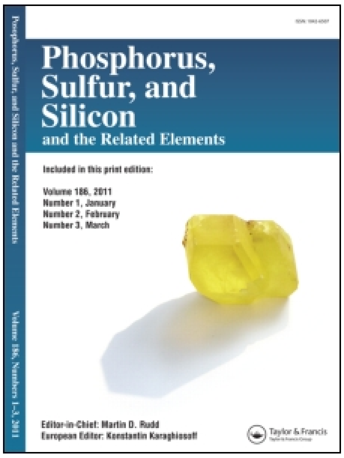

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART II.† THE REACTION OF TRIVALENT PHOSPHORUS ACID SALTS WITH THE BENZYLIC HALIDES SYSTEM‡

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The reaction of the benzylic halides systems with sodium dialkylphosphites as well as the sodium salt of dibenzylphosphine oxide in THF and alcohols as the solvents is described. According to the constitution of the starting materials, the formation of the P—C bond, dehalogenation or dimerization occurs. Probable mechanisms namely SET and X-philic substitution are discussed.

Key words: Benzylic halides system, dialkylphosphites, dibenzylphosphine oxide, Michaelis-Becker reaction, X-philic substitution.

INTRODUCTION

The most common and versatile pathway for the formation of the carbon-phosphorus bond is the Michaelis-Becker reaction,[1] involving the salts of trivalent phosphorus acids and an electrophile. Dialkyl phosphite anions give a satisfactory yield of the products of the Michaelis-Becker reaction only with primary alkyl halides. Secondary and tertiary alkyl halides give with dialkyl phosphite anions a poor yield or a complex mixture of the products.[2]

$$>P\text{-}O^- + R\text{-}X \longrightarrow R\text{-}P(O)< + X^-$$

Benzylphosphonates[3,4b] with a wide range of substituents in the benzyl ring as well as phosphonomethyl pyridines[5] are also available in the Michaelis-Becker reaction. The exceptions are nitro derivatives; there is reported a failure of an attempted direct preparation of a p-nitrobenzylphosphonate from p-nitrobenzyl chloride or bromide and trialkyl phosphites as well as the salts of dialkyl phosphites.[4] It is interesting enough that m-nitrobenzyl chloride or bromide gives with trialkyl phosphites m-nitrobenzylphosphonates.[4b,6] On the other hand A. Williams published the direct preparation of diethyl p-nitrobenzylphosphonate from p-nitrobenzyl bromide and triethyl phosphite (without yield and analytical data).[7]

B. A. Arbuzov[8] showed that benzyl halides treated with the sodium salt of diethyl phosphite give diethyl benzylphosphonate, regardless of the nature of the halide

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†Part I see lit. 11d.

‡Dedicated to Professor H. M. Walborsky on the occasion of his 70th birthday.

(benzyl chloride, -bromide and -iodide were studied). He showed also that diphenylchlormethane undergoes reaction with the sodium salt of diethyl phosphite to yield diethyl diphenylmethylphosphonate. In contrast to this tetraphenylethane was isolated from the reaction mixture of bromodiphenylmethane and sodium diethyl phosphite. Furthermore, B. A. Arbuzov[8] published that 9,10-dibromo-9,10-dihydrophenantrene in the reaction with sodium diethyl phosphite gives phenantrene, on the other hand chlorodinaphthylmethane, 9-chloro- as well as 9-bromofluorene are inert towards sodium diethyl phosphite.

The Michaelis-Becker reaction is often assumed to be a S_N2 process involving the nucleophilic phosphorus atom. However, the reaction between bromo-triphenylmethane and sodium diethyl phosphite was claimed to be a free radical process.[9]

Additionally, G. A. Russell[10] reported that dialkyl phosphite or thiophosphite anions react with p-nitrobenzyl chloride, and α,α-dimethyl-p-nitrobenzyl chloride to form p-nitrobenzylphosphonates or thiophosphonates. He showed that this reaction proceeds at least partially by the $S_{RN}1$ scheme. Thus, under standard conditions (20 h of sun lamp irradiation at −78–28°C in THF), the yield of p-nitrobenzylphosphonate was reduced from 34% to 9% by the presence of 5 mol% of $(t\text{-But})_2NO$. The experimental data he collected illustrate the effect of irradiation and inhibitors on the yield of this reaction.

For several years we have been interested in the different reactivity between the two types of phosphorus nucleophiles, namely $>P{-}O^-$ and $R{-}O{-}P<$ towards electophiles. To continue our studies of the mechanisms of the reactions involving phosphorus nucleophiles,[11] the reaction of dialkyl phosphite anions and the dibenzyl phosphinite ion $(PhCH_2)_2PO^-$ with the benzyl type halogenides is being studied now. In this paper we wish to present the preliminary results of this study.

