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Reactivity of the >P-O⁻ Nucleophiles Toward Arylmethyl Chloride Systems*†

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ABSTRACT: *The reactions of sodium dimethyl and diisopropyl phosphite, as well as dibenzylphosphinite with 4-nitrobenzyl chloride, 9-chlorofluorene, and diphenylchloromethane were studied in detail by the isolation and identification of all the products, and the examination of the effects of the solvents on the product distribution. The results of the performed experiments are compatible with the proposed mechanism: a >P-O⁻ anion acts toward an arylmethyl chloride as a base and abstracts a proton to form a carbanion, which can then participate in the SET processes to produce carbon-centered radicals. Additionally, the >P-O⁻ reagent can act as a carbon-centered radical trap if it is present in a high enough concentration.*
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INTRODUCTION

The reaction between salts of trivalent phosphorus acids and alkyl halides yielding products with a C–P bond is known as the Michaelis–Becker reaction [1,2]. Both benzylphosphonates with a wide range of substituents on the phenyl ring [3–5] and phosphonomethylpyridines [6–9] are also available for use in the Michaelis–Becker reaction. Exceptions are found with nitro derivatives; Kreutzkamp and Cordes [10] reported failures of attempted direct preparations of *p*-nitrobenzylphosphonates from *p*-nitrobenzyl chloride or bromide, and trialkyl phosphites, as well as the salts of dialkyl phosphites.

The anions of the >P-O⁻ type are of special interest; they are nucleophilic ambident reagents [11–13], strong bases [14,15], free radical traps, and are also considered as single electron donors [16–18]. On the other hand, compounds of the >P(O)H structure can act as proton [19,20] or hydrogen [21,22] sources, depending on the structure and reaction conditions.

Recently, we have been able to demonstrate that the anions of the >P-O⁻ type undergo a reaction with α-bromocarboxylates as well as with phosphonates yielding debrominated products [23–25]. Furthermore, according to the reduction potential of the *p*-substituted benzyl bromides and the solvent used, we have also been able to demonstrate that in the reaction of these starting materials with a nucleophilic reagent of the >P-O⁻ type, the formation of the P–C bond, debromination, and/or dimerization occur [26–28].

The results of our research strongly indicate that halophilic substitution is the principal process of the reaction in focus. This halophilic substitution results in carbanion formation, which, depending on the redox potentials, can participate in the proton and/or electron transfer processes producing debrominated products and/or dimers. Additionally, we have stud-

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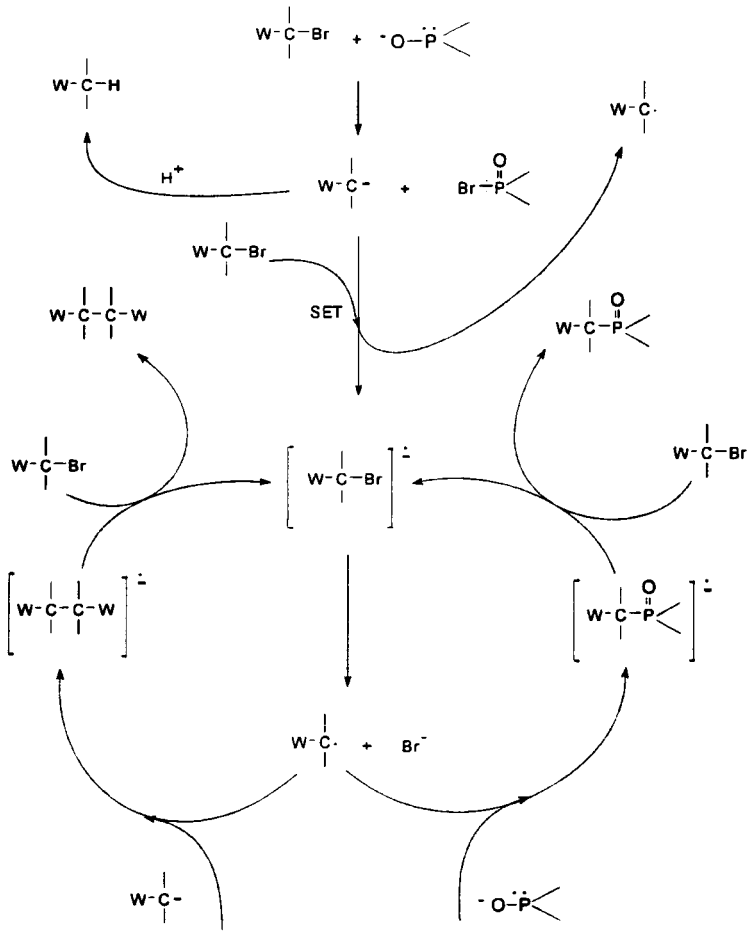
ied in detail the reaction of >P-O⁻ nucleophiles with bromodiphenylmethane, 9-bromofluorene, and triphenylmethyl bromide. In these cases, the results of the experiments carried out are compatible with the proposed X-philic substitution/SET tandem mechanism outlined in Scheme 1 [29].

