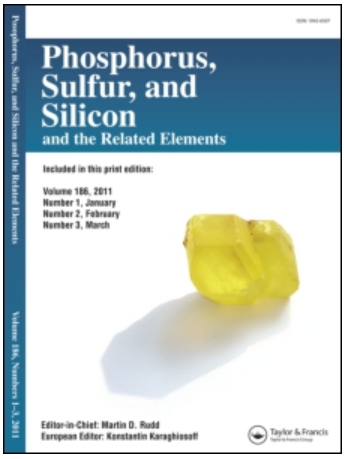

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART III.* THE >P—O⁻ IONS IN REACTION WITH ACTIVATED ALKYL BROMIDES. ATTACK ON BROMINE vs ELECTRON TRANSFER

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REACTIVITY OF THE ACIDS OF TRIVALENT PHOSPHORUS AND THEIR DERIVATIVES. PART III.* THE >P—O⁻ IONS IN REACTION WITH ACTIVATED ALKYL BROMIDES. ATTACK ON BROMINE vs ELECTRON TRANSFER

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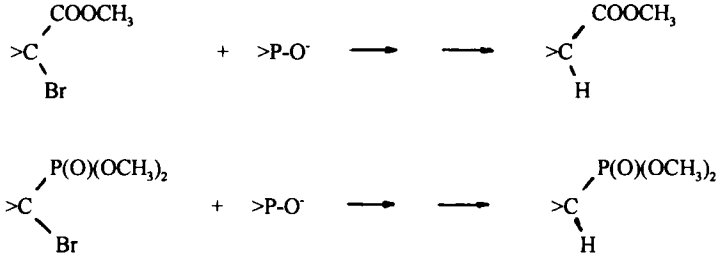
The mechanism of reductive debromination in the course of the reaction of sodium dialkyl (diaryl) phosphites as well as the sodium salt of dibenzylphosphine oxide with activated alkyl bromides in THF has been investigated. Probable mechanisms namely SET and X-philic substitution are discussed. The cyclopropyl system was chosen for the study of this reaction. The results of the carried out experiments (unrearranged products, no influence of light) suggest that the cyclopropyl radical intermediate (if it is formed) does not participate in the product-determining step of the reductive debromination under the action of the >P—O⁻ ions.

Key words: Bromocyclopropanes, reductive debromination, dialkyl phosphites, diaryl phosphites, dibenzylphosphine oxide, SET, X-philic substitution.

INTRODUCTION

The anions of the type >P—O⁻ are of special interest; they are nucleophilic ambient reagents,[1] strong bases[2] and single electron donors.[3] On the other hand the compounds of the structure >P(O)H can act as a proton[4] or a hydrogen[5] source; depending on the structure and reaction conditions.

For several years we have been interested in the varying reactivity of this type of phosphorus nucleophiles. In our previous studies of the reactions involving the phosphorus nucleophiles[3c,6] we found[7] that the anions of the type >P—O⁻ undergo reaction with α-bromocarboxylates and -phosphonates yielding debrominated products.



*Part II see D. Witt and J. Rachon, Phosphorus, Sulfur and Silicon, accepted for publication.

We showed that this type of reactivity gives the >P—O$^-$ ion with bromo and iodo derivatives, the chloro derivatives give Michaelis-Becker products resulting from an attack on carbon by the phosphor nucleophilic reagent.

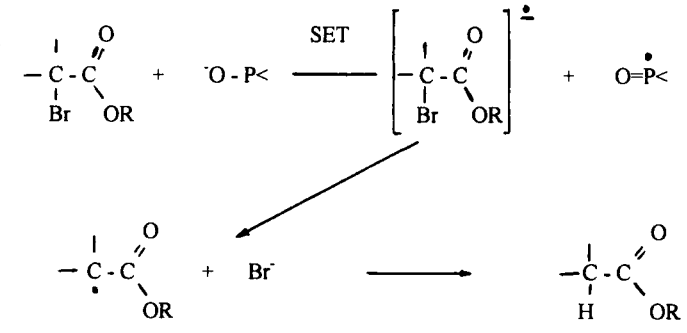
We found also that the compounds (acyclic, cyclic and bicyclic) possessing a C—Br bond where carbon atom is sp,[3] sp$^{2.3}$ and sp^2 hybridized undergo this type of reductive debromination.