RESULTS

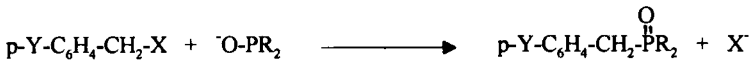
E. S. Lewis and co-workers[12] discovered that when dimethyl phosphite dissolved in THF or in benzene, is treated with sodium hydride at room temperature, the initially formed anion is virtually quantitatively alkylated by the remaining neutral ester before it can react with sodium hydride, yielding the monomethyl phosphite anion and dimethyl methylphosphonate. This major side reaction is less important with diethyl phosphite and is not detected with neopentyl ester.

To avoid this side reaction we chose for our experiments diisopropyl phosphite and dibenzylphosphine oxide.

When treated with the sodium salt of diisopropyl phosphite as well as with the sodium salt of dibenzylphosphine oxide in THF or isopropanol benzyl halogenides **1** (benzyl-, p-t-butyl-benzyl, p-phenyl-benzyl chlorides and bromides) give diisopropyl benzylphosphonates **3** or tribenzylphosphine oxides **3** respectively, see Table I. To check the influence of the halogen on the course and the yield of the product of the Michaelis-Becker reaction we ran some experiments with the sodium salt of dibenzylphosphine oxide and benzyl chloride, benzyl bromide and benzyl iodide in THF at room temperature.

From the reaction mixture of benzyl halides **1** and the sodium salt of dibenzyl-

TABLE I

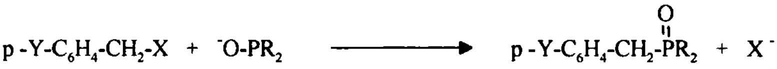


$$p\text{-}Y\text{-}C_6H_4\text{-}CH_2\text{-}X + {}^-O\text{-}PR_2 \longrightarrow p\text{-}Y\text{-}C_6H_4\text{-}CH_2\text{-}\overset{O}{\overset{\|}{P}}R_2 + X^-$$

1 3

X	Y	R	Solvent	% yield of 3	% recovery of 1
Cl	H	O-iPr	i-PrOH	26	73
			THF *	23	73
		CH_2Ph	i-PrOH	47	52
			THF	43	56
	$(CH_3)_3C$	O-iPr	i-PrOH *	24	74
			THF *	25	74
		CH_2Ph	i-PrOH	31	68
			THF	29	70
	C_6H_5	O-iPr	i-PrOH *	51	48
			THF *	46	53
		CH_2Ph	i-PrOH	52	46
			THF	55	45
Br	H	O-iPr	iPrOH	35	64
			THF	47	53
		CH_2Ph	iPrOH	46	53
			THF	47	51
	$(CH_3)C$	O-iPr	i-PrOH	40	58
			THF	32	68
		CH_2Ph	i-PrOH	41	57
			THF	31	68
	C_6H_5	O-i-Pr	i-PrOH	52	46
			THF	55	43
		CH_2Ph	i-PrOH	54	44
			THF	57	41

* Reaction was run at the boiling point of the solvent



$$p\text{-}Y\text{-}C_6H_4\text{-}CH_2\text{-}X + {}^-O\text{-}PR_2 \longrightarrow p\text{-}Y\text{-}C_6H_4\text{-}CH_2\text{-}\overset{O}{\overset{\|}{P}}R_2 + X^-$$

1 2 3

X: Cl; Br Y: H; t-Bu; Ph R: O-iPr; CH_2Ph

phosphine oxide we isolated only tribenzylphosphine oxide 3 and the starting materials. Benzyl iodide, however, gives a slightly higher yield of the product of the Michaelis-Becker reaction in comparison with chloro and bromo derivatives.

$$\underset{\mathbf{1}}{C_6H_5\text{-}CH_2\text{-}X} + \underset{\mathbf{2b}}{{}^-O\text{-}P(CH_2Ph)_2} \longrightarrow \underset{\mathbf{3}}{O{=}P(CH_2Ph)_3} + X^-$$

X	Yield % of **3**	% recovery of **1**
Cl	43	56
Br	47	51
I	55	44

In contrast to this the reaction of p-nitrobenzyl chloride **4a** with the diisopropyl phosphite anion is much more complex; we isolated from the reaction mixture of 1 equiv of the sodium salt of diisopropyl phosphite and 1 equiv of p-nitrobenzyl chloride in THF: diisopropyl p-nitrobenzylphosphonate **7** (21%), 4,4′-dinitrostyrene **6** (25%) along with the starting material p-nitrobenzyl chloride **4a** (50%).