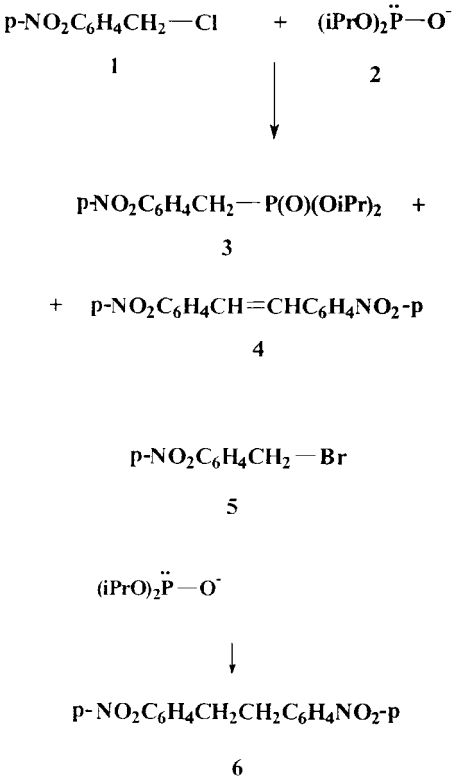
Russell et al. [30] reported that dialkyl phosphite anions react with *p*-nitrobenzyl chloride and α,α-dimethyl-*p*-nitrobenzyl chloride to form *p*-nitrobenzylphosphonates in moderate to good yield and *p*,*p*′-dinitrostilbene (in the case when *p*-nitrobenzyl chloride was used). The experimental data they collected illustrate the effect of irradiation and inhibitors on the yield of this reaction. Thus, under standard conditions (20 hours of sun lamp irradiation at −78°C in THF), the yield of the *p*-nitrobenzylphosphonate was reduced from 34 to 9% by the presence of 5 mol % of di-tert-butylnitroxide. He postulated that this reaction proceeds at least partially by a free-radical-chain $S_{RN}1$ process.

We showed previously [26] that *p*-nitrobenzyl chloride, without photostimulation, in reaction with the diisopropyl phosphite anion, yielded diisopropyl *p*-nitrobenzylphosphonate **3** and 4,4′-dinitrostilbene **4** in almost a 2:1 molar ratio of products (3 hours; THF; 20°C). In contrast to that result, the treatment of 1 equivalent of *p*-nitrobenzyl bromide in THF at 20°C with 1 equivalent of the diisopropyl phosphite anion, dimethyl phosphite anion, or the dibenzylphosphinite anion produced one major product, namely, 1,2-di(*p*-nitrophenyl)ethane **6** (Scheme 2).

What is the reasonable explanation for this different reactivity of *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide toward >P-O⁻ nucleophiles? In the case of *p*-nitrobenzyl bromide, the halophilic substitution resulting in carbanion formation is the principal process. The results of experiments by Russell et al. strongly suggest that in the reaction between p-nitrobenzyl chloride and the >P-O⁻ anions, the $S_{RN}1$ chain process operates. What is the initia-



SCHEME 1



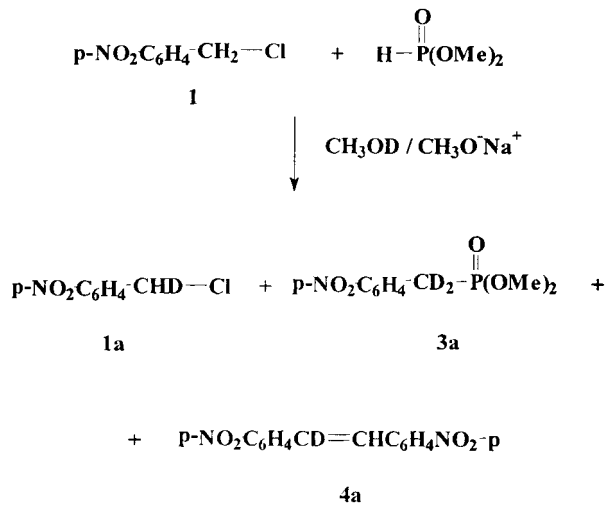
SCHEME 2

tion step in this case? To answer this question and to check the scope and limitations of this type of reactivity of the >P-O⁻ ions toward the C–Cl bond, we decided to study the reactions of other arylmethyl chloride systems: *p*-nitrobenzyl chloride, chlorodiphenylmethane, and 9-chlorofluorene. In this article, we present the results of these investigations.

