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Reactions of *p*-Nitrobenzyl Halides with Dialkyl Phosphite Anions in Dimethyl Sulfoxide*

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ABSTRACT

The reactions of p-$O_2NC_6H_4CH_2Cl$ with $(RO)_2PO^-$ in Me_2SO with R = Me, Et, Pr, Bu, CF_3CH_2, i-Pr or Ph involve the formation of p-$O_2NC_6H_4CH_2P(O)(OR)_2$ by S_N2 substitution followed by a further $S_{RN}1$ p-nitrobenzylation of p-$O_2NC_6H_4CH[P(O)(OR)_2]^-$ and p-$O_2NC_6H_4C(CH_2C_6H_4NO_2$-p)$[P(O)(OR)_2]^-$. With p-$O_2NC_6H_4CH_2Br$, the reactions proceed mainly to form p-$O_2NC_6H_4CH_2^-$, which undergoes reaction with p-$O_2NC_6H_4CH_2Br$ to form p-$O_2NC_6H_4CH_2CH_2C_6H_4NO_2$-p. Halophilic reaction of $(RO)_2PO^-$ with p-$O_2NC_6H_4CH(CH_3)X$ (X = Cl, Br) leading to the bibenzyl is the preferred reaction course. Reactions of $(RO)_2PO^-$ or p-$O_2NC_6H_4CH[P(O)(OR)_2]^-$ with p-$O_2NC_6H_4CH_2X$ in Me_2SO do not form significant amounts of p-$O_2NC_6H_4CHX^-$ that would yield p-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$-p. However, p-Cl-$C_6H_4CH[P(O)(OEt)_2]^-$ readily abstracts the benzylic proton from p-$O_2NC_6H_4CH_2X$ to form the stilbene, although p-$O_2NC_6H_4CH_2Br$ reacts with p-$O_2NC_6H_4$-$CH[P(O)(OR)_2]^-$ to form p-$O_2NC_6H_4CH(CH_2C_6H_4NO_2$-p)$P(O)(OR)_2$ in a reaction mixture not inhibited by $(t\text{-}Bu)_2NO^\bullet$. © 1998 John Wiley & Sons, Inc. Heteroatom Chem **9**:201–208, 1998

INTRODUCTION

The reactions of *p*-nitrobenzyl halides with nucleophiles lead to a variety of products depending upon the nature of the nucleophile, the nucleofuge, and the solvent. Among the competing processes are the following: (1) Electron transfer to the substrate forming the *p*-nitrobenzyl radical (Reaction 1)

$$O_2NC_6H_4CH_2Cl + e^- \rightarrow O_2NC_6H_4CH_2Cl\cdot^-$$

$$\rightarrow O_2NC_6H_4CH_2\cdot + Cl^- \quad (1)$$

and addition of the radical to a nucleophile leads to substitution by the $S_{RN}1$ chain reaction [1]. (2) S_N2 substitution by the nucleophile. (3) Halophilic attack by the nucleophile forming the *p*-nitrobenzyl anion (Reaction 2) [2].

$$O_2NC_6H_4CH_2Br + (RO)_2PO^- \rightarrow BrP(O)(OR)_2$$

$$+ O_2NC_6H_4CH_2:^- \quad (2)$$

The formation of p-$O_2NC_6H_4CH_2:^-$ in the presence of an electron acceptor ($ArNO_2$) invariable leads to *p,p′*-dinitrobibenzyl formation via Reaction 3 or 4 [3].

Dedicated to Prof. William McEwen on the occasion of his seventy-fifth birthday.

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$$2\ O_2NC_6H_4CH_2^- \rightleftarrows (O_2NC_6H_4CH_2)_2^{-2}$$

$$\xrightarrow{-2e} O_2NC_6H_4CH_2CH_2C_6H_4NO_2 \qquad (3)$$

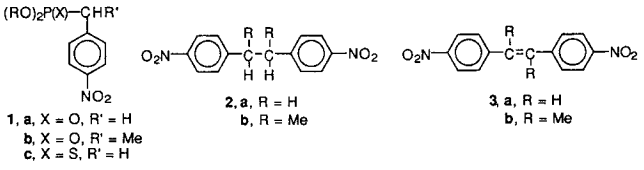
$$O_2NC_6H_4CH_2^- + O_2NC_6H_4CH\cdot_2$$

$$\rightarrow (O_2NC_6H_4CH_2)\cdot_2^- \qquad (4)$$

$$\xrightarrow{-e} O_2NC_6H_4CH_2CH_2C_6H_4NO_2$$

(4) Loss of a benzylic proton to form *p*-$O_2NC_6H_4CHX^-$. This anion upon addition of $O_2NC_6H_4CH_2^-$ forms $O_2NC_6H_4CH{=}CHC_6H_4NO_2$ in a radical chain reaction [4], a process that at one time was considered to proceed via α-elimination to produce *p*-$O_2NC_6H_4CH$: [5].

The reaction of *p*-$O_2NC_6H_4CH_2X$ with a stoichiometric amount of a dialkyl phosphite anion [$(RO)_2PO^-$] has in the past not been considered to be preparatively useful for the formation of the phosphonate **1,** since the reaction is often accompanied by, or yields mainly the bibenzyl **2** and/or the stilbene **3** [6,7].



