41. *The Thermal Decomposition of Quaternary Ammonium Hydroxides. Part III.*[1] *Methohydroxides containing Phenyl Substituents attached to α- and β-Carbon Atoms.*

By D. A. ARCHER, H. BOOTH, and (in part) P. C. CRISP.

The thermal decomposition of a number of simple quaternary hydroxides containing α- and β-phenyl groups has been studied by product analysis. The results demonstrate that replacement of an α-hydrogen atom by a phenyl group causes an acceleration of β-elimination, relative to substitution at *N*-methyl groups, although the effect is much weaker than that achieved by analogous replacement of a β-hydrogen atom.

Contrary to a report in the literature, thermal decomposition of the 1-methyl methohydroxide of 1,2,3,4-tetrahydro-2-phenylquinoline leads to considerable β-elimination. The 1-methyl methohydroxide of tetrahydro-3-phenylquinoline also suffers smooth Hofmann fission, but thermal decomposition of the 1-methyl methohydroxide of *cis*(?)-1,2,3,4-tetrahydro-2,3-diphenylquinoline leads exclusively to substitution at *N*-methyl groups. The results are discussed in terms of the preferred conformations of the methohydroxides.

EARLIER papers,[1,2] reporting experiments performed concurrently with work to be described below, were concerned with the thermal decomposition (Hofmann degradation) of quaternary hydroxides in which an aromatic ring was directly attached to the nitrogen atom. The starting point for the work was the report[3] that the thermal treatment of 1,2,3,4-tetrahydro-1-methylquinoline methohydroxide caused decomposition to occur exclusively by substitution at *N*-methyl groups (formation of methanol). It has recently been shown[1] that the decomposition involves appreciable β-elimination. von Braun, Seemann, and Schultheiss[4] showed that thermal decomposition of the methohydroxide of 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline (I) gave entirely 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline (but see later). This was surprising, since the presence of a phenyl group on the α-carbon atom would be expected to facilitate β-elimination by allowing delocalisation of π-electrons in the transition state. It was not expected that Hofmann degradation of compound (I) would be prevented by conformational features, since the reduced ring in it, and in its methohydroxide, is probably in a half-chair conformation (cf. ref. 1). Furthermore, examination of Courtauld models of the methohydroxide revealed that in neither of the two possible half-chair conformations does the phenyl ring at C-2 cause steric hindrance to the approach of hydroxyl ion to the 3-hydrogen atom. Therefore, since we originally had no reason to doubt the work of von Braun, Seemann, and Schultheiss, we embarked on an investigation of the effects of α-phenyl

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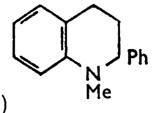
[1] Part II, Archer, Booth, Crisp, and Parrick, *J.*, 1963, 330.
[2] Archer and Booth, *J.*, 1963, 322.
[3] Feer and Koenigs, *Ber.*, 1885, **18**, 2388; Knorr, *Ber.*, 1899, **32**, 734.
[4] von Braun, Seemann, and Schultheiss, *Ber.*, 1922, **55**, 3803.

substituents on the ratio of elimination to substitution in the decomposition of simple quaternary hydroxides.



(I)

$Ph{\cdot}CHR{\cdot}NR'Me_2^+ \quad OH^-$

(II)

The thermal decomposition of *NNN*-trimethyl-1-phenylethylammonium hydroxide (II; $R = R' = Me$) gave 100% β-elimination, based upon the yield of styrene and the absence in the reaction products of *NN*-dimethyl-1-phenylethylamine. Since heat treatment of ethyltrimethylammonium hydroxide gave 95—100% β-elimination,[5] the α-phenyl substituent does not inhibit β-elimination in this simple case. It is of interest that thermal decomposition of *NNN*-trimethyl-2-phenylethylammonium hydroxide also proceeds exclusively by β-elimination.[6] A more accurate assessment of the influence of an α-phenyl substituent was obtained by allowing elimination from a 1-phenylethyl group to compete against elimination from an ethyl group. Decomposition of the hydroxide (II; $R = Me$, $R' = Et$) gave, in the non-volatile portion of the product, a mixture of styrene (~91 mol. %) and *NN*-dimethyl-1-phenylethylamine (~9 mol. %). Thus β-elimination from a 1-phenylethyl group occurs about ten times as readily as from an ethyl group. It has been shown that the rate of elimination from a 2-phenylethyl group is $2{\cdot}6 \times 10^4$ greater than that from an ethyl group.[7] The vastly superior accelerating influence of a β-phenyl group, as against an α-phenyl group, was confirmed when decomposition of the hydroxide (II; $R = Me$, $R' = Ph[CH_2]_2$) gave *NN*-dimethyl-1-phenylethylamine as the sole basic product. Now an α-substituted phenyl group can accelerate an E_2 elimination only by promoting π-electron overlap in the transition state. A β-phenyl group can exert a similar influence, but, in addition, it can strongly promote an E_2 elimination by its electron-attracting inductive effect, which increases the acidity of the β-hydrogen atoms. Our results are thus in agreement with the general theory developed by Ingold [8] for bimolecular elimination reactions.

Next, the thermal decomposition of *NNN*-trimethyl-1-phenylpropylammonium hydroxide (II; $R = Et$, $R' = Me$) was examined under reflux at 150—160°. Product analysis indicated that 86% β-elimination had occurred. The reduced tendency of this hydroxide to suffer β-elimination, as compared with the 1-phenylethyl compound, is an example of the well-recognised inhibitory effect of β-alkyl substitution. As decomposition of trimethylpropylammonium hydroxide causes about 90% β-elimination,[5] the α-phenyl group in the hydroxide (II; $R = Et$, $R' = Me$) does not appear to have any significant influence on the substitution–elimination ratio. However, the experiments are not accurately comparable, since Ingold and Vass [5] used distillation conditions. The only products isolated from the thermal decomposition of the hydroxide (II; $R = Me$, $R' = Ph$) were dimethylaniline and styrene. This result, 100% β-elimination, may be compared with the 72% β-elimination previously recorded for the decomposition of ethyldimethylaniline methohydroxide, the related hydroxide lacking an α-phenyl substituent. It is of interest that whereas low-temperature decomposition of solutions of sulphonium ethoxides containing α-phenyl substituents allows appreciable substitution at the α-carbon atom carrying the phenyl group,[9] decomposition of the corresponding ammonium hydroxides at relatively higher temperatures caused no intrusion from this reaction. Thermal decomposition of the hydroxide (II; $R = Et$, $R' = Ph$) was investigated in

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[5] Ingold and Vass, *J.*, 1928, 3125.

