The thionophosphate–thiolophosphate† photoisomerization proceeds predominantly through a non-chain radical pathway. Synthetically viable benzylation of tetrahydrofuran, propan-2-ol and olefins‡

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Received (in Cambridge, UK) 2nd May 2000, Accepted 7th December 2000
First published as an Advance Article on the web 11th January 2001

The photoirradiation of thionophosphates, $ROP(S)(OEt)_2$, derived from benzyl and vinylogously benzyl alcohols in CH_3CN, with a Hanovia medium-pressure mercury lamp in a quartz vessel leads to the formation of the corresponding thiolophosphates, $RSP(O)(OEt)_2$, through a non-chain radical pathway. This behavior of thionophosphates is unlike that of the related phosphates, which react through ionic dissociation–recombination processes. When the irradiation is conducted in solvents such as Pr^iOH, THF and toluene, benzylation of these solvents takes place in synthetically respectable yields. Irradiation of thionophosphates in CH_3CN leads to a convenient allylic benzylation of olefins.

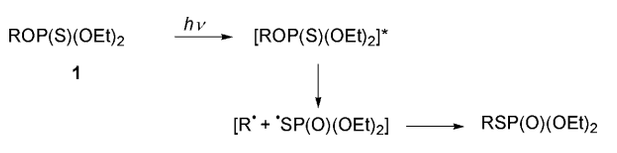
Introduction

The photochemistry of phosphates, $ROP(O)(OEt)_2$, has been studied extensively by Givens and shown to involve an ionic dissociation–recombination pathway.[1] In contrast, the photochemistry of thionophosphates, $ROP(S)(OEt)_2$, has received little attention. In the present manuscript, we disclose our results from such a study and show that (*a*) thionophosphates are photo-active only when the carbinol (methanol) carbon is substituted by an aryl or a vinylogous aryl function, (*b*) thionophosphates are conveniently isomerized to the corresponding thiolophosphates, $RSP(O)(OEt)_2$, in CH_3CN as solvent, (*c*) irradiation of thionophosphates in solvents such as Pr^iOH, tetrahydrofuran and toluene readily leads to their benzylation, (*d*) irradiation of thionophosphates in CH_3CN brings about allylic benzylation of olefins, and (*e*) non-chain radical pathways control all the above transformations.

Results and discussion

1. Isomerization to thiolophosphates

The irradiation in CH_3CN resulted in a smooth transformation of the thionophosphates, **1**, into the related thiolophosphates, **2** (Scheme 1). Some 65–70% of the initial thionophosphate reacted. The thiolophosphates were separated readily from the unchanged thionophosphates by chromatographic techniques including radial chromatography over silica gel. Except for the cinnamyl thionophosphate, all other thionophosphates were stable to thermal conditions[2] and silica gel chromatography. Cinnamyl thionophosphate isomerized[3] on chromatography over silica gel to furnish the same product mixture as that produced from irradiation (*vide infra*). However, the ratio of the isomeric products was different from that produced in the photochemical reaction.



Scheme 1 A general representation of the thionophosphate–thiolophosphate photoisomerization.

The species **3** and **4** were also formed in small amounts from the reaction of methyl mandelate-derived thionophosphate (mandelic acid is phenylglycolic acid). The corresponding thiolophosphate, however, was still the major product. While the structure of **3** was confirmed from spectroscopic characteristics, exact mass measurement analysis and comparison with literature data,[4] the structure of **4** was secured from a single-crystal X-ray structure determination (Fig. 2).[5] Cinnamyl thionophosphate underwent transformation both without and with allylic shift to furnish **5** and **6**, respectively. The efficacies of the rearrangements of 1-phenylethanol and 1-phenylcitronellol derivatives were somewhat low in comparison with those of methyl mandelate and cinnamyl alcohol derivatives, and longer irradiation (30 min) was required for ⩾65% conversion. The results are collected in Table 1.

1-Phenylhex-5-en-1-ol underwent both rearrangement to the corresponding thiolophosphate and elimination to generate a mixture of (*Z*)- and (*E*)-1-phenylhexa-1,5-dienes[6] in almost equal amounts. 1,2-Diphenylethyl thionophosphate reacted similarly to give the corresponding thiolophosphate and a mixture of (*Z*) and (*E*) stilbenes in almost equal amounts.

2. Irradiation in Pr^iOH

In view of the formation of **3** and **4** above, a radical pathway was considered to be more appropriate than an ionic dissociation–recombination alternative. This led us to study the reactions of selected thionophosphates in propan-2-ol, which is a good hydrogen-atom donor under radical conditions. It was expected to quench the phosphate radical derived from the thionophosphate to generate $(RO)_2P(O)SH$, or, a derivative thereof, and itself combine with the benzyl radical to result in a C–C bond formation.

† The IUPAC name for thionophosphates is thiophosphate *O*-esters and that for thiolophosphates is thiophosphate *S*-esters.
‡ ^1H and ^{13}C spectra of the adduct of TEMPO and the radical **14** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b003501g

DOI: 10.1039/b003501g

Table 1 Results of selected thionophosphate–thiolophosphate photoisomerizations

Thionophosphate from	Irradiation time (*t*/min)	Conversion (%)
Methyl mandelate	15	70
Cinnamyl alcohol	15	68
1-Phenylethanol	30	65
1,2-Diphenylethanol	30	67
1-Phenylcitronellol	30	65
1-Phenylhex-5-en-1-ol	30	65
Benzyl alcohol	30	65
4-(*tert*-Butyl)cyclohexanol	120	[a]
1-Phenylpropan-2-ol	120	[a]
trans-But-2-en-1-ol	120	[a]

[a] = No reaction. In all other cases, the reactions were very clean and the isolated yield of the thiolophosphate based on the consumed thionophosphate was 90% and above.

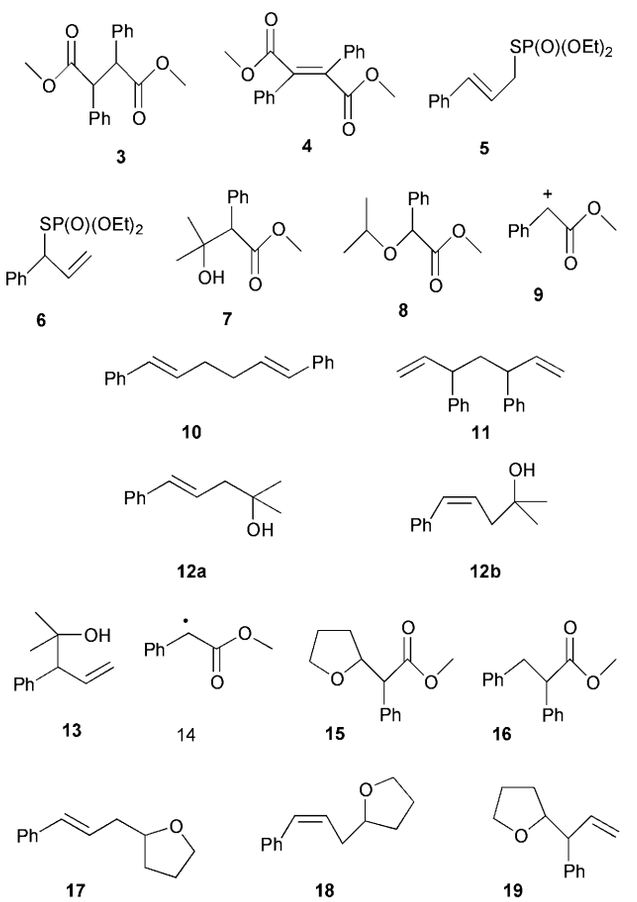


Fig. 1 Substrates **3**–**19** obtained from some reactions.

In the event, irradiation of a solution of methyl mandelate-derived thionophosphate in Pr^{i}OH for 30 min furnished the β-hydroxy ester **7** as the sole product; none of the cation-quenched product **8** was formed. This experiment demonstrated clearly that the benzyl cation **9** was not formed. This is to be contrasted with the results from the irradiation of $ArCH_2OP(O)(OEt)_2$ in solvents such as alcohols (ROH), moist CH_3CN, and benzene, when $ArCH_2OR$, $ArCH_2NHCOMe$, and $ArCH_2C_6H_5$, respectively, constituted the predominant products that arose from the reaction of $ArCH_2^+$ with the solvent molecules.[1] It is significant to note that we have never isolated any amide-like products from the reactions in CH_3CN. Likewise, C_6H_5-incorporated products were also not isolated from the reactions in benzene.

The cinnamyl thionophosphate also reacted with Pr^{i}OH.

Table 2 Results of the reactions of selected thionophosphates with Pr^{i}OH, THF, and toluene

Thionophosphate from	Solvent	Irradiation time (*t*/min)	Conversion (%)	Product yield (%)
Methyl mandelate	Pr^{i}OH	30	70	90
Methyl mandelate	THF	30	75	90
Methyl mandelate	Toluene	30	50	85
Cinnamyl alcohol	Pr^{i}OH	120	89	25
Cinnamyl alcohol	THF	120	91	20

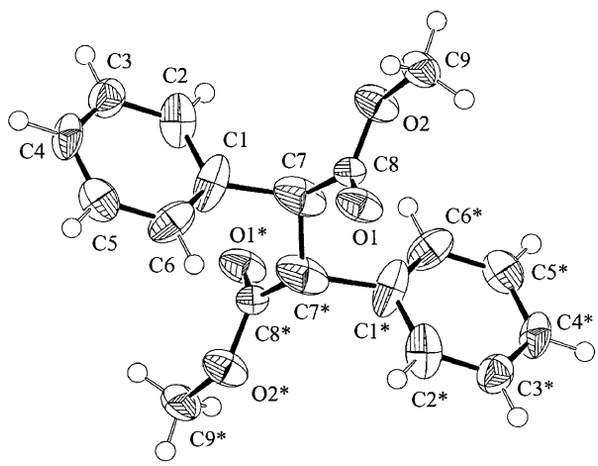


Fig. 2 ORTEP plot of the X-ray structure of **4**.

