Metal–Ammonia Reduction of Aromatic Nitrogen Heterocycles. Part I. Reductive Alkylation of Quinoline and Some Methyl Derivatives

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Reductive alkylation of quinoline with lithium and various alkylating agents in liquid ammonia affords exclusively 1-alkyl-1,4-dihydroquinolines. Quinolines substituted with Me in the 2-, 3-, 4-, or 8-positions behave similarly but the 1,2-dimethyl product is partly transformed into an exocyclic double bond isomer upon distillation. The structures of the reduction products have been established by spectroscopic and chemical methods and aspects of the mechanism of formation have been elucidated.

METAL–AMMONIA reduction of monocyclic and polycyclic aromatic hydrocarbons and their derivatives has been studied extensively.[1-4] Although isolated examples have been reported,[5-8] no systematic study of the metal–ammonia reduction of aromatic nitrogen heterocyclic compounds has been attempted.

The presence of one or more annular nitrogen atoms has a number of predictable consequences relating to the ease of reduction,[9] the reduction mechanism, and the nature of the products, which warrant further experimental investigation. Importance is also attached to studying the chemistry of the highly reactive reduction products which are likely to be inaccessible by other methods, but potentially useful in synthesis.

Our initial investigations, reported here, have employed the quinoline nucleus which is structurally suited to examine fundamental aspects of the topic. It has previously been reduced to different extents by a variety of methods.[10]

As early as 1881, Weidel[11] noted the occurrence of reductive coupling when quinoline was treated with sodium. The product was later correctly formulated[12] as 2,3'-biquinolyl, a result now explicable[13] in terms of radical anion intermediates generated on the metal surface. A claim[5] that sodium–ammonia reduction of quinoline and some derivatives produced products with the 1,4-dihydro structure is now believed[14] to be erroneous. Subsequently it was reported[6] that reduction of quinoline by sodium in liquid ammonia at −66° followed by quenching with ammonium chloride gave 1,2-dihydroquinoline in high yield.

A recent, more extensive study[7] of the metal–ammonia reduction of quinoline and its 6-methoxy derivative has shown that by varying the experimental conditions, preferential reduction of either the heterocyclic ring or the carbocyclic ring could be achieved, but mixtures containing up to five components were obtained probably due to the intervention of secondary reduction reactions. Since the products are difficult to separate and individual compounds are formed in very low yield, the process is not useful experimentally.

In the present study, reductive alkylation[15] has been utilised. This technique is analogous to the method (C) described[2] except that an alkylating agent rather than a proton source is used to quench the reactive intermediate(s). In contrast to the results above, primary reduction products were isolated in high yield.

RESULTS AND DISCUSSION

When a solution of quinoline in liquid ammonia at ca. −33° was treated with 2·5 mol. equiv. of lithium, the metal dissolved rapidly to give a deep blue-green solution. On quenching the mixture with an excess of an alkylating agent the colour was discharged and a white solid separated. After evaporating off the ammonia and working up the residue a single liquid product, shown spectroscopically and chemically to be a 1-alkyl-1,4-dihydroquinoline (2), was obtained.

Although the derivative 4-cyano-1-methyl-1,4-dihydroquinoline has been known since 1909[16] and a number of authentic substituted 1,4-dihydroquinolines have since been prepared,[17-19] it was only recently, and

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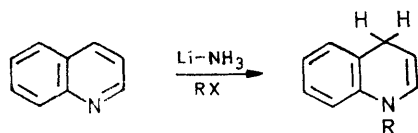[15] G. Hugel and M. Lerer, *Compt. rend.*, 1932, **195**, 249.

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while this work was in progress, that a simple 1-alkyl-1,4-dihydroquinoline (1-alkyl-1,4-DHQ) was first reported. Bunting and Meathrel [20] prepared 1-Me-1,4-DHQ in unspecified yield by reduction of 1-methylquinolinium iodide with sodium amalgam in water, but

(1)

(3) a; 2-Me
    b; 3-Me
    c; 4-Me
    d; 8-Me

(2) a; R = Me   (4) a; 1,2-Me₂
    b; R = Et   b; 1,3-Me₂
    c; R = Prⁿ   c; 1,4-Me₂
    d; R = Prⁱ   d; 1,8-Me₂
    e; R = Buⁿ
    f; R = PhCH₂
    g; R = MeOCH₂
    h; R = CO₂Me

the product could not be purified. Independently, Coates and Johnson [21] obtained the same compound in a reasonable yield by base catalysed isomerisation of the known 1-Me-1,2-DHQ. The compound was described [20,21] as an unstable yellow oil, sensitive to heat and air.