[6] von Braun, *Annalen*, 1911, **382**, 1; Hughes and Ingold, *J.*, 1933, 523.

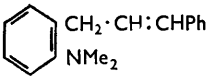
[7] Cope, Le Bel, Lee, and Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720.

[8] Cf. Ingold, Faraday Lecture, "The Mechanism of Olefin Elimination," *Proc. Chem. Soc.*, 1962, 265.

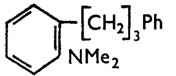
[9] Banthorpe, Hughes, and Ingold, *J.*, 1960, 4054.

detail, as this hydroxide resembles tetrahydro-1-methyl-2-phenylquinoline methohydroxide in structure. The outcome of the reaction varied with the method of decomposition. Thermal decomposition of a concentrated solution of the hydroxide under reflux at 160° caused β-elimination, substitution at the α-carbon atom carrying the phenyl group, and a rearrangement similar to the Hofmann–Martius rearrangement. The rearrangement, which has been reported briefly,[10] will be the subject of a further paper. Decomposition of the dry hydroxide (II; R = Et, R′ = Ph) at 100°/15 mm. gave in the basic fraction a mixture of *NN*-dimethylaniline (72 mol. %) and *N*-methyl-*N*-1-phenylpropylaniline (28 mol. %), the expected products of β-elimination and substitution at *N*-methyl groups. Now *NN*-dimethyl-*N*-propylaniline methohydroxide decomposes to the extent of only 15% β-elimination;[2] further evidence is thus provided for the acceleration of β-elimination by an α-phenyl substituent. Analysis of the neutral fraction from the decomposition of the hydroxide (II; R = Et, R′ = Ph) disclosed *trans*-1-phenylpropene (88 mol. %), *cis*-1-phenylpropene (8 mol. %), allylbenzene (2 mol. %) and 1-phenylpropan-1-ol (2 mol. %), the latter having been formed by substitution at the α-carbon atom carrying the phenyl group.

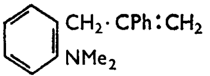
In none of the compounds hitherto examined was the presence of an α-phenyl substituent instrumental in preventing β-elimination; on the contrary, the results indicated a definite acceleration of β-elimination by the aromatic ring. We were thus led to doubt the findings of von Braun, Seemann, and Schultheiss with regard to the Hofmann degradation of compound (I). Repetition of this degradation at 100°/15 mm. gave a product which partly solidified, owing to the presence of the saturated base (I). However, the infrared spectrum of the product included maxima at 949 (sym. C–N stretching of NMe_2 in $ArNMe_2$), and 978 and 982 $cm.^{-1}$ (C–H out-of-plane deformn. of *trans*-R·CH=CHR′), none of which appears in the spectrum of pure compound (I). The presence of an unsaturated *NN*-dimethylaniline was thus indicated and the pure amine, probably *NN*-dimethyl-*o*-(3-phenylallyl)aniline (III) was readily isolated through its picrate; the tetrahydroquinoline (I) does not form a picrate.[4] The crude degradation product absorbed hydrogen in the presence of palladised charcoal, and the isolated liquid lacked the infrared bands at 978 and 982 $cm.^{-1}$, but retained that at 949 $cm.^{-1}$. From this liquid, the saturated base (IV) was easily isolated as its picrate. The volume of hydrogen absorbed in the hydrogenation indicated that the Hofmann degradation product contained ~65 mol. % of (III) and ~35 mol. % of (I). Again, therefore, the α-phenyl substituent was shown to facilitate β-elimination, since 1,2,3,4-tetrahydro-1-methylquinoline methohydroxide decomposed to the extent of only 20% by β-elimination under comparable conditions.



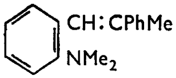
(III)



(IV)



(V)



(VI)

It was of interest to examine the thermal decomposition of 1,2,3,4-tetrahydro-1-methyl-3-phenylquinoline methohydroxide. The reduced heterocyclic ring in this hydroxide can assume two half-chair conformations, but the preferred conformation is presumably that in which the only β-hydrogen, at C-3, is axial, and therefore unfavourable to easy β-elimination. Half-chair–half-chair inversion of this conformation produces the less stable conformation in which the equatorial β-hydrogen is well disposed for easy elimination, but the ease of the inversion is not known, and nuclear magnetic resonance studies have not provided an answer.[11] However, ring inversion may be unnecessary for easy elimination, since an effect of β-phenyl substitution is the production of a relatively acidic β-hydrogen atom; whilst in such cases a *trans*-E_2 elimination is still preferred,[12] the

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[10] Archer and Booth, *Chem. and Ind.*, 1962, 1570.

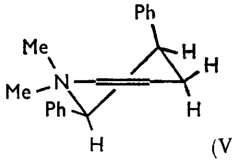
[11] Booth, unpublished work.

[12] Cram, Green, and Depuy, *J. Amer. Chem. Soc.*, 1956, **78**, 790.

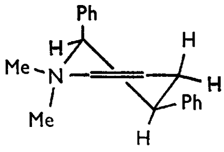
absence of a *trans*-orientated β-hydrogen does not prevent β-elimination (see, *e.g.*, refs. 13 and 14). In practice, Hofmann fission of 1,2,3,4-tetrahydro-1-methyl-3-phenylquinoline methohydroxide proceeded smoothly at 100—120°/15 mm. The product was not analysed quantitatively, but it gave, on distillation, an oil which appeared to be a homogeneous, unsaturated base. This base, which readily absorbed 1 mol. of hydrogen in the presence of palladised charcoal, was expected to be either (V) or (VI).

