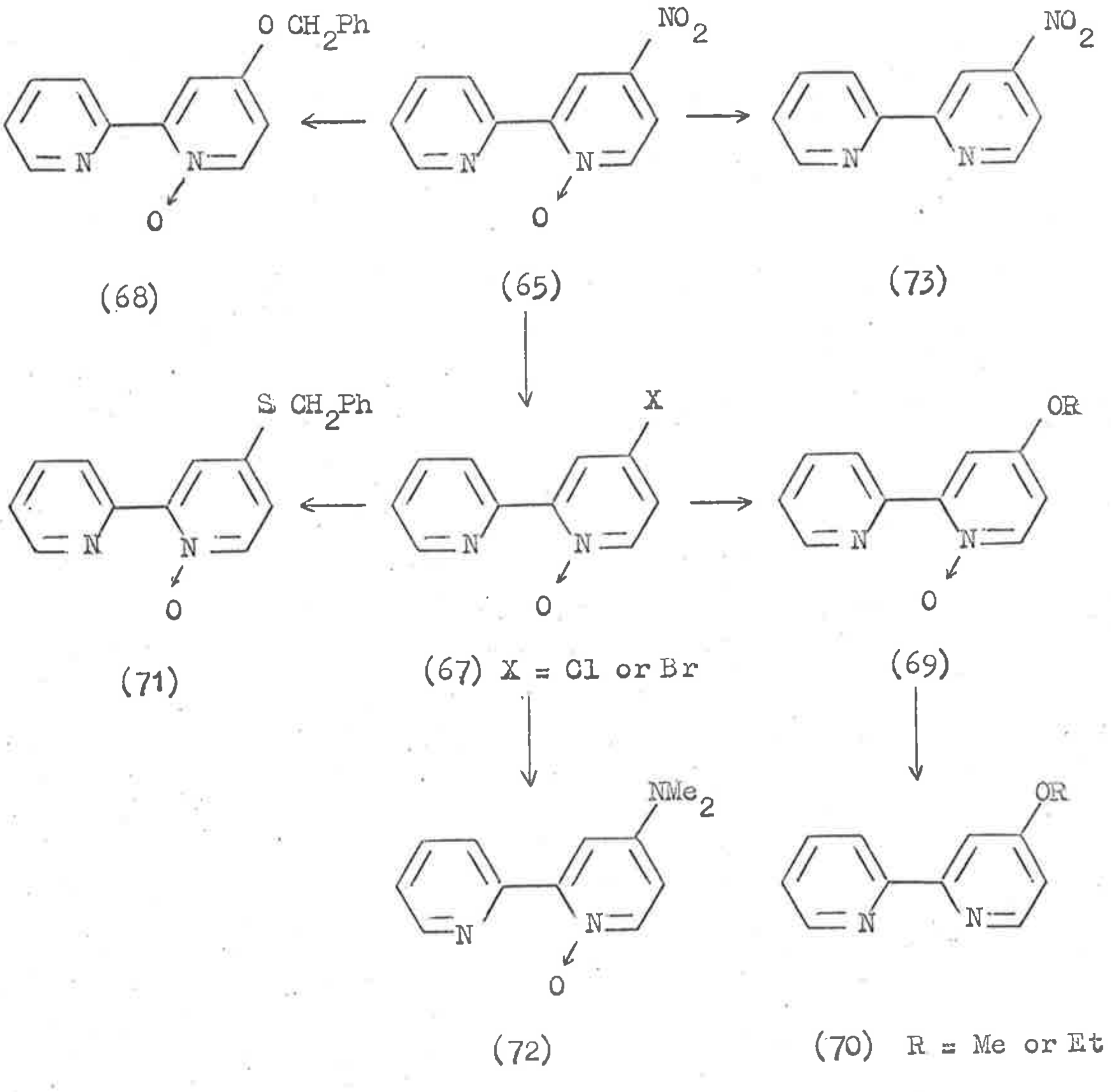
Carrying out the oxidation at a lower temperature or for a shorter time gave decreased yields of bipyridyl-N-oxides and a greater recovery of 2,2'-bipyridyl. Higher temperatures during the reaction increased the yields of di-N-oxides, while longer reaction times had little effect on the overall yields.

4-Nitro-2,2'-bipyridyl-1-oxide (65) was the key starting material to all compounds in this series, but as the nitro group is not a very good leaving group (compared with halogens for example), and as the conversion to 4-chloro-2,2'-bipyridyl-1-oxide (67) was in good yields, most other derivatives were prepared from this latter compound. The chlorine substitution of the nitro group proceeded smoothly using acetyl chloride by a method similar to that used by Maerker and Case,[163] which was found to be also applicable to the preparation of 4-bromo-2,2'-bipyridyl-1-oxide (67: X = Br) by using acetyl bromide. The only compound not prepared from the 4-chloro derivative was 4-benzyloxy-2,2'-bipyridyl-1-oxide (68) (See Scheme 18). Here, better yields were obtained by substitution of the nitro group with sodium benzyloxide in a reaction similar to that used by Ochiai[171] in the pyridine series.