The ions of the type >P—O$^-$ could *a priori* reduce α-bromocarboxylates by an attack on the bromine atom with the release of the enol anion as a nucleofuge (pathway A). Pathway A will be an example of the so called X-philic reaction.[8] Nucleophilic displacements on halogen are well known, as phosphorus nucleophiles are noteworthy for their proclivity to engage in such processes.[3b,9] This step might also be described as a positive bromine transfer reaction.

Pathway A:

We have to consider that substitution of the so-called "positive" bromine can also develop through SET (pathway B); the radical chain mechanism or cage process.

Pathway B:



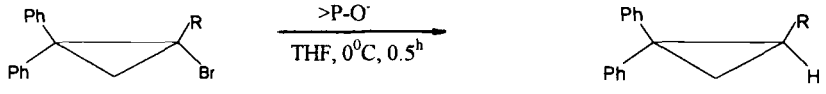
The intriguing mechanism of reductive debromination has been recently scrutinised in our laboratory. To distinguish between the X-philic substitution (pathway A) and SET (pathway B) we designed a new set of experiments. The results of these experiments are presented herein.

RESULTS AND DISCUSSION

The substrates for this stage of our investigation were the cyclopropyl systems. These provide a distinct advantage since, in contrast to other saturated hydrocarbon halides, cyclopropyl halides are extremely slow to solvolysis even in the presence of silver ions; the organometallic reagents prepared from them such as lithium,

magnesium, zinc, and mercury compounds are known to be configurationally stable. Another feature is that the cyclopropyl radical is a very reactive σ radical which with suitable substitution can rearrange to an allyl radical but when a good radical scavenger, solvent or substrate, is present in the reaction mixture, an unrearranged product will be the result. Additionally the cyclopropyl radical inverts its configuration at a rate of 10^{11} s^{-1}.

To answer the question about the neighbouring group participation in the reaction of reductive debromination under the action of the >P—O$^-$ ion we synthesized the set of 1-bromo-2,2-diphenylcyclopropyl-1 derivatives **1** and ran the reaction of sodium diethyl phosphite as well as sodium dibenzyl phosphinite in THF with them.



1 **2**

1 / 2	a	b	c	d	e	f	g	h
R	CH_3	CH_2OTos	Br	COOMe	$CONH_2$	CN	$P(O)(OMe)_2$	COO^-Na^+

The results of these experiments are summarized in Table I.

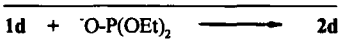
The examination of Table I shows that we obtained the reduced products in the case of the cyclopropyl systems **1c–1g** (R = Br, COOMe, $CONH_2$, CN, $P(O)(OCH_3)_2$); in the case of the cyclopropyl systems **1a–1b, 1h** (R = CH_3, CH_2OTos, COO^-Na^+), and additionally in the case of 1,1-dichloro-2,2-diphenylcyclopropane we isolated only the starting materials, thus for reductive debromination the electron-withdrawing group bound to the carbon bearing the bromine atom is indispensable. What we found would indicate the presence of carbanion intermediates in the reaction in focus. However it is postulated that the stability of free radicals is enhanced by the presence at the radical centre of both an electron-donating and electron-withdrawing group.[10]

TABLE I

Reaction of the 1-bromo-2,2-diphenylcyclopropane **1** with the anion of the type >P—O$^-$

Run	1	R	Solvent	$^-O-P<$	Yield of product **2** %
1	a	CH_3	THF	$^-O-P(OEt)_2$	0
2	b	CH_2OTos	THF	$^-O-P(OEt)_2$	0
3	c	Br	THF	$^-O-P(OEt)_2$	25
4	d	COOMe	MeOH	$^-O-P(CH_2Ph)_2$	94
5	d	COOMe	THF	$^-O-P(OEt)_2$	85
6	e	$CONH_2$	THF	$^-O-P(OiPr)_2$	42
7	f	CN	THF	$^-O-P(OiPr)_2$	41
8	g	$P(O)(OCH_3)_2$	THF	$^-O-P(OMe)_2$	100
9	h	COO^-Na^+	THF	$^-O-P(OEt)_2$	0

TABLE II



Conditions	Yield of **2d**
Normal	62 %
Darkness	57 %
Light of 500 W bulb	59 %

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.[11]

The formation of cyclopropyl halide radical anion pairs as intermediates is invoked in $S_{RN}1$ type substitution reactions by Rossi[12] and Meijs.[13] It seems that the photostimulated reaction of cyclopropyl bromides like 7-bromonorcarane with $Ph_2P^-M^+$ involves a radical chain, and halogen-containing radical anions as a chain carrier.

