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Studies on the Reaction of Benzoyl Peroxide with NN-Disubstituted Aromatic Amines and Other Related Compounds. Part IV.^{1,2} A Novel Formation of 1,2,3,4-Tetrahydroquinoline Derivatives.

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The reaction of benzoyl peroxide with NN-dimethylaniline in cumene or chloroform at ca. 0° in the presence of N-phenylmaleimide gives 1,2,3,4-tetrahydro-1-methylquinoline-N-phenyl-3,4-dicarboximide, formed via the *N*-methylanilinomethyl radical. This reaction provides a convenient way of differentiating between the PhNMe·CH₂ radical and the (PhNMe·CH₂)⁺ cation as intermediates. The latter does not react with *N*-phenylmaleimide, although it reacts with ethyl vinyl ether to give 4-ethoxy-1,2,3,4-tetrahydro-1-methylquinoline. The formation of quinoline derivatives by use of benzoyl peroxide succeeds also with N-methylmaleimide (instead of the N-phenyl compound) and with a number of other aromatic tertiary amines, including N-phenyl- and N-p-tolyl-pyrrolidine; yields of products obtained are of preparative value. Reduction of the products gives 2,3,3a,4,5,9b-hexahydro-2,3,3a,3b,4,5,6,11b-octahydro-2-phenyl-1H-dipyrrolo[1,2-5-methyl-2-phenyl-1H-pyrrolo[3,4-c]quinoline, a,3,4-c]quinoline, and derivatives thereof.

REACTION of benzoyl peroxide with *NN*-dimethylaniline can give rise to a variety of products, according to the nature of the solvent and other conditions.³⁻⁶ Both ions

¹ Part III, R. B. Roy and G. A. Swan, J. Chem. Soc. (C), 1968, 83.

 ² Preliminary communication, R. B. Roy and G. A. Swan, *Chem. Comm.*, 1968, 1446; G. A. Swan, *ibid.*, 1969, 20.
 ³ J. M. Fayadh, (the late) D. W. Jessop, and G. A. Swan, *J. Chem. Soc.* (C), 1966, 1605; R. B. Roy and G. A. Swan, *Chem. Comm.* 1026 (1966), 1605; Comm., 1966, 427.

and radicals appear to be involved, although it is not clear in all cases as to which products arise from ions and which from radicals. With a view to trapping intermediates we carrried out the reaction in the presence

⁴ R. Huisgen, W. Heydkamp, and F. Bayerlein, Chem. Ber., 1960, 93, 363.

⁵ L. Horner and C. Betzel, Annalen, 1953, 579, 175.

⁶ D. M. Graham and R. B. Mesrobian, Canad. J. Chem., 1963, 41, 2938.

of various unsaturated compounds. When N-phenylmaleimide (II) was used as the latter a crystalline product was obtained. Thus the reaction of benzoyl peroxide (1·44 mol.) with NN-dimethylaniline (4·3 mol.) in the presence of N-phenylmaleimide (1 mol.) in cumene at -5° yielded 1,2,3,4-tetrahydro-1-methylquinoline-Nphenyl-3,4-dicarboximide (V) (0·59 mol.).



This novel reaction also occurred with N-methylmaleimide (VIIb) and with other NN-disubstituted aromatic amines in which at least one of the N-substituents was methyl (VI). In this way the quinolines (VIIIa—f) were prepared. We failed to isolate a quinoline from the product obtained from benzoyl peroxide and NN-diethylaniline in the presence of N-phenylmaleimide, although a similar reaction brought about by γ -irradiation instead of peroxide succeeded.⁷ In the cases of reaction of benzoyl peroxide with N-ethyl-Nmethylaniline (VIa) and N-ethyl-N-methyl-p-toluidine (VIb), respectively, in the presence of N-phenylmaleimide, the products isolated were the N-ethylquinolines (VIIId) and (VIIIe), although the isomeric 1,2-dimethyl compounds could have been lost in the work-up.



Similarly N-phenylpyrrolidine (IXa) and N-p-tolypyrrolidine (IXb) yielded 1,2,3,3a,4,5-hexahydropyrrolo-[a]quinoline-N-phenyl-4,5-dicarboximide (Xa) and analogous compounds (Xb—d), of which (Xb) and (Xc) were each isolated in two stereoisomeric forms.

These reactions were best carried out at temperatures of -5 to 0° in cumene or chloroform, although they also succeeded (usually in lower yield) in acetonitrile.

⁷ J. M. Fayadh and G. A. Swan, J. Chem. Soc. (C), 1969, 1781.