Pure 1-Me-1,4-DHQ (2a) prepared by reductive methylation of quinoline in liquid ammonia was a liquid, repeatedly distillable under reduced pressure with negligible decomposition, and although unstable in air, it could be stored under nitrogen in the refrigerator for at least a year without appreciable deterioration.

In order to assess the generality of this reductive alkylation reaction, a series of 1-alkyl-1,4-DHQ's (2b—g) was prepared using a range of common alkylating agents. 1-Methoxycarbonyl-1,4-DHQ (2h) was also readily obtained using dimethyl carbonate under the same conditions. The reaction failed with t-butyl bromide where elimination would be a competing and probably favoured reaction. The reductive methylation of some methyl-substituted quinolines (3a—d) was also examined. The dimethyl-1,4-DHQ's (4a—d) were also obtained in very good yield. With 2-methylquinoline, a single product was initially isolated but after leaving, or upon distillation, a mixture of two compounds was obtained (see below). The compounds were not amenable to g.l.c. analysis, but the 100 MHz ¹H n.m.r. spectra of concentrated solutions showed no extraneous peaks and integrated correctly, indicating an acceptable state of purity.

The u.v. spectra * of the alkyl- and dialkyl-1,4-

DHQ's all showed maxima near 300 nm (log ε 3·1—3·9) (ethanol) in accord with values reported [19,22] for some more highly substituted 1,4-DHQ's. Bunting and Meathrel [20] quoted maxima only at 303 and 254 nm (CHCl₃) for their specimen of 1-Me-1,4-DHQ. The u.v. spectra clearly eliminate from consideration the isomeric 1,2-dihydro-structures which have maxima near 345 nm (ethanol).[23,24,21] The i.r. spectra all had strong absorptions at 1660 cm⁻¹ (C=C stretch) characteristic of heterocyclic enamines.[25]

The ¹H n.m.r. spectra conclusively define the compounds as substituted 1,4-DHQ's. The observed coupling constants agree well with tabulated [26] values and the chemical shifts and coupling constants closely resemble those given for 1-Me-1,4-DHQ in CDCl₃ [20] and (CD₃)₂SO.[21] Further compelling evidence for the proposed structures was obtained from spin decoupling experiments with compound (2a).

Significant variations were observed in the chemical shifts of H-2 and H-3 depending on the substituent on nitrogen. In cyclic enamines,[27] the degree of nitrogen lone pair conjugation with the double bond is reflected in the chemical shift of the vinyl proton, i.e. a decrease in conjugation results in deshielding. In the present series, H-3 is most deshielded in compounds (2d), (2h), and (4d) where electronic or steric effects would be most pronounced.

The product obtained by reductive methylation of 2-methylquinoline displayed unexpected properties. The spectra recorded using freshly isolated, but not distilled, compound were entirely in agreement with the proposed 1,4-dihydro-structure and this was confirmed by ¹H n.m.r. spin decoupling experiments.

However, after standing for some time or after distillation, significant changes in the spectra were observed: the intensity of the absorption at 297·5 nm decreased and a new absorption appeared at 280 nm; new absorptions appeared at 1627 and 890 cm⁻¹; new resonances in the ratio 1 : 1 : 4 : 3 appeared at δ 3·83, 3·75, 2·59, and 3·11. The spectral changes suggest that isomerisation occurs during distillation and that the
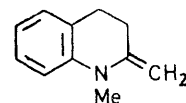
(5)

product (93%), b.p. 69—76° at 0·05 mmHg then consists of a mixture of 1,2-Me₂-1,4-DHQ (4a) and 1-methyl-2-methylene-1,2,3,4-tetrahydroquinoline (5). A double

* Spectral and analytical data and physical properties of the compounds (2a—h) and (4a—d) are listed in Supplementary Publication No. SUP 20817 (7 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index Issue.

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bond exocyclic to a 6-membered carbocyclic ring is energetically unfavoured,[28] but in a heterocyclic system such as (5) where mesomerism is possible, a greater measure of stability might be expected. Although not exactly analogous, a similar ready thermal isomerisation of methyl substituted dienamines has been reported.[29]

The structure proposed for (5) is supported by spectra. The i.r. absorption at 1627 cm^{-1}, after correction for ring size, is in agreement with values reported [30] for exocyclic double bonds in heterocyclic enamines. The protons of the exocyclic methylene group constitute an AB system for which only two lines are seen at δ 3·83 and 3·75 (2H). The C-3, C-4 protons resonate as a multiplet centred at δ 2·59 (4H) and the NMe protons give a singlet at δ 3·11 (3H). On spin decoupling, irradiation of the multiplet sharpened the resonances of the exocyclic protons confirming the expected allylic coupling with the C-3 protons. By integration, the distilled product contained 70% (4a), and 30% (5).

