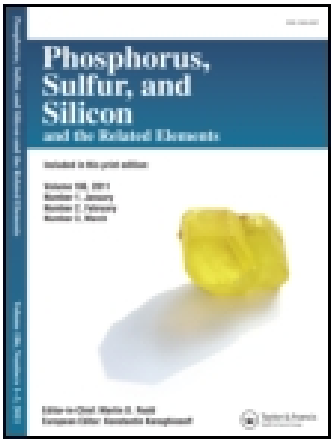

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART IX. THE >P-O⁻ AND >P-S⁻ NUCLEOPHILES IN THE REACTIONS OF HALOPHILIC SUBSTITUTION

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART IX.* THE >P-O$^-$ AND >P-S$^-$ NUCLEOPHILES IN THE REACTIONS OF HALOPHILIC SUBSTITUTION†

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(Received 25 March 1997)

The reaction of the >P-Y$^-$ (Y = O; S) nucleophiles with the compounds possessing a C-Br bond and electron-withdrawing groups is described. The isolation of the products derived from dialkyl bromophosphates, the results of the ^{31}P NMR studies, as well as the isolation of bromothiophosphate from the reaction mixture of >P-S$^-$ nucleophile and methyl α-bromocarboxylate, are further evidence for halophilic substitution as the principal process in the X-philic substitution/SET tandem mechanism operating in the reaction of these phosphorus nucleophiles with the bromoderivatives possessing electron-withdrawing groups.

Keywords: ^{31}P NMR studies; >P-Y$^-$ nucleophiles; Michaelis—Becker reaction; X-philic substitution/SET tandem mechanism

INTRODUCTION

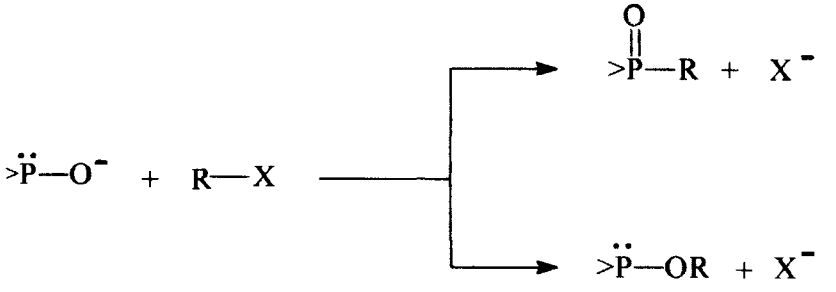
Dialkyl phosphites exist almost entirely in the phosphonate form $(RO)_2P(O)H$, which bears no lone pair electrons on phosphorus. Accordingly, the neutral esters are unreactive partners in nucleophilic substitution reactions, compared with trialkyl phosphites. The anions, however, displace halide ion smoothly in the Michaelis—Becker reaction, to give phosphonate esters, in presumably bimolecular

*Part VIII see lit. 6

†This paper is dedicated to Professor Czeslaw Wasielewski, whose untimely death occurred February 1996.

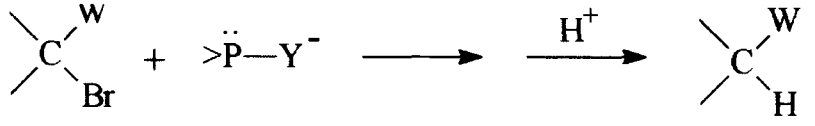
‡Corresponding author.

process, as indicated by the relative reactivity of the various halides.[1] Although the anion of a dialkyl phosphite is formally an ambient nucleophile, however, attack at oxygen occurs only very rarely. It is reported that alkylation on oxygen does occur when silver dialkyl phosphites react with triarylmethyl halides.[2]



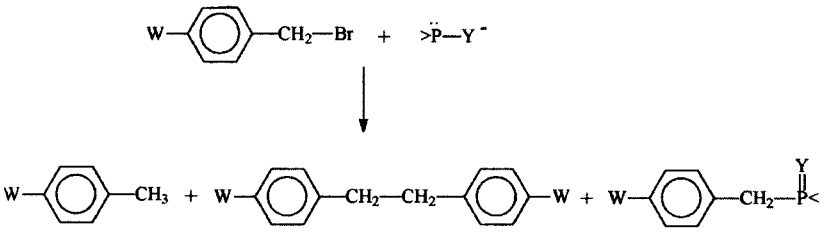
Additionally, it was shown by J. F. Bunnett that the >P-O⁻ as well as >P-S⁻ nucleophiles react with iodo- and bromobenzene to form substitution products. These reactions are believed, on good evidence, to occur by the radical chain $S_{RN}1$ mechanism[3] and serve to establish aryl carbon-phosphorus bond.