The mass spectra of all these quinoline derivatives contained a peak due to the molecular ion, but the base peak was the appropriate quinolinium ion (XI) in the



cases of most compounds (V) or (VIII). In the cases of compounds (X) the peak due to the quinolinium ion (XII) was not much smaller than that of the molecular ion, which was the base peak.

The quinoline structures could also be seen from n.m.r. spectra. Thus in the case of (VIIIc) the aromatic 5-proton showed up as a broad singlet (1H) at $\tau 2.75$ and the protons at C-7 and C-8 gave an AB system (2H), $\tau 3.02$ and 3.45, $J_{AB} 8.5$ c./sec. Also the spectrum of (VIIIb) showed an ABX system, with the X proton (*i.e.* that at C-3) coupled to another (*i.e.* at C-4) with J 10 c./sec. The doublet for the latter proton was at $\tau 5.95$. This latter spectrum was measured and interpreted by Dr. Keller and Dr. R. J. Stoodley, by use of a 90 MHz instrument in the Laboratory of Spectrospin, A.G., in Zürich.

By use of Dreiding models, the form of (V) with rings B and c *cis*-fused can be made without strain, and with a dihedral angle for the protons at C-3 and C-4 of 0°. On the other hand, construction of the *trans*-isomer involves considerable strain, and a dihedral angle of rather less than 180°. The quinolines are therefore tentatively formulated as being *cis*-fused. Burgess and McCullagh⁸ have prepared the *cis*-compound (XIII), which has a coupling constant of 9.5 c./sec. for the two protons at the ring junction.

In the case of the pyrroloquinolines (X) there is the additional possibility of isomerism arising from different relative configurations at positions 3a and 4.

The formation of quinoline derivatives from NNdimethylaniline might involve either the radical (I) or the cation (PhNMe:CH₂)⁺ (XV). Thus the radical (III) formed by addition of (I) to (II) could cyclise to give (IV) (cf. ref. 9), which could then be converted into (V) by hydrogen abstraction by some radical present in the system. In this case abstraction in (IV) by (III)

⁸ E. M. Burgess and L. McCullagh, J. Amer. Chem. Soc., 1966, **88**, 1580.

⁹ D. I. Davies and C. Waring, J. Chem. Soc. (C), 1968, 1865.

seems unlikely, as we did not detect the formation of (N-methylanilino)methyl-N-phenylsuccinimide (XVI).

If, on the other hand, the cation (XV) was the intermediate, the reaction would be looked on as a polar 1,4-cycloaddition, followed by loss of a proton.

Thermal decomposition of di-t-butyl peroxide in an excess of NN-dimethylaniline yields NN'-dimethyl-NN'diphenylethylenediamine, through dimerisation of the radical (I).¹⁰ When this reaction was carried out in the presence of N-phenylmaleimide the quinoline (V) was formed, suggesting that the latter is produced *via* the radical mechanism. Moreover, this quinoline is also formed by γ -irradiation or photolysis of a solution of *N*-phenylmaleimide in *NN*-dimethylaniline, where there is also evidence of the intervention of radical (I).⁷

PhNMe·CH2·NMePh H+ PhNMe:CH2+Ph·NHMe (XIV) (XV)

Although there was thus evidence that the radical (I) can react with (II) to give (V), it was desirable to show that the cation (XV) could not do so under the same conditions. A solution of NN'-dimethyl-NN'-diphenylmethylenediamine (XIV), N-phenylmaleimide (II), and benzoic acid in chloroform was kept for 2 days at room temperature, but the formation of the quinoline (V) could not be detected. The α -diamine (XIV) would presumably yield the cation (XV).¹¹ (N-Methylanilino)-N-phenylsuccinimide (XVIIa), formed by the addition of the N-methylaniline (produced in the reaction) to N-phenylmaleimide, was, however, isolated. The formation of (XV) from (XIV) can also be achieved by the action of an alkyl halide. If (XV) underwent polar, 1,4-cycloaddition, the product would have to lose a proton to yield (V), so that only a catalytic amount of alkyl halide should be required. When a chloroform solution containing NN'-dimethyl-NN'-di-p-tolylmethylenediamine and N-phenylmaleimide was treated with a



catalytic amount of benzyl chloride, (N-methyl-ptoluidino)-N-phenylsuccinimide (XVIIb), but no (VIIIb), was isolated from the products.

On the other hand when a solution of the α -diamine (XIV) and ethyl vinyl ether (XVIII) in chloroform was kept for 2 days in the presence of a catalytic amount of benzoic acid it gave a high yield of 4-ethoxy-1,2,3,4tetrahydro-1-methylquinoline (XIX). The structure of the latter followed from its mass spectrum, which showed the molecular ion corresponding to $C_{12}H_{17}NO$, with the base peak m/e 144, *i.e.* (XI; $R^2 = H, R^3 = Me$).



