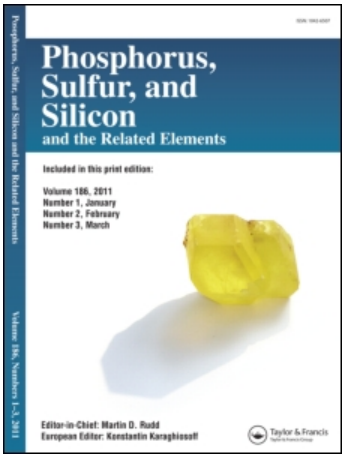

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART VIII.* REACTIVITY OF THE >P-O⁻ NUCLEOPHILES TOWARD ARYLMETHYLBROMIDE SYSTEMS. FURTHER EVIDENCE FOR THE X-PHILIC SUBSTITUTION/SET TANDEM MECHANISM

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART VIII.* REACTIVITY OF THE >P-O$^-$ NUCLEOPHILES TOWARD ARYLMETHYLBROMIDE SYSTEMS. FURTHER EVIDENCE FOR THE X-PHILIC SUBSTITUTION/SET TANDEM MECHANISM

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The reaction of sodium dimethyl and diisopropyl phosphite, as well as dibenzylphosphinite with bromodiphenylmethane, 9-bromofluorene and triphenylmethyl bromide was studied in detail by (1) isolating and identification of all products, (2) studying the effects of the solvents, as well as light on product distribution. The results of the experiments carried out are compatible with the proposed X-philic substitution/SET tandem mechanism. It was demonstrated that the triphenylmethyl radical can couple with the diethyl phosphite anion producing diethyl triphenylmethylphosphonate in the chain process.

Keywords: bromodiphenylmethane; triphenylmethyl bromide; 9-bromofluorene; Michaelis-Becker reaction; X-philic substitution/SET tandem mechanism

INTRODUCTION

The anions of the >P-O$^-$ type are of special interest; they are nucleophilic ambient reagents,[1] strong bases,[2] and single electron donors.[3] On the other hand

*Part VII see lit. 9

†Corresponding author.

the compounds of the >P(O)H structure can act as proton[4] or hydrogen[5] sources; depending on the structure and reaction conditions.

Recently we were able to demonstrate that the anions of the $>P\text{-}O^-$ type as well as $>P\text{-}S^-$ undergo reaction with α-bromocarboxylates as well as phosphonates yielding debrominated products.[6] The results of our investigations show that in the case of the carbon bromine bond, also bromine can be a target for nucleophilic attack by the phosphorus reagent of the $>P\text{-}O^-$ as well as $>P\text{-}S^-$ types with the release of the carbanion as nucleofuge. We were also able to demonstrate[7] that according to the reduction potential of p-substituted benzyl bromides and the solvent used in the reaction of these starting materials and the nucleophilic reagent of the $>P\text{-}O^-$ type the formation of the P-C bond, debromination and/or dimerization occur. The influence of light and product analyses[7,8] as well as the results of the free radical trap experiments[9] have resulted in a reasonable picture of the mechanism of the reaction between p-substituted benzyl bromides and $>P\text{-}O^-$ nucleophiles as outlined in Scheme 1.

The results of our research strongly speak for the X-philic substitution as the principal process in the reaction between p-substituted benzyl bromides (possessing electron-withdrawing groups) and $>P\text{-}O^-$ nucleophiles (eq 1). This nucleophilic attack of the $>P\text{-}O^-$ anion on the bromine atom results in benzyl anion formation **2**, which, depending on the redox potentials, can participate in the proton (eq 2) and/or electron transfer (eq 3) processes producing debrominated products **3** and/or dimers **7**.

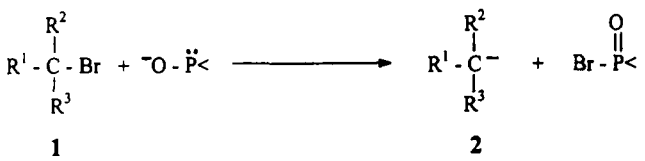
In order to check our postulate of X-philic substitution/SET tandem mechanism as well as the scope and limitations of this type of reactivity of the $>P\text{-}O^-$ ions, we decided to study other arylmethylbromide systems. We chose: bromodiphenylmethane, 9-bromofluorene and triphenylmethyl bromide.

In this paper we present the results of this investigation.

RESULTS AND DISCUSSION

Our principal experiments are summarized in Scheme 2 and Table I. They concern three phosphanion nucleophiles previously involved in X-philic substitution/SET tandem reactions, namely, $(MeO)_2P\text{-}O^-$; $(iPrO)_2P\text{-}O^-$, and $(PhCH_2)_2P\text{-}O^-$.

