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Organophosphorus Compounds. XI. Action of Trialkyl Phosphites on *p*-Quinoneimines

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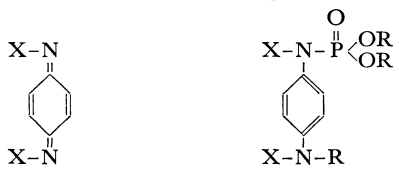
Although the action of trialkyl phosphites on *p*-quinones is well established,[1] their action on *p*-quinoneimines has hitherto not been investigated. We have found that trimethyl phosphite and triethyl phosphite react with *p*-quinoneimines (Ia, b) to give the corresponding phosphoramidate derivatives (IIa—d).

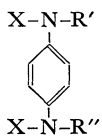
The IR spectrum of IIa, taken as example, revealed the absence of NH absorption and its NMR spectrum showed the following assignments:

(a) $\tau=7.04$ and $\tau=6.76$ (for protons of SO_2CH_3 groups, 2 singlets), (b) $\tau=6.6$ (for N–CH_3 protons, singlet), (c) $\tau=6.2$ (for protons of $P(O)(OCH_3)_2$ groups, doublet with $J_{HP}=11.4$ Hz), (d) $\tau=2.63$ (for aromatic protons, singlet). The integration ratio is 6 : 3 : 6 : 4.



Ia, X=SO_2CH_3
b, X=$SO_2C_6H_5$
c, X=COC_6H_5

IIa, R=CH_3; X=SO_2CH_3
b, R=C_2H_5; X=SO_2CH_3
c, R=CH_3; X=$SO_2C_6H_5$
d, R=C_2H_5; X=$SO_2C_6H_5$



IIIa, R′=X=H; R″=CH_3
b, R′=H; R″=CH_3; X=SO_2CH_3
c, R′=R″=CH_3; X=SO_2CH_3
d, R′=R″=H; X=$SO_2C_6H_5$
e, R′=R″=H; X=COC_6H_5

Adduct IIa, when treated with alcoholic alkali yielded IIIb. The identity of the latter compound was established by an unequivocal synthesis, namely by the methanesulphonylation of *N*-methyl-*p*-phenylenediamine (IIIa) in pyridine. Compound IIIb reacted with diazomethane to give IIIc, in contrast to compound IIa which is stable towards this reagent. When treated with concd. H_2SO_4, IIIb afforded IIIa. This reaction represents a new route for the preparation of *N*-alkyl-*p*-phenylenediamines when the adducts II are subjected to hydrolysis.

From the above results, it appears that *p*-quinoneimines (Ia, b) add trimethyl and/or triethyl phosphite in a 1 : 6 pattern with the creation of a new phosphorus-nitrogen bond, in a similar way to that for *p*-quinones[1] where a phosphorus-oxygen bond is likewise formed.

Quinoneimine Ic is reduced mainly to *p*-phenylenedibenzamide (IIIe), when treated with trialkyl phosphites under similar conditions. This disparity in behaviour of quinones Ia, b on the one hand and Ic on the other towards trialkyl phosphites is in accord with the differences in their behaviour towards a number of various reagents.[2]

1) F. Ramirez and S. Dershowitz, *J. Amer. Chem. Soc.*, **81**, 587 (1959); F. Ramirez, E. H. Chen and S. Dershowitz, *ibid.*, **81**, 4338 (1959); F. Ramirez, O. P. Madan and C. P. Smith, *J. Org. Chem.*, **30**, 2284 (1965); F. Ramirez, O. P. Madan and C. P. Smith, *Tetrahedron*, **22**, 567 (1966).

2) R. Adams and W. Reifschneider, *Bull. Soc. Chim. Fr.*, **1958**, 23.

Experimental

All melting points are uncorrected. The IR spectra were taken as KBr wafers in a Perkin-Elmer 237B Grating Spectrophotometer. The NMR spectra were run in $CDCl_3$ at 60 Mc, with TMS as internal reference.

Dimethyl [*p*-(*N*-Methylmethanesulphonamido)-phenyl](methanesulphonyl)phosphoramidate (IIa). A mixture of Ia[3] (0.001 mol), trimethyl phosphite[4] (0.001 mol) and dry bezene (10 m*l*) was kept under N_2 for 48 hr at 20°C. The crystalline product obtained was filtered and recrystallized from benzene to give IIa as colourless crystals, mp 150—152°C, yield 85%. (Found: C, 34.22; H, 4.91; N, 7.28; P, 7.95; S, 16.50%. Calcd for $C_{11}H_{19}N_2O_7PS_2$: C, 34.19; H, 4.95; N, 7.25; P, 8.01; S, 16.59%.) [IR: 7.81 (P=O),[5] 8.51 and 9.62 μ ($POCH_3$)[5]]

Similarly, triethyl phosphite[4] reacted with quinone Ia (in benzene at reflux for 6 hr) to give IIb as colourless crystals from chloroform - petrolerum ether (bp 40—60°C), mp 142—143°C, yield 80%. (Found: C, 39.21; H, 6.11; N, 6.47; P, 7.15; S, 14.90%. Calcd for $C_{14}H_{25}N_2O_7PS_2$: C, 39.24; H, 5.89; N, 6.53; P, 7.23; S, 14.96%.