This substitution, and all others with sodium alkoxide in alcohol on the bipyridyl-1-oxide system, proceeded quite smoothly and gave good yields of the 4-alkoxy-2,2'-bipyridyl-1-oxides (69). However, in early experiments in which an excess of sodium was used, products were always contaminated with 4-alkoxy-2,2'-bipyridyl (70), presumably because the N-oxide was reduced by the sodium-alcohol reagent. This was expected in the light of work by Schweizer and O'Neill[172] who deoxygenated pyridine-1-oxide with sodium methoxide in methyltrichloroacetate.

Using an equimolar ratio of reagents, the required N-oxide could be isolated and purified without any difficulty. One attempt to synthesize 4-alkoxy-2,2'-bipyridyl (70) from 4-nitro-2,2'-bipyridyl-1-oxide (65) in one step with a large excess of sodium methoxide, gave only a mixture of starting material, 4-methoxy-2,2'-bipyridyl (70), its 1-oxide (69) and several other compounds which were difficult to separate.



Scheme 18.

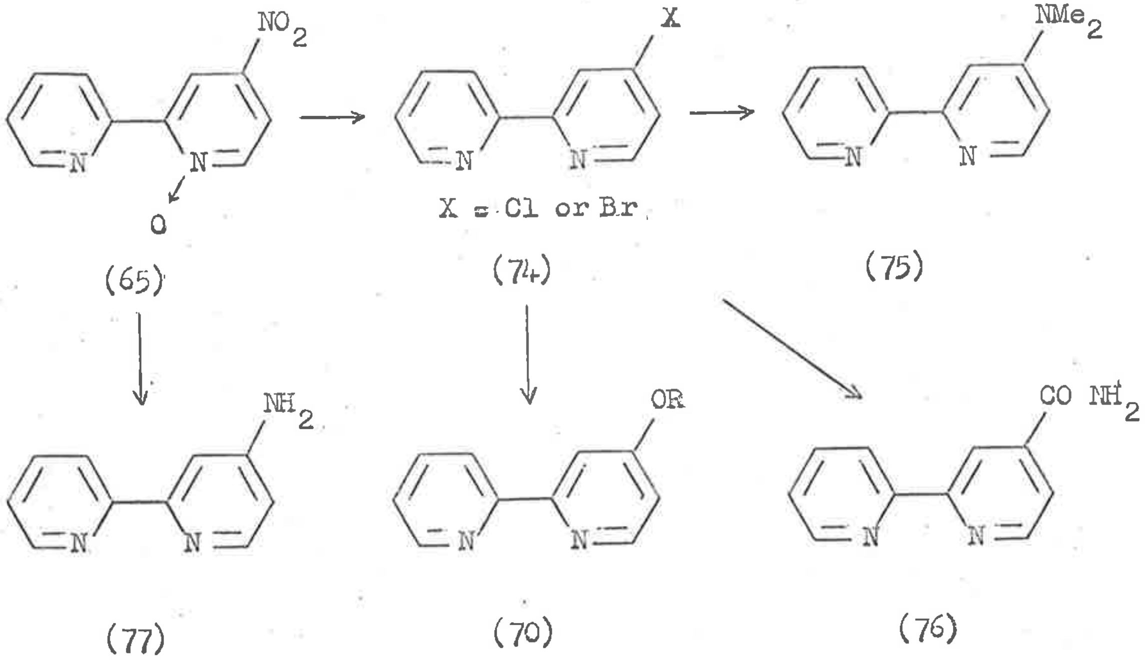
Sodium benzylsulphide was an even better nucleophile than alkoxide ions, and the yield of 4-benzylthio-2,2'-bipyridyl-1-oxide (71) was 80%, compared with 57% for the ethoxy (69; R = Et) and 43% for the methoxy (69; R = Me) derivatives.

The substitution of chlorine with dimethylamine proceeded very smoothly in a sealed tube at 100° to give a hydrochloride salt of the dimethylamino derivative. This was converted to the free base using ammonia, but this 4-dimethylamino-2,2'-bipyridyl-1-oxide was always contaminated with water, even when crystallized from petroleum ether. From analysis figures, freshly crystallized product appeared to contain approximately 1.5 moles of water, while a sample which was dried by standing under reduced pressure for a few hours or by warming, contained about one mole of water. However, this water content was never constant enough to give a consistent analysis. Added evidence for this bound water is given by the n.m.r. spectra. The untreated sample showed a sharp singlet at τ 7.06 (3 protons) corresponding presumably to the 1.5 moles of water, while the treated sample had this peak shifted downfield to τ 6.22 (2 protons) and was much broader. The nature of this water is still unknown. Confirmation of the structure of 4-dimethylamino-2,2'-bipyridyl-1-oxide (72) is provided by the n.m.r. and mass spectra.