(XV) (XVIII)

Schiff bases are inert towards typical dienophiles, but react readily with vinyl ethers in the presence of Lewis acids (e.g. boron trifluoride).12 The diene system, represented by (XX) in the conjugate acid, acquires



electrophilic properties, and the dienophile, e.g. (XVIII), acts as the electron donor. Thus (XIX) can be formed from (XV) and (XVIII), but a similar reaction would not be expected with N-phenylmaleimide, as this would not act as an electron donor. The reaction with ethyl vinyl ether is therefore regarded as a polar 1,4-cycloaddition,¹³ followed by proton loss.

The use of N-phenylmaleimide and ethyl vinyl ether as trapping agents should be useful in future work on the mechanism of oxidation of NN-dimethylaniline and related amines by various reagents. The reaction of the radical (I) with N-phenylmaleimide must be a very fast one.

Reactions of benzovl peroxide with NN-dimethylaniline or NN-dimethyl-p-toluidine were also carried out in the presence of cyclohexene, mesityl oxide, ethyl cinnamate, vinyl cyanide, maleic anhydride, or 1,4benzoquinone. Although in some cases new products were formed, we failed to isolate any crystalline quinoline derivatives, so the use of these compounds as trapping agents was not further pursued.

The reaction of benzoyl peroxide with N-p-tolylpyrrolidine (IXb) in the presence of N-methylmaleimide (VIIb) yielded not only (Xd), but also a compound, m.p. 325°, for which structure (XXI) is suggested. The latter was too insoluble in most organic solvents for its n.m.r. spectrum to be measured. Its mass spectrum showed the molecular ion corresponding to C₂₁H₂₃N₃O₄ and peaks at m/e 295 and 269, attributed to the ions (XXII) and (XXIII), respectively. Presumably the initially formed (Xd) underwent further reaction with benzoyl peroxide, with attack at the 1-position, but the resulting radical, corresponding to (III), failed to cyclise for steric reasons and therefore abstracted a hydrogen atom from some other molecule to yield (XXI).

¹⁰ H. B. Henbest and R. Patton, J. Chem. Soc., 1960, 3557. ¹¹ H. Böhme, W. Lehners, and G. Keitzer, Chem. Ber., 1958, 91, 340; H. Böhme and D. Eichler, ibid., 1967, 100, 2131.

¹² L. S. Povarov and B. M. Mikhailov, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 1963, 955; L. S. Povarov, Russ. Chem. Rev., 1967, 36, 656.

¹³ R. R. Schmidt, Tetrahedron Letters, 1968, 3443.



Reduction of (V) with lithium aluminium hydride gave 2,3,3a,4,5,9b-hexahydro-5-methyl-2-phenyl-1*H*pyrrolo[3,4-c]quinoline (XXIVa); and compounds



(XXIVb—d) were similarly prepared. Likewise (Xa) afforded 2,3,3a,3b,4,5,6,11b-octahydro-2-phenyl-1*H*-dipyrrolo[1,2,-*a*,3,4-*c*]quinoline (XXV). The mass spectra of (XXIVa) and (XXIVc) contained peaks corresponding to the molecular ions $C_{18}H_{20}N_2$ and $C_{19}H_{22}N_2$, respectively, and strong peaks at m/e 144 and 158 [*i.e.* (XI; $R^3 = Me, R^2 = H \text{ or } Me$], but the base peaks were at 158 and 172, respectively, and therefore formulated as (XXVI; $R^2 = H \text{ or } Me$).

Some attempts to synthesise (V) or (XXIVa) failed. Thus, although Dolby and Furukawa¹⁴ were able to replace the methyl group of 2-methylquinoline-*N*benzyl-3,4-dicarboximide by hydrogen by oxidation with chromic acid, we found the similar oxidation of 2-methyl-quinoline-*N*-phenyl-3,4-dicarboximide to be umpromising. Hydrolysis of ethyl α -cyano-1-methyl-3isatylideneacetate¹⁵ under acidic conditions gave 1,2dihydro-1-methyl-2-oxoquinoline-3,4-dicarboxylic acid (*cf.* ref. 16) but attempts to reduce the *N*-phenylimide of this compound to (XXIVa) failed.

