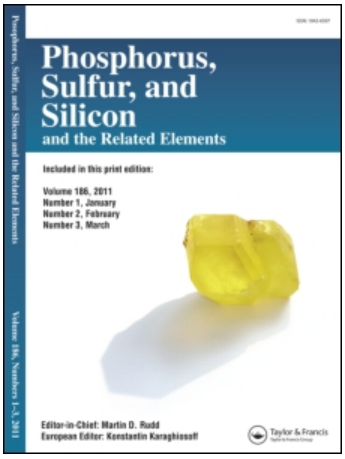

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART I. REDUCTIVE DEBROMINATION IN THE REACTIONS OF THE >P-O$^-$ IONS WITH 2-BROMOESTERS

Leszek Dembkowski[a]; Janusz Rachon[a]
[a] Department of Organic Chemistry, Technical University of Gdańsk, Gdańsk, Poland

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART I. REDUCTIVE DEBROMINATION IN THE REACTIONS OF THE >P—O⁻ IONS WITH 2-BROMOESTERS

LESZEK DEMBKOWSKI and JANUSZ RACHON
Department of Organic Chemistry, Technical University of Gdańsk, ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

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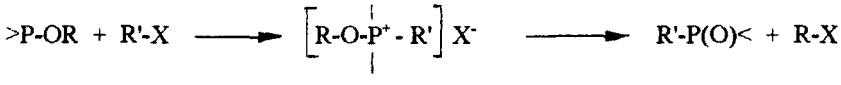
The reaction of α-bromocarboxylates with sodium dialkyl (diaryl) phosphites as well as sodium salt of dibenzylphosphine oxide in THF and alcohols as the solvents is described. Debromination of the starting materials occurs. Probable mechanisms namely SET and X-philic substitution are discussed.

Key words: α-Bromocarboxylates; debromination; dialkyl phosphites; diaryl phosphites; dibenzylphosphine oxide; Michaelis-Becker reaction; X-philic substitution.

INTRODUCTION

The energy of the formation of the phosphoryl group is a driving force in many reactions of the phosphorus compounds. The energy of the phosphoryl group is high and, apparently, because of this the most stable form of the acids of trivalent phosphorus is that with a four-coordinate phosphorus.

The most common and versatile pathways for the formation of carbon-phosphorus bonds are: the Michaelis-Arbuzov[1] rearrangement and Michaelis-Becker[2] reaction. The Michaelis-Arbuzov rearrangement,



generally proceeds by the S_N2 attack of the phosphite on carbon followed by an S_N2 reaction of the displaced anion on an alkyl group of the quasiphosphonium intermediate. The mechanism of the Michaelis-Becker reaction, often assumed to be S_N2 involving the nucleophilic phosphorus atom, is not established with certainty,

In addition to alkyl halides other organic halides also react with trialkyl phosphites according to the Michaelis-Arbuzov scheme. Esters of α-monohalomonocarboxylic acids likewise give α-carboxyalkylphosphonates[1c,d] and triaryl-bromo-methane gives triarylmethyl-phosphonates, respectively.[1c]

An analysis of the literature leads to several important observations. Dialkyl phosphite anions give only with primary alkyl halides a satisfactory yield of the Michaelis-Becker reaction. Secondary and tertiary alkyl halides give with dialkyl

phosphite anions poor yield or a complex mixture of the products,[3a,b] additionally the reaction between bromotriphenylmethane and sodium diethyl phosphite was claimed to be a free radical process.[3c,10b] For the synthesis of α-phosphonocarboxylates the Michaelis-Arbuzov reaction is the method of choice,[14] dialkyl phosphite anions give only with chloroacetate a satisfactory yield of the Michaelis-Becker reaction.[3d,10c] In the case of α-halogenopropionate the Michaelis-Becker reaction is reported to give a very poor yield or to result not in the assumed product.[3c] B. A. Arbuzov and co-workers published that ethyl 2-bromo-1,3-dioxoindan-2-carboxylate with sodium diethyl phosphite yield diphtalylethane and indanedione[3f]; it means that debromination and decarboxylation took place in the course of this reaction. The authors suggested the existence of radical intermediates in this process.

