  Bull. Chem. Soc. Jpn., 57, 2127—2131 (1984) 

# The Reaction of Butadienylphosphonates with a Oxosulfonium Ylide, Phosphonium Ylides, and Ketone Enolates

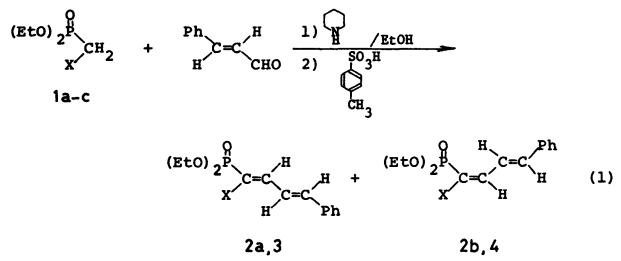
Toru MINAMI,* Takenobu YAMANOUCHI, Shigehumi TOKUMASU, and Ichiro HIRAO
*Department of Industrial Chemistry, Kyushu Institute of Technology, Sensuicho, Tobata, Kitakyushu 804*
(Received December 23, 1983)

The condensation of diethyl (ethoxycarbonylmethyl)phosphonate (**1a**) with cinnamaldehyde in the presence of piperidine gave a 1:1 mixture of diethyl (1*E*,3*E*)- (**2a**) and (1*Z*,3*E*)-(1-ethoxycarbonyl-4-phenyl-1,3-butadienyl)phosphonates (**2b**) in 82% yield, while a similar reaction using diethyl [cyanomethyl- (**1b**) and methylsulfonylmethyl]phosphonates (**1c**) exclusively gave diethyl (1*E*,3*E*)-[1-cyano- (**3**) and 1-methyl-sulfonyl-4-phenyl-1,3-butadienyl]phosphonates (**4**) in 78% and 93% yields, respectively. The reaction of the butadienylphosphonates **2**—**4** with dimethyloxosulfonium methylide (**5**) gave mixtures of (*E*)- and (*Z*)-(1-substituted 2-styrylcyclopropyl)phosphonates **7**—**9** in good yields. Similar treatment of the butadienylphosphonate **2** with phosphonium ylides **16a**—**c** led to (3-substituted 1-ethoxycarbonyl-2-styrylcyclopropyl)phosphonates **17a**—**c** in moderate yields. Reduction and oxidation of **7** were studied. The reaction of the phosphonates, **2** and **4**, with ketone enolates and ketones resulted in the formation of unexpected olefins **22**—**24** and dienes **20a, b**. The reaction mechanism is discussed.

In recent years, vinylphosphonates containing electronegative substituents on the $\alpha$-carbon atom as well as vinylphosphonium salts have been extensively used as versatile reagents for the synthesis of a variety of heterocyclic and carbocyclic compounds, functionalized unsaturated systems such as olefins, dienes and their analogues, and benzene derivatives.[1] As a continuation of the studies on vinylphosphonates, we have previously reported the synthesis of diethyl 4-phenyl-1,3-butadienylphosphonates bearing electronegative substituents and their reactions with oxosulfonium and phosphonium ylides.[2] Since we incorrectly assigned the structures of the reaction products in an earlier communication, we wish to revise the structures and to report further details of the results in this paper. Some studies on the reaction of the phosphonates with nucleophiles such as ketone enolates are also described.

## Results and Discussion

*The Reaction with Dimethyloxosulfonium Methylide and Phosphonium Ylides.* As described in previous communication,[2] the condensation of diethyl (ethoxycarbonylmethyl)phosphonate (**1a**) with cinnamaldehyde in the presence of piperidine gave a 1:1 mixture of diethyl (1*E*,3*E*)-(**2a**) and (1*Z*,3*E*)-(1-ethoxycarbonyl-4-phenyl-1,3-butadienyl)phosphonates (**2b**) in 82% yield, while the reaction using diethyl [cyanomethyl-(**1b**) and methylsulfonylmethyl]phosphonates (**1c**) afforded exclusively diethyl (1*E*,3*E*)-[1-cyano-(**3**) and 1-methylsulfonyl-4-phenyl-1,3-butadienyl]phosphonates (**4**) in 78% and 93% yields, respectively.



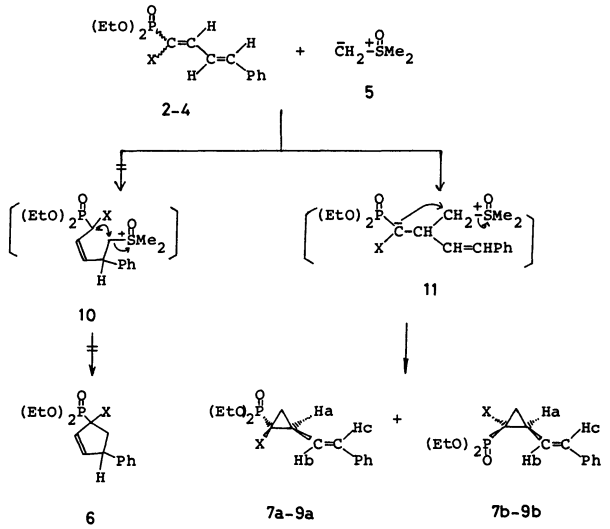

**1a, 2a, 2b**: X = $CO_2Et$
**1b, 3**: X = CN
**1c, 4**: X = $SO_2Me$

TABLE 1. THE REACTION OF DIETHYL (1-SUBSTITUTED 4-PHENYL-1,3-BUTADIENYL) PHOSPHONATES **2-4** WITH DIMETHYLOXOSULFONIUM METHYLIDE (**5**)

| Butadienyl-phosphonates | Products (Product ratio) | Yields/% |
|---|---|---|
| **2**[a] | **7a**+**7b** (1:1) | 91 |
| **3** | **8a**+**8b** (9:1) | 87 |
| **4** | **9a**+**9b** (1:4) | 41 |

a) A 1:1 mixture of **2a** and **2b**.

