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Participation of Anions of Dialkyl Phosphites and Thiophosphites in Aliphatic $S_{RN}1$ Reactions[1]

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Dialkyl phosphite or thiophosphite anions react with 2-chloro- or 2-(*p*-tolylsulfonyl)-2-nitropropane, *p*-nitrobenzyl chloride, and α,α-dimethyl-*p*-nitrobenzyl chloride to form in a free radical chain process the α-nitroalkyl or *p*-nitrobenzyl phosphonates or thiophosphonates which may be reduced to the amino derivatives. 2,2-Dinitropropane reacts with dialkyl phosphite or dimethyl thiophosphite ions to form the dialkyl phosphate or thiophosphate esters of acetone oxime. The relative reactivities of a series of anions toward $Me_2\dot{C}NO_2$, $p\text{-}O_2NPhCH_2\cdot$, and $p\text{-}O_2NPhC(Me)_2\cdot$ are reported.

Dialkyl phosphites are known to participate as nucleophiles in aromatic $S_{RN}1$ processes.[2] In a communication we have described the reaction of dimethyl and diethyl phosphite anions with the α-chloro and α-(*p*-tolylsulfonyl) derivatives of 2-nitropropane and nitrocyclopentane to yield the (α-nitroalkyl)phosphonates.[3] With X = *p*-MePhSO$_2$ the reaction was inhibited by (t-Bu)$_2$NO· or by oxygen.[3] The chain reaction leading to substitution was thus formulated as an $S_{RN}1$ process.[4,5] We have now extended these reactions to the dialkyl thiophosphite anion ((RO)$_2$PS$^-$) and to 2,2-dinitropropane, *p*-nitrobenzyl chloride, and α,α-dimethyl-*p*-nitrobenzyl chloride as the substrate.

$$R_2C(X)(NO_2) + (R'O)_2PO^-K^+ \xrightarrow[-45\text{–}25\ ^\circ C]{THF} R_2C(NO_2)P(O)(OR')_2 \tag{1}$$

1a, R = Me; R′ = Me (62%)
1b, R = Me; R′ = Et (75%)
1c, R$_2$ = –(CH$_2$)$_4$–; R′ = Et (80%)

$$R_2C(X)NO_2^{-}\cdot \rightarrow R_2\dot{C}NO_2 + X^-$$

$$R_2\dot{C}NO_2 + (R'O)_2PO^- \rightarrow (R'O)_2P(O)CR_2NO_2^{-}\cdot$$

$$(R'O)_2P(O)CR_2NO_2^{-}\cdot + R_2C(X)NO_2 \rightarrow R_2C(X)NO_2^{-}\cdot + (R'O)_2P(O)CR_2NO_2$$

Reaction of Me$_2$C(Cl)NO$_2$ with (EtO)$_2$PSLi yielded mainly (EtO)$_2$P(S)Cl, even with sunlamp irradiation in THF. Apparently the thiophosphite ion attacks the halogen atom of Me$_2$C(Cl)NO$_2$ in an S_N2 process. With 2-(*p*-tolylsulfonyl)-2-nitropropane, this S_N2 process was not observed and a 30% yield of the (α-nitroalkyl)thiophosphonate (**2b**) was obtained with (EtO)$_2$PSK in Me$_2$SO. Essentially the same yield of **2b** was observed in Me$_2$SO in the dark (3.5 h at 25 °C). The photostimulated reaction was strongly inhibited by 5 mol % (t-Bu)$_2$NO· (18% yield of product in 3.5 h) or by 40 mol % of *p*-O$_2$NPhNO$_2$ (9% yield in 3.5 h) and a more severe retardation by these inhibitors was observed in the dark reaction. The results are consistent with a thermally initiated electron-transfer process which can be further stimulated by irradiation.

$$Me_2C(X)NO_2 + (RO)_2PS^-K^+ \xrightarrow[h\nu,\ 3.5\ h]{Me_2SO} Me_2C(NO_2)P(S)(OR)_2 + X^- \tag{2}$$

2a, R = Me; 30% X = NO$_2$
2b, R = Et; 30% X = *p*-MePhSO$_2$

Reaction of (EtO)$_2$PO$^-$K$^+$ or (MeO)$_2$PO$^-$K$^+$ with Me$_2$C(NO$_2$)$_2$ did not follow reaction 1. Instead, the dialkyl phosphate esters of acetone oxime were the major products (reaction 3). The phosphate ester **3b** had been previously prepared by the reaction of (EtO)$_2$P(O)Cl with acetone oxime.[6] Reaction 3 is postulated to proceed by a nucleophilic attack of (RO)$_2$PO$^-$ on the nitro group to yield (RO)$_2$P(O)NO$_2$ and Me$_2$C=NO$_2^-$. A second displacement by the nitronate would yield (RO)$_2$P(O)ON(O)=CMe$_2$ which could transfer the nitrite oxygen to a second equivalent of the dialkyl phosphite anion. Reaction of Me$_2$C(NO$_2$)$_2$ with (EtO)$_2$PS$^-$K$^+$ for 2 h at –78–25 °C in THF yielded the thiophosphate ester **3d**. There was no effect of (t-Bu)$_2$NO· upon the yield of **3d**. Surprisingly, Me$_2$C(NO$_2$)$_2$ and (MeO)$_2$PS$^-$K$^+$ at –78 °C gave mainly **2a** (**2a**/**3c** $\simeq$ 20:1). The presence of (t-Bu)$_2$NO· completely suppressed the formation of **2a** at –78 °C. The α-nitroalkyl phosphonates or thiophosphonates were easily reduced by tin and hydrochloric acid to the α-aminoalkyl phosphonates or thiophosphonates which showed no tendency to form condensation polymers upon heating neat or in basic media.