EXPERIMENTAL

General directions as in Part II.17

1,2,3,4-Tetrahydro-1-methylquinoline-N-phenyl-3,4-dicarboximide (V).—A solution of benzoyl peroxide ($3\cdot0$ g.) in cumene (75 ml.) was added during 1.5 hr. to a stirred solution of NN-dimethylaniline (4.5 g.) and N-phenylmaleimide (1.5 g.) in cumene (25 ml.) at -5° under nitrogen. After a further 10 hr., sodium hydroxide solution (30%; 35 ml.) was added and the cold mixture was stirred for an additional 0.5 hr. The organic layer was separated, washed with water, and dried (MgSO₄). The cumene and unchanged amine were removed by distillation (finally at 12 mm. and from an oil-bath), leaving a residue (2.8 g.) which was chromatographed on alumina. Elution with light petroleum afforded 4,4'-bisdimethylaminodiphenylmethane, m.p. 91° (0.25 g.). Elution with benzene-light petroleum (1:4) gave 4-benzoyloxy-NN-dimethylaniline, m.p. 158° (0.075 g.). Elution with benzene-light petroleum (1:2) yielded the *dicarboximide* (V) as colourless crystals, m.p. 196° (1.5 g.) (from benzene-light petroleum).

The compounds listed in Tables 1 and 2 were prepared similarly, and were usually eluted from alumina by benzenelight petroleum (1:1) or benzene, and recrystallised from benzene-light petroleum.

Reaction of Di-t-butyl Peroxide with NN-Dimethylaniline in the Presence of N-Phenylmaleimide.—A mixture of NNdimethylaniline (6·3 ml.), N-phenylmaleimide (1 g.), and di-t-butyl peroxide (0·71 g.) was heated in a sealed tube for 40 hr. at 125—130°. Unchanged amine was removed by distillation at 11 mm., and the residue was chromatographed on alumina (30 g.). After elution of other materials with benzene-light petroleum (1:1) the 1,2,3,4tetrahydro-1-methylquinoline-N-phenyl-3,4-dicarboximide (V) was eluted with benzene, and after recrystallisation from benzene-light petroleum weighed 0·5 g. and was identical with the specimen already obtained.

(N-Methylanilino)-N-phenylsuccinimide (XVIIa).—A solution of N-methylaniline (0·11 g.) and N-phenylmaleimide (0·17 g.) in acetic acid (1·5 ml.) was kept overnight at room temperature. The resulting solid was collected, washed with acetic acid followed by light petroleum, and recrystallised from benzene–light petroleum to give the *product*, m.p. 172°, ν_{max} . 1710s cm.⁻¹ (C=O str.) (Found: C, 72·45; H, 6·2; N, 9·85. C₁₇H₁₆N₂O₂ requires C, 72·9; H, 5·7; N, 10·0%), m/e 280 (M⁺), 175, 173, 160, 133, and 132.

(N-Methyl-p-toluidino)-N-phenylsuccinimide (XVIIb).— Similarly prepared from N-methyl-p-toluidine the product had m.p. 186°, v_{max} 1705s cm.⁻¹ (Found: C, 74.05; H, 6.25; N, 8.9%; M^+ 294.1381. C₁₈H₁₈N₂O₂ requires C, 73.5; H, 6.1; N, 9.5%); M 294.1368, m/e 174, 173, 147, 146, 121, and 120.

Reaction of Benzoic Acid with NN'-Dimethyl-NN'-diphenylmethylenediamine in the Presence of N-Phenylmaleimide.— Benzoic acid (0.36 g.) was added to a solution of the base 0.66 g.) and N-phenylmaleimide (1.02 g.) in pure, dry chloroform (9 ml.). After 3 days at room temperature the solution was shaken with N-sodium hydroxide and dried (K₂CO₃); the solvent was removed, and the residue chromatographed on alumina. Light petroleum eluted a colourless oil. Benzene-light petroleum (1:1) eluted N-phenylmaleimide. The material eluted with benzene, when recrystallised four times from benzene-light petroleum afforded (N-methylanilino)-N-phenylsuccinimide (XVIIa).

Reaction of NN'-Dimethyl-NN'-di-p-tolylmethylenediamine Catalysed by Benzyl Chloride.—Benzyl chloride (13 mg.) was

¹⁶ H. Fiesselmann and W. Ehmann, *Chem. Ber.*, 1958, **91**, 1706.

¹⁷ R. B. Roy and G. A. Swan, J. Chem. Soc. (C), 1968, 80.

 ¹⁴ L. J. Dolby and S. Furukawa, J. Org. Chem., 1963, 28, 2512.
 ¹⁵ J. Harley-Mason and R. F. J. Ingleby, J. Chem. Soc., 1958, 3639.