We have investigated the reactions of *p*-$O_2NC_6H_4CH(R)X$ (R = H or Me, X = Cl or Br) with a variety of dialkyl phosphite anions in Me_2SO and have found that with X = Cl the reactions to produce **1a,c** are fairly efficient but that further radical chain reactions, easily inhibited by $(t\text{-Bu})_2NO^\bullet$, form the *p*-nitrobenzylation products **4** and **5.**

$O_2NC_6H_4C(R)'CH_2C_6H_4NO_2$
|
$P(X)(OR)_2$
4, a, X = O, R′ = H
b, X = S, R′ = H

$O_2NC_6H_4C(CH_2C_6H_4NO_2)_2$
|
$P(X)(OR)_2$
5, a, X = O
b, X = S

p-$O_2NC_6H_4CH(R)ON(CMe_3)_2$
6, a, R = H
b, R = Me

Compounds **1a,b,c** appear to be formed mainly by S_N2 reactions (not inhibited by [$(t\text{-Bu})_2NO^\bullet$], whereas **2–5** are formed from *p*-$O_2NC_6H_4CH_2Cl$ mainly by free radical reactions. In the presence of $(t\text{-Bu})_2NO^\bullet$, the yields of **2–5** are greatly reduced with the formation of the radical trapping products **6.** In Scheme 1, the $S_{RN}1$ substitution mechanism is given that, depending on the nucleophile, can lead to **1–5.**

$O_2NC_6H_4CH_2X^{\bullet-} \rightarrow O_2NC_6H_4CH^\bullet_2 + X^-$

$O_2NC_6H_4CH^\bullet_2 + (RO)_2PO^- \rightarrow O_2NC_6H_4CH_2P(O)(OR)_2^{\bullet-}$ (**1**$^{\bullet-}$)

$O_2NC_6H_4CH^\bullet_2 + O_2NC_6H_4CH_2{:}^- \rightarrow$ **2**$^{\bullet-}$

$O_2NC_6H_4CH^\bullet_2 + O_2NC_6H_4CHX{:}^- \xrightarrow{-HX} \rightarrow$ **3**$^{\bullet-}$

$O_2NC_6H_4CH^\bullet_2 + O_2NC_6H_4CHP(O)(OR)_2^- \rightarrow$ **4**$^{\bullet-}$

$O_2NC_6H_4CH^\bullet_2 + O_2NC_6H_4C[P(O)(OR)_2]CH_2C_6H_4NO_2^- \rightarrow$ **5**$^{\bullet-}$

1$^{\bullet-}$–**5**$^{\bullet-}$ + $O_2NC_6H_4CH_2X \rightarrow$ **1–5** + $O_2NC_6H_4CH_2X^{\bullet-}$

SCHEME 1 SRN1 substitution mechanism.

RESULTS AND DISCUSSION

Reactions of p-$O_2NC_6H_4CH_2Cl$

Dialkyl(R = Me, Et, Pr, Bu, CF_3CH_2, *i*-Pr) or diphenylphosphite anions were generated in Me_2SO solution by reaction of 1 equiv. of butyllithium with $(RO)_2P(O)H$. Essentially the same results were observed by the use of *tert*-butyllithium, KH, NaH, NaOEt, or $KOCMe_3$. Typically, each reaction involved the addition of *p*-$O_2NC_6H_4CH_2Cl$ to a solution of 1.2 equiv. of the anion followed by a 10 minute reaction period under three different conditions: (a) ordinary laboratory lighting at 25°C, (b) with 10–15% of $(t\text{-Bu})_2NO^\bullet$ present, and (c) with fluorescent sunlamp (275 W) irradiation at 35–40°C. The rate of addition of the *p*-$NO_2C_6H_4CH_2Cl$ had little effect on the reaction products as did inverse addition of the phosphite anion to a solution of *p*-nitrobenzyl chloride. Workup involved acidification, extraction by CH_2Cl_2, product identification by isolation and GCMS, and analysis by ^1H NMR using toluene or CH_2I_2 as an internal standard. Table 1 presents the results under the three sets of conditions (N = normal, I = inhibited, L = *hν*).

From Table 1, a number of conclusions can be drawn. Photolysis promotes the conversion of **1a** to **4a** and **4a** to **5a,** while the presence of $(t\text{-Bu})_2NO^\bullet$ essentially prevents the formation of **4a, 5a,** or **2a.** The formation of **2a, 4a,** and **5a** is somewhat more pronounced with sunlamp irradiation than without, but formation of *p*-$O_2NC_6H_4CH^\bullet_2$ appears to occur rapidly without irradiation. Compound **1a** is formed in the presence or absence of $(t\text{-Bu})_2NO^\bullet$, but the yield of total *p*-nitrobenzylation products (**1a, 4a, 5a**) in the 10 minute reaction period is routinely reduced by the presence of $(t\text{-Bu})_2NO^\bullet$. A significant recovery of *p*-$O_2NC_6H_4CH_2Cl$ was observed only in reactions inhibited by $(t\text{-Bu})_2NO^\bullet$.

The maximum yield of **4a** observed (Table 1) was for R = Me with photolysis where 73% of the *p*-$O_2NC_6H_4CH_2Cl$ was converted to **4a** and 21% to **1a** (0.315 mol of **4a** and 0.21 mol of **1a** per mol of *p*-$O_2NC_6H_4CH_2Cl$). Compound **1a** is quite acidic and its

TABLE 1 Reaction of p-$O_2NC_6H_4CH_2Cl$(PNBCl) with $(RO)_2POLi$ (1.2 equiv.) in Me_2SO

		% Yield					Recovered
R	*Conditions*[a]	**1a**	**2a**	**4a**	**5a**	**6a**	*PNBCl (%)*
Me	N	24	0.6	65	0	—	[b]
Me	I	60	0	9.0	0	[b]	[b]
Me	L	21	0.6	73	8.0	—	[b]
Et	N	13	3.7	60	4.5	—	[b]
Et	I	54	0	14	0	9.0	[b]
Et	L	11	7.3	64	9.0	—	[b]
Pr	N	13	2.4	47	4.5	—	[b]
Pr	I	65	0	24	0	9.0	[b]
Pr	L	11	3.7	64	14	—	[b]
Bu	N	16	2.4	50	5.5	—	[b]
Bu	I	64	0	12	0	7.5	[b]
Bu	L	13	3.9	59	14	—	[b]
Ph	N	45	0	33	0	—	[b]
Ph	I	57	0.6	2.0	0	[b]	21
Ph	L	43	1.2	38	0	—	
CF_3CH_2	N	63	0	0	0	—	9.0
CF_3CH_2	I	60	0	0	0	[b]	21
i-Pr	N	13	4.5	55	2.0	—	[b]
i-Pr	I	34	0	0	0	7.5	[b]
i-Pr	L	6	4.8	64	17	—	[b]
		with $KOCMe_3$ in Me_2SO					
Me	N	14	1.3	55	18	—	1.0
Me	I	58	0	10	0	6.0	9.0