$$Me_2C(NO_2)_2 + (RO)_2PX^-K^+ \xrightarrow[-78\text{–}25\ ^\circ C]{THF,\ h\nu,\ 2\ h} Me_2C{=}NOP(X)(OR)_2 \tag{3}$$

3a, R= Me; X = O (35%)
3b, R = Et; X = O (55%)
3c, R = Me; X = S (tr)
3d, R = Et; X = S (20%)

$$O_2NCMe_2P(X)(OR)_2 \xrightarrow{Sn/H_2O\text{-}HCl} NH_2CMe_2P(X)(OR)_2 \tag{4}$$

4a, X = O; R = Me (72%)
4b, X = O; R = Et (74%)
4c, X = S; R = Me (80%)

Reactions of *p*-nitrobenzyl or α,α-dimethyl-*p*-nitrobenzyl chlorides with (RO)$_2$PO$^-$M$^+$ or (RO)$_2$PS$^-$M$^+$ (M = Li, Na, K) in MeOH, EtOH, THF, Me$_2$SO, or HMPA yielded **5**.

$$p\text{-}O_2NPhCR_2P(X)(OR')_2$$

5a, R = H;R′ = Et; X = O
5b, R = H; R′ = Me; X = S
5c, R = H; R′ = Et; X = S
5d, R = Me; R′ = Et; X = O
5e, R = Me; R′ = Et; X = S

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[1] Electron Transfer Processes. 30. This work was supported by Grant CHE-7823866 from the National Science Foundation.

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[6] Allen, J. F., U.S. Patent 2816128, Dec 10, 1957; *Chem. Abstr.* **1958**, *52*, 5449e.

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Table I. Competition in the $S_{RN}1$ Reaction of Pairs of Anions with $Me_2C(O_2SPh\text{-}p\text{-}Me)NO_2$, $p\text{-}O_2NPhCH_2Cl$, and $p\text{-}O_2NPhC(CH_3)_2Cl$[a]

radical	A^-	B^-	counterion/ solvent	temp, °C	% yield of adducts from A	% yield of adducts from B
$Me_2\dot{C}NO_2$	$(EtO)_2PS^-$	$Me_2C{=}NO_2^-$	K^+/Me_2SO	25	36	25
$Me_2\dot{C}NO_2$	$(EtO)_2PO^-$	$Me_2C{=}NO_2^-$	K^+/Me_2SO	25	11	74
$Me_2\dot{C}NO_2$	$(EtO)_2PS^-$	$(EtO_2C)_2CMe^-$	K^+/Me_2SO	25	24	33
$Me_2\dot{C}NO_2$	$(EtO)_2PO^-$	$(EtO_2C)_2CMe^-$	K^+/Me_2SO	25	27	50
$Me_2\dot{C}NO_2$	$(EtO)_2PS^-$	$(EtO)_2PO^-$	K^+/THF	0	26	28
$Me_2\dot{C}NO_2$	$(EtO)_2PS^-$	$Me_2C{=}NO_2^-$	Li^+/Me_2SO	25	34	30
$Me_2\dot{C}NO_2$	$(EtO)_2PO^-$	$Me_2C{=}NO_2^-$	Li^+/Me_2SO	25	0	100
$Me_2\dot{C}NO_2$	$(EtO)_2PO^-$	$(EtO_2C)_2CMe^-$	Li^+/Me_2SO	25	0	94
$Me_2\dot{C}NO_2$	$Me_2C{=}NO_2^-$	$(EtO_2C)_2CMe^-$	Li^+/Me_2SO	25	87	13
$Me_2\dot{C}NO_2$	PhS^-	$Me_2C{=}NO_2^-$	Li^+/Me_2SO	25	57	9[b]
$Me_2\dot{C}NO_2$	PhS^-	$(EtO_2C)_2CMe^-$	Li^+/Me_2SO	25	44	5[c]
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PS^-$	$Me_2C{=}NO_2^-$	Li^+/DMF	0	55	14
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PO^-$	$Me_2C{=}NO_2^-$	Li^+/DMF	0	~5	25
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PS^-$	$(EtO)_2PO^-$	Li^+/DMF	0	49	0
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PS^-$	$Me_2C{=}NO_2^-$	$Li^+/EtOH$	−23	65	15
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PO^-$	$Me_2C{=}NO_2^-$	$Na^+/EtOH$	25	0	69
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PS^-$	$(EtO)_2PO^-$	$Na^+/EtOH$	25	59	0
$p\text{-}O_2NPhCH_2\cdot$	$(EtO)_2PO^-$	$Me_2C{=}NO_2^-$	Li^+/THF	25	15	18
$p\text{-}O_2NPhCMe_2\cdot$	$(EtO)_2PS^-$	$Me_2C{=}NO_2^-$	Li^+/Me_2SO	25	98	0
$p\text{-}O_2NPhCMe_2\cdot$	$(EtO)_2PS^-$	$(EtO_2C)_2CMe^-$	Li^+/Me_2SO	25	58	0
$p\text{-}O_2NPhCMe_2\cdot$	$(EtO)_2PS^-$	$(EtO)_2PO^-$	$K^+/HMPA$	25	42	~5

[a] Solutions were 0.1 M in substrate and each anion. All experiments performed with sunlamp irradiation. [b] Source of $O_2NCMe_2CMe_2NO_2$ is uncertain (see footnote c). [c] 11% of $O_2NCMe_2CMe_2NO_2$ isolated.