The stilbene formula (VI) was eliminated at once, from the ultraviolet spectrum, which had $\lambda_{max.}$ at 244 mμ (ε 14,100). The spectrum obtained was precisely the expected one for the styrene (V), which may be considered to possess the non-conjugated chromophores of *o*-methyl-*NN*-dimethylaniline ($\lambda_{max.}$ 248 mμ, ε 6300) [15] and α-methylstyrene ($\lambda_{max.}$ 244 mμ, ε 12,400).[16] Thus the conditions of degradation do not cause the entering double-bond to move into a position of conjugation with both aromatic rings.[17] It is, indeed, possible that structure (V) is more thermodynamically stable than (VI), as steric effects may prevent the latter from assuming a position in which full overlapping of π-orbitals occurs.[18]

These observations on the decomposition of α- and β-phenyl substituted quaternary ammonium hydroxides led us to expect that distillation of the methohydroxide of 1,2,3,4-tetrahydro-1-methyl-2,3-diphenylquinoline would cause smooth β-elimination. The stereoisomeric tetrahydro-2,3-diphenylquinolines were prepared by reducing 2,3-diphenylquinoline with sodium and ethanol, as described by Plant and Rosser.[19] The major product, isomer *A*, was smoothly converted into the 1-methyl derivative and thence, with some difficulty, successively into the 1,1-dimethyl methosulphate and 1-methyl methiodide. Plant and Rosser did not assign configurations to the isomeric tetrahydrodiphenylquinolines *A* and *B*. The nuclear magnetic resonance spectra of *A* and *B* have been determined and interpreted with the help of Dr. J. W. Lown, to whom we express our thanks. Isomer *A* gave more sharply defined spectra than isomer *B*. It is assumed in the first place that the reduced ring exists in a half-chair conformation (cf. flavanols [20]).



(VII)



(VIII)

The low-field doublet at 5·4 τ in the spectrum of *A* is due to the 2-hydrogen, which is coupled only to the 3-hydrogen. The coupling constant of 3·4 c./sec. corresponds to a dihedral angle of about 50—60°,[21] a situation which is satisfied by a *cis*-configuration in either of the two possible conformations related to (VII) and (VIII), but only by a *trans*-configuration in which both phenyl groups are axial. The latter possibility is, however, unlikely because of high repulsive 1,3-interactions between the phenyl group at C-2 and the quasi-axial hydrogen at C-4, and between the phenyl group at C-3 and the nitrogen lone-pair. Moreover, a fixed conformation is unlikely for the following reasons. The 4-hydrogen atoms appear in the spectrum as a doublet, suggesting that they are magnetically equivalent, and therefore that they form with the 3-hydrogen an A_2X rather than an ABX system. The equivalence of the 4-hydrogen atoms is due probably to rapid half-chair–half-chair inversion. It is tentatively concluded that isomer *A* has the *cis*-configuration, and that both conformations related to (VII) and (VIII) are present and

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[13] Masamune and Koshi, *Bull. Chem. Soc. Japan*, 1959, **32**, 1005.
[14] Cope, Berchtold, and Ross, *J. Amer. Chem. Soc.*, 1961, **83**, 3859.
[15] Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714.
[16] Braude and Timmons, *J.*, 1950, 2000.
[17] Cf. Weinstock and Bordwell, *J. Amer. Chem. Soc.*, 1955, **77**, 6706.
[18] Cf. Brown and Brown, *Tetrahedron Letters*, 1963, 191.
[19] Plant and Rosser, *J.*, 1929, 1861.
[20] Clark-Lewis and Jackman, *Proc. Chem. Soc.*, 1961, 165.
[21] Conroy, *Adv. Org. Chem.*, 1960, **2**, 11.

undergoing rapid interconversion (a reasonable expectation for a *cis*-molecule in which the substituents at positions 2 and 3 are identical). Now the 1-methyl metho-salts of the *cis*-base may exist preferentially in conformation (VIII), as the alternative (VII) involves a severe repulsive 1,3-interaction between the axial phenyl at C-3 and the quasi-axial *N*-methyl group. Whilst in conformation (VIII) the stereochemical requirement for easy E_2 elimination is not satisfied, this factor was expected to be overcome by the relatively high acidity of the 3-hydrogen atom, as in the examples quoted earlier. In the event however, thermal decomposition of the *cis*-methohydroxide caused no β-elimination, the only isolable product being *cis*-1,2,3,4-tetrahydro-1-methyl-2,3-diphenylquinoline. This result may be due to a combination of two factors arising from conformation (VIII): (a) lack of ideal stereochemistry for easy E_2 elimination, and (b) steric hindrance to the approach of hydroxyl ion to the axial 3-hydrogen atom. For comparison, it is interesting to note that heat treatment of *threo*- and *erythro*-*NNN*-trimethyl-1,2-diphenylpropylammonium iodide in sodium ethoxide results exclusively in β-elimination,[12] whereas decomposition of *NNN*-trimethyl-1,1,2-triphenylethylammonium hydroxide allows appreciable substitution at *N*-methyl groups.[22]

EXPERIMENTAL

The general remarks of Part I apply here.

Hofmann Degradation of NN-*Dimethyl*-1-*phenylethylamine*.—*NN*-Dimethyl-1-phenylethylamine, prepared by methylation of 1-phenylethylamine [23] with formaldehyde and formic acid, had b. p. 77°/14 mm., n_D^{20} 1·5020 (lit.,[24] b. p. 73·5°/14 mm.). The picrate had m. p. 138° (lit.,[24] 138°) and the methiodide had m. p. 145° (lit.,[25] 144·5—145·5°).

