Some Reactions of Dialkylamino Radicals

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The photolyses of tetramethyltetrazen and 1,1′-azopiperidine have been effected in some hydrocarbon solvents and the extent of the general reaction $R_2N\cdot + H{-}X \longrightarrow R_2NH + \cdot X$ has been examined by product study: radicals $R_2N\cdot$ prove to be but feeble dehydrogenating agents. Dimethylamino radicals do not dehydrogenate either 2,6-dimethoxy- or 2,6-dimethyl-phenol. Slight evidence of addition to anthracene was obtained. Attempts to prepare a radical $R_2N\cdot$ from 2,2,6,6-tetramethylpiperidine have been unsuccessful.

PREVIOUS work [1] has established that dimethylamino radicals, generated by the pyrolysis of tetramethyltetrazen in solutions at 150° or over are mild dehydrogenating agents, *e.g.*, of cumene and of benzyl alcohol, but at these high temperatures the occurrence of secondary reactions can easily obscure the natures of primary products. To study dehydrogenation by dimethylamino and similar radicals at lower temperatures we have therefore investigated photolyses of tetramethyltetrazen and of 1,1′-azopiperidine in appropriate solvents; again we find that radicals $R_2N\cdot$ are feeble dehydrogenating agents.

The irradiation of *N*-nitrosopiperidine did not effect decomposition under conditions in which alkyl nitrites suffer homolysis.[2] When tetramethyltetrazen was photolysed in boiling toluene 60% of the dimethyl groups were converted to volatile bases, probably mainly dimethylamine, about half of which had been formed by the dehydrogenation,

$$Me_2N\cdot + CH_3\cdot Ph \longrightarrow Me_2NH + \cdot CH_2\cdot Ph$$

since from the remaining liquid a 28% yield of bibenzyl was isolated together with 3% of *NN*-dimethylaminobenzylamine. The photolysis of azopiperidine in the same solvent yielded 22% of bibenzyl and 4% of 1,1′-bipiperidyl. The photolysis of tetramethyltetrazen in cumene yielded 38% of bicumyl which is consistent with the earlier pyrolytic study, but a photolysis of tetramethyltetrazen in cyclohexane gave only small traces of both bicyclohexyl and of cyclohexene. No evidence could be found for the occurrence of any reactions between dimethylamino or *N*-piperidyl radicals and benzene, but slight evidence of the addition of dimethylamino radicals to the 9,10-position in anthracene was forthcoming, though there was insufficient product for proper characterisation.

The actions of dimethylamino radicals on both 2,6-dimethoxy- and 2,6-dimethyl-phenols were also examined, since oxidations of these substances very readily yield sparingly soluble and easily recognisable 4,4′-diphenoquinones. However no trace of a diphenoquinone could be obtained from either phenol.

It was previously found [1] that the decomposition of tetramethyltetrazen in cyclohexanone gave an intractable mixture of condensation products, and consequently acetophenone was selected as a more amenable ketone for investigation. The basic products of this reaction again proved to be complex, but the neutral residue yielded, after steam distillation, significant amounts of both the racemic and *meso* forms of 2,3-dihydroxy-2,3-diphenylbutane but no 1,2-dibenzoylethane. This reduction to the pinacol possibly arises by a hydrogen transfer to photochemically excited acetophenone followed by dimerisation of the resulting phenylmethylcarbinol radicals [$Ph\cdot\dot{C}(OH)Me$]. Sources of such hydrogen would include methylene groups in the Schiff's base polymers which are invariably formed in reactions of dimethylamino radicals by the occurrence of the disproportionation

$$2\ Me_2N\cdot \longrightarrow Me_2NH + MeN{:}CH_2$$

To avoid this disproportionation we have attempted to prepare a radical $R_2N\cdot$ from 2,2,6,6-tetramethylpiperidine; this would contain no α C–H groups. Though the nitrosamine of this base could be prepared with difficulty, its reduction required vigorous conditions, and then yielded the original tetramethyl piperidine as well as its *N*-amino derivative. Attempts to oxidise the latter to the desired tetrazen have failed.

[1] B. R. Cowley and W. A. Waters, *J. Chem. Soc.*, 1961, 1230.
[2] A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, 1962, **17**, 35.

We also find that tetramethyltetrazen, unlike azodibenzoyl, does not undergo a Diels–Alder reaction with butadiene, cyclopentadiene, or hexachlorocyclopentadiene.

