Dehydrogenation of Some Aromatic Tertiary Amines by Gamma Radiation and by Peroxides

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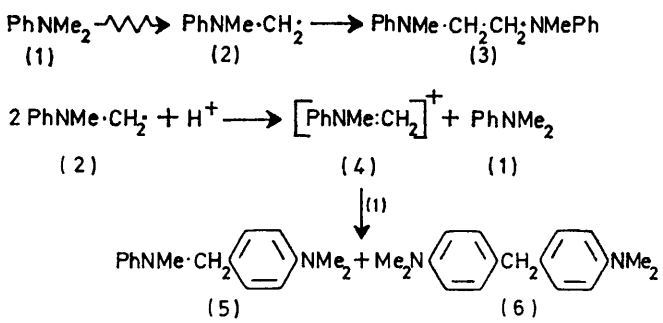
Thermal decomposition of di-t-butyl peroxide in *NN*-dimethylaniline (1) is known to yield a radical-coupling product, *i.e.* *NN'*-dimethyl-*NN'*-diphenylethylenediamine (3); but when the reaction was carried out in chlorobenzene as solvent several products were formed, arising both from radicals and from iminium ions. Gamma radiolysis of, or reaction of either t-butoxy-radicals or dibenzoyl peroxide with *N*-phenylpyrrolidine (9; Ar = Ph) yielded two stereoisomeric forms of 2,3,3a,3b,4,5,6,11b-octahydro-1-phenyl-1*H*-dipyrrolo[1,2-*a*:3',2'-*c*]quinoline (8; R = H), which presumably arose by dimerisation of 1-phenyl-Δ^2-pyrroline (12; Ar = Ph), formed by disproportionation of 1-phenylpyrrolidin-2-yl radicals (10; Ar = Ph). A similar type of reaction occurred in the gamma radiolysis of, or reaction of t-butoxy-radicals with 1-phenylpiperidine (24; R = H), and in the reaction of t-butoxy-radicals with 1,3,3a,4,5,6,7,7a-octahydro-2-phenyl-2*H*-isoindole (17; Ar = Ph) and 1,2,3,3a,4,5,6,6a-octahydro-2-*p*-tolylcyclopenta[*c*]pyrrole (20). On the other hand, gamma radiolysis of, or reaction of t-butoxy-radicals with *N*-phenylperhydroazepine (29) yielded a radical-coupling product (30).

GAMMA irradiation of *NN*-dimethylaniline (1) gives *N*-methylanilinomethyl radicals (2), which dimerise to give *NN'*-dimethyl-*NN'*-diphenylethylenediamine (3).[1] A similar conversion has been achieved by

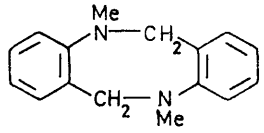


radicals generated by thermal decomposition of di-t-butyl peroxide.[2] However, if *NN*-dimethylaniline containing a trace of acid is irradiated[1] or treated with t-butoxy-radicals[3] the main products are *N*-(*p*-dimethylaminobenzyl)-*N*-methylaniline (5) and bis-(4-dimethylaminophenyl)methane (6), as the radicals (2) disproportionate in the presence of acid to yield the iminium ion (4).

Russian workers[4] claimed that the reaction of di-t-butyl peroxide with *NN*-dimethylaniline in chlorobenzene at 130° yielded *N*-t-butoxymethyl-*N*-methylaniline, *N*-*p*-dimethylaminobenzyl-*N*-methylaniline (5), and *N*-[*p*-(*p*-dimethylamino-*N*-methylbenzylamino)-benzyl]-*N*-methylaniline. We reinvestigated this reaction and isolated the second compound (5). The first compound also appeared to be present in small amount; but we were unable to isolate it pure, or in the yield stated by the Russians. We failed to find the third compound, but we did isolate 5,6,11,12-tetrahydro-5,11-dimethylphenhomazine (7),[5,6] the m.p. of which is close to that of the compound claimed by the Russians. From the n.m.r. spectrum of the mixed products we

[1] J. M. Fayadh and G. A. Swan, *J. Chem. Soc.* (*C*), 1969, 1775.
[2] H. B. Henbest and R. Patton, *J. Chem. Soc.*, 1960, 3557.
[3] G. A. Swan, *J. Chem. Soc.* (*C*), 1969, 2015.
[4] T. T. Vasil'eva and R. Kh. Freidlina, *Bull. Acad. Sci., U.S.S.R.*, 1968, 1039.
[5] R. B. Roy and G. A. Swan, *Chem. Comm.*, 1966, 427.
[6] G. A. Swan, *J. Chem. Soc.* (*C*), 1971, 2880.

concluded that *N*-*o*-dimethylaminobenzyl-*N*-methylaniline,[6] and *NN'*-dimethyl-*NN'*-diphenylethylenediamine (3) were also present. Evidently in chlorobenzene solution disproportionation of the radicals (2) occurs even in the absence of added acid.