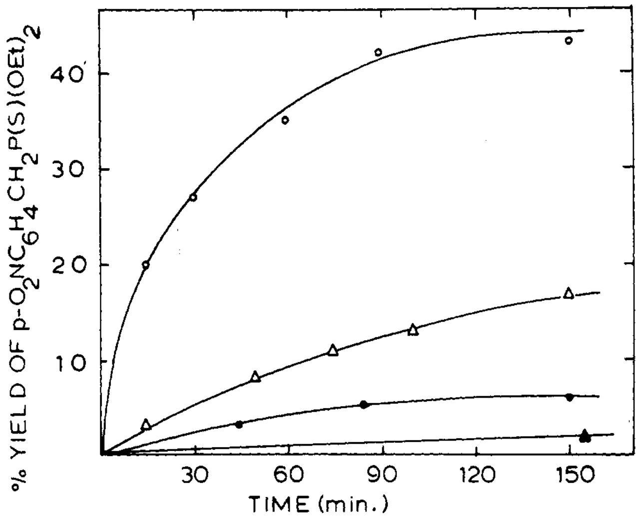

Figure 1. Yield of alkylation product from the reaction of $p\text{-}O_2NPhCH_2Cl$ (0.07 M) with $(EtO)_2PS^-Na^+$ (0.07 M) in EtOH at −23 °C: (○) sunlamp irradiation, (△) in ordinary laboratory lighting, (●) dark, (▲) sunlamp irradiation with 5 mol % $(t\text{-}Bu)_2NO\cdot$ added.

The reactions of $p\text{-}O_2NPhCH_2Cl$ proceed at least partially by the $S_{RN}1$ scheme. Thus, under standard conditions (Li^+, 20 h of sunlamp irradiation at −78–25 °C in THF), the yield of **5a** was reduced from 34% to 9% by the presence of 5 mol % of $(t\text{-}Bu)_2NO\cdot$. The yield of **5c** from a 15-min reaction at 0 °C in EtOH using $(EtO)_2PS^-Li^+$ was 58% with sunlamp irradiation, 50% with ordinary laboratory lighting, 29% in the dark, 12% in the dark in the presence of 15 mol % $(t\text{-}Bu)_2NO\cdot$, and 16% in the presence of O_2 with ordinary lighting. Figure 1 illustrates the effect of irradiation and inhibitors on the yield of **5c** at −23 °C in EtOH, using $(EtO)_2PS^-Na^+$. In a similar fashion the yield of **5e** from $(EtO)_2Ps^-Li^+$ in Me_2SO (2 h, 25 °C) was 64% with sunlamp irradiation but only 22% in the dark with 20 mol % $(t\text{-}Bu)_2NO\cdot$, while in DMF (30 min, 0 °C), the yield was 86% with sunlamp irradiation, 72% in the dark, and only 10% in the dark in the presence of 15 mol % of $(t\text{-}Bu)_2NO\cdot$. The yield of **5d** (K^+, 9 h of sunlamp irradiation at 25 °C in HMPA) was reduced from 51% to ~5% by the presence of 10 mol % of $(t\text{-}Bu)_2NO\cdot$.

The reaction of $(EtO)_2PO^-Na^+$ in EtOH at 25 °C for 18 h with $p\text{-}NO_2PhCH_2Cl$ yielded mainly (38%) *trans-p,p'*-dinitrostilbene and only 14% of **5a** with 25% recovery of $p\text{-}O_2NPhCH_2Cl$. In the presence of 15 mol % of $(t\text{-}Bu)_2NO\cdot$, none of the stilbene was formed[7] and the yield of **5a** was decreased to 8%.

The relative reactivities of $Me_2\dot{C}NO_2$ (from $Me_2C(O_2SPhMe\text{-}p)NO_2^-\cdot$), $p\text{-}O_2NPhCH_2\cdot$ (from $p\text{-}O_2NPhCH_2Cl^-\cdot$), and $p\text{-}O_2NPhC(Me)_2\cdot$ (from $p\text{-}O_2NPhC(Me)_2Cl^-\cdot$) were determined toward $(EtO)_2PS^-$, $(EtO)_2PO^-$, $Me_2C{=}NO_2^-$, and $(EtO_2C)_2CMe^-$ by competitive reactions (Table I). It has been previously established[8] that with $Me_2C(X)NO_2$ as the substrate, the ratio of the two products formed was determined by the values of k_A and k_B and it is assumed that a similar situation exists for $p\text{-}O_2NPhCH_2Cl$ and $p\text{-}O_2NPhC(Me)_2Cl$ although for $p\text{-}O_2NPhCH_2Cl$, S_N2 substitution may be a competing process.