In 1984 G. Hägele and co-workers published a new reductive Michaelis-Becker reaction; hexachlorobenzene reacts with sodium diethyl phosphite to form diethyl (pentachlorophenyl)phosphonite and sodium diethyl phosphate,[3g] the exact mechanism is unclear.

For several years we have been interested in different reactivity between these two types of phosphorus nucleophiles (>P̈—O⁻ and RO—P̈<) towards electrophiles. What is the difference between Michaelis-Becker and Michaelis-Arbuzov reactions? To continue our studies of the mechanism of the reactions involving the phosphorus nucleophiles,[4] the reaction of dialkyl- (diaryl) phosphite anions and the dibenzyl phosphinite ion "$(PhCH_2)_2\ddot{P}O^-$" with esters of α-halocarboxylic acids is being studied now.

RESULTS

When treated with the sodium salt of diethyl phosphite in THF, benzyl chloroacetate gives benzyl-diethylphosphonoacetate;

$$(EtO)_2\ddot{P}\text{-}O^- + \underset{\displaystyle Cl}{\overset{|}{CH_2}}\text{-}COOCH_2C_6H_5 \longrightarrow (EtO)_2P(O)\text{-}CH_2\text{-}COOCH_2C_6H_5 + Cl^-$$

in contrast to this benzyl bromoacetate and benzyl iodoacetate give a debrominated product, namely benzyl acetate.

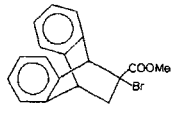
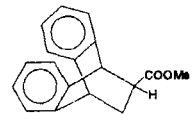
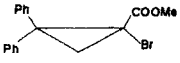
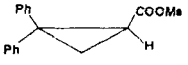
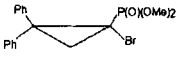
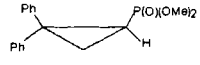
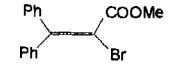
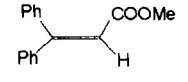
$$(EtO)_2\ddot{P}\text{-}O^- + X\text{-}CH_2\text{-}COOCH_2C_6H_5 \longrightarrow \longrightarrow CH_3\text{-}COOCH_2C_6H_5$$

X = Br; I

To check the scope and limitation of this debromination reaction we decided to investigate whether this kind of reactivity can be observed in other α-bromocarboxylates. A variety of α-bromocarboxylic esters was successfully reduced to the corresponding carboxylic esters by sodium diethyl phosphite as shown in Table I. Additionally, we found that α-bromo-phosphonate undergoes this reaction.