RESULTS AND DISCUSSION

From the reaction of 1 equivalent of *p*-nitrobenzyl chloride with 1 equivalent of dimethyl phosphite in methanol-O-d in the presence of sodium methoxide, we isolated: dimethyl (4-nitrophenyl)methyl-d_2-phosphonate **3a** (30%), 4,4′-dinitrostilbene **4a** (39%; the product of deuterium incorporation in the benzylic position is about 30%), and 4-nitro-α-deuterobenzyl chloride (28%) **1a** (Scheme 3). The deuterium incorporation in the isolated products was estimated on the basis of ^{1}H NMR spectroscopy. This analysis might be of a mixture of d_0, d_1, and d_2 compounds; however, the important point is the observed hydrogen-deuterium exchange under the reaction conditions.

The deuterated starting material (**1a**) isolated from this reaction mixture is derived from the initial proton abstraction product: the 4-nitrobenzyl chloride anion (after reaction with methanol-O-d).



SCHEME 3

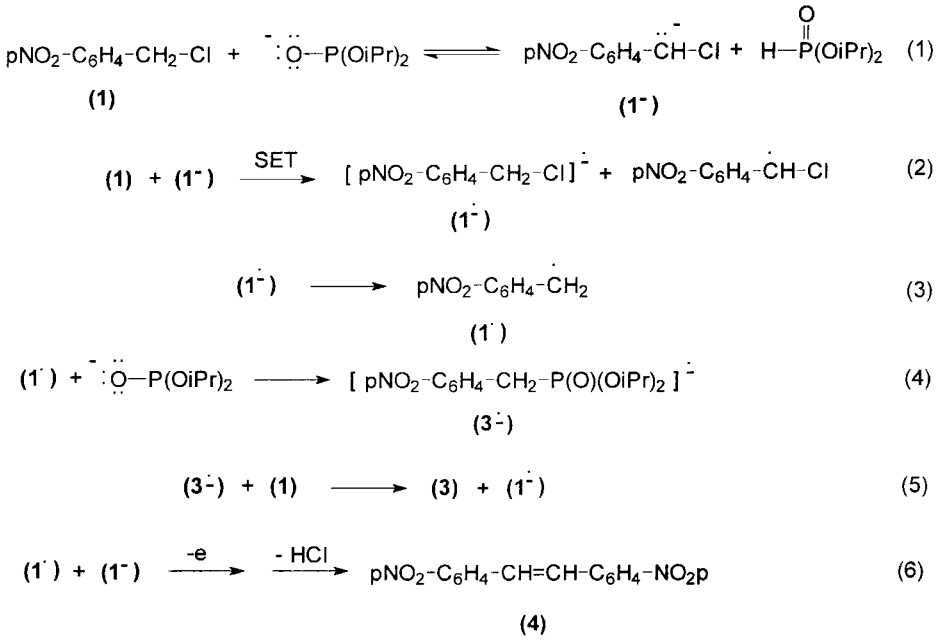
The 4-nitrobenzyl chloride anion as an intermediate can transfer a single electron to 4-nitrobenzyl chloride to provide the anion radical of 4-nitrobenzyl chloride (Equation 2 of Scheme 4), which fragments to produce the 4-nitrobenzyl radical (Equation 3). This radical can react with the nucleophiles present in the reaction mixture, in our case the >P-O⁻ anion, to produce the anion radical of the 4-nitrobenzylphosphonate (Equation 4), or the 4-nitrobenzyl chloride anion to produce the 1-chloro-1,2-di-*p*-nitrophenylethane anion radical (Equation 6). Subsequent electron transfer from these anion radicals to 4-nitrobenzyl chloride completes the propagation sequence (Equations 2, 5).

Another interesting feature of this reaction is that *p*-nitrobenzyl chloride, without photostimulation, in a reaction with dialkyl phosphite anions, yields 4-nitrobenzylphosphonates and 4,4′-dinitrostilbene in almost a 2:1 molar ratio of products (3 hours; THF; 20°C). The reaction sequence presented in Scheme 4 offers an explanation to these observations.

We have assumed that the >P-O⁻ anion is involved in an equilibrium state (Equation 1, of Scheme 4) and in the elimination of HCl from 1-chloro-1,2-di-*p*-nitrophenylethane to produce stilbene (Equation 6). As a consequence, the >P-O⁻ anion would never be present in a high enough concentration to couple effectively with the 4-nitrobenzyl radical. Additionally, Russell et al. were able to demonstrate in their elegant set of competitive experiments that the dialkyl phosphite anions are less reactive toward carbon-centered radicals as against other nucleophiles (nitronate, malonate, as well as thiophosphite anions) [17,30]. If the concentration of the >P-O⁻ anion was built up sufficiently, it could

