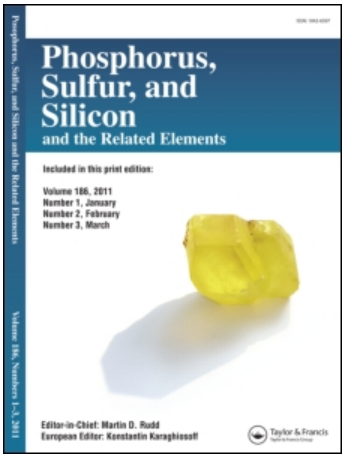

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART IV. THE REACTION OF DIALKYLPHOSPHITE ANIONS WITH NITROBENZYL BROMIDES

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART IV.* THE REACTION OF DIALKYLPHOSPHITE ANIONS WITH NITROBENZYL BROMIDES†

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The reaction of *o*-, *m*- and *p*-nitrobenzyl bromide with sodium dimethylphosphite as well as sodium diisopropylphosphite in THF and alcohols as the solvents is described. According to the constitution of the starting materials and the solvent used, the formation of the P—C bond, debromination or dimerization occurs. The principal process in *o*- and *p*-nitrobenzyl bromide and >P—O$^-$ anion systems is believed to be X-philic substitution, the dimer is formed through a secondary process via SET from the nitrobenzyl anion to nitrobenzyl bromide. Electron-transfer and proton-transfer processes in the nitrobenzyl bromide->P—O$^-$ systems are also discussed.

Key words: *o*-, *m*- and *p*-nitrobenzyl bromides, dialkyl phosphites, Michaelis-Becker reaction, X-philic substitution, SET.

INTRODUCTION

Benzylphosphonates with a wide range of substituents in the benzyl ring[1] as well as phosphonomethyl pyridines[2] are available in the Michaelis-Becker reaction. The exceptions are nitro derivatives; N. Kreutzkamp[3] reported a failure of an attempted direct preparation of a *p*-nitrobenzylphosphonate from *p*-nitrobenzyl chloride or bromide and trialkylphosphites as well as the salts of dialkyl phosphites.

The Michaelis-Becker reaction is often assumed to be a S_N2 process involving the nucleophilic phosphorus atom.

$$>P—O^- + R—X \rightarrow R—P(O)< + X^-$$

On the other hand G. A. Russell[4] reported that dialkyl phosphite anions react with *p*-nitrobenzyl chloride, and α,α-dimethyl-*p*-nitrobenzyl chloride to form *p*-nitrobenzylphosphonates. 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.

*Part III see lit. 11b.
†Dedicated to Professor Richard Neidlein on the occasion of his 65th birthday.

In our previous paper[5] we reported that the treatment of 1 equiv of *p*-nitrobenzyl bromide in THF or isopropanol at 20°C with 1 equiv of the diisopropyl phosphite anion, dimethyl phosphite anion as well as the dibenzylphosphinite anion produces one major product, namely 1,2-di(*p*-nitrophenyl)ethane; a compound with a P—C bond in the reaction mixture was not detected.

The ion of the type >P—O^- could a priori react with *p*-nitrobenzyl bromide either by the attack on the bromine atom, X-philic substitution (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).

Pathway A:

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

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

Pathway B:

$$p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2\text{—}Br + {}^-O\text{—}P< \rightarrow [p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2\text{—}Br]^{\cdot -} + O{=}\dot{P}<$$

$$[p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2\text{—}Br]^{\cdot -} \rightarrow p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2^{\cdot} + Br^-$$

$$2\ p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2^{\cdot} \rightarrow p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2CH_2\text{—}C_6H_4\text{—}NO_2\text{-}p$$

Pathway C:

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

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

$$\downarrow \quad \text{SET}$$

$$p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2^{\cdot} + [p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2\text{—}Br]^{\cdot -}$$

$$[p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2\text{—}Br]^{\cdot -} \rightarrow p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2^{\cdot} + Br^-$$

$$p\text{-}NO_2\text{—}C_6H_4\text{—}CH_2^{\cdot} + {}^-CH_2\text{—}C_6H_4\text{—}NO_2\text{-}p \rightarrow [p\text{-}NO_2\text{—}C_6H_4CH_2CH_2\text{—}C_6H_4\text{—}NO_2\text{-}p]^{\cdot -}$$

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

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

On the basis of the experiment with methanol-O-d as well as on the basis of the isolation of methyl dibenzylphosphinate from the reaction mixture,[5] pathway B was

excluded. To distinguish between the X-philic and the subsequent S_N2 substitution (pathway A) and SET (pathway C) we designed a set of experiments and these results we wish to present in this paper.

RESULTS

We ran the reaction of 1 equiv of *o*-, *m*- and *p*-nitrobenzyl bromide with 1 equiv of $R_2P—O^-$ anion (R = OMe, OiPr) in THF, iPrOH and methanol-O-d. The products distribution strongly depends on the position of the nitro substituent in the phenyl ring, see Table I.