TABLE I

Dehalogenation of 2-bromoesters

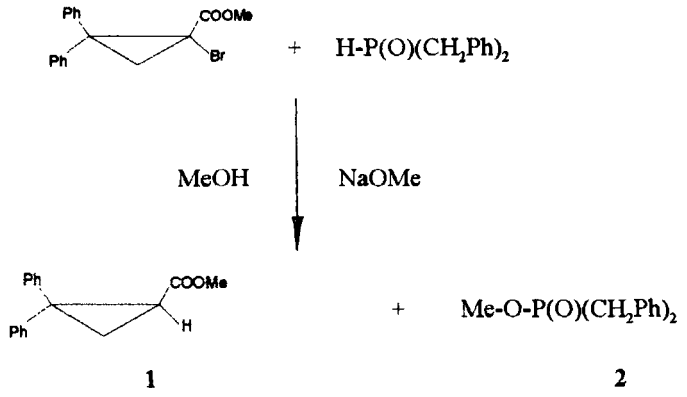
2-bromesters	O-P< equiv	solvent	yield %	products *
$BrCH_2COOCH_2Ph$	O-P(OEt)$_2$ 2	THF	75	
	O-P(OiPr)$_2$ 2	THF	72	CH_3COOCH_2Ph
	O-P(CH$_2$Ph)$_2$ 2	THF	50	
ICH_2COOCH_2Ph	O-P(OEt)$_2$ 2	THF	82	CH_3COOCH_2Ph
$CH_3CHBrCOOCH_2Ph$	O-P(OEt)$_2$ 2	THF	66	$CH_3CH_2COOCH_2Ph$
$(CH_3)_2CBrCOOCH_2Ph$	O-P(OEt)$_2$ 2	THF	84	$(CH_3)_2CHCOOCH_2Ph$
	O-P(CH$_2$Ph)$_2$ 2	THF	95	
$Ph_2CBrCOOCH_3$	O-P(CH$_2$Ph)$_2$ 2	THF	52	$Ph_2CHCOOCH_3$
	O-P(CH$_2$Ph)$_2$ 1	CH_3OH	65	
	O-P(OEt)$_2$ 2	THF	97	
	O-P(OMe)$_2$ 1	CH_3OH	79	
	O-P(OPh)$_2$ 2	THF	100	
	O-P(OMe)$_2$ 1	THF	76	
	O-P(OEt)$_2$ 2	THF	95	
	O-P(OPh)$_2$ 2	THF	53	
	O-P(CH$_2$Ph)$_2$ 1	CH_3OH	100	
	O-P(CH$_2$Ph)$_2$ 2	THF	100	
	O-P(OMe)$_2$ 2	THF	66	
	O-P(OEt)$_2$ 2	THF	93	
	O-P(OPh)$_2$ 2	THF	75	
	O-P(CH$_2$Ph)$_2$ 2	THF	96	

* The products were identyfied by comparison of the IR and NMR spectra with those of the autentic samples, dimethyl 2,2-diphenylcyclopropanephosphonate see[29]

We run the experiments in THF using the sodium salts of dimethyl phosphite, diethyl phosphite, diphenyl phosphite as well as dibenzylphosphine oxide. In all cases we isolated debrominated products. The amount of the used anion of phosphite as well as dibenzyl phosphinite has influence on the yield of a debrominated product. The treatment of 1 equiv of bromocarboxylate in THF at 20°C with 1

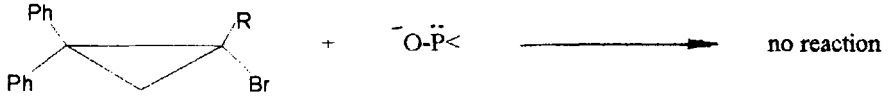
equiv of the phosphite anion as well as the phosphinite anion produces the debrominated product with 50–70% yield, the treatment of 1 equiv of bromocarboxylate in THF at 20°C with 2 equiv of the phosphite anion yields the debrominated product almost quantitatively.

The reaction goes very smoothly also in methanol and requires in this case only 1 equiv of the phosphorus reagent and 1 equiv of sodium methanolate as a base for quantitative yield of the debrominated product. The treatment of 1 equiv of methyl 1-bromo-2,2-diphenylcyclopropane carboxylate in methanol at 20°C with 1 equiv of dibenzylphosphine oxide in the presence of 1 equiv of sodium methanolate yields methyl 2,2-diphenylcyclopropanecarboxylate **1** and methyl dibenzylphosphinate **2**.



1 **2**

On the contrary 1-bromo-1-methyl-2,2-diphenylcyclopropane **3a** and also (1-bromo-2,2-diphenylcyclopropane)methyltosylate **3b** are inert towards phosphite and phosphonite anions. No debrominated product was detected. We isolated only starting materials.



3	R
a	CH_3
b	CH_2OTos

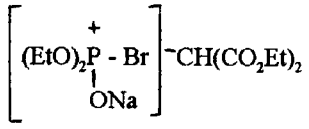
Additionally, we found that methyl 1-bromo-2,2-diphenyl-cyclopropanecarboxylate is inert toward triethyl phosphite as well as triphenyl phosphine under conditions applied here (THF or methanol, 20°C).