De-oxygenation of these bipyridyl-1-oxides was achieved either with phosphorous trichloride in chloroform or by hydrogen over metal catalysts. 4-Nitro-2,2'-bipyridyl-1-oxide (65) was converted to 4-nitro-2,2'-bipyridyl (73) in good yields using phosphorous trichloride with a method similar to that of Maerker and Case,[163] with 4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (63). However better yields were obtained with the mono-N-oxide because of its greater solubility in chloroform.

4-Chloro-2,2'-bipyridyl (74; X = Cl) was prepared very conveniently in one step from 4-nitro-2,2'-bipyridyl-1-oxide (65) by refluxing in a mixture of phosphorous trichloride and acetyl chloride.

This reaction gave about 50% yields and was also applicable to the



Scheme 19.

analogous bromo compounds using phosphorous tribromide and acetyl bromide. The 4-chloro-2,2'-bipyridyl (74) was then used as a convenient starting material for several other compounds (Scheme 19).

4-Ethoxy-2,2'-bipyridyl (70; R = Et) and 4-methoxy-2,2'-bipyridyl (70; R = Me) were prepared in reasonable yields by substitution of the chlorine group by sodium alkoxide. However, a more convenient method of preparation of these compounds involved treatment of 4-alkoxy-2,2'-bipyridyl-1-oxide (69) with W-7 Raney nickel under one atmosphere of hydrogen, although 4-ethoxy-2,2'-bipyridyl (70; R = Et) was only obtained in 33% yield because of difficulty in purification. 4-Benzyloxy-2,2'-bipyridyl (70; R = Ph) was prepared from its 1-oxide (68) by a similar hydrogenation.

Conversion of 4-chloro-2,2'-bipyridyl (74; X = Cl) to 4-dimethylamino-2,2'-bipyridyl (75) by aqueous dimethylamine solution in a sealed tube occurred readily, to give the hydrochloride salt which was hydrolyzed to the free base with ammonia.

Attempts to prepare 4-cyano-2,2'-bipyridyl using sodium cyanide in dimethylsulphoxide on 4-chloro-2,2'-bipyridyl (74 ; X = Cl) failed. Even though the solvent had been dried and distilled from calcium hydride, the only product isolated was 4-carboxamido-2,2'-bipyridyl (76), presumably formed by hydrolysis of 4-cyano-2,2'-bipyridyl. It should be straightforward to convert this amide group into both 4-cyano-2,2'-bipyridyl and 4-carboxy-2,2'-bipyridyl which were reported by Leont'ev, *et.al.*,[168] by dehydration and hydrolysis respectively.

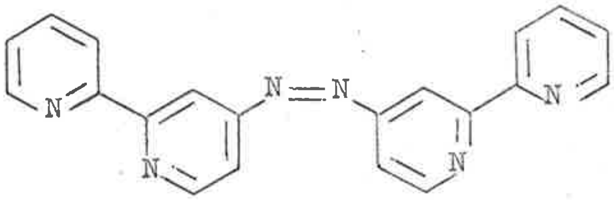
Perhaps the most difficult problem encountered in this series was the reduction of the nitro group in an attempt to prepare 4-amino-2,2'-bipyridyl (77) and its 1-oxide. With 4-nitropyridine-1-oxide, Ochiai[171] states that the N-oxide function was more stable to reduction than the nitro group, except under acidic conditions. Using chemical reducing methods, such as tin in acetic acid, the azoxy and azo dimers were formed exclusively. With catalytic reductions over palladium however, 4-aminopyridine was the product when hydrochloric acid was the solvent, and 4-aminopyridine-1-oxide was obtained in ethanol. 4-Nitroquinoline-1-oxide showed a greater tendency to form the azo dimer, apparently due to greater steric factors preventing catalytic reduction of the azo linkage.

Haginawa[162] claimed to obtain a hydrazo compound with an N-oxide function intact from the reduction of 4,4-dinitro-2,2'-bipyridyl-1,1'-dioxide (63) over catalysts in hydrochloric acid, but made no mention of any amino compounds obtained. The reduction of 4-nitro-3-picoline-1-oxide by Rao[173] with Raney nickel gave considerable quantities of azo compounds, but good yields of the amine were obtained with palladium catalyst in acetic acid.

Consequently, when the reduction of 4-nitro-2,2'-bipyridyl-1-oxide (65) was carried out with W-7 Raney nickel in ethanol, it was not surprising that a mixture of what appeared to be N,N'-bis(4-2,2'-bipyridyl)diimide (78) and the corresponding azoxy compound (79) was obtained.

However, reductions carried out over palladium on carbon both in ethanol and acetic acid produced a very similar mixture, from which no amino compounds were obtained. Maerker and Case[163] achieved the reduction of 4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (63) to 4,4'-diamino-2,2'-bipyridyl with iron in acetic acid. Equivalent conditions with 4-nitro-2,2'-bipyridyl-1-oxide only produced a purple water soluble substance, apparently an iron complex of the bipyridyl.