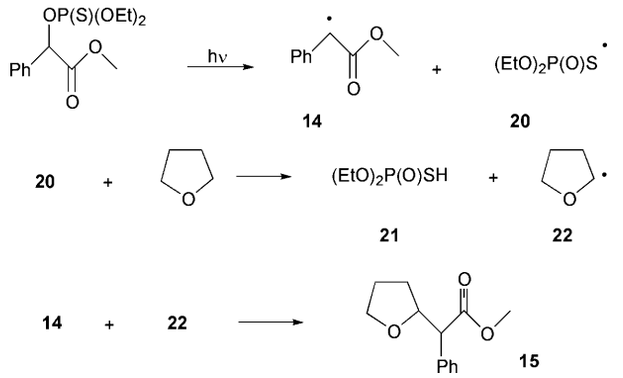
The dimers **10** and **11** (5%, combined) and the isomeric thiolophosphates **5** and **6** (40%, combined) were the other products that had formed along with the expected product **12** (25%). The product **13** that is isomeric with **12** was not formed. The reaction, therefore, had proceeded with very high regioselectivity. The formation of **12b** along with **12a** must be a consequence of photo-induced olefin isomerization. The 1,2-diphenylethyl thionophosphate underwent smooth elimination to furnish a mixture of (*Z*)- and (*E*)-stilbenes; Pr^{i}OH-incorporated product was not formed. 1-Phenylethanol furnished only the corresponding thiolophosphate.

3. Irradiations in tetrahydrofuran and toluene

The generation of radical species, *e.g.* **14**, from methyl mandelate-derived thionophosphate, was confirmed further by conducting the irradiation in non-alcoholic solvents such as tetrahydrofuran (THF) and toluene. The methyl mandelate derivative furnished **15** and **16**[7] from the reactions in THF and toluene, respectively. The reaction in THF was more efficient than the reaction in toluene. Cinnamyl thionophosphate furnished an inseparable mixture of products **17**–**19** (25%). The *E*- and *Z*-olefin geometries in **17** and **18** were determined from the ^{1}H coupling constants of the vinylic hydrogens, which were 15.6 and 11.7 Hz, respectively. The species **19** was a diastereomeric mixture. The dimeric species **10** and **11** (5%) and the thiolophosphates **5** and **6** (45%) were also formed. The results of the reactions of selected thionophosphates are collected in Table 2.

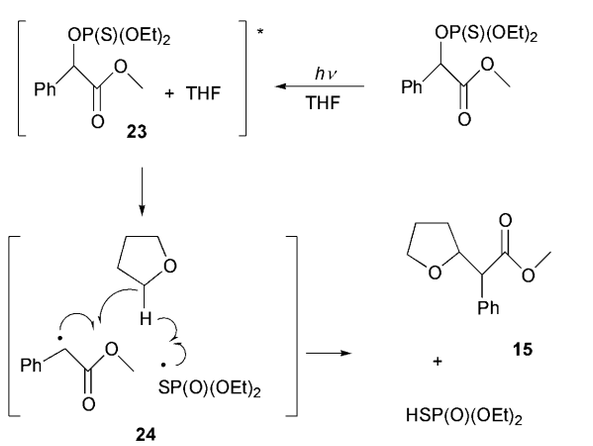
The thionophosphates of 1,2-diphenylethanol and 1-phenylethanol did not react in the desired manner. The 1,2-diphenylethanol derivative underwent elimination and furnished a mixture of (*Z*)- and (*E*)-stilbenes. A small amount of the corresponding thiolophosphate was also formed. 1-Phenylethanol furnished only the corresponding thiolophosphate.

The reactions in THF may be considered to proceed as shown in Scheme 2. It is the sulfur radical **20**, and not the carbon radical **14**, which abstracts a hydrogen atom from THF. In support of this, we have never isolated any methyl α-phenylacetate that would be formed if the carbon radical **14** were to



Scheme 2 A tentative mechanism for the benzylation of tetrahydrofuran.

abstract a hydrogen atom from THF. The products from the self-couplings of tetrahydrofuran-2-yl radical, **22**, and the carbon radical **14** were not formed either. The cross coupling, therefore, is greatly favored over self-coupling. This has some bearing on the reaction mechanism. The THF molecule that has diffused to form the exciplex **23** is probably readily available for hydrogen-atom abstraction by the sulfur radical. This is then followed by a fast capture of the so-generated tetrahydrofuran-2-yl radical by a benzyl radical as shown in Scheme 3.[8]



Scheme 3 A tentative rationale as to how only the cross-coupled products are formed.

4. Further evidence for radical participation

Dioxygen is an effective quench for radicals. A 10 mM CH_3CN solution (30 mL) of methyl mandelate-derived thionophosphate was bubbled with dioxygen for 30 min and then irradiated for 15 min. ^{1}H NMR analysis indicated 8 : 1 ratio of thiono- and thiolophosphate as against a ratio of 3.5 : 1 when the dioxygen was replaced by argon under otherwise identical conditions. The low thiono–thiolo conversion in the presence of dioxygen indicates involvement of radical(s).

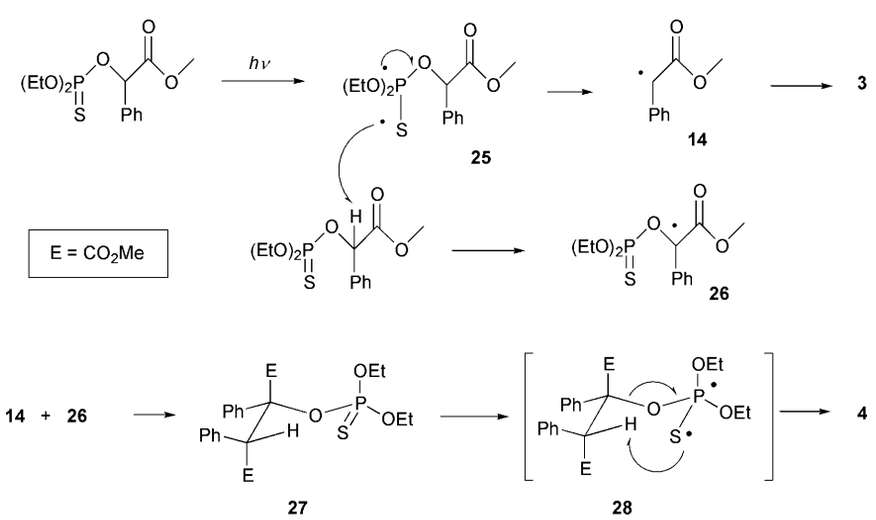
In yet another experiment, a 30 mL CH_3CN solution of methyl mandelate-derived thionophosphate and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), 10 mM in each, was degassed by bubbling with argon for 30 min and then irradiated for 15 min. Chromatographic purification allowed us to isolate the product of quench of the benzyl radical **14** with TEMPO. This experiment confirmed the participation of radicals beyond doubt.

5. A tentative mechanistic rationale for the formation of the species 3 and 4

With the participation of radical species confirmed, we can now speculate on the events in the formation of **3** and **4** as in Scheme 4. The benzylic hydrogen in methyl mandelate-derived thionophosphate is highly reactive. The carbon radical **26**, formed from its abstraction in an intermolecular process *via* diradical **25** as shown, is stable. The combination of radicals **14** and **26** would give yet another thionophosphate **27**, which would react through a six-membered ring transition state involving a hydrogen-atom transfer to deliver **4**. The self-coupling of the radical **14** generates **3**. The product of self-coupling of **26** was not formed. This may be due to the large steric crowding that would develop around the carbon–carbon bond that would form.

6. Reactions of thionophosphates formed from non-benzylic alcohols

The chemistry of the thionophosphates prepared from *trans*-4-*tert*-butylcyclohexanol, 1-phenylpropan-2-ol and *trans*-but-2-en-1-ol were studied to understand the role of the aromatic ring. There was no reaction even after irradiation for 2 h. It appears, therefore, that the light is absorbed first by the aromatic ring and then transmitted, in some way, to the P=S function. The failure of the 1-phenylpropan-2-ol derivative to undergo the thiono–thiolo isomerization suggests further that the aromatic chromophore must necessarily be present at the carbinol carbon for a meaningful reaction to occur. The study of thionophosphates prepared from these alcohols on reaction with diphenyl chlorothiophosphate turns out to be a distinct possiblity for future investigations.

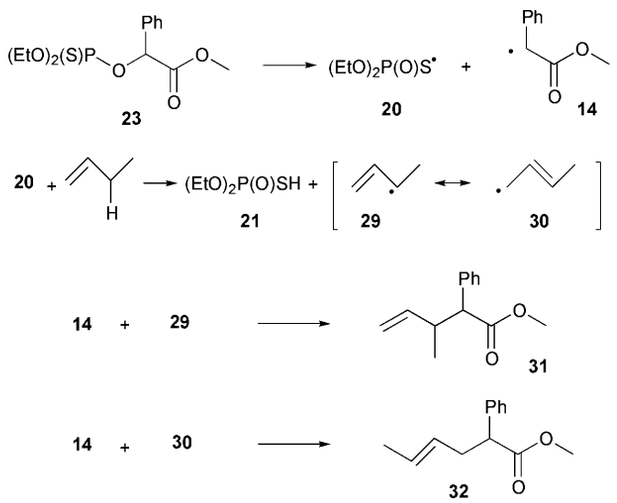


Scheme 4 A tentative mechanism leading to the formation of species **3** and **4**.

Table 3 Results of allylic benzylation of selected alkenes with methyl mandelate thionophosphate[a]

Olefin	Benzylation (%)[b]	**3** (%)[b]	**4** (%)[b]	Thiolophosphate (%)[b]	Recovered SM[b] (%)
Cyclopentene	38.2	7.6	6.8	17.8	24.8
Cyclohexene	32.0	6.6	6.6	23.0	29.2
Cyclooctene	34.4	5.5	6.9	30.8	32.1
Cycloocta-1,5-diene	33.0	7.5	9.1	20.2	28.0
1-Methylcyclohexene	38.4	8.4	7.8	18.4	25.0
Dec-1-ene	29.7	9.7	7.8	23.0	11.7

[a] The yields are based on the methyl mandelate-derived thionophosphate consumed. [b] SM = starting material.