EXPERIMENTAL

Purified, dry solvents were used throughout. M.p.s were taken on a Kofler hot stage apparatus and are uncorrected. Irradiations of tetrazens were carried out in Pyrex vessels using a Hanovia 250-w ultraviolet lamp, and the progress of the decompositions was followed, where possible, by the disappearance of the azo chromophore around 2800 Å.

Tetramethyltetrazen, prepared by the mercuric oxide oxidation of 1,1-dimethylhydrazine,[1] had b. p. 33·5°/15 mm., n_D^{25} 1·4628, $\lambda_{max.}$ (cyclohexane) 2780 Å (ε 8700), τ (CCl_4) 7·23 p.p.m. (sharp singlet). The *methobromide* was obtained as a colourless crystalline solid by treatment with methyl bromide in ether at 0° (Found: C, 27·9; H, 7·25. $C_5H_{15}N_4Br$ requires C, 28·4; H, 7·2%); it detonated violently on heating to *ca.* 70°, or on vigorous rubbing. The yellow *methiodide*, obtained similarly, decomposed slowly at room temperature (Found: C, 23·5; H, 5·6; I, 51·3. $C_5H_{15}N_4I$ requires C, 23·3; H, 5·9; I, 49·2%).

N-Aminopiperidine was prepared by the dropwise addition, over 30 min., of *N*-nitrosopiperidine (50 ml.) to a stirred, ice-cooled mixture of amalgamated zinc (200 g.) and 6N-hydrochloric acid (350 ml.). Stirring was continued for a further 30 min., and the whole was filtered and made just basic with conc. ammonia and then strongly basic with sodium hydroxide (direct basification with the latter led to the formation of an insoluble precipitate). The slightly cloudy solution was continuously extracted with ether for 10 hr., and the ether layer was dried ($MgSO_4$) and evaporated; the residual oil was twice distilled to give the hydrazine (50%), b. p. 146·8°/754 mm. Oxidation of the hydrazine with mercuric oxide as above gave 1,1′-azopiperidine, which, from aqueous methanol, formed colourless prisms (85%), m. p. 44·5° (lit.,[3] m. p. 45°), $\lambda_{max.}$ (methanol) 2800, 2500sh Å (ε 9400), τ (CCl_4) 8·43 p.p.m. (12β and γ protons, broad band), 6·91 p.p.m. (8α protons, multiplet).

1,1′-Bipiperidyl was prepared in poor yield by the dropwise addition of 1,5-dibromopentane to a refluxing mixture of anhydrous hydrazine and potassium hydroxide.[4] It had b. p. 52—53°/0·5 mm., τ (CCl_4) 8·53 p.p.m. (12β and γ protons, multiplet), 7·37 p.p.m. (8α protons, triplet) (Found: C, 71·1; H, 11·7; N, 17·05. Calc. for $C_{10}H_{20}N_2$: C, 71·4; H, 12·0; N, 16·65%). The picrate, prepared in methanol, crystallised from water as yellow prisms, m. p. 152·5—154° (lit.,[4] m. p. 153—154°).