The treatment of 1 equiv. of bromodiphenylmethane with 1 equiv. of the $>P\text{-}O^-$ anion (dimethyl, diisopropyl phosphite anions, dibenzylphosphinite anion) in THF produces 1,1,2,2-tetraphenylethane **7** as a major product and diphenylmethane **3** as a minor product (Table I runs 1,2,4). On the other hand, from

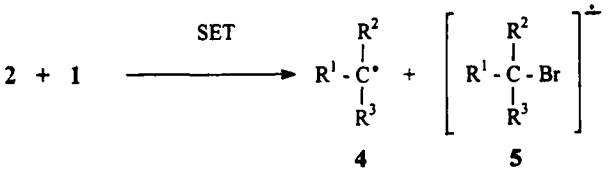


(1)

1 2

(2)

3



(3)

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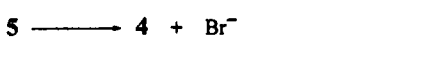

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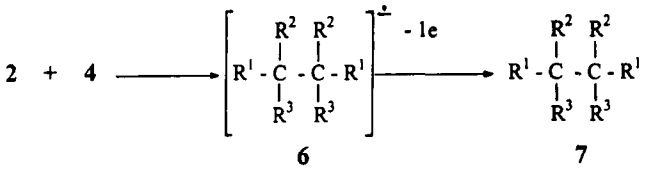
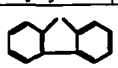


(5)

6 7

1, 2, 3, 4, 5, 6	R^1	R^2	R^3
	W-p-C_6H_4	H	H
	C_6H_5	C_6H_5	H
			H

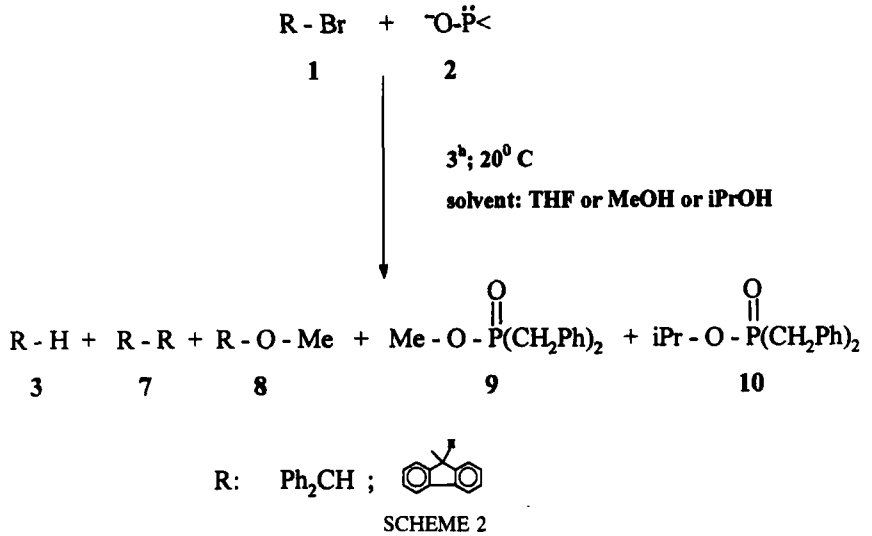
W = electron-withdrawing group

SCHEME 1

the reaction mixture of 1 equiv. of bromodiphenylmethane and 0.5 equiv. of sodium diisopropyl phosphite in THF we isolated the dimer (36%) and diphenylmethane (11%) besides benzhydrol (52%), which apparently was the hydrolysis product of the bromodiphenylmethane during the work up of the reaction mixture (Table I run 3).

When we carried out the reaction of bromodiphenylmethane with dimethyl phosphite in methanol in the presence of sodium methanolate we isolated only diphenylmethyl methyl ether **8** as a solvolysis product (Table I run 5). In contrast to that, from the reaction mixture of 1 equiv. of bromodiphenylmethane and sodium diisopropyl phosphite as well as sodium dibenzylphosphinite in i-PrOH we isolated one major product, namely diphenylmethane **3** (Table I runs 6, 7). Additionally, in case of dibenzylphosphine oxide, used as a precursor of $>P\text{-}O^-$ nucleophile, we isolated isopropyl dibenzylphosphinate **10** from the reaction mixture (Table I run 7).