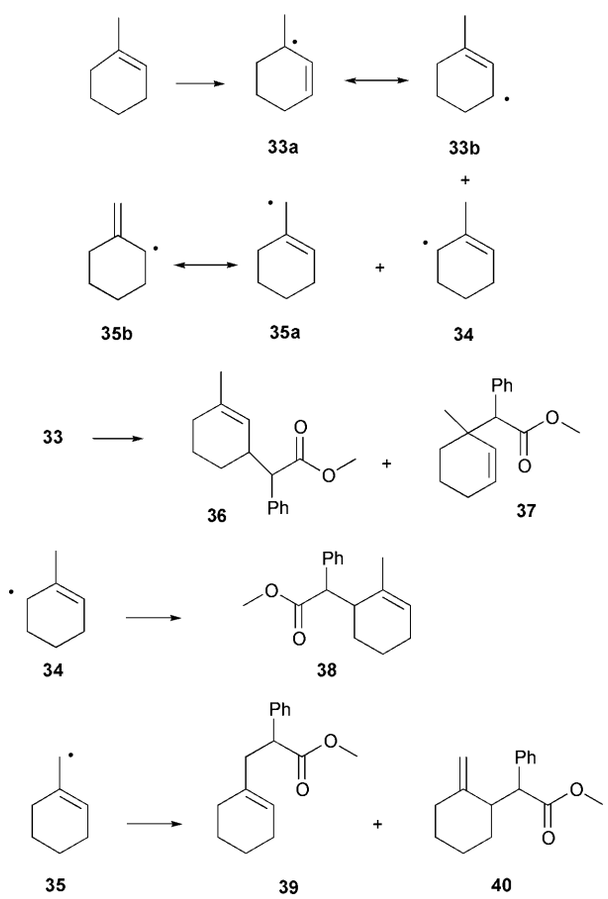
Scheme 5 The different possibilities in the allylic benzylation of but-1-ene.

7. Allylic benzylation of alkenes

The demonstrated ability of sulfur radicals to abstract a hydrogen atom from Pr^{i}OH, THF and toluene raised the possibility of using olefins as possible hydrogen-atom donors. The abstraction of a hydrogen atom from an allylic carbon will generate a radical that could, in principle, combine with the earlier formed benzyl radical in a subsequent step to generate a product of net allylic benzylation. This concept is illustrated in Scheme 5 with but-1-ene as a representative example. The first formed allylic radical **29**, which is in resonance with **30**, will be expected to combine with the radical **14** to generate a mixture of **31** and **32**.

The above premise was put to experimental test and we investigated the irradiation of selected thionophosphates and olefins such as cyclopentene, cyclohexene, 1-methylcyclohexene, cyclooctene, cycloocta-1,5-diene and dec-1-ene in CH_3CN. It was gratifying indeed to discover that the reactions proceeded just as expected. From all these reactions, the dimeric materials **3** and **4** and the corresponding thiolophosphates were also formed in small to significant amounts. The results of the reactions of methyl mandelate-derived thionophosphate with various olefins are collected in Table 3.

1-Methylcyclohexene could, in principle, furnish a total of five regioisomers, **36**–**40** (Scheme 6). The regioisomers **36** and **37** represent the products derived from the radical **33**. The regioisomer **38** will be derived from the radical **34**. Finally, the regioisomers **39** and **40** will be formed from the radical **35**. Of these five possible regioisomers, only the first three were formed. The isomer **37** was separated from the mixture. The isomers **36** and **38** were inseparable from each other even by chromatography over $AgNO_3$-impregnated silica gel. The ratio (**36** + **38**) : **37** was 4 : 1. Clearly, the radical coupling at the secondary carbons was 4 times faster than the coupling at the tertiary carbon. Hydrogen abstraction did not occur at the methyl group and, thus, the regioisomers **39** and **40** were not formed.



Scheme 6 Allylic benzylation of 1-methylcyclohexene.

Dec-1-ene reacted with methyl mandelate-derived thionophosphate and furnished an inseparable 3 : 2 mixture of the dec-2- and -1-ene, **41** and **42** (Fig. 3), which were benzylated at C-1 and C-3, respectively. The first formed allylic radical was resonance stabilized and it reacted through both ends.

The cinnamyl thionophosphate furnished a mixture of the (*E*)- and (*Z*)-3-(cyclohex-2-enyl)-1-phenylpropene, **43a** and **43b**, respectively, and a diastereomeric mixture of 3-(cyclohex-2-enyl)-3-phenylpropene, **44** on reaction with cyclohexene. The ratio **43a** : **43b** was estimated at ≈1 : 1 from the ^{1}H integrals of the olefinic hydrogens at C-1. The 1 : 1 diastereomeric mixture of **44** was separated into its components by radial chromatography. The product from 1-phenylethanyl thionophosphate and cyclohexene was a 1 : 1 mixture of diastereomeric 1-(cyclohex-2-enyl)-1-phenylethane, **45**.

The reaction of cycloocta-1,5-diene was likely to give two diastereomeric products, **46a** and **46b**. The structure assignment as to whether the product was **46a** or **46b** or a mixture of both was difficult due to the diastereomeric nature of the products. To resolve this problem indirectly, we chose to eliminate the diastereomeric component to simplify product composition and, hence, irradiated cycloocta-1,5-diene and benzyl thiono-

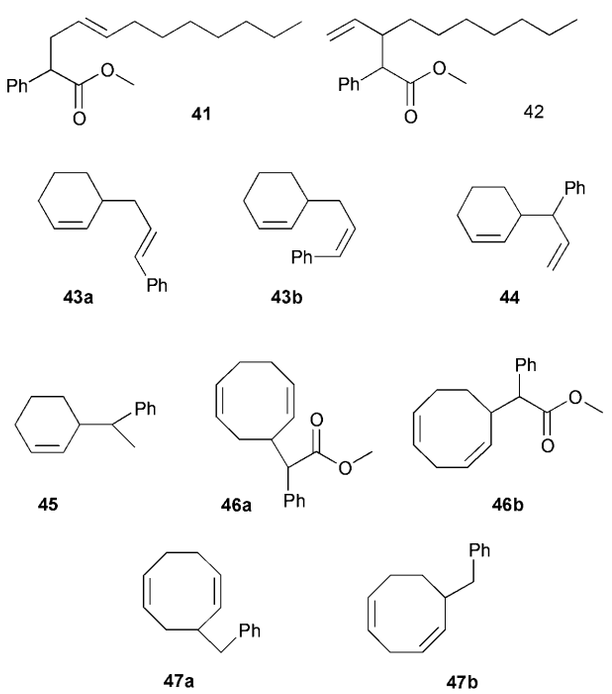
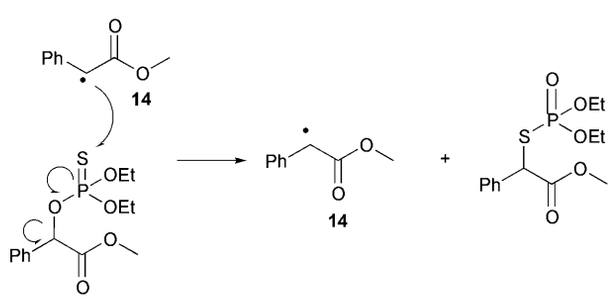


Fig. 3 Examples of allylic benzylations (substrates **41**–**47**).

phosphate under identical conditions and isolated a mixture of two compounds along with a small amount of 1,2-diphenylethane. Fortunately, these two compounds were separated easily by column chromatography over $AgNO_3$-impregnated silica gel and they were characterized as **47a** and **47b** from their individual spectroscopic data including 2D ^{1}H NMR. The product from allylic shift was, therefore, formed. In compliance with this, we conclude that a mixture of **46a** and **46b** was formed from the reaction of cycloocta-1,5-diene with methyl mandelate-derived thionophosphate.

8. Evidence in support of the non-chain radical protocol

The thionophosphate–thiolophosphate transformation proceeds in a non-chain radical fashion. This was demonstrated using methyl mandelate-derived thionophosphate as the substrate. If the reaction were to proceed in a chain fashion, one will expect the carbon radical **14** to add to the sulfur in the P=S bond and bring about further cleavage as shown in Scheme 7



Scheme 7 The requirement(s) of the radical-chain process for the thionophosphate–thiolophosphate isomerization.

to give the desired thiolophosphate with regeneration of the radical **14**. The crucial step in the design of such a radical chain is the ability of a benzylic radical to add to the sulfur in P=S. Though such radical additions to thione functions, C=S, are implicated in the literature,[9] we discover below that this is not so in as much as the addition to the sulfur in thionophosphates is concerned.

A solution of hexabutylditin (2.5 mol%) in toluene was added slowly to a refluxing solution of methyl mandelate-derived thionophosphate and benzyl bromide (5 mol%) in toluene. The *in situ*-generated benzyl radical from the reaction of tributyltin radical and benzyl bromide was expected to initiate the process by adding to the sulfur and, thus, bringing about the desired overall change. Product analysis indicated that while the thionophosphate was still present, all the benzyl bromide had been consumed. Clearly, the benzyl radical formed from benzyl bromide on reaction with tributyltin radical did not add to P=S. This result is interesting because the dimerization of benzyl radical took place even when its concentration was so very small. It points to the presence of some very strong force that acts against the addition of a benzyl radical to the P=S function. To reconfirm this finding, the following experiment was designed.

A solution of Bu_3SnH (1.2 equiv.) in benzene was added slowly with the help of a syringe pump to a mixture of methyl mandelate-derived thionophosphate and benzyl bromide (1.0 equiv.) at reflux. The benzyl bromide had apparently reduced to toluene as it was altogether absent in the mixture and the thionophosphate was recovered quantitatively. The benzyl radical, therefore, did not add to P=S. The tributyltin radical did not add to P=S either. This was confirmed further from a separate experiment in which a benzene solution of methyl mandelate-derived thionophosphate, Bu_3SnH (1.2 equiv.) and a catalytic amount of azoisobutyronitrile (AIBN) was refluxed for 2 h. The thionophosphate was recovered quantitatively. This last experiment was performed on 1-phenylcitronellyl§ thionophosphate as well, when, again, no reaction took place and the thionophosphate was recovered quantitatively.

The above observations established clearly that neither a carbon radical nor a tin radical adds to the P=S function present in thionophosphates. This being so, the transformation of a thionophosphate into the corresponding thiolophosphate could only be a non-chain radical process.

