Trapping of Radicals by Dialkyl Phosphite Ions; Synthesis of α-Nitroalkylphosphonates by $S_{RN}1$ Reactions

By Glen A. Russell* and James Hershberger

(*Department of Chemistry, Iowa State University, Ames, Iowa* 50011)

Summary Dialkyl phosphite ions and geminal chloro- or arylsulphonyl-nitroalkanes react by a free radical chain mechanism to form dialkyl α-nitroalkylphosphonates.

Dialkyl phosphite ions [$(RO)_2PO^-$] are known to be radical traps in aromatic $S_{RN}1$ reactions yielding arylphosphonates [equations (1)—(3)].[1] Alk-1-enyl radicals will also add readily to $(RO)_2PO^-$ in an $S_{RN}1$ reaction to

$$RX\cdot^- \rightarrow R\cdot + X^- \qquad (1)$$

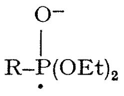
$$R\cdot + A^- \rightarrow RA\cdot^- \qquad (2)$$

$$RA\cdot^- + RX \rightleftharpoons RX\cdot^- + RA \qquad (3)$$

$$RX = ArI,\ A^- = (RO)_2PO^-$$

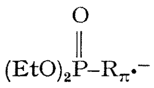
form the vinylphosphonate when RX is an alk-1-enylmercury halide.[2] However, alkylmercury halides and $(RO)_2PO^-$ will not undergo photo-stimulated $S_{RN}1$ reactions although $S_{RN}1$ reactions with $A^- = R_2C{=}NO_2^-$ occur readily.[3]

In competitive experiments n-$C_6H_{13}HgCl$ and $PhCH_2HgCl$ underwent a photo-stimulated $S_{RN}1$ reaction in Me_2SO with an equimolar mixture of $(EtO)_2PO^-$ and $Me_2C{=}NO_2^-$ to produce n-$C_6H_{13}CMe_2NO_2$ and $PhCH_2CMe_2NO_2$ without a trace of the corresponding phosponates. We conclude that although simple alkyl radicals do not add readily to $(EtO)_2PO^-$ to form the phosphoranyl radical anion (**1**), phenyl and vinyl radicals are readily trapped by $(EtO)_2PO^-$ with the formation of a phenyl–phosphorus bond. This suggests that aryl and vinyl radicals form an intermediate wherein the unpaired electron is in the π-system of the unsaturated group (**2**).[4]



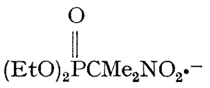
$$R\text{–}\overset{O^-}{\underset{\bullet}{P}}(OEt)_2$$

(**1**)



$$(EtO)_2\overset{O}{\overset{\|}{P}}\text{–}R_{\pi}\cdot^-$$

(**2**)



$$(EtO)_2\overset{O}{\overset{\|}{P}}CMe_2NO_2\cdot^-$$

(**3**)

1-Methyl-1-nitroethyl radicals formed in an $S_{RN}1$ process from 2-chloro-2-nitropropane or 2-(*p*-tolylsulphonyl)-2-nitropropane are readily trapped by $(RO)_2PO^-$ to yield the α-nitroalkylphosphonates[5] as the final product [reaction (4)] in what appears to be a general reaction [equation (5), Table].† The 1-methyl-1-nitroethyl radical is more reactive

$$O_2NCMe_2X + (RO)_2PO^- \xrightarrow[0\ ^\circ C,\ 2\ h]{THF} O_2NC(Me)_2P(O)(OR)_2 \qquad (4)$$

$$X = Cl,\ p\text{-}MeC_6H_4SO_2$$

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† A typical procedure for the formation of the α-nitroalkylphosphonates is as follows. 2-Chloro-2-nitropropane (9 mmol) was added to potassium t-butoxide (9 mmol) and diethyl phosphite (10 mmol) in 30 ml of dry tetrahydrofuran (THF) at −45 °C under nitrogen. As the solution warmed to 25 °C (1 h), potassium chloride precipitated. After vacuum distillation of the THF the residue was extracted from brine with diethyl ether. Removal of the ether gave 1·7 g of crude diethyl α-nitroisopropylphosphonate, b.p. 94—95 °C (0·2 Torr).

