

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

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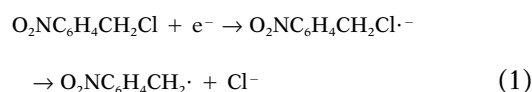
ABSTRACT

The reactions of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ with $(\text{RO})_2\text{PO}^-$ in Me_2SO with $\text{R} = \text{Me, Et, Pr, Bu, CF}_3\text{CH}_2, i\text{-Pr}$ or Ph involve the formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{P}(\text{O})(\text{OR})_2$ by $\text{S}_{\text{N}}2$ substitution followed by a further $\text{S}_{\text{RN}}1$ *p*-nitrobenzylation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}[\text{P}(\text{O})(\text{OR})_2]^-$ and $p\text{-O}_2\text{NC}_6\text{H}_4\text{C}(\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p)[\text{P}(\text{O})(\text{OR})_2]^-$. With $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$, the reactions proceed mainly to form $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2^-$, which undergoes reaction with $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$ to form $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}p$. Halophilic reaction of $(\text{RO})_2\text{PO}^-$ with $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{X}$ ($\text{X} = \text{Cl, Br}$) leading to the bibenzyl is the preferred reaction course. Reactions of $(\text{RO})_2\text{PO}^-$ or $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}[\text{P}(\text{O})(\text{OR})_2]^-$ with $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ in Me_2SO do not form significant amounts of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHX}^-$ that would yield $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2\text{-}p$. However, $p\text{-Cl-C}_6\text{H}_4\text{CH}[\text{P}(\text{O})(\text{OEt})_2]^-$ readily abstracts the benzylic proton from $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ to form the stilbene, although $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Br}$ reacts with $p\text{-O}_2\text{NC}_6\text{H}_4\text{-CH}[\text{P}(\text{O})(\text{OR})_2]^-$ to form $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}(\text{CH}_2\text{C}_6\text{-}$

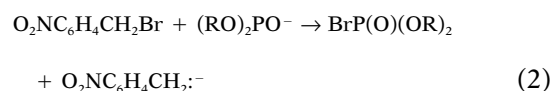
$\text{H}_4\text{NO}_2\text{-}p)\text{P}(\text{O})(\text{OR})_2$ in a reaction mixture not inhibited by $(t\text{-Bu})_2\text{NO}^\bullet$. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:201–208, 1998

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)



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



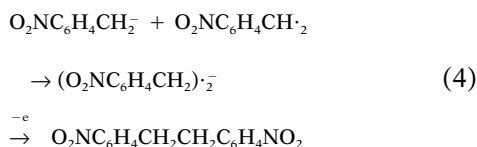
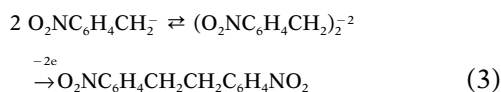
The formation of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2^-$ in the presence of an electron acceptor (ArNO_2) invariably leads to *p,p'*-dinitrobibenzyl formation via Reaction 3 or 4 [3].

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

*Electron Transfer Processes. Part 63. For Part 62, see *Acta Chem. Scand.*, in press.

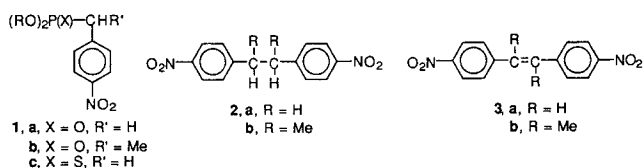
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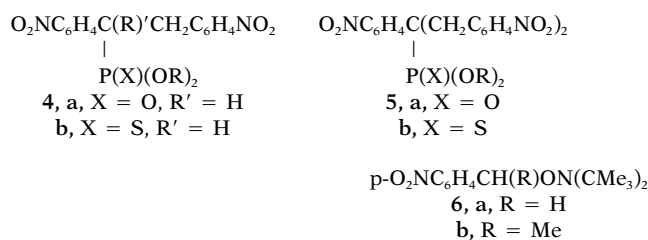


(4) Loss of a benzylic proton to form $p\text{-O}_2\text{NC}_6\text{H}_4\text{CHX}^-$. This anion upon addition of $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2^\bullet$ forms $\text{O}_2\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{NO}_2$ in a radical chain reaction [4], a process that at one time was considered to proceed via α -elimination to produce $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}$: [5].