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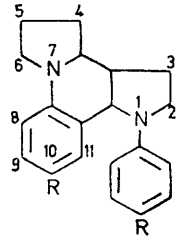

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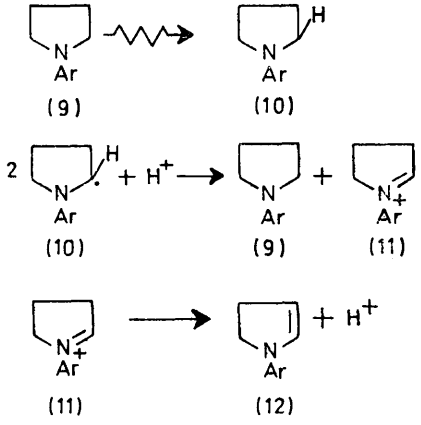
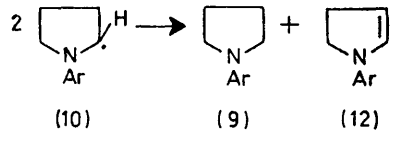
Gamma irradiation of *NN*-dimethylaniline in the presence of diethyl maleate yielded diethyl 1,2,3,4-tetrahydro-1-methylquinoline-3,4-dicarboxylate (presumably *trans*); and the same reaction could also be effected by t-butoxy-radicals.



SCHEME 1

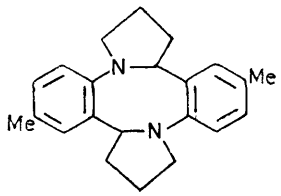


SCHEME 2

Gamma irradiation of pure 1-phenylpyrrolidine (9; Ar = Ph) yielded the same two stereoisomeric forms of 2,3,3a,3b,4,5,6,11b-octahydro-1-phenyl-1*H*-dipyrrolo-[1,2-*a*:3',2'-*c*]quinoline (8; R = H) which have been obtained by reduction of 1-phenylpyrrolidin-2-one with lithium aluminium hydride (0·25 mol. equiv.).[7] The same products were also obtained by treatment of 1-phenylpyrrolidine with t-butoxy-radicals; and the presence in the reaction mixture of a trace of acetic acid or triethylamine had no apparent effect on the products formed. It is probable that these products are formed by dimerisation of 1-phenyl-Δ^2-pyrroline (12; Ar = Ph); but it is uncertain whether the dimerisation occurs during the gamma irradiation or during the subsequent work-up (distillation and chromatography). The 1-phenyl-Δ^2-pyrroline could be formed by a process analogous to that which occurs in the case of *NN*-dimethylaniline (Scheme 1). However in the case of amines such as 1-phenylpyrrolidine, in which a β-hydrogen atom is present, direct disproportionation of the radicals (Scheme 2) is also possible; and in fact, as the presence of added acid is unnecessary Scheme 2 is here preferred. The formation of 1,2,3,3a,4,5-hexahydropyrrolo[*a*]quinoline-4,5-*N*-phenyldicarboximide by the gamma radiolysis of,[8] or by the action of t-butoxy-radicals[3] on 1-phenylpyrrolidine in the presence of *N*-phenylmaleimide is taken as evidence of the formation of 1-phenylpyrrolidin-2-yl radicals (10; Ar = Ph).

Treatment of 1-phenylpyrrolidine with dibenzoyl peroxide yielded the stereoisomeric form of (8; R = H), m.p. 165—166°, together with 1-*p*-benzoyloxyphenylpyrrolidine. Likewise, 1-*p*-tolylpyrrolidine afforded both known stereoisomeric forms of (8; R = Me).[7]

Theoretically, oxidation of a 1-arylpyrrolidine might yield a phenhomazine, *e.g.* 1-*p*-tolypyrrolidine could give



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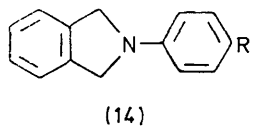

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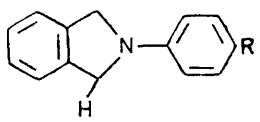

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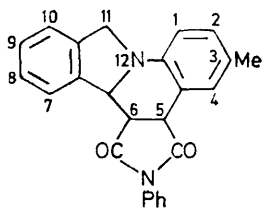

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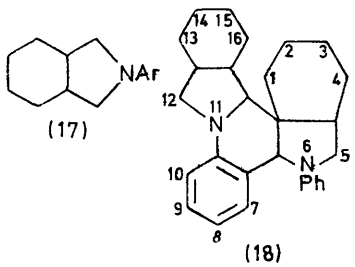

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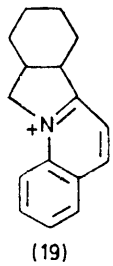

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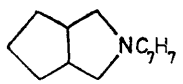

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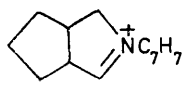

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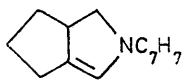


(22)

(13). However we failed to detect the formation of such compounds, presumably because the iminium ion (11) is in equilibrium with the enamine (12), which reacts

[7] G. A. Swan and J. D. Wilcock, preceding paper.
[8] J. M. Fayadh and G. A. Swan, *J. Chem. Soc.* (*C*), 1969, 1781.

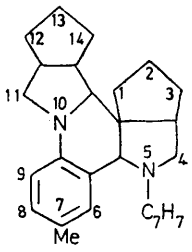
rapidly with (11) to afford a dimer of type (8). We therefore investigated the oxidation of 2-arylisoindolines (14). 2-Phenyl- and 2-*p*-tolyl-isoindoline are solids which are sparingly soluble in most solvents, so we were unable to study their radiolysis, or their reaction with t-butoxy-radicals, except (in the latter case) in chlorobenzene, in which case 2-phenylisoindolin-1-one (14; R = H, CO in place of CH_2 at position 1) and a lesser amount of *N*-phenylphthalimide, and the corresponding *p*-tolyl compounds, respectively, were obtained. The formation of the radicals (15) was however demonstrated by the production of 5,6,6a,11-tetrahydro-3-methyldibenzo[*a*,*e*]indolizine-5,6-*N*-phenyldicarboximide (16) from the reaction of 2-*p*-tolylisoindoline (14; R = Me) in the presence of *N*-phenylmaleimide.

