Nitroethylene: Synthesis of Novel 2-Nitroethylphosphonates

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Summary In benzene, standard refrigerated solutions of nitroethylene are stable; in benzene–t-butyl alcohol, the self-reactivity of nitroethylene is moderated leading to the selective synthesis of novel 2-nitroethylphosphonates by a rare P^{III} Michael addition.

IT is reported here that nitroethylene[1] is stable and that refrigerated standard solutions in benzene can be stored for at least six months without perceptible deterioration.[2]† Its tendency for lone pair initiated self-polymerization can be moderated using t-butyl alcohol as solvent.

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† The characteristic ^1H n.m.r. spectrum of nitroethylene {δ (neat) 6·55 [dd, *J* 7 and 15 Hz, $=C(NO_2)H$], 5·85 (dd, *J* 15 and 2 Hz, *syn*-H), and 5·22 [br d, *J* 7 Hz, *anti*-H (the 2 Hz *gem* coupling is hidden)]} was unchanged during this period of storage. The strength of standard nitroethylene solutions can be checked by the isolation of a colourless, crystalline adduct, m.p. 197—198 °C, with tetracyclone.

Whilst phosphite esters react with nitroethylene in benzene to give complex mixtures, reactions in benzene–t-butyl alcohol lead cleanly to novel 2-nitroethylphosphonates. Thus, when nitroethylene (75 mmol) in dry benzene (55 ml) was admixed gradually with $P(OMe)_3$ (60 mmol) in dry t-butyl alcohol (100 ml) at room temperature with stirring, the reaction was complete in 9 h (t.l.c.) and evaporation of the solvents followed by distillation gave an 88% yield of dimethyl 2-nitroethylphosphonate (**1**) (b.p. 124 °C, 0·05 mmHg), see equation (1).

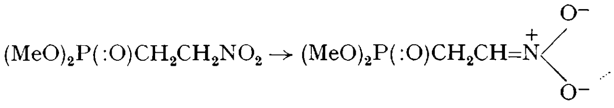
$$(MeO)_3P + H_2C{=}CHNO_2 \xrightarrow{Bu^tOH\text{–}benzene} (MeO)_2P({:}O)CH_2CH_2NO_2 \qquad (1)$$

(**1**)

Satisfactory analytical and spectral data were obtained for (**1**): i.r., ν_{max} (neat) 1560, 1380, 1252, and 1040 cm^{-1}, ^1H n.m.r. $\delta(CDCl_3)$ 2·6 (2H, m), 3·8 (6H, d, J 12 Hz), and 4·66 (2H, m); ^{13}C n.m.r. $\delta(CDCl_3)$ 22·21 (d, J_{C-P} 142 Hz), 52·35 (d, J_{C-P} 6 Hz), and 68·85 (d, J_{C-P} 0·8 Hz) p.p.m.[3]

The exclusive formation of (**1**) involving a Michael addition of P^{III} is particularly noteworthy in view of the well known tendency of reagents such as phosphites to bring about deoxygenation of the nitro group. A similar course was followed with $(PhO)_3P$ to give a 65% yield of crystalline diphenyl 2-nitroethylphosphonate, m.p. 62—63 °C. Triethyl and tri-isopropyl phosphites also gave the corresponding 2-nitroethylphosphonates.‡

Proton exchange of (**1**) in MeOH–NaOMe, monitored by ^1H n.m.r. spectroscopy, demonstrated clean formation of the nitronate (**2**), but did not affect the other acidic site of (**1**), see equation (2).



$$(MeO)_2P({:}O)CH_2CH_2NO_2 \rightarrow (MeO)_2P({:}O)CH_2CH{=}\overset{+}{N}\begin{smallmatrix}O^-\\ \\O^-\end{smallmatrix} \qquad (2)$$

(**1**) (**2**)

A typical procedure for proton exchange was as follows. Compound (**1**) was stirred at room temperature for 3 h with 1 equiv. of NaOMe in dry MeOH. The solvent was evaporated and the nitronate salt was washed with dry diethyl ether and dissolved in cold D_2O. The ^1H n.m.r. spectrum was clean and showed a 2H multiplet due to the $P–CH_2$ group, although there was no signal for the $CH_2–NO_2$ group.

The dianion can be generated in NaH–DME-(DME = 1,2-dimethoxyethane) as follows. A dry DME solution of (**1**) was mixed with an excess of NaH. The grey precipitate was stirred overnight, washed with dry benzene and the residue treated with D_2O to give deuteriated (**2**) which was immediately quenched with cold dil. H_2SO_4. Extraction with CH_2Cl_2 gave deuteriated (**1**) whose ^1H n.m.r. spectrum (using the $-CH_2NO_2$ and –OMe peaks as internal standards) showed 58% exchange of the $P–CH_2$ protons.

Nitroethylene in solution and 2-nitroethylphosphonates are potentially useful synthetic reagents and are presently being studied.

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‡ Satisfactory analytical and spectral (i.r. and n.m.r.) data have been obtained for this compound.

[1] G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1947, 1471; S. Ranganathan, D. Ranganathan, and A. K. Mehrotra, *J. Amer. Chem. Soc.*, 1974, **96**, 5261.

[2] This finding is at variance with earlier reports that highlighted the instability of this reagent [see ref. 1 and K. Noma, T. Okumura, and T. Sone, *Chem. High Polymers* (*Japan*), 1948, **5**, 99].

[3] See G. Mavel, 'N.M.R. Studies of Phosphorus Compounds,' in 'Annual Reports on N.M.R. Spectroscopy 5B,' ed. E. F. Mooney, Academic Press, New York, 1973.

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