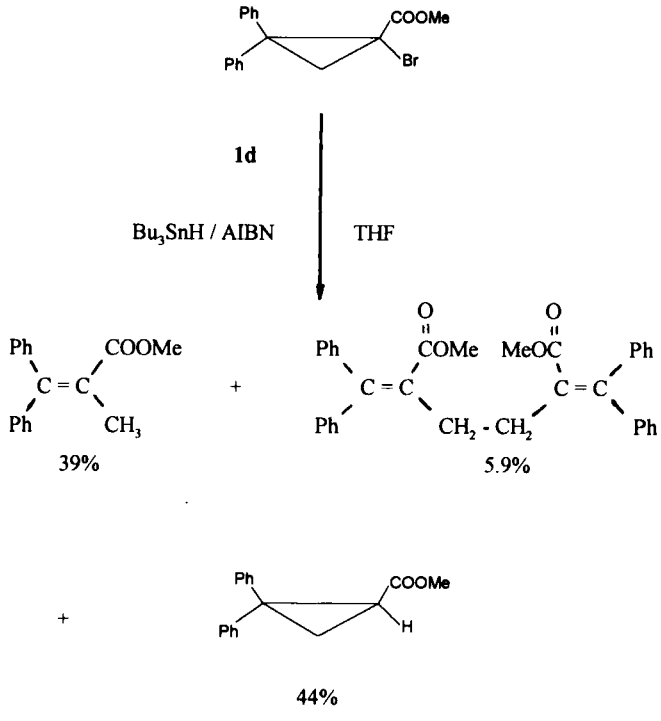
On the other hand Wreford[14] showed that the reaction of diorganophosphides with organic halides proceed in part by a radical mechanism and in part by a competing nonradical path. The preference for one mechanism or the other is highly dependent on the nature of the organic group, halide, and substituents bound to phosphorus.

In order to provide evidence for the SET mechanism operating in reductive debromination we ran the reaction of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** with sodium diethyl phosphite in THF under a variety of conditions (see Table II).

We found that the reaction was slightly inhibited when conducted in darkness. The yield of the debrominated product was almost the same independent of the conditions applied (the yields of the isolated products varied +, −5%).

The electrocyclic cyclopropyl radical-allyl radical rearrangement has been a subject of many theoretical investigations not all of which are in agreement. The first example of the rearrangement of the cyclopropyl radical to the allyl radical in solution was observed in the thermal decomposition of 1-methyl-2,2-diphenylcyclopropanecarbonyl peroxide.[15] The radical reacted by abstracting hydrogen from the solvent or by rearranging to the 1,1-diphenyl-2-methylpropenyl radical which dimerized to yield 1,1,6,6-tetraphenyl-2,5-dimethyl-1,5-hexadiene. The proportion of the dimeric product to that of cyclopropane is dependent on the solvent. If a good radical scavenger is used, then only the unrearranged cyclopropane derivative is obtained. A similar rearrangement with 2,2-diphenylcyclopropyl radicals that have a variety of 1-substituents has been observed.[16]

There is substantial evidence that the reduction of alkyl halides by organotin hydrides goes according to a radical mechanism.[17] We decided to check the reactivity and the behaviour of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate under the free radical condition in solution.



The treatment of 1 equiv of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate in THF with 2 equiv of tributyltin hydride (in the presence of the catalytic amount of 2,2′-azobis-(2-methylpropionitrile)) produces the mixture of the following products: methyl α-methyl-β,β-diphenylacrylate (39%), methyl 2,2-diphenylcyclopropanecarboxylate (44%) and 1,1,6,6-tetraphenyl-2,5-dicarboxymethyl-hexadien-1,5 (5.9%). The experiment shows that the cyclopropyl radical originating from methyl 1-bromo-2,2-diphenylcyclopropanocarboxylate opens up at least in 56% to give the allyl radical which abstracts hydrogen and/or dimerizes. This is not the case in the reaction in focus.