The reaction of these butadienylphosphonates with dimethyloxosulfonium methylide (**5**) gave mixtures of two isomeric products **7**—**9**, regardless of the stereochemistry of the starting butadienylphosphonates (Table 1). However, this reaction can be said to proceed nearly stereospecifically, since the reaction using single starting butadienylphosphonates **3** and **4** preferentially yielded **8a** and **9b**.



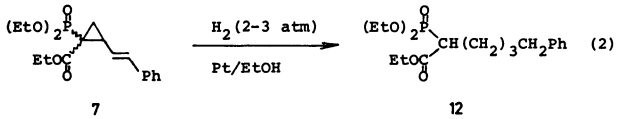

**2, 7a, 7b**: X = $CO_2Et$
**3, 8a, 8b**: X = CN
**4, 9a, 9b**: X = $SO_2Me$

Scheme 1.

Although we previously assigned the structures of the products to be diethyl (1-substituted 4-phenyl-2-cyclopentenyl)phosphonates **6**[2], we wish to revise them

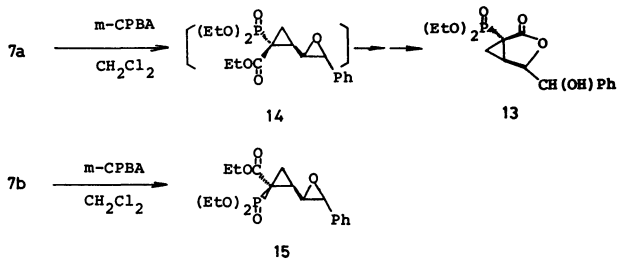
here into structures **7—9**, since further study of the products indicated that our previous structural assignment was incorrect. The products are composed of mixtures of two stereoisomers, (*E*)- and (*Z*)-(1-substituted 2-styrylcyclopropyl)phosphonates **7—9**, whose structural assignment rests upon the following spectroscopic and chemical evidence.

The $^1$H-NMR spectrum ($CDCl_3$) of **7a** shows methine Ha (m, 1H) at $\delta$ 2.15—3.0 and styryl Hb (dd, $J$=8.61, 15.93 Hz, 1H) and Hc (d, $J$=15.93 Hz, 1H) at $\delta$ 5.70—6.20 and at $\delta$ 6.68, while that of **7b** exhibits the corresponding peaks at $\delta$ 2.15—2.70 (m, Ha), 6.10—6.65 (dd, $J$=6.78, 15.93 Hz, Hb), and 6.71 (d, $J$=15.93 Hz, Hc). On the other hand, the $^{13}$C-NMR spectra of **7a** and **7b** reveal a styryl $\beta$-carbon at $\delta$ 124.7 ppm (s) and at $\delta$ 126.7 ppm (d, $^3J_{p\text{-}c}$=4.3 Hz), respectively. Similarly, the styryl $\beta$-carbon of **8a** and **9a** resonates at $\delta$ 123.3 ppm (s) and at $\delta$ 123.1 ppm (s), whereas the corresponding carbon of **8b** and **9b** is found at $\delta$ 124.0 ppm (d, $^3J_{p\text{-}c}$=3.4 Hz) and at $\delta$ 124.3 ppm (d, $^3J_{p\text{-}c}$=3.4 Hz). Comparing the styryl $\beta$ $^{13}$C chemical shifts in **7a—9a** and **7b—9b**, it is observed that those in the latter are at 0.7 to 2.0 ppm lower fields from those in the former. It is also found that the compounds **7b—9b** have a coupling between phosphorus and the styryl $\beta$-carbon of 3.4 to 4.3 Hz, while the compounds **7a—9a** show none of the corresponding coupling. On the basis of these results, it can be said that the stereochemistry of **7a** and **7b** is correlated to that of the compounds **8a** and **9a**, and of their isomers **8b** and **9b**, respectively. Since treatment of the butadienylphosphonates **3** and **4** with the ylide **5** predominantly led to **8a** and **9b** as mentioned above, it would be reasonable to assign their structures as diethyl (*E*)-(1-cyano-2-styrylcyclopropyl)- and (*E*)-(1-methylsulfonyl-2-styrylcyclopropyl)-phosphonates rather than as the corresponding (*Z*)-isomers, due to more sterically favorable structures. Accordingly, the stereochemistry of **7a** and **7b** was assigned as (*E*)- and (*Z*)-form, respectively. Furthermore, that the products **7a** and **7b** are stereoisomeric with each other and contain the cyclopropyl moiety in the molecules was evident from the fact that catalytic hydrogenation of the mixture in ethanol over platinum catalyst at low hydrogen pressure gave only diethyl (1-ethoxycarbonyl-5-phenylpentyl)phosphate (**12**) in good yield. For it is well known that the cyclopropyl ring easily undergoes the ring opening in a catalytic hydrogenation.[3]




7 12 (2)

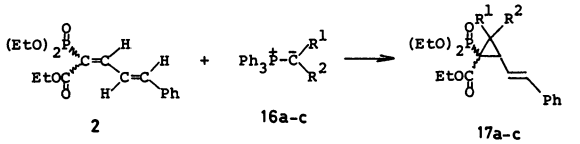
In addition, the structures of **7a** and **7b** were clearly established by their oxidations. Oxidation of **7a** with *m*-chloroperbenzoic acid converted into a lactone **13** in 91% yield, which would be formed *via* a cyclopropyloxirane **14**, while similar treatment of **7b** led to a cyclopropyloxirane **15** in 81% yield (Scheme 2). This result is obviously consistent with the above assigned structures **7a** and **7b**, since only the *E*-isomer **7a** in which the ethoxycarbonyl and the styryl groups are located *cis* to each other can lead to **13**.