The syrupy methohydroxide, prepared in the usual way (silver oxide) from the above methiodide (5 g.), was decomposed under reflux at 130—140° during 1 hr. The product was worked up by extraction with ether and was then separated into neutral and basic fractions by using ether and 10% hydrochloric acid. The neutral fraction (~1·7 g.), on treatment with bromine in carbon tetrachloride, gave styrene dibromide (4·5 g.), m. p. and mixed m. p. 73—74°. There was no basic fraction.

Hofmann Degradation of N-*Ethyl*-N-*methyl*-1-*phenylethylamine*.—A mixture of *NN*-dimethyl-1-phenylethylamine and an excess of ethyl iodide was heated under reflux for 12 hr., cooled, and poured into dry ether, when an oily methiodide separated. Attempts to crystallise the oil, and also the derived picrate and picrolonate, failed. However, N-*ethyl*-NN-*dimethyl*-1-*phenylethylammonium styphnate* crystallised from ethanol in prisms, m. p. 140—142° (Found: C, 51·6; H, 5·4; N, 13·1. $C_{18}H_{22}N_4O_8$ requires C, 51·3; H, 5·25; N, 13·3%). The syrupy methohydroxide, obtained from the oily methiodide, was decomposed under reflux at 130—140° during 2 hr. The product was separated into neutral and basic fractions. The basic fraction (~0·3 g.) was *NN*-dimethyl-1-phenylethylamine, as treatment with methyl iodide in ether gave the methiodide (0·56 g.), m. p. and mixed m. p. 143—144·5°. The neutral fraction (~2 g.) of styrene gave, with bromine in carbon tetrachloride, styrene dibromide (5·2 g.), m. p. and mixed m. p. 72—74°.

Hofmann Degradation of N-*Methyl*-N-1-*phenylethyl*-N-2-*phenylethylamine*.—*NN*-Dimethyl-2 phenylethylamine, prepared by methylation of 2-phenylethylamine with formaldehyde and formic acid, had b. p. 90—92°/17 mm., n_D^{20} 1·5030 (lit.,[26] b. p. 86—87°/8 mm., n_D^{20} 1·5032). The picrate had m. p. 135—136° (lit.,[27] 135—136·5°), and the methiodide m. p. 232° (lit.,[26] 232°). A mixture of the amine (10 g.), 1-bromo-1-phenylethane (20 g.), and acetone (100 ml.) was heated under reflux for 12 hr. and then cooled. The solid which separated was crystallised from acetone, giving NN-*dimethyl*-N-1-*phenylethyl*-N-2-*phenylethylammonium bromide* (20 g.) as needles, m. p. 163—164° (Found: C, 65·0; H, 7·2; N, 4·5. $C_{18}H_{24}BrN$ requires C, 64·7; H, 7·2; N, 4·2%). Poor yields of the salt were obtained from *NN*-dimethyl-1-phenylethylamine

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[22] Hughes and Ingold, *J.*, 1933, 68.
[23] Ingersoll, *Org. Synth.*, Coll. Vol. II, p. 503.
[24] Skita and Keil, *Ber.*, 1930, **63**, 34.
[25] Norcross and Openshaw, *J.*, 1949, 1174.
[26] Snyder, Carnahan, and Lovejoy, *J. Amer. Chem. Soc.*, 1954, **76**, 1301.
[27] Letsinger and Collat, *J. Amer. Chem. Soc.*, 1952, **74**, 621.

and 2-bromo-1-phenylethane. The syrupy methohydroxide, prepared from the above bromide (6·8 g.), was heated under reflux to 85°, when decomposition became vigorous, and then to 95° for 1 hr. The product was separated into neutral and basic fractions. The neutral fraction (~1·7 g.) of styrene was identified as the dibromide (4·4 g.), m. p. 72—74°. The basic fraction gave, on total distillation, *NN*-dimethyl-1-phenylethylamine (2·3 g.), n_D^{20} 1·5022; picrate, m. p. and mixed m. p. 137°; methiodide, m. p. 143—145°. Gas chromatography at 203° showed only one peak, at 5 min. 30 sec., in agreement with the authentic base. Under identical conditions, *NN*-dimethyl-2-phenylethylamine has a retention time of 6 min. 20 sec.

NN-*Dimethyl*-1-*phenylpropylamine*.—The following method gave better yields than the methods given [28,29] in the literature. A mixture of ammonium formate (25 g.) and propiophenone (17 g.) was slowly distilled until the b. p. of the liquid distilling reached 180°. The propiophenone layer of the distillate was returned to the flask and the distillation was repeated. The reaction mixture was cooled, washed with water (20 ml.), and heated under reflux with concentrated hydrochloric acid (15 g.) for 1 hr. The cooled solution was basified and extracted with ether. Evaporation of the dried (KOH) extracts gave crude 1-phenylpropylamine (14 g.). A mixture of the amine (14 g.), formic acid (25 g.), and formaldehyde (25 g., 40% solution) was heated under reflux until reaction commenced. After the reaction had subsided (20 min.), the mixture was heated under reflux for 8 hr. on a steam-bath. The cooled solution was treated with 10% hydrochloric acid (50 g.) and evaporated to dryness at 15 mm. The residue was basified and the liberated amine was extracted into ether. Distillation of the dried (KOH) ethereal extracts gave *NN*-dimethyl-1-phenylpropylamine (15 g., 85%), b. p. 93—94°/15 mm. (lit.,[28] 105—106°/22 mm.), n_D^{20} 1·5012 (lit.,[28] 1·5002); picrate m. p. 166° (lit.,[28] 165·5—166°); *methiodide*, hygroscopic plates, m. p. 162·5° (from ethanol–ether) (Found: C, 46·8; H, 6·8; N, 4·2. $C_{12}H_{20}IN$ requires C, 47·2; H, 6·6; N, 4·6%).