1-Alkyl-1,4-dihydroquinolines are tertiary heterocyclic enamines formally derived from intramolecular cyclisation of an appropriate secondary amino-aldehyde, a process which in practice would be difficult to achieve. The characteristic reactions [31] of heterocyclic enamines reflect their mesomeric nature. With electrophilic reagents, reaction usually occurs at the β-carbon, but occasionally on nitrogen.[32] Iminium salts obtained by protonation at the β-carbon react with nucleophiles at the α-carbon. In certain cycloaddition reactions which occur in a stepwise manner, these two modes of reaction take place consecutively.

Chemical evidence for the enamine structure of the compounds described above has been obtained using these characteristic reactions. 1-Alkyl-1,4-DHQ's react with toluene-p-sulphonyl chloride to form 3-substituted sulphone derivatives. Formic acid reduces enamines to fully saturated amine derivatives via a well established mechanism.[33] In this way, 1-methyl-1,2,3,4-tetrahydroquinoline (kairoline) was prepared from 1-Me-1,4-DHQ in a yield which compares favourably with other methods.[34-36] 1-Alkyl-1,4-DHQ's also undergo cycloaddition reactions with various reagents, and one example has already been reported.[37] In a later part of this series a full account of this and other interesting cycloaddition reactions will be given.

Mechanism.—Polarographic reduction of quinoline [38-41]

in aprotic solvents displays a single two-electron wave but almost certainly proceeds through a radical anion as this species can be detected (lifetime *ca.* 3 s in dimethylformamide at 25°) by rapid-scan cyclic voltammetry.[40] Quinoline radical anion is stable in hexamethylphosphoramide but dimerises in ethereal solvents.[42]

Different products from metal–ammonia reduction, depending on the conditions, have already been observed [7] for quinoline. When an alcohol is present initially (method B),[2] carbocyclic ring reduction predominates and is believed to involve 'trapping' of the weakly basic [43] radical anion as it is formed in the presence of methanol. When methanol is added later (method C),[2] reduction occurs mainly in the heterocyclic ring and is interpreted as a dianion reaction.

In the present instance, by analogy with naphthalene [44] which is π-isoelectronic with quinoline, a series of equilibria and reactions (Scheme) involving consecutive
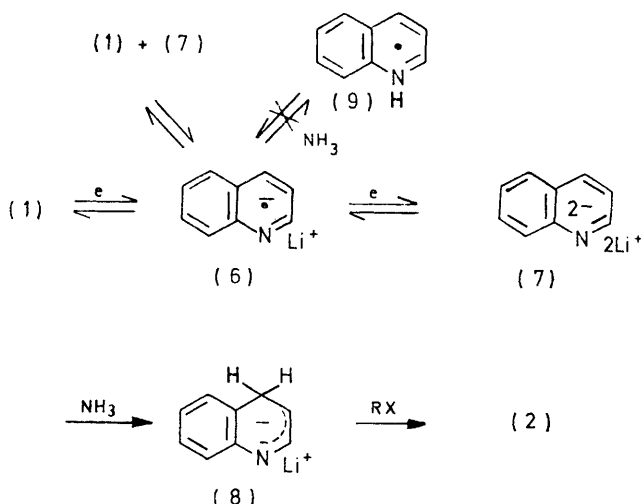
electron addition, protonation, and alkylation can account for the product formed. Experiments were carried out to determine the nature of the reacting species. In particular it was of interest to establish whether the radical anion (6) is present when a deficiency of metal is employed and if the dianion (7) resulting from addition of two electrons when two or more equivalents of metal are used, is stable as such in ammonia.

Alkylation of naphthalene radical anion [45] in 1,2-dimethoxyethane occurs through a radical mechanism

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involving electron transfer. Quinoline reacted with 1 equiv. of lithium in ammonia to form an intense yellow solution which when quenched with dimethyl sulphate gave unchanged quinoline and 1-Me-1,4-DHQ. Repetition with 3-methylquinoline, where ^{1}H n.m.r. analysis of the product was facilitated by the 3-Me resonances, gave a mixture (75% recovery) containing 3-methylquinoline (59%) and 1,3-Me$_2$-1,4-DHQ (41%). This result corresponds to addition of two electrons to half the substrate and its simplicity is evidence against a radical alkylation similar to the naphthalene example. Although direct addition of two electrons cannot be ruled out, disproportionation of the radical anion (6) seems more likely.