Scheme 2.

As shown in Scheme 1, these results imply that the ylide carbanion dose not attack on the $\delta$-carbon of the butadienylphosphonates **2—4**, but on the $\beta$-carbon to give the intermediate **11**, followed by the elimination of dimethyl sulfoxide to lead to the cyclopropylphosphonates **7—9**.

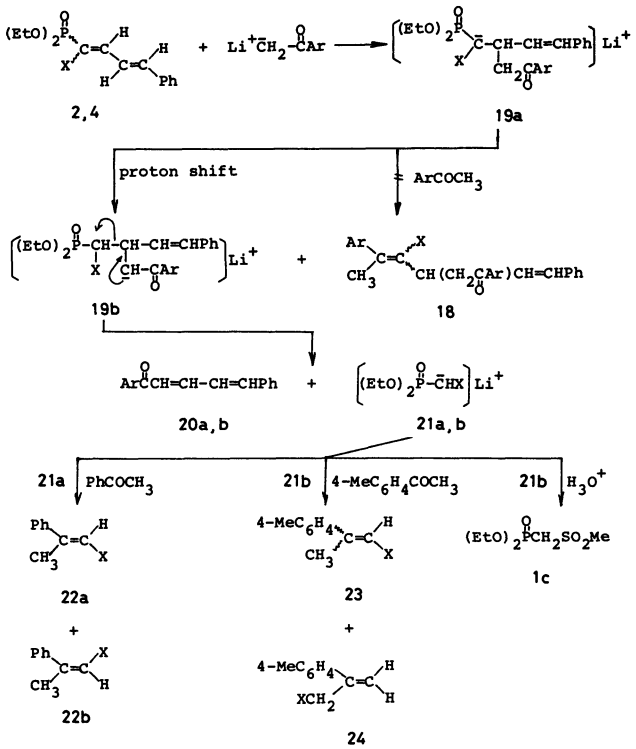
The reaction of **2** with various phosphonium ylides **16a—c** similarly produced diethyl (3-substituted 1-ethoxycarbonyl-2-styrylcyclopropyl)phosphonates **17a—c** in rather low yields (45%—58%) along with comparable yields of triphenylphosphine.




**16a, 17a**: $R^1 = R^2$ = Me
**16b, 17b**: $R^1$ = *p*-MeOC$_6$H$_4$, $R^2$ = H
**16c, 17c**: $R^1$ = *n*-C$_5$H$_{11}$, $R^2$ = H

+ $Ph_3P$ (3)

*The Reaction with Ketone Enolates.* Darling and co-workers[4] reported that diethyl butadienylphosphonate containing no substituent undergoes the Michael addition of ketone enolate anions at the $\delta$-position to give keto phosphonate carbanions (1,4-Michael adducts), but no Wittig-Horner reaction product was observed. On the other hand, Martin and Garrison[5] have recently reported that the reaction of [1-(methylthio)butadienyl]phosphonate with nucleophiles such as the enolate anion of formylcyclohexane and lithium dialkylcuprate(I)s similarly gives 1,4-Michael adducts, which subsequently undergo the Wittig-Horner reaction with ketones to yield dienes. Accordingly, it is of interest to examine the reactivity of the (4-phenylbutadienyl)phosphonates **2—4** bearing electronegative substituents toward ketone enolate anions, whether the phosphonates undergo 1,4-addition as previously reported or 1,2-addition as in the above-mentioned reaction with ylides. The reaction of **4** with equimolar amounts of the enolate anion of 4-methylacetophenone in the presence of excess 4-methylacetophenone unexpectedly gave 1-(4-methylphenyl)-5-phenyl-2,4-pentadien-1-one (**20b**), 1-methylsulfonyl-2-(4-methylphenyl)-1-propene (**23**), and 2-(4-methylphenyl)-3-methylsulfonyl-1-propene (**24**) in 41, 22, and 36% yields, respectively. Similar treatment of **2** with the enolate anion of acetophenone in the presence of acetophenone likewise led to 1,5-diphenyl-2,4-pentadien-1-one (**20a**), (*E*)- and (*Z*)-1-ethoxycarbonyl-2-phenyl-1-propene (**22a**) and (**22b**) in 51, 37, and 21% yields, respectively. On the other hand, the reaction of **4** with equimolar amounts of the enolate anion of 4-methylacetophenone resulted in the for-




Scheme 3.

mation of **20b** (37%) and diethyl (methylsulfonylmethyl)phosphonate (**1c**) (26%). On the basis of these results, the reaction of the butadienylphosphonates **2**, **4** with ketone enolates in the presence of excess ketones can be accounted for by a sequence of a nucleophilic attack of the enolate anions on the $\beta$-carbon of the butadienylphosphonates, the proton shift from methylene adjacent to the aroyl group to phosphoryl-stabilized carbanions in **19a** and decomposition of the resultant **19b** to butadienes **20** and the phosphonate carbanions **21**, which react with excess ketones to afford the olefins **22**—**24** (Scheme 3).

Thus, in contrast to the results reported by Darling *et. al.*[4] and Martin *et. al.*[5] the above results show that butadienylphosphonates containing the phenyl group at the $\delta$ position undergo a Michael addition of nucleophiles to the $\beta$-carbon but not to the $\delta$-carbon, primarily due to a large steric hindrance.