The mixture of 1 equiv of *m*-nitrobenzyl bromide and 1 equiv of sodium dimethylphosphite in THF produces one major product, namely dimethyl *m*-nitrobenzylphosphonate **2c** (Table I, run 6), using methanol-O-d as a solvent we isolated additionally from the reaction mixture ether **6c** as a solvolysis product (Table I, run 5). Sodium diisopropylphosphite and *m*-nitrobenzyl bromide in iPrOH give diisopropyl *m*-nitrobenzylphosphonate **2d** and *m*-nitrotoluene **5c** (Table I, run 8). The same mixture of the starting materials in THF gives a much more complex mixture of the

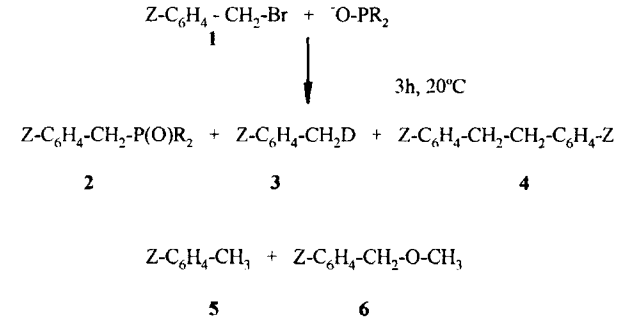


TABLE I

Reaction of the $^-O—PR_2$ nukleophile with *o*-, *m*- and *p*-nitrobenzyl bromide

Run	Z	R	solvent	% of isolated yield					
				1	2	3	4	5	6
1	o-NO_2	O-CH_3	CH_3OD	-	28	58	-	-	10
2			THF	-	24	-	75	-	-
3		O-iPr	THF	6	-	-	86	4	-
4			iPrOH	-	6	-	74	18	-
5	m-NO_2	O-CH_3	CH_3OD	10	51	-	-	-	37
6			THF	-	97	-	-	-	-
7		O-iPr	THF	13	52	-	28	5	-
8			iPrOH	8	69	-	-	21	-
9	p-NO_2	O-CH_3	CH_3OD	23	3	31	12	-	28
10			THF	9	8	-	82	-	-
11		O-iPr	THF	18	-	-	81	-	-
12			iPrOH	20	-	-	79	-	-

products: diisopropyl *m*-nitrobenzylphosphonate **2d**, dimer **4c** and a small amount of *m*-nitrotoluene **5c** (Table I, run 7).

In contrast *o*-nitrobenzyl bromide with sodium diisopropylphosphite and *p*-nitrobenzyl bromide with sodium dimethylphosphite as well as sodium diisopropylphosphite in THF yield one major product, namely dinitrobibenzyl **4a** (Table I, runs 3, 10, 11, 12).

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 **4e**, *p*-methyl-d-nitrobenzene **3e** along with the solvolysis product, namely *p*-nitrobenzyl methyl ether **6e** (see Table I, run 9).

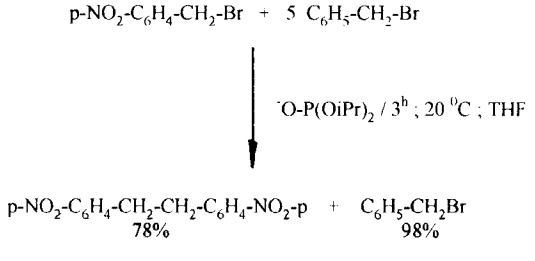
It is interesting enough, what was shown by T-S. Kam and co-workers,[6] that both *p*-nitrobenzyl bromide and *p*-nitrobenzyl iodide react rapidly with the alcohols to give the solvolysis products (*p*-nitrobenzyl ethers) in quantitative yields.

DISCUSSION

p-methyl-d_1-nitrobenzene **3e**, isolated from the reaction mixture of *p*-nitrobenzyl bromide and the anion $^-$O—P< carried out in methanol-O-d, is derived from the initial X-philic substitution product: the *p*-nitrobenzyl anion (quenched with methanol-O-d). The origin of the dimer **4e** in the reaction carried out is less clear and remains a puzzling aspect of the reactivity of *p*-nitrobenzyl bromide towards >P—O$^-$ ions.

The dimer can be produced as the product of the S_N2 reaction between *p*-nitrobenzyl bromide and *p*-nitrobenzyl anion (pathway A) as well as the product of the SET reaction (pathway C). The *p*-nitrobenzyl anion can a priori act as a nucleophilic reagent or a single electron donor.

If the initially formed *p*-nitrobenzyl anion in the reaction carried out acts as a nucleophilic reagent, it should react with any electrophile presents in the reaction mixture. We ran the reaction of 1 equiv of *p*-nitrobenzyl bromide, 5 equiv of benzyl bromide with 1 equiv of sodium diisopropyl phosphite in THF. From this reaction mixture we isolated 1,2-di(*p*-nitrophenyl) ethane **4e** (78%) and benzyl bromide (98%). The 1-phenyl-2-*p*-nitrophenylethane was not detected.



The results of this crossover experiment suggest strongly, that the *p*-nitrobenzyl anion, if it is formed, does not act as a nucleophilic reagent.

We also investigated the interaction of *p*-nitrobenzyl bromide with sodium diisopropyl phosphite in THF using UV absorption spectroscopy to monitor the course of reaction.