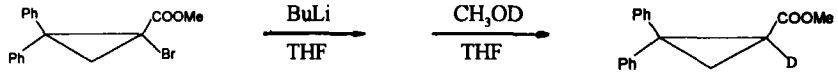
Methyl 1-bromo-2,2-diphenylcyclopropancarboxylate when treated with the >P—O$^-$ ion (also in the experiment run at the boiling point of THF) always gives the unrearranged product namely methyl 2,2-diphenylcyclopropanecarboxylate,[7] we have never observed hexadien- or acrylate-derivatives as the products of reductive debromination.

At this stage the results of our experiments suggest that the cyclopropyl radical intermediate (if it is formed) does not participate in the product-determining step of the reaction in focus.

As we discussed previously the ion of the type >P—O$^-$ could reduce 1-bromocyclopropanecarboxylate by an attack on the bromine atom with the release of the enol anion as a nucleofuge (pathway A). Cyclopropyl anion as well as cyclopropyl-allyl anion transformations have been the subjects of many investigations,[18] moreover cyclopropyl anions have a high synthetic potential.[19]

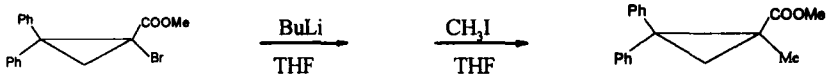
We decided to examine the reactivity and behaviour of the cyclopropyl anion originated from methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate. This anion

we prepared by the halogen-metal exchange. Methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate was treated with 2 equiv of BuLi in THF at −78°C. In one experiment the reaction mixture thus obtained was quenched with methanol-O-d yielding methyl 1-deuterio-2,2-diphenylcyclopropanecarboxylate **3**.



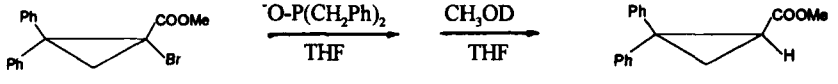
1d **3**

In the second experiment methyl iodide was added to the reaction mixture yielding methyl 1-methyl-2,2-diphenylcyclopropanecarboxylate **4**.



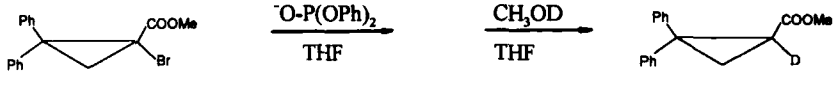
1d **4**

On the other hand when 1 equiv of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate was treated with 2 equiv of sodium dibenzyl phosphinite in THF than quenched with methanol-O-d, surprisingly, we isolated only methyl 2,2-diphenylcyclopropanecarboxylate from the reaction mixture—no deuterium incorporation was observed.



1d **2d**

This unexpected result of the last experiment could suggest the free radical process (abstraction of the hydrogen atom from the solvent) or another source of the protons in the reaction mixture. We decided to change the phosphor nucleophile in our experiment, so the salt of dibenzylphosphine oxide was replaced with the sodium diphenyl phosphite. The treatment of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate with the sodium salt of diphenyl phosphite followed by deuteriolysis yielded methyl 1-deuterio-2,2-diphenylcyclopropanecarboxylate.



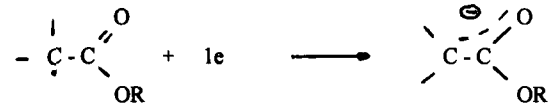
1d **3**

These two last experiments suggest the carbanion intermediate in this reaction and additionally show that dibenzylphosphine oxide (or compounds derived from it) is a proton source.

The reactions of free radicals either give stable products (termination reactions) or lead to other radicals, which themselves must usually react further (propagation reactions). The most common termination reactions are simple combinations of similar or different radicals. Another termination process is disproportionation.

There are four principal propagation reactions: abstraction of another atom or group (usually a hydrogen atom), addition to a multiple bond, decomposition and rearrangement. Apart from these reactions, free radicals can be oxidized to carbocations or reduced to carbanions.

One can argue that another competing reaction which may occur is the reduction of a radical resulting from the decomposition of the radical anion (pathway B) through an electron transfer from the nucleophile or radical anion into the enolate which is finally converted into carboxylic ester by proton abstraction.