[a]0.18 M $(RO)_2POLi$ and 0.15 M p-$O_2NC_6H_4CH_2Cl$. Reactions were conducted for 10 minutes in ordinary laboratory light at 25°C (N), with 10–15 mol% of $(t\text{-Bu})_2NO^\bullet$ (I) at 25°C or with fluorescent sunlamp irradiation (275 W) at 35–40°C (L).
[b]Not measured.

formation should therefore consume 2 equiv. of $(RO)_2PO^-$ to give 0.6 mol of the anion of **1a** from 1.2 equiv. of $(RO)_2PO^-$. In the presence of $(t\text{-Bu})_2NO^\bullet$, yields of **1a** close to 60% based on p-$O_2NC_6H_4CH_2Cl$ are observed (Table 1). In the absence of $(t\text{-Bu})_2NO^\bullet$, the anion of **1a** can undergo the $S_{RN}1$ reaction with the remaining 0.40 equiv. of p-$O_2NC_6H_4CH_2Cl$ to form **4a.** In the absence of any other reactions, 1 mol of p-$O_2NC_6H_4CH_2Cl$ should be converted to 0.2 mol of **1a** (20%) and 0.4 mol of **4a** (80%), yields which are approached in Table 1. In a two-stage, single-pot reaction involving the addition of a 2nd equiv. of BuLi followed by a 2nd equiv. of p-$O_2NC_6H_4CH_2Cl$, the yield of **4a** (R = Me) was 0.71 mol per 2 mol of p-$O_2NC_6H_4CH_2Cl$ and 1 mol of $(MeO)_2P(O)H$. Also formed in this experiment was 0.075 mol of **1a,** 0.037 mol of **5a,** 0.15 mol of **2a,** and 0.06 mol of **3a.**

The absence of the stilbene (**3a**) under the conditions of Table 1 is somewhat surprising since the stilbene has been previously reported to be formed in THF with $Me_3COK/(EtO)_2P(O)H$ [7], in EtOH with $EtONa/(EtO)_2P(O)H$ [7], or with $(i\text{-PrO})_2PO^-Na^+$ in THF [2b]. In EtOH or THF, the S_N2 substitution reaction is much slower. This allows competing reactions of p-$O_2NC_6H_4CHCl^-$ leading to the stilbene to become important. In these solvents, the slow formation of **1a** appears to proceed mainly by the $S_{RN}1$ chain mechanism [7,2b]. Surprisingly, further *p*-nitrobenzylation of **1a** to **4a** has never been reported in THF solution.

With $(t\text{-BuO})_2POLi$ in Me_2SO, the substitution reactions are slower with **4a** greatly predominating over **1a** under all conditions. There is a considerable reduction in yield by the presence of 10 mol% $(t\text{-Bu})_2NO^\bullet$, and the stilbene **3a** is observed even with photolysis (~5%). With the hindered anion, the S_N2 substitution reactions are slower and the $S_{RN}1$ chain makes a more important contribution. Because of the slow consumption of p-$O_2NC_6H_4CH_2Cl$, the formation and reaction of p-$O_2NC_6H_4CHCl^-$ also becomes important. These results also suggest that in Me_2SO, $\mathbf{1a}^-$ is more reactive than $(RO)_2POLi$ toward p-$O_2NC_6H_4CH^\bullet{}_2$. It has been previously reported that in Me_2SO the presence of Li^+ greatly reduces the reactivity of $(EtO)_2PO^-$ toward $Me_2\dot{C}NO_2$, presumably because of ion pairing [8].

Dialkyl thiophosphites $[(RO)_2PS^-]$ reacted simi-

lar to their oxygen analogues in Me_2SO producing a mixture of **1c, 4b,** and **5b** with the formation of **4b** and **5b** retarded by the presence of $(t\text{-Bu})_2NO^\bullet$ (Table 2). With the better radicophile $(RO)_2PS^-$ [7,8], the formation of **2a** was not observed. A powerful inhibition in the formation of **1c** (R = Et) was previously reported for 5% $(t\text{-Bu})_2NO^\bullet$ in EtOH at −23°C, although in Me_2SO, the reaction appears to occur mainly by the S_N2 mechanism [7].

Reactions of p-$O_2NC_6H_4CH(Cl)CH_3$

Reaction of $(MeO)_2PO^-$ with *p*-$O_2NC_6H_4CH(Cl)CH_3$ in Me_2SO gave a mixture of **1b, 2b,** and small amounts of the phosphorylated dimer analogous to **4a.** The stilbene **3b** was not detected in either Me_2SO or THF solution. With the more hindered benzylic halide, apparently the S_N2 substitution to yield **1b** is slower and a halophilic reaction leading to *p*-$O_2NC_6H_4CHCH_3^-$ is now a major reaction pathway. Table 3 summarizes some typical results.