To confirm further the above non-chain protocol, we irradiated a 10 mM solution of methyl mandelate-derived thionophosphate in CH_3CN for 3 min and then waited for 12 min before the solvent was removed. The thiono–thiolo ratio was determined to be 67 : 1, which indicated very little conversion. The above ratio is far from the 3.5 : 1 ratio observed on irradiation for 15 min. The low conversion on shorter irradiation can be explained only by the participation of a non-chain protocol. With a chain protocol, both the reactions will be expected to exhibit similar conversions.

9. Attempts at the cleavage of cyclopropane rings

The successful experiments with cinnamyl thionophosphate led us to explore the chemistry of cyclopropylmethanol derivatives as well. This was due largely to the understanding that a cyclopropane ring is similar to an olefin. In the event, we irradiated **48** (Fig. 4) in CH_3CN and noted absolutely no reaction. This shows the significance of a true π-bond over a cyclopropane ring system; the ring does not allow the transfer of energy absorbed by the aromatic unit to the thionophosphate function.

This above failure is not too difficult to understand. The transmittance of energy from the aromatic unit to the thionophosphate function across an olefinic linkage is made simple due to the all-parallel nature of the p orbitals in the aromatic ring system, the two p orbitals of the olefinic tether and the C–O bond axis in the thionophosphate function. In the cyclopropane derivative, if the p orbitals of the aromatic ring system are parallel to the adjacent cyclopropane carbon–carbon bond axis, they are near orthogonal to the cyclopropane carbon–carbon bond axis at the other carbinol-bearing carbon. This is likely to break the flow of energy from the aromatic core to the thionophosphate function. The transfer of energy, therefore, takes place through the bonds and not through the space. This

§ Citronellyl = 3,7-dimethyloct-6-enyl.

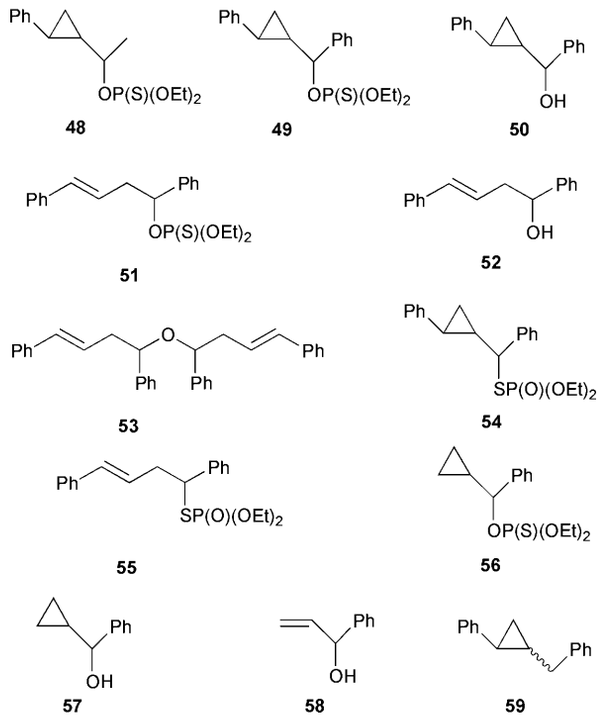


Fig. 4 Attempts at the cleavage of cyclopropane rings.

hypothesis explains the failure of 1-phenylpropan-2-yl thionophosphate to undergo isomerization to the corresponding thiolophosphate (*vide supra*).

We considered we could overcome the above difficulty by substituting a phenyl group on the carbinol carbon itself and studying **49**. However, the preparation of **49** from the alcohol **50** was difficult. We isolated a host of products, **51**–**55**, but not the expected thionophosphate from the employment of our standard conditions. The formation of the products **51**–**55** can be explained from a combination of events such as (a) ionization leading to the formation of a cyclopropylmethyl cation, (b) cleavage of the cyclopropane ring in this cation that leads to the formation of yet another cation, and (c) the quenching of the rearranged cation by the phosphate ion through both oxygen and sulfur. The species **49**, therefore, is too unstable under the thionophosphate-forming reaction conditions to allow its isolation. The all-*E* **51**–**53** and **55** show that the cyclopropane ring cleaved with very high stereoselectivity.

The alcohols corresponding to the thionophosphates **48** and **49** were prepared from $NaBH_4$ reduction of the corresponding ketones which, in turn, were prepared from the corresponding α,β-unsaturated ketones following Corey's cyclopropanation method.[10]

In attempts to suppress or even stop the above rapid ionization, we also considered studying the substrate **56** that lacks the phenyl substituent on the cyclopropane ring. However, the alcohol **57** could not be prepared from the attempted cyclopropanation of **58** under the Simmons–Smith conditions (CH_2I_2, Zn/Cu, Et_2O, reflux, 2 h). Other methods of cyclopropanation were not attempted.

Finally, in our attempts to generate a cyclopropylmethyl radical to witness the cleavage of the cyclopropane ring and its further quench by a carbon radical, we irradiated a mixture of methyl mandelate thionophosphate and **59**[11] (*cis*/*trans* mixture) in CH_3CN to observe only thiono–thiolo isomerization. The substrate **59** was recovered and no ring-cleaved product was formed. This result is surprising particularly because methyl mandelate-derived thionophosphate has been found by us (*vide supra*) to react with toluene. It appears as if the phosphate radical can quench the carbon radical faster than it can abstract a hydrogen atom from **59**.

Conclusions

Thionophosphates were conveniently isomerized into the corresponding thiolophosphates under photochemical conditions. The isomerizations followed exclusively non-chain radical pathways. The reactions in Pr^iOH and THF constitute convenient benzylation protocols for these substrates. The irradiation of a thionophosphate and an olefin in acetonitrile readily leads to an allylic benzylation of the latter. All these reactions are, however, limited to alcohols that are either benzylic or vinologously benzylic. The light absorbed by the aromatic core is transmitted to the thionophosphate function through the bonds that trigger the observed transformations.

Experimental

Starting materials

The thionophosphates studied were derived from methyl mandelate, 1-phenylhex-5-enol, cinnamyl alcohol, 1-phenylethanol, 1,2-diphenylethanol,[12] 1-phenylcitronellol,[13] *trans*-4-*tert*-butylcyclohexanol, (*E*)-but-2-en-1-ol, 1-phenylpropan-2-ol and 1-(2-phenylcyclopropyl)ethanol on reaction of their sodium salts with diethyl chlorothiophosphate at 0–25 °C. It is important to note that the earlier employed method[1] that uses pyridine as base for the preparation of phosphates was completely ineffective. Cyclopentene, cyclohexene and dec-1-ene were distilled before use. Cyclooctene, cycloocta-1,5-diene and 1-methylcyclohexene were used as received.

General

^1H, ^{13}C and ^{31}P data were recorded on Bruker DPX-200, Bruker DRX-300 and JEOL JNM-LA400 series of instruments for samples in $CDCl_3$. Signal positions are reported in ppm (δ scale) relative to $SiMe_4$ for ^1H, $CDCl_3$ for ^{13}C and H_3PO_4 for ^{31}P spectra. The mixtures were purified for their components by either gravity column chromatography over silica gel (100–200 mesh) or radial chromatography using plates coated with silica gel 60 PF_{254} (E. Merck). The components were eluted with mixtures of hexanes and EtOAc. IR spectra were measured on a Perkin-Elmer 1320 spectrometer.

Argon was bubbled through all the solutions for 30 min before irradiation. Irradiation was carried out using a Hanovia 450W medium-pressure mercury lamp (product no. 679A0360, arc length 4.3 inches). The center of the magnetically stirred reaction solution (15–30 mL in a quartz tube of id 2.0 cm) was kept at a distance of 11–12 cm from the center of the light source. Water at 25 °C was circulated through the outer jacket of the lamp-housing (all-quartz). The reaction solutions were only slightly warm to the touch after the irradiation.

For the thiono–thiolo isomerization, a 10 mM solution of a thionophosphate in CH_3CN was irradiated for 15–30 min. For reactions with solvents such as Pr^iOH, THF and toluene and for the allylic benzylation of olefins in CH_3CN, 20 mM solutions of the thionophosphates were used. The molar ratio of thionophosphate and olefin was 1 : 2 and the irradiation time 2 h.

General procedure for the formation of thionophosphates

To an ice-cold stirred suspension of NaH (1.2 mmol) in dry THF (2 mL) was added a solution of an alcohol (1.0 mmol) in THF (2 mL). The resultant mixture was stirred till hydrogen evolution ceased (30–60 min). A solution of diethyl chlorothiophosphate (1.1 mmol) in THF (2 mL) was added, the reaction mixture allowed to warm to room temperature, and stirring was continued until the reaction was complete (3–10 h) by TLC. The reaction mixture was diluted with Et_2O (10 mL), mixed with saturated aq. NH_4Cl (5 mL) and stirred for 10 min. The layers were separated and the aqueous layer was extracted with Et_2O (2 × 5 mL). The combined Et_2O solution was dried, filtered and

concentrated. The residue was chromatographed over silica gel and the desired product isolated in near quantitative yield.

Reaction of methyl mandelate-derived thionophosphate with benzyl bromide and hexabutylditin

A solution of hexabutylditin (0.025 mmol) in toluene (3.5 mL) was slowly added to a refluxing solution of the thionophosphate (1.0 mmol) and benzyl bromide (0.05 mmol) in toluene (9 mL) over a period of 2 h using a syringe pump. Reflux was continued for an additional 1 h. The solvent was removed and the residue was chromatographed to isolate the starting thionophosphate quantitatively.

Reaction of methyl mandelate-derived thionophosphate with benzyl bromide, tributyltin hydride and AIBN

A solution of Bu_3SnH (1.2 mmol) and AIBN (0.06 mmol) in benzene (3.5 mL) was added to a refluxing solution of the thionophosphate (1.0 mmol) and $PhCH_2Br$ (1.0 mmol) in benzene (9 mL) over a period of 2 h using a syringe pump. The reaction mixture was refluxed for an additional 1 h before the solvent was removed.