DISCUSSION

The anions of the type $>\ddot{P}—O^-$ are of special interest; they are nucleophilic ambient reagents,[2a,5] strong bases[6] and single electron donors.[4c,7] On the other hand the compounds of the structure >P(O)H can act as proton[8] or hydrogen[9] sources; depending on the structure and reaction conditions.

In the literature one can find some examples of C—halogen bond reduction by the action of the anions of trivalent phosphorus acids or their esters. However, the mechanistic details of most of these reductions are still not clearly delineated.

The reaction of diethyl bromomalonate and sodium diethyl phosphite in ether was reported to yield tetraethyl 1,1,2,2-ethanetetracarboxylate.[10a] A. E. Arbuzov and V. S. Abramov suggested the free radical mechanism for this reaction.[10a] Takemura and Tuma reinvestigated this reaction.[11] They noticed that the addition of ethanol to the reaction of diethyl bromomalonate with sodium diethyl phosphite in ether gave a smaller yield of tetraethyl 1,1,2,2-ethanetetracarboxylate. The major products of the reaction were diethyl malonate and triethyl phosphate. These were the only products when the reaction was carried out in ethanol as a solvent. They proposed initial displacement on bromine and formation of the ion pair **4**.



4

Zwierzak[12] studied the reaction between α-bromoderivatives of 2,4-dichloroacetophenone and diethyl phosphite. He observed partial monodebromination, particularly in the case of α,α-dibromo- and α,α,α-tribromosubstituted ketones. He assumed that first there was an attack of the diethyl phosphite molecule on "positive" bromine.

B. A. Arbuzov and co-workers[13] in series of papers showed that sodium diethyl phosphite in reaction with α-halogen ketones gives epoxyphophonates, enol phosphates or a mixture of these products depending on the structure of the starting materials and reaction conditions. On the other hand B. A. Arbuzov[13b,c,e] and W. S. Abramov[14] showed that α-chloroketones with diethyl phosphite (without a basic catalyst) yielded α-hydroxy-β-chloro-phosphonates which treated with a base can be transformed into epoxyphosphonates.

Ohshiro and co-workers developed a method for reduction of gem-dibromocyclopropanes and gem-dibromoalkenes with diethyl phosphite and triethylamine into the corresponding monobromides, without complete stereoselectivity.[15] He extended this method for reduction of gem-bromochlorocyclopropanes, trichloromethane derivatives and α-bromoketones.[16] The treatment of gem-bromochlorocyclopropanes with diethyl phosphite and triethylamine gave the corresponding chlorocyclopropanes exclusively. Furthermore, α-bromo-α,β-unsaturated ketones or 1,1-dibromo-2-trimethylsiloxycyclopropanes were shown to be converted to β,γ-unsaturated ketones with diethyl phosphite and triethylamine.[17] Ohshiro developed also a unique reductive deconjugation of α-bromo-α,β-unsaturated esters or lac-

tones to β,γ-unsaturated esters or lactones, respectively, with a combination of diethyl phosphite and triethylamine.[18]

He claims the attack of diethyl phosphite or its anion on bromine or chlorine to be the first step in the reduction reaction.

G. F. Meijs[19] reported that the diethyl phosphite ion reacts with 7,7-dibromobicyclo-[4.1.0] heptane (even in the dark) giving the reduced product; exo-7-bromobicyclo-[4.1.0]-heptane in a quantitative yield and uncontaminated by the endo isomer. The same type of reaction gives also the diphenylphosphide ion,[20] a known $S_{RN}1$ nucleophile[21] but the Meijs' results are suggestive of nonradical intermediates; the exact mechanism is unclear. On the other hand the nucleophilic attack of the ionic phosphorus reagent on the bromine atom in geminal dibromo derivatives used by Meijs should produce carbenoid intermediates with characteristic reactivity.[22]

As we showed above the esters of α-bromocarboxylic acids treated with sodium dialkyl (diaryl) phosphites as well as sodium dibenzyl phosphinite yield debrominated products under very mild conditions.