We also prepared 2-phenyl-, 2-*p*-tolyl-, 2-*m*-tolyl-, and 2-(3,5-dimethylphenyl)-1,3,3a,4,5,6,7,7a-octahydro-2*H*-isoindole (17), by reduction with lithium aluminium hydride of the product formed by reaction of the appropriate aniline with *cis*-hexahydrophthalic anhydride. All these isoindoles were solid at room temperature. Reaction of 1,3,3a,4,5,6,7,7a-octahydro-2-phenyl-2*H*-isoindole (17; Ar = Ph) with t-butoxy-radicals yielded a crystalline compound, formulated as the di-isoindolo-[2,1-*a*:7a,1-*c*]quinoline (18). A one-proton singlet at τ 5·25 in the n.m.r. spectrum of this compound was attributed to H-6a; and an intense peak in the mass spectrum at *m/e* 224 was assigned to the ion (19).

We then prepared the cyclopenta[*c*]pyrrole (20), hoping that the replacement of the saturated six-membered carbon ring by a five-membered ring might stabilise the iminium ion (21) relative to the enamine (22), because the double-bond endocyclic to one five-membered ring, but exocyclic to the other fused five-membered ring might be less favoured. However, the product obtained by treatment of this with t-butoxy-radicals appeared to be a dimer of the same type as before, *i.e.* the biscyclopenta[3,4:3′,4′]pyrrolo[1,2-*a*:2′,-3′-*c*]quinoline (23). The n.m.r. spectrum of (23) showed a one-proton singlet at τ 5 (H-5a) and two 3-proton singlets at τ 7·7 and 8·0, attributed to the methyl group in the 5-*p*-tolyl group and that at position 7, respectively, the latter being shielded by the aromatic ring of the 5-*p*-tolyl group.

Gamma irradiation of pure 1-phenylpiperidine (24; R = H) yielded a small quantity of a crystalline compound formulated as the benzo[*h*]pyrido[2,1-*f*][1,6]-naphthyridine (25; R = H). The latter was also obtained by reaction of 1-phenylpiperidine with t-butoxy-radicals, although in this case it was also possible to demonstrate the formation of 1,1′-diphenyl-2,2′-bipiperidyl (26), identical with a specimen obtained from 2,2′-bipyridyl by hydrogenation, followed by treatment with sodamide and bromobenzene. Here again presumably radicals (27) are formed; and these disproportionate to yield 1,2,3,4-tetrahydro-1-phenylpyridine (28), most of which gives rise to gummy products.

Gamma irradiation of, or reaction of t-butoxy-radicals with *N*-phenylperhydroazepine (29) yielded the radical-coupling dimer (30). The latter reaction in the presence of *N*-phenylmaleimide yielded the azepino[1,2-*a*]quinoline-6,7-*N*-phenyldicarboximide (31).



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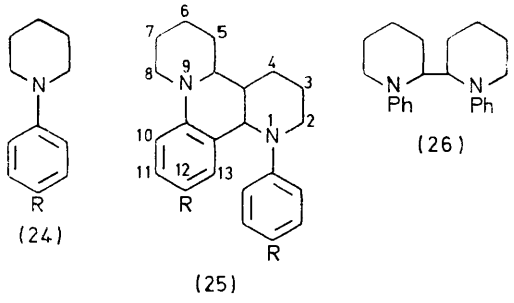
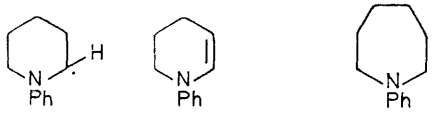
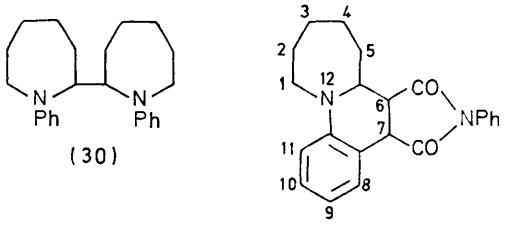


(24) (25) (26)



(27) (28) (29)



(30) (31)

EXPERIMENTAL

For general directions, see ref. 1.

Hopkin and Williams Ltd. alumina (neutral) M.F.C. grade was used for column chromatography, except where otherwise stated.

Reaction of NN-*Dimethylaniline with Di-t-butyl Peroxide in Chlorobenzene.*—The reaction was carried out as described.[4] Distillation of the product gave a fraction, b.p. 68—70° at 1 mmHg, which contained *NN*-dimethylaniline and *N*-t-butoxymethyl-*N*-methylaniline. The residue was chromatographed on B.D.H. aluminium oxide, all material eluted by light petroleum being collected. The n.m.r. spectrum of this material showed singlets at the following τ values, corresponding to the CH_2 groups of the respective compounds named: 6·52 (*NN′*-dimethyl-*NN′*-diphenylethylenediamine) (3), 5·75 (5,6,11,12-tetrahydro-5,11-dimethylphenhomazine) (7), 5·6 (*N*-*p*-dimethylaminobenzyl-*N*-methylaniline) (5), and 5·42 (*N*-*o*-dimethylaminobenzyl-*N*-methylaniline). When this material was

rechromatographed on alumina, it was possible to isolate (7) and (5) from fractions of the light petroleum eluate; these products, after recrystallisation from light petroleum were identical in i.r. and n.m.r. spectra with authentic samples.[6,9]

A similar result was obtained when the reaction was carried out under nitrogen, or in a sealed tube. Chlorobenzene and *NN*-dimethylaniline which had been carefully freed from any traces of acidic impurities also gave the same results.