The treatment of *p*-nitrobenzyl bromide with sodium diisopropyl phosphite in THF

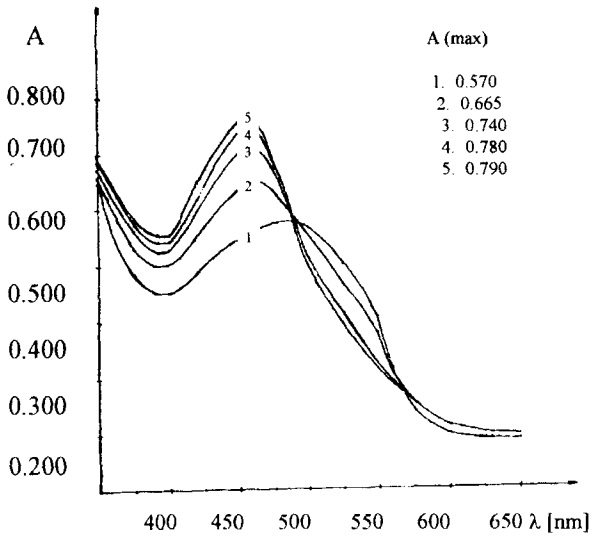


FIGURE 1 Variation of absorption spectra of a reaction solution consisting of 4-nitrobenzyl bromide/ $^{-}O—P(OiPr)_2$ in THF, as function of time: spectrum 1, 2 min; 2,20 min; 3, 38 min; 4, 56 min; 5, 74 min.

gave rise to a pale red solution having a small absorption at 510 nm followed by the consecutive development of the peak at 460 nm (see Figure 1). This spectral absorption we assigned to the *p*-nitrobenzyl anion.

E. Buncel and B. C. Menon[7] published the results of the spectrophotometric study of the proton transfer and electron transfer process in the reaction of *p*-nitrotoluene with bases. The initially formed species in this system is the *p*-nitrobenzyl anion. The authors proposed that the 430–450 nm absorption observed is due to the *p*-nitrobenzyl anion.

Light may speed up a radical anion substitution process. Numerous instances of light effects have been found, some of them very substantial. In general, it appears that visible, or near ultraviolet light is effective in promoting these reactions and, indeed, all that is required is illumination by ordinary fluorescent light.[8,9]

In order to provide evidence for the SET mechanism operating in the reaction of nitrobenzyl bromides with the ions of >P—O^{-} we ran the reaction in THF under a variety of conditions.

As we showed above the treatment of *p*-nitrobenzyl bromide with sodium diisopropylphosphite as well as dimethylphosphite produces one major product, namely 1,2-di(*p*-nitrophenyl)ethane **4e**. We decided to run the reaction for 30 minutes in THF at −45°C with 1 equiv of *o*-, *m*-, and *p*-nitrobenzyl bromides and sodium diisopropylphosphite under a variety of conditions: in the darkness, day light and irradiation with 500 W bulb. The results of these experiments are summarised in Table II.

From the reaction mixture in the case of *o*-, and *p*-nitrobenzyl bromide in this set of experiments we isolated mainly dimer **4** as a major product and the starting material. In the case of *m*-nitrobenzyl bromide we isolated from the reaction mixture diisopropyl *m*-nitrobenzylphosphonate, a dimer and a small amount of *m*-nitrotolu-

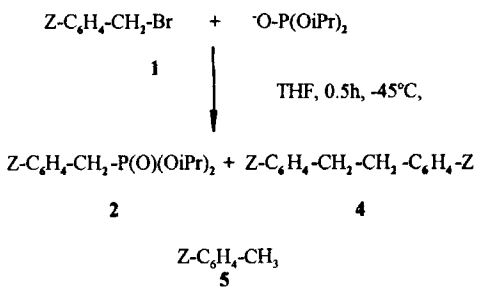


TABLE II

Light influence on the products distribution of the reaction of *o*-, *m*- and *p*-nitrobenzyl bromide with sodium diisopropylphosphite

Z	Conditions	% of isolated yield			
		1	2	4	5
o-NO_2	darkness	56	-	35	7
	day light	36	-	58	2
	hν	2	-	97	-
m-NO_2	darkness	67	15	7	8
	day light	65	12	15	6
	hν	61	10	26	-
p-NO_2	darkness	69	-	30	-
	day light	38	-	61	-
	hν	5	-	94	-

ene. As one can see from Table II we found a substantial influence of light on the yield of isolated dimer **4**. The yield of diisopropyl *m*-nitrobenzylphosphonate was not affected by the illumination of the reaction mixture by the light.

The results of these experiments strongly suggest that the SET process operates in the case of the dimer formation. On the other hand the UV investigation as well as the isolation of nitrotoluene from the reaction mixture carried out in alcohols as solvents speak for the nitrobenzyl anion as an intermediate in the investigated reaction.

At this point of our study it was very important to check if the light would have any influence on the product distribution of the reaction carried out in methanol. We ran this kind of experiments and the results are summarised in Table III. Unfortunately *p*-nitrobenzyl bromide **1e** precipitates from methanol solution at 0°C, it was the reason why we had to perform the experiments at this temperature with THF as a cosolvent.

As one can see from the data collected in Table III, we found that the yield of the solvolysis product, that is methyl *p*-nitrobenzyl ether **6e,** was almost the same, independent of the conditions applied (the yields of the isolated product varied +, −3% at 20°C and +, −2% at 0°C). In contrast to that we found a substantial influence of light on the yield of dimer **4**. The reaction of the dimer formation was inhibited when conducted in darkness; under these conditions we isolated from the

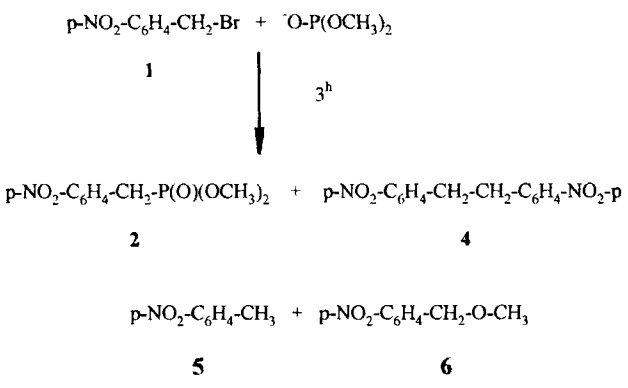


TABLE III

Light influence on the products distribution of the reaction of *p*-nitrobenzyl bromide with sodium dimethylphosphite in MeOH

