

Amine Oxidation. Part XII.¹ Reactions of Some *NN*-Dimethylbenzylamine *N*-Oxides with Acetic Anhydride and of Some *N*-Acetoxy-*NN*-dimethylbenzylammonium Perchlorates with Acetate Ion. The Polonovski Reaction

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The reactions of acetic anhydride with *NN*-dimethylbenzylamine *N*-oxide and five of its substituted derivatives (the Polonovski reaction) to give *NN*-dimethylacetamide, an *N*-benzyl-*N*-methylacetamide, and a benzaldehyde have been studied by use of n.m.r. and g.l.c. The effect of the substituents on the relative proportions of debenzylation and demethylation is discussed in terms of a variable transition state in the product-determining step for debenzylation: with an electron-donating group, such as 4-OMe, it is iminium ion-like whereas with the electron-withdrawing 4-NO₂ it has carbanionic character. The preparations of *N*-acetoxy-*NN*-dimethylbenzylammonium perchlorate and its 4-Cl and 4-NO₂ derivatives are described. The thermal stability of these salts and their reactions with acetate ion are reported. These data agree with an *N*-acetoxyammonium ion being the first intermediate in the Polonovski reaction, and with the overall conversion of this ion into acetamides being an ionic process induced by acetate ion. No evidence for any radical intermediates was obtained.

The reactions of pyridine and alkylpyridine *N*-oxides with acetic anhydride have been thoroughly studied, and convincing evidence for both ionic and radical reaction³) the generally accepted mechanism is the sequence of ionic processes [illustrated for an *NN*-dimethylbenzylamine *N*-oxide in reactions (i)—(ix)]

TABLE 1

Yields (% based on *N*-oxide) of products from the reactions of some substituted *NN*-dimethylbenzylamine *N*-oxides with acetic anhydride

Substrate XC ₆ H ₄ ·CH ₂ ·N ⁺ (O ⁻)Me ₂	Products			Ratio of Me ₂ NAc to XC ₆ H ₄ ·CH ₂ ·NMeAc
	Me ₂ NAc	XC ₆ H ₄ ·CH ₂ ·NMeAc	XC ₆ H ₄ ·CHO	
X				
4-MeO *	73.7	17.6		4.2
4-MeO †	49.4	24.4	58.7	2.0
4-Me *	66.7	13.4		5.0
H *	70.7	23.1		3.1
H †	82.4	28.4	82.4	2.9
4-Cl *	78.0	12.0		6.5
4-Cl †	76.1	11.2	74.2	6.8
3-CF ₃ *	76.7	12.6		6.1
4-NO ₂ *	45.7	7.1		6.4
4-NO ₂ †	32.8	4.8		6.8

* Yields measured by ¹H n.m.r. † Yields measured by g.l.c.

TABLE 2

Yields (% based on *N*-acetoxyammonium salt) of acetamides from the reactions of some substituted *N*-acetoxy-*NN*-dimethylbenzylammonium perchlorates with acetate ion

Substrate XC ₆ H ₄ ·CH ₂ ·N ⁺ (OAc)Me ₂	Solvent	Products			Ratio of Me ₂ NAc to XC ₆ H ₄ ·CH ₂ ·NMeAc
		Me ₂ NAc	XC ₆ H ₄ ·CH ₂ ·NMeAc	Total	
X					
H *	HOAc	28.7	7.9	36.6	3.6
H †	HOAc	33.3	11.9	45.2	2.8
H *	Ac ₂ O	76.1	25.0	101.1	3.1
4-Cl *	Ac ₂ O	72.9	19.2	92.1	3.8
4-NO ₂ *	Ac ₂ O	90.6	17.1	107.7	5.3

* Yields measured by ¹H n.m.r. † Yields measured by g.l.c.

mechanisms has been obtained.² For the corresponding reaction of aliphatic tertiary amine *N*-oxides (Polonovski

¹ Part XI, J. R. Lindsay Smith and L. A. V. Mead, *J.C.S. Perkin II*, 1976, 1172.

² (a) T. Koenig, *J. Amer. Chem. Soc.*, 1966, **88**, 4045; (b) V. J. Traynelis in, 'Mechanisms of Molecular Migrations,' vol. II, ed. B. S. Thyagarajan, Interscience, New York, 1969, p. 1; (c) H. Iwamura, M. Iwamura, T. Nishida, and S. Sato, *J. Amer. Chem. Soc.*, 1970, **92**, 7474; (d) H. Iwamura, M. Iwamura, T. Nishida, and I. Miura, *Tetrahedron Letters*, 1970, 3117; (e) T. Cohen and

proposed by Huisgen and his co-workers,⁴ although this is less well established.

