

## Nitroethylene: Synthesis of Novel 2-Nitroethylphosphonates

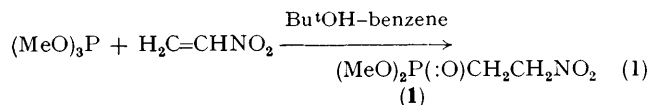
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*Summary* In benzene, standard refrigerated solutions of nitroethylene are stable; in benzene-t-butyl alcohol, the self-reactivity of nitroethylene is moderated leading to the selective synthesis of novel 2-nitroethylphosphonates by a rare P<sup>III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

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

† The characteristic <sup>1</sup>H n.m.r. spectrum of nitroethylene { $\delta$  (neat) 6.55 [dd, *J* 7 and 15 Hz, =C(NO<sub>2</sub>)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.

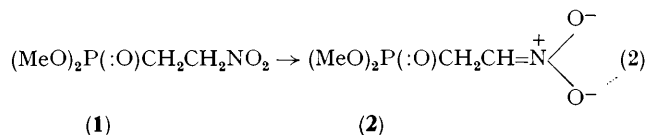
Whilst phosphite esters react with nitroethylene in benzene to give complex mixtures, reactions in benzene-t-butyl alcohol lead cleanly to novel 2-nitroethylphosphonates. Thus, when nitroethylene (75 mmol) in dry benzene (55 ml) was admixed gradually with  $\text{P}(\text{OMe})_3$  (60 mmol) in dry t-butyl 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).



Satisfactory analytical and spectral data were obtained for (**1**): i.r.,  $\nu_{\text{max}}$  (neat) 1560, 1380, 1252, and 1040  $\text{cm}^{-1}$ ,  $^1\text{H}$  n.m.r.  $\delta(\text{CDCl}_3)$  2.6 (2H, m), 3.8 (6H, d,  $J$  12 Hz), and 4.66 (2H, m);  $^{13}\text{C}$  n.m.r.  $\delta(\text{CDCl}_3)$  22.21 (d,  $J_{\text{C-P}}$  142 Hz), 52.35 (d,  $J_{\text{C-P}}$  6 Hz), and 68.85 (d,  $J_{\text{C-P}}$  0.8 Hz) p.p.m.<sup>3</sup>

The exclusive formation of (**1**) involving a Michael addition of  $\text{P}^{\text{III}}$  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  $(\text{PhO})_3\text{P}$  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.<sup>‡</sup>

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



A typical procedure for proton exchange was as follows. Compound (**1**) was stirred at room temperature for 3 h with 1 equiv. of  $\text{NaOMe}$  in dry  $\text{MeOH}$ . The solvent was evaporated and the nitronate salt was washed with dry diethyl ether and dissolved in cold  $\text{D}_2\text{O}$ . The  $^1\text{H}$  n.m.r. spectrum was clean and showed a 2H multiplet due to the  $\text{P}-\text{CH}_2$  group, although there was no signal for the  $\text{CH}_2-\text{NO}_2$  group.

The dianion can be generated in  $\text{NaH}-\text{DME}$  ( $\text{DME}=1,2\text{-dimethoxyethane}$ ) as follows. A dry DME solution of (**1**) was mixed with an excess of  $\text{NaH}$ . The grey precipitate was stirred overnight, washed with dry benzene and the residue treated with  $\text{D}_2\text{O}$  to give deuteriated (**2**) which was immediately quenched with cold dil.  $\text{H}_2\text{SO}_4$ . Extraction with  $\text{CH}_2\text{Cl}_2$  gave deuteriated (**1**) whose  $^1\text{H}$  n.m.r. spectrum (using the  $-\text{CH}_2\text{NO}_2$  and  $-\text{OMe}$  peaks as internal standards) showed 58% exchange of the  $\text{P}-\text{CH}_2$  protons.

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

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

<sup>1</sup> 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.

<sup>2</sup> 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].

<sup>3</sup> 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.