$$\underset{\mathbf{4a}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Cl} + \underset{\mathbf{5a}}{Na^+\,{}^-O\text{-}P(OiPr)_2}$$

$$\downarrow$$

$$\underset{\mathbf{6}}{p\text{-}NO_2\text{-}C_6H_5\text{-}CH=CH\text{-}C_6H_4\text{-}NO_2\text{-}p} + \underset{\mathbf{7}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}P(O)(OiPr)_2}$$

On the other hand the treatment of 1 equiv of p-nitrobenzyl bromide in THF at 20°C with 1 equiv of the diisopropyl phosphite anion as well as the dibenzylphosphinite anion produces one major product. We isolated from the reaction mixture 1,2-di(p-nitrophenyl)ethane **8**; we could not find any compound with a P—C bond. When the reaction was carried out in i-PrOH the same product was isolated.

$$\underset{4b}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br} \xrightarrow[\text{THF or i-Pr-OH}]{{}^-O\text{-}P<} \underset{\mathbf{8}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p}$$

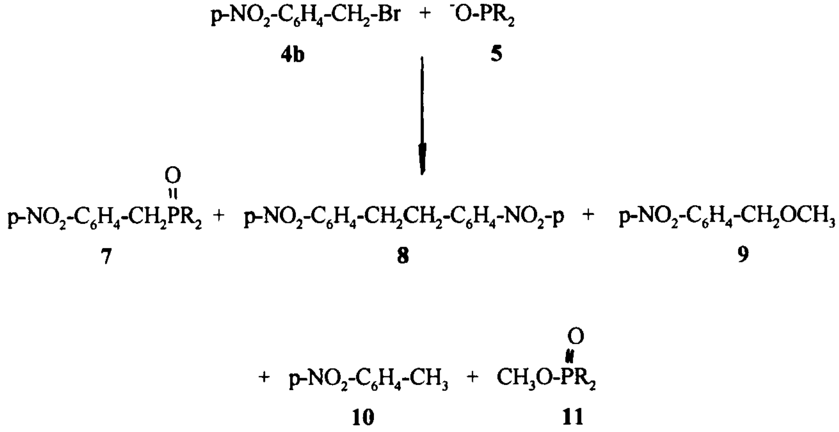
Moreover, treatment of 1 equiv of p-nitrobenzyl bromide with 3 equiv of the sodium salt of diisopropyl phosphite in THF produces diisopropyl p-nitrobenzylphosphonate **7** (R = O—iPr; 23%) and 1,2-di(p-nitrophenyl)ethane **8**.

When we used methanol as a solvent and sodium methanolate as a base, p-nitrobenzyl bromide with dibenzylphosphine oxide as well as dimethyl phosphite produces a more complex mixture of products, namely 1,2-di(p-nitrophenyl)ethane **8**, p-nitrotoluene **10** along with the solvolysis product methyl p-nitrobenzyl ether **9** and the starting material **4b**. Additionally in the case of dibenzylphosphine oxide we isolated methyl dibenzylphosphinate **11** (Table II, run 6).

TABLE II

The products of the reaction of p-nitrobenzyl bromide with the ion of the type $^{-}O{-}PR_2$

Run	R	Ratio 5/4b	Solvent	% of isoladed yield					
				4b	7	8	9	10	11
1	O-i-Pr	1	THF	18		81			
2		1	i-Pr-OH	20		79			
3		3	THF		23	74			
4	CH_2Ph	1	THF	57		42			
5		1	i-Pr-OH	51		48			
6		1	MeOH	22		12	28	35	48
7	O-Me	1	MeOH	29		12	26	28	



$$\underset{\textbf{4b}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br} + \underset{\textbf{5}}{^{-}O\text{-}PR_2} \longrightarrow \underset{\textbf{7}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\overset{O}{\overset{\|}{P}}R_2} + \underset{\textbf{8}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p} + \underset{\textbf{9}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2OCH_3}$$

$$+ \underset{\textbf{10}}{p\text{-}NO_2\text{-}C_6H_4\text{-}CH_3} + \underset{\textbf{11}}{CH_3O\text{-}\overset{O}{\overset{\|}{P}}R_2}$$

The yields of the products of the reaction between p-nitrobenzyl bromide and phosphite as well as phosphinite anions in THF and alcohols are shown in Table II.