Reduction with 5% palladium on barium carbonate in ethanol



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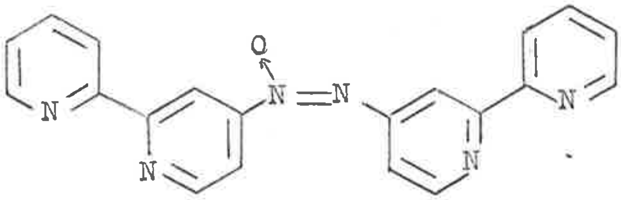
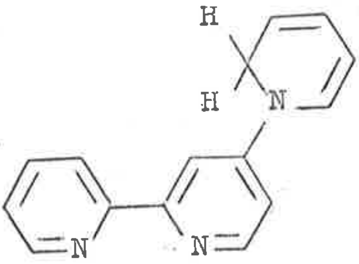


(79)

gave a pale yellow solid in reasonable yield. The structure of this compound has been assigned as 4-(N"-1",2"-dihydropyridyl)-2,2'-bipyridyl (80) on the basis of the mass spectra.



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The mass spectra shows a molecular ion at 235 and a stable (M-1) peak (44%) corresponding to the aromatized system. The n.m.r. spectrum shows the two aliphatic protons adjacent to the tertiary nitrogen as broad peaks at 6.55 and 7.05.

4-Amino-2,2'-bipyridyl (77) was finally obtained by reduction of 4-nitro-2,2'-bipyridyl-1-oxide (65) with sodium borohydride in aqueous methanol catalyzed by a trace of palladium on carbon using a method similar to Neilson, Wood, and Wylie.[174] It is interesting to note that although these authors claim this reaction does not proceed *via* azo compounds, small quantities of the azoxy compounds (79) was obtained from this reduction.

EXPERIMENTAL

1. General.

Nuclear magnetic resonance (n.m.r.) spectra were determined with a Varian DP.60 spectrometer, calibrated relative to tetramethylsilane using side-band technique. Mass spectra were measured with an Hitachi Perkin-Elmer RMU-6D single focusing mass spectrometer. Infrared spectra were measured with a Perkin-Elmer 137 or 237 spectrophotometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

2. Oxidation and Nitration of 2,2'-bipyridyl.

Hydrogen peroxide (75 ml; 0.66 moles of 30% aqueous solution) was added with rapid stirring to a cold solution of 2,2'-bipyridyl (15.0 g; 0.096 moles) in 75 ml of A.R. glacial acetic acid and heated at 50° (± 1°) for 12 hours with occasional shaking. Excess peracetic and acetic acids were removed from the resulting light yellow liquid by distillation at 20 mm pressure on a boiling water-bath. The thick oily residue was cooled in an ice/salt-bath and quickly dissolved in 40 ml of concentrated sulphuric acid (occasionally this addition was very exothermic). A mixture of concentrated sulphuric acid (40 ml) and fuming nitric acid (60 ml) was added to the solution, which was then heated at 100° for two hours. The cooled acidic solution was poured onto 200 g of ice and adjusted to pH 5.5 with sodium hydroxide and sodium bicarbonate solutions. The orange-brown precipitate was filtered off and extracted with boiling ethanol (4 x 250 ml). The remaining yellow solid was 4,4'-dinitro-2,2'-bipyridyl-1,1'-dioxide (2.5 g; 10%) which crystallized from ethanol as yellow needles, m.p. 273-274° (lit.[162] 274°).

The ethanolic extract was concentrated to about 400 ml, and on cooling, yielded 4-nitro-2,2'-bipyridyl-1-oxide (4.4 g; 21%) as yellow needles, m.p. 183°. This sample had the same melting point and identical infrared spectrum as a sample characterized by Sasse.[70]

The aqueous residue (pH 5.5) was basified with ammonia and then continuously extracted with chloroform. The dried chloroform extract yielded a dark red solid on evaporation. Extraction with petroleum ether (b.p. 60-80°) gave impure 2,2'-bipyridyl (1.0 g; 7%). The remaining solid was crystallized from ethanol to give 4-nitro-2,2'-bipyridyl-1,1'-dioxide (7.2 g; 34%), purified further by recrystallization from water as fine yellow needles, m.p. 243°. (Found: C, 51.4; H, 3.1; N, 17.6; O, 27.4. $C_{10}H_7N_3O_4$ requires : C, 51.5; H, 3.0; N, 17.8; O, 27.5%).

3. Preparation of 4-substituted-2,2'-bipyridyl-1-oxides.

(i) 4-Chloro-2,2'-bipyridyl-1-oxide. - 4-Nitro-2,2'-bipyridyl-1-oxide (1.0 g) and acetyl chloride (20 ml) were refluxed on a boiling water-bath for two hours, and then poured onto 50 g of ice. The aqueous solution was neutralized with 10% sodium hydroxide solution and extracted with chloroform (3 x 50 ml). The residue obtained on evaporation of the chloroform was crystallized from petroleum ether (b.p. 60-80°) to yield

4-chloro-2,2'-bipyridyl-1-oxide (0.75 g; 79%) as colourless needles, m.p. 97-98°. (Found: C, 57.5; H, 3.6; N, 13.5. $C_{10}H_7N_2OCl$ requires: C, 58.1; H, 3.4; N, 13.6%).