Hofmann Degradation of NN-*Dimethyl*-1-*phenylpropylamine*.—The syrupy methohydroxide from the above methiodide (18 g.), was decomposed at 150—160° under reflux during 3 hr. The product was isolated by extraction into ether and then separated into basic and non-basic fractions. The basic fraction (1·30 g.), n_D^{23} 1·4996, was shown by infrared analysis, conversion into the picrate (m. p. 166°), and quantitative conversion into the methiodide (m. p. 162°), to be *NN*-dimethyl-1-phenylpropylamine. The non-basic fraction (5·15 g.) had n_D^{20} 1·5460 and its behaviour on infrared analysis and gas chromatography was identical with that of the mixture of phenylpropenes obtained in the degradation of *N*-methyl-*N*-3-phenylpropylaniline.[2] The infrared spectrum showed no absorption at 3600 cm.$^{-1}$ (OH stretching).

N-*Methyl*-N-1-*phenylethylaniline*.—A mixture of *N*-methylaniline (23 g.) and 1-bromo-1-phenylethane (37 g.) was heated at 100° for 48 hr. The mixture was treated with 20% hydrochloric acid (50 ml.) and washed several times with ether. The aqueous solution was basified and extracted with ether. The dried (KOH) extracts were distilled, giving N-*methyl*-N-1-*phenylethylaniline* (29 g.), b. p. 166—168°/14 mm., n_D^{23} 1·5967 (Found: N, 6·5. $C_{15}H_{17}N$ requires N, 6·6%. Values for C and H were consistently low, but no bromine was present), $\lambda_{max.}$ (in EtOH) 207, 260, and 309 mμ (ε 25,600, 15,200, and 2260), $\lambda_{max.}$ (in conc. HCl) 256, 260, 263, and 269 mμ (ε 705, 738, 696, and 426). The base did not appear to form a picrate, picrolonate or styphnate. The *hydrochloride* crystallised from ethanol–ether in rhombs, m. p. 162·5° (Found: C, 72·8; H, 7·4; N, 5·6. $C_{15}H_{18}ClN$ requires C, 72·7; H, 7·2; N, 5·6%).

Hofmann Degradation of N-*methyl*-N-1-*phenylethylaniline*.—A mixture of *NN*-dimethylaniline and 1-bromo-1-phenylethane was kept in the dark for 3 days. Addition of ether was followed by filtration of the mixture. The residue of N-*methyl*-N-1-*phenylethylaniline methobromide*, obtained in high yield, crystallised from ethanol–ether as plates, m. p. 124° (Found: C, 62·7; H, 6·6; N, 4·3. $C_{16}H_{20}BrN$ requires C, 62·7; H, 6·5; N, 4·6%), $\lambda_{max.}$ (in EtOH) 256, 260, 263, and 270 mμ (ε 720, 755, 676 and 400). The syrupy quaternary hydroxide, derived from the above methobromide using Ag_2O, was decomposed under reflux at 140° during 2 hr. The product was isolated by extraction into ether and was separated into basic and non-basic fractions. The basic fraction had n_D^{23} 1·5575 and was shown by infrared analysis and quantitative formation of picrate (m. p. 163—164°) to be entirely dimethylaniline. The non-basic fraction, with bromine, gave styrene dibromide (85%), m. p. 72—74°. Decomposition of

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[28] Bunnett, Marks, and Moe, *J. Amer. Chem. Soc.*, 1953, **75**, 985.

[29] Sauers, *J. Amer. Chem. Soc.*, 1958, **80**, 4721.

the methohydroxide at 90°/15 mm. also gave dimethylaniline and styrene as the only identifiable products.

N-*Methyl*-N-1-*phenylpropylaniline*.—*N*-1-Phenylpropylaniline, prepared from benzylideneaniline and ethylmagnesium iodide by the method of Campbell *et al.*[30] had b. p. 184—186°/14 mm. (lit.,[31] b. p. 192°/20 mm.), n_D^{23} 1·5885, $\nu_{max.}$ (liquid film) 3500 cm.$^{-1}$; hydrochloride, m. p. 187° (lit.,[31] m. p. 187°). A mixture of the base (20 g.), dimethyl sulphate (16 g.), anhydrous sodium carbonate (11 g.), and acetone (100 ml.) was heated under reflux for 48 hr. and then diluted with water (50 ml.). Acetone was removed by distillation and the residue was extracted with ether. Distillation of the dried (KOH) ethereal extracts gave N-*methyl*-N-1-*phenylpropylaniline* as an oil (18 g.), b. p. 178—180°/14 mm., n_D^{23} 1·5890 (Found: C, 85·5; H, 8·4; N, 6·2. $C_{16}H_{19}N$ requires C, 85·3; H, 8·4; N, 6·2%), $\lambda_{max.}$ (in EtOH) 256 and 296 mμ (ε 14,750 and 2570) $\lambda_{max.}$ (in conc. HCl) 250, 259, 263, and 269 mμ (ε 934, 946, 895, and 556). The *hydrochloride* had m. p. 172—174° (sealed tube) (Found: N, 5·1. $C_{16}H_{20}ClN$ requires N, 5·3%). The derived N-*methyl methosulphate*, from the base and dimethyl sulphate in the cold, crystallised from ethanol–ether in prisms, m. p. 125° (Found: C, 61·7; H, 6·8; N, 3·7; S, 9·0. $C_{18}H_{25}NO_4S$ requires C, 61·5; H, 7·1; N, 4·0; S, 9·1%), $\lambda_{max.}$ (in EtOH) 253, 260, 264, and 271 mμ (ε 1120, 1170, 1035, and 698). The base appeared to decompose when treated with cold methyl iodide.