Reaction of methyl mandelate-derived thionophosphate with tributyltin hydride and AIBN

A solution of Bu_3SnH (1.2 mmol) and AIBN (0.06 mmol) in benzene (3.5 mL) was added to a refluxing solution of the thionophosphate (1.0 mmol) over a period of 2 h using a syringe pump. Reflux was continued for an additional 1 h before the solvent was removed.

Methyl mandelate-derived thionophosphate (1, R = PhCH-CO_2Me). Liquid, δ_H 7.60–7.25 (5H, m), 5.89 (1H, d, *J* 11.6 Hz), 4.30–4.10 (2H, m), 4.05–3.80 (2H, m), 3.72 (3H, s), 1.35 (3H, t, *J* 7.0 Hz), 1.14 (3H, t, *J* 7.0 Hz); δ_C 169.7 (d, *J* 6.4 Hz), 135.4 (d, *J* 6.0 Hz), 129.7, 129.1, 127.8, 77.9 (d, *J* 3.2 Hz), 65.1 (d, *J* 5.6 Hz), 64.8 (d, *J* 5.8 Hz), 53.0, 16.1 (t, *J* 8.3 Hz); δ_P 67.2.

Methyl mandelate-derived thiolophosphate (2, R = PhCH-CO_2Me). Liquid, δ_H 7.50–7.30 (5H, m), 5.04 (1H, d, *J* 11.3 Hz), 4.20–4.10 (1H, m), 4.08–3.90 (3H, m), 3.74 (3H, s), 1.27 (3H, t, *J* 7.0 Hz), 1.24 (3H, t, *J* 7.0 Hz); δ_C 170.8 (d, *J* 6.4 Hz), 136.6 (d, *J* 6.0 Hz), 129.3, 129.0, 128.7, 64.3 (d, *J* 6.2 Hz), 62.2 (d, *J* 6.9 Hz), 53.5, 52.3 (d, *J* 3.2 Hz), 16.2 (d, *J* 7.3 Hz); δ_P 23.4.

Dimethyl 2,3-diphenylsuccinate 3a. More polar, solid, mp 231–234 °C; δ_H 7.18–6.97 (5H, m), 4.25 (1H s), 3.69 (3H, s); δ_C 173.7, 135.6, 128.5, 128.4, 128.3, 127.5, 54.7, 52.4 (Calc. for $[M - MeOH]^+$: *m*/*z*, 266.0943. Observed *m*/*z*, 266.0918).

Dimethyl 2,3-diphenylsuccinate 3b. Less polar, solid, mp 235–238 °C; δ_H 7.50–7.24 (5H, m), 4.38 (1H, s), 3.39 (3H, s); δ_C 171.8, 136.3, 128.7, 128.3, 127.9, 54.9, 52.0 (Calc. for $[M - MeOH]^+$: *m*/*z*, 266.0943. Observed *m*/*z*, 266.0923).

1-Phenylethyl thionophosphate (1, R = $PhCHCH_3$). Liquid, δ_H 7.40–7.20 (5H, m), 5.65–5.50 (1H, m), 4.20–4.00 (2H, m), 4.00–3.80 (2H, m), 1.62 (3H, d, *J* 6.6 Hz), 1.30 (3H, t, *J* 7.2 Hz), 1.14 (3H, t, *J* 7.2 Hz); δ_C 141.7, 141.6, 128.4, 128.0, 126.1, 77.4, 64.08, 64.02, 63.96, 23.90, 23.83, 15.83, 15.73, 15.69, 15.58; δ_P 66.8.

1-Phenylethyl thiolophosphate (2, R = $PhCHCH_3$). Liquid, δ_H 7.40–7.25 (5H, m), 4.48 (1H, dq, *J* 10.8, 7.1 Hz), 4.17–3.88 (4H, m), 1.75 (3H, dd, *J* 7.1, 1.0 Hz), 1.24 (3H, dt, *J* 7.1, 0.7 Hz), 1.23 (3H, dt, *J* 7.1, 0.7 Hz); δ_C 143.5 (d, *J* 4.9 Hz), 128.6, 127.5, 127.0, 63.8 (d, *J* 5.7 Hz), 45.8 (d, *J* 4.1 Hz), 24.6 (d, *J* 7.5 Hz), 15.9 (d, *J* 6.6 Hz); δ_P 26.4.

Cinnamyl thionophosphate (1, R = $PhCH{=}CHCH_2$). Liquid, δ_H 7.41–7.22 (5H, m), 6.68 (1H, d, *J* 15.8 Hz), 6.29 (1H, td, *J* 15.8, 6.3 Hz), 4.72 (2H, dd, *J* 10.1, 6.3 Hz), 4.22–4.07 (4H, dq, *J* 7.1, 9.6 Hz), 1.33 (6H, t, *J* 7.1 Hz); δ_C 136.1, 133.9, 128.6, 128.1, 126.6, 123.6 (d, *J* 7.6 Hz), 68.4 (d, *J* 4.7 Hz), 64.3 (d, *J* 5.5 Hz), 15.9 (d, *J* 7.5 Hz); δ_P 68.0.

Cinnamyl thiolophosphate (2, R = $PhCH{=}CHCH_2$). Liquid, δ_H 7.44–7.20 (5H, m), 6.60 (1H, d, *J* 15.7 Hz), 6.33–6.18 (1H, td, *J* 15.7, 7.4 Hz), 4.30–4.03 (4H, m), 3.65 (2H, dd, *J* 14.9, 7.4 Hz), 1.34 (6H, t, *J* 7.1 Hz); δ_C 136.2, 133.4, 128.5, 127.8, 126.3, 124.7 (d, *J* 4.7 Hz), 63.5 (d, *J* 5.8 Hz), 33.35 (d, *J* 4.2 Hz), 15.9 (d, *J* 7.2 Hz); δ_P 27.3.

1-Phenylallyl thiolophosphate 6. Liquid, δ_H 7.36–7.25 (5H, m), 6.26–6.08 (1H, m), 5.30–5.16 (2H, m), 4.99 (1H, dd, *J* 11.1, 7.8 Hz), 4.22–3.84 (4H, m), 1.25 (6H, t, *J* 7.0 Hz); δ_C 140.4 (d, *J* 5.3 Hz), 137.8 (d, *J* 6.2 Hz), 128.6, 127.8, 127.6, 126.3, 116.7, 63.4 (d, *J* 4.0 Hz), 52.8, 15.8 (d, *J* 7.5 Hz); δ_P 25.5.

1-Phenylcitronellol. Diastereomeric mixture, liquid, δ_H 7.35–7.23 (5H, m), 5.11–5.02 (1H, 2t, *J* 7.1 Hz), 4.76–4.70 (1H, 2t, *J* 4.5, 6.4 Hz), 2.05–1.85 (3H, m), 1.68–1.57 (6H, 4s), 1.52–1.30 (2H, m), 1.26–1.10 (1H, m), 0.96–0.93 (3H, 2d, *J* 6.6 Hz); δ_C 145.45, 144.95, 131.17, 131.14, 128.40, 128.39, 127.47, 127.34, 125.95, 125.72, 124.71, 124.68, 72.8, 72.3, 46.7, 46.3, 37.5, 36.8, 29.3, 29.1, 25.6, 25.4, 25.2, 20.1, 19.2, 17.6 (Calc. for $C_{16}H_{24}O$: C, 82.69; H, 10.42. Found: C, 82.50; H, 10.30%).

1-Phenylcitronellyl thionophosphate. Diastereomeric mixture, liquid, δ_H 7.38–7.26 (5H, m), 5.54–5.43 (1H, m), 5.10–5.02 (1H, m), 4.15–3.93 (2H, m), 3.85–3.65 (2H, m), 2.09–1.73 (2H, m), 1.70–1.56 (6H, 4s), 1.26 (6H, dt, *J* 7.1, 1.0 Hz), 1.50–1.00 (5H, m), 0.98–0.93 (3H, 2d, *J* 6.6 Hz); δ_C 141.21, 140.60, 131.29, 131.20, 128.37, 128.31, 128.14, 128.03, 126.92, 126.68, 124.57, 80.09, 80.03, 79.75, 79.69, 63.99, 63.93, 63.88, 45.61, 45.53, 44.93, 44.86, 37.19, 36.67, 28.84, 28.67, 25.69, 25.27, 25.16, 19.74, 19.27, 17.62, 15.83, 15.75, 15.58, 15.50; δ_P 66.6, 66.5.

1-Phenylcitronellyl thiolophosphate. Diastereomeric mixture, liquid, δ_H 7.36–7.21 (5H, m), 5.10–4.90 (1H, m), 4.38–4.30 (1H, m), 4.10–3.98 (1H, m), 3.98–3.82 (2H, m), 3.82–3.72 (1H, m), 2.10–1.70 (2H, m), 1.68–1.54 (6H, 4s), 1.45–1.14 (11H, m), 0.90 (3H, d, *J* 6.6 Hz); δ_C 143.26, 142.29, 131.38, 131.27, 128.50, 128.47, 128.44, 127.62, 127.52, 127.42, 127.33, 124.46, 124.41, 63.24, 63.18, 49.12, 49.09, 48.80, 48.77, 45.54, 45.45, 45.01, 44.93, 37.10, 36.20, 30.29, 25.62, 25.15, 19.49, 18.88, 17.61, 15.90, 15.87, 15.82, 15.79; δ_P 25.8, 25.6.

1,2-Diphenylethyl thionophosphate (1, R = $PhCH_2CHPh$). Liquid, δ_H 7.30–7.10 (10H, m), 5.62 (1H, dt, *J* 11.7, 6.4 Hz), 3.94–3.84 (2H, m), 3.82–3.74 (1H, m), 3.72–3.56 (1H, m), 3.27 (1H, dd, *J* 13.7, 7.7 Hz), 3.08 (1H, ddd, *J* 13.7, 6.2, 1.9 Hz), 1.13 (3H, dt, *J* 7.1, 0.7 Hz), 1.00 (3H, dt, *J* 7.1, 1.0 Hz); δ_C 139.82 (d, *J* 2.5 Hz), 136.5, 129.6, 128.1, 128.0, 126.7, 126.4, 81.7 (d, *J* 5.8 Hz), 63.74 (d, *J* 5.8 Hz), 63.64 (d, *J* 5.0 Hz), 44.3 (d, *J* 8.2 Hz), 15.57 (d, *J* 8.2 Hz), 15.43 (d, *J* 8.2 Hz); δ_P 66.9.