(ii) 4-Ethoxy-2,2'-bipyridyl-1-oxide. - 4-Chloro-2,2'-bipyridyl-1-oxide (0.5 g) was dissolved in "super-dry" ethanol (10 ml) and freshly cut sodium (0.06 g) added. The solution was refluxed for one hour, and then evaporated to dryness. The residue was extracted with petroleum ether (b.p. 60-80°) (2 x 100 ml) which, on concentration and cooling, yielded white needles of 4-ethoxy-2,2'-bipyridyl-1-oxide (0.2 g; 57%). Recrystallization from petroleum ether gave pure product, m.p. 83-84°. (Found: C, 66.5; H, 5.5; N, 12.7. $C_{12}H_{12}N_2O_2$ requires: C, 66.6; H, 5.6; N, 13.0%). The picrate crystallized from ethanol as yellow needles, m.p. 153°C.

(iii) 4-Methoxy-2,2'-bipyridyl-1-oxide. - This was prepared as colourless needles, m.p. 117°, in 43% yield by the same method as that described for 4-ethoxy-2,2'-bipyridyl-1-oxide. (Found: C, 64.6; H, 5.2; N, 13.5. $C_{11}H_{10}N_2O_2$ requires: C, 65.3; H, 5.0; N, 13.9%). The picrate crystallized from ethanol as yellow needles, m.p. 166°. Found: C, 47.0; H, 3.2. $C_{17}H_{13}N_5O_9$ requires: C, 47.3; H, 3.0%).

(iv) 4-Benzylthio-2,2'-bipyridyl-1-oxide. - 4-Chloro-2,2'-bipyridyl-1-oxide (0.35 g) was added slowly to a solution of sodium benzylsulphide (from 0.21 g of benzylmercaptan and sodium ethoxide from 0.045 g of sodium in 10 ml of "super-dry" ethanol) and then refluxed for one hour. On cooling, 3 g of solid carbon dioxide was added to the yellow liquid, which was filtered and evaporated to dryness. The residue was dissolved in chloroform and centrifuged. On evaporation of the chloroform solution, a dark red liquid containing product and benzylmercaptan remained. The latter was removed by steam distillation, leaving a yellow solid which was crystallized from ethyl acetate to give 4-benzylthio-2,2'-bipyridyl-1-oxide (0.40 g; 80%) as shiny yellow plates, m.p. 139°. (Found: C, 69.8; H, 4.8; N, 9.3. $C_{17}H_{14}N_2OS$ requires: C, 69.4; H, 4.8; N, 9.5%).

(v) 4-Dimethylamino-2,2'-bipyridyl-1-oxide. - 4-Chloro-2,2'-bipyridyl-1-oxide (0.50 g) was suspended in 33% w/v aqueous dimethylamine (10 ml), and heated in a sealed tube at 100° for 24 hours. The aqueous solution was evaporated to dryness, the residue dissolved in chloroform, and ammonia gas bubbled through. The precipitated ammonium chloride was removed and the chloroform solution evaporated to dryness leaving a brown solid which was extracted with boiling petroleum ether (2 x 200 ml). This extract was concentrated to about 50 ml, from which the product crystallized on cooling. Further crystallizations from petroleum ether gave yellow needles, m.p. 131° (phase changes at 80° and 105°). On drying at 65°/0.3 mm for 2 hours over phosphorous pentachloride, no phase changes were observed.

The n.m.r. spectrum ($CDCl_3$) showed a dimethylamino absorption at 6.94 (singlet), seven aromatic protons from 1.12 to 3.48, and a sharp singlet at 7.06 corresponding to three protons. The dried sample had the same spectrum except the latter absorption was shifted to 6.22 (2 protons) and was broader. The mass spectrum showed a molecular peak at m/e 215 (1%) and a strong (M-16) peak at m/e 199 (70%).

(vi) 4-Benzyloxy-2,2'-bipyridyl-1-oxide. - 4-Nitro-2,2'-bipyridyl-1-oxide (0.50 g) was added to a solution of sodium benzyloxide (prepared from 0.06 g of sodium in 15 ml of benzyl alcohol), and left to stand for eight hours. Excess benzyl alcohol was removed by distillation and steam distillation, and the dark red residue extracted with hot petroleum ether, which yielded on cooling, pale yellow needles of 4-benzyloxy-2,2'-bipyridyl-1-oxide, m.p. 138-140° (0.23 g; 36%). (Found: C, 73.4; H, 5.1; N, 9.9. $C_{17}H_{14}N_2O_2$ requires: C, 73.4; H, 5.1; N, 10.1%).

(vii) 4-Bromo-2,2'-bipyridyl-1-oxide. - This was prepared as colourless needles, m.p. 115°, in 83% yield by the same method as described for 4-chloro-2,2'-bipyridyl-1-oxide, using acetyl bromide in place of acetyl chloride. (Found: C, 47.9; H, 3.0; N, 10.9. $C_{10}H_7N_2OBr$ requires: C, 47.7; H, 2.8; N, 11.2%).