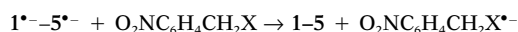
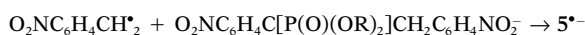
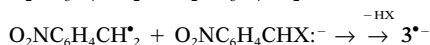
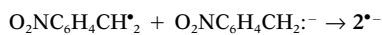
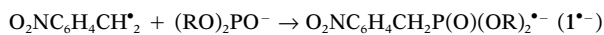
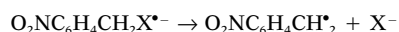
The reaction of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ with a stoichiometric amount of a dialkyl phosphite anion $[(\text{RO})_2\text{PO}]^-$ has in the past not been considered to be preparatively useful for the formation of the phosphonate **1**, since the reaction is often accompanied by, or yields mainly the bibenzyl **2** and/or the stilbene **3** [6,7].



We have investigated the reactions of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH(R)X}$ ($\text{R} = \text{H}$ or Me , $\text{X} = \text{Cl}$ or Br) with a variety of dialkyl phosphite anions in Me_2SO and have found that with $\text{X} = \text{Cl}$ the reactions to produce **1a,c** are fairly efficient but that further radical chain reactions, easily inhibited by $(t\text{-Bu})_2\text{NO}^\bullet$, form the p -nitrobenzyl products **4** and **5**.



Compounds **1a,b,c** appear to be formed mainly by $\text{S}_\text{N}2$ reactions (not inhibited by $[(t\text{-Bu})_2\text{NO}^\bullet]$, whereas **2–5** are formed from $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ mainly by free radical reactions. In the presence of $(t\text{-Bu})_2\text{NO}^\bullet$, the yields of **2–5** are greatly reduced with the formation of the radical trapping products **6**. In Scheme 1, the $\text{S}_\text{RN}1$ substitution mechanism is given that, depending on the nucleophile, can lead to **1–5**.



SCHEME 1 $\text{S}_\text{RN}1$ substitution mechanism.

RESULTS AND DISCUSSION

Reactions of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$

Dialkyl ($\text{R} = \text{Me}$, Et , Pr , Bu , CF_3CH_2 , $i\text{-Pr}$) or diphenylphosphite anions were generated in Me_2SO solution by reaction of 1 equiv. of butyllithium with $(\text{RO})_2\text{P(O)H}$. 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 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ 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 $(t\text{-Bu})_2\text{NO}^\bullet$ present, and (c) with fluorescent sunlamp (275 W) irradiation at $35\text{--}40^\circ\text{C}$. The rate of addition of the $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ 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 ($\text{N} = \text{normal}$, $\text{I} = \text{inhibited}$, $\text{L} = h\nu$).

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 $(t\text{-Bu})_2\text{NO}^\bullet$ 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 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2^\bullet$ appears to occur rapidly without irradiation. Compound **1a** is formed in the presence or absence of $(t\text{-Bu})_2\text{NO}^\bullet$, but the yield of total p -nitrobenzyl products (**1a**, **4a**, **5a**) in the 10 minute reaction period is routinely reduced by the presence of $(t\text{-Bu})_2\text{NO}^\bullet$. A significant recovery of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ was observed only in reactions inhibited by $(t\text{-Bu})_2\text{NO}^\bullet$.