G. L. Deets, *J. Amer. Chem. Soc.*, 1972, **94**, 932; (f) V. J. Traynelis, K. Yamauchi, and J. P. Kimball, *ibid.*, 1974, **96**, 7289; (g) V. J. Traynelis, J. P. Kimball, and K. Yamauchi, *J. Org. Chem.*, 1975, **40**, 1313.

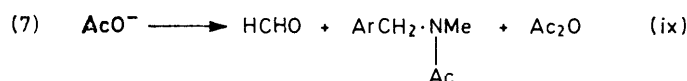
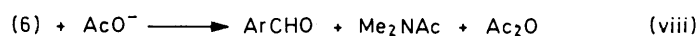
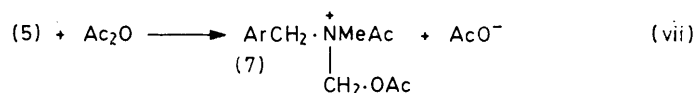
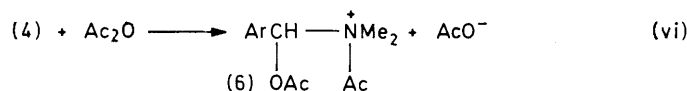
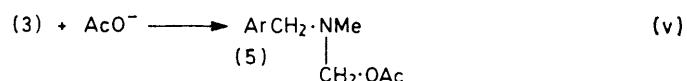
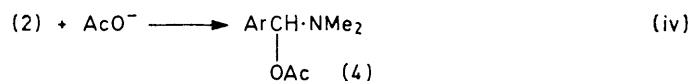
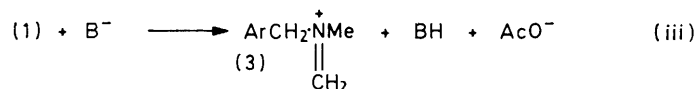
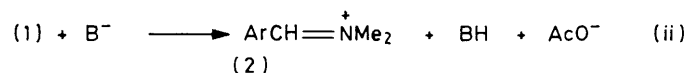
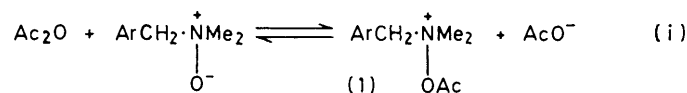
³ M. Polonovski and M. Polonovski, *Compt. rend.*, 1927, **184**, 331; *Bull. Soc. chim. France*, 1927, **41**, 1190.

⁴ R. Huisgen, F. Bayerlein, and W. Heydkamp, *Chem. Ber.*, 1959, **92**, 3223.

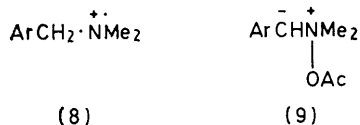
Alternative routes involving radical⁵ and ylide⁶ intermediates, such as (8) and (9), have also been proposed.

We report here, as an extension of our earlier studies,⁷ the reactions of some ring-substituted *NN*-dimethylbenzylamine *N*-oxides with acetic anhydride, and the

treated with a large excess of acetic anhydride, and the yields of the products were estimated by ¹H n.m.r. spectroscopy (mesitylene as internal standard). With four of the reactions the yields were also measured by g.l.c. (mesitylene, bibenzyl, or 4-nitrobiphenyl as standard). These yields and the ratio of debenzylation



synthesis and reactions of some *N*-acetoxy-*NN*-dimethylbenzylammonium perchlorates.



RESULTS

Reactions of Substituted NN-Dimethylbenzylamine N-Oxides.—Six *NN*-dimethylbenzylamine *N*-oxides were

⁵ J. C. Craig, F. P. Dwyer, A. N. Glazer, and E. C. Horning, *J. Amer. Chem. Soc.*, 1961, **83**, 1871.

to demethylation are recorded in Table I. The total yield of the two amides in each reaction accounted for >89% of the *N*-oxide substrate, except in the reactions of 4-*NN*-trimethylbenzylamine *N*-oxide and *NN*-dimethyl-4-nitrobenzylamine *N*-oxide. In the last reaction, although the aromatic proton signals of the products account for 105% of the starting *N*-oxide and there are no unaccounted-for absorbances, the combined amide yield is *ca.* 50%.

⁶ Y. Hayashi, Y. Nagano, S. Hongyo, and K. Teramura, *Tetrahedron Letters*, 1974, 1299.

⁷ P. A. Bather, J. R. Lindsay Smith, and R. O. C. Norman, *J. Chem. Soc. (C)*, 1971, 3060.

acid, acetic [³H]acid, acetic anhydride, or acetonitrile). The n.m.r. spectrum of the solution was recorded and shown to remain unchanged even after heating at 80 °C for 4 h (acetic anhydride solutions were only heated at 80 °C for *ca.* 10 min). The addition of water or sodium acetate followed by warming rapidly converted the salts into

products which were analysed by n.m.r. spectroscopy and g.l.c.

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