New Products of the Reaction of *NN*-Dimethylaniline with Benzoyl Peroxide

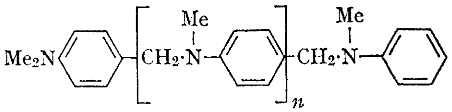
By R. B. ROY and G. A. SWAN

(*Department of Organic Chemistry, University of Newcastle upon Tyne, Newcastle upon Tyne,* 1)

IT has already been shown that the following products can be obtained from *NN*-dimethylaniline, by the action of benzoyl peroxide in benzene or chloroform, followed by treatment with water: formaldehyde,[1] *N*-methylaniline,[1] *p*-benzoyloxy-*NN*-dimethylaniline,[1] *N*-*p*-dimethylaminobenzyl-*N*-methylaniline,[2] and 4,4′-bisdimethylaminodiphenylmethane.[1,2] In addition, an unstable Würster salt of *NNN′N′*-tetramethylbenzidine has been claimed to be a major product of the reaction in toluene at −25° in the absence of oxygen.[3]

On the assumption that the reaction could take two different courses, one ionic and the other radical in nature, we studied the products formed in a variety of solvents and also at different temperatures and with certain other variations in reaction conditions. The amine was in excess and yields quoted are based on benzoyl peroxide. The products studied were those more complex than dimethylaniline and reference to reaction products (*e.g.*, "main product") disregards *N*-methylaniline. This work has resulted in the isolation of the following apparently hitherto unknown compounds, using chromatography on alumina:

(1) *N′*-*p*-Dimethylaminobenzyl-*N′*-methyl-*N*-*p*-aminobenzyl-*N*-methylaniline (I), m.p. 102°. Formed in acetonitrile (30°) and in very low yield in benzene (30°), toluene (45°), chloroform (0—45°) and dichloromethane (0—45°).



(I) $n = 1$; (II) $n = 2$; (V) $n = 0$.

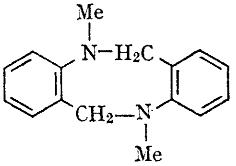
p-(OHC)MeN·C_6H_4·CH_2·NMe·Ph (III)

p-Me·C_6H_4·NMe·CH_2·NMe·C_6H_4·Me-*p* (VI)

(2) *N″*-*p*-Dimethylaminobenzyl-*N″*-methyl-*N′*-*p*-aminobenzyl-*N′*-methyl-*N*-*p*-aminobenzyl-*N*-methylaniline (II), m.p. 144°. Formed in small amount in toluene, chloroform, pyridine, or dichloromethane at 0—45° and in styrene at 0°.

(3) *N′*-Formyl-*N′*-methyl-*N*-*p*-aminobenzyl-*N*-methylaniline (III), m.p. 139—140°. Formed in small amount in carbon tetrachloride (−5°) in the absence of oxygen.

(4) 5,6,11,12-Tetrahydro-5,11,dimethylphenhomazine (IV), m.p. 103°. Formed in 70% yield in cumene (0°) and in low yield in tetralin (0°) and decalin (0°).



(IV)

In addition, we isolated 2-hydroxy-*N*-methylbenzamide and confirmed the formation of *p*-benzoyloxy-*NN*-dimethylaniline in several solvents (27% yield in acetonitrile at −5° under nitrogen; also the main product in acetone at 0°). *NNN′N′*-Tetramethylbenzidine was obtained from reactions carried out in a variety of solvents, particularly at low temperature, in the absence of oxygen, but the yield was always low.

The optimum conditions for the formation of *N*-*p*-dimethylaminobenzyl-*N*-methylaniline (V), (64%) in benzene were in the temperature range 5—45°, with a molecular ratio of dimethylaniline to benzoyl peroxide of 3 : 1. Compound (V) was also obtained as the main product with a ratio of 3 : 1 at 5—45° in acetonitrile, toluene, chloroform, and dichloromethane; and also in styrene at 0°. In carbon tetrachloride (0°) 4,4′-bisdimethylaminodiphenylmethane was the main product; chloride ion was also formed and the base presumably arises as a secondary product from (V) (see ref. 2).

Horner and Betzel[1] obtained small amounts of a compound $C_{18}H_{24}N_2$, m.p. 149°, by reaction of benzoyl peroxide with *NN*-dimethyl-*p*-toluidine in ethyl acetate (30°, under nitrogen) or chloroform (35°, in oxygen). By a similar reaction in chloroform (yield 79% at 5°, in air), cumene (0°), tetralin (0°) or ethyl acetate (0°) we obtained a compound $C_{18}H_{22}N_2$, m.p. 149°, which was identical with an authentic sample of 5,6,11,12-tetrahydro-2,5,8,11-tetramethylphenhomazine, kindly supplied by

Dr. Cooper and Professor Partridge.[4] When the reaction was carried out at 5° or 45° in benzene or acetonitrile the latter compound was not obtained, but *NN'*-dimethyl-*NN'*-di-*p*-tolylmethanediamine (VI), identical with an authentic sample,[5] was isolated.