Similar results were obtained when 9-bromofluorene was used in the reaction with the $>P\text{-}O^-$ nucleophiles. From the reaction mixture of 1 equiv. of sodium dialkyl phosphite as well as sodium dibenzylphosphinite with 1 equiv. of 9-bromofluorene in THF we isolated two products: dimer **7** as a major and fluorene **3** as a minor product (Table I runs 8, 9, 11). The treatment of 1 equiv. of 9-bromofluorene with 0,5 equiv. of the phosphite anion gives only 48% conversion; we isolated 52% of 9-bromofluorene from this reaction mixture (Table I run 10). Again in the case of methanol as well as isopropanol as solvent in the reaction of 1 equiv. of 9-bromofluorene and 1 equiv. of dimethyl-, diisopropyl phosphite and dibenzylphosphine oxide in the presence of sodium alcoholates we isolated fluorene almost in quantitative yields (Table I runs 12, 13, 14). In case of dibenzylphosphine oxide used in the reaction under investigation, we additionally isolated methyl dibenzylphosphinate **9** (Table I run 13).



SCHEME 2

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.[10] In order to provide evidence for the SET mechanism operating in the reactions of bromodiphenylmethane as well as 9-bromofluorene with the >P-O$^-$ ions we carried out the reactions for 35 minutes in THF at −45°C with 1 equiv. of bromodiphenylmethane, 9-bromofluorene and sodium diisopropyl phosphite under a variety of conditions: in darkness, day light and irradiation with 500 W bulb. The results of these experiments are summarized in Table II.

As it can be seen from Table II, we found a substantial influence of light on the yield of isolated dimers **7**. We observed a dramatic influence of light on the yield of 1,1,2,2-tetraphenylethane; 0% in the case of the reaction conducted in darkness vs 62% yield in the case of illumination of the reaction flask by 500 W bulb (Table II runs 1–3). In the experiment carried out in darkness, we found only debrominated product **3** in the reaction mixture, namely diphenylmethane (Table II run 1). We also observed a substantial influence of light on the yield of bifluorene formation; 32% in the case of the reaction conducted in darkness vs 77% yield in the case of illumination of the reaction flask by 500 W bulb (Table II runs 4–6).

Another interesting feature of this set of experiments is that the yield of debrominated products **3** decreases with an increase in the yield of the dimers **7**. Again we found a substantial influence of light on the isolated yield of debro-

TABLE I Reaction of the >P-O$^-$ nucleophiles with bromodiphenylmethane and 9-bromofluorene in THF and alcohols

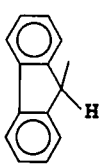
Run	*R*	*>P-O$^-$ ratio >P-O$^-$/R-Br*	*Solvent*	*% isolated yield of*				
				3	7	8	9	10
1		$^-$O-P(OMe)$_2$ 1		26	72			
2		$^-$O-P(OiPr)$_2$ 1		24	74			
3		$^-$O-P(OiPr)$_2$ 0.5	THF	11	36			
4	Ph_2CH	$^-$O-P(CH$_2$Ph)$_2$ 1		27	71			
5		$^-$O-P(OMe)$_2$ 1	MeOH			99		
6		$^-$O-P(OiPr)$_2$ 1	iPrOH	97				
7		$^-$O-P(CH$_2$Ph)$_2$ 1		99				84
8		$^-$O-P(OMe)$_2$ 1		26	73			
9		$^-$O-P(OiPr)$_2$ 1		28	72			
10		$^-$O-P(OiPr)$_2$ 0.5	THF	15	32			
11		$^-$O-P(CH$_2$Ph)$_2$ 1		25	74			
13		$^-$O-P(CH$_2$Ph)$_2$ 1		98			94	
14		$^-$O-P(OiPr)$_2$ 1	iPrOH	97				

TABLE II Light influence on the products distribution of the reaction of bromodiphenylmethane and 9-bromofluorene with sodium diisopropyl phosphite (THF; 35'; −45°C)

Run	*R*	*Conditions*	*% isolated yield of*		
			1	3	7
1	Ph_2CH	Darkness	67*	31	–
2		Normal	49*	12	37
3		Light of 500 W bulb	31*	5	62
4		Darkness	43	24	32
5		Normal	32	18	48
6		Light of 500 W bulb	15	7	77

*based on the yield of benzhydrol

minated products **3** but this time in a reversed order. This last observation strongly suggests that diphenylmethyl anion **2** ($R^1 = R^2 = Ph$) as well as 9-fluorenyl anion **2** ($R^1 = R^2 = C_6H_4\text{-}C_6H_4$; $R^3 = H$) are consumed during the dimers' **7** formation; the dimer formation is a secondary process via SET (this reaction is light sensitive) from carbanions **2** and arylmethylbromides **1** (Scheme 1 eq 3–5).