Studies on the effects of $\delta$ substituents on reactivities of butadienylphosphonates and their synthetic applications are in progress.

## Experimental

*General.* $^1$H-NMR and $^{13}$C-NMR spectra were taken in $CDCl_3$ solution on a JEOL JNM-FX-60 operating at 60 and 15.04 MHz with $Me_4Si$ as an internal standard. IR spectra were recorded with a Shimadzu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected. Distillations of products were carried out with a Kugelrohr apparatus, and bath temperatures are reported.

*General Procedure for the Preparation of Diethyl (1-Substituted 4-phenyl-1,3-butadienyl)phosphonates* **2**—**4**. A solution of a phosphonate **1** (0.05 mol) and cinnamaldehyde (6.61 g, 0.05 mol) in 100 ml of dry ethanol containing catalytic amounts of piperidine was refluxed for *ca.* 30 h until disappearance of the carbonyl absorption at 1675 cm$^{-1}$ in the IR spectrum. After removal of solvent ethanol, the residue was dissolved in 100 ml of dry benzene containing catalytic amounts of *p*-toluenesulfonic acid and the solution was refluxed for 3 h. After the usual work-up, bulb-to-bulb distillation of the residue gave a butadienylphosphonate.

*Diethyl (1E,3E)-(2a) and (1Z,3E)-(1-Ethoxycarbonyl-4-phenyl-1,3-butadienyl)phosphonate (2b).* The reaction was carried out as described above by using diethyl (ethoxycarbonylmethyl)phosphonate (**1a**) (11.21 g, 0.05 mol) to give 13.87 g (82%) yield of a 1:1 mixture of **2a** and **2b** [bp 178 °C/1 mmHg (1 mmHg≈133.322 Pa)]. Pure samples of each were obtained by preparative TLC. The product **2a** had the following properties: IR (neat): 1710, 1610, 1580, 1560, 1235, 1020 cm$^{-1}$; $^1$H NMR $\delta$=1.34 (6H, t, $J$=6.96 Hz, $POCH_2\underline{CH_3}$), 1.36 (3H, t, $J$=6.96 Hz, $OCH_2\underline{CH_3}$), 3.80—4.52 (6H, m, $PO\underline{CH_2}CH_3$ and $O\underline{CH_2}CH_3$), 6.80—8.10 (8H, m, olefinic and phenyl H); $^{13}$C NMR $\delta$=14.0, 16.1 (d, $^3J_{p\text{-}c}$=6.9 Hz), 60.8, 62.2 (d, $^2J_{p\text{-}c}$=6.0 Hz), 119.9 (d, $^1J_{p\text{-}c}$=186.5 Hz), 124.1 (d, $^3J_{p\text{-}c}$=19.8 Hz), 127.7, 128.6, 129.7, 135.3, 145.9, 154.6 (d, $^2J_{p\text{-}c}$=7.7 Hz), 164.4 (d, $^2J_{p\text{-}c}$=13.8 Hz); MS $m/z$ 338 ($M^+$). The product **2b** had the following properties: IR (neat): 1710, 1610, 1580, 1560, 1235, 1020 cm$^{-1}$; $^1$H NMR $\delta$=1.34 (9H, t, $J$=6.96 Hz, $POCH_2\underline{CH_3}$ and $OCH_2\underline{CH_3}$), 3.80—4.50 (6H, m, $PO\underline{CH_2}CH_3$, and $O\underline{CH_2}CH_3$), 6.80—8.50 (8H, m, olefinic and phenyl H); $^{13}$C NMR $\delta$=14.2, 16.3 (d, $^3J_{p\text{-}c}$=6.9 Hz), 61.1, 62.2 (d, $^2J_{p\text{-}c}$=5.2 Hz), 119.4 (d, $^1J_{p\text{-}c}$=185.7 Hz), 124.9 (d, $^3J_{p\text{-}c}$=6.0 Hz), 128.1, 128.7, 129.9, 135.6, 146.7, 156.6 (d, $^2J_{p\text{-}c}$=7.7 Hz), 165.8 (d, $^2J_{p\text{-}c}$=13.8 Hz); MS $m/z$ 338 ($M^+$).

Found (for a mixture of **2a** and **2b**): C, 60.05; H, 6.90. Calcd for $C_{17}H_{23}O_5P$: C, 60.35; H, 6.85%.

*Diethyl (1E,3E)-(1-Cyano-4-phenyl-1,3-butadienyl)phosphonate (3).* The reaction was carried out as described above by using diethyl cyanomethylphosphonate (**1b**) (8.86 g, 0.05 mol) to afford 11.36 g (78%) yield of **3** as a single product. Its structural assignment was made on the basis of the close similarity of its $^1$H- and $^{13}$C-NMR spectra to those of **2a**, as shown below. The product **3** had the following properties: bp 168 °C/2 mmHg; IR (neat): 2160, 1605, 1205 cm$^{-1}$; $^1$H-NMR $\delta$=1.39 (6H, dt, $J$=0.55 Hz, 6.96 Hz, $OCH_2\underline{CH_3}$), 3.80—4.45 (4H, m, $O\underline{CH_2}CH_3$), 7.0—8.05 (8H, m, olefinic and phenyl H); $^{13}$C NMR $\delta$=16.2 (d, $^3J_{p\text{-}c}$=6.0 Hz), 63.4 (d, $^2J_{p\text{-}c}$=6.0 Hz), 101.1 (d, $^1J_{p\text{-}c}$=202.0 Hz), 114.5 (d, $^2J_{p\text{-}c}$=12.0 Hz), 123.5 (d, $^3J_{p\text{-}c}$=18.1 Hz), 128.3, 129.0, 130.9, 134.5, 147.5, 159.4 (d, $^2J_{p\text{-}c}$=6.9 Hz); MS $m/z$ 291 ($M^+$).