Hofmann Degradation of N-*Methyl*-N-1-*phenylpropylaniline*.—An aqueous solution of the above methosulphate (50 g.) was allowed to percolate slowly through a column (5 ft. by ½ in.) of Amberlite I.R.A. 400 resin (200 g.; OH^- form), the alkaline eluate being collected. Washing was continued with water until the eluate was no longer alkaline. The eluate was evaporated at 40°/15 mm. and the resulting syrupy quaternary hydroxide was then decomposed at 80—100°/15 mm. The product was worked up by extraction into ether and then separated into basic and non-basic fractions. The basic fraction was examined by gas chromatography on a 1 m. column, operated at 220°, packed with a support derived from " Tide " (method D of ref. 32) and coated with 10% Apiezon M. The only bases detected were *NN*-dimethylaniline and *N*-methyl-N-1-phenylpropylaniline. Total distillation of the basic fraction gave a liquid (n_D^{22} 1·5659) corresponding on a calibration curve with 72 mol. % of dimethylaniline and 28 mol. % of *N*-methyl-*N*-1-phenylpropylaniline. A prepared mixture of the two bases in the proportions mentioned had an infrared spectrum (liquid film, " Infracord ") superimposable on that of the basic fraction. Distillation of the fraction at 120°/14 mm. gave dimethylaniline (picrate, m. p. and mixed m. p. 163°) and a residue of *N*-methyl-*N*-1-phenylpropylaniline [hydrochloride, m. p. 170—172° (sealed tube)].

The non-basic fraction, on total distillation, had n_D^{23} 1·5450, and showed weak absorption at 3600 cm.$^{-1}$ (OH stretching). Gas chromatography indicated the presence of *trans*-1-phenylpropene (~90%), *cis*-1-phenylpropene (~8%), and 1-phenylpropan-1-ol (~2%). The presence of allylbenzene (~2%) was demonstrated by nuclear magnetic resonance spectroscopy on the neat liquid (doublets at 6·73 and 5·28 τ, *J* 6·2 and 14 c./sec., due to benzylic and terminal olefinic protons, respectively.)

1,2,3,4-*Tetrahydro*-1-*methyl*-2-*phenylquinoline*.—(*a*) 1,2-Dihydro-1-methyl-2-phenylquinoline[33,34] (22·4 g.) was hydrogenated in methanol over Raney nickel at 60—75° and an initial pressure of 110 atm. After 22 hr. the solution was filtered and methanol was removed on a steam-bath. The residue of 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline crystallised from ethanol in needles (8·9 g., 39%), m. p. 105° (lit.,[4] 105°), $\lambda_{max.}$ (in EtOH) 212, 254, and 306 mμ (ε 24,800, 23,600, and 3100), $\lambda_{max.}$ (in conc. HCl) 252, 258, 262 and 269 mμ (ε 473, 606 715, and 578), $\nu_{max.}$ (in CCl_4) 904 and 923 cm.$^{-1}$ (ε 11 and 26).

(*b*) Acetophenone (56 g.) was converted by the method of Pfitzinger[35] into 2-phenylquinoline-4-carboxylic acid, m. p. 211°, $\lambda_{max.}$ (in EtOH) 207, 263, and 337 mμ (ε 45,900, 35,380, and 8270). Distillation of the acid gave 2-phenylquinoline (45 g.), needles (from ethanol), m. p. 85—86°, $\lambda_{max.}$ (in EtOH) 207, 257, and 322 mμ (ε 36,400, 40,200, and 7600). Treatment of 2-phenylquinoline (10 g.) in refluxing ethanol (250 ml.) with sodium (30 g.), added in small

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[30] Campbell, Helbing, Florkowski, and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 3868.

[31] Busch and Rinck, *Ber.*, 1905, **38**, 1761.

[32] Decora and Dinneen, *Analyt. Chem.*, 1960, **32**, 164.

[33] Freund, *Ber.*, 1904, **37**, 4668.

[34] Meisenheimer, Stotz, and Bauer, *Ber.*, 1925, **58**, 2326.

[35] Pfitzinger, *J. prakt. Chem.*, 1897, **56**, 283.

pieces during 2 hr., followed by the usual method of working-up, gave crude 1,2,3,4-tetrahydro-2-phenylquinoline (10·2 g.) as an oil. Reduction of 2-phenylquinoline to the tetrahydro-base was also achieved by hydrogenation in ethanol over Raney nickel at 55—65°/110 atm.[36] A mixture of tetrahydrophenylquinoline (10·2 g.), methyl iodide (9 g.), acetone (50 ml.) and sodium carbonate (7 g.) was heated under reflux for 12 hr. The usual method of working-up gave 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline (9·5 g.), m. p. 105°.

Hofmann Degradation of 1,2,3,4-*Tetrahydro*-1-*methyl*-2-*phenylquinoline*.—The foregoing tertiary base was converted in good yield into the methiodide by heating with an excess of methyl iodide in boiling methanol for 8 days. The methiodide crystallised from water in prisms, m. p. 185° (lit.,[4] 185°), $\lambda_{max.}$ (in EtOH) 251, 258, 263, and 269 mμ (ε 569, 736, 892, and 780). A stirred suspension of the methiodide (6·0 g.) in water (200 ml.) was treated, during 24 hr., with silver oxide, freshly prepared from silver nitrate (20 g.). The mixture was filtered and the filtrate, which gave a negative iodide test, was evaporated to a syrup at 40°/15 mm. The methohydroxide was decomposed at 90—100°/15 mm. The product (3·7 g.), isolated by ether-extraction and distillation, was partly solid and was a mixture of 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline and *NN*-dimethyl-*o*-(3-phenylallyl)aniline, $\lambda_{max.}$ (in EtOH) 215, 254, 294, and 305 mμ (ε 21,600, 16,500, 2480, and 2330), $\nu_{max.}$ (in CCl_4) 908, 925, 949, 978, and 982 cm.$^{-1}$ (ε 12, 21, 71, 46, and 33). Crystallisation of the mixture from ethanol gave crude 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline, m. p. 100—102°. Treatment of the mixture with picric acid in ethanol gave NN-*dimethyl*-o-(3-*phenylallyl*)*aniline picrate* as prisms, m. p. 144—145·5° (Found: C, 59·4; H, 5·1; N, 12·3. $C_{23}H_{22}N_4O_7$ requires C, 59·2; H, 4·7; N, 12·0%).