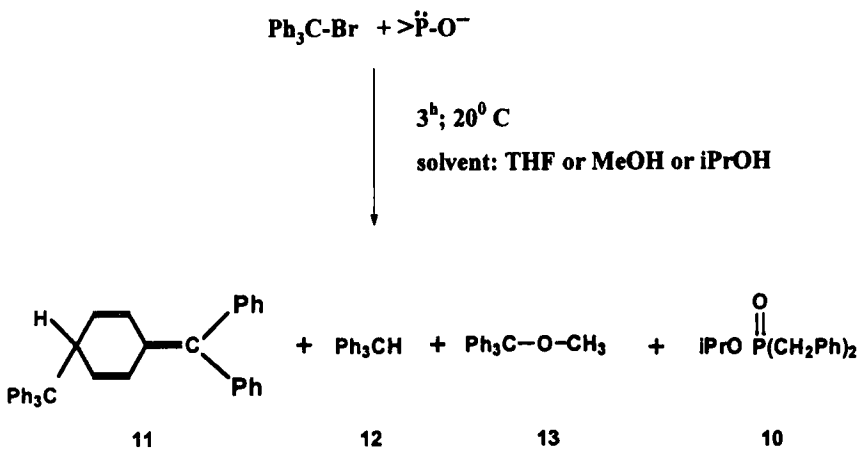
As one can see from Tables I and II at this stage of our research the results of this set of experiments are in full agreement with the proposed X-philic substitution/SET tandem mechanism presented in Scheme 1.

Dialkyl phosphite anions give a satisfactory yield of the Michaelis—Becker reaction only with primary alkyl halides. Secondary and tertiary halides with dialkyl phosphite anions give poor yield or a complex mixture of the products. Additionally the reaction between bromotriphnylmethane and sodium diethyl phosphite was claimed to be a free radical process. [11]Twenty years later[12] electron spin resonance spectroscopy was used to obtain confirmatory evidence for the presence of free radicals in the reaction mixture of triphenylbromomethane and sodium diethyl phosphite.

We decided to reinvestigate this reaction to get information whether in the case of triphenylbromomethane and the $>P\text{-}O^-$ type nucleophiles the proposed X-philic substitution/SET tandem mechanism operates.

We carried out the reactions of 1 equiv. of triphenylmethyl bromide with 1 equiv. of the $>P\text{-}O^-$ type anions in MeOH, iPrOH and THF. The results of this set of experiments are presented in Scheme 3 and collected in Table III.

Treatment of triphenylmethyl bromide with dimethyl phosphite in the presence of sodium methanolate in methanol produces only methyl triphenylmethyl ether **13** as a solvolysis product (Table III run 3). In contrast to that treatment of triphenylmethyl bromide with diisopropyl phosphite as well as dibenzylphosphine oxide in the presence of sodium isopropanolate in iPrOH produces a quantitative yield of triphenylmethane **12** (Table III run 4, 5). Additionally from



SCHEME 3

the reaction mixture of triphenylmethyl bromide, dibenzylphosphine oxide and sodium isopropanolate in iPrOH we isolated isopropyl dibenzylphosphinate **10** (Table III run 5).

On the other hand the reaction of sodium dimethyl phosphite as well as sodium diisopropyl phosphite with triphenylmethyl bromide in THF produces dimer **11** as a major product and triphenylmethane **12** as a minor one (Table III runs 1, 2).

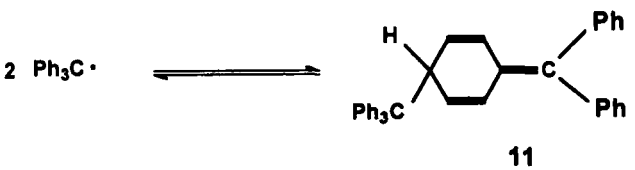
Triphenylmethane isolated from the reaction mixture of triphenylmethyl bromide and the $>P\text{-}O^-$ anions carried out in iPrOH and also in THF is derived from the initial X-philic substitution product: the triphenylmethyl anion (quenched with iPrOH or water during work up). The former Arbuzov observation, [11] as well as the electron spin resonance spectroscopy experiment[12] speak for the presence of free radicals in the reaction mixture.

TABLE III Reaction of triphenylmethyl bromide with $>P\text{-}O^-$ nucleophiles [$-P^-O(OMe)_2$; P^-O-;$P(OiPr)_2$; $^-O\text{-}P(CH_2Ph)_2$]

Run	*>P-O⁻*	*Solvent*	*% isolated yield of*			
10	11	12	13			
1	$^-O\text{-}P(OMe)_2$			84	15	
2	$^-O\text{-}P(OiPr)_2$	THF		87	12	
3	$^-O\text{-}P(OMe)_2$	MeOH				98
4	$^-O\text{-}P(OiPr)_2$				97	
5	$^-O\text{-}P(CH_2Ph)_2$	iPrOH	96		98	

The results of the experiments from Table III as well as Arbuzov's observation are in full agreement with the proposed mechanism outlined in Scheme 1. The nucleophilic attack of the >P-O$^-$ nucleophile on the bromine atom of the triphenylmethyl bromide results in the triphenylmethyl anion **2** formation (eq 1; $R^1 = R^2 = R^3 = C_6H_5$), which in the protic solvents is transferred into triphenylmethane **3** (eq 2; $R^1 = R^2 = R^3 = C_6H_5$). However, in THF it can participate in the SET process producing triphenylmethyl radical **4** (eq 3 and 4; $R^1 = R^2 = R^3 = C_6H_5$). The key step in our X-philic substitution/SET tandem mechanism is the formation of dimer anion radical **6** as the consequence of the reaction between carbon centered radicals **4** and carbanions **2** (Scheme 1 eq 5).