Run	Solvent Temp.	Conditions	% of isolated yield				
			1	**2**	**4**	**5**	**6**
1	MeOH 20°C	Darkness	20	4	-	47	27
2		Normal	22	3	12	32	29
3		hν	14	2	41	15	26
4	MeOH / THF = 1.5/1 0°C	Darkness	61	-	-	32	5
5		day light	63	-	10	20	4
6		hν	43	-	37	12	6

reaction mixture instead of dimer **4e**, *p*-nitrotoluene **5e** with 47% yield at 20°C (Table III, run 1) and 32% at 0°C (Table III, run 4).

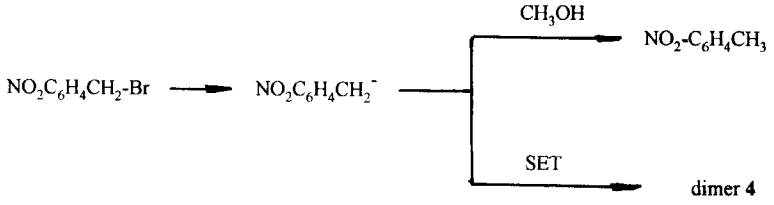
The illumination of the reaction flask with the 500 W bulb gives a different distribution of the products: in this case from the reaction mixture we isolated dimer **4e** with 41% or 37% yield and *p*-nitrotoluene with only 15% or 12% yield (Table III, runs 3 and 6). On the other hand from Table III one can see a big influence of the temperature on the yield of ether **6e** (a solvolysis product) in contrast to dimer **4e**.

In this particular case we deal with two competing processes: the electron transfer from- and proton transfer into- the *p*-nitrobenzyl anion. The *p*-nitrobenzyl anion, in the reaction investigated herein, can logically be derived only by the X-philic substitution reaction. The reaction of phosphite ions causes a nucleophilic attack on bromine in a nitrobenzyl bromide, effecting the nucleophilic displacement on bromine with the release of nitrobenzyl anion as a nucleofuge. This type of nucleophilic displacements on halogen is well known, and phosphorus nucleophiles are noteworthy for their proclivity to engage in such processes.[10]

Recently we have also shown that the anions of the type >P—O^- cause a nucleophilic attack on bromine in activated alkyl bromides (possessing an electron-withdrawing group bound to the carbon bearing the bromine atom), with the release of an enol anion as nucleofuge.[11]

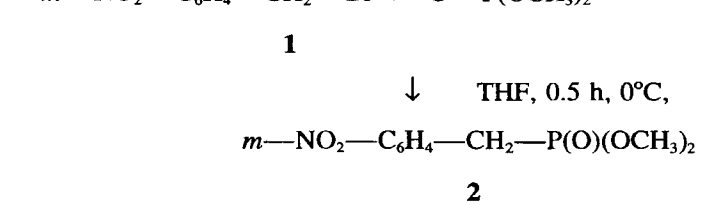
The electron transfer processes are known to be generally fast and light can ad-

ditionally speed them up, whereas the proton transfer processes can often be slow and in the reaction under investigation shouldn't be affected by light.



Hence, considering the reaction one might have expected the electron transfer to be competitive with the proton transfer and to lead to the preferential formation of dimer **4** (as a result of the SET process) under the irradiation condition. On the other hand the reaction conducted in the dark might reduce the competing SET component and allow the proton transfer to proceed. This indeed turned out to be the case. Under these conditions, the reaction of *p*-nitrobenzyl bromide with sodium dimethylphosphite furnished up to 47% yield of proton transfer derived *p*-nitrotoluene **5** (see Table III, runs 1 and 4).

As we showed above (see Table I) the treatment of *m*-nitrobenzyl bromide with sodium dimethylphosphite in THF as well as in methanol produces mainly dimethyl *m*-nitrobenzylphosphonate **2** (Table I, runs 5 and 6), neither dimer **4** nor toluene **5** were detected. Additionally, we found that the formation of dimethyl *m*-nitrobenzylphosphonate was not inhibited when conducted in darkness. The yield of phosphonate **2** was almost the same, independent of the conditions applied (the yields of the isolated products varied +, −4%).



In contrast, the treatment of *m*-nitrobenzyl bromide with sodium diisopropylphosphite produces beside diisopropyl *m*-nitrobenzylphosphonate **2d**, dimer **4c** (in THF, Table I, run 7) or *m*-nitrotoluene **5c** (in iPrOH, Table I, run 8). These results suggest that the bulky phosphorus nucleophile of the type >P—O⁻ because of the steric hindrance will attack preferentially the bromine atom in *m*-nitrobenzyl bromide instead of the benzyl carbon atom.

If this postulate is correct then the use of phosphorus nucleophile of the type

TABLE IV

Light influence on the yield of dimethyl *m*-nitrobenzylphosphonate

Conditions	% of isolated yield	
	1	2
darkness	35	63
day light	37	61
hν	34	64

>P—O^- possessing bulky substituents should give increase in the dimer **4c** or toluene **5c** formation as a result of the nucleophilic attack on the bromine atom and decrease of the >P(O)—C derivatives as a result of the nucleophilic attack on the carbon atom in the reaction in focus. This is precisely what was observed (see Table V).