We were looking for an experiment which could distinguish between those systems in which substitution occurs by a direct mechanism such as S_N2 (pathway A) or by free radicals (pathway B). We chose the trapping of intermediates as the technique because it could, in principle, distinguish between the two mechanistic classes and could also provide quantitative information concerning the contribution of each if they occurred in competition in a given reacting system.

The fact that the $^-O—P<$ ions are powerful nucleophiles, strong bases, and good reducing agents limited the choice available for potential radical traps. We chose dicyclohexylphosphine as a free radical trap, whose pK_a in THF is 35.7, precluding its reaction as a proton donor to the $^-O—P<$ ion, and the P—H bond dissociation energy (77 kcal/mol) making it a good hydrogen atom donor to carbon free radicals. The treatment of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate with the sodium salt of diphenyl phosphite in THF (1 hour; 20°C) in the presence of dicyclohexylphosphine followed by deuteriolysis (quenching the reaction mixture with methanol-O-d) yielded methyl 1-deuterio-2,2-diphenylcyclopropanecarboxylate in 40% of the isolated yield compared to 47% of the isolated yield of **2d** in the control experiment run under the same conditions in the absence of dicyclohexylphosphine.

1d **3**

The absence of a significant effect of dicyclohexylphosphine on the rates of those reactions as well as the deuterium incorporation into the product permits the exclusion of a chain mechanism of the $S_{RN}1$ type for these substrates (pathway B).

In order to gain further insight into the reductive debromination mechanism by the action of the $>P—O^-$ ion 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 an AMD Intectra 604 apparatus. IR spectra were taken on a Jena-Zeiss IR 10 Apparatus. ^{1}H NMR and ^{31}P NMR spectra were recorded with a Varian apparatus 200 MHz.

Dibenzylphosphine oxide,[20] 1-Bromo-1-methyl-2,2-diphenylcyclopropane **1a**,[21] (1-Bromo-2,2-diphenylcyclopropane)-methyltosylate **1b**,[21]

1,1-Dibromo-2,2-diphenylcyclopropane **1c**,[22] Methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d**,[23] Dimethyl 1-bromo-2,2-diphenylcyclopropanephosphonate **1g**[7] 1,1-Dichloro-2,2-diphenylcyclopropane[25] were prepared according to the literature.

1-Bromo-2,2-diphenylcyclopropanecarboxamide **1e**. The mixture of 1-bromo-2,2-diphenylcyclopropanecarboxylic acid (20.5 mmol, 6.5 g) and 60 mL of $SOCl_2$ was refluxed for 4 hours. The reaction mixture was evaporated under reduced pressure. The residue was dissolved in 100 mL of $CHCl_3$ and ammonia passed through the solution for 40 minutes, then washed with water and dried over $MgSO_4$. The solvent was evaporated, the residue was washed with ether and recrystallized from ethanol to give 4.56 g (70%) 1-bromo-2,2-diphenylcyclopropanecarboxamide, m.p. 202–203°C.

IR (KBr) ν = 3440, 3290 NH; 1660, 1590 $CONH_2$ cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 2.05 (d, J = 6.3 Hz, 1H, CH_2); 2.85 (d, J = 6.3 Hz, 1H, CH_2); 5.60 (bs, 1H, CO—NH_2); 6.72 (bs, 1H, CO—NH_2); 7.10–7.50 (m, 10H, C_6H_5)
MS exact mass calc. for $C_{16}H_{14}BrNO$: 315.02587; found: 315.02581

1-Bromo-2,2-diphenylcyclopropyl cyanide **1f**. To a refluxing solution of α-bromoacrylonitrile (0.15 Mol, 19.8 g) in 200 mL hexane was added diphenyldiazomethane (0.155 mol. 26.5 g) in 150 mL of hexane. Heating was continued until the solution decolorized (about 5 hours) and the reaction mixture was left overnight at room temperature. The crystals were filtered and recrystallized from methanol.

Yield 21.7 g (48.5%) of 1-bromo-2,2-diphenyl-cyclopropyl cyanide. m.p. 112–115°C
IR (KBr) ν = 2250 CN cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 2.25 (d, J = 6.8 Hz, 1H, CH_2); 2.58 (d, J = 6.8 Hz, 1H, CH_2); 7.24–7.59 (m, 10H, C_6H_5)
Anal calc. for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06. Found: C, 64.51; H, 4.26%

Reductive debromination of 1-bromocyclopropane **1**. *General procedure*: 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 1 mmol of 1-bromocyclopropane **1** was added, and the mixture was stirred for 30 minutes at 0°C. 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 vacuum and the product was purified by radial chromatography. 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.