compete with the 4-nitrobenzyl chloride anion for the 4-nitrobenzyl radical and generate the 4-nitrobenzylphosphonate by a chain sequence. If this concept is correct, we would expect to find a much higher yield of the 4-nitrobenzylphosphonate **3** in the reaction carried out with an excess of the >P-O$^-$ anion present. This expectation has been verified by experiment. The reaction of 1 equivalent of 4-nitrobenzyl chloride with 10 equivalent of sodium diisopropyl phosphite in THF produced only one product, namely, diisopropyl 4-nitrobenzylphosphonate (see Table 1, run 2). The results of this set of experiments show that the >P-O$^-$ anions are indeed able (if present in high enough concentrations) to compete with the 4-nitrobenzyl chloride anion for 4-nitrobenzyl radicals and to generate the phosphonates by a chain sequence. At this point, one can also argue that a high phosphite concentrations may also be conducive to a rapid S_N2 substitution occurring in competition with the radical anion processes. On the other hand, it is well known that exposure to light doesn't affect S_N2 reactions. However, the action of light can speed up a radical anion substitution process. Numerous instances of the light effect have been found, some of them very substantial. In order to provide evidence for the SET mechanism operating in this reaction, we ran the reaction of *p*-nitrobenzyl chloride with a 10-fold excess of the $(i\text{-PrO})_2PO^-$ nucleophile for 20 minutes in THF at −78°C under a variety of conditions: in darkness, in daylight, and with irradiation by use of a 500 W bulb. The results of these experiments are summarized in Table 2. As one can see from the data shown in Table 2, we found a substantial influence of light on the yield of isolated phosphonate ester **3**.

Aminoxyl radicals are known to scavenge carbon-centered radicals, as well as diphenylphosphinoyl and dimethoxyphosphinoyl radicals, at almost diffusion-controlled rates. We performed the reaction between *p*-nitrobenzyl chloride and a 10-fold ex-



SCHEME 4

TABLE 1 The Products Distribution of the Reaction between Sodium Diisopropylphosphite and 4-Nitrobenzyl Chloride at Different Ratios

			% of yield		
Run	**1** (*mmol*)	**2** (*mmol*)	**1**	**4**	**3**
1	2.5	2.5	50	26	21
2	1.25	12.5	–	–	92

TABLE 2 Light Influence on the Products Distribution of the Reaction between 4-Nitrobenzyl Chloride and a 10-Fold Excess of Sodium Diisopropylphosphite

		% of yield		
Run	*Conditions*	**1**	**3**	**4**
1	Darkness	87	9	0
2	Daylight	51	42	0
3	Light of 500 W bulb	0	91	0

cess of sodium diisopropylphosphite in the presence of di-*tert*-butylnitroxide (daylight; without supplemental illumination). From this reaction mixture we isolated *N*,*N*-di-*tert*-butyl-*Q*-*p*-nitrobenzylhydroxylamine (46%) but the O-phosphorylated *N*,*N*-di-*tert*-butylhydroxylamine was not detected.

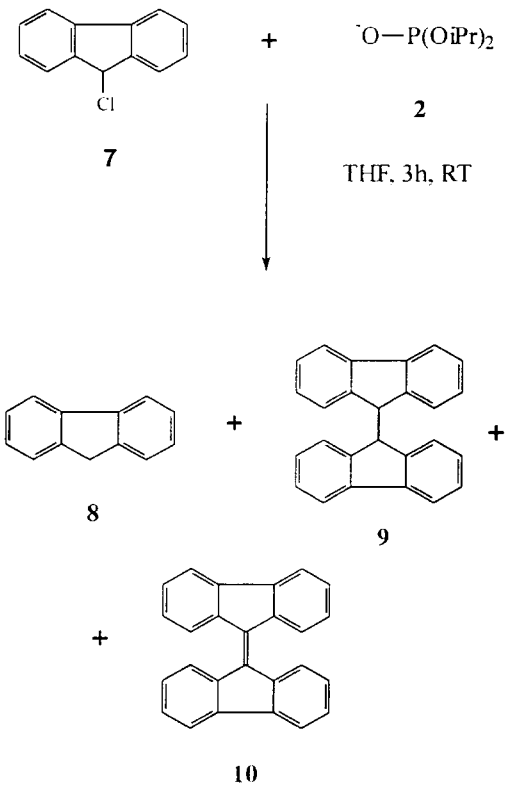
The influence of light on the yield of the phosphonate ester **3**, as well as the isolation from the reaction mixture of *N*,*N*-di-*tert*-butyl-*O*-*p*-nitrobenzylhydroxylamine, arising from the coupling of di-*tert*-butylnitroxide with the *p*-nitrobenzyl radical, strongly suggests that the reaction proceeds via the $S_{RN}1$ mechanism. A 10-fold excess of >P-O⁻ nucleophile allows the reaction to proceed via this mechanism as well.