Gamma Irradiation of NN-*Dimethylaniline in the Presence of Diethyl Maleate.*—A solution of diethyl maleate (5 ml) in purified *NN*-dimethylaniline [1] (95 ml) was gamma-irradiated for 74 days. The bulk of the unchanged amine and ester was removed under reduced pressure, and the residue was chromatographed on alumina. Elution with light petroleum afforded unchanged amine. Elution with benzene gave an oil, b.p. 186—190° at 10 mmHg (3·3 g), which yielded a picrate, m.p. 172—174° (Found: C, 51·05; H, 4·65; N, 10·9. $C_{16}H_{21}NO_4,C_6H_3N_3O_7$ requires C, 50·7; H, 4·6; N, 10·75%). This was shaken with a mixture of ether and saturated aqueous lithium hydroxide solution, the ethereal layer was dried (K_2CO_3), and the ether was removed, and the residue distilled under reduced pressure to give *diethyl* 1,2,3,4-*tetrahydro*-1-*methylquinoline*-3,4-*dicarboxylate*, $\nu_{max.}$ 1725 (C=O str.) and 745 cm^{-1} (Found: M^+, 291. $C_{16}H_{21}NO_4$ requires *M*, 291); *m/e* 144 ($C_{10}H_{10}N$, *N*-methylquinolinium ion); τ 2·6—3·5 (m, Ar), 7·7 (s, N·*Me*), 6·5 (m, $N{\cdot}CH_2$), and pairs of interesting triplets (around 8·8) and quartets (around 5·8) representing 2 × CO_2Et. The signals due to the protons at positions 3 and 4 appeared to be covered by the intersecting quartets around τ 5·8.

Reaction of NN-*Dimethylaniline with Di-t-butyl Peroxide in the Presence of Diethyl Maleate.*—A mixture of *NN*-dimethylaniline (6·3 ml), di-t-butyl peroxide (0·71 g), and diethyl maleate (1·0 g) was heated in a sealed tube for 24 h at 130—135°, then worked up as before, yielding an oil (0·65 g) identical with the ester obtained above.

Gamma Irradiation of 1-*Phenylpyrrolidine* (9; Ar = Ph). —1-Phenylpyrrolidine [10] was shaken for 2 days with 3N-sodium hydroxide, separated, dried (K_2CO_3), and distilled. The purified base (40 ml) was irradiated for 17 days (total dose 1·8 × 10^{23} eV); and the bulk of the unchanged 1-phenylpyrrolidine was then removed by distillation under reduced pressure. The residue (1·58 g) was chromatographed on alumina. Light petroleum eluted 1-phenylpyrrolidine. Elution with benzene–light petroleum (1 : 1) then afforded the known stereoisomeric form of 2,3,3a,3b,-4,5,6,11b-octahydro-1-phenyl-1*H*-dipyrrolo[1,2-*a*:3′,2′-*c*]-quinoline (8; R = H) which is faster running in t.l.c., m.p. 165—166° (from benzene-light petroleum), identical in t.l.c. behaviour, and in n.m.r., i.r., and u.v. spectra with an authentic sample [7] (yield 65 mg; $G < 0{\cdot}1$). Further elution with benzene–ether (1 : 1) yielded an oil, which ultimately solidified, and which when recrystallised from benzene–light petroleum gave the slower-running stereoisomeric form of (8; R = H), m.p. 150—152°, identical with an authentic sample [7] (yield 60 mg, $G < 0{\cdot}1$).

Reaction of 1-*Phenylpyrrolidine with Di-t-butyl Peroxide.*— (*a*) Purified 1-phenylpyrrolidine (7·35 g) was heated with di-t-butyl peroxide (0·73 g) in a sealed tube for 44 h at 140°. When worked up as above, the product yielded the same two isomeric forms of (8; R = H) as did the radiolysis.

(*b*) A similar reaction was carried out in the presence of acetic acid (0·2 g); and the product in ether was shaken with sodium hydroxide solution, then dried (K_2CO_3), before being worked up as above, yielding the same products.

(*c*) A similar experiment, in the presence of triethylamine (0·2 ml) afforded the same products.

Reaction of 1-*Phenylpyrrolidine with Di-t-butyl Hyponitrite.*—Purified 1-phenylpyrrolidine (2·84 g) when heated with di-t-butyl hyponitrite [11] (0·36 g) for 24 h at 55° yielded the same products as above.