4. Preparation of 4-substituted-2,2'-bipyridyls.

(i) 4-Nitro-2,2'-bipyridyl. - 4-Nitro-2,2'-bipyridyl-1-oxide (1.0 g) was added to a solution of phosphorous trichloride (5 g) in anhydrous chloroform (30 ml), and refluxed for one hour. This was poured onto ice and left to stand for eight hours. The mixture was then neutralized and extracted with chloroform which, on evaporation, gave a yellow residue of crude product. 4-Nitro-2,2'-bipyridyl (0.75 g; 81%) was crystallized from ethanol as colourless needles, m.p. 118°. (Found: C, 59.9; H, 4.0; N, 20.5. $C_{10}H_7N_3O_2$ requires: C, 59.7; H, 3.5; N, 20.9%).

(ii) 4-Chloro-2,2'-bipyridyl. - 4-Nitro-2,2'-bipyridyl-1-oxide (1.0 g) acetyl chloride (20 ml) and phosphorous trichloride (5 ml) were refluxed for one hour. The solution was poured onto 100 g of ice and neutralized. The mixture was extracted with chloroform, the chloroform evaporated, and the dark residue extracted with petroleum ether. The petroleum ether extract was evaporated to dryness and the remaining solid sublimed at 60°/0.2 mm to give pure 4-chloro-2,2'-bipyridyl (0.46 g; 55%) as colourless needles, m.p. 84-85°. (Found: C, 62.6; H, 3.7; N, 14.2. $C_{10}H_7N_2Cl$ requires: C, 62.9; H, 3.7; N, 14.7%).

Alternatively, the product may be purified by crystallization from petroleum ether (b.p. 40-60°).

(iii) 4-Bromo-2,2'-bipyridyl. - This was prepared in 46% yield by the same method described for 4-chloro-2,2'-bipyridyl using acetyl bromide and phosphorous tribromide in place of acetyl chloride and phosphorous trichloride. 4-Bromo-2,2'-bipyridyl crystallized from petroleum ether (b.p. 40-60°) as colourless needles, m.p. 52°.

(Found: C, 52.0; H, 3.3; N, 12.0. $C_{10}H_7N_2Br$ requires: C, 51.1; H, 3.0; N, 11.9%).

The picrate crystallized from ethanol as yellow needles, m.p. 174-175°. (Found: C, 41.9; H, 2.2; N, 15.5. $C_{16}H_{10}N_5O_7Br$ requires: C, 41.4; H, 2.2; N, 15.1%.)

(iv) 4-Ethoxy-2,2'-bipyridyl. - 4-Ethoxy-2,2'-bipyridyl-1-oxide (0.50 g) and W-7 Raney nickel (ca. 0.5 g) were shaken in ethanol (25 ml) under one atmosphere of hydrogen for 12 hours (58 cc of hydrogen absorbed). The solution was filtered and evaporated to dryness to leave an oily residue of crude 4-ethoxy-2,2'-bipyridyl, which was purified by distillation at 0.5 mm (bath temperature 140°) to give a clear oil (0.15 g; 33%). The picrate crystallized from ethanol as yellow needles, m.p. 179°. (Found: C, 50.2; H, 3.5; N, 16.4. $C_{18}H_{15}N_5O_8$ requires: C, 50.4; H, 3.5; N, 16.3%).

(v) 4-Methoxy-2,2'-bipyridyl. - This was prepared from 4-chloro-2,2'-bipyridyl (0.5 g) and excess sodium (0.1 g) in methanol by the same method described for 4-methoxy-2,2'-bipyridyl-1-oxide. The product crystallized from petroleum ether (b.p. 40-60°) as colourless needles (0.24 g; 49%), m.p. 61°. (Found: C, 71.2; H, 5.6; N, 15.0. $C_{11}H_{10}N_2O$ requires: C, 71.0; H, 5.4; N, 15.0%).

(vi) 4-Dimethylamino-2,2'-bipyridyl. - 4-Chloro-2,2'-bipyridyl (0.50 g) was suspended in 33% w/v aqueous dimethylamine (10 ml) and heated in a sealed tube at 50° for 12 hours. The aqueous solution was evaporated to dryness, the residue dissolved in chloroform, and ammonia gas bubbled through. Precipitated ammonium chloride was removed, the chloroform solution washed with water, dried, and evaporated to dryness. The residue crystallized from petroleum ether to give 4-dimethylamino-2,2'-bipyridyl (0.21 g; 40%) as pale yellow needles, m.p. 100°. (Found: C, 72.7; H, 6.8; N, 21.2. $C_{12}H_{13}N_3$ requires: C, 72.3; H, 6.6; N, 21.2%).

The picrate crystallized from ethanol as yellow needles, m.p. 208°. (Found: C, 50.3; H, 3.8; N, 19.1. $C_{18}H_{16}N_6O_7$ requires: C, 50.6; H, 3.8; N, 19.6%).