Reactions of p-$O_2NC_6H_4CH_2Br$

In Me_2SO, the reaction of *p*-$O_2NC_6H_4CH_2Br$ with 1.2 equiv. of $(MeO)_2PO^-$ gives mainly the bibenzyl (**2a**) with small amounts of **1a** and **4a** (Table 4). The presence of 10–50 mol% of $(t\text{-Bu})_2NO^\bullet$ inhibited the formation of **2a,** indicating that the reaction proceeds mainly by the $S_{RN}1$ routes of Scheme 1. However, the formation of **2a** was not completely inhibited by 50 mol% of $(t\text{-Bu})_2NO^\bullet$ under conditions where a 15% yield of **6a** was observed. In THF, little **1a** was observed, and the yield of **2a** was only reduced by ~50% by the presence of 50 mol% of $(t\text{-Bu})_2NO^\bullet$. The formation of *p*-$O_2NC_6H_4CH^\bullet_2$ in reactions of *p*-$O_2NC_6H_4CH_2Br$ with $(MeO)_2PO^-$ appears to be quite rapid, particularly in THF. With limited amounts of $(t\text{-Bu})_2NO^\bullet$ present (e.g., 10 mol%), a large fraction of the **2a** may thus be formed after the nitroxide has been consumed. However, with 50 mol% of $(t\text{-Bu})_2NO^\bullet$, it appears from the yield of **6a** (Table 4) that $(t\text{-Bu})_2NO^\bullet$ was present at the end of the 10 minute reaction period and that significant quantities of **2a** are formed in the presence of the nitroxide. In THF, and to a lesser extent in Me_2SO, there appears to be a route to **2a** not involving *p*-$O_2NC_6H_4CH^\bullet_2$. This could involve S_N2 attack upon the benzyl bromide by $O_2NC_6H_4CH_2:^-$ formed in the halophilic reaction of $(MeO)_2PO^-$ with the bromide or possibly by the coupling of two molecules of the carbanion to yield the easily oxidized dianion, Reaction 3 [3].

TABLE 2 Reaction of $(RO)_2PS^-Li^+$ with *p*-$O_2NC_6H_4CH_2Cl$ in Me_2SO

		% Yield		
R	*Conditions*[a]	**1c**	**4b**	**5b**
Et	N	32	25	6
Et	I	42	11	9
Et	L	29	31	9
Bu	N	37	20	4
Bu	I	62	5	2
Bu	L	39	30	2

[a]See Table 1.

TABLE 3 Reaction of $(MeO)_2POLi$ (1.2 equiv) with *p*-$O_2NC_6H_4CH(CH_3)Cl$ in Me_2SO and THF

		% Yield		
Solvent	*Condition*[a]	**1b**	**2b**[b]	*p-$O_2NC_6H_4CH(CH_3)Cl$*
ME_2SO	N	29	29	[c]
Me_2SO	I	33	0	[c,d]
Me_2SO	L	32	28	[c]
THF	N	7.5	35	27
THF	I	6.2	26	42[d]
THF	L	7.8	39	18

[a]See Table 1.
[b]Mixture (~1:1) of two diastereomers.
[c]Not determined.
[d]5–7% of trapping product **6b** formed.

Reaction of p-$O_2NC_6H_4CH(CH_3)Br$

The bibenzyl **2b** (as a 1:1 mixture of two diastereomers) was the major product observed. In Me_2SO, the formation of **2b** was significantly retarded by 10 mol% of $(t\text{-Bu})_2NO^\bullet$. Table 5 summarizes typical results.

p-Nitrobenzylation of **1a** *and* **4a**

Conversion of **1a** (R = Me) or **4a** (R = Me) to their anions by BuLi, NaH, or $KOCMe_3$ in Me_2SO or THF

TABLE 4 Reaction of $(MeO)_2POLi$ (1.2 equiv) with *p*-$O_2NC_6H_4CH_2Br$ (PNBB)

		% Yield			
Solvent	*Condition*[a]	**1a**	**2a**	**4a**	*PNBB*
Me_2SO	N	5	42	11	30
Me_2SO	I[b]	3	16	0	35
Me_2SO	I[c]	0	13	0	26
Me_2SO	L	4	37	12	33
THF	N	1	59	0	15
THF	I[b]	2	58	0	10
THF	I[d]	0	26	0	23
THF	L	2	58	0	12

[a]See Table 1.
[b]10 mol% $(t\text{-Bu})_2NO^\bullet$; 5–10% of **6a** formed.
[c]50 mol% $(t\text{-Bu})_2NO^\bullet$; 15% of **6a** formed.
[d]50 mol% $(t\text{-Bu})_2NO^\bullet$; 36% of **6a** formed.

TABLE 5 Reaction of $(MeO)_2POLi$ with p-$O_2NC_6H_4CH(CH_3)Br$ in Me_2SO and THF

		% Yield		
Solvent	*Conditions*[a]	**1b**	**2b**[b]	*p-O₂NC₆H₄CH(CH₃)Br*
Me_2SO	N	0.3	38	15
Me_2SO	I	tr	14	27[c]
Me_2SO	L	0.4	32	23
THF	N	4.0	96	0
THF	I	2.1	71	8.7[c]
THF	L	1.6	83	7.0

[a]See Table 1.
[b]Mixture (~1:1) of two diastereomers.
[c]5–6% of trapping product **6b** formed.

followed by reaction with p-$O_2NC_6H_4CH_2Cl$ or p-$O_2NC_6H_4CH_2Br$ resulted in further p-nitrobenzylation. Table 6 summarizes results clearly indicating that these processes are mainly radical in nature with p-$O_2NC_6H_4CH_2Cl$. Formation of the stilbene **3a** was appreciable only when an excess of $KOCMe_3$ (2 equiv.) was employed. With p-$O_2NC_6H_4CH_2Br$, a minor side reaction of **4a** was observed to yield **7** in yields up to 20%, presumably by a halophilic reaction of the anion to yield p-$O_2NC_6H_4C(Br)[P(O)(OMe)_2]CH_2C_6H_4NO_2$-$p$, which underwent elimination to yield the stilbene phosphonate.