On the other hand it is well known that the triphenylmethyl radical is stable enough to exist in solution at room temperature, though in equilibrium with a dimeric form (Scheme 4).[15]



11

SCHEME 4

In this particular case the dimer **11** formation in the reaction under investigation can occur by triphenylmethyl radical dimerization.

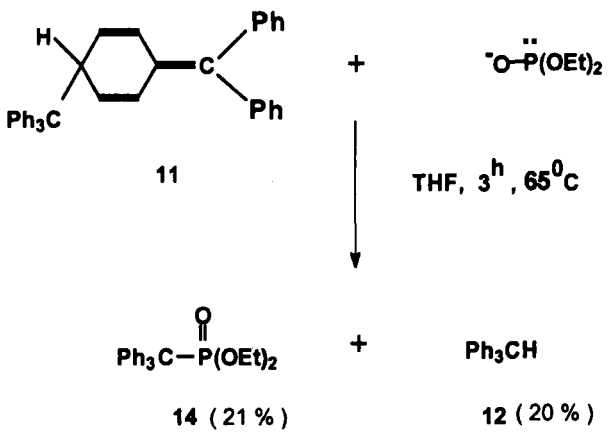
Nevertheless, the dialkyl phosphite anions are known to be radical traps in aromatic $S_{RN}1$ reactions yielding arylphosphonates[13], also alk-1-enyl as well as nitroalkyl radicals add readily to >P-O$^-$ nucleophiles.[14]

It was of interest to answer the question, why triphenylmethyl radical does not couple with the >P-O$^-$ type anions to produce triphenylmethylphosphonates by a chain mechanism, in the reaction in focus?

We decided first of all to check if diethyl phosphite anion is a good enough trap for triphenylmethyl radical.

The treatment of 1 equiv of 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene **11** with 1 equiv of sodium diethylphosphite in THF at room temperature for 24 hours resulted in the isomerization of the dimer **11** into p-benzhydryltetraphenylmethane **15**. It was recognized earlier that all quinonoid dimers of type **11** investigated so far rearrange easily to the benzoid products of type **15** via a 1,5-H shift, both by base[27] and by acid catalysis.[28] This rearrangement is commonly acknowledged as additional proof for a quinoid structure such as **11** for the Gomberg's trityl. Yet it is well known that warming a solution of the quinonoid dimer **11** gives rise in the triphenylmethyl radical concentration.[16]

We ran the reaction of 1 equiv. of dimer **11** with 1 equiv. of sodium diethyl phosphite in boiling THF. From this reaction mixture we isolated triphenylmethane **12** (20%), dimer **11** (57%) and diethyl triphenylmethylphosphonate **14** with 21% yield (Scheme 5).



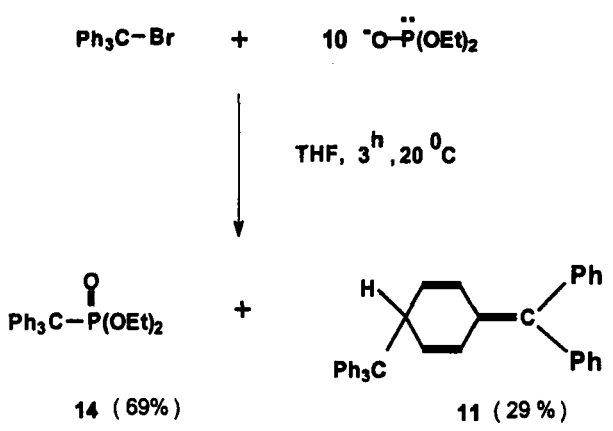
SCHEME 5

Triphenylmethylphosphonate isolated from this experiment shows that diethyl phosphite anion is able to react with triphenylmethyl radical producing triphenylmethylphosphonate anion radical, which can transfer one electron to the triphenylmethyl radical to form phosphonate and triphenylmethyl anion. Triphenylmethane **12** is derived from the initial one electron reduction product: the triphenylmethyl anion (quenched with water during work up). It should be pointed out that we isolated from the reaction mixture triphenylmethylphosphonate **14** and triphenylmethane **12** with almost the same yield 21% and 20% respectively, which is in full agreement with the picture of the reaction presented above.