(vii) 4-Carboxamido-2,2'-bipyridyl. - To 4-chloro-2,2'-bipyridyl (1.0 g) dissolved in dimethylsulphoxide (15 ml) (dried and distilled from calcium hydride), was added sodium cyanide (0.5 g). This solution was heated at 180-190° for eight hours. After cooling, water (30 ml) was added, and the solution extracted with ether (3 x 50 ml). The ether solution was washed with water (2 x 100 ml), evaporated to dryness, and the residue extracted with ethanol. On concentration and cooling of this ethanolic solution, 4-carboxamido-2,2'-bipyridyl crystallized as pale yellow plates (0.29 g; 28%), m.p. 200°. (Found: C, 66.5; H, 4.8; N, 20.8. $C_{11}H_9N_3O$ requires: C, 66.3; H, 4.6; N, 21.1%).

(viii) 4-Benzyloxy-2,2'-bipyridyl. - This was prepared from 4-benzyloxy-2,2'-bipyridyl-1-oxide (0.25 g) and phosphorous trichloride, by the same method as described for 4-nitro-2,2'-bipyridyl. 4-Benzyloxy-2,2'-bipyridyl (0.18 g; 77%) crystallized from petroleum ether (b.p. 40-60°) as colourless needles, m.p. 91-92°. (Found: C, 77.4; H, 5.5; N, 10.2. $C_{17}H_{14}N_2O$ requires: C, 77.8; H, 5.4; N, 10.7%).

5. Reduction of Nitro compounds.

(i) 4-Amino-2,2'-bipyridyl and 4-acetylamino-2,2'-bipyridyl. - A suspension of 10% palladium/carbon (0.10 g) in water (50 ml) was added to a solution of sodium borohydride (1.0 g) in water (25 ml), and to this was added a suspension of 4-nitro-2,2'-bipyridyl-1-oxide (0.50 g) in methanol (100 ml). The mixture was warmed slightly and left to stand with occasional shaking for 20 minutes. Excess sodium borohydride was destroyed with hydrochloric acid, the solution filtered and made basic, and then extracted with chloroform (3 x 50 ml) which on evaporation gave a dark brown solid. Crystallization of this solid from ethanol gave orange yellow needles of N,N'-bis 4-(2,2'-bipyridyl) diimide-N-oxide, m.p. and mixed m.p. 198°. Evaporation of the mother liquors to dryness and recrystallization of the remaining solid from petroleum ether, gave 4-amino-2,2'-bipyridyl (0.29 g; 75%) as colourless needles, m.p. 129°. (Found: C, 70.5; H, 5.4; N, 24.1. $C_{10}H_9N_3$ requires: C, 70.2; H, 5.3; N, 24.6%).

Acetylation of this amine with acetic acid-acetic anhydride mixture (1:1) gave 4-acetylamino-2,2'-bipyridyl, which was purified by crystallization from water as pale yellow needles, m.p. 187°. (Found: C, 67.9; H, 5.2; N, 19.8. $C_{12}H_{11}N_3O$ requires: C, 67.6; H, 5.2; N, 19.7%).

(ii) Reduction with Raney nickel and palladium/carbon. - Reduction of 4-nitro-2,2'-bipyridyl-1-oxide with both W-7 Raney nickel and 10% palladium/carbon catalysts in ethanol under one atmosphere of hydrogen at room temperature, gave similar mixtures of products, melting between 190-220°C. Infrared spectra of these mixtures showed no absorption above 3100 cm^{-1}.

Fractional recrystallization from ethanol gave a compound m.p. 198° with analysis figures corresponding closely to $C_{20}H_{14}N_6O$. The n.m.r. spectrum ($CDCl_3$) showed only seven aromatic protons from 1.14 to 2.62. The mass spectrum showed a molecular ion at m/e 354 (1.5%) and a stable (M-16) peak at m/e 338 (36%). Infrared and ultraviolet absorption of this compound and the mixture above were similar.

(iii) Reduction with palladium/barium carbonate. - 4-Nitro-2,2'-bipyridyl-1-oxide (0.50 g), 5% palladium/barium carbonate (0.35 g) and ethanol (100 ml) were stirred under one atmosphere of hydrogen at 45° for 36 hours. The solution was filtered, evaporated to dryness, and the light brown residue crystallized from ethanol to give pale orange needles (0.27 g), m.p. 129°.

The infrared spectrum ($CHCl_3$) showed no absorption above 3100 cm^{-1}. Ultraviolet absorption (ethanol) showed maximum at 382, 368, 278, and 258 mu. The n.m.r. spectrum ($CDCl_3$) showed broad absorption due to two aliphatic protons adjacent to a nitrogen atom at 6.55 and 7.05. The mass spectrum showed a molecular ion at m/e 235 (8%) and a stable (M-1) peak at m/e 234 (44%).

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APPENDIX

Nomenclature of organosilicon compounds.