The reaction of 9-bromofluorene with the >P-O⁻ anions produces mainly 9,9′-bifluorenyl (in THF as a solvent) or fluorene (in alcohol as a solvent) [29]. In contrast to that result, the reaction of 9-chlorofluorene with sodium diisopropylphosphite in THF produces a complex mixture of products: fluorene **8**, 9,9′-bifluorenyl **9**, and 9,9′-bifluorenylidene **10** (see Scheme 5 and Table 3).

As one can see from the data collected in Table 3, treatment of 1 equivalent of 9-chlorofluorene with 1 equivalent of the phosphite anion gives only a 53% conversion. We recovered 47% of 9-chlorofluorene from this reaction mixture and three products: fluorene **8** (3%), 9,9′-bifluorenyl **9** (16%), and 9,9′-bifluorenylidene **10** (32%). On the other hand, treatment of 1 equivalent of 9-chlorofluorene with 2 equivalents of the phosphite anion gives 80% conversion with one major product, 9,9′-bifluorenylidene **10** (54%), and two minor products, 9,9′-bifluorene **9** (19%) and fluorene **5** (5%). Additionally, we carried out the reaction of 1 equivalent of 9-chlorofluorene with 1 equivalent of dimethyl phosphite in methanol-O-d in the presence of sodium methanolate (3 hours, 20°C). From this reaction mixture we isolated 9-chloro-9-deutero-fluorene (97%).

The formation of 9,9′-bifluorenylidene **10** in the reaction, as well as the ability of the 9-chlorofluorene to undergo proton exchange in the basic medium, is in full agreement with the idea that the >P-O⁻ anion participates in an acid-base equilibrium with 9-chlorofluorene. On the other hand, the 9-chlorofluorene anion can transfer an electron to 9-chlorofluorene to form the fluorene radical, which can then react with the nucleophilic reagents present in high enough concentration in the reaction mixture to produce anion radicals of the products and/or, as a stable radical, can dimerize as well as undergo one electron reduction to form 9,9′-bifluorene and fluorene. This behavior of the 9-fluorene radical has been observed during electrolysis of 9-chlorofluorene [31]. Additionally, Bordwell [32] has reported 9,9′-bifluorenyl formation as a result of the recombination of the 9-fluorenyl radical obtained from oxidation of the 9-fluorenyl anion.

The structure of diphenylchloromethane seems to be sufficiently similar to that of 9-chlorofluorene, so we expected similar reactivity of diphenylchloromethane toward dialkylphosphite anions. To our surprise, the >P-O⁻ anions showed no detectable reactivity relative to the diphenylchloromethane. We carried out a set of experiments using different R_2P-O⁻ anions (R = OMe, OEt, OiPr, CH_2Ph) in THF, as well as the use of toluene at 20°C and also at the boiling point of the solvent. In all cases, the starting material, diphenylchloromethane, was recovered.



SCHEME 5

TABLE 3 The Products Distribution of the Reaction between 9-Chlorofluorene and Sodium Diisopropyl Phosphite at Different Ratios

			% of yield			
Run	**7** (*mmol*)	**2** (*mmol*)	**7**	**8**	**9**	**10**
1	5	5	47	3	16	32
2	5	10	20	5	19	54

At this point, it was very important to check if diphenylchloromethane was able to exchange its proton in the benzylic position. The treatment of 1 equivalent of diphenylchloromethane with 1 equivalent of dimethyl phosphite in methanol-O-d in the presence of sodium methanolate at −20°C yielded diphenylmethyl-d-chloride (deuterium incorporation 98%).

^{31}P NMR spectroscopy offers the exceptional opportunity to distinguish between the structure of the >P-O$^-$ nucleophile and the >P(O)H acid. Using ^{31}P NMR spectroscopy, the mode of interaction between sodium diisopropylphosphite and diphenylchloromethane was examined. While the ^{31}P NMR spectrum of sodium diisopriopylphosphite in THF displayed a single resonance at δ_P = 152.7, the addition of diphenylchloromethane at 20°C produced a ^{31}P NMR spectrum displaying two signals at δ_P = 152.7 and δ_P = 4.7, which were identified as the resonances of the $(iPrO)_2$P-O$^-$ anion and the diisopropyl phosphite, respectively (see Figure 1).

This ^{31}P NMR spectrum shows that a >P-O$^-$ anion participates in the acid-base equilibrium with diphenylchloromethane.

Taking into consideration the proton exchange ability of the diphenylchloromethane and the ^{31}P NMR experiments presented in Figure 1, one can conclude that the >P-O$^-$ anion is able to abstract a proton from diphenylchloromethane, producing a diphenylchloromethane anion. If this is so, why do we observe such a different reactivity of this anion in comparison with that of 4-nitrobenzyl chloride, as well as that of the 9-chlorofluorene anion?