For several years, we have been interested in the reactivity of >P-Y⁻ (Y = O; S) nucleophiles. Recently we were able to demonstrate that these anions undergo reactions with α-bromocarboxylates as well as phosphonates yielding debrominated products.[4]



Y : O; S
W : COOR; P(O)(OR)$_2$

Furthermore, we were also able to demonstrate 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-Y⁻ (Y = O; S) type, the formation of the P-C bond, debromination and/or dimerization occur.[5]



W : NO_2, CN, SO_2Ph, COOEt, COOMe, Br

The influence of light and product analyses, as well as the results of the free radical trap experiments have resulted in a reasonable picture of X-philic substitution/SET tandem mechanism of the reaction between bromoalkanes possessing electron-withdrawing groups and the $>P\text{-}Y^-$ (Y = O; S) nucleophiles as outlined in Scheme 1.

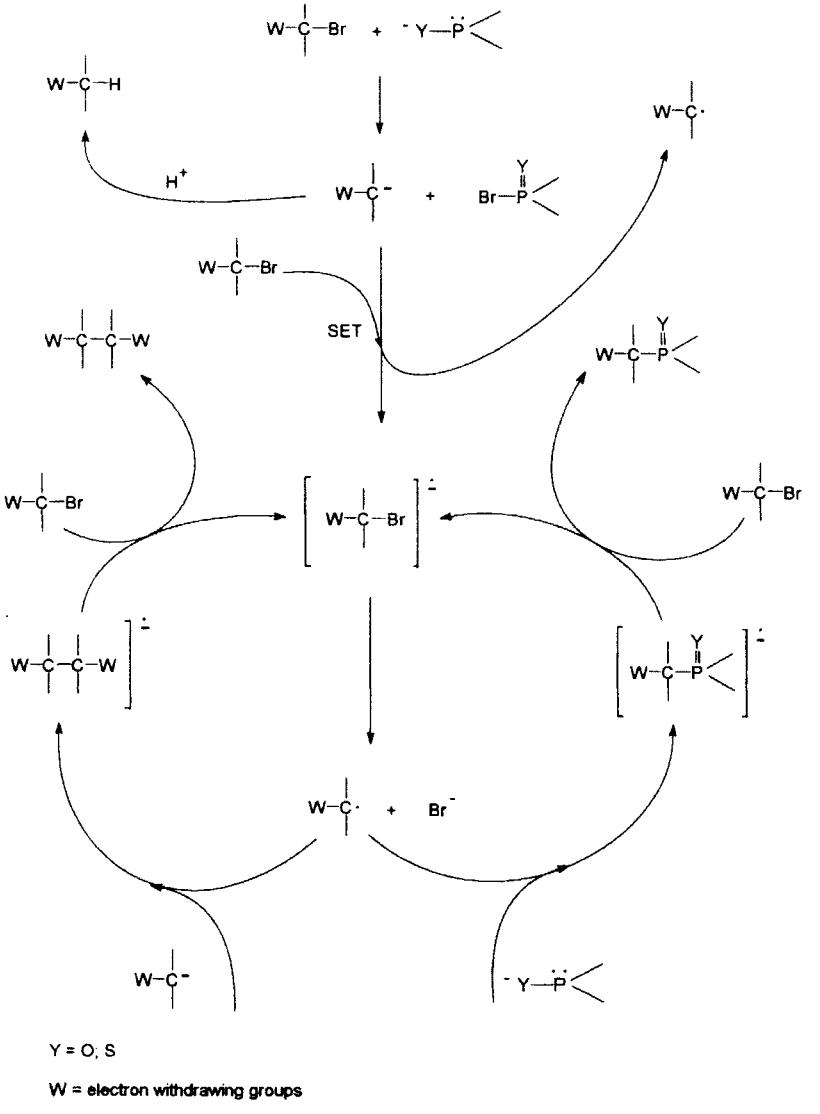
The results of our research strongly speak for the halophilic substitution as the principal process in the reaction in focus. This nucleophilic attack of the $>P\text{-}Y^-$ (Y = O; S) anion on the bromine atom results in carbanion formation, which, depending on the redox potentials, can participate in the proton and/or electron transfer processes producing debrominated products and/or dimers. In the course of our investigations we couldn't find evidence for the single electron transfer from the $>P\text{-}Y^-$ (Y = O; S) nucleophiles to bromoalkanes. On the other hand, however, we were able to demonstrate that these phosphorus anions are very good carbon centred radical traps.[5d]