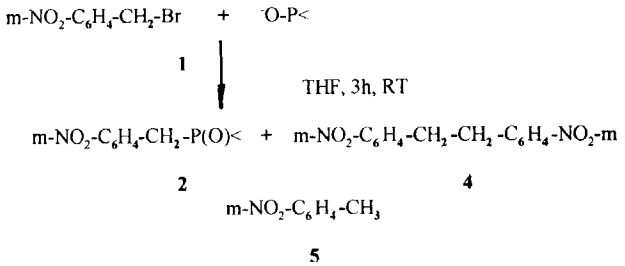
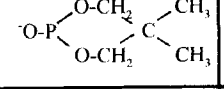
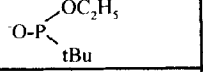


Table V lists the yields of the isolated products of the reaction between *m*-nitrobenzyl bromide and the different >P—O^- ions. The compounds with the C—P=O structure are formed in the S_N2 reaction. The examination of the data in this table reveals that the degree of conversion depends on the steric effects. The S_N2 reaction is known to involve an attack by the nucleophile from a position opposite to that of bromine. The great decrease in rate can be attributed to steric hindrance, a sheer physical blockage to the attack of the nucleophile. The steric effect might reduce the S_N2 process involving the phosphorus nucleophile of the type >P—O^- and allow the X-philic substitution to proceed. This indeed turned out to be the case.

From the reaction mixture of one equiv of *m*-nitrobenzyl bromide and one equiv of sodium dimethylphosphite, the smallest nucleophile in this series, we isolated only one major product namely dimethyl *m*-nitrobenzylphosphonate (Table V, run 1). The treatment of *m*-nitrobenzyl bromide with sodium diisopropyl phosphite produces two major products: diisopropyl *m*-nitrobenzylphosphonate and dimer **4c** (Table V, run 2). On the other hand from the reaction mixture of the sodium salt of monoethyl *t*-butylphosphonite and *m*-nitrobenzyl bromide we isolated mainly dimer **4c** (Table V, run 5) and in the case of sodium di-*t*-butylphosphite *m*-nitrotoluene **5c** (Table V, run 6).

TABLE V

Reaction of the >P—O^- nucleophiles with *m*-nitrobenzyl bromide

Run	⁻O-P<	% of isolated yield			
		1	2	4	5
1	$^-O\text{-}P(OCH_3)_2$	-	97	-	-
2	$^-O\text{-}P(OiPr)_2$	13	52	28	5
3		26	72	-	-
4	$^-O\text{-}P(CH_2Ph)_2$	52	20	21	2
5		81	-	10	4
6	$^-O\text{-}P(OtBu)_2$	86	-	-	12

The deuterium incorporation into the methyl group of the *p*-nitrotoluene[5] as well as the UV experiment speak strongly for the carbanion and against the free radical as an intermediate in the reaction in focus. We ran the control experiment with the *p*-nitrotoluene in methanol-O-d in the presence of sodium dimethylphosphite. In this experiment we did not observe any proton deuterium exchange or dimer formation.

Additionally the isolation of methyl dibenzylphosphinate from the reaction mixture of *p*-nitrobenzyl bromide and dibenzylphosphine oxide in methanol[5] is in agreement with the X-philic substitution. On the other hand on the basis of the results of the crossover experiment as well as the light influence on the dimer formation, pathway A can be excluded and the SET mechanism (pathway C) is the most plausible one. By considering all the above pieces of evidence one can find that the nucleophilic displacement of the bromine with the release of the nitrobenzyl anion is the first step in the reaction under investigation. The initially formed nitrobenzyl anion in the reaction carried out can act as a single electron donor (if a suitable acceptor in the reaction mixture is present) to yield the dimer as a final product or can act as a base (the proton transfer reaction) to yield nitrotoluene as a final product.

On the basis of several electrochemical studies[12] it seems that the combination of *o*- and *p*-nitrobenzyl bromide/*o*- and *p*-nitrobenzyl anion is a much better combination for the SET process than *m*-nitrobenzyl bromide/*m*-nitrobenzyl anion; what is in full agreement with our results presented in this paper.

In order to check our postulate of this mechanism as well as to check the scope and limitations of this type of reactivity of >P—O^- ions, we decided to study other benzyl systems possessing electron withdrawing groups in the phenyl ring with different redox potential. This work is in progress and the results will be published successively.

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphospholan,[13] monoethyl *t*-butylphosphonite[14] and di-*t*-butyl phosphite[15] were prepared according to the published procedures. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran or toluene was dried with sodium-potassium alloy. Isopropanol was dried with calcium hydride. Melting points were uncorrected. Mass spectra (FD) were recorded on an AMD Intectra 604 apparatus. IR spectra were taken on a Jena-Zeiss IR 10 apparatus. ^{31}PNMR and ^{1}HNMR spectra were recorded with a Varian apparatus at 60, 200 or 500 MHz. The UV experiments were performed with the use of a 0.1-cm cuvette adapted for the introduction of reagents under argon. Concentration of 4-nitrobenzyl bromide and the sodium salt of diisopropylphosphite in THF was $8 \cdot 10^{-3}$ M. The spectra were recorded on a Beckman UV 5270 spectrophotometer over the range 350–650 nm.

The Michaelis-Becker Reaction Between Nitrobenzyl Bromide **1** *and the Sodium Salt of Diisopropyl Phosphite as Well as Dimethyl Phosphite: 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 dimethyl phosphite in 10 mL of THF. When the evolution of hydrogen had ceased, nitrobenzyl bromide **1** (4-nitrobenzyl bromide, 3-nitrobenzyl bromide, 2-nitrobenzyl bromide) (2.5 mmol, 0.54 g) in 5 mL of THF were added and the reaction mixture was stirred for 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. The yields are summarized in Table I.