The question to be answered is if in the case of reaction between triphenylmethyl bromide and sodium diethyl phosphite X-philic substitution/SET tandem mechanism operates, why don't we observe diethyl triphenylmethylphosphonate **14** formation. The reaction sequence presented in Scheme 1 appears to offer an answer to this question.

First let us assume that diethyl bromophosphate, electrophile formed via eq 1 (X-philic substitution) is rapidly scavenged by diethyl phosphite anion. As a consequence, $(EtO)_2P\text{-}O^-$ anion would never be present in high enough concentration to couple with the triphenylmethyl radical. When the concentration of this anion builds up sufficiently, it can compete for triphenylmethyl radical and

generate diethyl triphenylmethylphosphonate by a chain sequence. If this scheme is correct we would expect to find the diethyl triphenylmethylphosphonate **14** among the products in the reaction carried out with excess of sodium diethyl phosphite. This expectation was verified by experiment. We carried out the reaction of 1 equiv. of triphenylbromomethane with 10 equiv. of sodium diethyl phosphite in THF. From this reaction mixture we isolated diethyl triphenylmethylphosphonate (69%) and dimer **11** (29%), Scheme 6.



SCHEME 6

Additional work, to obtain evidence for the presence of the >P(O)Br type intermediate in the reaction in focus and also to obtain proof for the secondary process, i.e. the reaction between >P(O)Br electrophile and >P-O$^-$ nucleophile, is under way. The results will be published successively.

Acknowledgments

Financial assistance from the Internal Grants Committee of Technical University of Gdansk; Department of Chemistry is gratefully acknowledged.

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. 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. 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.

The Reaction Between Diphenylbromomethane or 9-Bromoflourene and >P-O$^-$ Nucleophiles: General Procedure

A. In THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF dimethyl phosphite, diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 10 mL of THF were added. When the evolution of hydrogen had ceased, diphenylbromomethane or 9-bromofluorene **1** (2.5 mmol) 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 vacuum and the products were separated by radial chromatography. The yields are shown in Table I.

Run 1

diphenylmethane **3a** (eluted with hexane) 0.109 g (26%)

m.p. 21–22°C (lit. 22–24°C).[17]

^{1}H NMR ($CDCl_3$) δ = 3.63 (s, CH_2, 2H), 6.50–7.10 (m, C_6H_5, 10H)

1,1,2,2-tetraphenylethane **7a** (eluted with chloroform) 0.301 g (72%)

m.p. 212–213°C (lit. 214–215°C).[18]

^{1}H NMR ($CDCl_3$) δ = 4.56 (s, CH, 2H), 6.52–7.16 (m, C_6H_5, 20H)

Run 2

diphenylmethane **3a** (eluted with hexane) 0.101 g (24%)

1,1,2,2-tetraphenylethane **7a** (eluted with chloroform) 0.309 g (74%)

Run 4

diphenylmethane **3a** (eluted with hexane) 0.114 g (27%)

1,1,2,2-tetraphenylethane **7a** (eluted with chloroform) 0.297 g (71%)

Run 8

fluorene **3b** (eluted with hexane) 0.108 g (26%)

m.p. 113–115°C (lit. 114–116°C).[19]

^{1}H NMR ($CDCl_3$) δ = 3.96 (s, CH_2, 2H), 7.30–7.52 (m, aromatic, 4H), 7.54–7.68 (m, aromatic, 2H), 7.80–7.92 (m, aromatic, 2H)

9,9′-bifluorene **7b** (eluted with chloroform) 0.302 g (73%)

m.p. 239–241°C (lit. 246°C).[20]

^{1}H NMR ($CDCl_3$) δ = 4.86 (s, CH, 2H), 6.97 (d, J = 7.62 Hz, aromatic, 4H), 7.04–7.20 (m, aromatic, 4H), 7.20–7.38 (m, aromatic, 4H), 7.67 (d, J = 7.49 Hz, aromatic, 4H)

Run 9
fluorene **3b** (eluted with hexane) 0.116 g (28%)
9,9′-bifluorene **7b** (eluted with chloroform) 0.297 g (72%)
Run 11
fluorene **3b** (eluted with hexane) 0.104 g (25%)
9,9′-bifluorene **7b** (eluted with chloroform) 0.306 g (74%)

B. In Methanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol and into the resultant mixture dimethyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 5 mL of methanol and diphenylbromomethane or 9-bromofluorene **1** (2.5 mmol) 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 vacuum and the products were separated by radial chromatography. The yields are shown in Table I.