Additionally, we studied in detail the reaction of sodium dimethyl and diisopropyl phosphite, as well as dibenzylphosphinite with bromodiphenylmethane, 9-bromofluorene and triphenylmethyl bromide. Also in this case the results of the experiments are compatible with the proposed X-philic substitution/SET tandem mechanism.[6]

The first step in our postulated X-philic substitution/SET tandem mechanism, bromine is a target for nucleophilic attack by the phosphorus reagent with the release of the carbanion as nucleofuge and $>P(Y)Br$ (Y = O; S) formation. We designed a new set of experiments to get the evidence for the compounds of the $>P(Y)Br$ (Y = O; S) structure as the intermediates in the reaction under investigation. In this paper we present the results of this investigation.

RESULTS AND DISCUSSION

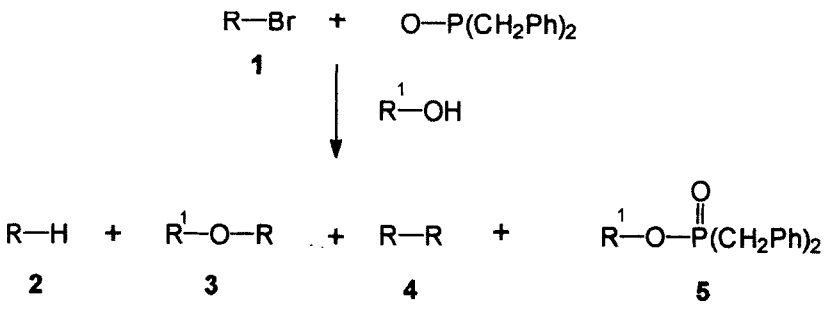
We ran the reaction of 1 equiv of bromoderivative **1** (methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate; p-nitrobenzyl bromide; bromodiphenylmethane; 9-bromofluorene and triphenylmethane) with 1 equiv. of sodium



dibenzylphosphinite in alcohols (methanol; isopropanol) as solvents Scheme 2.

The products distribution of these reactions strongly depends on the constitution of the bromoderivatives **1** used as the starting materials. The results of this set of experiments are collected in Table I.

As one can see from this table, we isolated from the reaction mixture: debrominated product **2**, ether **3** as a solvolysis product and dimer **4**. Furthermore,



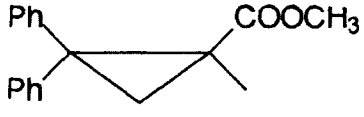
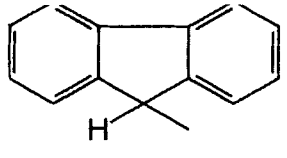
in every experiment carried out we isolated methyl or isopropyl dibenzylphosphinate **5** depending on the alcohol used, respectively.

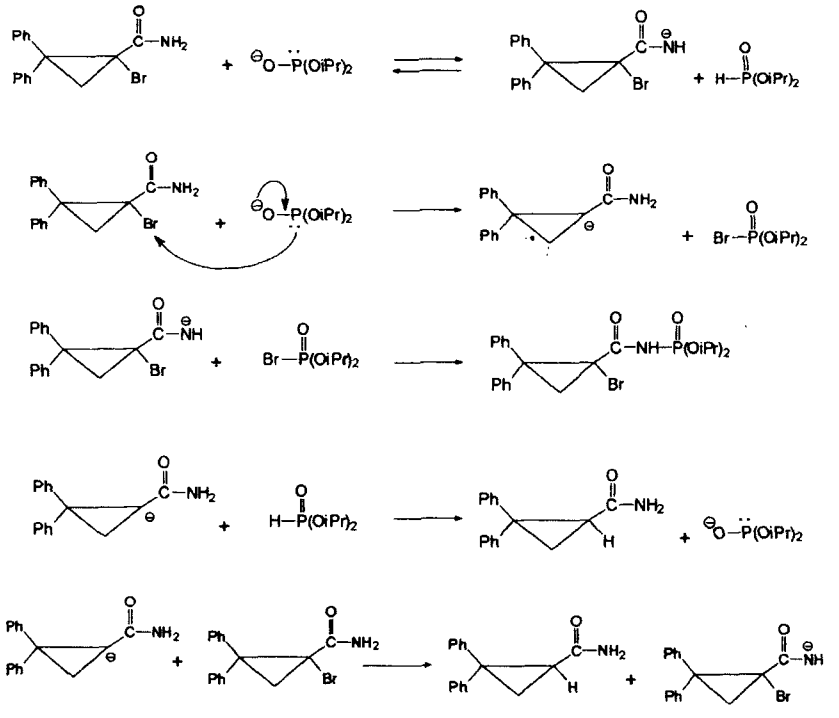
The alkyl dibenzylphosphinate **5**, isolated from the reaction mixture of bromoderivatives **1** and dibenzylphosphinite anion carried out in methanol or isopropanol, is derived from the initial X-philic substitution product, i.e. bromophosphinate, which undergoes a solvolysis process.