$$Me_2\dot{C}NO_2 + A^- \xrightarrow{k_A} Me_2C(A)NO_2^-\cdot \xrightarrow{-e} Me_2C(A)NO_2$$

$$Me_2\dot{C}NO_2 + B^- \xrightarrow{k_B} Me_2C(B)NO_2^-\cdot \xrightarrow{-e} Me_2C(B)NO_2$$

The data of Table I for $Me_2\dot{C}NO_2$ complement the relative reactivities previously reported in Me_2SO with K^+[2.2.2]cryptand and Li^+ at various concentrations as the counterions.[8] With K^+ as the counterion in Me_2SO, a reactivity series of $Me_2C{=}NO_2^-$, $(EtO_2C)_2CMe^-$ > $(EtO)_2PS^-$ > $(EtO)_2PO^-$ is observed.[9] With Li^+ in Me_2SO

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[7] For a discussion of the formation of *p,p'*-dinitrostilbene by the $S_{RN}1$ mechanism, see Russell, G. A.; Pecoraro, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 3331.

[8] Russell, G. A.; Ros, F.; Mudryk, B. *J. Am. Chem. Soc.* **1980**, *102*, 7601.

(0.1 M in Li^+A^- and Li^+B^-), the reactivities are $Me_2C{=}NO_2^- \sim (EtO)_2PS^- > (EtO_2C)_2CMe^- \gg (EtO)_2PO^-$. Preferential ion pairing of $(EtO)_2PO^-$ with Li^+ has decreased the reactivity of the phosphite and affected the relative reactivities of the other anions.

With $p\text{-}NO_2PhCH_2\cdot$ in Na^+/EtOH or Li^+/DMF, a reactivity series of $(EtO)_2PS^- > Me_2C{=}NO_2^- \gg (EtO)_2PO^-$ is observed. In Li^+/THF one experiment yielded a relative reactivity of $Me_2C{=}NO_2Li \simeq (EtO)_2POLi$. Here, both anions are essentially completely ion paired, and preferentially ion pairing does not contribute to the apparent relative reactivities. Toward $p\text{-}O_2NPhC(Me_2)\cdot$, $(EtO)_2PS^-$ is much more reactive than $Me_2C{=}NO_2^-$ or $(EtO_2C)_2CMe^-$ (Li^+/Me_2SO) or $(EtO)_2PO^-$ (K^+/Me_2SO). All of the results are consistent with $(EtO)_2PS^-$ being a better trap than $(EtO)_2PO^-$ for α-nitroalkyl radicals, particularly when ion pairing is important.

Experimental Section

2-Chloro-2-nitropropane,[10] 2-(*p*-tolylsulfonyl)-2-nitropropane,[11] 1-(*p*-tolylsulfonyl)-1-nitrocyclopentane,[11] 2,2-dinitropropane,[12] *p*-nitro-α,α-dimethylbenzyl chloride,[13] dimethyl thiophosphite,[14] and diethyl thiophosphite[15] were prepared according to literature procedures. Lithium *tert*-butoxide (mol wt 80.1) was prepared and found to have a neutralization equivalent of 78.5. Solvents were dried and distilled over CaH_2. Reactants were deoxygenated before mixing by a nitrogen stream of bubbles for 15–30 min. Sunlamp irradiation utilized a 275-W lamp 30–50 cm from the reaction flask, while for dark reactions the reaction flask was wrapped with aluminum foil.

Diethyl 2-Nitro-2-propylphosphonate (1b).[16] 2-Chloro-2-nitropropane (9 mmol) or 2-(*p*-tolylsulfonyl)-2-nitropropane (9 mmol) was added to 10 mmol of $(EtO)_2PO^-K^+$ in 30 mL of THF at −45 °C under nitrogen and the mixture was stirred for 30 min at −45 °C, 30 min at −20 °C and 30 min at 0 °C. The THF was vacuum evaporated and the residue extracted from brine with ether. Evaporation of the ether gave a residue shown by ^1H NMR to contain 75% of **1b** from 2-chloro-2-nitropropane and 92% of **1b** from 2-(*p*-tolylsulfonyl)-2-nitropropane. Repetition using 135 mmol of 2-chloro-2-nitropropane gave a distilled yield of **1b** of 63%: bp 94–95 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 1.38 (t, J = 6 Hz, 6 H), 1.75 (d, J_{PH} = 16 Hz, 6 H), 4.0–4.5 (m, 4 H); ^{13}C NMR (proton decoupled, $CDCl_3$) δ 85.6 (d, J_{PC} = 150 Hz), 63.5 (d, J_{PC} = 7.3 Hz), 22.1 (s), 15.7 (d, J_{PC} = 4.9 Hz); ^{31}P NMR (proton decoupled, $CDCl_3$) δ (H_3PO_4) 17.2 (s); IR (neat) 2950 (m), 1550 (vs), 1470 (w), 1400 (m), 1370 (m), 1340 (w), 1260 (s), 1160 (w), 1045 (vs, br), 1015 (vs, br), 970 (s, br), 855 (s) 770 (w) cm^{-1}; mass spectrum, *m/e* 179.0837 ($M^+ - NO_2 = C_7H_{16}O_3P$ requires 179.08295).

Anal. Calcd for $C_7H_{16}NO_5P$: C, 37.34; H, 7.16. Found: C, 37.62; H, 7.27.