N-*Nitrosotetramethylpiperidine*.—The method of Hall[5] for the preparation of triacetonamine was improved as follows. Phorone and twice its weight of water were saturated with ammonia till the two liquid phases became homogeneous, and the solution was then heated in a pressure bottle at 100° for 24 hr. Evaporation of the reaction mixture under reduced pressure gave almost pure triacetonamine hydrate, which on fractionation gave triacetonamine, b. p. 90—90·5°/10 mm. It crystallised on cooling, and when recrystallised from light petroleum (b. p. 40—60°) formed long prisms, m. p. 36° (lit.,[5] m. p. 36°), $\nu_{max.}$ (CCl_4) 1715 cm.$^{-1}$ (C=O), N–H stretch hardly detectable. Reduction by the Wolff–Kishner method[6] gave 2,2,6,6-tetramethylpiperidine (80%), b. p. 154·5—156°/762 mm. (lit.,[6] b. p. 151—152°/750 mm.), n_D^{20} 1·4455 (lit.,[6] n_D^{20} 1·4455) (Found: C, 76·9; H, 13·3; N, 10·2. Calc. for $C_9H_{19}N$: C, 76·5; H, 13·6; N, 9·9%); the expected absorption for N–H stretching was not observed in the infrared region in carbon tetrachloride solution, but the presence of NH was confirmed by the n.m.r. signal for this proton at τ 9·42 p.p.m., which disappeared after treatment of the amine with D_2O. The *hydrochloride*, prepared in ether saturated with hydrogen chloride, crystallised from ether–ethanol as prisms, subl. >220° (Found: C, 60·9; H, 11·2; N, 8·4; Cl, 19·35. $C_9H_{20}NCl$ requires C, 60·8; H, 11·35; N, 7·9; Cl, 19·95%). Attempted nitrosation of tetramethylpiperidine using sodium nitrite and mineral acid or acetic acid, or using amyl nitrite and acetic acid, all failed, the amine being recoverable. The following modification of methods using nitrous fumes[7] was successful. Nitrogen(III) oxide, generated from sodium nitrite and conc. sulphuric acid, was bubbled for 2 hr. through a solution, at room temperature, of the amine (5 ml.) in acetic acid (15 ml.) contained in a vessel, stoppered except for a narrow outlet orifice (the use of larger amounts of amine, or the admission of air, leading to nitrogen(IV) oxide formation, gave reduced yields). The solution was diluted with water (60 ml.), and the resulting oil was extracted with ether till the extracts were colourless. The ethereal solution was washed with water, dil. aqueous potassium hydrogen carbonate, and water, and was then dried and fractionated, yielding golden-yellow 1-*nitroso*-2,2,6,6-*tetramethylpiperidine* (60%), b. p. 91—92°/12 mm., $\lambda_{max.}$ (hexane) 2380 Å (ε 5400), 3970 Å (ε 86) (Found: C, 63·5; H, 10·6; N, 16·6. $C_9H_{18}N_2O$ requires C, 63·5; H, 19·7; N, 16·5%).

Reduction of N-*Nitrosotetramethylpiperidine*.—Reduction to the *N*-amino compound to any significant extent failed with sodium in ethanol,[8] and with lithium aluminium hydride, alone,[9] or with added aluminium chloride; in each case most of the nitrosamine was recovered. The following method of Jucker and Lindenmann[10] gave partial reduction, and then only when carried out at elevated temperatures rather than at 0°.[10] A suspension of the nitrosamine (3·0 g.) and zinc dust (9·5 g.) in water (20 ml.) kept at about 80° was treated dropwise with 50% acetic acid (10 ml.) over 45 min.: the yellow oil slowly dissolved. The whole was filtered hot and made basic with aqueous sodium hydroxide. Ether extraction of the resulting emulsion and evaporation of the dried ethereal extracts gave an oil which was fractionated at 20 mm. with steady increase in b. p. up to 80° to give very impure 1-amino-2,2,6,6-tetramethylpiperidine (2 g.), of which a cut (250 mg.) boiling near 80° corresponded to about a 9 : 1 mixture with the related amine (Found: C, 70·7; H, 12·1; N, 17·35. $C_9H_{20}N_2$ requires C, 69·2; H, 12·9; N, 17·9%).

Reactions of Tetramethyltetrazen.—(i) *Toluene*. Dry

[3] L. Knorr, *Annalen*, 1883, **221**, 297.
[4] M. Rink and R. Lux, *Naturwiss.*, 1958, **45**, 516.
[5] H. K. Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5444.
[6] N. J. Leonard and E. W. Nommensen, *J. Amer. Chem. Soc.*, 1949, **71**, 2808.
[7] R. Huisgen and J. Reinertshofer, *Annalen*, 1952, **575**, 174; M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, 1951, **73**, 4199.
[8] H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *J. Amer. Chem. Soc.*, 1955, **77**, 790.
[9] C. Hanna and F. W. Schueler, *J. Amer. Chem. Soc.*, 1952, **74**, 3693.
[10] E. Jucker and A. Lindenmann, *Helv. Chim. Acta*, 1962, **45**, 2316.

nitrogen was bubbled through an irradiated solution of the tetrazen (4·0 ml., 31 mmole) in refluxing toluene (100 ml.) for 24 hr., the effluent gas stream being passed through two 75 ml. portions of 1·00N-hydrochloric acid. The evolved base (37·9 m. equiv.) was estimated titrimetrically with alkali (using screened Methyl Orange as indicator), but was not investigated further. The toluene layer was extracted with known amounts of standard hydrochloric acid, and the basic material thus removed (16 m. equiv., estimated on an aliquot as above) was liberated as an oil with alkali and taken up in chloroform. Evaporation of the dried ($MgSO_4$) chloroform solution, followed by steam distillation of the residue, gave a colourless oil (0·17 g.), isolated with ether, and identified as *NN'*-dimethylbenzylamine by comparison of its infrared spectrum with that of authentic amine, and by conversion to its picrate of m. p. and mixed m. p. 182·5—183·5°. The material involatile with steam was a brown, intractable gum (0·06 g.). The neutral toluene layer was evaporated to a residue (1·86 g.) which crystallised, melting at 40—45°, and consisted essentially of bibenzyl. Purification by chromatography on alumina from light petroleum (b. p. 40—60°) gave pure bibenzyl (1·55 g., 28% *).