***N*-Methyl-*N*,*N*′-dimethanesulphonyl-*p*-phenylenediamine (IIIb).** Compound IIa (0.1 g) was treated with 10% alcoholic NaOH (10 m*l*) and the mixture was refluxed for 6 hr. Alcohol was evaporated and the mixture was cooled and acidified with 10% aq. HCl. The precipitate was filtered off and crystallized from acetic acid to give IIIb as colourless crystals, mp 175—176°C, yield 90%. Compound IIIb proved to be identical (mixed mp), with that obtained by the following procedure: To a cold solution of IIIa[6] (1.2 g) in pyridine (5 m*l*), was added methanesulphonyl chloride (2.3 g) and the reaction mixture was left overnight at room temperature. Acidification with 10% aq. HCl precipitated IIIb, mp 175—176°C (from acetic acid). (Found: C, 38.94; H, 5.16; N, 10.19; S, 23.03%. Calcd for $C_9H_{14}N_2O_4S_2$: C, 38.83; H, 5.07; N, 10.06; S, 23.03%.) [IR: 3.12 μ (N–H)].

***N*-Methyl-*p*-phenylenediamine (IIIa).** A solution of IIIb (0.5 g) in concd. H_2SO_4 (sp. gr. 1.98) was kept at room temperature for 24 hr. The resulting solution was cooled, made alkaline with 15% aq. NaOH, and extracted with two 25 m*l* portions of ether. The combined extracts were dried over $MgSO_4$ (anhydrous) and evaporated to dryness. The oily residue thus formed was crystallized from pentane to give IIIa as colourless crystals, mp 35—36°C.[6]

***N*,*N*′-Dimethyl-*N*,*N*′-dimethanesulphonyl-*p*-phenylenediamine (IIIc).** To a suspension of IIIb (0.1 g) in dry ether (10 m*l*), was added an ethereal solution of diazomethane. Methanol (1 m*l*) was added and the reaction vessel was kept in a refrigerator for 72 hr. The ethereal solution was evaporated and the solid residue thus obtained (*ca.* 90%) was crystallized from acetic acid to give IIIc, mp 220°C, yield 80%. (Found: C, 40.98; H, 5.44; N, 9.49; S, 21.85%. Calcd for $C_{10}H_{16}N_2O_4S_2$: C, 41.07; H, 5.51; N, 9.58; S, 21.93%.) [IR: N–H absent.]

Dimethyl [*p*-(*N*-Methylbenzenesulphonamido)-phenyl](benzenesulphonyl)phosphoramidate (IIc). A mixture of Ib[3] (0.001 mol), trimethyl phosphite (0.001 mol) and dry benzene (10 m*l*) was kept under N_2 at room temperature for 24 hr. The ppt (A) thus formed was filtered. The colourless oil that remained after evaporation of the volatile materials was solidified in a refrigerator. Crystallization from benzene - petroleum ether (bp 40—60°C) gave IIc as colourless crystals, mp 78°C, yield 70%. (Found: C, 49.34; H, 4.49; N, 5.42; P, 6.11; S, 12.51%. Calcd for $C_{21}H_{23}N_2O_7PS_2$: C, 49.40; H, 4.54; N, 5.48; P, 6.07; S, 12.56%.) Spectral characteristics: bands at 7.78 (P=O), 8.55 and 9.62 ($POCH_3$), and 10.1 μ (P–N);[7] a $3H^1$ singlet at 6.88, a $6H^1$ doublet (J_{HP}=11.4 Hz) at 6.25, and a $14H^1$ multiplet at 2.66 τ.

Compound (A) upon recrystallization from acetic acid gave *p*-phenylenedibenzenesulphonamide (IIId),[3] mp 243°C, yield 15%.

IId was obtained similarly, together with a small amount of IIId (*ca.* 10%), by the action of triethyl phosphite on quinone Ib. Compound IId was crystallized from benzene - petroleum ether mp 85°C, yield 60%. (Found: C, 52.10; H, 5.24; N, 5.07; P, 5.59; S, 11.55%. Calcd for $C_{24}H_{29}N_2O_7PS_2$: C, 52.16; H, 5.29; N, 5.07; P, 5.60; S, 11.60%.)

Action of Trimethyl Phosphite on Quinone Ic. To a solution of quinone Ic[8] (0.32 g) in dry benzene (10 m*l*) was added trimethyl phosphite (0.13 g) and the mixture was refluxed for 10 hr. After cooling a colourless crystalline product was separated. It was filtered off, washed with ethanol, dried, crystallized from dimethylformamide and proved to be *p*-phenylenedibenzamide (IIIe), mp 340°C,[8] yield 95%.

3) R. Adams and A. S. Nagarkatti, *J. Amer. Chem. Soc.*, **72**, 4601 (1950).

4) T. Milobendzki and A. Sachnowski, *Chem. Polski*, **15**, 34 (1917); *Chem. Abstr.*, **13**, 2865 (1919); A. H. Ford-Moore and B. J. Perry, Organic Synthese, Vol. 31, p. 111 (1951).

5) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

6) A. Bernthsen and A. Goske, *Ber.*, **20**, 924 (1887).

7) N. B. Colthup, L. H. Daly and S. E. Wiberely, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York (1964), pp. 304, 405.

8) R. Adams and J. L. Anderson, *J. Amer. Chem. Soc.*, **72**, 5154 (1950).