 TABLE 1

 Reactions of benzoyl peroxide with amines in the presence of N-substituted maleimides

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		Benzoyl		N-Phenyl-	N-Methyl-		
		peroxide	Amine	maleimide	maleimide		Yield
	Product	(g.)	(g.)	(g.)	(g.)	Solvent	(g.)
(V)	1,2,3,4-Tetrahydro-1-methylquinoline-N-phenyl-3,4- dicarboximide	3.0	$4 \cdot 5$	1.5		Cumene	1.5 °
(VIIIa)	1,2,3,4-Tetrahydro-1-methylquinoline-N-methyl-3,4- dicarboximide	3.0	$4 \cdot 5$		1.5	Cumene	0.8
(VIIIb)	1,2,3,4-Tetrahydro-1,6-dimethylquinoline-N-phenyl- 3,4-dicarboximide	3.0	$4 \cdot 5$	1.5		Chloroform	1.59
(VIIIc)	1,2,3,4-Tetrahydro-1,6-dimethylquinoline-N-methyl- 3,4-dicarboximide	3.0	4.5		1.5	Chloroform	1.5
(VIIId)	1-Ethyl-1,2,3,4-tetrahydroquinoline-N-phenyl-3,4-di- carboximide	3.0	4 ·0	$1 \cdot 2$		Cumene	0.8
(VIIIe)	1-Ethyl-1,2,3,4-tetrahydro-6-methylquinoline-N-phenyl 3,4-dicarboximide	- 3.0	4·0 ª	1.4		Cumene	1.0 ×
(VIIIf)	1,2,3,4-Tetrahydro-1-phenylquinoline-N-phenyl-3,4- dicarboximide	3.0	4 ·0 ^b	$1 \cdot 2$		Cumene	0.2
(Xa)	1,2,3,3a,4,5-Hexahydropyrrolo[a]quinoline-N-phenyl- 4,5-dicarboximide	3.0	4·0 °	$1 \cdot 2$		Chloroform	0.25
		$2 \cdot 5$	4·0 °	1.3		Acetonitrile	0·3 i
(Xb)	 (i) 1,2,3,3a,4,5-Hexahydropyrrolo[a]quinoline-N-methyl- (ii) 4,5-dicarboximide 	1.5	0 ∘ 2∙0		0.8	Cumene	$\left\{\begin{array}{c} 0.25^{j} \\ 0.05^{k} \end{array}\right.$
(Xc)	 (i) 1,2,3,3a,4,5-Hexahydro-7-methylpyrrolo[a]quinoline- (ii) N-phenyl-4,5-dicarboximide 	1.6	2.5 d	0.8		Acetonitrile	$\begin{cases} 0.21\\ 0.08m \end{cases}$
(Xd)	1,2,3,3a,4,5-Hexahydro-7-methylpyrrolo[a]quinoline- N-methyl-4,5-dicarboximide	2.0	3.0 ª		1.5	Acetonitrile	$\begin{cases} 0.6^n \\ 0.05^n \end{cases}$
(XXI)	-	J				+ cumene	0.35

^a Prepared by reduction of N-acetyl-N-methyl-p-toluidine with lithium aluminium hydride. ^b Prepared by the method of C. S. Gibson and D. C. Vining (J. Chem. Soc., 1923, 123, 831), but further purified by chromatography on alumina (elution with light petroleum). ^c Conveniently prepared (cf. J. von Braun and G. Lemke, Ber., 1922, 55, 3536) by heating a mixture of aniline (9·3 g.), sodium carbonate (30 g.), water (200 ml.), and 1,4-dichlorobutane (15·8 g.) under reflux for 11 hr. The cooled mixture was extracted with ether, the solvent removed from the dried extract, and the residue heated under reflux for 1 hr. with acetic anhydride, cooled, treated with dilute hydrochloric acid, and extracted with ether. The aqueous layer was basified (30% NaOH), and extracted with ether. The residue obtained by removal of ether from the extract was chromatographed on alumina, the N-phenylpyrrolidine (11 g.) being eluted by light petroleum. ^d Prepared as in c, but by use of p-toluidine instead of aniline (cf. L. C. Craig and R. M. Hixon, J. Amer. Chem. Soc., 1931, 53, 187). ^e Yields 1·3 and 0·2 g., respectively, with chloroform and acetonitrile as solvents; p-benzoyloxy-NN-dimethylaniline (0·1 and 1·3 g., respectively) was also formed. ^f Also 5,6,11,12-tetrahydro-5,11-dimethylphenhomazine, m.p. 103° (3 mg.) (eluted with light petroleum), and p-benzoyloxy-NN-dimethylaniline, m.p. 158° (0·25 g.) [eluted before (VIIIa) by benzene-light petroleum]. ^e Also 5,6,11,12-tetrahydro-2,5,8,11-tetramethylphenhomazine, m.p. 149° (0·8 g.) (eluted with light petroleum). ^h Not obtained when chloroform or acetonitrile used as solvent. ⁱ Elution with benzene-light petroleum (1: 3) afforded N-p-benzoyloxyphenylpyrrolidine, m.p. 215° (0·2 g.), to be described in a later paper. ^{j, k} Eluted by benzene-light petroleum (1: 3) and benzene, respectively; and recrystallised from benzene. ^l, ^m Eluted by benzenelight petroleum (1: 1) and benzene, respectively. ^m Recrystallised from benzene. ^e Eluted by ether-benzene (1: 4).