The ion of the type $>\ddot{P}O^-$ could *a priori* reduce α-bromocarboxylates either by attack on the carbonyl oxygen (pathway A) or on the bromine atom (pathway B).

Pathway A:

Pathway B:

A direct attack of a phosphite molecule on the carbonyl oxygen should produce enol phosphate, which in methanol or during work up could be transferred into carboxylic ester. We couldn't find enol phosphate in the reaction mixture of any of our experiments.

On the other hand we discovered that dimethyl 1-bromo-2,2-diphenylcyclopropane phosphonate treated with sodium dimethyl phosphite as well as sodium dibenzyl phosphinite gives dimethyl 2,2-diphenylcyclopropanephosphonate.

As we pointed out above for the quantitative debromination (reaction in THF) 2 equiv. of the phosphorus reagent are required. For the pathway A there isn't a reasonable explanation of this observation.

The pathway B is an example of so called X-philic reaction.[23] Nucleophilic displacements on halogen are well known, and phosphorus nucleophiles are noteworthy for their proclivity to engage in such processes.[7,23,24]

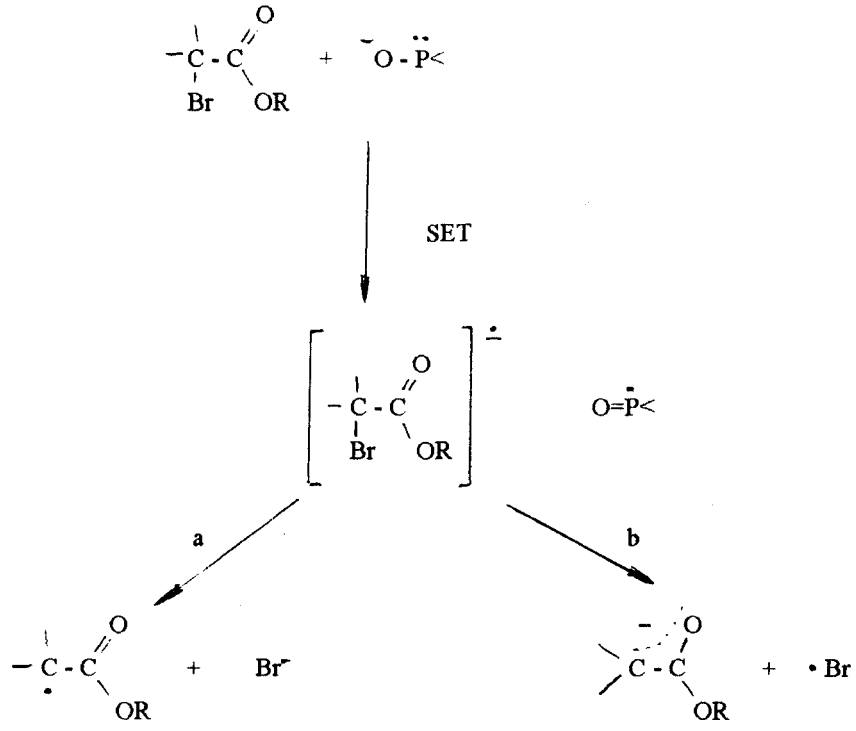
The reaction of phosphite or phosphinite ions cause a nucleophilic attack on bromine in an α-bromo-carboxylic ester, effecting the nucleophilic displacement on bromine with the release of an enol anion as nucleofuge. This step might also be described as a positive bromine transfer reaction.

The bromophosphonate originating in this process as an intermediate is a powerful electrophilic reagent which can react with any nucleophiles present in the reaction mixture (phosphite, a phosphinite anion, and enol anion or methanol). This can explain the observed stoichiometry of this reaction.