The maximum yield of **4a** observed (Table 1) was for $\text{R} = \text{Me}$ with photolysis where 73% of the $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$ was converted to **4a** and 21% to **1a** (0.315 mol of **4a** and 0.21 mol of **1a** per mol of $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{Cl}$). Compound **1a** is quite acidic and its

TABLE 1 Reaction of *p*-O₂NC₆H₄CH₂Cl(PNBCl) with (RO)₂POLi (1.2 equiv.) in Me₂SO

<i>R</i>	Conditions ^a	% Yield					Recovered PNBCl (%)
		1a	2a	4a	5a	6a	
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 ₃ CH ₂	N	63	0	0	0	—	9.0
CF ₃ CH ₂	I	60	0	0	0	^b	21
<i>i</i> -Pr	N	13	4.5	55	2.0	—	^b
<i>i</i> -Pr	I	34	0	0	0	7.5	^b
<i>i</i> -Pr	L	6	4.8	64	17	—	^b
with KOCMe ₃ in Me ₂ SO							
Me	N	14	1.3	55	18	—	1.0
Me	I	58	0	10	0	6.0	9.0

^a0.18 M (RO)₂POLi and 0.15 M *p*-O₂NC₆H₄CH₂Cl. Reactions were conducted for 10 minutes in ordinary laboratory light at 25°C (N), with 10–15 mol% of (*t*-Bu)₂NO• (I) at 25°C or with fluorescent sunlamp irradiation (275 W) at 35–40°C (L).

^bNot 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*-Bu)₂NO•, yields of **1a** close to 60% based on *p*-O₂NC₆H₄CH₂Cl are observed (Table 1). In the absence of (*t*-Bu)₂NO•, the anion of **1a** can undergo the S_{RN}1 reaction with the remaining 0.40 equiv. of *p*-O₂NC₆H₄CH₂Cl to form **4a**. In the absence of any other reactions, 1 mol of *p*-O₂NC₆H₄CH₂Cl 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*-O₂NC₆H₄CH₂Cl, the yield of **4a** (R = Me) was 0.71 mol per 2 mol of *p*-O₂NC₆H₄CH₂Cl 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 Me₃COK/(EtO)₂P(O)H [7], in EtOH with EtONa/(EtO)₂P(O)H [7], or with (*i*-PrO)₂PO[−]Na⁺ in THF [2b]. In EtOH or THF, the S_N2 substitution reaction is much slower. This allows competing reac-

tions of *p*-O₂NC₆H₄CHCl[−] 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*-BuO)₂POLi in Me₂SO, 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*-Bu)₂NO•, 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*-O₂NC₆H₄CH₂Cl, the formation and reaction of *p*-O₂NC₆H₄CHCl[−] also becomes important. These results also suggest that in Me₂SO, **1a**[−] is more reactive than (RO)₂POLi toward *p*-O₂NC₆H₄CH₂•. It has been previously reported that in Me₂SO the presence of Li⁺ greatly reduces the reactivity of (EtO)₂PO[−] toward Me₂CNO₂, presumably because of ion pairing [8].

Dialkyl thiophosphites [(RO)₂PS[−]] reacted simi-

lar to their oxygen analogues in Me₂SO producing a mixture of **1c**, **4b**, and **5b** with the formation of **4b** and **5b** retarded by the presence of (*t*-Bu)₂NO• (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*-Bu)₂NO• in EtOH at −23°C, although in Me₂SO, the reaction appears to occur mainly by the S_N2 mechanism [7].

Reactions of *p*-O₂NC₆H₄CH(Cl)CH₃

Reaction of (MeO)₂PO[−] with *p*-O₂NC₆H₄CH(Cl)CH₃ in Me₂SO gave a mixture of **1b**, **2b**, and small amounts of the phosphorylated dimer analogous to **4a**. The stilbene **3b** was not detected in either Me₂SO 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*-O₂NC₆H₄CHCH₃[−] is now a major reaction pathway. Table 3 summarizes some typical results.