1,2-Diphenylethyl thiolophosphate (2, R = $PhCH_2CHPh$). Liquid, δ_H 7.30–7.08 (10H, m), 4.44 (1H, td, *J* 11.7, 7.8 Hz), 4.00–3.85 (2H, m), 3.77–3.63 (2H, m), 3.33–3.28 (1H, dd, *J* 13.7, 7.6 Hz), 3.25–3.19 (1H, ddd, *J* 13.7, 7.6, 1.4 Hz), 1.16 (3H, dt, *J* 7.1, 0.5 Hz), 1.13 (3H, dt, *J* 7.1, 0.5 Hz); δ_C 142.1, 138.1, 129.4, 128.4, 128.2, 127.7, 127.5, 126.6, 63.2 (d, *J* 5.7 Hz), 52.6 (d, *J* 3.3 Hz), 44.7 (d, *J* 8.2 Hz), 15.84 (d, *J* 7.4 Hz), 15.75 (d, *J* 9.9 Hz); δ_P 25.8.

1-Phenylhex-5-enyl thionophosphate [1, R = $PhCH(CH_2)_3$-$CH{=}CH_2$]. Liquid, δ_H 7.35–7.28 (5H, m), 5.80–5.70 (1H, m), 5.44–5.38 (1H, m), 5.01–4.92 (2H, m), 4.16–4.06 (1H, m),

4.06–3.98 (1H, m), 3.89–3.79 (1H, m), 3.79–3.70 (1H, m), 2.10–2.04 (2H, q, *J* 7.1 Hz), 2.05–1.95 (1H, m), 1.85–1.77 (1H, m), 1.53–1.43 (1H, m), 1.43–1.33 (1H, m), 1.27 (3H, t, *J* 7.1 Hz), 1.06 (3H, t, *J* 7.1 Hz); δ_C 140.53 (d, *J* 3.3 Hz), 138.19, 128.28, 128.03, 126.59, 114.84, 81.18 (d, *J* 5.8 Hz), 63.98, 64.00 (d, *J* 4.2 Hz), 63.95 (d, *J* 4.2 Hz), 37.10 (d, *J* 7.4 Hz), 33.21, 24.41, 15.77 (d, *J* 8.3 Hz), 15.54 (d, *J* 7.4 Hz); δ_P 67.2.

1-Phenylhex-5-enyl thiolophosphate [2, R = PhCH(CH$_2$)$_3$-CH=CH$_2$]. Liquid, δ_H 7.33–7.24 (5H, m), 5.78–5.68 (1H, m), 5.00–4.92 (2H, m), 4.27–4.20 (1H, m), 4.10–4.00 (1H, m), 3.99–3.87 and 3.86–3.76 (3H, m), 2.08–1.90 (4H, m), 1.52–1.41 (1H, m), 1.37–1.26 (1H, m), 1.21–1.17 (6H, m); δ_C 142.5, 138.0, 128.5, 127.5, 115.0, 63.3, 50.8, 37.6, 37.5, 33.1, 26.8, 15.88, 15.84, 15.80, 15.76; δ_P 26.3.

Benzyl thionophosphate (1, R = PhCH$_2$). Liquid, δ_H 7.40–7.25 (5H, m), 5.08 (2H, d, *J* 10.0 Hz), 4.15–4.02 (4H, m), 1.28 (6H, dt, *J* 7.2, 0.8 Hz); δ_C 135.8 (d, *J* 7.4 Hz), 128.3, 128.2, 127.8, 69.3 (d, *J* 4.9 Hz), 64.1 (d, *J* 5.8 Hz), 15.7 (d, *J* 7.4 Hz); δ_P 68.0.

Benzyl thiolophosphate (2, R = PhCH$_2$). Liquid, δ_H 7.38–7.25 (5H, m), 4.03 (2H, d, *J* 14.2 Hz), 4.17–4.07 (2H, m), 4.07–3.97 (2H, m), 1.28 (6H, dt, *J* 7.1, 0.8 Hz); δ_C 137.5, 128.9, 128.6, 127.6, 63.5 (d, *J* 5.8 Hz), 35.0 (d, *J* 3.3 Hz), 15.9 (d, *J* 7.4 Hz); δ_P 26.8.

***trans*-4-(*tert*-Butyl)cyclohexyl thionophosphate.** Liquid, δ_H 4.33–4.22 (1H, m), 4.11–4.02 (4H, m), 2.07 (2H, br d, *J* 9.0 Hz), 1.76 (2H, br d, *J* 12.0 Hz), 1.45–1.30 (2H, m), 1.29 (6H, t, *J* 7.0 Hz), 1.10–0.85 (3H, m), 0.86 (9H, s); δ_C 78.96, 78.90, 63.92, 63.86, 46.7, 33.61, 33.57, 32.2, 27.5, 25.4, 15.87, 15.80; δ_P 66.4.

1-Methyl-2-phenylethyl thionophosphate. Liquid, δ_H 7.30–7.20 (5H, m), 4.85–4.77 (1H, m), 4.12–3.82 (4H, m), 3.05–3.00 (1H, dd, *J* 13.7, 6.6 Hz), 2.84–2.78 (1H, dd, *J* 13.7, 6.6 Hz), 1.30 (3H, d, *J* 6.1 Hz), 1.29 (3H, dt, *J* 7.1, 0.8 Hz), 1.22 (3H, t, *J* 7.1 Hz); δ_C 137.3, 129.6, 128.3, 126.5, 77.1 (d, *J* 5.8 Hz), 63.9 (t, *J* 5.0 Hz), 43.6 (d, *J* 6.6 Hz), 20.9 (d, *J* 3.3 Hz), 15.86 (d, *J* 4.1 Hz), 15.78 (d, *J* 5.0 Hz); δ_P 66.5.

(*E*)-But-2-enyl thionophosphate. Liquid, δ_H 5.85–5.77 (1H, m), 5.65–5.58 (1H, m), 4.51–4.46 (2H, m), 4.18–4.06 (4H, m), 1.74–1.72 (3H, dd, *J* 6.4, 1.2 Hz), 1.40–1.26 (6H, m); δ_C 131.4, 125.6, 77.4, 68.6, 64.2, 17.7, 15.8; δ_P 67.8.

Methyl 3-hydroxy-3-methyl-2-phenylbutanoate 7. Liquid, δ_H 7.38–7.26 (5H, m), 3.68 (3H, s), 3.60 (1H, s), 1.34 (3H, s), 1.07 (3H, s); δ_C 174.6, 135.3, 129.5, 128.3, 127.6, 71.7, 60.4, 52.0, 29.5, 26.6 (Calc. for $C_{12}H_{16}O_3$: C, 69.19; H, 7.75. Found: C, 68.98; H, 7.81%).

(*E*)-2-Methyl-5-phenylpent-4-en-2-ol 12a and (*Z*)-2-methyl-5-phenylpent-4-en-2-ol 12b. ≈1 : 1 Mixture. Characteristic signals for the *E*-derivative: δ_H 6.46 (1H, d, *J* 15.9 Hz), 6.32–6.25 (1H, td, *J* 15.9, 7.3 Hz), 2.52 (2H, dd, *J* 7.5, 1.7 Hz). Characteristic signals for the *Z*-derivative: δ_H 6.60 (1H, d, *J* 11.7 Hz), 5.84–5.78 (1H, td, *J* 11.7, 7.5 Hz), 2.38 (2H, d, *J* 7.5 Hz). The methyl groups appear at δ_H 1.27 in one isomer and at δ_H 1.25 in the other.

Methyl α-phenyl-α-(tetrahydrofuran-2-yl)acetate 15. Liquid, δ_H 7.33–7.26 (5H, m), 4.58–4.46 (1H, m), 3.98–3.77 (2H, m), 3.70 (3H, s), 3.51 (1H, d, *J* 9.9 Hz), 1.92–1.74 (2H, m), 1.74–1.61 (1H, m), 1.51–1.34 (1H, m); δ_C 173.0, 135.9, 128.7, 128.4, 127.7, 80.6, 68.5, 57.5, 52.1, 29.5, 25.4 (Calc. for $C_{13}H_{16}O_3$: C, 70.87; H, 7.33. Found: C, 70.65; H, 7.18%).

Methyl 2,3-diphenylpropanoate 16. Liquid, δ_H 7.27–7.10 (10H, m), 3.88–3.82 (1H, dd, *J* 8.7, 6.9 Hz), 3.6 (3H, s), 3.45–3.38 (1H, dd, *J* 13.5, 8.7 Hz), 3.06–2.99 (1H, dd, *J* 13.5, 6.9 Hz); δ_C 173.8, 139.0, 138.6, 128.9, 128.6, 128.3, 127.9, 127.4, 126.4, 53.6, 52.0, 39.8 (Calc. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.80; H, 6.84%).

2-[(*E*)-3-Phenylprop-2-enyl]tetrahydrofuran 17. Liquid, δ_H 7.36–7.17 (5H, m), 6.46 (1H, d, *J* 15.6 Hz), 6.28–6.20 (1H, td, *J* 15.6, 7.1 Hz), 3.98–3.88 (2H, m), 3.78–3.72 (1H, m), 2.53–2.38 (2H, m), 2.10–1.75 (4H, m) (Calc. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.77; H, 8.45%).

2-[(*Z*)-3-Phenylprop-2-enyl]tetrahydrofuran 18. Liquid, δ_H 7.35–7.20 (5H, m), 6.53 (1H, d, *J* 11.7 Hz), 5.76–5.70 (1H, td, *J* 11.7, 7.1 Hz), 3.98–3.84 (2H, m), 3.77–3.70 (1H, m), 2.68–2.60 (1H, m), 2.56–2.49 (1H, m), 2.03–1.95 (1H, m), 1.92–1.83 (2H, m), 1.55–1.46 (1H, m) (Calc. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.80; H, 8.42%).