$$p\text{-}O_2NC_6H_4C[P(O)(OMe)_2]{=}CHC_6H_4NO_2\text{-}p$$
7

$$p\text{-}ClC_6H_4CH_2P(O)(OMe)_2$$
8

From Table 6, it is apparent that the anions p-$O_2NC_6H_4CH[P(O)(OMe)_2]^-$ or p-$O_2NC_6H_4C(CH_2C_6H_4NO_2\text{-}p)[P(O)(OEt)_2]^-$ do not readily remove a benzylic proton from p-$O_2NC_6H_4CH_2Cl$ or p-$O_2NC_6H_4CH_2Br$ because the stilbene was not an important product in the absence of an excess of $KOCMe_3$. However, when the anion p-$ClC_6H_4CH[P(O)(OMe)_2]^-$ was prepared from the **8** and BuLi, reaction with p-$O_2NC_6H_4CH_2Cl$ for 10 minutes in Me_2SO formed mainly the stilbene **3a** with recovery of **8.** A 1:1.2:1 ratio of **8**:BuLi:p-$O_2NC_6H_4CH_2X$ with sunlamp photolysis at 35–40°C gave 95% of **8** and 43% of **3a** with X = Cl and 88% of **8** with 70% of **3a** for X = Br. With X = Br ~5% of the p-nitrobenzylation product was also observed. The predominant reaction of p-$ClC_6H_4CHP(O)(OMe)_2^-$ with p-$O_2NC_6H_4CH_2X$ is to remove a benzylic proton.

There are some quantitative differences in addition to halophilic reactivity between the substitution reactions of p-$O_2NC_6H_4CH_2Br$ and p-$O_2NC_6H_4CH_2Cl$ with $\mathbf{1a}^-$ in Me_2SO, particularly in the presence of 10–15 mol% of $(t\text{-}Bu)_2NO^\bullet$. When the conversion of $\mathbf{1a}^-$ to **4a** and **5a** is examined (Table 6), the inhibitory effect of the nitroxide is observed for p-$O_2NC_6H_4CH_2Cl$ but not for p-$O_2NC_6H_4CH_2Br$. Apparently, conversion of $\mathbf{1a}^-$ to **4a** involves the electron transfer chain reaction only for p-$O_2NC_6H_4CH_2Cl$ with p-$O_2NC_6H_4CH_2Br$ now reacting rapidly by the S_N2 pathway. In fact, in the presence of 1 equiv. of $(t\text{-}Bu)_2NO^\bullet$, we have observed the conversion of $\mathbf{1a}^-$ (R = Me) to **4a** in 80% yield by 1 equiv. of p-$O_2NC_6H_4CH_2Br$ (10 min, 25°C, Me_2SO). Under similar conditions with p-$O_2NC_6H_4CH_2Cl$, the yield of **4a** was only 14%. For the conversion of $\mathbf{4a}^-$ to **5a,** the $S_{RN}1$ process appears to be the main reaction course for both halides.

EXPERIMENTAL

General Procedures

Reactions were generally performed with stirring under argon using 2 mmol of the p-nitrobenzyl derivative in 13 mL of solvent. Photostimulated reactions were irradiated by a 275 W Sylvania fluorescent sunlamp approximately 25 cm from the Pyrex reaction vessel. After acidification and extraction by methylene chloride, toluene or diiodomethane was added as an internal standard and the yields measured by ^1H NMR integration using response factors determined by least squares with four authentic samples. All NMR spectra were recorded in $CDCl_3$. For ^1H NMR spectra at 300 MHz, the hydrogen of $CHCl_3$ was used as the standard (δ = 7.260). ^{13}C NMR at 75.4 MHz used the central line of $CDCl_3$ as the standard (δ = 77.00) while ^{31}P NMR spectra were recorded at 81.0 MHz using 85% phosphoric acid as an external standard.

The general procedure for preparation of the salts of the nucleophiles by BuLi or t-BuLi involved purging of 10 mL of the solvent by argon for 5 minutes followed by the slow addition by hypodermic syringe of a solution of the organolithium reagent (2.4 mmol; 1.7–2.5 M in hexane or pentane) followed by stirring for 5 minutes. The dialkyl phosphite or phosphonate (2.4 mmoL) was added and the solution stirred for 10 minutes before 2 mmol of the p-nitrobenzyl halide in 3 mL of solvent was slowly added by hypodermic syringe over a 2 minute period. Solid bases were weighed into the reaction tube and the solvent added by syringe under an argon atmosphere.

Dialkyl p-Nitrobenzylphosphonates, **1a.** Compound **1a** with R = CF_3CH_2 was isolated by column chromatography as a white solid, mp 89.0–89.5°C by use of hexane (20%)-ethyl acetate (80%) as eluent: ^1H NMR δ 3.433 (d, J_{PH} = 23.1 Hz, 2H), 4.319 (dq,

TABLE 6 Reactions of the Anions of **1a** and **4a** with p-$O_2NC_6H_4CH_2X$ (PNBX)