Radical anions readily transfer an electron to substrates of more positive reduction potential.[46] Treatment of 4-methylquinoline with 2 equiv. of lithium in ammonia, followed by addition of quinoline, which has a more positive reduction potential,[39] after times as short as *ca.* 20 s at —70°, produced only 1,4-Me$_2$-1,4-DHQ on methylation. Since no electron transfer could be detected it can be inferred that the radical anion (6) is only a transient species under these conditions. Rapid addition of a second electron, in spite of the lower electron affinity of a radical anion compared with its parent, is apparently facilitated by the gain in stability achieved by association of the resulting dianion with two cations.[47]

No evidence could be found, either from the expected deep colour,[48] or from production of a dialkylated product, for the accumulation of the dianion (7), even when a large excess of metal was employed. From the nature of the product, the only stable species present, whatever the ratio of metal, appears to be the monoanion (8). We conclude that although the dianion (7) is formed, because of its high basicity, it is capable, unlike the radical anion (6), of abstracting a proton from ammonia. The extent of its formation in an equilibrium is not a prime consideration provided that its protonation is irreversible. Evidence for the intermediacy of the dianion (7) was obtained however, by its capture under modified conditions.[49] Simultaneous addition of quinoline and an excess of Me$_2$SO$_4$ to a solution of lithium in ammonia at —70° produced a mixture of 1-Me-1,4-DHQ and 1,4-Me$_2$-1,4-DHQ in the ratio 1 : 1·5. The latter compound clearly arises from (7), methylation at C-4 competing with protonation under these conditions.

Previous work with other dianions [44,49,50] has assumed protonation from ammonia and this has been verified in the present example using [^{2}H$_3$]ammonia as solvent in which case the methylation product was [4-^{2}H]-1-Me-1,4-DHQ. This result also excludes an alternative mechanism,[6] the initial formation of a 1-Me-1,2-DHQ

followed by base induced isomerisation [21] to the more stable 1-Me-1,4-DHQ, since no deuterium incorporation was evident at C-2.

The explanation for protonation at the 4-position appears to be related to the charge distribution in the dianion (7) and the relative stabilities of the two anionic sites. One charge would be mainly localised on the electronegative nitrogen atom, probably as a tight ion pair, while the other charge is likely to concentrate at the 4-position thereby achieving maximum charge separation. The latter should be the more basic of the two and consequently the site of protonation.

That the final alkylation is a standard nucleophilic displacement was demonstrated by use of a 1 : 1 mixture of n-propyl and isopropyl bromide. ^{1}H N.m.r. analysis of the product showed a ratio of n-propyl (93%) to isopropyl (7%) in accordance with the tenfold rate difference normally observed between primary and secondary alkyl halides.[51]

EXPERIMENTAL

General.—M.p.s were determined on a Kofler micro heating stage. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer as thin films or mulls in Nujol. U.v. spectra were recorded in ethanol on a Unicam SP 800 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian HA100 instrument using [^{2}H]chloroform as solvent except where otherwise stated and tetramethylsilane as internal reference.

Quinoline (Fluka, Purum) was dried over KOH and distilled. 2-Methylquinoline (BDH) was purified through the phosphate salt.[52] 3-Methylquinoline was prepared by the method of Willmott and Simpson [53] and purified through the dichromate salt.[54] 4-Methylquinoline (P & B) and 8-methylquinoline (BDH) were distilled before use. All the quinolines were shown to be pure by g.l.c. and n.m.r.

The alkyl bromides were distilled, and immediately before use were passed through 4 × 1 cm columns of alumina (Merck, A1 basic). Dimethyl sulphate, chloromethyl methyl ether, benzyl bromide, and dimethyl carbonate were all distilled before use. All other reagents were purified where necessary by standard procedures. Alumina (Merck, A1 neutral) was used for column chromatography. Commercial ammonia was distilled from sodium directly into the reaction vessel and high purity lithium wire (Merck) was employed in the reductions.