Reaction of 1-*Phenylpyrrolidine with Dibenzoyl Peroxide* (with R. B. Roy).—A solution of dibenzoyl peroxide [12] (3·0 g) in purified chloroform (20 ml) was added during 1·5 h to a stirred solution of 1-phenylpyrrolidine (4·0 g) in chloroform (15 ml) at 0°. After 9 h at 0° the mixture was basified (NaOH), the organic layer was separated, washed with water, and dried ($MgSO_4$), and the bulk of the unchanged 1-phenylpyrrolidine was removed by distillation under reduced pressure. The residue (1·8 g) was chromatographed on B.D.H. aluminium oxide. Elution with light petroleum afforded a solid, m.p. 144° (0·25 g), which was chromatographed on silica. Elution with benzene–ether (4 : 1) gave the faster-running form of (8; R = H), m.p. 166—167° (0·20 g), identical spectroscopically, and in t.l.c. behaviour with an authentic sample [7] (Found: C, 82·9; H, 7·8; N, 9·1. Calc. for $C_{20}H_{22}N_2$: C, 82·8; H, 7·6; N, 9·6%). Further elution of the alumina column with benzene–light petroleum (3 : 7) yielded 1-p-*benzoyloxypyrrolidine*, m.p. 215° (from benzene–light petroleum) (0·05 g) (Found: C, 76·6; H, 6·2; N, 5·3%; M^+ 267. $C_{17}H_{17}NO_2$ requires C, 76·4; H, 6·2; N, 5·3%; *M*, 267); $\nu_{max.}$ 1730 cm^{-1} (C=O str.).

Similar experiments were carried out with acetonitrile, cumene, and benzene (in this case at 5°) in place of chloroform, the yields of the two products being 0·25 and 0·1, 0·25 and 0·08, and 0·1 and 0·25 g, respectively.

Reaction of 1-p-*Tolylpyrrolidine with Dibenzoyl Peroxide* (with R. B. Roy).—A similar reaction using dibenzoyl peroxide (3 g) in acetonitrile (60 ml) and 1-*p*-tolylpyrrolidine (4·0 g) in acetonitrile (25 ml) yielded mainly the slower-running isomer of 2,3,3a,3b,4,5,6,11b-octahydro-10-methyl-1-*p*-tolyl-1*H*-dipyrrolo[1,2-*a*:3′,2′-*c*]quinoline (8; R = Me), m.p. 114—115° (0·1 g) (Found: C, 82·6; H, 8·6; N, 8·9%; M^+, 318. Calc. for $C_{22}H_{26}N_2$: C, 83·0; H, 8·2; N, 8·8%; *M*, 318). A similar reaction in cumene afforded a mixture of both known streoisomeric forms, m.p. 144—145 and 115—116°, respectively, separable by chromatography on silica.[7]

Reaction of 2-*Phenylisoindoline with Di-t-butyl Peroxide.*— Di-t-butyl peroxide (0·73 g) was added during 6 h to a solution of 2-phenylisoindoline [13] (3·9 g, 4 mol. equiv.) in chlorobenzene (15 ml) at 130—132°. The solvent was removed under reduced pressure, the residue was heated with benzene, and the mixture was filtered. The resulting solid was recrystallised from benzene–light petroleum, affording unchanged 2-phenylisoindoline. The combined filtrate from the benzene solution and the mother liquor from the recrystallisation were chromatographed on

[9] J. M. Fayadh, D. W. Jessop, and G. A. Swan, *J. Chem. Soc.* (*C*), 1966, 1605.
[10] R. B. Roy and G. A. Swan, *J. Chem. Soc.* (*C*), 1969, 1886.
[11] H. Kiefer and T. G. Traylor, *Tetrahedron Letters*, 1966, 6163.
[12] R. B. Roy and G. A. Swan, *J. Chem. Soc.* (*C*), 1968, 80.
[13] A. H. Sommers, *J. Amer. Chem. Soc.*, 1956, **78**, 2439.

alumina. Benzene eluted further unchanged 2-phenylisoindoline. Elution with ether afforded a product which when recrystallised from benzene–light petroleum had m.p. 148—150° (60 mg), consisting of a mixture of 2-phenylisoindolin-1-one and *N*-phenylphthalimide, M^+ 223 ($C_{14}H_9NO_2$) and 209 ($C_{14}H_{11}NO$); $\nu_{max.}$ 1700 cm^{-1}; $\lambda_{max.}$ 228 and 280 nm; τ 1·8—2·8 (m, Ar) and 5·1 (s, CH_2); *cf.* ref. 14.

Reaction of 2-p-*Tolylisoindoline with Di-t-butyl Peroxide.*—2-*p*-Tolylisoindoline (3·13 g, 3 mol. equiv.) was similarly treated with di-t-butyl peroxide (0·73 g) in chlorobenzene (20 ml). Elution with benzene yielded *N*-*p*-tolylphthalimide, m.p. 182—184° (from ethanol) (9 mg), identical with an authentic specimen. Elution with benzene–ether (3 : 1) at first gave a red compound, m.p. 264—266°; $\nu_{max.}$ 1685 cm^{-1}; M^+ 420. Further elution with the same solvent afforded 2-*p*-tolylisoindolin-1-one, m.p. 132—133° (from ethanol) (45 mg); $\nu_{max.}$ 1685 cm^{-1}; (Found: M^+, 223. Calc. for $C_{15}H_{13}NO$: *M*, 223); $\lambda_{max.}$ 228 and 287 nm; τ 5·2 (s, CH_2) and 7·7 (s, Me). The same products were obtained when the reaction was carried out under nitrogen, or in the presence of benzoic acid (0·7 g).