It is well known that carboxamides can be phosphorylated with chloro as well as bromo phosphates and phosphinates under basic conditions.[7]

Since dialkyl bromophosphates can react with carboxamides and compounds of the Br-P(O) < structure are postulated in our concept of X-philic substitution/SET tandem mechanism, one can expect that using α-bromocarboxamide in the reaction with the $>P\text{-}O^-$ nucleophiles, N-phosphorylated carboxamide should

TABLE I The products distribution in the reaction of the bromoderivatives **1** with sodium dibenzylphosphinite in alcohols as solvents.

Run	*R*	*R'*	*% of isolated yield*				
			1	*2*	*3*	*4*	*5*
1		Me	–	100	–	–	100
2	p-NO_2-C_6H_4-CH_2-	Me	23	34	11	29	38
3	Ph_2CH-	iPr	–	99	–	–	84
4		Me	–	98	–	–	94
5	Ph_3C-	iPr	–	98	–	–	96



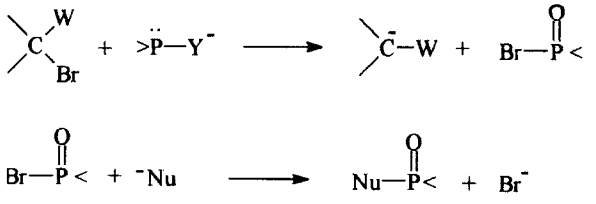
be produced. We decided to verify this hypothesis by experiment. The treatment of 1-bromo-2,2-diphenylcyclopropanecarboxamide with sodium diisopropyl phosphite in THF produces two major products; namely: 2,2-diphenylcyclopropanecarboxamide (debrominated product) and (N-diisopropylphosphoryl)-1-bromo-2,2-diphenylcyclopropanecarboxyamide (phosphorylated product). Isolation of the phosphorylated amide from the reaction mixture strongly supports our idea of halophilic substitution and the compound of BrP(O) < structure as an intermediate. However, the question can be asked, why, if the bromophosphate is formed only α-bromocarboxamide is phosphorylated?

The reaction sequence presented in Scheme 3 appears to offer a complete answer to this question.

The α-bromocarboxamides are much stronger N-H acids than appropriate carboxamides, in other words α-bromocarboxamide will be much faster deprotonated by the base than appropriate carboxamide. In the reaction mixture we have pretty strong bases, namely sodium diisopropyl phosphinate and anion of the 2,2-diphenylcyclopropanecarboxamide as a result of the halophilic substitution. Both of these bases can preferentially deprotonate α-bromo-2,2-diphenylcarbox-

amide to furnish a nucleophilic reagent which is phosphorylated by diisopropyl bromophosphate.

Previously we have observed that the treatment of 1 equiv. of bromocarboxylate, as well as bromophosphonate in THF at 20°C with 1 equiv. of the >P-O$^-$ anions produces the debrominated product with 50%–70% yield. On the other hand, the treatment of 1 equiv. of the same bromoderivatives in THF at 20°C with 2 equiv. of the phosphite anions yield the debrominated products almost quantitatively. The reaction proceeds very smoothly also in alcohols, as we showed earlier,[4a] and requires in this case only 1 equiv. of the phosphorus reagent and 1 equiv. of sodium alcoholate as a base for quantitative yield of the debrominated product. This observation can be explained in terms of halophilic substitution and the formation of bromophosphate. The bromophosphates are powerful electrophilic reagents which can react with the >P-O$^-$ nucleophiles, present in the reaction mixture, or suffer solvolysis when the reaction is run in alcohol as a solvent.