Reactions of *p*-O₂NC₆H₄CH₂Br

In Me₂SO, the reaction of *p*-O₂NC₆H₄CH₂Br with 1.2 equiv. of (MeO)₂PO[−] gives mainly the bibenzyl (**2a**)

TABLE 2 Reaction of (RO)₂PS[−]Li⁺ with *p*-O₂NC₆H₄CH₂Cl in Me₂SO

R	Conditions ^a	% Yield		
		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

^aSee Table 1.

TABLE 3 Reaction of (MeO)₂POLi (1.2 equiv) with *p*-O₂NC₆H₄CH(CH₃)Cl in Me₂SO and THF

Solvent	Condition ^a	% Yield		
		1b	2b	<i>p</i> -O ₂ NC ₆ H ₄ CH(CH ₃)Cl
Me ₂ SO	N	29	29	^c
Me ₂ SO	I	33	0	^{c,d}
Me ₂ SO	L	32	28	^c
THF	N	7.5	35	27
THF	I	6.2	26	42 ^d
THF	L	7.8	39	18

^aSee Table 1.

^bMixture (~1:1) of two diastereomers.

^cNot determined.

^d5–7% of trapping product **6b** formed.

with small amounts of **1a** and **4a** (Table 4). The presence of 10–50 mol% of (*t*-Bu)₂NO• 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*-Bu)₂NO• 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*-Bu)₂NO•. The formation of *p*-O₂NC₆H₄CH₂• in reactions of *p*-O₂NC₆H₄CH₂Br with (MeO)₂PO[−] appears to be quite rapid, particularly in THF. With limited amounts of (*t*-Bu)₂NO• 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*-Bu)₂NO•, it appears from the yield of **6a** (Table 4) that (*t*-Bu)₂NO• 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 Me₂SO, there appears to be a route to **2a** not involving *p*-O₂NC₆H₄CH₂•. This could involve S_N2 attack upon the benzyl bromide by O₂NC₆H₄CH₂•[−] 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].

Reaction of *p*-O₂NC₆H₄CH(CH₃)Br

The bibenzyl **2b** (as a 1:1 mixture of two diastereomers) was the major product observed. In Me₂SO, the formation of **2b** was significantly retarded by 10 mol% of (*t*-Bu)₂NO•. 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 KOCMe₃ in Me₂SO or THF

TABLE 4 Reaction of (MeO)₂POLi (1.2 equiv) with *p*-O₂NC₆H₄CH₂Br (PNBB)

Solvent	Condition ^a	% Yield			
		1a	2a	4a	PNBB
Me ₂ SO	N	5	42	11	30
Me ₂ SO	I ^b	3	16	0	35
Me ₂ SO	I ^c	0	13	0	26
Me ₂ SO	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

^aSee Table 1.

^b10 mol% (*t*-Bu)₂NO•; 5–10% of **6a** formed.

^c50 mol% (*t*-Bu)₂NO•; 15% of **6a** formed.

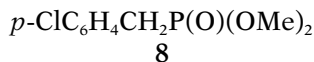
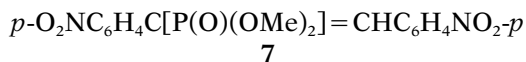
^d50 mol% (*t*-Bu)₂NO•; 36% of **6a** formed.

TABLE 5 Reaction of (MeO)₂POLi with *p*-O₂NC₆H₄CH(CH₃)Br in Me₂SO and THF

Solvent	Conditions ^a	% Yield		
		1b	2b ^b	<i>p</i> -O ₂ NC ₆ H ₄ CH(CH ₃)Br
Me ₂ SO	N	0.3	38	15
Me ₂ SO	I	tr	14	27 ^c
Me ₂ SO	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

^aSee Table 1.^bMixture (~1:1) of two diastereomers.^c5–6% of trapping product **6b** formed.

followed by reaction with *p*-O₂NC₆H₄CH₂Cl or *p*-O₂NC₆H₄CH₂Br resulted in further *p*-nitrobenzylation. Table 6 summarizes results clearly indicating that these processes are mainly radical in nature with *p*-O₂NC₆H₄CH₂Cl. Formation of the stilbene **3a** was appreciable only when an excess of KOCMe₃ (2 equiv.) was employed. With *p*-O₂NC₆H₄CH₂Br, 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*-O₂NC₆H₄C(Br)-[P(O)(OMe)₂]CH₂C₆H₄NO₂-*p*, which underwent elimination to yield the stilbene phosphonate.