Reductive Alkylation Experiments.—The reaction vessel used was a three necked 500 ml round bottom flask and was equipped with a dry-ice condenser, nitrogen inlet, a rubber septum seal, and a magnetic stirrer (preferably glass encased). Ammonia (250 ml) was distilled into the flask and a solution of the quinoline (0·03 mol) in dry ether (20 ml) was added. Lithium (0·075 g atom) was added all at once and dissolved rapidly. The deep blue-green solution was stirred at *ca.* —33° for 30 min under nitrogen and was then

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cooled to *ca.* −70° by immersing the flask in a dry-ice–ethanol bath. The appropriate alkylating agent (0·04—0·08 mol; see below) was introduced through the septum in a slow stream from a syringe. The deep colour was discharged and after stirring for a further 15 min, the solution usually became colourless and a large amount of a white solid separated. The cooling bath was removed and the ammonia was evaporated off with the aid of a hot air blower. The residue was treated with distilled water (50 ml) and the oily product was extracted with ether (4 × 25 ml). The ethereal solution was washed with water (3 × 10 ml) and dried (Na₂SO₄) for 1—2 h in the refrigerator. The solvent was removed at 15 mmHg and the remaining oil was distilled rapidly under vacuum. A small amount of a thick brown sludge remained in the pot. The distillate was then immediately redistilled and the b.p. and yield recorded. In most cases virtually no residue remained after the second distillation. The products were sealed in flasks under nitrogen and stored in the refrigerator. In all manipulations, air was rigorously excluded.

For the substrate quinoline, dimethyl sulphate, ethyl, n-propyl, isopropyl, and n-butyl bromides, chloromethyl methyl ether, and dimethyl carbonate (0·08 mol) were used. With benzyl bromide (0·033 mol) the addition was made at −33°. For the substrates 3-, 4-, and 8-methylquinoline, dimethyl sulphate (0·08 mol) was used, while with 2-methylquinoline a smaller excess of lithium was employed (0·066 g atom) and dimethyl sulphate (0·08 mol) was again used. The following products were obtained (b.p. °/mmHg, yield %): (2a) 56—60/0·05, 88 (lit.,²¹ 67/0·3); (2b) 63—67/0·03, 80; (2c) 74—77/0·05, 89; (2d) 62—64/0·02, 78; (2e) 80—84/0·02, 84; (2f) 129—132/0·05, 45; (2g) 78—81/0·15, 79; (2h) 82—88/0·05, 78; (4a) see text; (4b) 67—72/0·05, 87; (4c) 65—66/0·05, 93; (4d) 63—64/0·1, 87.

1-*Methyl*-3-(4-*methylphenylsulphonyl*)-1,4-*dihydroquinoline*.—1-Methyl-1,4-dihydroquinoline (1·45 g) and triethylamine (1·25 g) were dissolved in dry tetrahydrofuran (50 ml). The solution was cooled (ice-bath) and stirred under N₂ while a solution of toluene-*p*-sulphonyl chloride (1·91 g) in THF (15 ml) was added dropwise. After *ca.* 5 min the solution became dark red and triethylamine hydrochloride began to separate. The mixture was stirred at 25° for 2 h after which it was chilled and the hydrochloride salt filtered off and washed with THF. The filtrate was concentrated and the red-brown semi-solid which remained was chromatographed over alumina using 30% chloroform in petroleum (b.p. 60—80°) as eluant. A yellow solid (1·86 g) was obtained from the main fraction, and gave 1-methyl-3-(4-methylphenylsulphonyl)-1,4-dihydroquinoline (1·6 g, 53·5%) as plates (from petroleum–THF), m.p. 129—130°.

1-*Ethyl*-3-(4-*methylphenylsulphonyl*)-1,4-*dihydroquinoline*.—This was prepared in the same manner from 1-ethyl-1,4-dihydroquinoline and crystallised from petroleum–THF as plates, m.p. 166—167°.

Reduction of 1-*Methyl*-1,4-*dihydroquinoline with Formic Acid.*—A solution of 98% formic acid (1·1 g) in THF (2·5 ml) was added in portions during 30 min to a solution of 1-methyl-1,4-dihydroquinoline (2·9 g) in THF (2·5 ml), heated under N₂ on a water-bath. The deep red solution was heated under reflux for 20 h and was then cooled and poured into water (50 ml). Solid KOH was added until the solution was strongly alkaline and the oil which separated was extracted with ether (4 × 25 ml). The ether solution was washed with cold water (3 × 10 ml), dried

(Na₂SO₄), and the solvent removed to leave a brown oil (2·95 g). 1-Methyl-1,2,3,4-tetrahydroquinoline (1·91 g, 65%) distilled as an oil, b.p. 51—55° at 0·05 mmHg (lit.,³⁶ 96° at 3 mmHg). The methiodide, prepared with methyl iodide in acetonitrile, crystallised from acetone as rods, m.p. 179—179·5° (lit.,⁵⁵ 172—174°, also ³⁵ 174°).