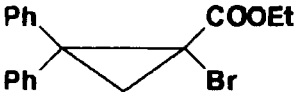
Nu : any nucleophile present in the reaction mixture

Unfortunately we were not able to isolate the Br-P(O)< type compounds from the reaction mixture of any of our experiment, which would be the direct proof, because of their very high reactivity and the presence of other nucleophiles in the raction medium. However, we decided to investigate the crude reaction mixture of the selected bromoderivatives possessing electron-withdrawing groups with sodium diethyl phosphite in THF employing ^{31}P NMR spectroscopy.

As the models for this study we chose: ethyl 1-bromo-2,2-diphenylcyclopropanecarboxylate; p-nitrobenzyl bromide; diphenylbromomethane; 9-bromofluorene and triphenylbromomethane. The ^{31}P NMR spectra of all above mentioned crude reaction mixtures show three major resonance lines responsible for three major phosphorus products in these reactions. The chemical shifts registered in this set of experiments are collected in Table II.

As one can see from the data collected in Table II, the spectra reflecting the reaction course between bromoderivatives and sodium diethyl phosphite at room

TABLE II The chemical shifts of the ^{31}P NMR spectra of the crude reaction mixture of selected bromoderivatives with sodium diethyl phosphite.

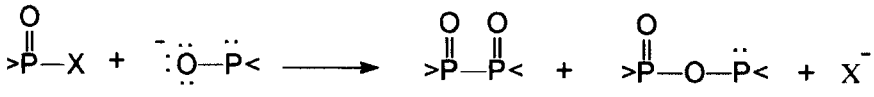
Run	*Bromoderivatives*	*δ [ppm]* of the ^{31}P NMR resonance lines*		
1		−12.86	+6.37	+6.59
2	p-$NO_2C_6H_5CH_2Br$	−12.86	+6.46	+6.60
3	Ph_2CHBr	−12.86	+6.40	+6.59
4	9-bromofluorene	−12.86	+6.40	+6.59
5	Ph_3CBr	−12.86	+6.46	+6.60
6	$(EtO)_2P(O)Br$	−12.84	+6.39	+6.59

*Relative to 85% aqueous ortophosphoric acid

temperature in THF show the signals attributed to the final phosphorus products which we identified with authentic samples as being: tetraethyl pyrophosphate (δ = −12.86), diethyl phosphite (δ = +6.40, +6.46) and tetraethyl hypophosphate (δ = +6.60). Moreover, the ^{31}P NMR spectra of the reaction mixture of diethyl bromophosphate and sodium diethyl phosphite at room temperature in THF exhibits the same picture. Also in this case we have three resonance lines attributed to the three final products; namely: tetraethyl pyrophosphate, diethyl phosphite and tetraethyl hypophosphate.

Evidence obtained from ^{31}P NMR spectroscopic studies confirms our postulate of the halophilic substitution being the principal process in our proposed X-philic/SET tandem mechanism, followed by the reaction between the bromophosphate (as a result of the halophilic substitution) and >P-O$^-$ nucleophiles.

From the theoretical point of view sodium diethyl phosphite being an ambient nucleophile in the reaction with diethyl bromophosphate should produce hypophsphate and/or a mixed anhydride



Several research groups were involved in the mechanistic study of the reaction between phosphorus electrophiles of the >P(O)X (X: halogen) and phosphorus nucleophiles of the >P-O$^-$ type.[8] In contrast to the theoretical expectations the isolation of the tetraalkyl hypo- as well as pyrophosphate from the reaction mixture of dialkyl chlorophosphate and dialkyl phosphite anion are reported. The tetraalkyl hypophosphate is the product of the nucleophilic attack of the phosphorus lone electron pair on the electrophilic phosphorus of the dialkyl

chlorophosphate. The origin of the pyrophosphate produced in this reaction is less clear and remains a puzzling aspect of the reactivity of the dialkyl chlorophosphates towards $>P\text{-}O^-$ ions. However, J. Michalski, A. Zwierzak and W. J. Stec discovered an interesting feature of the reaction between diethyl chlorophosphate and sodium diethyl phosphite: the treatment of 1 equiv. of diethyl chlorophosphate with 1 equiv. of diethyl phosphite anion yields among other products tetraethyl pyrophosphate. On the other hand, no pyrophosphate is produced in the case of the treatment of 1 equiv. of diethyl chlorophosphate with 2 equiv. of sodium diethyl phosphite.[8e,f,g]

First of all, we ascertained that the reaction mixtures of diethyl chlorophosphate as well as diethyl bromophosphate and sodium diethyl phosphite have the same ^{31}P NMR picture, i.e., exhibiting three resonance lines responsible for diethyl phosphite, hypophosphate and pyrophosphate.