TABLE 2

Products from Table 1

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												<u> </u>				I					
	Found (%)		und (%) Reg			Required $(\%)$ where $(cm - 1)$			•			H-4 in (VIII) (VIII) or or H-5 L		M+		<i>m/e</i> for (XI) or (XII)					
Com-		<u> </u>			Molecular		~					ArCH.	NCH.	CO·N·CH.	in(X)	$(\mathbf{X})^{*}$	·		· · · ·	Molecular	· · · · ·
pound	M.p.	Ċ	н	N	formula	С	н	N	w	s	s	(s)	(s)	(s)	(d)	(c./sec.)	Found	Calc.	Found	formula	Calc.
(V) (VIIIa) (VIIIb)	196° 175 199	73·6 67·5 74·1	5·7 6·0 5·8	$9.6 \\ 12.3 \\ 9.4$	C ₁₈ H ₁₆ N ₂ O ₂ C ₁₃ H ₁₄ N ₂ O ₂ C ₁₉ H ₁₈ N ₂ O ₂	73·9 67·8 74·5	5·5 6·0 5·9	$9.6 \\ 12.2 \\ 9.2$	1780 1775 1775	1707 1690 1710	75 4 765	7.75	7·4 7·2 7·25	7.02	6·1 5·86 5·95	10 8·5 10	292 (18%) 230 (34%) 306 · 1355	3 06·1368	144 (100%)) 144 (100%)) 158-0965	· C ₁₀ H ₁₀ N C ₁₁ H ₁₂ N	158-0969
(VIIIc)	183	68.8	6.5	11.5	C14H14N2O2	68.8	6.6	11.5	1765	1697		7.7	7.24	7.03	6.07	9	244 (40%)		158 (100%)	C.,H.,N	
(VIIId) a	184 176	74-5	5.85	9.0	C ₁₉ H ₁₈ N ₂ O ₂	74.5	5.9	9·2							5.93	9	306 (96%)		158 (22%)	$C_{11}H_{12}N$ (R ₂ = H,	
																			144 (22%)	$ \begin{array}{l} \mathbf{R}_3 = \mathrm{Et} \\ \mathbf{C}_{10} \mathbf{H}_{10} \mathbf{N} \\ (\mathbf{R}_2 = \mathbf{H}, \\ \mathbf{R}_3 = \mathrm{Me} \end{array} $	
(VIIIe) b (VIIIf) c	$112 \\ 122 \\ 123 \\ 123$	74·8 77·1	6·2 5·15	8·7 8·3	C ₂₀ H ₂₀ N ₂ O ₂ C ₂₃ H ₁₈ N ₂ O ₂	75·0 77·95	$6.25 \\ 5.1$	8·75 9·0	1775 1775	$1705 \\ 1705$		7.77			6 ·0 2	10	320 (100%) 354·1372 (9%)) 354·1368	172 (17%) 206 (5%)	$C_{12}H_{14}N C_{15}H_{12}N$	
(Xa)	204	75.9	$5 \cdot 2$	9 ·0	$C_{20}H_{18}N_2O_2$	75.5	5.6	8.8	1770	1700							318-1378	318-1368	170 (51%)		
(Xb) (i)	$\frac{168}{169}$	70·0	6·4	11.3]				1768	1700							(100%) 256.1212 · (100%))	170 (46%)	C12H12N	
(Xb) (ii)	134 135	71-3	6.6	11·5	$\left\{ C_{15}H_{16}N_{2}O_{2}\right\}$	70 ∙3	6.2	11.0	1770	1695	763						256·1212 (100%)	256·1212	170 (70%)		
(Xc) (i)	158	77.3	$6 \cdot 2$	8.0)				1770	1700		7.7			5.85	10	332-1528	1	184.1123		
(Xc) (ii)	210	76 ·1	6.2	8.2	$C_{21}H_{20}N_2O_2$	76.0	6.0	8.4	1768	1700		7.75			6 ∙0 4	8	(100%) 332.1518 (100%)	}332.1525	(75%) 184.1127 (92%)	C ₁₃ H ₁₄ N	184-1126
(Xd) d	164	71.1	7 ∙0	11.3	$C_{16}H_{18}N_2O_2$	71.1	6.7	10.4	1764	1690	804	7 ·72		7.11	6.0	8	270·1372 (100%)	270-1368	184 (34%)	C13H14N	
•(XXI)	325				$C_{21}H_{23}N_3O_4$				1765	1695	810(1	w)					381-1677	381-1688			
																	(46%)				