DISCUSSION

The anions of the type $>P{-}O^{-}$ are of special interest; they are nucleophilic ambient reagents,[13] strong bases[14] and single electron donors.[10,11c,15] On the other hand the compounds of the structure >P(O)H can act as proton[16] or hydrogen[17] sources depending on the structure and reaction conditions.

The interaction of nitrobenzyl derivatives with bases and/or nucleophiles can give rise to processes involving charge transfer, electron transfer, proton transfer and σ-complex formation, as well as to nucleophilic substitution when a displaceable group is present. For example, the reaction of 4-nitrobenzyl chloride with sodium hydroxide which gives a high yield of 4,4′-dinitrostilbene **6** was originally presumed to proceed by carbene formation.[20] A careful reinvestigation of this reaction revealed that the kinetic and product data were in agreement with a single electron transfer mechanism involving carbenoid as a electron donor.[21]

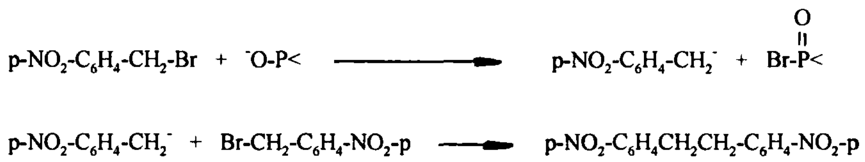
The p-nitrobenzyl halogenides are capable of undergoing the $S_{RN}1$ reaction with a wide range of nucleophiles.[10,18] Additionally, it is well known and documented that p- and o-nitrotoluene form spontaneously radical anions in the presence of strong bases.[19] It was also demonstrated that phenyl, vinyl and nitroalkyl radicals are readily trapped by dialkyl phosphite ions with the formation of the carbon-phosphorus bond.[22]

An analysis of the literature leads to several important observations. The reaction of 4-nitrobenzyl chloride proceeds smoothly with the hydroxide ion in ethanol as well as in dioxan to furnish the major product, namely 4,4'-dinitrostilbene **6** and other minor dimeric products (1,2-di(p-nitrophenyl)ethane **8** about 2%–5% and 1,2-di(p-nitrophenyl)acetylene about 10%) via an electron transfer pathway,[21] whereas both 4-nitrobenzyl bromide and 4-nitrobenzyl iodide react with the hydroxide ion in ethanol to give the solvolysis product, namely 4-nitrobenzyl ethyl ether and 4,4'-dinitrobibenzyl ether when the reaction is carried out in dioxan.[21,23] However, T-S. Kam[21c] showed that when the reactions are conducted in two-phase media with a phase transfer catalysis the competing solvolytic component is reduced and allows the electron transfer reaction to proceed. Under these conditions, the reaction of p-nitrobenzyl bromide **4b** furnishes up to 60% yield of ET derived dimeric products (4,4'-dinitrostilbene **6** as a major product along with 4,4'-dinitrophenylacetylene (10%) and 1,4-di(p-nitrophenyl)ethane **8** (2%)). Even the otherwise extremely labile iodide affords about 41% yield of dimeric products (stilbene **6** as a major product and bibenzyl **8** as a minor one).

The product which is isolated in the reaction of p-nitrotoluene with the alkoxide ion is actually 1,2-di(p-nitrophenyl)ethane **8** and/or 4,4'-dinitrostilbene **6**. The last one is believed to be formed through secondary processes via p,p'-dinitrobibenzyl **8**.[24]

As we showed above p-nitrobenzyl bromide in the reaction with phosphite as well as phosphinite ions in THF or in i-Pr—OH produces p,p'-dinitrobibenzyl **8** as the sole product. When the reaction is carried out in methanol p-nitrotoluene **10** (28–35%), p,p'-dinitrobibenzyl **8** (12%) along with the solvolysis product p-nitrobenzyl methyl ether **9** (26–28%) are produced (Table II, run 6 and 7).

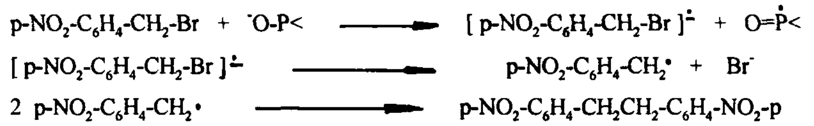
Pathway A:



$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br + {}^-O\text{-}P< \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^- + Br\text{-}\overset{\overset{O}{\|}}{P}<$$

$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^- + Br\text{-}CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p \longrightarrow p\text{-}NO_2\text{-}C_6H_4CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p$$

Pathway B:

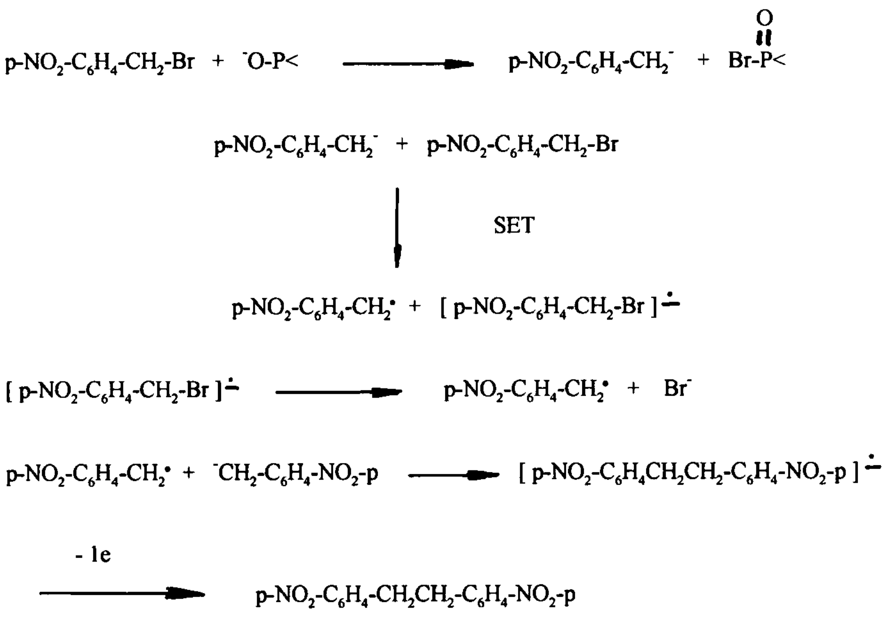


$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br + {}^-O\text{-}P< \longrightarrow [\,p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br\,]^{\bullet-} + O{=}\dot{P}<$$

$$[\,p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br\,]^{\bullet-} \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{\bullet} + Br^-$$

$$2\ p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{\bullet} \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p$$

Pathway C:



$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br + {}^{-}O\text{-}P< \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{-} + Br\text{-}\overset{O}{\overset{\|}{P}}<$$

$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{-} + p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br$$

$$\Big\downarrow \text{ SET}$$

$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{\bullet} + [\,p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br\,]^{\dot{-}}$$

$$[\,p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2\text{-}Br\,]^{\dot{-}} \longrightarrow p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{\bullet} + Br^{-}$$

$$p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2^{\bullet} + {}^{-}CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p \longrightarrow [\,p\text{-}NO_2\text{-}C_6H_4CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p\,]^{\dot{-}}$$

$$\xrightarrow{-\,1e} p\text{-}NO_2\text{-}C_6H_4\text{-}CH_2CH_2\text{-}C_6H_4\text{-}NO_2\text{-}p$$

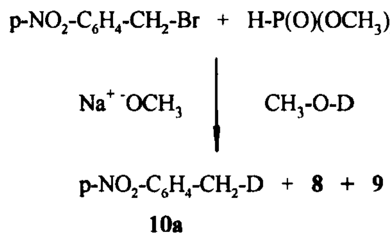
It is interesting enough that in our experiments with p-nitrobenzyl bromide p,p'-dinitrobibenzyl **8** was isolated without any trace of 4,4'-dinitrostilbene **6**, which would suggest the free radical intermediate and additionally excludes the SET process with carbenoid as an electron donor.[21] The p,p'-dinitrobibenzyl could be formed either via the p-nitrobenzyl radical (two possibilities: dimerization; addition to the p-nitrobenzyl anion) and also via the p-nitrobenzyl anion (its reaction with p-nitrobenzyl bromide, S_N2 process).

The ion of the type >P—O⁻ could a priori react with p-nitrobenzyl bromide either by the attack on the bromine atom (pathway A) or through SET; the radical chain mechanism or cage process with the >P—O⁻ ion as a single electron donor (pathway B) or the p-nitrobenzyl anion as a single electron donor (pathway C).

The major difference between these three pathways is that in pathway A and C the p-nitrobenzyl anion as an intermediate is proposed, whereas in pathway B the p-nitrobenzyl radical.