Dimethyl 2-Nitro-2-propylphosphonate (1a). The above procedure utilizing 40 mmol of $Me_2C(Cl)NO_2$ and $(MeO)_2PO^-K^+$ gave a 60% yield of **1a**: bp 80–81 °C (0.1 torr); ^1H NMR ($CDCl_3$) δ 1.82 (d, J_{PH} = 14 Hz, 6 H), 3.93 (d, J_{PH} = 18 Hz, 6 H); IR (neat) 1270, 1550 (NO_2) cm^{-1}; mass spectrum, *m/e* (relative intensity) 197 (2, M^+), 151.0524 (84, $M^+ - NO_2 = C_5H_{12}O_3P$ requires 151.0520), 109 (100).

Anal. Calcd for $C_5H_{12}NO_5P$: C, 30.46; H, 6.14; N, 7.10. Found: C, 30.61; H, 6.30; N, 7.05.

1-Nitro-1-(diethoxyphosphinyl)cyclopentane (1c). Reaction of 9 mmol of 1-(*p*-tolylsulfonyl)-1-nitrocyclopentane with 18 mmol of $(EtO)_2PO^-K^+$ according to the above procedure gave 75% of **1e** isolated by Kugelrohr distillation at 95 °C (0.4 torr): ^1H NMR ($CDCl_3$) δ 1.35 (t, J = 7 Hz, 6 H), 1.5–3.0 (m, 8 H), 3.9–4.4 (m, 4 H); IR (neat) 1260, 1545 (NO_2) cm^{-1}; mass spectrum, *m/e* 205.09936 ($C_9H_{10}NO_5P$ requires 205.09943).

Anal. Calcd for $C_9H_{18}NO_5P$: C, 43.03; H, 7.22. Found: C, 43.03; H, 7.37.

Diethyl 2-Nitro-2-propylthiophosphonate (2b). Addition of 4.9 mmol of 2-(*p*-tolylsulfonyl)-2-nitropropane in 11 mL of Me_2SO to 9.8 mmol of $(EtO)_2PS^-K^+$ in 29 mL of Me_2SO at 25 °C gave after 3.5 h a 29% yield of **2b**, isolated after hydrolysis of the reaction product by ether extraction and short-path distillation at 70 °C (0.15 torr) and purified by GC on a OV-3 column at 150 °C: ^1H NMR (CCl_4) δ 1.35 (t, J = 8 Hz, 6 H), 1.79 (d, J_{PH} = 16 Hz, 6 H), 4.15 (dq, J_{HH} = 8 Hz, J_{PH} = 11 Hz, 4 H); IR (CCl_4) 1550 (NO_2) cm^{-1}; mass spectrum, *m/e* 241.05270 ($C_7H_{16}NO_4Ps$ requires 241.05377).

Anal. Calcd for $C_7H_{16}NO_4PS$: C, 34.84; H, 6.70; P, 12.84. Found: C, 35.02; H, 6.72; P, 12.65.

Reaction of 3 mmol of $Me_2C(Cl)NO_2$ and $(EtO)_2PS^-K^+$ in 30 mL of THF at −60 °C with sunlamp irradiation for 4 h gave upon distillation only 5% of **2a** and 43% of $(EtO)_2P(S)Cl$: bp 85–87 °C (10 torr); $n^{25}{}_D$ = 1.4669 (lit.[17] bp 71.5–72 °C (7 torr); $n^{25}{}_D$ = 1.4684).

Dimethyl 2-Nitro-2-propylthiophosphonate 2a. Addition of 28 mmol of 2,2-dinitropropane in 10 mL of THF to 40 mmol of $(Me_2O)_2PO^-K^+$ in 50 mL of THF at −45 °C with sunlamp irradiation yielded, after 1 h at −45 °C and 1 h at 25 °C, 30% of **2a** isolated by short-path distillation (80–82 °C (0.9 torr)) of the ethereal extract obtained from the reaction product after vacuum removal of the THF and hydrolysis in 30% brine: ^1H NMR ($CDCl_3$) δ 1.85 (d, J_{PH} = 16 Hz, 6 H), 3.78 (d, J_{PH} = 14 Hz, 6 H); IR (neat) 1550, 1320 (NO_2) cm^{-1}; mass spectrum, *m/e* (relative intensity) 213 (2.9), 183 (43), 167 (21), 135 (68), 125 (51), 95 (52), 93 (84), 73 (100).

Diethyl Phosphate Ester of Acetone Oxime (3b). To 40 mmol of $(EtO)_2PO^-K^+$ in 30 mL THF at −78 °C was added 18 mmol of $Me_2C(NO_2)_2$ in 10 mL THF over 10 min. After 1 h at −78 °C with sunlamp irradiation, the solution was warmed to 25 °C and irradiated for an additional 1 h. The THF was removed by rotatory evaporation, the residue extracted from 30% brine by Et_2O, and the ether extract washed and dried ($MgSO_4$). Vacuum distillation gave a 55% yield of **3a**: bp 95–97 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 1.36 (t, J = 8 Hz, 6 H), 2.01 (s, 6), 4.20 (dq, 4 H); ^1H NMR (C_6D_6) δ 1.34 (t, J = 8 Hz, 6 H), 1.56 (s, 3 H), 1.62 (s, 3 H), 4.15 (dq, 4 H); ^{13}C NMR (proton decoupled, $CDCl_3$) δ 164.6 (d, J_{PC} = 13 Hz), 64.4 (d, J_{PC} = 5.8 Hz), 21.4 (s), 16.2 (s), 16.1 (s); ^{31}P NMR (proton decoupled, $CDCl_3$) δ 139.2 (H_3PO_4); IR (neat) 1650 (C=N) cm^{-1}; mass spectrum, *m/e* (relative intensity) 167 (0.13), 153 (1.93), 125 (9.9), 81 (8.5), 56 (100). The material had identified spectroscopic properties to those of the product of the reaction of $Me_2C{=}NOH$ and $(EtO)_2P(O)Cl$.