From Table 6, it is apparent that the anions *p*-O₂NC₆H₄CH[P(O)(OMe)₂][−] or *p*-O₂NC₆H₄C(CH₂C₆H₄NO₂-*p*)[P(O)(OEt)₂][−] do not readily remove a benzylic proton from *p*-O₂NC₆H₄CH₂Cl or *p*-O₂NC₆H₄CH₂Br because the stilbene was not an important product in the absence of an excess of KOCMe₃. However, when the anion *p*-Cl-C₆H₄CH[P(O)(OMe)₂][−] was prepared from the **8** and BuLi, reaction with *p*-O₂NC₆H₄CH₂Cl for 10 minutes in Me₂SO formed mainly the stilbene **3a** with recovery of **8**. A 1:1.2:1 ratio of **8**:BuLi:*p*-O₂NC₆H₄CH₂X 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*-ClC₆H₄CHP(O)(OMe)₂[−] with *p*-O₂NC₆H₄CH₂X is to remove a benzylic proton.

There are some quantitative differences in addition to halophilic reactivity between the substitution reactions of *p*-O₂NC₆H₄CH₂Br and *p*-O₂NC₆H₄CH₂Cl with **1a**[−] in Me₂SO, particularly in

the presence of 10–15 mol% of (*t*-Bu)₂NO•. When the conversion of **1a**[−] to **4a** and **5a** is examined (Table 6), the inhibitory effect of the nitroxide is observed for *p*-O₂NC₆H₄CH₂Cl but not for *p*-O₂NC₆H₄CH₂Br. Apparently, conversion of **1a**[−] to **4a** involves the electron transfer chain reaction only for *p*-O₂NC₆H₄CH₂Cl with *p*-O₂NC₆H₄CH₂Br now reacting rapidly by the S_N2 pathway. In fact, in the presence of 1 equiv. of (*t*-Bu)₂NO•, we have observed the conversion of **1a**[−] (R = Me) to **4a** in 80% yield by 1 equiv. of *p*-O₂NC₆H₄CH₂Br (10 min, 25°C, Me₂SO). Under similar conditions with *p*-O₂NC₆H₄CH₂Cl, the yield of **4a** was only 14%. For the conversion of **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 CDCl₃. For ¹H NMR spectra at 300 MHz, the hydrogen of CHCl₃ was used as the standard (δ = 7.260). ¹³C NMR at 75.4 MHz used the central line of CDCl₃ as the standard (δ = 77.00) while ³¹P 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 = CF₃CH₂ 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 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ (PNBX)