We decided to run a new experiment with p-nitrobenzyl bromide and dimethyl phosphite in the presence of sodium methoxide in methanol-O-d. If in this reaction the p-nitrobenzyl radical derived from p-nitrobenzyl bromide was an intermediate, then the radical would react with the solvent to abstract the hydrogen atom from the methyl group to yield R—H. If, on the other hand, the p-nitrobenzyl anion was an intermediate, then it would be quenched by methanol-O-d to give the deuterated product R—D.[25]

The treatment of p-nitrobenzyl bromide with dimethyl phosphite in the presence of sodium methanolate in methanol-O-d produces a complex mixture of products: p,p'-dinitrobibenzyl **8**, p-methyl-d-nitrobenzene **10a** along with the solvolysis product, namely p-nitrobenzyl methyl ether **9**.



The deuterium incorporation into the methyl group of p-nitrotoluene **10a** speaks strongly for the carbanion and against the free radical as an intermediate.

On the basis of the experiment with methanol-O-d as well as the isolation of methyl dibenzylphosphinate **11** (Table II, run 6) pathway B can be excluded.

By considering all the above pieces of evidence one can find that the nucleophilic displacements on the bromine with the release of the p-nitrobenzyl anion is the first step and the S_N2 mechanism (pathway A) is the most plausible one. However, one cannot completely exclude the major competing SET mechanism (pathway C) for p,p′-dinitrobibenzyl **8** formation.

In order to check the scope and limitations of this type of reactivity of $^-$O—P< ions, we decided to study other benzyl systems possessing electron withdrawing groups in the phenyl ring. We chose p-cyanobenzyl bromide as well as p-carboethoxybenzyl bromide. Furthermore, to find further evidence supporting the proposed mechanism and to distinguish between X-philic and the subsequent S_N2 substitution (pathway A) and SET (pathway C) we designed a new set of experiments. This work is in progress and the results will be published successively.

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 sodium-potassium alloy. Melting points were uncorrected. IR spectra were taken on a Jena-Zeiss IR 10 apparatus. ^{1}H-NMR spectra were recorded with a Varian apparatus at 60 or 200 MHz.

The Michaelis-Becker reaction between benzyl halogenide **1** *and the sodium salt of diisopropyl phosphite as well as dibenzylphosphine oxide. General procedure.*

A. *In THF solution.* To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF were added 2.5 mmol of diisopropyl phosphite or dibenzylphosphine oxide in 10 mL of THF. When the evolution of hydrogen had ceased, 2.5 mmol of benzyl halogenide **1** (benzyl-chloride, bromide; 4-t-butyl-benzyl chloride, bromide; 4-phenyl-benzyl chloride, bromide) in 5 mL of THF were added and the reaction mixture was stirred 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were purified by radial chromatography (silica gel; the starting materials were eluted with hexane, the products with ether). The yields are shown in Table I.

Diisopropyl benzylphosphonate

IR (film) ν = 1265 P=O; 1010 P—O—C cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.14 (t, J = 6 Hz, C—CH_3, 12H), 2.95 (d, J = 21 Hz, CH_2P, 2H), 4.36 (m, O—CH, 2H), 690 (s, C_6H_5, 5H)
MS exact mass calcd. for $C_{13}H_{21}O_3P$ 256.1228 found 256.1226

Diisopropyl (4-t-butyl-phenyl)-methylphosphonate

IR (film) ν = 1265 P=O, 1010 P—O—C cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.14 (t, J = 6 Hz, C—CH_3, 12H); 1.23 (s, t-Bu, 9H), 2.95 (d, J = 21 Hz, CH_2P, 2H), 4.40 (m, OCH, 2H), 6.90 (s, C_6H_4, 4H)
MS exact mass calcd. for $C_{17}H_{29}O_3P$ 312.1854 found 312.1852

Diisopropyl (4-phenyl-phenyl)-methylphosphonate: m.p. 50–52°C

IR (KBr) ν = 1260 P=O, 1015 P—O—C cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.16 (t, J = 6 Hz, C—CH_3, 12H), 2.95 (d, J = 21 Hz, CH_2P, 2H), 4.40 (m, O—CH, 2H), 6.84–7.43 (m, C_6H_5—C_6H_4, 9H)
MS exact mass calcd. for $C_{19}H_{25}O_3P$ 332.1541 found 332.1542

Tribenzylphosphine oxide: m.p. 209–211°C, (lit. 210–212°C)[26]

IR (KBr) ν = 1200 P=O cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 2.86 (d, J = 13 Hz, CH_2, 6H), 6.80–7.10 (m, C_6H_5, 15H)

(4-t-butyl-phenyl)methyl-dibenzylphosphine oxide: m.p. 177–179°C

IR (KBr) ν = 1200 P=O cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.16 (s, t-Bu, 9H), 2.80 (d, J = 13 Hz, CH_2, 6H), 6.60–7.10 (m, aromat, 14H)
MS exact mass calcd. for $C_{25}H_{29}OP$ 376.1956 found 376.1956

