The Behaviour of *p*-Nitrobenzyl Compounds in Basic Media

By SAMIR B. HANNA

(Department of Chemistry, The University of Missouri at Rolla, Rolla, Missouri, U.S.A)

As a continuation of our investigations[1] on the mechanisms of formation of *pp'*-dinitrostilbene (I) from *p*-nitrobenzyl compounds we have now studied the behaviour of *p*-nitrobenzylpyridinium chloride (II) and bromide (III) in aqueous alkaline solution. Recently, Rothberg and Thornton reported that *p*-nitrobenzyltrimethylammonium bromide was recovered quantitatively after allowing it to react on a steam bath for 72 hrs.[2] This is rather surprising since *p*-nitrobenzyl chloride in alkaline aqueous dioxan,[1] and *p*-nitrobenzyldimethylsulphonium tosylate in alkaline aqueous solution[3] are known to give quantitative yields of the stilbene (I) *via* α-elimination.

When aqueous solutions of the pyridinium salts (0·1 M) were mixed with sodium hydroxide solutions (0·1 and 0·5M) at 25° an intense orange colour developed followed by the appearance of a yellowish brown precipitate and the characteristic smell of pyridine. Thin-layer chromatography on silica, and column chromatography on alumina, showed the product to be a pure substance. The melting point of the crystallised material was 193—194°. Infrared analysis showed the absence of the characteristic nitro-group frequencies, but showed a strong carbonyl peak at 1700 cm.^{-1} Nuclear magnetic resonance showed two aldehydic protons at $\tau - 0{\cdot}083$ and $-0{\cdot}17$. The product is, therefore, neither the stilbene (I) nor *p*-$NO_2\cdot C_6H_4\cdot CH_2N{=}CH{-}CH{=}CH{-}CH_2\cdot CHO$, a derivative of glutacondialdehyde, as would be expected from an alkali-induced pyridinium salt decomposition.[4] Fisher reported that treatment of (III) with aqueous hypobromite yielded 82% *p*-nitrobenzoic acid,[5] while *p*-nitrotoluene was reported as the product of treating *p*-nitrobenzylpyridinium perchlorate with boiling sodium hydroxide.[6] Elemental analysis on our product leads us to the molecular

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[1] S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, **1961**, 217; S. B. Hanna, Y. Iskander, and A. Salama, *ibid.*, p. 221.

[2] I. Rothberg and E. R. Thornton, *J. Amer. Chem. Soc.*, 1963, **85**, 1704; 1964, **86**, 3296.

[3] C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, 1961 ,**83**, 4033.

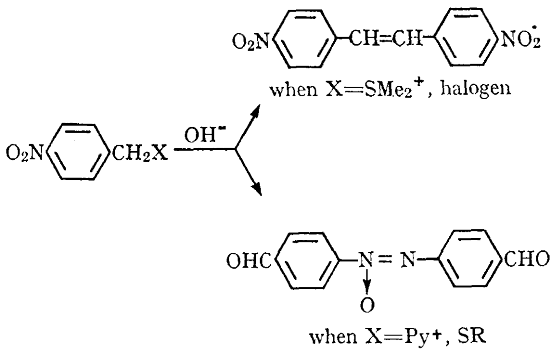
[4] F. Krohnke, *Ber.*, 1938, **71**, 2588.

[5] H. Fisher, *J. Amer. Chem. Soc.*, 1934, **56**, 2056.

[6] A. Pollard and R. Robinson, *J. Chem. Soc.*, 1927, 2779.

formula $C_{14}H_{10}N_2O_3$. Together with the m.p. (*cf.* ref. 7), infrared, and n.m.r. evidence we believe that the product is *p*-azoxybenzaldehyde (IV). This was confirmed by the undepressed m.p. when mixed with an authentic sample,[7] and by the identical infrared spectra. This compound was reported as the product of alkaline hydrolysis of some *p*-nitrobenzyl thio-ethers.[8]

It is still not clear why the product is (I) when halide or dimethyl sulphide are the leaving groups, but is (IV) when pyridine or thiols are the severed entities. Further investigation to determine the exact role of pyridine in the above reaction is under way. It suffices to mention now that the stilbene (I) was formed alone, and quantitatively, on treating *p*-nitrobenzyldimethylsulphonium bromide with sodium hydroxide in 50% aqueous pyridine.



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[8] Y. Iskander and Y. Riad, *J. Chem. Soc.*, 1951, 2054; 1961, 2397.