	Reactants, equiv						*Products (% Yield)*[b]					
R	**1a**	**4a**	*Base*	*PNBX*	*Solvent*	*Conditions*[a]	**1a**	**4a**	**5a**	**2a**	**3a**	*PNBX*
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	N	0	97	tr	1	0	0
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	I	58	31	0	0	5	43
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	L	0	98	1	tr	0	0
Me	1.0	—	*t*-BuLi, 1.2	Cl, 1.0	Me_2SO	N	0	94	3	0	0	0
Me	1.0	—	*t*-BuLi, 1.2	Cl, 1.0	Me_2SO	I	54	34	0	0	0	41
Me	1.0	—	*t*-BuLi, 1.2	Cl, 1.0	Me_2SO	L	0	98	1	1	0	0
Me	1.0	—	KH, 1.2	Cl, 1.0	Me_2SO	N	0	82	6	1	0	2
Me	1.0	—	KH, 1.2	Cl, 1.0	Me_2SO	I	58	25	0	0	0	61
Me	1.0	—	KH, 1.2	Cl, 1.0	Me_2SO	L	0	84	4	0	0	15
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me_2SO	N	0	93	4	tr	0	0
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me_2SO	I	66	32	0	0	6	36
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me_2SO	L	0	97	3	tr	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Me_2SO	N	0	82	4	3	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Me_2SO	I	61	26	0	5	0	39
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Me_2SO	L	0	95	5	2	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	THF	N	17	61	8	19	1	2
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	THF	I	23	40	5	16	1	19
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	THF	L	0	40	6	34	0	2
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	Me_2SO	N	19	66	0	14	30	0
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	Me_2SO	I	43	43	0	6	71	5
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	Me_2SO	L	0	55	16	7	7	0
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	THF	N	14	46	2	19	25	15
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	THF	I	12	42	1	8	25	27
Me	1.0	—	$KOCMe_3$, 2.0	Cl, 1.7	THF	L	0	48	2	24	37	1.7
Me	1.0	—	BuLi, 1.2	Br, 1.0	Me_2SO	N	0	95	tr	tr	0	0
Me	1.0	—	BuLi, 1.2	Br, 1.0	Me_2SO	I	0	95	0	0	3	0
Me	1.0	—	BuLi, 1.2	Br, 1.0	Me_2SO	L	0	97	3	tr	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	Me_2SO	N	0	93	3	1	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	Me_2SO	I	0	87	0	tr	4	0
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	Me_2SO	L	0	96	4	1	0	0
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	THF	N	37	51	3	10	2	13
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	THF	I	12	39	2	8	tr	19
Me	1.0	—	$KOCMe_3$, 1.2	Br, 1.0	THF	L	12	62	6	16	0	13
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	*t*-BuOH	N	18	53	14	5	2	0
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	*t*-BuOH	I	25	41	6	5	5	5
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	*t*-BuOH	L	14	42	16	8	tr	6
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Et_2O	N	17	70	2	8	3	8
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Et_2O	I	54	23	2	3	3	46
Me	1.0	—	$KOCMe_3$, 1.2	Cl, 1.0	Et_2O	L	11	74	4	11	2	2
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me_2SO	N	18	73	11	6	0	8
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me_2SO	I	69	26	0	9	0	50
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me_2SO	L	14	72	12	5	0	0
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	THF	N	49	45	0	8	0	33
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	THF	I	49	36	0	5	0	41
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	THF	L	41	40	1.4	12	0	31
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	EtOH	N	90	0	0	0	0	93
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	EtOH	I	77	0	0	0	0	90
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	EtOH	L	92	4	0	0	3	84
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	EtOH	L, 12 h	81	5	0	0	3	56
Me	—	1.0	BuLi, 1.2	Cl, 1.0	Me_2SO	N	—	22	44	17	12	14
Me	—	1.0	BuLi, 1.2	Cl, 1.0	Me_2SO	I	—	42	26	0	3	21
Me	—	1.0	BuLi, 1.2	Cl, 1.0	Me_2SO	L	—	0	87	tr	9	4
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me_2SO	N	—	9	45	30	0	3[c]
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me_2SO	I	—	15	35	25	0	3[c]
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me_2SO	L	—	5	44	18	0	3[c]
Me	—	1.0	BuLi, 1.2	Br, 1.0	THF	N	—	74	11	7	0	56
Me	—	1.0	BuLi, 1.2	Br, 1.0	THF	I	—	66	8	7	0	57
Me	—	1.0	BuLi, 1.2	Br, 1.0	THF	L	—	72	6.5	7	0	59
Me	—	1.0	BuLi, 1.2	Br, 1.0	THF	N, 1 h	—	33	14	27	0	13[c]
Me	—	1.0	BuLi, 1.2	Br, 1.0	THF	L, 1 h	—	19	7	25	0	6[c]

TABLE 6 *Continued*

	Reactants, equiv						*Products (% Yield)*[b]					
R	**1a**	**4a**	*Base*	*PNBX*	*Solvent*	*Conditions*[a]	**1a**	**4a**	**5a**	**2a**	**3a**	*PNBX*
Et	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	N	tr	86	tr	3	0	tr
Et	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	I	tr	38	tr	7	0	tr
Et	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	L	tr	64	tr	2	0	tr
Et	1.0	—	BuLi, 1.2	Br, 1.0	Me_2SO	N	0	88	3	3	0	tr
CF_3CH_2	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	N	8.5	48	11	1	0	9
CF_3CH_2	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	I	17	11	0	0	0	68
CF_3CH_2	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	L	11	50	26	1	0	0
Ph	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	N	7	49	13	1	0	8
Ph	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	I	46	25	3	1	0	57
Ph	1.0	—	BuLi, 1.2	Cl, 1.0	Me_2SO	L	tr	57	25	2	0	0
Me[d]	1.0(**1c**)	—	$KOCMe_3$, 1.2	Cl, 1.0	Me_2SO	N	29[d]	59[d]	4[d]	11	8	0

[a]See Table 1.
[b]**2a** and **3a** based on *p*-$O_2NC_6H_4CH_2X$; **4a** and **5a** based on limiting reagent.
[c]Also isolated, 10–20% of **7.**
[d]The P(S) analogs of **1a, 4a, 5a** (**1c, 4b, 5b**).