The attack of "soft" phosphorus on oxygen in an unlikely process for α-bromo carboxylates. This is due to the lack of polarization for the oxygen atom which is "hard" as compared with the polarizable or "soft" bromine atom.

We have to consider that substitution of the so-called "positive" bromine can also develop through SET (pathway C); the radical chain mechanism or cage process with two possible ways of radical anion fragmentation (a or b).

Pathway C:



It is conceivable that R—X radical anions could undergo the cleavage of the C—X bond either by the loss of halide ion (X^-) and a carbon-centered radical ($\cdot R$) - fragmentation a—or by the loss of a carbanion (R^-) and a halogen atom ($\cdot X$) - fragmentation b. Product studies of several reactions leave no doubt that the radical anion intermediates formed by the addition of an electron to the alkyl or benzyl halide cleave preferentially by path a, which is understandable since the electron affinity of the halogen atom is much greater than that of carbon.

On the other hand in path b we will have the same enol anion intermediate as in the case of X-philic substitution (pathway B).

To find further evidence supporting the proposed mechanism and to distinguish between X-philic substitution (pathway B) and SET (pathway C) we designed a new set of experiments. This work is in progress and the results will be published successively.

EXPERIMENTAL

Dialkyl phosphites and diphenyl phosphite were purchased from Aldrich and distilled before use. Sodium hydride (Aldrich) was washed with hexane to remove paraffin oil. Tetrahydrofuran was dried with sodium-potassium alloy. Melting points were uncorrected. Mass spectra (FD) were recorded on a AMD Intectra 604 apparatus. IR spectra were taken on Jena-Zeiss IR 10 apparatus. ^{1}H-NMR spectra were recorded with a Varian apparatus at 60 or 200 MHz. ^{31}P NMR spectra were recorded with a Bruker (100 MHz) apparatus.

Methyl-2-bromodibenzobicyclo[2.2.2]octadiene-2-carboxylate was prepared according to Reference 25.
Methyl-1-bromo-2,2-diphenylcyclopropanecarboxylate was prepared according to Reference 26.
Methyl-bromodiphenylacetate was prepared according to Reference 27.
Methyl-bromodiphenylacrylate was prepared according to Reference 28.

Dimethyl 1-bromo-2,2-diphenylcyclopropanephosphonate. To a refluxing solution of dimethyl α-bromovinylphosphonate (11.82 g, 55 mmol) in 150 mL of hexane-petroleum mixture (1:1) was added diphenyldiazomethane (7.1 g, 36.6 mmol) dissolved in petroleum ether (100 mL). Heating was continued until the solution decolorized (about 4 h) and the reaction mixture left overnight at room temperature. The crystals were filtered and recrystalized from ether/hexane. Yield 9,45 g (68%) of dimethyl 1-bromo-2,2-diphenylcyclopropanephosphonate, m.p. 95–98°C.

IR (KBr) ν = 1246 (P═O), 1050 (P—O—C) cm^{-1}
^{1}H NMR, 100 MHz, ($CDCl_3$) δ = 2.05 (dd, J_{PH} = 6.35 Hz, J_{HH} = 6.47 Hz, 1H, CH); 2.55 (dd, J_{PH} = 14.35 Hz, J_{HH} = 6.47 Hz, 1H, CH); 3.22 (d, J_{PH} = 10.71 Hz, 3H, OCH_3); 3.77 (d, J_{PH} = 10.92 Hz, 3H, OCH_3); 7.10–7.70 (m, 10H, C_6H_5)
^{31}P NMR, 100 MHz ($CDCl_3$) δ = 18.24
MS exact mass calcd. for $C_{17}H_{18}BrO_3P$: 380.0177; found: 380.0173.