The structural assignment of (I) was based on the formula $C_{24}H_{29}N_3$ (mass spectrum), infrared spectrum (strong bands at 685, 742, and 799 cm.$^{-1}$) and n.m.r. spectrum, τ 7·16 (CH_3) and 5·72 (CH_2). This was confirmed by synthesis. *N-p*-Aminobenzylaniline condensed with *p*-dimethylaminobenzaldehyde to give an anil, m.p. 157—158°, which was reduced by sodium borohydride to *N'-p*-dimethylaminobenzyl-*N-p*-aminobenzylaniline, m.p. 121°. When the latter was formylated and the resulting amide reduced with lithium aluminium hydride, the product was identical with compound (I) above.

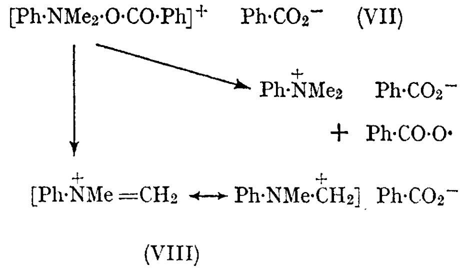
The structure of (II) was based on the formula, $C_{32}H_{38}N_4$ (mass spectrum), infrared spectrum (strong band at 805 cm.$^{-1}$, comparatively weak bands at 690 and 750 cm.$^{-1}$) and n.m.r. spectrum, τ 7·13 (CH_3) and 5·63 (CH_2), ratio of CH_3, CH_2, and aromatic protons, 15 : 6 : 17.

The structure of (III) was based on the formula, $C_{16}H_{18}N_2O$ and the mass spectrum which contains a strong peak at $m = 148$ ($C_9H_{10}NO$). The mass spectrum of (V), as well as (I) and (II) all show a strong, corresponding peak at $m = 134$ ($C_9H_{12}N$).

Compound (IV) was shown by the mass spectrum to have the formula $C_{16}H_{18}N_2$. Its infrared spectrum showed a very strong band at 743 cm.$^{-1}$ Its n.m.r. spectrum showed peaks for *N*–CH_3 (τ, 7·18) and CH_2 (τ, 5·75) protons and was very like that of 5,6,11,12-tetrahydro-2,5,8,11-tetramethylphenhomazine, except that the peak at τ 7·8 (Ar–CH_3) was missing. The ultraviolet spectra of these two compounds were also similar and the mass spectrum of each showed strong peaks at $\left(\frac{m}{2} + 1\right)$ and $\left(\frac{m}{2} - 1\right)$.

The smooth formation of (IV) from dimethylaniline is a rather remarkable reaction. It may be significant that all the solvents in which the formation of (IV) (or the corresponding 2,5,8,11-tetramethyl compound) have been observed are ones which may form radicals by hydrogen abstraction (see refs. 6 and 7).

It has been suggested that an intermediate of the type (VII) might be formed either by reaction of a diacyl peroxide with an amine, or by the action of an acid anhydride on an amine oxide.[8] It has also been suggested that (VII) could decompose in either of two ways, although there is evidence against this being the branching point between radical and ionic mechanisms.[9] We have now shown that treatment of *NN*-dimethylaniline *N*-oxide, in the presence of excess of *NN*-dimethylaniline, in benzene, toluene, or acetonitrile at 0°, with acetic anhydride yields (V) and *NNN'N'*-tetramethylbenzidine, the latter also being obtained in cumene. The formation of the former product seems to imply the intervention of the mesomeric ion (VIII) in both the (*NN*-dimethylaniline + benzoyl peroxide) and (*NN*-dimethylaniline *N*-oxide + acetic anhydride) systems. The formation of tetramethylbenzidine seems to imply the intervention of radicals in both systems. Recent kinetic results have been interpreted in terms of radical, rather than ionic mechanisms,[3,10] but our work shows how complex the situation is.



(*Received, May 23rd,* 1966; *Com.* 347.)

---

[1] L. Horner and C. Betzel, *Annalen*, 1953, **579**, 175.

[2] J. M. Fayadh, D. W. Jessop, and G. A. Swan, *Proc. Chem. Soc.*, 1964, 236.

[3] D. M. Graham and R. B. Mesrobian, *Canad. J. Chem.*, 1963, **41**, 2938.

[4] F. C. Cooper and M. W. Partridge, *J. Chem. Soc.*, 1957, 2888.

[5] J. von Braun, *Ber.*, 1908, **41**, 2145.

[6] D. H. Hey and J. Peters, *J. Chem. Soc.*, 1960, 79 and 88.

[7] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, 1945, **10**, 394 and 401.

[8] R. Huisgen, F. Bayerlein, and W. Heydkamp, *Chem. Ber.*, 1959, **92**, 3223.

[9] R. Huisgen, W. Heydkamp, and F. Bayerlein, *Chem. Ber.*, 1960, **93**, 363.

[10] F. Hrabák and M. Vacek, *Coll. Czech. Chem. Comm.*, 1965, **30**, 573.