J_{PH} = 10.2 Hz, J_{FH} = 7.8 Hz, 4H), 7.467 (dd, J_{HH} = 8.7 Hz, J_{PH} = 2.7 Hz, 2H), 8.197 (d, 8.7 Hz, 2H); ^{13}C NMR δ 33.37 (d, J_{PC} = 140.3 Hz), 62.35 (qd, J_{FC} = 38.0 Hz, J_{PC} = 6.3 Hz), 122.30 (qd, J_{FC} = 277.6 Hz, J_{PC} = 7.6 Hz), 123.91 (d, J_{PC} = 3.4 Hz), 130.69 (d, J_{PC} = 6.9 Hz), 136.92 (d, J_{PC} = 9.8 Hz), 147.44 (d, J_{PC} = 2.3 Hz); ^{31}P NMR δ 28.255; GC and HRMS *m/z* (relative intensity) 381.020 (45, calcd for $C_{11}H_{10}NO_5PF_6$ 381.0201), 364(100), 341(53), 317(28), 286(9), 267(20), 212(12), 186(8), 136(32), 106(18), 69(24). Anal. calcd for $C_{11}H_{10}NO_5PF_6$: C, 34.66; H, 2.64; N, 3.67. Found: C, 34.72; H, 2.81; N, 3.54. Compounds **1a** with R = Me, Et, Pr, Bu, or Ph were isolated and had the expected ^{1}H and ^{13}C NMR spectra as well as HRMS and satisfactory elemental analysis. With R = Me, **1a** had mp 75.0–76.5°C, while with R = Ph, the mp was 78.0–79.5°C. With R = Et, Pr, or Bu, compounds **1a** were isolated as yellow oils after column chromatography.

Dialkyl p-Nitrobenzylthiophosphonates, **1c.** Compound **1c** with R = Me had mp 58.5–59.5°C (Ref. [7] mp 59–63°C) and consistent ^{1}H and ^{13}C NMR spectra. Compound **1c** with R = Et was isolated as a yellow oil with an ^{1}H and ^{13}C spectra consistent with literature values [7]; GC and HRMS *m/z* (relative intensity) 289.0533 (100, calcd for $C_{11}H_{16}NO_4PS$ 289.0538), 153(26), 137(43), 124(40), 89(7), 78(10). Compound **1c** with R = Bu was isolated by column chromatography as a yellow oil by use of hexane (90%)-ethyl acetate (10%) as the eluent: ^{1}H NMR 0.871 (t, J = 7.2 Hz, 6H), 1.306 (sextet, J = 7.5 Hz, 4H), 1.548 (p, J = 7.2 Hz, 4H), 3.430 (d, J_{PH} = 20.1 Hz), 3.881–4.044 (m, 4H), 7.437 (dd, J_{HH} = 8.7 Hz, J_{PH} = 2.7 Hz, 2H), 8.138 (dd, J_{HH} = 8.7 Hz, J_{PH} = 0.6 Hz, 2H); ^{13}C NMR 13.45, 18.59, 32.12 (d, J_{PC} = 7.0 Hz), 42.18 (d, J_{PC} = 108.2 Hz), 66.70 (d, J_{PC} = 7.47 Hz), 123.25 (d, J_{PC} = 3.5 Hz), 130.88 (d, J_{PC} = 6.3 Hz), 139.545 (d, J_{PC} = 8.6 Hz), 146.91 (d, J_{PC} = 4.8 Hz).

Dialkyl 1,2-Di(p-nitrophenyl)ethylphosphonates, **4a.** Compound **4a** with R = Me was isolated as a white solid, mp 203–204°C: ^{1}H NMR δ 3.147–3.655 (m, 3H), 3.507 (d, J_{PH} = 10.8 Hz, 3H), 3.692 (d, J_{PH} = 10.8 Hz, 3H), 7.078 (d, J = 2.7 Hz), 7.357 (dd, J_{HH} = 8.7 Hz, J_{PH} = 1.8 Hz, 2H), 7.964 (d, J = 8.4 Hz, 2H), 8.064 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 35.93 (d, J_{PC} = 2.7 Hz), 44.91, 46.76, 53.13 (d, J_{PC} = 7.8 Hz), 53.77 (d, J_{PC} = 7.2 Hz), 123.74, 142.33 (d, J_{PC} = 6.3 Hz), 145.45 (d, J_{PC} = 15.0 Hz), 146.85, 147.35 (d, J_{PC} = 3.9 Hz); ^{31}P NMR δ 27.94. GC and HRMS *m/z* (relative intensity) 380.0768 (27, calcd for $C_{16}H_{17}N_2O_7P$ 380.0773), 270(28), 254(100), 178(31), 165(13), 136(14), 110(35), 93(38), 69(91). Anal. calcd for $C_{16}H_{17}N_2O_7P$: C, 50.53; H, 4.51; N, 7.37. Found: C, 50.21; H, 4.53; N, 7.10. Compounds **4a** with R = Et, Pr, Bu, or Ph were isolated as solids by column chromatography. All the compounds gave the expected ^{1}H and ^{13}C NMR spectra and satisfactory elemental and HRMS analysis. The observed mps were R = Et, 127–128°C; R = Pr, 127–128°C; R = Bu, 119.0–121.5°C; and R = Ph, 147.0–148.5°C.