N.m.r. spectra were measured at 60 Mc./sec. for solutions in deuteriochloroform.

σ τ 8-86 (t, CH₂CH₂, J 7 c./sec.); m/e 291 (100%).
 δ τ 8-9 (t, CH₂CH₂, J 6-5 c./sec.); m/e 158 (11%), presumably C₁₂H₁₂N.
 σ m/e 78 (100%).
 d τ 3-07 and 3-57 (AB, H-8 and H-9, J 8.5 c./sec.) and 2.74 (s, H-6).
 σ m/e Found: 269-1288 (100%).
 Calc. for C₁₂H₁₂N₂O₂ (XXIII), 269-1289; also 295 (1%), presumably C₁₈H₁₂N₂O₂ (XXIII).

added to a solution of the base ¹⁸ (0.25 g.) and N-phenylmaleimide (0.17 g.) in chloroform (3 ml.). After 4 days at room temperature the solution was worked up as in the previous experiment, to yield (N-methyl-p-toluidino)-Nphenylsuccinimide (XVIIb), m.p. 184—185°.

4-Ethoxy-1,2,3,4-tetrahydro-1-methylquinoline (XIX).---Benzoic acid (0.2 g.) was added to a solution of NN'dimethyl-NN'-diphenylmethylenediamine (XIV) 18 (3.15 g.) and ethyl vinyl ether (6 ml.) in pure, dry chloroform (40 ml.). After 56 hr. at room temperature the solution was shaken three times with N-sodium hydroxide, dried (K₂CO₃), and distilled to yield fractions (a) b.p. $< 125^{\circ}/11$ mm. (0.9 g.) and (b) b.p. 125-155°/11 mm. (1.7 g.). The latter was redistilled and the distillate of b.p. 120°/2 mm. was chromatographed on alumina. The eluate obtained with light petroleum was redistilled to afford the base (XIX), b.p. 120° (bath)/1 mm., v_{max} (film) 1088br,vs (O-C str.) and 748vs cm.⁻¹ (ortho-substituted aromatic ring) (Found: C, 75.15; H, 9.1. C₁₂H₁₇NO requires C, 75.4; H, 8.9%), m/e 191 (M+, 100%) and 144 [presumably $\rm C_{16}H_{16}N$ (XI; $R^2 = H, R^3 = Me$], $\tau 8.82$ (t, $CH_3 \cdot CH_2, J 7$ c./sec.), 8.5—7.7 [m, $CH_2 \cdot CH_2 \cdot CH(OEt)$], 7.15 (s, $CH_3 \cdot N$), ca. 6.8 (m, N·CH₂·CH₂), 6.45 (q, CH₃·CH₂·O, J 7 c./sec.), 5.7 (poorly resolved t, CHOEt·CH₂), and 3·6-1·6 (m, aromatic).

2,3,3a,4,5,9b-Hexahydro-5-methyl-2-phenyl-1H-pyrrolo[3,4c]quinoline (XXIVa).—Excess of an ethereal solution of lithium aluminium hydride was dropped into a suspension of 1,2,3,4-tetrahydro-1-methylquinoline-N-phenyl-3,4-dicarboximide (V) (0·12 g.) in ether, and the mixture was heated under reflux for 5 hr., cooled, and decomposed with a saturated solution of potassium sodium tartrate. The residue left by removal of ether from the dried organic layer was boiled in benzene (charcoal) and filtered, and the filtrate was diluted with light petroleum; crystals of the base (XXIVa) separated, m.p. 99—100° (Found: C, 81·6; H, 7·6; N, 10·8. $C_{18}H_{20}N_2$ requires C, 81·8; H, 7·6; N, 10·6%), v_{max} . 765s, 750s, and 696s cm.⁻¹.