Methyl α-(cyclopent-2-enyl)-α-phenylacetate. Diastereomeric mixture, liquid, δ_H 7.43–7.18 (5H, m), 5.87–5.68 and 5.32–5.26 (2H, m), 3.65 (3H, s), 3.55–3.24 (2H, m), 2.45–2.10 (2H, m), 1.83–1.17 (2H, m); δ_C 174.4, 174.3, 139.5, 139.4, 133.9, 133.1, 132.8, 129.4, 129.3, 128.2, 123.0, 58.3, 57.9, 52.1, 52.0, 50.4, 50.1, 32.5, 32.1, 29.6, 28.3; ν_{max} (film) 2920, 1718, 1440, 1420, 1160 cm^{-1} (Calc. for $C_{14}H_{16}O_2$: *M*, 216.1149. Observed M^+, 216.1157. Calc. for $C_{14}H_{16}O_2$: C, 77.74; H, 7.46. Found: C, 77.62; H, 7.35%).

Methyl α-(cyclohex-2-enyl)-α-phenylacetate. Diastereomeric mixture, liquid, δ_H 7.37–7.18 (5H, m), 5.85–5.75, 5.70–5.60 and 5.20–5.10 (2H, m), 3.66 and 3.65 (3H, s), 3.32 (1H, d, *J* 11.1), 2.95–2.75 (1H, m), 2.03–1.25 and 1.10–0.95 (6H, m); δ_C 174.0, 173.9, 137.7, 137.4, 129.2, 129.0, 128.8, 128.5, 128.4, 127.9, 127.3, 57.5, 51.8, 38.5, 38.4, 27.9, 26.4, 25.3, 25.2, 21.1, 20.7; ν_{max} (film) 2920, 1720, 1442, 1425, 1150 cm^{-1} (Calc. for $C_{15}H_{18}O_2$: *M*, 230.1306. Observed M^+, 230.1300. Calc. for $C_{15}H_{18}O_2$: C, 78.22; H, 7.88. Found: C, 78.11; H, 7.73%).

Methyl α-(cyclooct-2-enyl)-α-phenylacetate. Diastereomeric mixture, low-melting solid, δ_H 7.40–7.18 (5H, m), 5.83–5.71, 5.57–5.46, 5.36–5.27 and 5.02–4.93 (2H, m), 3.65 and 3.62 (3H, s), 3.49–3.16 (2H, 2H), 2.42–1.93 (2H, m), 1.77–1.17 and 1.03–0.85 (8H, m); δ_C 174.3, 174.0, 138.0, 137.7, 131.6, 131.3, 130.4, 128.6, 128.4, 127.3, 127.2, 57.9, 57.7, 51.9, 51.8, 39.5, 38.8, 34.7, 33.0, 29.5, 26.9, 26.8, 25.6, 25.3 (Calc. for $C_{17}H_{22}O_2$: *M*, 258.1618. Observed M^+, 258.1610. Calc. for $C_{17}H_{22}O_2$: C, 79.02; H, 8.59. Found: C, 78.88; H, 8.45%).

Methyl α-(1-methylcyclohex-2-enyl)-α-phenylacetate 37. Liquid, δ_H 7.42–7.26 (5H, m), 5.70–5.56 (2H, m), 3.64 (3H, s), 3.54 (1H, s), 1.94–1.25 (6H, m), 1.09 (3H, s); δ_C 173.2, 133.4, 130.2, 130.1, 127.8, 127.7, 127.1, 127.0, 60.9, 59.9, 51.45, 51.41, 38.3, 37.9, 33.4, 33.1, 25.08, 24.87, 24.82, 24.52, 18.88, 18.66 (Calc. for $C_{16}H_{20}O_2$: C, 78.64; H, 8.26. Found: C, 78.45; H, 8.16%).

Methyl α-(3-methylcyclohex-2-enyl)-α-phenylacetate 36 and methyl α-(2-methylcyclohex-2-enyl)-α-phenylacetate 38. Diastereomeric mixture, liquid, δ_H 7.39–7.25 (m), 5.49 (br s), 5.40 (br s), 5.33 (br s), 4.87 (br s), 3.78 (d, *J* 10.0 Hz), 3.68–3.65 (4s), 3.58 (d, *J* 10.0 Hz), 3.30–3.26 (2d, *J* 11.0, 11.5 Hz), 2.83 (br s), 2.05–1.70 (m), 1.69, 1.67, 1.58, 1.53 (4s), 1.50–1.20 (m); δ_C 174.1, 137.77, 137.54, 136.38, 136.05, 128.78, 128.72, 128.49, 128.44, 128.42, 128.35, 128.32, 127.2, 123.0, 121.8, 57.68, 57.63, 51.98, 51.83, 51.76, 38.79, 38.67, 30.0, 27.7, 25.9, 23.98, 23.89, 21.5, 21.0, 18.3.

Methyl 2-phenyldodec-4-enoate 41 and methyl 3-heptyl-2-phenylpent-4-enoate 42. Diastereomeric mixture for **42**; liquid,

δ_H 7.37–7.23 (m), 5.67–5.58 (m), 5.49–5.39 (m), 5.37–5.21 (m), 5.14–5.07 (m), 4.85–4.74 (m), 3.66–3.59 (4s), 3.46–3.41 (2d, *J* 11.0 Hz), 2.84–2.68 (m), 2.50–2.36 (m), 1.95–1.90 (q, *J* 6.8 Hz), 1.40–1.0 (m), 0.89–0.82 (2t, *J* 7.0 Hz).

3-(Cyclohex-2-enyl)-1-phenylpropene 43a and 43b. Liquid, δ_H 7.36–7.19 (m), 6.49–6.46 (d, *J* 12.0 Hz), 6.42–6.38 (d, *J* 15.8 Hz), 6.26–6.19 (td, *J* 16.0, 6.8 Hz), 5.74–5.67 (m), 5.64–5.59 (dt, *J* 8.3, 1.7 Hz), 2.43–2.28 (m), 2.28–2.18 (m), 2.02–1.98 (m), 1.84–1.75 (m), 1.75–1.65 (m), 1.60–1.45 (m), 1.38–1.22 (m); δ_C 137.77, 137.73, 131.34, 131.27, 131.09, 129.74, 129.25, 128.77, 128.46, 128.08, 127.52, 127.42, 126.83, 126.43, 125.94, 39.82, 35.91, 35.49, 34.95, 28.91, 28.88, 25.27, 25.25, 21.42, 21.39 (Calc. for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.60; H, 9.02%).

3-(Cyclohex-2-enyl)-3-phenylpropene 44. More polar, liquid, δ_H 7.32–7.18 (5H, m), 6.03–5.94 (1H, m), 5.65–5.60 (1H, m), 5.33–5.30 (1H, dd, *J* 10.2, 2.2 Hz), 5.05–5.00 (2H, m), 3.05 (1H, t, *J* 9.3 Hz), 2.51–2.44 (1H, m), 1.99–1.94 (2H, m), 1.87–1.78 (1H, m), 1.76–1.71 (1H, m), 1.56–1.47 (1H, m), 1.37–1.25 (1H, m); δ_C 143.4, 140.9, 129.7, 128.4, 128.1, 127.9, 126.1, 115.1, 56.4, 39.7, 27.5, 25.3, 21.5 (Calc. for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.68; H, 9.05%).

3-(Cyclohex-2-enyl)-3-phenylpropene 44. Less polar, liquid, δ_H 7.32–7.17 (5H, m), 6.06–5.97 (1H, m), 5.80–5.72 (2H, m), 5.10–5.04 (2H, m), 3.04 (1H, t, *J* 9.3 Hz), 2.47–2.41 (1H, m), 1.99–1.95 (2H, m), 1.71–1.65 (1H, m), 1.51–1.39 (2H, m), 1.17–1.07 (1H, m); δ_C 143.7, 140.6, 129.5, 128.4, 128.1, 127.8, 126.1, 115.7, 56.2, 39.6, 27.7, 25.4, 21.6 (Calc. for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.65; H, 9.02%).

1-(Cyclohex-2-enyl)-1-phenylethane 45. Diastereomeric mixture, liquid, δ_H 7.31–7.16 (10H, m), 5.82–5.79 (1H, m), 5.76–5.71 (1H, m), 5.65–5.60 (1H, m), 5.39–5.35 (1H, m), 2.62–2.53 (2H, m), 2.35–2.18 (2H, m), 2.00–2.18 (4H, m), 1.85–1.40 (8H, m), 1.28 (3H, d, *J* 7.0 Hz), 1.24 (3H, d, *J* 7.0 Hz); δ_C 130.73, 129.62, 128.14, 127.76, 127.52, 125.82, 45.03, 44.68, 41.84, 27.60, 26.51, 25.40, 25.27, 21.96, 21.37, 18.81, 18.54 (Calc. for $C_{14}H_{18}$: C, 90.25; H, 9.75. Found: C, 90.10; H, 9.58%).

Methyl α-(cycloocta-2,6-dienyl)-α-phenylacetate 46a (diastereomeric mixture) and methyl α-(cycloocta-2,5-dienyl)-α-phenylacetate 46b (diastereomeric mixture). Liquid, δ_H 7.38–7.25 (m), 5.67–5.50 (m), 5.47–5.37 (m), 5.07–5.02 (dd, *J* 11.5, 6.8 Hz), 3.66 (s), 3.65 (s), 3.57–3.45 (m), 3.43–3.36 (2d, *J* 10.5 Hz), 2.60–2.48 (m), 2.44–2.26 (m), 2.23–2.13 (m), 2.03–1.92 (m); δ_C 173.96, 173.84, 137.50, 137.36, 130.89, 130.32, 129.58, 129.19, 128.91, 128.86, 128.72, 128.64, 128.47, 128.44, 127.56, 127.49, 127.42, 127.34, 58.38, 58.06, 51.97, 51.94, 42.17, 42.09, 33.07, 31.89, 27.91, 27.78, 27.46 (Calc. for $C_{17}H_{20}O_2$: C, 79.64; H, 7.87. Found: C, 79.48; H, 7.69%).

3-Benzylcycloocta-1,5-diene 47a. Liquid, δ_H 7.30–7.17 (5H, m), 5.59–5.51 (3H, m), 5.43–5.38 (1H, dd, *J* 11.7, 6.3 Hz), 3.05–2.96 (1H, m), 2.75–2.70 (1H, dd, *J* 13.4, 6.8 Hz), 2.60–2.55 (1H, dd, *J* 13.4, 7.8 Hz), 2.53–2.44 (1H, m), 2.39–2.25 (3H, m), 2.24–2.13 (2H, m); δ_C 140.7, 133.6, 129.1, 128.8, 128.2, 128.0, 127.7, 125.9, 43.1, 41.0, 33.7, 28.2, 27.6 (Calc. for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.67; H, 9.04%).