Found: C, 61.81; H, 6.20; N, 4.92. Calcd for $C_{15}H_{18}O_3NP$: C, 61.85; H, 6.23; N, 4.81%.

*Diethyl (1E,3E)-(1-Methylsulfonyl-4-phenyl-1,3-butadienyl)-phosphonate (4).* The reaction was carried out as described above by using diethyl (methylsulfonylmethyl)phosphonate (**1c**) (11.51 g, 0.05 mol) to produce 10.70 g (93%) yield of **4** as a sole product, whose structural assignment was similarly made by comparison of its $^1$H- and $^{13}$C-NMR spectra with those of **2b**. The compound **4** had the following properties: Mp 113—114 °C; IR (KBr) 1610, 1575, 1550, 1300, 1240, 1120 cm$^{-1}$; $^1$H NMR $\delta$=1.31 (6H, t, $J$=7.05 Hz, $OCH_2\underline{CH_3}$), 3.13 (3H, s, $SO_2\underline{Me}$), 3.80—4.50 (4H, quint., $O\underline{CH_2}CH_3$), 6.75—8.40 (8H, m, olefinic and phenyl H); $^{13}$C NMR $\delta$=16.0 (d, $^3J_{p\text{-}c}$=6.9 Hz), 42.9, 62.8 (d, $^2J_{p\text{-}c}$=5.2 Hz), 122.3 (d, $^3J_{p\text{-}c}$=6.0 Hz), 128.0, 128.7, 128.8 (d, $^1J_{p\text{-}c}$=179.7 Hz), 130.4, 134.7, 149.1, 154.5 (d, $^2J_{p\text{-}c}$=6.0 Hz) MS Found: $m/z$ 344.0821. Calcd for $C_{15}H_{21}O_5SP$: 344.0846 ($M^+$).

*General Procedure for the Synthesis of (1-Substituted 2-styrylcyclopropyl)phosphonates* **7—9**. To a solution of dimethyloxosulfonium methylide (**5**) (5 mmol) in 15 ml of dry DMSO was added a butadienylphosphonate (5 mmol) in 5 ml of dry DMSO. The reaction mixture was then stirred at 50 °C for 5 h. After conventional work-up, distillation of the residue produced a mixture of two stereoisomers. Pure samples of each were obtained by preparative TLC.

*Diethyl (E)-(1-ethoxycarbonyl-2-styrylcyclopropyl)phosphonate (**7a**)*: Yield 0.81 g (2.30 mmol, 46%); bp 190 °C/1 mmHg; IR (neat) 1705, 1580, 1240 cm$^{-1}$; $^1$H NMR $\delta$=0.90—2.10 (11H, m, $CH_3$ and cyclopropyl methylene H), 2.15—3.0 (1H, m, Ha), 3.60—4.50 (6H, m, $\underline{CH_2}CH_3$), 5.70—6.20 (1H, dd, $J$=8.61 Hz, 15.93 Hz, Hb), 6.68 (1H, d, $J$=15.93 Hz, Hc), 7.0—7.60 (5H, phenyl H); $^{13}$C NMR $\delta$=14.3, 16.5 (d, $^3J_{p\text{-}c}$=6.0 Hz), 19.4, 27.9 (d, $^1J_{p\text{-}c}$=187.4 Hz), 30.3, 61.7, 62.7 (d, $^2J_{p\text{-}c}$=5.2 Hz), 124.7, 126.1, 127.6, 128.6, 134.0, 136.8, 167.5; MS $m/z$ 352 ($M^+$).

*Diethyl (Z)-(1-ethoxycarbonyl-2-styrylcyclopropyl)phosphonate (**7b**)*: Yield 0.79 g (2.24 mmol, 45%); bp 190 °C/1 mmHg; IR (neat): 1705, 1580, 1240 cm$^{-1}$; $^1$H NMR $\delta$=0.90—1.50 (9H, m, Me), 1.50—2.15 (2H, m, cyclopropyl methylene H), 2.15—2.70 (1H, m, Ha), 3.75—4.50 (6H, m, $\underline{CH_2}CH_3$),6.10—6.65 (1H,dd, $J$=6.78 Hz, 15.93 Hz, Hb), 6.71 (1H, d, $J$=15.93 Hz, Hc), 6.90—7.50 (5H, m, phenyl H); $^{13}$C NMR $\delta$=14.1, 16.4 (d, $^3J_{p\text{-}c}$=6.0 Hz), 21.2, 27.9 (d, $^1J_{p\text{-}c}$=187.4 Hz), 33.7 (d, $^2J_{p\text{-}c}$= 2.6 Hz), 61.7, 62.4 (d, $^2J_{p\text{-}c}$=6.0 Hz), 126.1, 126.7 (d, $^3J_{p\text{-}c}$= 4.3 Hz), 127.4, 128.5, 133.5, 136.9, 169.6; MS $m/z$ 352 ($M^+$).

Found (for a mixture of **7a** and **7b**): C, 60.96; H, 7.39%. Calcd for $C_{15}H_{25}O_5P$: C, 61.36; H, 7.15%.