Run 2

1,2-di(2-nitrophenyl)ethane **4a** (eluted with chloroform) 0.255 g (75%) m.p. 127–128°C (lit. 126–127°C)[16]
^{1}HNMR ($CDCl_3$) δ = 3.06 (s, CH_2, 4H), 6.80–7.40 (m, aromat, 6H), 7.40–7.80 (m, aromat, 2H) dimethyl (2-nitrophenyl)methyl phosphonate **2a** (eluted with chloroform) 0.147 g (24%) m.p. 63–64°C (lit. 64°C)[17]
IR (KBr) ν = 1265 P=O, 1060 P—O—C, 1520, 1355 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.18 (d, J = 22.38 Hz, CH_2P, 2H), 3.66 (d, J = 10.30 Hz, $POCH_3$, 6H), 7.36–7.50 (m, aromat, 2H), 7.50–7.60 (m, aromat, 1H), 7.94 (d, J = 8.30 Hz, aromat, 1H)
^{31}PNMR ($CDCl_3$) δ = 27.12

Run 3

2-nitrotoluene **5a** (eluted with hexane) 0.014 g (4%)
2-nitrobenzyl bromide **1a** (eluted with hexane) 0.032 g (6%)
1,2-di(2-nitrophenyl)ethane **4a** (eluted with chloroform) 0.293 g (86%)

Run 6

dimethyl (3-nitrophenyl)methyl phosphonate **2c** (eluted with chloroform) 0.595 g (97%) m.p. 53–54°C
IR (KBr) ν = 1265 P=O, 1055 P—O—C, 1530, 1360 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.25 (d, J = 21.9 Hz, CH_2P, 2H), 3.70 (d, J = 11.3 Hz, $POCH_3$, 6H), 7.44–7.54 (m, aromat, 1H), 7.60–7.70 (m, aromat, 1H), 8.06–8.14 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.58
Acid hydrolysis of this material yielded a (3-nitrophenyl)methyl phosphonic acid m.p. 187–188°C (lit. 186–187°C).[18]

Run 7

3-nitrotoluene **5c** (eluted with hexane) 0.017 g (5%)
3-nitrobenzyl bromide **1c** (eluted with hexane) 0.070 g (13%)
1,2-di(3-nitrophenyl)ethane **4c** (eluted with hexane:chloroform 1:2) 0.095 g (28%) m.p. 169–171°C
^{1}HNMR ($CDCl_3$) δ = 2.93 (s, CH_2, 4H), 6.83–7.26 (m, aromat, 4H), 7.56–7.86 (m, aromat, 4H) diisopropyl (3-nitrophenyl)methyl phosphonate **2d** (eluted with chloroform) 0.392 g (52%)
IR (Film) ν = 1260 P=O, 1030 P—O—C, 1530, 1360 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.229 (d, J = 6.18 Hz, $POCH_3$, 6H), 1.305 (d, J = 6.18 Hz, $POCH_3$, 6H), 3.238 (d, J = 21.70Hz, CH_2P, 2H), 4.55–4.70 (m, POCH<, 2H), 7.46–7.60 (m, aromat, 1H), 7.62–7.76 (m, aromat, 1H), 8.06–8.24 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 22.93
Acid hydrolysis of this material yielded a (3-nitrophenyl)methyl phosphonic acid m.p. 187–188°C (lit. 186–187°C).[18]

Run 10

4-nitrobenzyl bromide **1e** (eluted with hexane) 0.049 g (9%)
1,2-di(4-nitrophenyl)ethane **4e** (eluted with chloroform) 0.280 g (82%) m.p. 180–182°C (lit. 178–181°C)[19]
dimethyl (4-nitrophenyl)methyl phosphonate **2e** (eluted with chloroform) 0.049 g (8%) m.p. 74–75°C (lit. 75°C)[20]
^{31}PNMR ($CDCl_3$) δ = 27.24

Run 11

4-nitrobenzyl bromide **1e** (eluted with hexane) 0.097 g (18%)
1,2-di(4-nitrophenyl)ethane **4e** (eluted with chloroform) 0.276 g (81%)

B. In Isopropanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of iPrOH and to the resultant mixture diisopropyl phosphite (2.5 mmol, 0.42 g, 0.42 mL) in 10 mL of iPrOH and nitrobenzyl bromide **1** (4-nitrobenzyl bromide, 3-nitrobenzyl bromide, 2-nitrobenzyl bromide; 2.5 mmol, 0.54 g) 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. The products were identified by comparison of the IR and NMR spectra with those of authentic samples. The yields are shown in Table I.