6-Benzylcycloocta-1,4-diene 47b. Liquid, δ_H 7.28–7.15 (5H, m), 5.71–5.58 (2H, 2m, 2- and 4-H), 5.43–5.35 (1H, m, 1-H), 5.18–5.12 (1H, m, 5-H), 3.14–3.04 (1H, m, 6-H), 2.86–2.56 (5H, m, 3-H_2, C8-H, PhCH_2), 1.97–1.90 (1H, m, 8-H), 1.55–1.47 (1H, m, 7-H), 1.18–1.10 (1H, m, 7-H); δ_C 141.2, 133.8, 129.8, 129.0, 128.6, 128.4, 128.1, 125.7, 42.3, 37.1, 29.9, 29.8, 24.5 (Calc. for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.69; H, 9.06%).

1-Phenylhexa-1,5-diene. Mixture of *E* and *Z* isomers, liquid, δ_H 7.34–7.18 (m), 6.44–6.37 (unsym t), 6.22 (t, *J* 6.4 Hz), 6.20 (t, *J* 6.8 Hz), 5.92–5.78 (m), 5.67 (t, *J* 7.1 Hz), 5.64 (t, *J* 7.1 Hz), 5.08–4.96 (m), 2.47–2.40 (dq, *J* 7.3, 1.7 Hz), 2.33–2.25 (m), 2.65–2.17 (m); δ_C 138.05, 137.99, 137.71, 137.59, 132.02, 130.16, 130.05, 129.15, 128.72, 128.44, 128.10, 126.85, 126.49, 125.93, 114.95, 114.89, 33.92, 33.52, 32.39, 27.89 (Calc. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.87; H, 8.75%).

Phenyl-(2-phenylcyclopropyl)methanol 50. More polar isomer, solid, mp 48–50 °C; δ_H 7.53–7.09 (10H, m), 4.36 (1H, d, *J* 7.5 Hz), 3.25 (1H, br s), 2.10–2.03 (1H, m), 1.63–1.57 (1H, m), 1.27–1.22 (1H, m), 1.14–1.09 (1H, m); δ_C 143.4, 142.0, 128.2, 128.1, 127.3, 125.90, 125.85, 125.43, 76.3, 29.8, 20.8, 13.6 (Calc. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.49; H, 7.08%).

Phenyl-(2-phenylcyclopropyl)methanol 50. Less polar isomer, solid, mp 42–44 °C; δ_H 7.72–7.24 (10H, m), 4.24 (1H, d, *J* 7.8 Hz), 3.55 (1H, br s), 2.17–2.14 (1H, m), 1.67–1.57 (1H, m), 1.15–1.03 (2H, 2m); δ_C 143.4, 142.3, 128.2, 128.1, 127.2, 125.9, 125.7, 125.3, 76.7, 30.3, 21.6, 13.3 (Found: C, 85.53; H, 7.10%).

***trans*-1,4-Diphenylbut-3-enyl thionophosphate 51.** Liquid, δ_H 7.40–7.19 (10H, m), 6.43 (1H, d, *J* 15.8 Hz), 6.16–6.08 (1H, td, *J* 15.8, 7.3 Hz), 5.57–5.51 (1H, m), 4.13–3.72 (1H each, 4m), 2.92–2.84 (1H, m), 2.78–2.71 (1H, m), 1.21 (3H, t, *J* 7.1 Hz), 1.06 (3H, t, *J* 7.1 Hz); δ_C 140.0, 137.2, 133.2, 128.43, 128.35, 128.19, 127.2, 126.6, 126.1, 124.8, 80.6 (d, *J* 5.8 Hz), 64.1 (d, *J* 3.3 Hz), 64.0 (d, *J* 3.3 Hz), 41.4 (d, *J* 7.4 Hz), 15.7 (d, *J* 8.2 Hz), 15.6 (d, *J* 7.4); δ_P 67.0.

Bis-[(*E*)-1,4-diphenylbut-3-enyl] ether 53. Liquid, δ_H 7.39–7.20 (20H, m), 6.47 (2H, d, *J* 15.9 Hz), 6.10–6.03 (2H, td, *J* 15.9, 7.1 Hz), 5.87–5.83 (2H, dd, *J* 7.8, 6.3 Hz), 2.92–2.84 (2H, m), 2.78–2.70 (2H, m); δ_C 137.4, 136.7, 134.2, 129.0, 128.8, 128.5, 127.6, 126.5, 126.2, 123.1, 85.0, 38.1 (Calc. for $C_{32}H_{30}O$: C, 89.25; H, 7.03. Found: C, 89.13; H, 6.91%).

The adduct of TEMPO and the radical 14. Solid, mp 73–75 °C; δ_H 7.43 (2H, d, *J* 7.1 Hz), 7.35–7.28 (3H, m), 5.21 (1H, s), 3.65 (3H, s), 1.60–1.20 (6H, m), 1.23 (3H, s), 1.14 (3H, s), 1.07 (3H, s), 0.72 (3H, s); δ_C 172.4, 138.1, 128.2, 127.8, 126.8, 88.5, 59.8, 51.7, 40.12, 29.99, 33.4, 32.7, 20.1, 17.0.

Acknowledgements

We thank the Council of Scientific & Industrial Research, Government of India for financial support, and Professors H. Ila and H. Junjappa for encouragement.

References

1 R. S. Givens and L. W. Kueper, III, *Chem. Rev.*, 1993, **93**, 55 and references cited therein. Also see: W. W. Epstein and M. Garrossian, *J. Chem. Soc.*, *Chem. Commun.*, 1987, 532.
2 Heating of a toluene solution in a pressure tube at 140 °C (bath temperature) for 4–5 h gave only the starting material without any noticeable decomposition.
3 C. D. Poulter and D. S. Mautz, *J. Am. Chem. Soc.*, 1991, **113**, 4895; A. W. Herriott, *J. Org. Chem.*, 1975, **40**, 801.
4 Y. Ito, S. Fujiim, T. Konoeke and T. Saegusa, *Synth. Commun.*, 1976, **6**, 429; C. T. Ng, X. Wang and T.-Y. Luh, *J. Org. Chem.*, 1988, **53**, 2536.
5 Selected crystal data for dimethyl 2,3-diphenylfumarate **4**: CCDC reference number 137237. See http://www.rsc.org/suppdata/p1/b0/b003501g/ for crystallographic data in CIF or other electronic format. $M = 296.32$, monoclinic, $a = 5.845(5)$, $b = 17.134(4)$, $c = 7.935(7)$ Å, $\beta = 107.54(6)°$, $Z = 2$, $D_c = 1.299$ g cm^{-3}, $\mu = 0.91$ cm^{-1}. 1533 Data collected at room temperature on a Rigaku AFC6S diffractometer. 1395 Reflections were used to solve and refine the structure to $R = 0.076$ and $R_w = 0.051$. C7–C7* = 1.402(14) Å, C8–O1 = 1.190(7) Å, C8–C7–C7* = 111.0(9)°, O1–C8–C7 = 125.9(7)°, O1–C8–C7–C7* = −35.9(14)°, C6–C1–C7–C7* = 46.7(11)°, O2–C8–C7–C7* = 149.8(10)°, O1–C8–O2–C9 = 0.8(11)°, C7–C8–O2–

C9 = 175.2(6)°. For the preparation of the *Z*-isomer of **4** (*i.e.* the diphenylmaleate) and the data on it, see: H. Oda, M. Morishita, K. Fugami, H. Sano and M. Kosugi, *Chem. Lett.*, 1996, 811.
6 R. C. Larock and K. Takagi, *J. Org. Chem.*, 1984, **49**, 2701; Y. Yamamoto, K. Maruyama and K. Matsumoto, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 548.
7 S. Ghosh, S. N. Pardo and R. G. Salomon, *J. Org. Chem.*, 1982, **47**, 4692; M. N. Fox and C.-C. Chen, *J. Chem. Soc.*, *Chem. Commun.*, 1985, 23.
8 For an asymmetric C–H insertion of a carbenoid into tetrahydrofuran, see: H. M. L. Davies and T. Hansen, *J. Am. Chem. Soc.*, 1997, **119**, 9075.
9 D. H. R. Barton, D. Crich and W. B. Motherwell, *Tetrahedron*, 1985, **41**, 3901; D. Crich, *Aldrichim. Acta*, 1987, **20**, 35; D. H. R. Barton, D. Briden, I. F. Picot and S. Z. Zard, *Tetrahedron*, 1987, **43**, 2733. For an alternative mechanism, see: V. K. Yadav, A. Yadav, P. Pande and K. K. Kapoor, *Indian J. Chem.*, *Sect. B*, 1994, **33**, 1129.
10 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353; A. Merz and G. Mark, *Angew. Chem.*, *Int. Ed. Engl.*, 1973, **12**, 845; L. A. Yanovskaya, V. A. Dombrovsky, O. S. Chizhov, B. M. Zolotarev, O. A. Subbotin and V. F. Kucherov, *Tetrahedron*, 1972, **28**, 1565; D. N. Boykin, A. B. Turner and R. E. Lutz, *Tetrahedron Lett.*, 1967, 817; Y. D. Vankar, G. Kumaravel and C. T. Rao, *Synth. Commun.*, 1989, **19**, 2181.
11 The substrate **59** was prepared from Simmons–Smith cyclopropanation of 1,3-diphenylpropene which, in turn, was made available from the Wittig reaction of benzaldehyde and the triphenylphosphorane prepared from 2-phenylethyl bromide. However, see: R. Hollis, L. Hughes, V. W. Bowry and K. U. Ingold, *J. Org. Chem.*, 1992, **57**, 4284.
12 1,2-Diphenylethanol was prepared from the reaction of PhCHO with $PhCH_2MgBr$ in Et_2O following standard reaction conditions in >90% yield.
13 1-Phenylcitronellol was prepared from the reaction of (±)-citronellal with phenylmagnesium bromide in Et_2O following standard reaction conditions in >90% yield.