*Diethyl (E)-(1-Cyano-2-styrylcyclopropyl)phosphonate (**8a**)*: Yield 1.19 g (3.9 mmol, 78.3%); bp 175 °C/2 mmHg; IR (neat): 2215, 1250 cm$^{-1}$; $^1$H NMR $\delta$=1.38 (6H, t, $J$=7.05 Hz, $CH_2\underline{CH_3}$), 1.55—2.20 (2H, m, cyclopropyl methylene H), 2.20—3.0 (1H, m, Ha), 3.90—4.50 (4H, m, $\underline{CH_2}CH_3$), 5.65—6.15 (1H, dd, $J$=8.61 Hz, 15.75 Hz, Hb), 6.76 (1H, d, $J$= 15.75 Hz, Hc), 7.31 (5H, s, phenyl H); $^{13}$C NMR $\delta$=12.4 (d, $^1J_{p\text{-}c}$=196.0 Hz); 16.2 (d, $^3J_{p\text{-}c}$=6.0 Hz), 20.1, 28.5, 63.7 (d, $^2J_{p\text{-}c}$=6.9 Hz), 116.8 (d, $^2J_{p\text{-}c}$=3.4 Hz), 123.3, 126.1, 127.9, 128.4, 135.2, 135.7; MS $m/z$ 305 ($M^+$).

*Diethyl (Z)-(1-Cyano-2-styrylcyclopropyl)phosphonate (**8b**)*: Yield 0.133 g (0.44 mmol, 8.7%); bp 175 °C/2 mmHg; IR (neat): 2215, 1250 cm$^{-1}$; $^1$H NMR $\delta$=1.0—1.56 (6H, m, $CH_2\underline{CH_3}$), 1.56—2.20 (2H, m, cyclopropyl methylene H), 2.25—3.0 (1H, m, Ha), 3.70—4.55 (4H, m, $\underline{CH_2}CH_3$), 6.0—6.50 (1H, dd, $J$=8.70 Hz, 15.94 Hz, Hb), 6.78 (1H, d, $J$= 15.94 Hz, Hc), 7.30 (5H, br.s, phenyl H); $^{13}$C NMR $\delta$=12.3 (d, $^1J_{p\text{-}c}$=197.7 Hz), 16.3 (d, $^3J_{p\text{-}c}$=6.0 Hz), 21.2, 32.3, 63.6 (d, $^2J_{p\text{-}c}$=6.0 Hz), 119.0 (d, $^2J_{p\text{-}c}$=4.3 Hz), 124.0 (d, $^3J_{p\text{-}c}$=3.4 Hz), 126.3, 128.3, 128.7, 135.1, 136.3; MS $m/z$ 305 ($M^+$).

Found (for a mixture of **8a** and **8b**): C, 62.55; H, 6.68; N, 4.54%. Calcd for $C_{16}H_{20}O_3NP$: C, 62.94; H, 6.60; N, 4.59%.

*Diethyl (Z)-(1-Methylsulfonyl-2-styrylcyclopropyl)phosphonate (**9a**)*: Yield 0.146 g (0.41 mmol, 8.2%); Oil; IR (neat): 1310, 1230, 1130 cm$^{-1}$; $^1$H NMR $\delta$=1.38 (6H, t, $J$=7.14 Hz, $CH_2\underline{CH_3}$), 1.55—2.40 (2H, m, cyclopropyl methylene H), 2.40—3.20 (1H, m, Ha), 3.08 (3H, s, $SO_2\underline{Me}$), 3.90—4.60 (4H, m, $\underline{CH_2}$-$CH_3$), 5.95—6.70 (1H, dd, $J$=8.79 Hz, 15.93 Hz, Hb), 6.81 (1H, d, $J$=15.93 Hz, Hc), 7.31 (5H, s, phenyl H); $^{13}$C NMR $\delta$=16.4 (d, $^3J_{p\text{-}c}$=6.0 Hz), 17.2, 30.0, 42.4, 42.5 (d, $^1J_{p\text{-}c}$= 176.6 Hz), 63.5 (d, $^2J_{p\text{-}c}$=6.0 Hz), 64.2 (d, $^2J_{p\text{-}c}$=6.9 Hz), 123.1, 126.3, 128.1, 128.7, 136.0, 136.3; MS Found: $m/z$ 358.1005. Calcd for $C_{16}H_{23}O_5SP$: 358.1004 ($M^+$).

*Diethyl (E)-(1-Methylsulfonyl-2-styrylcyclopropyl)phosphonate (**9b**)*: Yield 0.582 g (1.62 mmol, 32.8%); mp 77 °C; IR (KBr) 1300, 1230, 1130 cm$^{-1}$; $^1$H NMR $\delta$=1.0—1.60 (6H, m, $CH_2\underline{CH_3}$), 1.60—2.30 (2H, m, cyclopropyl methylene H), 2.60—3.30 (1H, m, Ha), 3.15 (3H, s, $SO_2\underline{Me}$), 6.0—6.50 (1H, dd, $J$= 8.42 Hz, 15.75 Hz, Hb), 6.75 (1H, d, $J$=15.75 Hz, Hc), 7.30 (5H, s, phenyl H); $^{13}$C NMR $\delta$=16.3 (d, $^3J_{p\text{-}c}$=6.0 Hz), 19.2, 28.8 (d, $^2J_{p\text{-}c}$=2.5 Hz), 41.3, 42.3 (d, $^1J_{p\text{-}c}$=183.2 Hz), 63.3 (d, $^2J_{p\text{-}c}$=6.9 Hz), 63.7 (d, $^2J_{p\text{-}c}$=6.1 Hz), 124.3 (d, $^3J_{p\text{-}c}$=3.4 Hz), 126.1, 127.7, 128.6, 134.6, 136.5; MS Found: $m/z$ 358.0985. Calcd for $C_{16}H_{23}O_5SP$: 358.1004 ($M^+$).