Run 4

2-nitrotoluene **5a** (eluted with hexane) 0.062 g (18%)
1,2-di(2-nitrophenyl)ethane **4a** (eluted with chloroform) 0.252 g (74%)
diisopropyl (2-nitrophenyl)methyl phosphonate **2b** (eluted with chloroform) 0.045 g (6%)
IR (film) ν = 1280 P=O, 1020 P—O—C, 1510, 1330 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 1.228 (d, J = 6.19 Hz, $POCH_3$, 6H), 1.304 (d, J = 6.19 Hz, $POCH_3$, 6H), 3.162 (d, J = 22.18 Hz, CH_2P, 2H), 4.55–4.70 (m, POCH<, 2H), 7.38–7.48 (m, aromat, 2H), 7.52–7.62 (m, aromat, 1H), 7.94 (d, J = 8.30 Hz, aromat, 1H)
^{31}PNMR ($CDCl_3$) δ = 23.12

Run 8

3-nitrotoluene **5c** (eluted with hexane) 0.072 g (21%)
3-nitrobenzyl bromide **1c** (eluted with hexane) 0.043 g (8%)
diisopropyl (3-nitrophenyl)methyl phosphonate **2d** (eluted with chloroform) 0.520 g (69%)

Run 12

4-Nitrobenzyl bromide **1e** (eluted with hexane) 0.108 g (20%)
1,2-di(4-nitrophenyl)ethane **4e** (eluted with chloroform) 0.269 g (79%)

Reaction of Nitrobenzyl Bromide with Dimethylphosphite in the Presence of $NaOCH_3$ in Methanol-O-d: General Procedure

C. Methanol-O-d Solution

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 nitrobenzyl bromide **1** (4-nitrobenzyl bromide, 3-nitrobenzyl bromide, 2-nitrobenzyl bromide; 2.5 mmol, 0.54 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 NH_4Cl saturated solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography. The yields are given in Table I.

Run 1

2-methyl-d-nitrobenzene **3a** (eluted with hexane) 0.200 g (58%)
IR (film) ν = 1520, 1355 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.58 (t, J = 2.24 Hz, CH_2D, 2H), 7.26–7.40 (m, aromat, 2H), 7.44–7.56 (m, aromat, 1H), 7.91–8.00 (m, aromat, 1H)
Deuterium incorporation minimum value 98%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
2-nitrobenzyl methyl ether **6a** (eluted with hexane:chloroform 2:1) 0.042 g (10%) dimethyl (2-nitrophenyl)methyl-d_2-phosphonate **2g** (eluted with chloroform) 0.173 g (28%) m.p. 64–65°C
IR (KBr) ν = 1265 P=O, 1060 P—O—C, 1520, 1355 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.66 (d, J = 10.30 Hz, $POCH_3$, 6H), 7.36–7.50 (m, aromat, 2H), 7.50–7.60 (m, aromat, 2H), 7.945 (d, J = 8.30 Hz, aromat, 1H)
^{31}PNMR ($CDCl_3$) δ = 27.14

Run 5

3-nitrobenzyl bromide **1c** (eluted with hexane:chloroform 9:1) 0.054 g (10%)
3-nitrobenzyl methyl ether **6a** (eluted with hexane:chloroform 2:1) 0.155 g (37%)
dimethyl (3-nitrophenyl)methyl-d_2-phosphonate **2h** (eluted with chloroform) 0.315 g (51%) m.p. 53–54°C
IR (KBr) ν = 1265 P=O, 1055 P—O—C, 1530, 1360 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.70 (d, J = 11.30 Hz, $POCH_3$, 6H), 7.44–7.54 (m, aromat, 1H), 7.60–7.70 (m, aromat, 1H), 8.06–8.14 (m, aromat, 2H)

^{31}PNMR ($CDCl_3$) δ = 27.60

Acid hydrolysis of this material yielded a (3-nitrophenyl)methyl phosphonic acid m.p. 187–188°C (lit. 186–187°C).[18]

Run 9

4-methyl-d-nitrobenzene **3e** (eluted with hexane:chloroform 9:1) 0.108 g (31%) m.p. 53–55°C
IR (KBr)ν = 1520, 1355 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 2.45 (t, J = 2.24 Hz, CH_2D, 2H), 7.26–7.36 (m, aromat, 2H), 8.06–8.16 (m, aromat, 2H)
Deuterium incorporation minimum value 96%, determined by the use of a mass spectroscopic analysis and ^{1}HNMR.
4-nitrobenzyl bromine **1e** (eluted with hexane:chloroform 9:1) 0.123 g (23%)
4-nitrobenzyl methyl ether **6e** (eluted with hexane:chloroform 2:1) 0.117 g (28%)
1,2-di(4-nitrophenyl)ethane **4e** (eluted with chloroform) 0.041 g (12%)
dimethyl (4-nitrophenyl)methyl-d_2-phosphonate **2i** (eluted with chloroform) 0.020 g (3%) m.p. 74–75°C
IR (KBr) ν = 1260 P=O, 1040 P—O—C, 1530, 1350 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.73 (d, J = 10.92 Hz, $POCH_3$, 6H), 7.08–7.18 (m, aromat, 2H), 7.75–7.85 (m, aromat, 2H)
^{31}PNMR ($CDCl_3$) δ = 27.31

Influence of Light on the Michaelis-Becker Reaction Between Nitrobenzyl Bromide **1** *and the Sodium Salt of Diisopropyl Phosphite in THF Solution: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF was added diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF. When the evolution of hydrogen had ceased the solution was cooled to −45°C and 4-nitrobenzyl bromide **1e** (2.5 mmol, 0.54 g) in 5 mL of THF was added and the reaction mixture was stirred for 30 min. at −45°C 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.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by a 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions: day light, in darkness and in the presence of light (500 W bulb) are summarized in Table II.

Influence of Light on the Reaction of 4-Nitrobenzyl Bromide **1e** *with Dimethylphosphite in the Presence of $NaOCH_3$ in Methanol: General Procedure*

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol and into the resultant mixture dimethyl phosphite (2.5 mmol, 0.275 g, 0.23 mL) in 5 mL of methanol and 4-nitrobenzyl bromide **1e** (2.5 mmol, 0.54 g) in 10 mL of methanol were added. The reaction mixture was stirred for 3 hours at room temperature, then diluted with 75 mL of ether, washed with 50 mL NH_4Cl saturated solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by a 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions: day light, in darkness and in the presence of light (500 W bulb) are summarized in Table III.