Reaction of sodium diethyl phosphite and benzyl chloroacetate in THF. To a suspension of NaH (6 mmol; 0.144 g) in 20 mL of THF was added diethyl phosphite (5 mmol; 0.65 mL). When the evolution of hydrogen had ceased, benzyl chloroacetate (2.5 mmol; 0.461 g) at 0°C was added. The reaction mixture was stirred at this temperature 0,5 h, then diluted with ether (25 mL), washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed and the residue separated by radial chromatography (silica gel; hexane:CH_2Cl_2 = 1:1). The following compounds were obtained:

Benzyl chloroacetate 0.18 g, (39%), spectral data were identified with those of an authentic sample.
Benzyl diethoxyphosphonylacetate[30] 0.43 g, (60%)
IR (film) ν = 1730 (C═O), 1290 (P═O), 1050 (P—O—C) cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.29 (t, J_{HH} = 7.05 Hz, 3H, CH_3); 3.01 (d, J_{PH} = 21.57 Hz, 2H, CH_2P); 4.12 (dq, J_{HH} = 7.05 Hz, J_{PH} = 7.09 Hz, 2H, CH_2—O); 5.17 (s, 2H, CH_2Ph); 7.27–7.39 (m, 5H, C_6H_5).

Reaction of sodium diethyl phosphite with benzyl bromoacetate in THF. To a suspension of NaH (6 mmol; 0.144 g) in 20 mL of THF was added diethyl phosphite (5 mmol; 0.65 mL). When the evolution of hydrogen had ceased, benzyl bromoacetate (2.5 mmol; 0.57 g) at 0°C was added. The reaction mixture was stirred at this temperature 0.5 h, then diluted with ether (25 mL), washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed and the residue separated by radial chromatography (silica gel; hexane:CH_2Cl_2 = 1:1.5) to yield 0.3 g (80%) benzyl acetate.

IR (film) ν = 1730 (C═O) cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.88 (s, 3H, CH_3); 4.83 (s, 2H, CH_2—Ph); 6.93 (s, 5H, C_6H_5).

Reaction of sodium diethyl phosphite with benzyl iodoacetate in THF. To a suspension of NaH (6 mmol; 0.144 g) in 20 mL of THF was added diethyl phosphite (5 mmol; 0.65 mL). When the evolution of hydrogen had ceased, benzyl iodoacetate (2.5 mmol; 0.69 g) at 0°C was added. The reaction mixture was stirred at this temperature 0.5 h, then diluted with ether (25 mL), washed with NH_4Cl solution,

and dried over $MgSO_4$. The solvent was removed and the residue separated by radial chromatography (silica gel; hexane:CH_2Cl_2 = 1:1.5) to yield 0.26 g (69%) of benzyl acetate.

Reductive debromination of 2-bromoesters. General procedure.

A. In THF solution. To a suspension of NaH (2.25 mmol, 0.054 g) in THF (20 mL) were added 2 mmol of dialkyl phosphite or dibenzylphosphine oxide. After 10 minutes the appropriate amount (1 or 2 mmol) of 2-bromoester was added, and the mixture was stirred overnight at room temperature. The reaction mixture was 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 product was purified by radial chromatography (silica gel; hexane:CH_2Cl_2 = 1:1).

The products were identified by comparison of the IR and NMR spectra with those of the authentic samples. The yields are shown in Table I.

B. In methanol solution. NaH (1.2 mmol, 0.03 g) was dissolved in 20 mL of methanol and to the resultant mixture was added 1 mmol of dialkyl phosphite or dibenzylphosphine oxide. After 10 minutes 1 mmol of 2-bromoester was added and the reaction mixture left overnight at room temperature. The methanol was removed in vacuum, the residue was dissolved in 50 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and the product was purified by radial chromatography (silica gel; hexane:CH_2Cl_2 = 1:1). The products were identified by comparison of the IR and NMR spectra with those of authentic samples. The yields are shown in Table I.