NN-*Dimethyl*-o-(3-*phenylpropyl*)*aniline Picrate*.—The above mixture of degradation products (19·7 mg.), dissolved in ethanol containing 10% palladised charcoal, absorbed 2·02 ml., (0·66 mol.) of hydrogen at 23°/760 mm. A second hydrogenation on the mixture (2·5 g.) gave a mixture of 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline and *NN*-dimethyl-*o*-(3-phenylpropyl)aniline, $\lambda_{max.}$ (in EtOH) 214, 254, and 301 mμ (ε 19,200, 8200, and 1740), $\nu_{max.}$ (in CCl_4) 908, 923, and 948 cm.$^{-1}$ (ε 13, 17, and 60). Treatment of the mixture with ethanol gave crude 1,2,3,4-tetrahydro-1-methyl-2-phenylquinoline, m. p. 101—102°. Addition of picric acid to the mixture in ethanol gave NN-*dimethyl*-o-(3-*phenylpropyl*)*aniline picrate*, m. p. 115·5—116·5° (Found: C, 58·9; H, 5·0; N, 12·0. $C_{23}H_{24}N_4O_7$ requires C, 58·9; H, 5·1; N, 11·9%).

1,2,3,4-*Tetrahydro*-3-*phenylquinoline*.—The method of Hubner[37] was used to prepare 3-phenylquinoline-4-carboxylic acid, m. p. 273°, $\lambda_{max.}$ (in dimethylformamide) 260 and 287 mμ (ε 14,150 and 6950). Decarboxylation[38] at 300—320° gave 3-phenylquinoline, m. p. 52°, $\lambda_{max.}$ (in EtOH) 207 and 252 mμ (ε 33,800 and 34,200). 3-Phenylquinoline (9·4 g.) was hydrogenated in ethanol (50 ml.) over Raney nickel at 60—70° and an initial pressure of 80 atm. After 12 hr., the solution was filtered and ethanol was removed on a steam-bath. The residue of 1,2,3,4-tetrahydro-3-phenylquinoline crystallised from aqueous ethanol in needles (6·26 g., 65%), m. p. 86—87° (lit.,[39] 83°), $\lambda_{max.}$ (in EtOH) 208, 251, and 304 mμ (ε 33,750, 8850, and 2730).

Hofmann Degradation of 1,2,3,4-*Tetrahydro*-1-*methyl*-3-*phenylquinoline*.—A mixture of the above base (5·16 g.), methyl iodide (30 g.), anhydrous sodium carbonate (1·4 g.), and acetone (45 ml.) was heated under reflux for 1·5 hr. The usual method of working-up gave 1,2,3,4-tetrahydro-1-methyl-3-phenylquinoline methiodide as needles (6·45 g., 70%), m. p. 183—184° (lit.,[39] 172°) (Found: C, 55·6; H, 5·5; N, 3·6. Calc. for $C_{17}H_{20}IN$: C, 55·9; H, 5·5; N, 3·8%), $\lambda_{max.}$ 258, 263, and 270 (infl.) mμ (ε 550, 580, and 390). The methohydroxide from the methiodide (4 g.) was decomposed at 110—120°, giving NN-*dimethyl*-o-(2-*phenylallyl*)*aniline* as a pale-yellow oil (1·10 g., 40%), b. p. 205—210°/12 mm. (Found: C, 85·9; H, 8·1; N, 6·0. $C_{17}H_{19}N$ requires C, 86·0; H, 8·1; N, 5·9%), $\lambda_{max.}$ (in EtOH) 206 and 244 mμ (ε 30,600 and 14,100); *picrate*, needles, m. p. 156—158° (from ethanol) (Found: C, 59·0; H, 4·8; N, 12·1. $C_{23}H_{22}N_4O_7$ requires C, 59·2; H, 4·75; N, 12·0%).

NN-*Dimethyl*-o-(2-*phenylpropyl*)*aniline*.—The above unsaturated base (0·81 g.) was hydrogenated as its hydrochloride in methanol (30 ml.) over 5% palladised charcoal (0·1 g.) at room

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[36] Cf. Protiva, Pericha, Borovicka, and Jilek, *Coll. Czech. Chem. Comm.*, 1950, **15**, 532.

[37] Hubner, *Ber.*, 1906, **39**, 982.

[38] Hubner, *Ber.*, 1908, **41**, 482.

[39] von Braun, Petzold, and Seemann, *Ber.*, 1922, **55**, 3785.

temperature and pressure (0·99 mol. absorbed). The solution was filtered, heated to remove methanol, and distilled from a bulb-tube. NN-*Dimethyl*-o-(2-*phenylpropyl*)*aniline* was a pale yellow oil (0·46 g., 56%) (Found: C, 85·5; H, 8·7; N, 6·0. $C_{17}H_{21}N$ requires C, 85·3; H, 8·8; N, 5·85%), $\lambda_{max.}$ (in EtOH) 207 and 251 mμ (ε 22,600 and 4450); *picrate*, swords, m. p. 134—136° (from ethanol) (Found: C, 58·7; H, 5·0; N, 12·2. $C_{23}H_{24}N_4O_7$ requires C, 59·0; H, 5·2; N, 12·0%).

cis- *and* trans-1,2,3,4-*Tetrahydro*-2,3-*diphenylquinoline*.—Deoxybenzoin (25 g.) was converted by the method of Pfitzinger [35] into 2,3-diphenylquinoline-4-carboxylic acid (18·22 g., 53%), m. p. 295°, $\lambda_{max.}$ (in dimethylformamide) 261 and 324 mμ (ε 29,300 and 5500). The acid (54 g., in 10—12-g. batches) was heated in an oil-bath at 320—350° until evolution of carbon dioxide ceased (10—12 min.). The crude 2,3-diphenylquinoline (41 g., 88%), which was recovered by ether-extraction, crystallised from ethanol as needles, (28·3 g.), m. p. 94—96°, $\lambda_{max.}$ (in EtOH) 208, 236, 258, and 329 mμ (ε 40,400, 40,100, 34,000, and 4900). 2,3-Diphenylquinoline (10 g.) was reduced by sodium and ethanol according to the directions of Plant and Rosser.[19] The products were *cis*-1,2,3,4-tetrahydro-2,3-diphenylquinoline (6·0 g.), needles, m. p. 131°, $\lambda_{max.}$ (in EtOH) 208, 249, and 305 mμ (ε 44,800, 10,250, and 3270), and *trans*-1,2,3,4-tetrahydro-2,3-diphenylquinoline (0·3 g.), plates, m. p. 92°, $\lambda_{max.}$ (in EtOH) 208, 252, and 304 mμ (ε 48,400, 12,460, and 3460).