Using 1,1-dichloro-2,2-diphenylcyclopropane in this experiment only starting material was isolated.

Run 1

The starting material was isolated namely 1-bromo-1-methyl-2,2-diphenylcyclopropane (flash chromatography; eluated with benzene) m.p. 80–81°C (Lit.[21] 82–84°C)

^{1}H NMR (CCl_4) δ = 1.58 (d, J = 6.00 Hz, 1H, CH_2); 1.63 (s, 3H, CH_3); 1.85 (d, J = 6.00 Hz, 1H, CH_2); 6.80–7.43 (m, 10H, C_6H_5)

Run 2

The starting material was isolated namely (1-bromo-2,2-diphenylcyclopropane)-methyltosylate (flash chromatography; eluated with benzene) m.p. 115–117°C (Lit.[21] 121°C)

^{1}IR (KBr) ν = 1370, 1190 SO_2 cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.94 (s, 2H, CH_2OTos); 2.46 (s, 3H, CH_3); 4.03 (d, J = 11.05 Hz, 1H, CH_2); 4.17 (d, J = 11.05 Hz, 1H, CH_2); 7.10–7.80 (m, 14H, aromat)

Run 3

1-bromo-2,2-diphenylcyclopropane (eluated with pentane:ether 100:1) m.p. 72–74°C (Lit.[22] 79.5–81.5°C)

^{1}H NMR (500 MHz) ($CDCl_3$) δ = 1.82 (dd, J = 6.60 Hz, J = 4.88 Hz, 1H, CH_2); 1.88 (dd, J = 7.81 Hz, J = 6.60 Hz, 1H, CH_2); 3.69 (dd, J = 7.81, J = 4.88, 1H, CHBr); 7.16–7.53 (m, 10H, C_6H_5)

Run 4

Methyl 2,2-diphenylcyclopropanecarboxylate (eluated with hexane: CH_2Cl_2 = 1:1) ^{1}H NMR and IR spectra were identical with the authentic sample.[7]

Run 5

Methyl 2,2-diphenylcyclopropanecarboxylate (eluated with hexane: CH_2Cl_2 = 1:1) ^{1}H NMR and IR spectra were identical with the authentic sample.[7]

Run 6

2,2-diphenylcyclopropanecarboxamide (eluated with CH_2Cl_2: ethyl acetate = 20:1) m.p. 177–179°C (Lit.[24] 178–179°C)

IR (KBr) ν = 3450, 3295 NH; 1650, 1610 CO—NH_2 cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.56 (dd, J = 8.27 Hz, J = 4.87 Hz, 1H, CH_2); 2.05 (dd, J = 5.96 Hz, J = 4.87 Hz, 1H, $CHCONH_2$); 2.27 (dd, J = 8.27 Hz, J = 4.87 Hz, 1H, CH_2); 5.44 (bs, 2H, $CONH_2$); 7.05–7.40 (m, 10H, C_6H_5)

1-bromo-2,2-diphenylcyclopropane-(N-di*iso*propoxyphosphonyl)-carboxamide (eluated with CH_2Cl_2: ethyl acetate = 20:1) 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}
^{1}H NMR ($CDCl_3$) δ = 1.02 (d, J = 6.13 Hz, 3H, CH_3); 1.21 (d, J = 6.13 Hz, 3H, CH_3); 1.36 (d, J = 6.13 Hz, 3H, CH_3); 1.42 (d, J = 6.13 Hz, 3H, CH_3); 1.91 (d, J = 6.60 Hz, 1H, CH_2); 2.94 (d, J = 6.60 Hz, 1H, CH_2); 4.28 (m, 1H, CH); 4.84 (m, 1H, CH); 7.10–7.80 (m, 10H, C_6H_5); 9.50 (d, J_{PH} = 9.81 Hz, 1H, NH).
^{31}P NMR ($CDCl_3$) δ = −5.41
MS exact mass calc. for $C_{22}H_{27}NO_4PBr$: 479.08616 found 479.08566

Run 7

2,2-diphenylcyclopropyl cyanide (eluated with pentane: CH_2Cl_2 = 1.5:1), m.p. 104–106°C (Lit.[24] 107–108°C)