If in the case of the reaction between bromoderivatives posseessing electron-withdrawing groups and sodium diethyl phosphite X-philic substitution/SET tandem mechanism operates, then diethyl bromophosphate as a result of the first step (halophilic substitution) should be produced which should exhibit the behaviour towards sodium diethyl phosphite observed by J. Michalski, A. Zwierzak and W. J. Stec.

This expectation was verified by experiment. We carried out the reaction of 1 equiv. of methyl 1-bromo-2,2-cyclopropanecarboxylate with 4 equiv. of sodium diethyl phosphite in THF and examined this reaction mixture by ^{31}P NMR spectroscopy.

As can be seen from Figure 1 no resonance line of tetraethyl pyrophosphate was present, which means that no pyrophosphate was produced in this last reaction. The results of this experiment are in full agreement with the previous observations[8e,f,g] and strongly support our idea of the halophilic substitution as a first step in X-philic/SET tandem mechanism. It is well known that halogenothiophsphates are much less reactive than halogenophosphates.[8d,8f,9] This knowledge prompted us to use thiophosphite in the reaction under investigation, with the hope for possible isolation of the bromothiophosphate from the reaction mixture. We chose a cyclic thiophosphite, namely sodium 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan as a $>P\text{-}S^-$ nucleophilic reagent.

We carried out the reaction of 1 equiv. of methyl 1-bromo-2,2-dipheylcyclopropanecarboxylate with 2 equiv. of sodium 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan under standard conditions (in THF; 20°C). From the reaction mixture we isolated the debrominated product, namely methyl 2,2-diphenylcyclopropanecarboxylate and 2-bromo-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorian (Scheme 4).

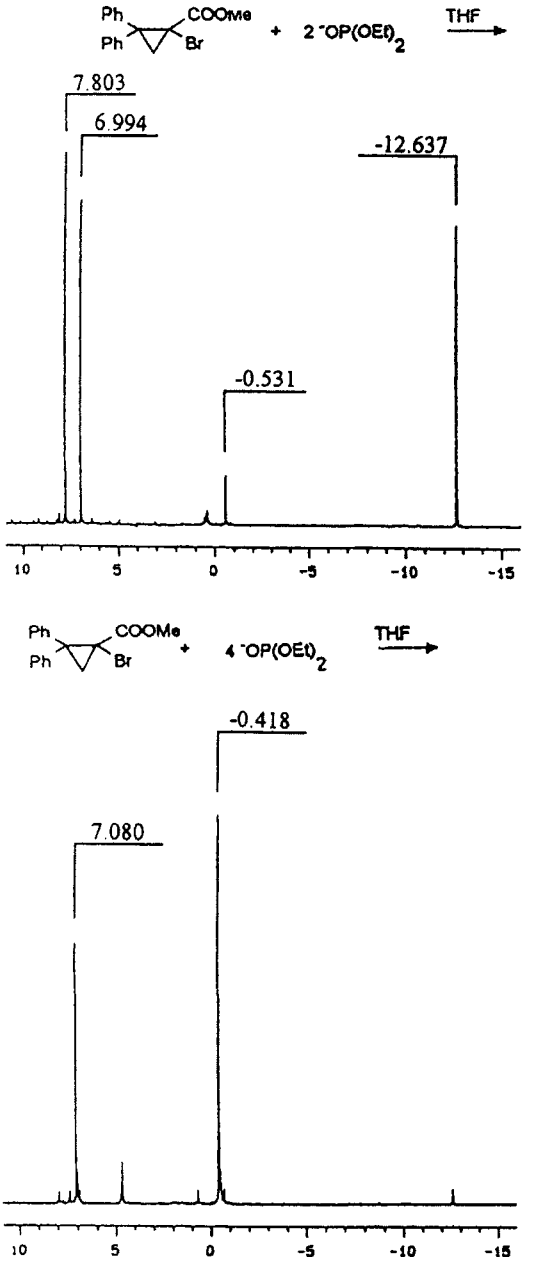
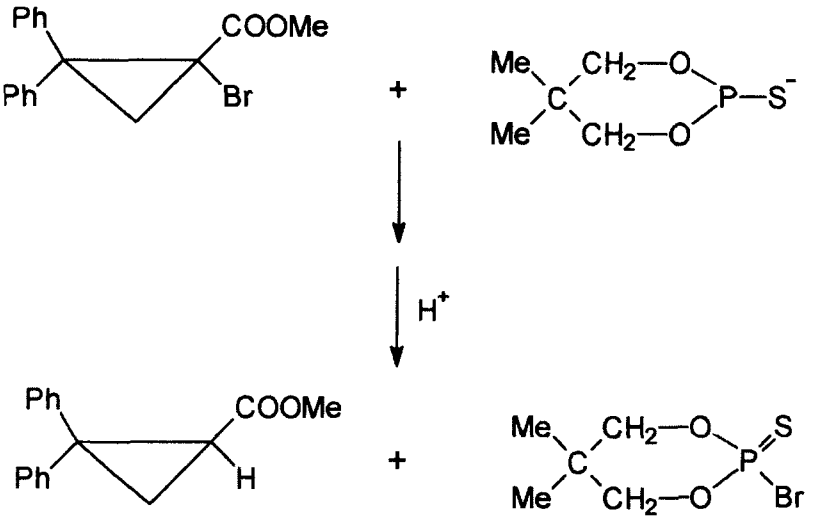