$$O_2NCR^1_2X + (R^2O)_2PO^- \rightarrow O_2NCR^1_2P(O)(OR^2)_2 \qquad (5)$$

a, $R^1 = R^2 = Me$, $X = Cl$
b, $R^1 = Me$, $R^2 = Et$, $X = Cl$
c, $R^1 = Me$, $R^2 = Et$, $X = MeC_6H_4SO_2$-*p*
d, $R^1 = [CH_2]_4$, $R^2 = Et$, $X = Cl$
e, $R^1 = [CH_2]_4$, $R^2 = Et$, $X = MeC_6H_4SO_2$-*p*

TABLE Synthesis of the α nitroalkylphosphonates $O_2NCR^1_2$-$P(O)(OR^2)_2$ [a]

	Temp /°C	Time	Yield[b]/% N m r	Yield[b]/% Distilled
a	−45 to 25	1 h	—	60
b	−45 to 25	1 h	75	63
b	25	1 h[c]	0[d]	—
c	0	45 min	66	—
c	0	45 min[c]	0[e]	—
c	0	45 min[f]	0	—
c	0—25	2 h	92	—
d	−45 to 25	1 5 h	80	—
e	0—25	2 h	75	62

[a] All reactions were carried out using tetrahydrofuran as solvent [b] Satisfactory elemental analyses were obtained [c] With oxygen [d] All of the 2 chloro 2-nitropropane was consumed [e] 87% of the 2 (*p*-tolylsulphonyl)-2-nitropropane was recovered [f] With 5% Bu^t_2NO

than simple alkyl radicals towards $(RO)_2PO^-$ because the intermediate radical anion [(**3**), $RA\cdot^-$ equations (2) and (3)] now has the unpaired electron in an MO of the nitro group rather than localized on phosphorus as in the phosphoranyl radical (**1**)

Reaction (4) can be demonstrated to be a chain process An easy thermal initiation reaction [presumably electron transfer between $(R^2O)_2PO^-$ and $R^1_2C(NO_2)X$] makes it difficult to inhibit this free radical process by di-t-butyl nitroxide in all cases However reaction of 2-(*p*-tolyl)-2-nitropropane with $(EtO)_2PO^-$ showed clear inhibition by the nitroxide (Table) In addition, the α-nitroalkylphosphonates were not formed when the reactions were performed in the presence of oxygen The thermal initiation reaction, as judged by reactions performed in the presence of oxygen or di-t-butyl nitroxide, occurred much more rapidly with X = Cl than with X = *p*-$MeC_6H_4SO_2$

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[1] J F Bunnett *Accounts Chem Res* 1978, **11** 413
[2] G A Russell and J Hershberger submitted to *J Amer Chem Soc*
[3] G A Russell J Hershberger and K Owens *J Amer Chem Soc* 1979 **101** 1312
[4] This assignment is consistent with e s r investigations of $PhP(OR)_3$ (G Boekestein E H J M Jansen and H M Buck *J C S Chem Comm* 1974 118 A G Davies M J Parrott and B P Roberts *ibid* p 973) and $R_2C{=}CHP(OR)_3$ radicals (J A Baban, C J Cooksey and B P Roberts *J C S Perkin II* 1979 781) which indicate that the unpaired electron is associated with the phenyl or vinyl group rather than localized at the phosphorus atom A similar conclusion was reached in regard to the radical anions of PhPO(OH) and $PhPO(OH)_2$ (S P Mishra and M C R Symons *Tetrahedron Letters* 1973 4061, *J C S Chem Comm* 1974, 606, *J C S Perkin II* 1976 21)
[5] α Nitroalkylphosphonates have not been extensively investigated The synthesis of $(EtO)_2P(O)CMe_2NO_2$ by the permanganate oxidation of the amino compound has been reported (K A Petrov V A Chauzov L V Pastukhova and W N Bogdanov, *Zhur obshchei Khim* , 1976, **46**, 1246)