IR (KBr) ν = 2250 CN cm^{-1}
^{1}H NMR ($CDCl_3$) δ = 1.83 (dd, J = 9.28 Hz, J = 5.37 Hz, 1H, CH_2); 2.06 (dd, J = 5.86, J = 5.37 Hz, 1H, CHCN); 2.25 (dd, J = 9.28 Hz, J = 5.86 Hz, 1H, CH_2); 7.24–7.50 (m, 10H, C_6H_5)

Run 8

Dimethyl 2,2-diphenylcyclopropanephosphonate (eluated with ether) ^{1}H NMR and IR spectra were identical with authentic sample.[7]

Run 9

1-bromo-2,2-diphenylcyclopropanecarboxylic acid, ^{1}H NMR and IR spectra were identical with authentic sample.[23]

Reductive debromination of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *with sodium diethyl phosphite under a variety of conditions. Searching for evidence supporting SET mechanism.* To a suspension of NaH (2.25 mmol, 0.054 g) inTHF (20 mL) was added diethyl phosphite (2 mmol, 0.28 g, 0.26 mL). When the evolution of hydrogen had ceased (about 10 minutes), methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) was added and the reaction mixture was stirred for 30 minutes at 0°C. Then the mixture was diluted with 50 mL of ether, washed with NH_4Cl solution

and dried over $MgSO_4$. The solvent was removed in vacuum and the product, methyl 2,2-diphenylcyclopropanecarboxylate was isolated by radial chromatography (silica gel, hexane: CH_2Cl_2 = 1:1).

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

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. Moreover, we found that light (500 W bulb) had no influence on the reaction rate.

Reaction of tri-n-butyltin hydride with methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *in THF.* A solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g), AIBN (catalytic amount) and tri-*n*-butyltin hydride (2 mmol, 0.582 g, 0.53 mL) in 50 mL of THF was refluxed for 24 hours. The solvent was removed by evaporation under reduced pressure, and the residue was separated by flash chromatography (benzene) to yield: methyl α-methyl-β,β-diphenylacrylate 0.098 g (39%)

IR (film) ν = 1715 C=O cm^{-1}
^1H NMR ($CDCl_3$) δ = 2.03 (s, 3H, CH_3); 3.47 (s, 3H, $COOCH_3$); 7.00–7.60 (m, 10H, C_6H_5)
Methyl 2,2-diphenylcyclopropanecarboxylate 0.112 g (44%), spectral data were identical with those of the authentic sample.[7]
1,1,6,6-tetraphenyl-2,5-dicarboxymethyl-hexadien-1,5 0.03 g (5.9%)
IR (KBr) ν = 1715 C=O cm^{-1}
^1H NMR ($CDCl_3$) δ = 2.56 (s, 4H, CH_2CH_2); 3.41 (s, 3H, $COOCH_3$); 6.90–7.60 (m, 10H, C_6H_5)
MS exact mass calc. for $C_{34}H_{30}O_4$: 502.21441; found: 502.21432

Reaction of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *with sodium methyl phosphite in boiling THF.* To a suspension of NaH (2.25 mmol, 0.054 g) in THF (50 mL) was added dimethyl phosphite (2 mmol, 0.22 g, 0.183 mL). When the evolution of hydrogen had ceased, methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) was added. The reaction mixture was refluxed for 24 hours, then diluted with 75 mL of ether, washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and the residue separated by radial chromatography (silica gel, pentane: CH_2Cl_2 = 1:1) to yield 0.24 g (96%) of methyl 2,2-diphenylcyclopropanecarboxylate.

Methyl 1-deuterio-2,2-diphenylcyclopropanecarboxylate **3**. Butyllithium (2.25 mmol, 1.4 mL of a 1.6 M solution in hexane) was added at −78°C to a solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) in THF (50 mL). The reaction mixture was stirred for 15 minutes, 5 mL of methanol-O-d was added and the reaction mixture was allowed to reach room temperature. It was subsequently diluted with 50 mL of ether and washed with NH_4Cl solution. The organic layer was dried over $MgSO_4$, the solvent was removed in vacuum and the residue was purified by flash chromatography (silica gel, benzene) to give the desired product (0.23 g, 91% yield)