FIGURE 1 ^{31}P-NMR spectra of the reactions as shown.



The 2-bromo2-thino-5,5-dimethyl-1,3,2-dioxaphosphorinan isolated from the reaction mixture was identified by comparison of the ^{1}H and ^{31}P NMR spectra with an authentic sample.

The isolation of the products derived from dialkyl bromophosphates, the results of the ^{31}P NMR studies, as well as the isolation of bromothiophosphate from the reaction mixture are further evidence for our postulate of halophilic substitution as the principal process in the X-philic substitution/SET tandem mechanism operated in the reaction of the $>P\text{-}Y^{-}$ (Y = O,S) nucleophiles with the bromoderivatives possessing electron-withdrawing groups.

EXPERIMENTAL

Dialkyl phosphites were purchased from Aldrich and distilled before use. Dibenzylphosphine oxide,[10] 2-bromo-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan,[8f] 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan,[11] diethyl chlorophosphate,[12] diethyl bromophosphate,[13] tetraethyl hypophosphate,[14] tetraethyl pyrophosphate,[15] were prepared by the known methods. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran was dried with sodium-potassium alloy. Isopropanol was dried with calcium hydride. Melting points were uncorrected. IR specta were taken on Jena-Zeiss IR 10 apparatus. ^{31}P and ^{1}H NMR spectra were recorded with a Varian apparatus at 60, 200 or 500 MHz.

The Reaction of the Bromoderivatives 1 with Sodium Dibenzylphosphinite in Alcohols as a Solvent: General Procedure

NaH (3.0 mmol, 0.072 g) was dissolved in 15 mL of alcohol and to the resultant mixture dibenzylphosphine oxide (2.5 mmol, 0.576 g) in 10 mL of alcohol and bromoderivative **1** (methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate, 4-nitrobenzyl bromide, diphenylbromomethane, 9-bromofluorene, triphenylbromomethane) (2.5 mmol) 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.

^{31}P NMR Investigation of the Reaction of Sodium Diethyl Phosphite with Bromoderivatives 1 in THF Solution: General Procedure

To a suspension of NaH (3.0 mmol, 0.072 g) in 20 mL of THF diethyl phosphite (2.5 mmol, 0.32 mL, 0.345g) was added. When the evolution of hydrogen had ceased bromoderivatives **1** (ethyl 1-bromo-2,2-diphenylcyclopropanecarboxylate) (1.25 mmol, 0.43 g) or (4-nitrobenzyl bromide, diphenylbromomethane, 9-bromofluorene, triphenylbromomethane) (2.5 mmol) in 5 mL of THF were added. The reaction mixture was stirred for 3 hours at room temperature. A sample of reaction mixture was taken off and after addition of 10% of C_6D_6 ^{31}P NMR was recorded. The signals of the spectra were identified by addition of external standard of authentic samples. The chemical shifts are collected in Table II.

