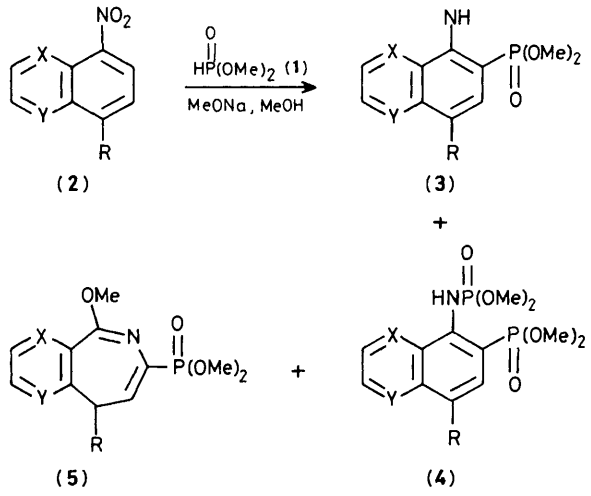
A New Reaction of Bicyclic Nitroarenes with Dimethyl Phosphite

W. Danikiewicz and M. Makosza*

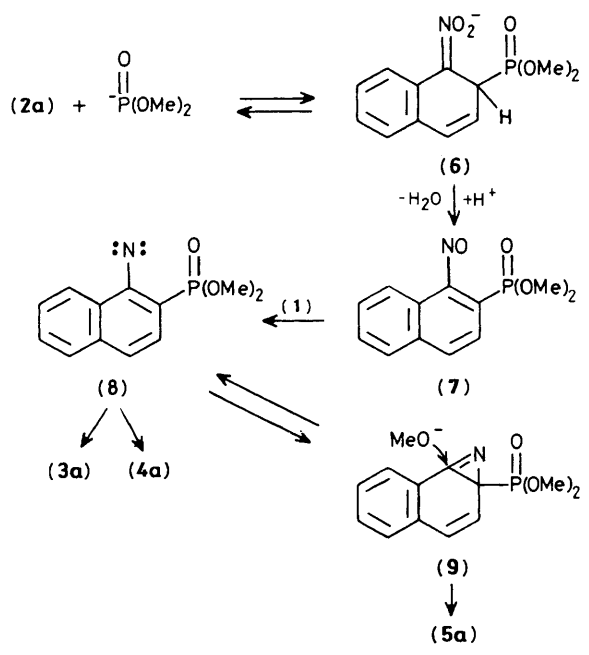
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

In the reaction of dimethyl phosphite anion with 1-nitronaphthalene, nucleophilic substitution of hydrogen takes place according to a redox stoicheiometry, giving substituted dimethyl naphthalenephosphonates and benzazepines; other bicyclic nitroarenes react in a similar way.

Trialkyl phosphites react with nitroarenes *via* attack on the nitro group leading, *via* nitrenes, to azepines or other heterocyclic compounds.[1] Formation of stable σ-complexes of dialkylphosphite anions with polynitroarenes has also been reported.[2] We now report the reactions of dimethyl phosphite (**1**) with bicyclic nitroarenes in strongly basic medium, which proceed *via* addition of the phosphite anion to the nitroarenes, and further transformations of the σ-complexes, also involving a nitrene intermediate. The process can be considered to be a nucleophilic substitution of hydrogen according to redox stoicheiometry (Scheme 1 and Table 1). Since procedure B gives mainly mixtures of (**3a—e**) and (**4a—e**), and compounds



Scheme 1



Scheme 2

Table 1.

