Dehydrogenation accompanying Certain Cyclo-addition Reactions of β-Nitrostyrene

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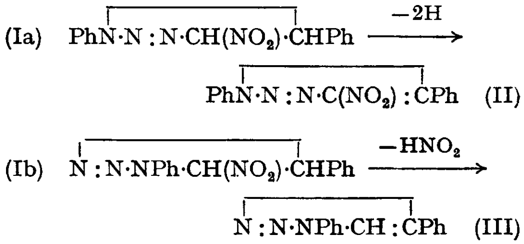
THE reaction of phenyl azide with β-nitrostyrene in toluene as solvent (reflux; 17 hr.) has recently been reported to yield, *inter alia*, 4-nitro-1,5-diphenyl-Δ^2-1,2,3-triazolene (Ia).[1] We have obtained the same compound† (mixed m.p., i.r., t.l.c.) in cyclohexane as solvent (reflux; 156 hr.), but observe that certain properties, notably its thermal stability and its stability to acids and bases,[1] are difficult to reconcile with such a structure.[2] Analytical and ^{1}H n.m.r. spectroscopic [aromatic protons only; multiplet, centred at τ 2·5 (in $CDCl_3$)] data indicate a triazole rather than a triazolene structure,[2] now confirmed by establishing identity (mixed m.p., i.r., t.l.c.) with 4-nitro-1,5-diphenyl-1,2,3-triazole† similarly obtained from phenyl azide and β-bromo-β-nitrostyrene.[1] The orientation pattern follows from conversion to 1,5-diphenyl-1,2,3-triazole by reduction to the primary amine, diazotisation in ethanolic solution and warming,[1] *i.e.*, reductive deamination.[3]

The addition of phenyl azide to β-nitrostyrene, by contrast with similar additions to enamines and enol ethers,[2] is sluggish and nonspecific, giving 1,4-diphenyl-1,2,3-triazole[1] in addition to 4-nitro-1,5-diphenyl-1,2,3-triazole. The alternative reactions involved can be regarded as 1,3-dipolar additions giving primary adducts (Ia) and (Ib), neither of which is stable under the reaction conditions. (Ia) undergoes aromatisation by dehydrogenation to (II), an unusual reaction in cyclo-additions involving β-nitrostyrene; (Ib) aromatises to (III) by loss of nitrous acid, a reaction probably associated with the relative acidity of the benzylic proton. The formation of (II) and its reduction to the primary amine provide a useful route to 4-amino-1,5-diaryl-1,2,3-triazoles isomeric with the 5-amino-1,4-diaryl-1,2,3-triazoles obtainable from the appropriate aryl azide and arylacetonitrile.[4]



$$\text{(Ia)}\quad \text{PhN·N:N·CH(NO}_2\text{)·CHPh} \xrightarrow{-2\text{H}} \text{PhN·N:N·C(NO}_2\text{):CPh}\quad \text{(II)}$$

$$\text{(Ib)}\quad \text{N:N·NPh·CH(NO}_2\text{)·CHPh} \xrightarrow{-\text{HNO}_2} \text{N:N·NPh·CH:CPh}\quad \text{(III)}$$

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[1] G. Rembarz, B. Kirchhoff, and G. Dongowski, *J. prakt. Chem.*, **1966**, **33**, 199.

[2] See R. Fusco, G. Bianchetti, and D. Pocar, *Gazzetta*, **1961**, **91**, 849, 933; M. E. Munk and Y. K. Kim, *J. Amer. Chem. Soc.*, **1964**, **86**, 2213; R. Huisgen, L. Möbius, and G. Szeimies, *Chem. Ber.*, **1965**, **98**, 1138. For similar cases in pyrazolene chemistry, see W. E. Parham, H. G. Braxton, and C. Serres, *J. Org. Chem.*, **1961**, **26**, 1831, and references therein.

[3] See R. Pütter in Houben-Weyl's "Methoden der Organischen Chemie," 4th edn., vol. 10/3, ed. E. Müller, G. Thieme Verlag, Stuttgart, 1965, p. 116 *et seq.*

[4] See E. Lieber, T. S. Chao, and C. N. Ramachandra Rao, *J. Org. Chem.*, **1957**, **22**, 654, and references therein.