^{31}P NMR Investigation of the Reaction of Sodium Diethyl Phosphite with Diethyl Bromophosphate or Diethyl Chlorophosphate in THF Solution: General Procedure

To a suspension of NaH (3.0 mmol, 0.072 g) in 20 mL of THF diethyl phosphite (2.5 mmol, 0.32 mL, 0.345 g) was added. When the evolution of hydrogen had ceased, diethyl halophosphate (2.5 mmol) in 5 mL of THF were added. The reaction mixture was stirred for 3 hours at room temperature. A sample of the reaction mixture was taken off, evaporated and the ^{31}P NMR spectra in $CDCl_3$ was recorded. In both cases three resonance lines responsible for diethyl phosphite (7.75 ppm), tetraethyl hypophosphate (6.84 ppm) and tetraethyl pyrophosphate (-12.84 ppm) were observed.

^{31}P NMR Investigation of the Reaction of Excess Sodium Diethyl Phosphite with Ethyl 1-bromo-2,2-diphenylcyclopropanecarboxylate in THF Solution

To a suspension of NaH (6.0 mmol, 0.144 g) in 20 mL of THF diethyl phosphite (5.0 mmol, 0.64 mL, 0.69 g) was added. When the evolution of hydrogen had ceased ethyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1.25 mmol, 0.43 g) in 5 mL of THF was added. The reaction mixture was stirred for 3 hours at room temperature. A sample of reaction mixture was taken off, evaporated and the ^{31}P NMR spectra in $CDCl_3$ was recorded. The ^{31}P NMR spectra are presented in Figure 1.

Isolation of 2-Bromo-2-Thiono-5,5-Dimethyl-1,3,2-Dioxaphosphorinan from The Reaction Mixture of Methyl 1-Bromo-2,2-Diphenylcyclopropanecarboxylate and Sodium 2-Mercapto-5,5-Dimethyl-1,3,2-Dioxaphosphorinan in THF Solution.

To a suspension of NaH (3.0 mmol, 0.072 g) in 15 mL of THF 2-mercapto-5,5-dimethyl-1,3,2-dioxaphosphorinan (2.5 mmol, 0.413 g) was added. When the evolution of hydrogen had ceased, methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1.25 mmol, 0.413 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 either, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and 2-bromo-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinan 0.050 g (8%) was separated by radial chromatography (silica gel; hexane: CH_2Cl_2 = 1:1)

^1H NMR ($CDCl_3$) δ = 0.93 (s, CH_3, 3H), 1.33 (s, CH_3, 3H), 3.91 (dd, $J_{H\text{-}H}$ = 10.74 Hz, $J_{P\text{-}H}$ = 30.03 Hz, P-O-CH, 2H), 4.26 (dd, $J_{H\text{-}H}$ = 10.74 Hz, $J_{P\text{-}H}$ = 4.64 Hz, P-O-CH, 2H)

^{31}P NMR ($CDCl_3$) δ = 43.27

The NMR spectra were identical with those of an authentic sample.[8f]

The Reaction of 1-Bromo-2,2-Diphenylcyclopropanecarboxamide with Sodium Diethyl Phosphite in THF Solution

To a suspension of NaH (3.0 mmol, 0.072 g) in 20 mL of THF diethyl phosphite (2.5 mmol, 0.32 mL, 0.345 g) was added. When the evolution of hydrogen had ceased, 1-bromo-2,2-diphenylcyclopropanecarboxamide (1.25 mmol, 0.395 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 following compounds were obtained:

2,2-diphenylcyclopropanecarboxamide 0.125 g (42%)

m.p. 177–179°C (lit. 178–179°C).[16]

(N-diisoprophylphosphoryl)-l-bromo-2,2-diphenylcyclopropanecarboxyamide 0.234 g (39%) m.p. 180–184°C

IR (KBr) ν = 3440, 3130 NH; 1700 C=O; 1270, 1230 P=O; 1040 P-O-C cm^{-1}

^1H NMR ($CDCl_3$) δ = 1.02 (d, J = 6.13 Hz, CH_3, 3H), 1.21 (d, J = 6.13 Hz, CH_3, 3H), 1.36 (d, J = 6.13 Hz, CH_3, 3H), 1.42 (d, J = 6.13 Hz, CH_3, 3H), 1.91 (d, J = 6.60 Hz, cyclo-CH, 1H), 2.94 (d, J = 6.60 Hz, cyclo-CH, 1H), 4.28 (m, >CH, 1H), 4.84 (m, >CH, 1H), 7.10–7.80 (m, C_6H_5, 10H), 9.50 (d, J = 9.81 Hz, NH, 1H)

^{31}P NMR ($CDCl_3$) δ = −5.41

MS exact mass calcd. for $C_{22}H_{27}BrNO_4P$ 479.0816 found 479.0856

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