2,3,3a,4,5,9b-Hexahydro-2,5-dimethyl-1H-pyrrolo[3,4-c]quinoline (XXIVb).—Similarly prepared from (VIIIa), the crude base was an oil, which gave a dipicrate, m.p. 160—161° (decomp.) (from ethanol) (Found: C, 46·0; H, 4·0. $C_{25}H_{24}$ -N₈O₁₄ requires C, 45·6; H, 3·4%). A solution of this (0·2 g.) in hot acetone (30 ml.) was mixed with water (25 ml.), cooled rapidly, and passed through a column of Dowex 1 [previously treated successivly with 2N-hydrochloric acid, water, and acetone-water (1:1)]. The eluate when recrystallised from ethanol afforded the hydrochloride, m.p. 224° (decomp.), basification of which yielded an oil.

2,3,3a,4,5,9b-Hexahydro-5,8-dimethyl-2-phenyl-1H-

¹⁹ W. Schäfer and P. Neubert, Tetrahedron, 1969, 25, 315.

pyrrolo[3,4-c]quinoline (XXIVc).—Similarly prepared from (VIIIb) (0.12 g.), this base was eluted by light petroleum, and had m.p. 132° (80 mg.) (Found: C, 81.95; H, 7.85; N, 10.1. $C_{19}H_{22}N_2$ requires C, 82.0; H, 7.9; N, 10.1%).

2,3,3a,4,5,9b-Hexahydro-2,5,8-trimethyl-2-phenyl-1H-

pyrrolo[3,4-c]*quinoline* (XXIVd).—The product of reduction of (VIIIc) was chromatographed on alumina, and the eluate obtained with light petroleum was treated with dry hydrogen chloride in ether, yielding the *dihydrochloride*, which when recrystallised from ethanol and dried at 100°/1 mm. had m.p. 225° (decomp.) (Found: C, 58.05; H, 7.8; N, 9.55. C₁₄H₂₂Cl₂N₂ requires C, 58.1; H, 7.6; N, 9.7%). Basification of this afforded an oil, ν_{max} . 806s cm.⁻¹, which gave a picrate, m.p. 160° (decomp.) (from ethanol).

2,3,3a,3b,4,5,6,11b-Octahydro-2-phenyl-1 \dot{H} -dipyrrolo[1,2a,3,4-c]quinoline (XXV).—Similarly prepared from (Xa), and recrystallised from benzene–light petroleum, this base had m.p. 142—143° (Found: C, 83.0; H, 7.7; N, 9.9. C₂₀H₂₂N₂ requires C, 82.8; H, 7.6; N, 9.7%), ν_{max} . 753s, 745s, and 692s cm.⁻¹.

2-Methylquinoline-N-phenyl-3,4-dicarboximide.— The imide was prepared essentially as described ¹⁴ for the N-benzylimide, except that aniline was used instead of benzylamine; it was eluted from alumina by benzene, and had m.p. 166° (Found: C, 74.8; H, 4.2; N, 9.7. $C_{18}H_{12}N_2$ -O₂ requires C, 75.0; H, 4.2; N, 9.7%).

1,2-Dihydro-1-Methyl-2-oxoquinoline-N-phenyl-3,4-dicarboximide.—Ethyl a-cyano-1-methyl-3-isatylideneacettate 15 (2.5 g.), when hydrolysed as described by Fiesselmann and Ehmann¹⁶ for the preparation of 1,2-dihydro-2-oxoquinoline-3,4-dicarboxylic acid yielded 1,2-dihydro-1-methyl-2-oxoquinoline-3,4-dicarboxylic acid, which separated from water as pale yellow, shining crystals, m.p. 293-294° (1.3 g.) (Found: C, 57.95; H, 3.85; N, 5.95%; M^+ . 247.0481. $C_{12}H_{9}NO_{5}$ requires C, 58.3; H, 3.65; N, 5.65%; M, 247.0481); strong m/e 159 (presumably $C_{10}H_9NO$). This acid (0.5 g.) was heated under reflux for 2 hr. with aniline (0.7 g.) and collidine (1 ml.). The cooled product was treated with water, and the resulting solid was collected, dried, and chromatographed on alumina. Elution with chloroform afforded the imide (0.1 g.), which after recrystallisation from benzene-light petroleum had m.p. 270°, v_{\max} 1645 and 1680 cm.⁻¹ (Found: C, 71·35; H, 4·7. C₁₈H₁₂N₂O₃ requires C, 71·05; H, 3·95%); *m/e* 304 (*M*⁺, 19%), 186 (9%) (presumably C₁₁H₈NO₂; cf. ref. 19), and 78 (100%).

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¹⁸ J. von Braun, Ber., 1908, **41**, 2145.