<i>R</i>	<i>Reactants, equiv</i>				<i>Solvent</i>	<i>Conditions^a</i>	<i>Products (% Yield)^b</i>					
	1a	4a	<i>Base</i>	<i>PNBX</i>			1a	4a	5a	2a	3a	<i>PNBX</i>
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me ₂ SO	N	0	97	tr	1	0	0
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me ₂ SO	I	58	31	0	0	5	43
Me	1.0	—	BuLi, 1.2	Cl, 1.0	Me ₂ SO	L	0	98	1	tr	0	0
Me	1.0	—	<i>t</i> -BuLi, 1.2	Cl, 1.0	Me ₂ SO	N	0	94	3	0	0	0
Me	1.0	—	<i>t</i> -BuLi, 1.2	Cl, 1.0	Me ₂ SO	I	54	34	0	0	0	41
Me	1.0	—	<i>t</i> -BuLi, 1.2	Cl, 1.0	Me ₂ SO	L	0	98	1	1	0	0
Me	1.0	—	KH, 1.2	Cl, 1.0	Me ₂ SO	N	0	82	6	1	0	2
Me	1.0	—	KH, 1.2	Cl, 1.0	Me ₂ SO	I	58	25	0	0	0	61
Me	1.0	—	KH, 1.2	Cl, 1.0	Me ₂ SO	L	0	84	4	0	0	15
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me ₂ SO	N	0	93	4	tr	0	0
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me ₂ SO	I	66	32	0	0	6	36
Me	1.0	—	NaH, 1.2	Cl, 1.0	Me ₂ SO	L	0	97	3	tr	0	0
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Me ₂ SO	N	0	82	4	3	0	0
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Me ₂ SO	I	61	26	0	5	0	39
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Me ₂ SO	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 ₂ SO	N	19	66	0	14	30	0
Me	1.0	—	KOCMe ₃ , 2.0	Cl, 1.7	Me ₂ SO	I	43	43	0	6	71	5
Me	1.0	—	KOCMe ₃ , 2.0	Cl, 1.7	Me ₂ SO	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 ₂ SO	N	0	95	tr	tr	0	0
Me	1.0	—	BuLi, 1.2	Br, 1.0	Me ₂ SO	I	0	95	0	0	3	0
Me	1.0	—	BuLi, 1.2	Br, 1.0	Me ₂ SO	L	0	97	3	tr	0	0
Me	1.0	—	KOCMe ₃ , 1.2	Br, 1.0	Me ₂ SO	N	0	93	3	1	0	0
Me	1.0	—	KOCMe ₃ , 1.2	Br, 1.0	Me ₂ SO	I	0	87	0	tr	4	0
Me	1.0	—	KOCMe ₃ , 1.2	Br, 1.0	Me ₂ SO	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	<i>t</i> -BuOH	N	18	53	14	5	2	0
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	<i>t</i> -BuOH	I	25	41	6	5	5	5
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	<i>t</i> -BuOH	L	14	42	16	8	tr	6
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Et ₂ O	N	17	70	2	8	3	8
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Et ₂ O	I	54	23	2	3	3	46
Me	1.0	—	KOCMe ₃ , 1.2	Cl, 1.0	Et ₂ O	L	11	74	4	11	2	2
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me ₂ SO	N	18	73	11	6	0	8
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me ₂ SO	I	69	26	0	9	0	50
Me	1.0	—	NaOEt, 1.2	Cl, 1.0	Me ₂ SO	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 ₂ SO	N	—	22	44	17	12	14
Me	—	1.0	BuLi, 1.2	Cl, 1.0	Me ₂ SO	I	—	42	26	0	3	21
Me	—	1.0	BuLi, 1.2	Cl, 1.0	Me ₂ SO	L	—	0	87	tr	9	4
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me ₂ SO	N	—	9	45	30	0	3 ^c
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me ₂ SO	I	—	15	35	25	0	3 ^c
Me	—	1.0	BuLi, 1.2	Br, 1.0	Me ₂ SO	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

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

^aSee Table 1.^b2a and 3a based on *p*-O₂NC₆H₄CH₂X; 4a and 5a based on limiting reagent.^cAlso isolated, 10–20% of 7.^dThe P(S) analogs of 1a, 4a, 5a (1c, 4b, 5b).