Anal. Calcd for $C_7H_{16}NO_4P$: H, 7.65; N, 6.70; P, 14.83. Found: H, 7.43; N, 6.54; P, 14.55.

Dimethyl Phosphate Ester of Acetone Oxime (3a). The above procedure utilizing $(MeO)_2PO^-K^+$ gave a 30% yield of $O_2NCMe_2CMe_2NO_2$ (mp 210 °C) and a 35% yield of **3a**: bp 40 °C (0.3 torr); ^1H NMR ($CDCl_3$) δ 2.01 (s, 6 H), 3.65 (d, J_{PH} = 14 Hz, 6 H); ^1H NMR (C_6D_6) δ 1.65 (s, 3 H), 1.68 (s, 3 H), 3.62 (d, J_{PH} = 12 Hz, 6 H); ^{13}C NMR (proton decoupled, C_6D_6) δ 165.2 (d, J_{PC} = 12.4 Hz), 54.5 (d, J_{PC} = 5 Hz), 20.7 (s), 15.6 (s); IR (neat) 1640 (C=N) cm^{-1}; mass spectrum, *m/e* (relative intensity) 181 (0.01), 109 (9.7), 79 (4.1), 56 (100).

Diethyl Thiophosphate Ester of Acetone Oxime (3d). Addition of 10 mmol of 2,2-dinitropropane in 10 mL of THF to 20 mmol of $(EtO)_2PS^-K^+$ in 35 mL of THF at −78 °C under nitrogen gave, after sunlamp irradiation for 1 h at −78 °C and 1 h at 25 °C, a 20% yield of **3d** isolated by short-path distillation (95 °C (0.6 torr)) of the ethereal extract obtained from the reaction product after removal of the THF under vacuum and hydrolysis with 30% brine: ^1H NMR ($CDCl_3$) δ 1.34 (t, J = 8 Hz, 6 H), 2.02 (s, 6 H), 4.12 (dq, 4 H); ^1H NMR (C_6D_6) δ 1.32 (t, J = 8 Hz, 6 H),

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(9) For the free ions (K^+[2.2.2]cryptand) in Me_2SO, the relative reactivities toward $Me_2\dot{C}NO_2$ are $(EtO_2C)_2CMe^-$ (10), $(EtO_2C)_2CH^-$ (6), $Me_2{=}NO_2^-$ (1), $(EtO)_2PS^-$ (0.9), $(EtO)_2PO^-$ (0.5).[8]

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1.62 (s, 3 H), 1.68 (s, 3 H), 4.05 (dq, 4 H); IR (neat) 1640 (C=N) cm^{-1}; mass spectrum, *m/e* (relative intensity) 225 (0.3), 169 (8), 141 (7), 97 (55), 56 (100).

Diethyl 2-Amino-2-propylphosphonate (4b). Treatment of 20 mmol of **1b** in 5 mL of ethanol (80%)–H_2O (20%) with 5 g of Sn and 9 mL of concentrated hydrochloric acid, followed by 30 min under reflux, gave a product which, after neutralization by 20% aqueous NaOH, filtration, and ether extractions, yielded upon distillation 74% of **4b**: bp 70–72 °C (0.2 torr); ^1H NMR ($CDCl_3$) δ 1.32 (d, J_{PH} = 16 Hz, 6 H), 1.32 (s, 2 H), 1.37 (t, J = 8 Hz, 6 H), 4.23 (dq, 4 H); ^{13}C NMR (proton decoupled, $CDCl_3$) 60.7 (d, J_{PC} = 8.6 Hz), 47.5 (d, J_{PC} = 148 Hz), 23.7 (d, J_{PC} = 5.8 Hz), 15.1 (d, J_{PC} = 4.9 Hz); ^{31}P (proton decoupled, $CDCl_3$) δ 32.64 (H_3PO_4); IR (neat) 3330, 3290, 1230 (primary amine) cm^{-1}; mass spectrum, *m/e* (relative intensity) 195.10244 (0.13, required for $C_7H_{18}NO_3P$ 195.10247), 111 (6.4), 83 (11), 58 (100).

Dimethyl 2-Amino-2-propylphosphonate (4a). Repetition of the above reduction procedure with **1a** yielded **4a** in 72% yield: ^1H NMR ($CDCl_3$) δ 1.25 (d, J_{PH} = 18 Hz, 6 H), 1.34 (s, 2 H), 3.80 (d, J_{PH} = 13 Hz, 6 H); IR (neat) 3380, 3280, 1240 cm^{-1}; mass spectrum, *m/e* (relative intensity) 167 (0.03), 152 (0.44), 93 (3.76), 58 (100).