Reaction of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate with dibenzylphosphine oxide in the presence of $NaOCH_3$ in methanol. To the solution of $NaOCH_3$ in methanol (prepared from 0.028 g, 1.2 mmol of Na and 20 mL of methanol) dibenzylphosphine oxide (1 mmol, 0.23 g) and methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.33 g) were added. The reaction mixture was stirred 8 hours at 20°C, than evporated under reduced pressure. The residue was dissolved in 50 mL of CH_2Cl_2, washed with NH_4Cl solution and dried over $MgSO_4$. The methylene chloride was evaporated to dryness and the products were separated using flash chromatography: Methyl 2,2-diphenylcyclopropanecarboxylate[31] (benzene as eluent) 0.26 g (100%), ^1H NMR ($CDCl_3$) δ = 1.54 (dd, J_{HH} = 8.15 Hz, J_{HH} = 4.80 Hz, 1H, CH_2); 2.10 (dd, J_{HH} = 5.92 Hz, J_{HH} = 4.80 Hz, 1 H, CH—COOMe); 2.48 (dd, J_{HH} = 8.15 Hz, J_{HH} = 5.92 Hz, 1 H, CH_2); 3.42 (s, 3H, OCH_3); 7.05–7.46 (m, 10 H, C_6H_5).

Methyl dibenzylphosphinate (acetone as eluent) 0.26 g (100%) m.p. 62–65°C Lit. 75°C,[32] IR (KBr) ν = 1230 P=O; 1065 P—O—C cm^{-1}
^1H NMR ($CDCl_3$) δ = 3.08 (d, J_{PH} = 16.28 Hz, 4H, CH_2Ph); 3.57 (d, J_{PH} = 10.50 Hz, 3H, OCH_3); 7.20–7.40 (m, 10H, C_6H_5)
^{31}P NMR ($CDCl_3$) δ = 49.80
Anal. Calcd. for $C_{15}H_{17}O_2P$: C, 69.21; H, 6.58. Found: C, 68.91; H, 6.26%.

Attempted reaction between sodium diethyl phosphite and 1-bromo-2,2-diphenylcyclopropane **3** *in THF.* Diethyl phosphite (2 mmol; 0.26 mL) was added with stirring to the suspension of sodium hydride (2.25 mmol; 0.054 g) in THF (20 mL). When the evolution of hydrogen had ceased, 1-bromo-2,2-diphenylcyclopropane **3** (1 mmol) was added. The reaction mixture was stirred overnight at room temperature, then diluted with ether (25 mL), washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed and the residue separated by radial chromatography (silica gel, hexane: CH_2Cl_2 = 1:1) to yield the starting materials (93–98%).

Attempted reaction between triethyl phosphite and methyl 1- bromo-2,2-diphenylcyclopropanecarboxylate in THF. Triethyl phosphite (2 mmol, 0.33 g, 0.35 mL) was added to the solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.33 g) in THF (20 mL). The reaction mixture was stirred overnight at room temperature, then diluted with ether (25 mL), washed with NH_4Cl solution, and dried over $MgSO_4$. The solvent was removed and the residue separated by radial chromatography (silica gel, hexane:CH_2Cl_2 = 1:1) to yield 0.33 g of 1-bromo-2,2-diphenylcyclopropanecarboxylate (100%).

Triethyl phosphite (2 mmol, 0.33 g, 0.35 mL) was added to the solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.33 g) in THF (20 mL). The reaction mixture was reflux for 10 hours. The starting materials were isolated using radial chromatography (silica gel, hexane: CH_2Cl_2 = 1:1) in 98% of yield.

Attempted reaction between triphenylphosphine and methyl 1- bromo-2,2-diphenylcyclopropanecarboxylate in THF. Triphenylphosphine (2 mmol, 0.53 g) was added to the solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.33 g) in THF (20 mL). The reaction mixture was reflux

for 4 hours and then stirred overnight at room temperature. The starting materials were isolated using radial chromatography (silica gel, hexane:CH_2Cl_2 = 1:1) in 97% of yield.

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