Influence of Light on the Reaction of 4-Nitrobenzyl Bromide **1e** *with Dimethylphosphite in the Presence of $NaOCH_3$ in Methanol/THF (1.5/1) Solution: General Procedure*

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol/THF solution into the resultant mixture dimethyl phosphite (2.5 mmol, 0.275 g, 0.23 mL) in 5 mL of methanol/THF solution and 4-nitrobenzyl bromide **1e** (2.5 mmol, 0.54 g) in 10 mL of methanol/THF solution were added. The reaction mixture was stirred for 3 hours at room temperature, then diluted with 75 mL of ether, washed with 50 ml NH_4Cl saturated solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by a 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions (day light), in darkness and in the presence of light (500 W bulb) are summarized in Table III.

Influence of Light on the Reaction of 3-Nitrobenzyl Bromide **1c** *with Dimethylphosphite in THF: General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF were added 2.5 mmol of dimethyl phosphite in 10 mL of THF. When the evolution of hydrogen had ceased the solution was cooled to 0°C and 3-nitrobenzyl bromide (2.5 mmol, 0.54 g) in 5 mL of THF was added. The reaction mixture was stirred for 3 hours, 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.

The above experiment was repeated: a) in a flask shielded from all light, b) in a flask irradiated by a 500 W bulb.

The yields and conditions for the reactions carried out under normal conditions: day light, in darkness and in the presence of light (500 W bulb) are summarized in Table IV.

Reaction of the $>P—O^-$ *Nukleophiles with 3-Nitrobenzyl Bromide* **1c**: *General Procedure*

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF were added 2.5 mmol of hydrogen phosphite (dimethyl phosphite, diisopropyl phosphite, 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphospholan, dibenzylphosphine oxide, monoethyl *t*-butylphosphite, di-*t*-butyl phosphite) in 10 mL of THF. When the evolution of hydrogen had ceased, (2.5 mmol, 0.54 g) of 3-nitrobenzyl bromide **1c** in 5 mL of THF were added and the reaction mixture was stirred for 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. The yields are summarized in Table V.

Run 1 see Table I run 6

Run 2 see Table I run 7

Run 3

3-nitrobenzyl bromide **1c** (eluted with hexane) 0.140 g (26%)
2-(3-nitrophenyl)methyl-2-oxa-5,5-dimethyl-1,3,2-dioxaphospholan **2f** (eluted with chloroform) 0.513 g (72%) m.p. = 83–84°C
IR (KBr) ν = 1260 P═O, 1040 P—O—C, 1530, 1360 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 0.870 (s, CH_{3a}, 3H), 0.930 (s, CH_{3e}, 3H), 3.385 (d, J = 21.90 Hz, CH_2P, ZH), 3.72–3.82 (m, $POCH_a$, 2H), 4.24–4.32 (m, $POCH_e$, 2H), 7.28–7.40 (m, aromat, 1H), 7.48–7.56 (m, aromat, 1H), 7.68–7.72 (m, aromat, 1H), 8.10–8.20 (m, aromat, 1H), ^{31}PNMR ($CDCl_3$) δ = 21.56

Acid hydrolysis of this material yielded a (3-nitrophenyl)methyl phosphonic acid m.p. 187–188°C (lit. 186–187°C).[18]

Run 4

3-nitrotoluene **5c** (eluted with hexane) 0.007 g (2%)
3-nitrobenzyl bromide **1c** (eluted with hexane) 0.281 g (52%)
1,2-di(3-nitrophenyl)ethane **4c** (eluted with hexane:chloroform 1:2) 0.071 g (21%)
(3-nitrophenyl)methyl-dibenzyl-phosphine oxide **2g** (eluted with chloroform) 0.183 g (20%) m.p. = 172–173°C
IR (KBr) ν = 1210 P═O, 1530, 1360 NO_2 cm^{-1}
^{1}HNMR ($CDCl_3$) δ = 3.04 (d, J = 13.45 Hz, CH_2P, 6H), 7.50–8.20 (m, aromat, 14H)
^{31}PNMR ($CDCl_3$) δ = 40.15
Anal. Calcd. for $C_{21}H_{20}NO_3P$: C, 69.03; H, 5.52; found: C, 69.17, H, 5.61

Run 5

3-nitrotoluene **5c** (eluted with hexane) 0.014 g (4%)
3-nitrobenzyl bromide **1c** (eluted with hexane) 0.437 g (81%)
1,2-di(3-nitrophenyl)ethane **4c** (eluted with hexane:chloroform 1:2) 0.034 g (10%)

Run 7

3-nitrotoluene **5c** (eluted with hexane) 0.041 g (12%)
3-nitrobenzyl bromide **1c** (eluted with hexane) 0.464 g (86%)

The Control Experiment with p-Nitrotoluene in Methanol-O-d at the Presence of Sodium Dimethylphosphite

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 *p*-nitrotoluene **1e** (2.5 mmol, 0.343 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 NH_4Cl saturated solution and dried over $MgSO_4$. The solvent was removed in the vacuum and the products were separated by radial chromatography. Deuterium incorporation was not observed by the use of a mass spectroscopic analysis and ^{1}HNMR. The same result was obtained when the reaction mixture was stirred for 24 hours at room temperature.

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