Reaction of 2-p-*Tolylisoindoline with Di-t-butyl Peroxide in the Presence of* N-*Phenylmaleimide.*—Di-t-butyl peroxide (0·73 g) was added during 4 h to a solution of 2-*p*-tolylisoindoline (3·13 g, 3 mol. equiv.) and *N*-phenylmaleimide (0·865 g, 1 mol. equiv.) in chlorobenzene (50 ml) at 130—132°. The solvent was removed under reduced pressure, and the residue was chromatographed on alumina. Elution with benzene–light petroleum gave 2-*p*-tolylisoindoline. Elution with benzene yielded 5,6,6a,11-*tetrahydro*-3-*methyldibenzo*[a,e]*indolizine*-5,6-N-*phenyldicarboximide* (16), m.p. 210—212° (from benzene–light petroleum) (60 mg) (Found: C, 78·8; H, 5·2; N, 6·9%; M^+, 380. $C_{25}H_{20}N_2O_2$ requires C, 78·9; H, 5·25; N, 7·35%; *M*, 380); $\nu_{max.}$ 1790w and 1720s cm^{-1} (C=O str.); *m/e* 232 ($C_{17}H_{14}N$, quinolinium-type ion).

1,3,3a,4,5,6,7,7a-*Octahydro*-2-*phenyl*-2H-*isoindole* (17; Ar = Ph).—*cis*-*N*-Phenylcyclohexane-1,2-dicarboximide [15] was reduced with lithium aluminium hydride in ether to give the product, m.p. 48° (from ethanol) (lit.,[16] 48°) (Found: C, 83·6; H, 9·4; N, 6·9%; M^+, 201. Calc. for $C_{14}H_{19}N$: C, 83·6; H, 9·4; N, 7·0%; *M*, 201).

1,3,3a,4,5,6,7,7a-*Octahydro*-2-p-*tolyl*-2H-*isoindole* (17; Ar = *p*-tolyl).—Similar reduction of cis-N-p-*tolylcyclohexane*-1,2-*dicarboximide*, m.p. 136—138° (Found: C, 74·2; H, 7·0; N, 5·8. $C_{15}H_{17}NO_2$ requires C, 74·1; H, 7·0; N, 5·75%) yielded the *product*, m.p. 60—61° (Found: C, 83·75; H, 9·8; N, 6·6%; M^+, 215. $C_{15}H_{21}N$ requires C, 83·7; H, 9·75; N, 6·5%; *M*, 215).

1,3,3a,4,5,6,7,7a-*Octahydro*-2-m-*tolyl*-2H-*isoindole* (17; Ar = *m*-tolyl).—Similar reduction of cis-N-m-*tolylcyclohexane*-1,2-*dicarboximide*, m.p. 114—116° (Found: C, 74·1; H, 7·1%) yielded the *product*, m.p. 41—42° (Found: C, 83·7; H, 9·8; N, 6·5%; M^+, 215).

1,3,3a,4,5,6,7,7a-*Octahydro*-2-(3,5-*dimethylphenyl*)-2H-*isoindole* (17; Ar = 3,5-dimethylphenyl).—Similar reduction of cis-N-(3,5-*dimethylphenyl*)*cyclohexane*-1,2-*dicarboximide*, m.p. 62—64° (Found: C, 75·05; H, 7·5; N, 5·4. $C_{16}H_{19}NO_2$ requires C, 74·7; H, 7·4; N, 5·45%), yielded the *product*, m.p. 72—74° (Found: C, 84·1; H, 10·2; N, 6·4%; M^+, 229. $C_{16}H_{23}N$ requires C, 83·8; H, 10·0; N, 6·1%; *M*, 229).

1,2,3,3a,4,5,6,6a-*Octahydro*-2-p-*tolylcyclopenta*[c]*pyrrole* (20).—Similar reduction of cis-N-p-*tolylcyclopentane*-1,2-*dicarboximide*, m.p. 125° (Found: C, 73·45; H, 6·25; N, 6·15%; M^+, 229. $C_{14}H_{15}NO_2$ requires C, 73·35; H, 6·55; N, 6·1%; *M*, 229), yielded the *product*, m.p. 45—46° (Found: C, 83·75; H, 9·65; N, 6·95%; M^+, 201. $C_{14}H_{19}N$ requires C, 83·55; H, 9·45; N, 6·95%; *M*, 201).

Reaction of 1,3,3a,4,5,6,7,7a-*Octahydro*-2-*phenyl*-2H-*isoindole with Di-t-butyl Peroxide.*—A mixture of the isoindole (3·0 g, 3 mol. equiv.) and di-t-butyl peroxide (0·73 g) was heated in a sealed tube for 20 h at 140°. The product which was eluted from alumina by benzene, after recrystallisation from benzene-light petroleum afforded 1,2,3,4,4a,5,6,6a,12,12a,13,14,15,16,16a,16b-*hexadecahydro*-6-*phenyldi-isoindolo*[2,1-a:7a,1-c]*quinoline* (18), m.p. 218—220° (210 mg) (Found: C, 84·5; H, 8·5; N, 6·8%; M^+, 398. $C_{28}H_{34}N_2$ requires C, 84·2; H, 8·54; N, 7·0%; *M*, 398); $\lambda_{max.}$ 216, 257, and 316 nm.