Run 5
diphenylmethyl methyl ether **8** (eluted with hexane:chloroform 4:1) 0.486 g (99%)
IR (Film) ν = 1120 C-O-C cm^{-1}
^1H NMR ($CDCl_3$) δ = 3.03 (s, OCH_3, 3H), 4.76 (s, CH, 1H), 6.53–7.06 (m, C_6H_5, 10H)
Run 12
fluorene **3b** (eluted with hexane) 0.415 g (99%)
Run 13
fluorene **3b** (eluted with hexane) 0.104 g (98%)
methyl dibenzylphosphinate **9** (eluted with chloroform) 0.607 g (94%)
m.p. 63–65°C (lit. 75°C).[21]
IR (KBr) ν = 1230 P=O, 1065 P-O-C cm^{-1}
^1H NMR ($CDCl_3$) δ = 3.08 (d, J = 16.28 Hz, CH_2P, 4H), 3.57 (d, J = 10.50 Hz, P-O-CH_3, 3H), 7.20–7.40 (m, C_6H_5, 10H)
^{31}P NMR δ = 49.80

C. In Isopropanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of iPrOH and to the resultant mixture diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 10 mL of iPrOH and diphenylbromomethane or 9-bromofluorene **1** (2.5 mmol) in 5 mL

of THF were added. 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 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 6

diphenylmethane **3a** (eluted with hexane) 0.408 g (97%)

Run 7

diphenylmethane **3a** (eluted with hexane) 0.416 g (99%)

isopropyl dibenzylphosphinate **10** (eluted with chloroform) 0.606 g (84%)

m.p. 70–72°C

IR (KBr) ν = 1230 P═O, 1060 P-O-C cm^{-1}

^1H NMR ($CDCl_3$) δ = 1.03 (d, J = 6.00 Hz, CH_3, 6H), 2.93 (d, J = 16.18 Hz, CH_2P, 4H), 4.16–4.50 (m, CH, 1H), 6.80–7.26 (m, C_6H_5, 10H)

^{31}P NMR δ = 47.10

Anal. Calcd. for $C_{17}H_{21}O_2P$: C, 70.82; H, 7.34; found: C, 70.53, H, 7.52

Run 14

fluorene **3b** (eluted with hexane) 0.403 g (97%)

The Reaction of 2 equiv. of Diphenylbromomethane or 9-Bromofluorene with 1 equiv. of Sodium Diisopropyl Phosphite in THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF diisopropyl phosphite (2.5 mmol, 0.42 g, 0.42 mL) in 10 mL of THF was added. When the evolution of hydrogen had ceased, diphenylbromomethane or 9-bromofluorene **1** (5.0 mmol) 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 vacuum and the products were separated by radial chromatography. The yields are shown in Table I.

Run 3

diphenylmethane **3a** (eluted with hexane) 0.093 g (11%)

1,1,2,2-tetraphenylethane **7a** (eluted with chloroform) 0.301 g (36%)

benzhydrol (eluted with chloroform) 0.479g (52%) from hydrolysis of **1a**

m.p. 66–67°C (lit. 65–67°C).[22]

^1H NMR ($CDCl_3$) δ = 1.96 (s, OH, 1H), 5.76 (s, CH, 1H), 7.03–7.50 (m, C_6H_5, 10H)

Run 10

fluorene **3b** (eluted with hexane) 0.125 g (15%)
9-bromofluorene **1b** (eluted with hexane:chloroform, 4:1) 0.638 g (52%)
9,9′-bifluorene **7b** (eluted with chloroform) 0.264 g (32%)

Influence of Light on the Reaction Between Diphenylbromomethane or 9-bromofluorene 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 diisopropyl phosphite (2.5 mmol, 0.42 g) in 10 mL of THF was added. When the evolution of hydrogen had ceased the solution was cooled to −45°C and diphenylbromomethane or 9-bromofluorene **1** (2.5 mmol) in 5 mL of THF were added and the reaction mixture was stirred for 35 min. at −45°C, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in 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 the 500 W bulb.

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

The Reaction Between Triphenylbromomethane and >P-O⁻ nucleophiles: General Procedure

A. In THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF dimethyl phosphite or diisopropyl phosphite (2.5 mmol) in 10 mL of THF were added. When the evolution of hydrogen had ceased, triphenylbromomethane (2.5 mmol) in 5 mL of THF was 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 vacuum and the products were separated by radial chromatography. The yields are shown in Table III.