Dimethyl 2-Amino-2-propylthiophosphonate (4c). Reduction of **2a** gave an 80% yield of **4c**: ^1H NMR ($CDCl_3$) δ 1.32 (d, J_{PH} = 18 Hz, 6 H), 1.82 (br s, 2 H), 3.78 (d, J_{PH} = 14 Hz, 6 H); IR (neat) 3290, 3380 cm^{-1}; mass spectrum, *m/e* (relative intensity) 183 (0.07), 128 (0.16, $^{34}SC_2H_7O_2P$), 126 (3.62, $^{32}SC_2H_7O_2P$), 93 (8.6), 58 (100).

Diethyl (*p*-Nitrobenzyl)phosphonate (5a). Addition of 18 mmol of *p*-O_2NPhCH_2Cl in 14 mL of THF to 18.4 mmol of $(EtO)_2PO^-K^+$ in 60 mL of THF with sunlamp irradiation at −78 °C followed by a reaction period of 7 h at −80 °C and 12 h of warming to 25 °C gave a brown solution, which was added to dilute hydrochloric acid and extracted with ether to give upon distillation a 26% recovery of *p*-O_2NPhCH_2Cl and 26% of **5a**: bp 147–150 °C (0.1 torr); $n^{25}{}_D$ = 1.5209 (lit.[18] bp 148–153 °C (0.1 torr); $n^{25}{}_D$ = 1.5220).

Reaction of *p*-O_2NPhCH_2Cl with $(EtO)_2PO^-Na^+$ (from $(EtO)_2POH$ and NaOEt) in EtOH for 18 h at 25 °C with sunlamp irradiation gave 14% of **5a**, 25% recovery of *p*-O_2NPhCH_2Cl, and 38% of *p*-O_2NPhCH=$CHPh$-*p*-NO_2, mp 295–300 °C (lit.[19] mp 293 °C).

Dimethyl (*p*-Nitrobenzyl)thiophosphonate (5b). Reaction of 25 mmol of *p*-O_2NPhCH_2Cl with 20 mmol of $(MeO)_2PS^-Na^+$ in 133 mL of MeOH with sunlamp irradiation for 18 h at 25 °C gave, after pouring of the mixture into water, ether extraction, and distillation, 25% recovery of *p*-O_2NPhCH_2Cl and 39% of **5b**: bp 153–156 °C (0.15 torr); mp 59–62 °C; ^1H NMR ($CDCl_3$) δ 3.48 (d, J_{PH} = 20 Hz, 2 H), 3.70 (d, J_{PH} = 14 Hz, 6 H), 7.45 (dd, J_{HH} = 9 Hz, J_{PH} = 3 Hz, 2 H), 8.17 (d, J = 9 Hz, 2 H); IR (CCl_4) 1520, 1343 (NO_2) cm^{-1}; mass spectrum, *m/e* 261.02244 (required for $C_9H_{12}NO_4PS$, 261.02247).

Anal. Calcd for $C_9H_{12}NO_4PS$: C, 41.37; H, 4.64; P, 11.85. Found: C, 41.48; H, 4.51; P, 11.57.

Repetition of the experiment in EtOH gave a 70% yield (by ^1H NMR) of diethyl (*p*-nitrobenzyl)thiophosphonate.

Diethyl (*p*-Nitrobenzyl)thiophosphonate (5c). Reaction of 21 mmol of *p*-O_2NPhCH_2Cl with 23 mmol of $(EtO)_2PS^-Na^+$ in 130 mL of EtOH with sunlamp irradiation for 6 h at 0 °C followed by treatment with water and ether gave after distillation 14% of *p*-O_2NPhCH_2Cl and 67% of **5c**: bp 172 °C (0.7 torr); ^1H NMR (CCl_4) δ 1.23 (t, J = 7 Hz, 6 H), 3.38 (d, J_{PH} = 20 Hz, 2 H), 4.01 (dq, J_{HH} = 7 Hz, J_{PH} = 10 Hz, 4 H), 7.41 (dd, J_{HH} = 9 Hz, J_{PH} = 3 Hz, 2 H), 8.12 (d, J = 9 Hz, 2 H); IR (neat) 1520, 1345 (NO_2) cm^{-1}; mass spectrum, *m/e* 289.05414 (required for $C_{11}H_{16}NO_4PS$, 289.05377).

Anal. Calcd for $C_{11}H_{16}NO_4PS$: C, 45.66; H, 5.59; P, 10.70. Found: C, 45.86; H, 5.65; P, 10.57.

Diethyl (α,α-Dimethyl-*p*-nitrobenzyl)phosphonate (5d). Reaction of 1.4 mmol of *p*-$O_2NPhCMe_2Cl$ with 1.4 mmol of $(EtO)_2PO^-K^+$ in 6.3 mL of HMPA with sunlamp irradiation for 9 h at 25 °C gave after hydrolysis, ether extraction, and distillation 34% of **5d**: bp 113–120 °C (0.07 torr); ^1H NMR ($CDCl_3$) δ 1.23 (t, J = 7 Hz, 6 H), 1.70 (d, J_{PH} = 17 Hz, 6 H), 4.04 (p, J_{HH} = J_{PH} = 7 Hz, 4 H), 7.82 (dd, J_{HH} = 10 Hz, J_{PH} = 3 Hz, 2 H), 8.33 (d, J = 10 Hz, 2 H); IR (neat) 1520, 1350 (NO_2), 1245 (P=O) cm^{-1}; mass spectrum, *m/e* 301.10708 (required for $C_{13}H_{20}NO_5P$, 301.10792).