Reaction of 1,3,3a,4,5,6,7,7a-*Octahydro*-2-*phenyl*-2H-*isoindole with Di-t-butyl Peroxide in the Presence of* N-*Phenylmaleimide.*—A mixture of the isoindole (3·0 g, 3 mol equiv.), di-t-butyl peroxide (0·73 g), and *N*-phenylmaleimide (0·86 g, 1 mol. equiv.) was heated in a sealed tube for 20 h at 140°. The product eluted from alumina by benzene–ether (1 : 1) when recrystallised from benzene–light petroleum afforded 5,6,6a,6b,7,8,9,10,10a,11-*decahydrodibenzo*[a,e]*indolizine*-5,6-N-*phenyldicarboximide*, m.p. 246—248° (0·11 g) (Found: C, 77·8; H, 6·7; N, 7·3%; M^+, 372. $C_{25}H_{24}N_2O_2$ requires C, 77·4; H, 6·4; N, 7·5%; *M*, 372); *m/e* 224 ($C_{16}H_{18}N$, quinolinium-type ion); $\nu_{max.}$ 1710 cm^{-1}.

Reaction of 1,2,3,3a,4,5,6,6a-*Octahydro*-2-p-*tolylcyclopenta*[c]*pyrrole with Di-t-butyl Peroxide.*—A mixture of the pyrrole (3·01 g, 3 mol. equiv.) and di-t-butyl peroxide (0·73 g) was heated in a sealed tube for 20 h at 140°. The product eluted from alumina by benzene–light petroleum (2 : 1), when recrystallised from ethanol–light petroleum afforded 2,3,3a,4,5,5a,11,11a,12,13,14,14a,14b,14c-*tetradecahydro*-7-*methyl*-5-p-*tolyl*-1H-*biscyclopenta*[3,4:3′,4′]*pyrrolo*[1,2-a:2′3′-c]*quinoline* (23), m.p. 136—138° (225 mg) (Found: C, 84·5; H, 8·6; N, 7·05%; M^+, 398. $C_{28}H_{34}N_2$ requires C, 84·4; H, 8·55; N, 7·05%; *M*, 398); *m/e* 224 ($C_{16}H_{18}N$, quinolinium-type ion); $\lambda_{max.}$ 217, 255, and 311 nm.

Reaction of 1,2,3,3a,4,5,6,6a-*Octahydro*-2-p-*tolylcyclopenta*[c]*pyrrole with Di-t-butyl Peroxide in the Presence of* N-*Phenylmaleimide.*—A mixture of the pyrrole (3·01 g, 3 mol. equiv.), di-t-butyl peroxide (0·73 g), and *N*-phenylmaleimide (0·86 g, 1 mol. equiv.) was heated in a sealed tube for 24 h at 140°. The product eluted from alumina by benzene–ether (1 : 1), when recrystallised from benzene–light petroleum afforded 6,6a,6b,7,8,9,9a,10-*octahydro*-5H-*benzo*[e]*cyclopenta*[a]*indolizine*-5,6-N-*phenyldicarboximide*, m.p. 182—184° (250 mg) (Found: C, 77·75; H, 6·6; N, 7·5%; M^+, 304. $C_{24}H_{24}N_2O_2$ requires C, 77·4; H, 6·4; N, 7·5%; *M*, 304); *m/e* 224; $\nu_{max.}$ 1710 cm^{-1}.

Gamma Irradiation of 1-*Phenylpiperidine* (24; R = H).—1-Phenylpiperidine, prepared by Bunnett and Brotherton's method [17] was irradiated without further purification. Another sample, purified as follows, when irradiated gave identical products. The 1-phenylpiperidine was boiled under reflux with acetic anhydride, distilled, then shaken with sodium hydroxide solution, separated from the aqueous layer, dried (K_2CO_3), redistilled, again shaken for 2 days with sodium hydroxide solution, separated,

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[15] R. Stoermer and H. J. Steinbeck, *Ber.*, 1932, **65**, 413.
[16] H. Daniel and F. Weygand, *Annalen*, 1964, **671**, 111.
[17] J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, 1957, **22**, 832.

dried (K_2CO_3), and once again redistilled immediately before irradiation.

1-Phenylpiperidine (40 ml) was irradiated for 29 days (total dose $2\cdot6 \times 10^{23}$ eV); and the bulk of the unchanged base was removed by distillation under reduced pressure. The residue (2·3 g) was chromatographed on alumina. Elution with light petroleum afforded some unchanged 1-phenylpiperidine. Elution with benzene yielded 1,3,4,-4a,4b,5,6,7,8,13b-*decahydro*-1-*phenyl*-2H-*benzo*[h]*pyrido*-[2,1-f][1,6]*naphthyridine* (25; R= H), m.p. 138—140° (from benzene–light petroleum) (0·12 g; $G < 0\cdot1$); *m/e* 318 (M^+, $C_{22}H_{26}N_2$) and 184 ($C_{13}H_{14}N$, quinolinium-type ion); τ 5·24br (s, H-13b).

Reaction of 1-*Phenylpiperidine with Di-t-butyl Peroxide.*—A mixture of 1-phenylpiperidine (8·05 g) and di-t-butyl peroxide (0·73 g) was heated in a sealed tube for 40 h at 150°, then worked up as above, yielding the same product (25; R = H) (75 mg). In one experiment 1,1′-diphenyl 2,2′-bipiperidyl (26) was also isolated. Its spectra were closely similar to those of a sample synthesised as below.