Run 1 triphenylmethane **12** (eluted with hexane) 0.092 g (15%) m.p. 91–93°C (lit. 92–93°C).[23]

^1H NMR ($CDCl_3$) δ = 5.26 (s, CH, 1H), 6.10–7.20 (m, C_6H_5, 15H)

1-diphenylmethylen-4-trityl-2,5-cyclohexadiene **11** (eluted with chloroform) 0.501 g (84%) m.p. 146–148°C (lit. 145–147°C).[24]

^1H NMR ($CDCl_3$) δ = 5.00 (s, CH, 1H), 5.80–6.43 (m, dienyl, 4H), 6.78–7.46 (m, C_6H_5, 25H)

Run 2 triphenylmethane **12** (eluted with hexane) 0.073 g (12%) 1-diphenylmethylen-4-trityl-2,5-cyclohexadiene **11** (eluted with chloroform) 0.529 g (87%)

B. In Methanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of methanol and into the resultant mixture dimethyl phosphite (2.5 mmol, 0.23 mL) in 5 mL of methanol and triphenylbromomethane (2.5 mmol, 0.808 g) in 10 mL of methanol was 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 vacuum and the products were separated by radial chromatography. The yield is shown in Table III.

Run 3 methyl trityl ether **13** (eluted with chloroform) 0.481 g (98%) m.p. 82–83°C (lit. 82°C).[25]

IR (KBr) ν = 1130 C-O-C cm^{-1}

^1H NMR ($CDCl_3$) δ = 2.90 (s, O-CH_3, 3H), 6.70–7.26 (m, C_6H_5, 15H)

C. In Isopropanol Solution

NaH (3.0 mmol, 0.072 g) was dissolved in 10 mL of iPrOH and to the resultant mixture diisopropyl phosphite or dibenzylphosphine oxide (2.5 mmol) in 10 mL of iPrOH and triphenylbromomethane (2.5 mmol, 0.808 g) in 5 mL of THF was added. 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 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 III.

Run 4

triphenylmethane **12** (eluted with hexane) 0.593 g (97%) Run 5

triphenylmethane **12** (eluted with hexane) 0.599 g (98%)

isopropyl dibenzylphosphinate **10** (eluted with chloroform) 0.692 g (96%)

The Reaction Between 1-Diphenylmethylene-4-trityl-2,5-cycklohexadiene 11 and Sodium Diethyl Phosphite in THF Solution.

A. In THF at 20°C

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF diethyl phosphite (2.5 mmol, 0.345 g, 0.32 mL) in 10 mL of THF was added. When the evolution

of hydrogen had ceased, 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (2.5 mmol, 1.217 g) in 5 mL of THF was added and the reaction mixture was stirred for 24 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 vacuum and the products were separated by radial chromatography yielded:

4-benzhydryl-tetraphenylmethane **15** (eluted with chlorophorm) 1.168 g (96%)

m.p. 224–226°C (lit. 225–227°C).[28]

^1H NMR ($CDCl_3$) δ = 5.36 (s, CH, 1H), 6.80–7.66 (m, C_6H_5, 29H)

B. In Boiling THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 10 mL of THF diethyl phosphite (2.5 mmol, 0.345 g, 0.32 mL) in 10 mL of THF was added. When the evolution of hydrogen had ceased, 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene (2.5 mmol, 1.217 g) in 5 mL of THF was added and the reaction mixture was stirred for 3 hours at boiling point of the solvent, then diluted with 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and the products were separated by radial chromatography yielded:

triphenylmethane **12** (eluted with hexane) 0.244 g (20%)

1-diphenylmethylen-4-trityl-2,5-cyclohexadiene **11** (eluted with chloroform) 0.694 g (57%)

diethyl triphenylmethylphosphonate **14** (eluted with chloroform) 0.399 g (21%)

m.p. 121–122°C (lit. 121–122°C).[26]

IR (KBr) ν = 1265 P=O, 1015 P-O-C cm^{-1}

^1H NMR ($CDCl_3$) δ = 0.96 (t, J = 6.00 Hz, CH_3, 6H), 3.40–4.06 (m, O-CH_2, 4H), 6.70–7.30 (m, C_6H_5, 15H)

^{31}P NMR ($CDCl_3$) δ = 26.67

The Reaction of 1 equiv. of Triphenylbromomethane with 10 equiv. of Sodium Diethyl Phosphite in THF Solution

To a suspension of NaH (15.0 mmol, 0.360 g) in 10 mL of THF diethyl phosphite (12.5 mmol, 1.725 g, 1.61 mL) in 10 mL of THF was added. When the evolution of hydrogen had ceased, triphenylbromomethane (1.25 mmol, 0.404 g) in 5 mL of THF was 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 vacuum and the prod-

ucts were separated by radial chromatography; it yielded: 1-diphenylmethylen-4-trityl-2,5-cyclohexadiene **11** (eluted with chloroform) 0.088 g (29%) and diethyl triphenylmethylphosphonate **14** (eluted with chloroform) 0.328 g (69%)

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