$J_{\text{PH}} = 10.2$ Hz, $J_{\text{FH}} = 7.8$ Hz, 4H), 7.467 (dd, $J_{\text{HH}} = 8.7$ Hz, $J_{\text{PH}} = 2.7$ Hz, 2H), 8.197 (d, 8.7 Hz, 2H); ¹³C NMR δ 33.37 (d, $J_{\text{PC}} = 140.3$ Hz), 62.35 (qd, $J_{\text{FC}} = 38.0$ Hz, $J_{\text{PC}} = 6.3$ Hz), 122.30 (qd, $J_{\text{FC}} = 277.6$ Hz, $J_{\text{PC}} = 7.6$ Hz), 123.91 (d, $J_{\text{PC}} = 3.4$ Hz), 130.69 (d, $J_{\text{PC}} = 6.9$ Hz), 136.92 (d, $J_{\text{PC}} = 9.8$ Hz), 147.44 (d, $J_{\text{PC}} = 2.3$ Hz); ³¹P NMR δ 28.255; GC and HRMS m/z (relative intensity) 381.020 (45, calcd for C₁₁H₁₀NO₅PF₆ 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 C₁₁H₁₀NO₅PF₆: 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 ¹H and ¹³C 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 ¹H and ¹³C NMR spectra. Compound 1c with R = Et was isolated as a yellow oil with an ¹H and ¹³C spectra consistent with literature values [7]; GC and HRMS m/z (relative intensity) 289.0533 (100, calcd for C₁₁H₁₆NO₄PS 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: ¹H 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, $J_{\text{PH}} = 20.1$ Hz), 3.881–4.044 (m, 4H), 7.437 (dd, $J_{\text{HH}} = 8.7$ Hz, $J_{\text{PH}} = 2.7$ Hz, 2H), 8.138 (dd, $J_{\text{HH}} =$

8.7 Hz, $J_{\text{PH}} = 0.6$ Hz, 2H); ¹³C NMR 13.45, 18.59, 32.12 (d, $J_{\text{PC}} = 7.0$ Hz), 42.18 (d, $J_{\text{PC}} = 108.2$ Hz), 66.70 (d, $J_{\text{PC}} = 7.47$ Hz), 123.25 (d, $J_{\text{PC}} = 3.5$ Hz), 130.88 (d, $J_{\text{PC}} = 6.3$ Hz), 139.545 (d, $J_{\text{PC}} = 8.6$ Hz), 146.91 (d, $J_{\text{PC}} = 4.8$ Hz).

Dialkyl 1,2-Di(*p*-nitrophenyl)ethylphosphonates, 4a. Compound 4a with R = Me was isolated as a white solid, mp 203–204°C: ¹H NMR δ 3.147–3.655 (m, 3H), 3.507 (d, $J_{\text{PH}} = 10.8$ Hz, 3H), 3.692 (d, $J_{\text{PH}} = 10.8$ Hz, 3H), 7.078 (d, $J = 2.7$ Hz), 7.357 (dd, $J_{\text{HH}} = 8.7$ Hz, $J_{\text{PH}} = 1.8$ Hz, 2H), 7.964 (d, $J = 8.4$ Hz, 2H), 8.064 (d, $J = 8.7$ Hz, 2H); ¹³C NMR δ 35.93 (d, $J_{\text{PC}} = 2.7$ Hz), 44.91, 46.76, 53.13 (d, $J_{\text{PC}} = 7.8$ Hz), 53.77 (d, $J_{\text{PC}} = 7.2$ Hz), 123.74, 142.33 (d, $J_{\text{PC}} = 6.3$ Hz), 145.45 (d, $J_{\text{PC}} = 15.0$ Hz), 146.85, 147.35 (d, $J_{\text{PC}} = 3.9$ Hz); ³¹P NMR δ 27.94. GC and HRMS m/z (relative intensity) 380.0768 (27, calcd for C₁₆H₁₇N₂O₇P 380.0773), 270(28), 254(100), 178(31), 165(13), 136(14), 110(35), 93(38), 69(91). Anal. calcd for C₁₆H₁₇N₂O₇P: 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 ¹H and ¹³C 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: ¹H 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, $J_{\text{HH}} = 9.0$ Hz, $J_{\text{PH}} = 2.4$ 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, $J_{\text{PC}} = 6.1$ Hz), 16.12 (d, $J_{\text{PC}} = 6.8$ Hz), 36.10, 52.31 (d, $J_{\text{PC}} = 108.1$ Hz), 63.02 (d, $J_{\text{PC}} = 7.5$ Hz), 63.90 (d, $J_{\text{PC}} = 7.5$ Hz), 123.40 (d, $J_{\text{PC}} = 2.8$ Hz), 123.65, 129.59, 130.38 (d, $J_{\text{PC}} = 10.95$ Hz), 142.44 (d, $J_{\text{PC}} = 5.3$ Hz), 145.87 (d, $J_{\text{PC}} = 16.8$ Hz), 146.71, 147.29 (d, $J_{\text{PC}} = 3.9$ Hz); ^{31}P NMR δ 94.307; GC and HRMS m/z (relative intensity) 424.0848 (45, calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_6\text{PS}$ 424.0858), 254(54), 225(4), 154(46), 121(100). Compound **4c** with $\text{R} = \text{Bu}$ was isolated as a yellow oil by column chromatography: ^1H 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, $J_{\text{HH}} = 9.0$, $J_{\text{PH}} = 2.4$ 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, $J_{\text{PC}} = 6.7$ Hz), 32.19 (d, $J_{\text{PC}} = 6.9$ Hz), 36.14, 52.31 (d, $J_{\text{PC}} = 108.1$ Hz), 66.74 (d, $J_{\text{PC}} = 7.8$ Hz), 67.52 (d, $J_{\text{PC}} = 7.8$ Hz), 123.34 (d, $J_{\text{PC}} = 2.8$ Hz), 123.60, 129.56, 130.34 (d, $J_{\text{PC}} = 6.3$ Hz), 142.55 (d, $J_{\text{PC}} = 5.4$ Hz), 145.87 (d, $J_{\text{PC}} = 16.7$ Hz), 146.66, 147.21 (d, $J_{\text{PC}} = 3.9$ Hz).