The nuclear magnetic resonance spectrum of the *cis*-base was determined with a Varian 4300 spectrometer with a 56·45 Mc. oscillator. In deuterochloroform (internal reference, tetramethylsilane), the base showed a doublet at 5·6 τ, singlet at 6·2 τ, multiplet (>5 peaks) at 6·8 τ, and doublet at 7·2 τ, the areas being in the ratios 1 : 1 : 1 : 2. After acidification and exchange with D_2O, the spectrum showed (i) a doublet at 5·4 τ, *J* 3·4 c./sec. (proton at C-2), (ii) a multiplet at 6·6 τ (proton at C-3), and (iii) a doublet at 7·2 τ, *J* 6·6 c./sec. (protons at C-4). The singlet at 6·2 τ in neutral solution is assigned to NH as it sharpened on acidification and disappeared after exchange with D_2O.

cis-1,2,3,4-*Tetrahydro*-1-*methyl*-2,3-*diphenylquinoline*.—*cis*-1,2,3,4-Tetrahydro-2,3-diphenylquinoline (4 g.), methyl iodide (15 g.), anhydrous sodium carbonate (1·0 g.), and acetone (50 ml.) were heated under reflux for 12 hr. The cooled solution was diluted with water (20 ml.), heated to remove acetone and methyl iodide, and filtered. The residue was crystallised from ethanol and finally sublimed at 150°/0·5 mm., giving cis-1,2,3,4-*tetrahydro*-1-*methyl*-2,3-*diphenylquinoline* as prisms (2·5 g., 60%), m. p. 182—183° (sealed tube) (Found: C, 87·9; H, 7·15; N, 5·0. $C_{22}H_{21}N$ requires C, 88·25; H, 7·05; N, 4·7%), $\lambda_{max.}$ (in EtOH) 209, 250, and 306 mμ (ε 49,700, 11,610, and 4070), $\lambda_{max.}$ (in conc. HCl) 258, 263, and 270 mμ (ε 954, 954, and 886).

cis-1,2,3,4-*Tetrahydro*-1-*methyl*-2,3-*diphenylquinoline Methiodide*.—The foregoing base was recovered after treatment with excess of methyl iodide in boiling acetone or nitromethane, and after treatment with methyl iodide in acetone at 100°/10 atm. A mixture of the base (6 g.), dimethyl sulphate (20 g.), and nitromethane (50 ml.) was heated under reflux for 3 days. The blue solution was poured into ether (500 ml.), when a blue gum containing some crystals was slowly precipitated. Recrystallisation of some of the crystals gave pale green prisms, m. p. 229°, probably impure 1-methyl methosulphate of *cis*-1,2,3,4-tetrahydro-1-methyl-2,3-diphenylquinoline (Found: S, 7·8. $C_{24}H_{27}NO_4S$ requires S, 7·5%) (analyses for carbon and hydrogen were unsatisfactory) $\lambda_{max.}$ (in EtOH) 210 (infl.), 258, 263, and 270 (infl.) mμ (ε 26,000, 1420, 1420, and 1140). An aqueous solution of the blue gum gave no turbidity with sodium carbonate solution. The gum was separated from ether by decantation and extracted with boiling water (3 × 30 ml.). The combined extracts were filtered, and saturated with potassium iodide. The methiodide which separated was filtered, dissolved in dry chloroform, and reprecipitated by addition of dry ether. Recrystallisation of the solid (3·4 g.), from ethanol gave cis-1,2,3,4-*tetrahydro*-1-*methyl*-2,3-*diphenylquinoline methiodide* (3 g.), needles, m. p. 202—203° (Found: C, 62·3; H, 5·6; N, 3·4. $C_{23}H_{24}IN$ requires C, 62·6; H, 5·4; N, 3·1%), $\lambda_{max.}$ (in EtOH) 258, 263, and 270 mμ (ε 1130, 1140, and 890). The spectrum was unchanged by aqueous sodium carbonate, which caused no turbidity.

Hofmann Degradation of cis-1,2,3,4-*Tetrahydro*-1-*methyl*-2,3-*diphenylquinoline*.—The above methiodide (3 g.) was suspended in aqueous ethanol (500 ml.; 50%) and the solution was stirred overnight, in the dark, with an excess of freshly prepared silver oxide. The filtered solution, which gave a negative test for iodide, was alkaline to litmus and showed the typical ultraviolet spectrum of the quaternary salt. Ethanol was removed by heating the solution under reduced pressure at 30—50°, and the residual solution was washed with ether. Evaporation of the ether yielded nothing. The aqueous quaternary hydroxide was evaporated to a syrup at 30—40°/15 mm. and the syrup was decomposed at 160—170°/760 mm. during 3 hr. Ether-extraction yielded *cis*-1,2,3,4-tetrahydro-1-methyl-2,3-diphenylquinoline (1·5 g.), m. p. 178—179°, mixed m. p. 179—180·5°, $\lambda_{max.}$ (in EtOH) 252 and 305 mμ (ε 10,400 and 3380). Sublimation gave the pure base, m. p. and mixed m. p. 181—182°, $\lambda_{max.}$ (in EtOH) 252 and 307 mμ (ε 11,510 and 4070).

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