Anal. Calcd for $C_{13}H_{20}NO_5P$: C, 51.82; H, 6.70; N, 4.65; P, 10.28. Found: C, 51.90; H, 6.80; N, 4.43; P, 9.99.

Diethyl (α,α-Dimethyl-*p*-nitrobenzyl)thiophosphonate (5e). Reaction of 1.4 mmol of *p*-$O_2NPhCMe_2Cl$ with 1.4 mmol of $(EtO)_2PS^-Li^+$ in 12 mL of Me_2SO with sunlamp irradiation for 2 h at 25 °C gave after hydrolysis, ether extraction, and distillation 64% of **5e**: bp 146–150 °C (0.2 torr); mp 60–63 °C; ^1H NMR (CCl_4) δ 1.21 (t, J = 7 Hz, 6 H), 1.64 (d, J_{PH} = 18 Hz, 6 H), 3.95 (dq, J_{PH} = 10 Hz, J_{HH} = 7 Hz, 4 H), 7.59 (dd, J_{HH} = 10 Hz, J_{PH} = 3 Hz, 2 H), 8.14 (d, J = 10 Hz, 2 H); IR (neat) 1520, 1345 (NO_2) cm^{-1}.

Anal. Calcd for $C_{13}H_{20}NO_4PS$: C, 49.19; H, 6.36; P, 9.76. Found: C, 49.46; H, 6.47; P, 9.52.

Competitive $S_{RN}1$ Alkylations. Solutions were prepared to be 0.1 M in each of two anions and the substrate by the addition of 1 equiv of the conjugate acid of each anion to 2 equiv of the base ($Me_3CO^-Li^+$, $Me_3CO^-K^+$, or EtO^-Na^+) followed after 20–30 min by the fast addition with stirring of 1 equiv of $Me_2C(O_2SPh$-*p*-$Me)NO_2$, *p*-O_2NPhCH_2Cl, or *p*-$O_2NPhCMe_2Cl$. The reactions were stirred under nitrogen with sunlamp illumination until 80–100% of the substrate had been consumed. The reaction products were extracted from water or brine by ether which was removed by vacuum evaporation to give a crude product mixture which was analyzed by ^1H NMR ($CDCl_3$), using CH_2Br_2 or Me_2SO as an internal standard, or by GC, using $PhCH_2OPh$ as the standard. GC correcting factors were determined for each pure alkylation product.

Registry No. 1a (R = Me; R′ = Me), 53753-43-8; **1b** (R = Me; R′ = Et), 60171-51-9; **1c** (R = $(CH_2)_4$; R′ = Et), 74895-95-7; **2a** (R = Me), 80866-07-5; **2b** (R = Et), 80866-08-6; **3a** (R = Me; X = O), 65289-21-6; **3b** (R = Et; X = O), 25461-75-0; **3c** (R = Me; X = S), 80866-09-7; **3d** (R = Et; X = S), 80866-10-0; **4a** (R = Me; X = O), 53753-41-6; **4b** (R = Et; X = O), 16814-09-8; **4c** (R = Me; X = S), 80866-11-1; **5a** (R = H; R′ = Et; X = O), 2609-49-6; **5b** (R = H; R′ = Me; X = S), 80879-49-8; **5c** (R = H; R′ = Et; X = S), 80866-12-2; **5d** (R = Me; R′ = Et; X = O), 80866-13-3; **5e** (R = Me; R′ = Et; X = S), 80866-14-4; $(MeO)_2PSK$, 80866-15-5; $(EtO)_2POK$, 54058-00-3; $(MeO)_2POK$, 54057-98-6; $(EtO)_2PSK$, 71774-85-1; $(EtO)_2P(S)Cl$, 2524-04-1; $(EtO)_2PONa$, 2303-76-6; $(MeO)_2PSNa$, 80866-16-6; $(EtO)_2PSNa$, 2303-75-5; $(EtO)_2PSLi$, 75924-85-5; $Me_2\dot{C}NO_2$, 17440-63-0; O_2N-*p*-C_6H_4-$\dot{C}H_2$, 19019-93-3; O_2N-*p*-C_6H_4-$\dot{C}Me_2$, 80866-17-7; $(EtO_2)POLi$, 72726-66-0; $Me_2C = NO_2Li$, 3958-63-2; PhSLi, 2973-86-6; $Me_2C = NO_2K$, 28273-55-4; $(EtO_2C)_2CMeK$, 30014-62-1; $(EtO_2C)_2CMeLi$, 41597-29-9; $Me_2C = NO_2Na$, 24163-39-1; 2-chloro-2-nitropropane, 594-71-8; 2-(*p*-tolylsulfonyl)-2-nitropropane, 21272-86-6; 1-(*p*-tolylsulfonyl)-1-nitrocyclopentane, 74895-94-6; 2,2-dinitropropane, 595-49-3; 2,3-dinitro-2,3-dimethyl butane, 3964-18-9; *p*-nitrobenzyl chloride, 100-14-1; *trans*-*p*,*p*′-dinitrostilbene, 736-31-2; α,α-dimethyl-*p*-nitrobenzyl chloride, 14500-58-4.

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