(4-phenyl-phenyl)methyl-dibenzylphosphine oxide: m.p. 153–155°C

IR (KBr) ν = 1200 P=O cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 2.86 (d, J = 13 Hz, CH_2, 6H), 6.70–7.40 (m, aromat, 19H)
MS exact mass calcd. for $C_{27}H_{25}OP$ 396.1643 found 396.1643

B. *In isopropanol solution.* NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of iPrOH and to the resultant mixture 2,5 mmol of diisopropyl phosphite or dibenzylphosphine oxide in 10 mL of iPrOH and 2.5 mmol of benzyl halogenide **1** (benzyl-chloride, bromide; 4-t-butylbenzyl-chloride, bromide; 4-phenylbenzyl-chloride, bromide) in 5 mL of THF were added. The reaction mixture was stirred 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography (silica gel; the starting materials were eluted with hexane, the products with ether). The products were identified by comparison of the IR and NMR spectra with those of authentic samples. The yields are shown in Table I.

Reaction of 4-nitrobenzyl chloride **4a** *with the sodium salt of diisopropyl phosphite in THF.* To a suspension of NaH (3 mmol, 0.072 g) in 20 mL of THF was added diisopropyl phosphite (2.5 mmol, 0.42 g). When the evolution of hydrogen had ceased, 4-nitrobenzyl chloride (2.5 mmol, 0.43 g) in 5 mL of THF was added. The reaction mixture was stirred 3 hours at room temperature, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the residue separated by radial chromatography (silica gel). The following compounds were obtained:

4-nitrobenzyl chloride **4a** (eluted with hexane) 0.214 g (50%), spectral data were identified with those of an authentic sample.
4,4'-dinitrostilbene **6** (eluted with hexane:chloroform = 2:1) 0.084 g (25%), m.p. 293–299°C (lit. 293°C)[27]
diisopropyl p-nitrobenzylphosphonate **7** (eluted with chloroform) 0.158 g (21%)

IR (film) ν = 1230 P=O, 1035 P—O—C, 1360, 1530 NO_2 cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.20 (t, J = 6 Hz, C—CH_3, 12H), 3.10 (d, J = 21 Hz, CH_2P, 2H), 4.46 (m, O—CH, 2H), 7.13 (d, J = 8 Hz, aromat, 2H), 7.80 (d, J = 8 Hz, aromat, 2H)
MS exact mass calcd. for $C_{13}H_{20}NO_5P$ 301.1079 found 301.1079

Reaction of 4-nitrobenzyl bromide with the ion of the type O—$P<$. General procedure

A. *In THF solution.* To a suspension of NaH (2.75 mmol, 0.066 g) in 10 mL of THF were added 2,5 mmol of dialkyl phosphite or dibenzylphosphine oxide in 5 mL of THF. When the evolution of hydrogen had ceased 4-nitrobenzyl bromide (2.5 mmol, 0.54 g) in 10 mL of THF was added. The reaction mixture was stirred 3 hours at 20°C, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography.

Run 1

4-nitrobenzyl bromide **4b** (eluted with hexane) 0.097 g (18%)

1,2-di(p-nitrophenyl) ethane **8** (eluted with chloroform) 0.276 g (81%) m.p. 180–182°C (lit. 178–181°C)[19b]

^{1}H NMR (CDCl$_3$) δ = 2.90 (s, CH$_2$, 4H), 6.83 (d, J = 8 Hz, aromat, 4H), 7.66 (d, J = 8 Hz, aromat, 4H)

Run 3

Diisopropyl p-nitrobenzylphosphonate **7** (eluted with chloroform) 0.173 g (23%)

1,2-di(p-nitrophenyl)ethane **8** (eluted with chloroform) 0.252 g (74%)

Run 4

4-nitrobenzyl bromide **4b** (eluted with hexane) 0.308 g (57%)

1,2-di(p-nitrophenyl)ethane **8** (eluted with chloroform) 0.143 g (42%)

B. *In alcohol solution.* NaH (2.75 mmol, 0.066 g) was dissolved in 10 mL of alcohol (methanol or isopropanol) and to the resultant mixture were added 2.5 mmol of dialkyl phosphite or dibenzylphosphine oxide in 10 mL of alcohol. After 10 minutes 2.5 mmol of 4-nitrobenzyl bromide (0.54 g) in 5 mL of THF were added. The reaction mixture was stirred 3 hours at 20°C, then diluted with 75 mL of ether, washed with NH$_4$Cl solution and dried over MgSO$_4$. The solvent was removed in the vacuum and the residue separated by radial chromatography.