It is well known that the success of the electron transfer reaction is the result of a less negative reduction potential of the alkyl, aryl halides [33,34,35,36]. To evaluate the feasibility of the SET process in the reactions in focus, we decided to measure the reduction potentials of the benzyl type chlorides used in this investigation: 4-nitrobenzyl chloride (A), 9-chlorofluorene (B), and diphenylchloromethane (C). Table 4 and Figure 2 show the most relevant information concerning the electrochemical reduction of the substrates A, B, C.

Cyclic voltammetry of the investigated substrates showed one or two irreversible waves according to the relative reducibility of the benzyl type chloride R-Cl (A, B, C) and of the radical R. All of them undergo reduction in the range of potential −0.8–2.2 V. Only in the case of 4-nitrobenzyl chloride does the second process seem to be reversible. But what is of interest is that the ease of reduction, as shown by the peak potential of the wave, is in the order 4-nitrobenzyl chloride (A) ≫ 9-chlorofluorene (B) ≫ diphenylchloromethane (C).

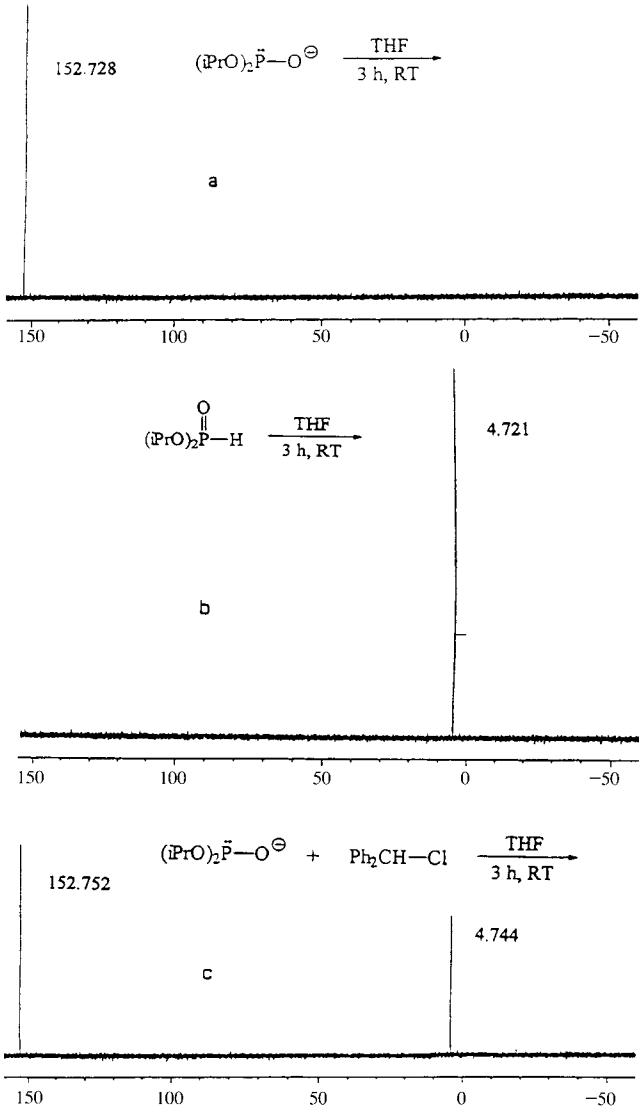


FIGURE 1 ^{31}P NMR spectra recorded in THF of: (a) sodium diisopropyl phosphite; (b) diisopropyl phosphite; (c) sodium diisopropyl phosphite:diphenylchloromethane = 1:1.

The redox data shown in Table 4 explains the inertness of diphenylchloromethane toward >P-O$^-$ nucleophiles. As one can see from this data, 4-nitrobenzyl chloride and 9-chlorofluorene possess less negative reduction potentials than diphenylchloromethane, and the electron transfer reaction is feasible, resulting in 4-nitrobenzyl as well as 9-fluorene radical formation. In contrast to that, the diphenylchloromethane possesses a very negative reduction potential and probably is not able to participate in the electron transfer reaction. This is precisely what was observed.

CONCLUSIONS

The results of our previous investigations [23–29] have shown that, in the case of the carbon–bromine

TABLE 4 Cyclic Voltammetric Peak Potentials[a] Determined for the Substrates 4-Nitrobenzyl Chloride (A), 9-Chlorofluorene (B), Diphenylchloromethane (C)

Compound	*A*	*B*	*C*
I Process			
E^1_{pc} (V vs. SCE)	−0.887 V (ir)[b]	−1.430 V (ir)	−2.095 V (ir)
II process			
E^2_{pC}	−1.160 V		
E^2_{pa} (V vs. SCE)	−1.097 V		
Other			
E_{pa} (V vs. SCE)		−0.558 V	

[a]Measured at static mercury drop electrode, in DMF + 0.1 M TEAP at 25°C.
[b]ir, irreversible.