Dialkyl [1,2-Di(p-nitrophenyl)ethyl]thiophosphonates, **4b.** Compound **4b** with R = Et was isolated as a yellow solid, mp 86.5–88.0°C by column chromatography using hexane (80%)-ethyl acetate (20%) as the eluent: ^{1}H NMR δ 1.090 (t, J = 7.2 Hz, 3H), 1.266 (t, J = 7.2 Hz, 3H), 3.265–3.400 (m, 1H),

3.577–3.702 (m, 2H), 3.737–3.856 (m, 1H), 3.880–4.016 (m, 1H), 4.038–4.216 (m, 2H), 7.199 (d, J = 8.7 Hz, 2H), 7.469 (dd, J_{HH} = 9.0 Hz, J_{PH} = 2.4 Hz, 2H), 8.027 (d, J = 8.7 Hz, 2H), 8.120 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 15.92 (d, J_{PC} = 6.1 Hz), 16.12 (d, J_{PC} = 6.8 Hz), 36.10, 52.31 (d, J_{PC} = 108.1 Hz), 63.02 (d, J_{PC} = 7.5 Hz), 63.90 (d, J_{PC} = 7.5 Hz), 123.40 (d, J_{PC} = 2.8 Hz), 123.65, 129.59, 130.38 (d, J_{PC} = 10.95 Hz), 142.44 (d, J_{PC} = 5.3 Hz), 145.87 (d, J_{PC} = 16.8 Hz), 146.71, 147.29 (d, J_{PC} = 3.9 Hz); ^{31}P NMR δ 94.307; GC and HRMS *m/z* (relative intensity) 424.0848 (45, calcd for $C_{18}H_{21}N_2O_6PS$ 424.0858), 254(54), 225(4), 154(46), 121(100). Compound **4c** with R = Bu was isolated as a yellow oil by column chromatography: ^{1}H NMR δ 0.813 (t, J = 7.2 Hz, 3H), 0.895 (t, J = 7.2 Hz, 3H), 1.138–1.464 (m, 6H), 1.526–1.6191 (m, 2H), 3.256–3.383 (m, 1H), 3.587–3.787 (m, 3H), 3.825–3.909 (m, 1H), 3.931–4.116 (m, 2H), 7.140 (d, J = 8.4 Hz, 2H), 7.464 (dd, J_{HH} = 9.0, J_{PH} = 2.4 Hz, 2H), 8.012 (d, J = 8.7 Hz, 2H), 8.105 (d, J = 8.70 Hz, 2H); ^{13}C NMR δ 13.42, 13.50, 18.53, 18.67, 32.06 (d, J_{PC} = 6.7 Hz), 32.19 (d, J_{PC} = 6.9 Hz), 36.14, 52.31 (d, J_{PC} = 108.1 Hz), 66.74 (d, J_{PC} = 7.8 Hz), 67.52 (d, J_{PC} = 7.8 Hz), 123.34 (d, J_{PC} = 2.8 Hz), 123.60, 129.56, 130.34 (d, J_{PC} = 6.3 Hz), 142.55 (d, J_{PC} = 5.4 Hz), 145.87 (d, J_{PC} = 16.7 Hz), 146.66, 147.21 (d, J_{PC} = 3.9 Hz).

Dimethyl 1-(p-Nitrobenzyl)-1,2-di(p-nitrophenyl)ethylphosphonate, **5a** (*R = Me*). The compound was isolated as a white solid, mp 193.5–195.0°C by column chromatography using ethyl acetate as the eluent: ^{1}H NMR δ 3.517 (d, J_{PH} = 10.5 Hz, 6H), δ 3.55–3.73 (m, 4H; the diastereotopic benzylic hydrogens form the AB part of an ABX system (X = P); the symmetrical six-line pattern requires $J_{AX} \cong J_{BX} \cong J_{AB} \cong \nu_A - \nu_B \cong$ 15.6 Hz), 7.164 (d, J = 8.7 Hz, 4H), 7.767 (dd, J_{HH} = 9.0 Hz, J_{PH} = 2.1 Hz, 2H), 8.048 (d, J = 8.7 Hz, 4H), 8.254 (d, J = 9.0 Hz, 2H); GC and HRMS *m/z* (relative intensity) 571.1736 (44, calcd for $C_{27}H_{30}N_3O_9P$ 571.1719), 453(100), 389(60), 271(38), 178(15), 123(89), 83(26).

N,N-Di-tert-butyl-O-(p-nitrobenzyl)hydroxylamines, **6.** Compound **6a** has been previously described [2b]. The *O*-(1-*p*-nitrophenylethyl) analog **6b** was isolated as a liquid by thin-layer chromatography: ^{1}H NMR δ 1.03 (s, 9H), 1.32 (s, 9H), 1.50 (d, J = 6.9 Hz, 3H), 4.93 (q, J = 6.6 Hz, 1H), 7.48 (d, J = 8.7 Hz, 2H), 8.18 (d, J = 8.7 Hz, 2H); ^{13}C NMR δ 22.9, 30.5, 30.7, 61.9, 62.1, 82.3, 123.4, 127.4, 146.8, 152.9; GCMS *m/z* (relative intensity) 166 [7, M^+–N $(CMe_3)_2$], 150(100), 120(12), 104(15), 92(16).

Dimethyl 1,2-Di(p-nitrophenyl)vinylphosphonate, **7.** The compound was isolated by column chromatography using hexane (10%)-ethyl acetate (90%) as the eluent as a pale yellow solid, mp 124.0–125.5°C: ^{1}H NMR δ 3.79 (d, J_{PH} = 11.1 Hz, 6H), 7.87 (d, J = 8.7 Hz, 2H), 7.42 (dd, J = 8.7, 1.5 Hz), 7.77 (d, J_{PH} = 24.0 Hz, 1H), 8.48 (d, J = 9.0 Hz, 2H), 8.23 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 53.2 (*d*, J_{PC} = 6.2 Hz), 123.70, 124.3 (d, J_{PC} = 1.6 Hz), 129.3, 130.1 (d, J_{PC} = 22.0 Hz) 141.5 (d, J_{PC} = 7.5 Hz), 142.7 (d, J_{PC} = 10.1 Hz), 147.77 (d, J_{PC} = 8.1 Hz); ^{31}P NMR δ 18.13; GC and HRMS *m/z* (relative intensity) 378.0619 (100, calcd for $C_{16}H_{15}N_2O_7P$ 378.0617), 377(28), 361(25), 331(12), 269(4), 253(9), 278(8), 222(8), 176(21), 165(7), 150(6), 111(4), 109(9).

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