The perchlorate salt, prepared in absolute ethanol, crystallised from methanol–ether as glistening plates, m.p. 150—151°.

Reductive Methylation of 3-*Methylquinoline using a Deficiency of Lithium.*—3-Methylquinoline (0·02 mol) was reduced in liquid ammonia (250 ml) with lithium (0·02 g atom). The reaction was quenched with dimethyl sulphate (0·025 mol) and worked up in the usual way to give an oil (2·23 g) with b.p. 70—80° at 0·1 mmHg. ¹H N.m.r. analysis showed that it consisted of a mixture of 3-methylquinoline (59%) and 1,3-dimethyl-1,4-dihydroquinoline (41%).

Attempts to Intercept Radical Anion of 4-*Methylquinoline.*—Four separate experiments were carried out in which the time interval between the addition of the two substrates and the temperature of the reaction was varied. 4-Methylquinoline (0·03 mol) in dry ether (20 ml) was added to solutions of lithium (0·06 g atom) in liquid ammonia (250 ml) at −33° and −70°. After the time intervals listed below, a solution of quinoline (0·03 mol) in dry ether (10 ml) was added as rapidly as possible.

Time	Temperature
60 min	−33° (control)
5 min	−33°
1 min	−70°
ca. 20 s	−70°

The reactions were quenched with dimethyl sulphate and worked up in the usual way. The oils obtained were distilled and their ¹H n.m.r. spectra recorded. In each case only 1,4-dimethyl-1,4-dihydroquinoline and quinoline were found.

Reductive Methylation of Quinoline using a Large Excess of Lithium.—Quinoline (0·03 mol) was reduced in liquid ammonia (250 ml) with lithium (0·21 g atom). The reaction was quenched with dimethyl sulphate (0·3 mol) and worked up in the usual way. The product (3·17 g, 73%) had b.p. and spectra identical with 1-methyl-1,4-dihydroquinoline.

Interception of Quinoline Dianion.—Lithium (0·12 g atom) was dissolved in liquid ammonia (200 ml) and the solution was cooled to −70°. A solution of quinoline (0·03 mol) and dimethyl sulphate (0·13 mol) in ether (30 ml) was then added as rapidly as possible. The reaction mixture was worked up in the usual way and an oil (3·81 g), b.p. 55—63° at 0·075 mmHg was obtained. The ¹H n.m.r. spectrum revealed the presence of 1-methyl-1,4-dihydroquinoline, 1,4-dimethyl-1,4-dihydroquinoline, and unchanged quinoline. By integration, the 1,4-dimethyl compound amounted to 60% of the reduced material.

Reductive Methylation of Quinoline in [²H₃]*Ammonia.*—[²H₃]Ammonia was prepared after the method of Bouclier and Partier ⁵⁶ from magnesium nitride (101 g) and deuterium oxide (120 ml) and was distilled from sodium into the reaction vessel. Quinoline (0·01 mol) was reduced with lithium (0·025 g atom) in [²H₃]ammonia (*ca.* 30 ml). The reaction was quenched with dimethyl sulphate (0·027 mol)

⁵⁵ L. Knorr, *Ber.*, 1899, **32**, 734.
⁵⁶ P. Bouclier and J. Portier, *Bull. Soc. chim. France*, 1967, 738.

and worked up in the usual way, except that D_2O (10 ml) was used instead of water. The crude oil was flash distilled under vacuum to give a colourless product (1·19 g, 82%). The ^1H n.m.r. spectrum was identical with that of 1-methyl-1,4-dihydroquinoline, but the doublet due to the C-4 protons was reduced in intensity. By integration the intensity corresponded to 1·4H, *i.e.* 60% deuterium incorporation.

Reductive Alkylation of Quinoline using Lithium and a Mixture of n-Propyl and Isopropyl Bromides.—Quinoline (0·03 mol) was reduced with lithium (0·075 g atom) in liquid ammonia (250 ml). The reaction was quenched with a mixture of n-propyl (0·04 mol) and isopropyl (0·04 mol) bromides. Following work-up in the usual way, an oil (4·4 g, 85%), b.p. 67—72° at 0·05 mmHg was obtained. The ^1H n.m.r. spectrum revealed that the product was a mixture of 1-n-propyl-1,4-dihydroquinoline (93%) and 1-isopropyl-1,4-dihydroquinoline (7%).