Run 2

4-nitrobenzyl bromide **4b** (eluted with hexane) 0.108 g (20%)

1,2-di(p-nitrophenyl)ethane **8** (eluted with chloroform) 0.269 g (79%)

Run 5

4-nitrobenzyl bromide **4b** (eluted with hexane) 0.275 g (51%)

1,2-di(p-nitrophenyl)ethane **8** (eluted with chloroform) 0.163 g (48%)

Run 6

p-nitrotoluene **10** (eluted with hexane:ether = 9:1) 0.120 g (35%), m.p. 52–54°C (lit. 52–54°C)[29]

IR (KBr) ν = 1520, 1355 NO$_2$ cm^{-1}

^{1}H NMR (CDCl$_3$) δ = 2.40 (s, CH$_3$, 3H), 7.00 (d J = 8 Hz, aromat, 2H), 7.76 (d, J = 8 Hz, aromat, 2H)

4-nitrobenzyl bromide **4b** (eluted with hexane:chloroform = 9:1) 0.119 g (22%)

methyl p-nitrobenzyl ether **9** (eluted with hexane:chloroform = 2:1) 0.117 g (28%)

IR (film) ν = 1525, 1355 NO$_2$; 1125 CH$_2$OCH$_3$ cm^{-1}

^{1}H NMR (CDCl$_3$) δ = 3.30 (s, OCH$_3$, 3H), 4.36 (s, CH$_2$O, 2H), 7.10 (d, J = 8 Hz, aromat, 2H), 7.76 (d, J = 8 Hz, aromat, 2H)

1,2-di(p-nitrophenyl)ethane **8** (eluted with chloroform) 0.041 g (12%)

methyl dibenzylphosphinate **11** (eluted with chloroform) 0.312 g (48%), m.p. 63–65°C (lit. 75°C)[28]

IR (KBr) ν = 1230 P=O, 1065 P—O—C cm^{-1}

^{1}H NMR (CDCl$_3$) δ = 3.00 (d, J = 16 Hz, CH$_2$, 4H), 3.60 (d, J = 10 Hz, OCH$_3$, 3H), 7.20–7.40 (m, C$_6$H$_5$, 10H)

Run 7

p-nitrotoluene **10** (eluted with hexane:chloroform = 9:1) 0.096 g (28%)

4-nitrobenzyl bromide **4b** (eluted with hexane:chloroform = 9:1) 0.157 g (29%)

methyl p-nitrobenzyl ether **9** (eluted with hexane:chloroform = 2:1) 0.109 g (26%)

1,2-di(p-nitrophenyl)ether **8** (eluted with chloroform) 0.040 g (12%)

Reaction of 4-nitrobenzyl bromide with dimethyl phosphite in the presence of NaOCH$_3$ in methanol-O-d. NaH (2.75 mmol, 0.066 g) was dissolved in 15 mL of methanol-O-d and to the resultant mixture 2.5 mmol of dimethyl phosphite (0.275 g) were added. After 10 minutes 2.5 mmol of 4-nitrobenzyl bromide (0.54 g) in 10 mL of methanol-O-d were added. The reaction mixture was stirred 3 hours at 20°C, then diluted with 75 mL of ether, washed with NH$_4$Cl solution and dried over MgSO$_4$. The solvent was removed in the vacuum and the residue was separated by radial chromatography. The following compounds were obtained:

4-methyl-d-nitrobenzene **10a** (eluted with hexane:CHCl$_3$ = 9:1) 0.104 g (30%), m.p. 53–55°C

IR (KBr) ν = 1520, 1355 NO_2 cm^{-1}
^1H NMR ($CDCl_3$) δ = 2.26 (t, J = 2 Hz, CH_2D, 2H), 6.86 (d, J = 8 Hz, aromat, 2H), 7.60 (d, J = 8 Hz, aromat, 2H)
Anal. Calcd. for $C_7H_6DNO_2$: C, 60.86; HD, 5.84, Found: C, 60.85; H, 5.73

Deuterium incorporation minimum value 96%, determined by using mass spectroscopic analysis and by NMR
4-nitrobenzyl bromide **4b** (eluted with hexane:$CHCl_3$ = 9:1) 0.151 g (28%), spectral data were identified with those of an authentic sample.
4-nitrobenzyl methyl ether **9** (eluted with hexane:$CHCl_3$ = 2:1) 0.113 g (27%),
1,2-di(4,4'-dinitrophenyl)ethane **8** (eluted with $CHCl_3$) 0.039 g (12%), spectral data were identified with those of an authentic sample.

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