Substrate	Method[a]	Product, % yield[b,c] (3)	(4)	(5)
(2a)	A	24	18	30
	B	19	48	4
(2b)	A	8	—	52
	B	26	—	11
(2c)	A	13	—	25
	B	30	9	4
(2d)	A	12	51	2
(2e)	A	18	32	2

[a] Method A: (**2a—e**) (5 mmol) and (**1**) (20 mmol) in MeOH (5 ml) were added dropwise to 1 M MeONa in MeOH (15 ml) at 5 °C. After 15—60 min the mixture was poured into saturated aqueous sodium hydrogen carbonate, and the products were extracted with ethyl acetate and separated by column chromatography. Method B; 1 M MeONa in MeOH (15 ml) was added dropwise to (**2a—e**) (5 mmol) and (**1**) (20 mmol) in MeOH (10 ml) at 40 °C. The mixture was refluxed for 10 min, cooled, and worked up as in A. [b] Yields of isolated products. [c] The ^1H and ^{13}C n.m.r. spectra were consistent with the assigned structures; satisfactory microanalyses were obtained.

(**4a—e**) are readily hydrolysed to give (**3a—e**), hydrolysis of the crude mixture gives (**3a—e**). The process thus provides a simple route to aminoaryl phosphonates.

The structures of the products were established by chemical and spectroscopic means. Compound (**3a**) was deaminated *via* reduction of the diazonium salt, and the dimethyl naphthalene-2-phosphonate obtained identified by ^1H and ^{13}C n.m.r. spectra. The position of the phosphonate moiety in the benzazepine (**5a**) is evident because no coupling between phosphorus and C-5, -6, -9, and -10 of the aromatic ring (1-nitronaphthalene numbering) was observed, showing that phosphorus and these atoms are separated by more than three bonds.†

The reactions proceed apparently as shown in Scheme 2.

The initially formed σ-complex (**6**) is converted into the nitroso compound (**7**).[3] Rapid deoxygenation of (**7**) with (**1**) gives the nitrene (**8**) which is in equilibrium with the azirine (**9**); compound (**8**) reacts with (**1**) giving (**4a**) or is reduced to give the amine (**3a**), whereas ring opening of (**9**) upon addition of MeO^- leads to the benzazepine derivative (**5a**). Conversion of the nitroso compound to the nitrene, its equilibrium with the azirine, and the formation of the azepine derivative from the latter, have analogy in work of Cadogan.[1b] However, the formation of the dialkyl nitrosoarenephosphonates, and the direct synthesis of dialkyl aminoarenephosphonates *etc.* are unprecedented, and provide a simple route to these interesting compounds.

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References

1 (a) 'Organophosphorus Reagents in Organic Synthesis,' ed. J. I. G. Cadogan, Academic Press, London, 1979, ch. 6; (b) T. de Boer, J. I. G. Cadogan, H. M. McWilliam, and A. G. Rowley, *J. Chem. Soc., Perkin Trans. 2*, 1975, 554.
2 P. P. Onys'ko and Yu. G. Gololobov, *Zh. Obshch. Khim.*, 1980, **50**, 729.
3 This process resembles formation of intermediate nitrosoarenes in the reactions of aryl acetonitriles with nitroarenes in basic protic media: R. B. Davis and L. C. Pizzini, *J. Org. Chem.*, 1960, **25**, 1884; M. Makosza, M. Jagusztyn-Grochowska, M. Ludwikow, and M. Jawdosiuk, *Tetrahedron*, 1974, **30**, 3723.

† Compound (**5a**): ^1H n.m.r., δ ($CDCl_3$) 3.10 (d, *J* 7.1 Hz, 2H), 3.61 (d, *J* 11.0 Hz, 6H), 3.91 (s, 3H), 6.26 (dt, *J* 7.1 and 13.2 Hz, 1H), and 7.06—7.67 (m, 4H); ^{13}C n.m.r., δ ($CDCl_3$) 32.1 (dd, J_{CP} 16.1 Hz), 53.1 (dq, J_{CP} 5.8 Hz), 53.7 (q), 126.7 (d), 126.9 (d), 127.5 (dd, J_{CP} 22.9 Hz), 128.3 (d), 129.0 (s), 132.2 (d), 135.9 (d, J_{CP} 221.8 Hz), 141.7 (d, J_{CP} 2.9 Hz), and 163.4 (d, J_{CP} 21.5 Hz).