*Diethyl (1-Ethoxycarbonyl-3,3-dimethyl-2-styrylcyclopropyl)-phosphonate (**17a**)*. To a solution of isopropylidenetriphenylphosphorane (**16a**) (5 mmol), *in situ* generated from isopropyltriphenylphosphonium bromide (1.97 g, 5 mmol) and butyllithium (5.5 mmol), in 15 ml of THF was added **2** dissolved in 10 ml of THF at room temperature. The solution was then refluxed for 6 h. After conventional work-up, the residue was chromatographed on silica gel using benzene and chloroform as eluent. The first fraction gave 0.80 g (61%) yield of triphenylphosphine. Distillation of the oily product obtained from the second fraction gave **17a** (1.11 g, 58%), which is composed of two stereoisomers. The separation of the two isomers was not attempted. The compound **17a** had the following properties: bp 170 °C/1 mmHg; IR (neat): 1720, 1600, 1260 cm$^{-1}$, $^1$H NMR $\delta$=1.0—1.60 (15H, m, Me), 2.39—2.96 (1H, m, CH-), 3.85—4.55 (6H, m, $OCH_2$), 6.25—6.75 (1H, dd, $J$=8.42 Hz, 15.80 Hz, olefinic H), 6.75—7.0 (1H, 2xd, olefinic H), 7.20—7.55 (5H, m, phenyl H); MS Found: $m/z$ 380.1773. Calcd for $C_{20}H_{29}O_5P$: 380.1771 ($M^+$).

*Diethyl [1-Ethoxycarbonyl-3-(4-methoxyphenyl)-2-styrylcyclopropyl]phosphonate (**17b**)*. The reaction was carried out as described above using **2** (0.66 g, 2 mmol) and 4-methoxybenzylidenetriphenylphosphorane (**16b**) (2 mmol). After the usual work-up, the residue was similarly chromatographed on silica gel to give 0.26 g (50%) of triphenylphosphine and 0.41 g (45%) of **17b**: Oil; IR (neat): 1720, 1260 cm$^{-1}$; $^1$H NMR $\delta$=1.27 (9H, t, $J$=7.1 Hz, $CH_2\underline{CH_3}$), 1.1—2.45 (2H, m, CH-), 3.71 (3H, s, $OCH_3$), 3.75—4.40 (6H, m, $\underline{CH_2}CH_3$), 5.75—6.25 (1H, dd, olefinic H), 6.55—6.90 (1H, 2xd, olefinic H), 7.0—7.55 (9H, m, aromatic H); MS Found: $m/z$ 458.1904. Calcd for $C_{25}H_{31}O_6P$: 458.1858 ($M^+$).

*Diethyl (1-Ethoxycarbonyl-3-pentyl-2-styrylcyclopropyl)phosphonate (**17c**)*. The reaction was carried out as described above using **2** (0.66 g, 2 mmol) and *n*-hexylidenetriphenylphosphorane (**16c**). After the usual work-up, the residue was similarly chromatographed on silica gel to give 0.43 g (51%) of **17c**: Oil; IR (neat): 1710, 1610, 1250 cm$^{-1}$; $^1$H NMR $\delta$= 0.85—2.20 (22H, m, $CH_3$, $CH_2$, CH-), 3.85—4.45 (6H, m, $OCH_2$), 6.05—6.40 (1H, m, olefinic H), 6.50—6.85 (1H, m, olefinic H), 7.27 (5H, s, phenyl H); MS Found: $m/z$ 422.2269. Calcd for $C_{23}H_{35}O_5P$: 422.2222 ($M^+$).

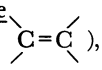
*Hydrogenation of* **7**. The hydrogenation of **7** (1:1 mixture of **7a** and **7b**) (0.35 g, 1 mmol) was accomplished in 10 h in ethanol over Pt ($PtO_2$, 20 mg) to afford **12** (0.28 g, 79%) as a colorless oil: IR (neat): 1720, 1260 cm$^{-1}$; $^1$H NMR $\delta$= 1.13—2.25 (15H, m, $CH_3$ and $CH_2$), 2.61 (2H, t, $J$=8.06 Hz, $CH_2\underline{CH_2}Ph$), 2.80—3.25 (1H, m, CH-), 3.85—4.40 (6H, quint. $OCH_2$), 7.19 (5H, s, phenyl H); MS Found: $m/z$ 356.1717. Calcd for $C_{18}H_{29}O_5P$; 356.1751.

*Oxidation of* **7a**. A solution of a mixture of **7a** (0.16 g, 0.45 mmol) and *m*-chloroperbenzoic acid (70%, 0.19 g, 1.67 equiv) in 5 ml of $CH_2Cl_2$ was refluxed for 10 h. After the usual work-up, the residue was chromatographed on preparative TLC with ether as eluent to give 0.14 g (91%) of *1-diethoxyphosphinyl-4-(α-hydroxybenzyl)-3-oxabicyclo[3.1.0]-hexan-2-one* (**13**): Oil; IR (neat): 3300, 1770, 1260 cm$^{-1}$; $^1$H NMR $\delta$=1.35 (6H, t, $J$=6.96 Hz, $CH_3$), 1.02—2.18 (2H, m, cyclopropyl $CH_2$), 2.30—2.85 (1H, cyclopropyl CH-), 3.40—3.75 (1H, br., OH, $D_2O$ exchangeable), 3.90—4.60 (5H, m, $OCH_2$ and lactone CH-), 4.85—5.10 (1H, br., -$\underline{CH}$ (OH)Ph), 7.37 (5H, s, phenyl H); $^{13}$C NMR $\delta$=16.2, 16.4 (d, $^3J_{p\text{-}c}$= 6.9 Hz), 23.3 (d, $^1J_{p\text{-}c}$=200.3 Hz), 24.7, 63.2 (d, $^2J_{p\text{-}c}$=6.0 Hz), 63.6 (d, $^2J_{p\text{-}c}$=5.2 Hz), 73.5, 82.5, (d, $^3J_{p\text{-}c}$=2.6 Hz), 126.3, 128.0, 128.6, 138.7, 171.6 (d, $^2J_{p\text{-}c}$=10.3 Hz); MS Found: $m/z$ 341.1175. Calcd for $C_{16}H_{22}O_6P$: 341.1154 ($M^+$+1).