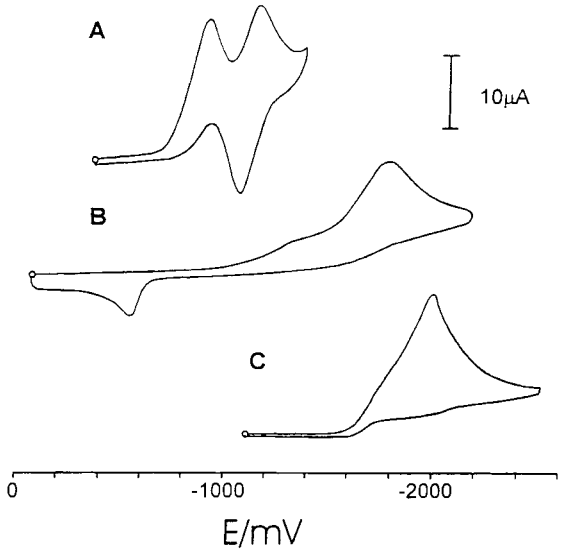


FIGURE 2 Cyclic voltammetry of A, B, and C (1 mM) on static mercury drop electrode in DMF + TEAP at 25°C, scan rate 0.1 Vs^{-1}. Vertical scale in μA; horizontal scale in V vs. SCE.

bond, bromine can be a target for nucleophilic attack by the phosphorus reagent of the >P-O⁻ type with the release of the carbanion as a nucleofuge. This carbanion can initiate the SET process or participate in a proton transfer reaction. In contrast to that, in the case of the carbon–chlorine bond, the chlorine atom is not a good target for the halophilic substitution by the >P-O⁻ reagent. This anion acts rather as a base and abstracts a proton to form the carbanion that can participate in the single electron transfer processes, producing a carbon centered radical. In both cases, the anion of the >P-O⁻ type can act as a carbon-centered radical trap and not as a single electron donor.

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran was dried with a sodium-potassium alloy. Melting points were uncorrected. The IR spectra were taken on a Jena-Zeiss IR 10 apparatus. ^{31}P NMR and ^{1}H NMR spectra were recorded with a Varian apparatus at 60, 200, or 500 MHz.

Reaction of 4-Nitrobenzyl Chloride **1** *with Dimethyl Phosphite in the Presence of $NaOCH_3$ in Methanol-O-d.*

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol-O-d and into the resultant mixture, dimethyl phosphite (2.5 mmol, 0.275 g, 0.23 mL) in 5 mL of methanol-O-d and 4-nitrobenzyl chloride **1** (2.5 mmol, 0.428 g) in 10 mL of methanol-O-d were added. The reaction mixture was stirred for 3 hours at room temperature, then diluted with 75 mL of ether, washed with 50 mL of saturated NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in a vacuum and the products were separated by radial chromatography to yield: 4-chloromethyl-d-nitrobenzene **1a** (eluted with hexane), 0.121 g (28%), m.p. 72–74°C IR (KBr) ν (cm^{-1}) = 1520, 1355 NO_2 ^{1}H NMR ($CDCl_3$) δ = 4.63 (t, $^2J_{H\text{-}D}$ = 2.54 Hz, CHD, 1H), 7.50–7.62 (m, aromat, 2H), 8.18–8.28 (m, aromat, 2H) 4,4′-dinitrostilbene **4a** (eluted with chloroform), 0.132 g (39%), m.p. 295–300°C IR (KBr)ν (cm^{-1}) = 3050 CH=CH, 1520, 1355 NO_2 ^{1}H NMR ($CDCl_3$) δ = 6.71 (s, CH, 1.4H), 6.85 (d, $^3J_{HH}$ = 8.00 Hz, aromat, 4H), 7.67 (d, $^3J_{HH}$ = 8.00 Hz, aromat, 4H) dimethyl (4-nitrophenyl)methyl-d_2-phosphonate **3a** (eluted with chloroform), 0.185 g (30%), m.p. 74–75°C IR (KBr) ν (cm^{-1}) = 1260 P=O, 1040 P–O–C, 1530, 1350 NO_2 ^{1}H NMR ($CDCl_3$) δ = 3.73 (d, $^3J_{PH}$ = 10.92 Hz, P–O–CH_3, 6H), 7.08–7.18 (m, aromat, 2H), 7.75–7.85 (m, aromat, 2H) ^{31}P NMR ($CDCl_3$) δ = 27.31

The Reaction Between 4-Nitrobenzyl Chloride **1** *or 9-Chlorofluorene* **7** *and the Sodium Salt of Diisopropyl Phosphite* **2** *with Variable Ratios of 1/2 or 7/2 in THF solution*

General Procedure. To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF, a solution of diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased, 4-nitrobenzyl chloride **1** or 9-chlorofluorene **7** (2.5 mmol) in 5 mL of THF was added, and the reaction mixture was stirred for 3 hours at room temperature, diluted with 50 mL of ether, washed

with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in a vacuum, and the products were separated by radial chromatography. The products were identified by comparisons of spectral data with those of the authentic samples.