Dimethyl 1-(p-Nitrobenzyl)-1,2-di(p-nitrophenyl)ethylphosphonate, 5a ($\text{R} = \text{Me}$). The compound was isolated as a white solid, mp 193.5–195.0°C by column chromatography using ethyl acetate as the eluent: ^1H NMR δ 3.517 (d, $J_{\text{PH}} = 10.5$ Hz, 6H), δ 3.55–3.73 (m, 4H; the diastereotopic benzylic hydrogens form the AB part of an ABX system ($\text{X} = \text{P}$); the symmetrical six-line pattern requires $J_{\text{AX}} \cong J_{\text{BX}} \cong J_{\text{AB}} \cong \nu_{\text{A}} - \nu_{\text{B}} \cong 15.6$ Hz), 7.164 (d, $J = 8.7$ Hz, 4H), 7.767 (dd, $J_{\text{HH}} = 9.0$ Hz, $J_{\text{PH}} = 2.1$ 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 $\text{C}_{27}\text{H}_{30}\text{N}_3\text{O}_9\text{P}$ 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 chromatogra-

phy: ^1H 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, $\text{M}^+ - \text{N}(\text{CMe}_3)_2$], 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: ^1H NMR δ 3.79 (d, $J_{\text{PH}} = 11.1$ Hz, 6H), 7.87 (d, $J = 8.7$ Hz, 2H), 7.42 (dd, $J = 8.7$, 1.5 Hz), 7.77 (d, $J_{\text{PH}} = 24.0$ 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, $J_{\text{PC}} = 6.2$ Hz), 123.70, 124.3 (d, $J_{\text{PC}} = 1.6$ Hz), 129.3, 130.1 (d, $J_{\text{PC}} = 22.0$ Hz), 141.5 (d, $J_{\text{PC}} = 7.5$ Hz), 142.7 (d, $J_{\text{PC}} = 10.1$ Hz), 147.77 (d, $J_{\text{PC}} = 8.1$ Hz); ^{31}P NMR δ 18.13; GC and HRMS m/z (relative intensity) 378.0619 (100, calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{O}_7\text{P}$ 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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