(ii) *Cumene*. A solution of the tetrazen (1·0 ml., 8 mmole) in cumene (20 ml.) was similarly irradiated for 20 hr. After removal of the cumene *in vacuo* the residue was dissolved in ether and the basic products were extracted with dil. hydrochloric acid but were not further examined. The neutral ether layer gave slightly impure bicumyl on evaporation (0·70 g., 38%); it crystallised from methanol, as prisms, m. p. and mixed m. p. 117—118°, with authentic bicumyl.

(iii) *Cyclohexane*. A cooled solution of the tetrazen (4·0 ml., 31 mmole) in cyclohexane (100 ml.) was irradiated for 30 hr., the volatile bases being swept out with nitrogen into dil. hydrochloric acid as described in (i). The cyclohexane solution was washed with acid: the combined acidic solutions contained 48 m. equiv. of base. The bases were regenerated with alkali, extracted with ether, and the ethereal solution was evaporated. The residue, a small amount of foul-smelling base probably containing tetramethylhydrazine, was not further examined. The neutral cyclohexane layer was shown to contain less than 10 mg. of cyclohexene by vapour phase chromatography (v.p.c.) at 40° on 15% ββ'-oxydipropionitrile on Embacel (H_2-flame detector), and less than 1 mg. of bicyclohexyl by v.p.c. at 95° on 1½% silicone oil on Embacel (β-ray detector); authentic bicyclohexyl, b. p. 230—232°/760 mm., was made by the Wurtz reaction on bromocyclohexane. Evaporation of the cyclohexane left only a small amount of involatile residue.

(iv) *Anthracene*. A solution of the tetrazen (2·0 ml., 15·5 mmole) and anthracene (5 g.) in refluxing benzene (100 ml.) was irradiated for 48 hr. Much crystalline material precipitated during this time and was identified as the anthracene photo-dimer. The benzene filtrate was extracted with dil. hydrochloric acid, and the extracts were made alkaline and shaken out with benzene; the benzene solution afforded an amine residue (0·038 g.), containing some volatile material (probably the hydrazine). Addition of a little cold methanol gave a tan-coloured precipitate (60 mg.), which was crystallised from benzene–methanol as prisms, considered to be 9,10-dimethylamino-9,10-dihydroanthracene, which melted at 226—228°, showing some resolidification above this temperature and remelting at 243—245°. Its light absorption spectrum in ethanol–hydrochloric acid had peaks at 2690 and 2760 Å, but none at longer wavelengths; when a portion was heated at 250° for 30 min. these absorption maxima disappeared and were replaced by a single peak at 2530 Å and typical anthracene fine structure above 3200 Å. There was insufficient material for proper characterisation. The neutral benzene solution gave further anthracene dimer, but no other product.

(v) *Acetophenone*. The tetrazen (2·0 ml., 15·5 mmole) was irradiated in the ketone (20 ml.) for 6 days. The solution was diluted with ether and the basic fraction was isolated (2·2 g., phenyl C–H and phenyl C=O absorption in the infrared region). Distillation of this at 0·2 mm. gave three fractions (<95, 95—110, 130—140°), 0·49 g. in all, and left a dark involatile gum, all of which proved intractable when investigated, either directly, or as their picrates or semicarbazones. The neutral products, after removal of acetophenone by steam distillation, were partially crystalline (1·49 g.). Trituration with ether–light petroleum gave a solid (0·66 g.), which on two crystallisations from light petroleum (b. p. 60—80°) gave colourless (±)-2,3-dihydroxy-2,3-diphenylbutane as prisms, m. p. 123—125° (lit.,[11] m. p. 122°), $\nu_{max.}$ (Nujol) 3540 cm.$^{-1}$ (OH stretch) (Found: C, 78·9; H, 7·4. Calc. for $C_{16}H_{18}O_2$: C, 79·3; H, 7·5%). The mother-liquors from the trituration and crystallisations were combined and chromatographed on alumina; elution with light petroleum–ether (3 : 2) gave *meso*-2,3-dihydroxy-2,3-diphenylbutane (0·47 g.), which when twice crystallised from light petroleum (b. p. 60—80°) gave prisms, m. p. 118—119° (lit.,[11] m. p. 117—118°), $\nu_{max.}$ (Nujol) 3520 cm.$^{-1}$ (OH stretch) (Found: C, 79·6; H, 7·6%), and then further racemic glycol (0·56 g. in all). Only small amounts of other products were eluted on further chromatography. None contained 1,2-dibenzoylethane (by comparison with reference material on thin layer chromatoplates).