1,1′-*Diphenyl*-2,2′-*bipiperidyl* (26).—2,2′-Bipyridyl was hydrogenated in acetic acid over Adams catalyst. The resulting 2,2′-bipiperidyl (1·52 g) was boiled under reflux in ether for 1 h with sodamide (1·56 g, 4 mol equiv.). Bromobenzene (3·14 g, 2 mol. equiv.) was added, and the mixture was boiled under reflux for a further 2 h. The basic fraction was chromatographed on alumina. Elution with benzene–light petroleum (2 : 1) yielded the *product*, m.p. 140—142° (Found: C, 82·4; H, 8·7; N, 8·7%; M^+, 320. $C_{22}H_{28}N_2$ requires C, 82·5; H, 8·7; N, 8·7%; *M*, 320); *m/e* 159, 160, and 161.

Reaction of 1-p-*Tolylpiperidine with Di-t-butyl Peroxide.*—A mixture of 1-*p*-tolylpiperidine [10] (7 g, 4 mol. equiv.) and di-t-butyl peroxide (1·46 g) was heated in a sealed tube for 23 h at 130°. Chromatography on alumina, and elution with benzene afforded 1,3,4,4a,4b,5,6,7,8,13b-*decahydro*-12-*methyl*-1-p-*tolyl*-2H-*benzo*[h]*pyrido*[2,1-f][1,6]-*naphthyridine* (25; R = Me), m.p. 180—182° (from ethanol) (0·1 g) (Found: C, 83·5; H, 8·8; N, 8·0%; M^+, 346. $C_{24}H_{30}N_2$ requires C, 83·25; H, 8·65; N, 8·1%; *M*, 346); *m/e* 198 ($C_{14}H_{16}N$, quinolinium-type ion); $\lambda_{max.}$ 219, 309, and 312 nm.

Reaction of 1-p-*Tolypiperidine with Di-t-butyl Peroxide in the Presence of* N-*Phenylmaleimide.*—A mixture of 1-*p*-tolylpiperidine (7 g), di-t-butyl peroxide (1·46 g), and *N*-phenylmaleimide (1·73 g) was treated as above. Elution with benzene yielded (25; R = Me), m.p. 180—182° (0·1 g) (Found: C, 83·5; H, 8·8; N, 8·0%; M^+, 346). Elution with benzene–ether (3 : 1) afforded 1,2,3,4,5,6-*hexahydro*-8-*methyl*-4aH-*benzo*[c]*quinolizine*-5,6-N-*phenyldicarboximide*, m.p. 194—196° (Found: C, 76·2; H, 5·95; N, 7·9%; M^+, 346. $C_{22}H_{22}N_2O_2$ requires C, 76·3; H, 6·35; N, 8·1%; *M*, 346); *m/e* 198 ($C_{19}H_{16}N$, quinolinium-type ion).

N-*Phenylperhydroazepine* (29).—This was prepared by following Bunnett and Brotherton's method [17] for the preparation of 1-phenylpiperidine, using perhydroazepine in place of piperidine; and had b.p. 150—152° at 14 mmHg (lit.,[18] 146—148° at 12 mmHg) (Found: C, 82·15; H, 9·6; N, 7·95. Calc. for $C_{12}H_{17}N$: C, 82·3; H, 9·7; N, 8·0%).

Gamma Irradiation of N-*Phenylperhydroazepine.*—The base (40 ml) was irradiated for 25 days. The bulk of the unchanged amine was removed by distillation under reduced pressure; and the residue was chromatographed on alumina. Elution with light petroleum yielded unchanged amine. Elution with benzene gave an oil, which solidified on trituration with benzene–hexane, and which on recrystallisation from the same solvent afforded 1,1′-*diphenylperhydro*-2,2′-*biazepinyl* (30), m.p. 116—118° (0·3 g) (Found: C, 82·55; H, 9·25; N, 8·1%; M^+, 348. $C_{24}H_{32}N_2$ requires C, 82·75; H, 9·2; N, 8·05%; *M*, 348); *m/e* 175, 174; $\lambda_{max.}$ 212, 263, and 308 nm; τ 2·5—3·4 (10H, m, Ar), 5·85 (2H, m), 6·55 (4H, m), and 8·40 (16H, m). Elution with ether gave an oil, which when rechromatographed on silica gel (elution with ether) yielded more of the same compound (0·08 g).

Reaction of N-*Phenylperhydroazepine with Di-t-butyl Peroxide.*—A mixture of the base (8·75 g, 5 mol. equiv.) and di-t-butyl peroxide (1·46 g) was heated in a sealed tube for 23 h at 140°. The product, when worked up as above, yielded the base (30) (0·4 g).

Reaction of N-*Phenylperhydroazepine with Di-t-butyl Peroxide in the Presence of* N-*Phenylmaleimide.*—A mixture of the base (8·75 g, 5 mol. equiv.), di-t-butyl peroxide (1·40 g), and *N*-phenylmaleimide (1·73 g, 1 mol. equiv.) was heated in a sealed tube for 24 h at 140°, and worked up as above. Elution with benzene yielded 1,2,3,4,5,5a,6,7-*octahydroazepino*[1,2-a]*quinoline*-6,7-N-*phenyldicarboximide* (31), m.p. 188—190° (from benzene–light petroleum) (60 mg) (Found: C, 76·35; H, 6·4; N, 8·9%; M^+, 346. $C_{22}H_{22}N_2O_2$ requires C, 76·3; H, 6·35; N, 8·9%; *M*, 346); *m/e* 198 ($C_{14}H_{16}N$, quinolinium-type ion); $\nu_{max.}$ 1775w and 1705s cm^{-1} (C=O str,).

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