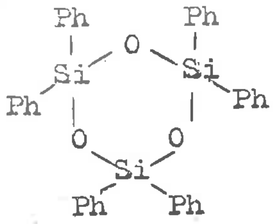
The nomenclature used for the organosilicon compounds in Chapter I is that recommended by the Commission of Nomenclature of Organic Chemistry of the I.U.P.A.C. and adopted by the Chemical Society.[175] The basis for naming all of these compounds is the compound silane, (SiH_4).

Hydroxy derivatives of silane are denoted by the suffix "-ol", as in silanol ($H_3Si{-}OH$), and silanediol ($H_2Si(OH)_2$).

Compounds with silicon-oxygen-silicon bonds are termed siloxanes; for example disiloxane ($H_3Si{-}O{-}SiH_3$).

Any organic derivatives of these compounds have the normal prefix in alphabetical order denoting these substituents. For example, if the four hydrogens of silane are replaced by phenyl or p-tolyl groups, the compounds are called tetraphenylsilane and tetra-(p-tolyl)silane respectively. Similarly, silanol, silanediol, and siloxanes are used as the basis for naming their derivatives. Cyclic compounds have the prefix "cyclo", for example hexphenylcyclotrisiloxane (81). Radicals are named as derivatives of silyl etc., e.g. the triphenylsilyl radical $Ph_3Si{-}$.

(81)



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PRELIMINARY NOTE

The cleavage of tetraphenylsilane by Raney nickel

Raney nickel catalysts have been used frequently to hydrogenate organic groups bonded to silicon[1]. A relevant example[2] is the preparation of tetracyclohexylsilane by the hydrogenation of tetraphenylsilane in the presence of W-7 Raney nickel at 100° and 60–100 atm.

We have found that tetraphenylsilane reacts with excess Raney nickel at atmospheric pressure and at temperatures between *ca.* 20° and 101° to give benzene and cyclohexane. Thus, a solution of tetraphenylsilane (0.018 mole) in boiling dioxane (200 ml; containing *ca.* 10% methanol) was treated for four hours with W-7 Raney nickel[3] (prepared from 125 g of 1:1 nickel–aluminium alloy; washed first with methanol and then with dioxane) to give 17% benzene and 49% cyclohexane*. The same quantity of catalyst reacted with 0.015 mole of tetraphenylsilane at room temperature during 48 hours to give 35% benzene and 2% cyclohexane*; 60% of the silane was recovered. Catalysts containing less hydrogen (*e.g.*, W-1 Raney nickel[4]) gave more benzene and less cyclohexane without lowering the total yield of these hydrocarbons, indicating that the primary product of the hydrogenolysis of tetraphenylsilane was benzene. By-products isolated in yields below 1% include biphenyl, triphenylsilanol, and tetracyclohexylsilane. The fate of the silicon atom in this reaction has not been determined, but *ca.* 50% of the silicon introduced as silane was found in the residue left after digestion of the spent catalyst with hydrochloric acid**. Silicon hydrides were not detected*, but in view of the alkaline nature of the catalyst (*cf.* ref. 3) this was not to be expected[5].

We have also measured the poisoning coefficient[6] of tetraphenylsilane[7] (0.11) and conclude that chemisorption of this compound occurs mainly via the silicon atom, as for electronic[8] and steric reasons adsorption involving one of the phenyl groups should be less favoured than, for example in triphenylamine (poisoning co-

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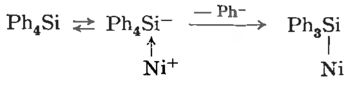
* Determined by gas chromatography using a 12-feet column packed with B.D.S. (10%) on gaschrom P.

** This determination was carried out by Dr. K. Norrish with a vacuum fluorescent X-ray spectrograph on a sample fused in lithium borate glass.

efficient[7] 0.022), which reacts with W-7 Raney nickel under similar conditions to give mainly hydrogenated products and only a little benzene[7]. In the absence of lone electrons or suitably occupied *d*-orbitals[9] we envisage chemisorption of tetraphenylsilane to occur mainly by dative bonding from the catalyst to the silicon atom. The resulting species (I) may be stabilised either by desorption or by expulsion of an anion to give (II). One factor which may influence the balance between these processes is the stability of the leaving anion, and this may explain why tetracyclohexylsilane and cyclohexyltrimethylsilane are unaffected by W-7 Raney nickel while phenyltrimethylsilane yields benzene, cyclohexane, methane and a little cyclohexyltrimethylsilane*.



$$\mathrm{Ph_4Si} \rightleftarrows \underset{\substack{\uparrow \\ \mathrm{Ni^+}}}{\mathrm{Ph_4Si^-}} \xrightarrow{-\mathrm{Ph^-}} \underset{\substack{| \\ \mathrm{Ni}}}{\mathrm{Ph_3Si}}$$

(I) (II)

The intermediate (II) is thought to undergo hydrogenolysis by mechanisms analogous to those operating in hydrogenolyses such as the Raney nickel desulphurisation[10]. The formation of some biphenyl in the hydrogenolysis of tetraphenylsilane is compatible with this view (*cf.* ref. 11).

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