When acetophenone alone was irradiated for 6 days in a control experiment neither of the glycol isomers was obtained.

(vi) 2,6-*Dimethoxy- and* 2,6-*dimethyl-phenol*. The tetrazen (2·1 ml.) and 2,6-dimethoxyphenol (0·25 g., 1 mol.) were dissolved in benzene (50 ml.) and irradiated for 24 hr. under reflux; a dark precipitate and a red solution formed. The whole was evaporated and the residue treated with N-hydrochloric acid to remove basic material, but the latter was not investigated. A small amount of dark oil remained undissolved, which was shown to contain no 2,6,2',6'-tetramethoxydiphenoquinone. A similar reaction of the tetrazen with 2,6-dimethylphenol again failed to lead to the formation of the analogous tetramethyldiphenoquinone.

(vii) 1,3-*Dienes*. The tetrazen (2·8 ml.) was completely recovered when its solution in benzene (20 ml.) was saturated at room temperature with butadiene over 5 hr. It was likewise unaffected when treated at 0° for 3 days with an excess of either cyclopentadiene or hexachlorocyclopentadiene. When the tetrazen was first quaternised, either to the hydrochloride or the methiodide, and then treated with cyclopentadiene, again there was no evidence of condensation.

Reactions of Azopiperidine.—(i) *Toluene*. Azopiperidine (5·0 g., 25·5 mmole) in refluxing toluene (200 ml.) was

* Based on the reaction: $Me_2N_4Me_2 + 2PhMe \longrightarrow 2Me_2NH + N_2 + (PhCH_2)_2$.

[11] Beilstein, "Handbuch der organischen Chemie," 2nd Suppl. vol. 6, 979.

completely decomposed when irradiated for 7 hr. (In refluxing toluene, without irradiation, there was no decomposition in 7 hr.). The colourless solution was then shown to contain 46 m. equiv. of amines by analysis of aliquots with standard sulphuric acid. The amines were completely extracted with acid, regenerated with alkali, and isolated therefrom by repeated shaking with ether. The dried ethereal solution was fractionated to give, first, piperidine (1·3 g., but much loss would occur in the work-up due to its miscibility with water), b. p. 106—110°/754 mm., picrate m. p. and mixed m. p. 151·5—152·5°, and then, at reduced pressure, an oil, b. p. 52—56°/0·1 mm., identified as 1,1′-bipiperidyl (0·17 g., 4%), τ (CCl_4) 8·53, 7·36 p.p.m. (Found: C, 71·9; H, 11·4; N, 16·4%), the picrate being identical with authentic picrate, mixed m. p. 150—153°, and finally a high-boiling viscous liquid, b. p. 100—160°/0·1 mm. (0·19 g.), with benzenoid absorption bands in its infrared spectrum and strong phenyl proton absorption at τ 2·75 p.p.m. in its n.m.r. spectrum. This fraction and the picrate mixture from it proved intractable. The neutral toluene solution was evaporated and the residue, which crystallised, was digested with light petroleum (b. p. 40—60°), in which some polymeric material remained undissolved, and the solution was chromatographed on on alumina to give pure bibenzyl (0·52 g., 22%).

(ii) *Benzene*. A solution of azopiperidine (1·5 g., 7·65 mmole) in benzene (60 ml.) was similarly irradiated for 6 hr., during which time a red-brown colour developed; the solution contained 12·2 m. equiv. of base. Extraction of the benzene solution with acid, followed by liberation of the amines with alkali, led to material incompletely soluble in ether, some of the products being tarry. The ether-soluble fraction had very weak ultraviolet absorption, indicating the absence of 1-phenylpiperidine; *NN*-diethylaniline, for example, a suitable model compound, has $\lambda_{max.}$ (methanol) 2600 Å (ε 11,000). The neutral benzene layer was evaporated giving a trace of gummy residue in which, by thin-layer chromatography, biphenyl was shown to be absent.

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