The previous experiment was repeated with different ratios of 1/2 and 7/2. The results are summarized in Table 1 and Table 3.

Table 3 Run 1. fluorene **8** (eluted with hexane), 0.012 g (3%), m.p. 113–115°C (116°C, Ref. [37]) 9-chlorofluorene **7** (eluted with hexane), 0.236 g (47%), m.p. 89–91°C (90°C, Ref. [38]) 9,9′-bifluorenyl **9** (eluted with chloroform), 0.066 g (16%), m.p. 239–241°C (240–242°C, Ref. [39]) bifluorenylidene **10** (eluted with chloroform), 0.131 g (32%), m.p. 185–187°C (182–187°C, Ref. [40])

Influence of Light on the Reaction Between 4-Nitrobenzyl Chloride **1** *and a 10-fold Excess of Sodium Diisopropyl Phosphite in THF Solution*

General Procedure. To a suspension of NaH (30.0 mmol, 0.72 g) in 50 mL of THF was added diisopropyl phosphite (25 mmol, 4.2 g) in 10 mL of THF. When the evolution of hydrogen had ceased, 4-nitrobenzyl chloride **1** (2.5 mmol, 0.43 g) in 5 mL of THF was added and the reaction mixture was stirred for 20 minutes at −78°C, then diluted with 50 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in a vacuum and the products were separated by radial chromatography.

The above experiment was repeated in a flask shielded from all light and in a flask irradiated by the 500 W bulb. The yields for the reactions carried out under normal conditions, daylight, darkness, and in the presence of light (500 W bulb), are summarized in Table 2.

The Reaction Between 4-Nitrobenzyl Chloride and a 10-fold Excess of the Sodium Salt of Diisopropyl Phosphite in the Presence of Di-t-Butyl Nitroxide in THF Solution

To a suspension of NaH (15.0 mmol, 0.36 g) in 10 mL of THF, a solution of diisopropyl phosphite (12.5 mmol, 2.10 g) in 50 mL of THF was added. When the evolution of hydrogen had ceased, di-*t*-butyl nitroxide (1.25 mmol, 0.18 g) and 4-nitrobenzyl chloride (1.25 mmol, 0.22 g) in 5 mL of THF were added. The reaction mixture was stirred for 3 hours at room temperature, diluted with 75 mL of ether, washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed in a vacuum, and the products were separated by radial chromatography. *N,N*-di-*t*-butyl-*O*-(4-nitrobenzyl)-hydroxylamine (0.16 g, 46%) was eluted with chloroform, IR (film) ν (cm^{-1}) = 1210, C-O-N, 1350, 1525 NO_2; ^1H NMR ($CDCl_3$) δ = 1.18 (s, CH_3, 18 H), 4.82 (s, CH_2-O-N<, 2H), 7.39 (d, $^3J_{HH}$ = 8.80 Hz, aromatic, 2H), 8.10 (d, $^3J_{HH}$ = 8.80 Hz, aromatic, 2H). Anal. calcd for $C_{15}H_{24}N_2O_3$: C, 64.26%; H, 8.36%; found: C, 64.31%; H, 8.24%.

Cyclic Voltammetry

Cyclic voltammetry (CV) experiments were performed at 25°C in a three-electrode measuring cell with a static mercury drop electrode of 0.56 mm diameter used as a working electrode and a platinum wire (ϕ = 0.8 mm) reported versus a NaCl saturated calomel electrode (SEC) that was connected to the measurement cell by a salt bridge filled with 0.1 M tetraethylammonium perchlorate (TEAP) in DMF. All measurements were made using a potentiostat EP-20A (UNIPAN, Poland) and voltage generator EG-20 (UNIPAN, Poland). The XY-recorder 4100 (Laboratorny Prystroye, Czech Republic) was used to record CVs. The apparatus was equipped with an automatic feedback unit to eliminate the potential due to the solution resistance. To test IR drop compensation, CV curves were recorded at 25°C for the standard ferricenium/ferrocene reversible system in DMF. The difference obtained between the peak and half-peak potential was $[E_{p/2} - E_p] = 0.056$ V, a value very close to theoretical value of 0.0565 V for 25°C.[41] It can be concluded that the IR drop does not affect the result under the experimental condition.

Reagents. The solvent (DMF) was purified according to a procedure described in the literature [42]. TEAP was crystallized twice from methanol/water (10:1 v/v) and dried for 48 hours at 50°C under reduced pressure before use.

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