IR (KBr) ν = 1720 cm^{-1}
^1H NMR ($CDCl_3$) δ = 1.60 (d, J = 4.80 Hz, 1H, CH_2); 2.15 (d, J = 4.80 Hz, 1H, CH_2); 3.47 (s, 3H, $COOCH_3$); 7.00–7.50 (m, 10H, C_6H_5)
Anal. Calc. for $C_{17}H_{15}DO_2$: C, 80.57; HD, 6.79. Found: C, 80.01; HD, 7.07%

Methyl 1-methyl-2,2-diphenylcyclopropanecarboxylate **4**. Buthyllithium (2.25 mmol, 1.4 mL of a 1.6 M solution in hexane) was added at −78°C to a solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) in THF (50 mL). The reaction mixture was stirred for 15 minutes, a solution of iodomethane (2.0 mmol, 0.284 g, 0.125 mL) was added, and the reaction mixture was allowed to reach room temperature. It was subsequently diluted with ether (50 mL) and washed with water. The organic layer was dried over $MgSO_4$, the solvent was removed in vacuum and the residue was purified by flash chromatography (silica gel, benzene) to give the desired product (0.24 g, 90% yield): m.p. 89–90°C

IR (KBr) ν = 1710 C=O cm^{-1}
^1H NMR ($CDCl_3$) δ = 1.21 (s, 3H, CH_3); 1.48 (d, J = 4.91 Hz, 1H, CH_2); 2.29 (d, J = 4.91 Hz, 1H, CH_2); 3.37 (s, 3H, $COOCH_3$); 7.10–7.47 (m, 10H, C_6H_5)

Reaction of sodium dibenzyl phosphinite with methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *in THF quenched with methanol-O-d.* Dibenzylphosphine oxide (2 mmol, 0.46 g) was added with stirring to the suspension of sodium hydride (2,25 mmol, 0.054 g) in 30 mL of THF. When the evolution of hydrogen had ceased, a solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) in THF (10 mL) was added. The reaction mixture was stirred for 30 minutes and then 5 mL of methanol-O-d was added, after 30 minutes it was subsequently diluted with ether (50 mL) and washed with D_2O. The organic layer was dried over $MgSO_4$, the solvent was removed in vacuum and the residue

separated by radial chromatography (silica gel, hexane: CH_2Cl_2 = 1:1) to yield methyl 2,2-diphenyl-cyclopropanecarboxylate 0.23 g (91%). The product was identified by comparison of the IR and NMR spectra with those of the authentic sample.[7]

Reaction of sodium diphenyl phosphite with methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *in THF quenched with methanol-O-d.* To a suspension of NaH (2.25 mmol, 0.056 g) in THF (20 mL) was added diphenyl phosphite (2 mmol, 0.468 g, 0.38 mL). When the evolution of hydrogen had ceased, a solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate in THF (10 mL) was added. The reaction mixture was stirred for 1 hour at room temperature and then 5 mL of methanol-O-d were added, after 10 minutes it was subsequently diluted with ether (50 mL), washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and the residue separated by radial chromatography (silica gel, pentane: CH_2Cl_2 = 1:1) to yield 0.15 g (45%) of the starting material and 0.12 g (47%) of methyl 1-deuterio-2,2-diphenyl-cyclopropanecarboxylate.

Reaction of sodium diphenyl phosphite with methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate **1d** *in the presence of dicyclohexylphosphine in THF.* To a suspension of NaH (2.25 mmol, 0.056 g) in THF (20 mL) was added diphenyl phosphite (2 mmol, 0.46 g, 0.38 mL). When the evolution of hydrogen had ceased, a solution of methyl 1-bromo-2,2-diphenylcyclopropanecarboxylate (1 mmol, 0.331 g) and dicyclohexylphosphine (1 mmol, 0.198 g, 0.19 mL) in THF (10 mL) was added. The reaction mixture was stirred for 1 hour at room temperature then 5 mL of methanol-O-d were added, after 5 minutes subsequently it was diluted with ether (75 mL), washed with NH_4Cl solution and dried over $MgSO_4$. The solvent was removed in vacuum and the residue was separated by radial chromatography (silica gel, pentane: CH_2Cl_2 = 1:1) to yield 0.19 g (57%) of the starting material and 0.103 g (41%) of 1-deuterio-2,2-diphenylcyclopropanecarboxylate.

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