*Oxidation of 7b.* A solution of **7b** (0.20 g, 0.568 mmol) and *m*-chloroperbenzoic acid (70%, 0.21 g, 1.50 equiv.) was treated under the same condition as **7a.** After a similar work-up, the residue was chromatographed on preparative TLC with ether as eluent to give 0.170 g (81%) of *(E)-2-[(Z)-1-ethoxycarbonyl-1-diethoxyphosphinylcyclopropyl]-3-phenyloxirane (15)*: Oil; IR (neat): 1720, 1260, 1020 $cm^{-1}$; $^1H$ NMR $\delta$=0.80—2.10 (12H, m, $CH_3$, cyclopropyl $CH_2$ and CH-), 3.20—3.50 (1H, m, -CH-CHPh), 3.50—4.50 (7H, m, $OCH_2$ and -CH-CHPh), 7.28 (5H, s, phenyl H); $^{13}C$ NMR $\delta$=13.9, 16.1 (d, $^3J_{p-c}$=5.2 Hz), 19.3, 24.6 (d, $^1J_{p-c}$=194.3 Hz), 30.4 (d, $^2J_{p-c}$=2.6 Hz), 58.6, 60.0 (d, $^3J_{p-c}$=3.4 Hz), 61.7, 62.4 (d, $^2J_{p-c}$=6.0 Hz), 125.6, 128.1, 136.5, 169.0 (d, $^2J_{p-c}$=7.7 Hz); MS Found: *m/z* 368.1359. Calcd for $C_{18}H_{27}O_7P$: 368.1362 ($M^+$).

*Reaction of 4 with 4-Methylacetophenone in the Presence of Lithium Diisopropylamide (LDA). A. The Reaction Using Excess Amounts of 4-Methylacetophenone*: To a cooled solution of LDA (1.1 mmol) in THF (15 ml) at −75 °C was added 4-methylacetophenone (0.30 g, 2.24 mmol). The solution was stirred for 1 h at this temperature. Then the butadienylphosphonate **4** (0.33 g, 0.96 mmol) was added to the solution and the mixture was stirred at −75 °C for 0.5 h and at refluxing temperature for 10 h. After a conventional work-up, the residue was chromatographed on preparative TLC with $CHCl_3$ as eluent to give **20b** (97 mg, 41%), **23** (44 mg, 22%) and **24** (73 mg, 36%), respectively.

*1-(4-Methylphenyl)-5-phenyl-2,4-pentadien-1-one (20b)*: Mp 84—85 °C; IR (KBr): 1640 $cm^{-1}$; $^1H$ NMR $\delta$=2.36 (3H, s, Me), 6.60—7.60 (11H, m, aromatic and olefinic H), 7.88 (2H, d, *J*=8.10 Hz, the other aromatic H); MS Found: *m/z* 248.1216. Calcd for $C_{18}H_{16}O$: 248.1201 ($M^+$).

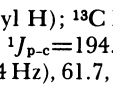
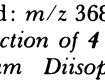
*1-Methylsulfonyl-2-(4-methylphenyl)-1-propene (23)*: Oil; IR (neat): 1300, 1120 $cm^{-1}$; $^1H$ NMR $\delta$=2.38 (3H, s, Me), 2.56 (3H, d, *J*=1.17 Hz,  ), 3.04 (3H, s, $SO_2Me$), 6.38—6.60 (1H, q, *J*=1.17 Hz, olefinic H), 6.80—7.50 (4H, m, aromatic H); MS Found: *m/z* 210.0746. Calcd for $C_{11}H_{14}O_2S$: 210.0715 ($M^+$). This compound was consistent with an authentic sample independently prepared from **1c** and 4-methylacetophenone.

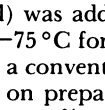
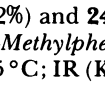
*2-(4-Methylphenyl)-3-methylsulfonyl-1-propene (24)*: Mp 56—57 °C; IR (KBr): 1300, 1120 $cm^{-1}$; $^1H$ NMR $\delta$=2.35 (3H, s, Me), 2.71 (3H, s, $SO_2Me$), 4.17 (2H, s, $CH_2SO_2Me$), 5.50 (1H, s, olefinic H), 5.72 (1H, s, olefinic H), 6.90—7.50 (4H, m, phenyl H); MS Found: *m/z* 210.0738. Calcd for $C_{11}H_{14}O_2S$: 210.0715 ($M^+$). This compound was consistent with an authentic sample prepared from **1c** and 4-methylacetophenone.

*B. The Reaction Using an Equimolar Amount of 4-Methylacetophenone.* The reaction was similarly carried out at −75 °C for 1 h and at room temperature for 10 h using the procedure described above with **4** (0.34 g, 0.99 mmol), 4-methylacetophenone (0.15 g, 1.12 mmol) and LDA (1.1 mmol) in dry THF (20 ml). After the usual work-up, similar treatment of the residue gave **20b** (90 mg, 37%) and **1c** (60 mg, 26%).

*Reaction of 2 with Acetophenone in the Presence of LDA.* The reaction was carried out as described above using **2** (0.34 g, 1 mmol), acetophenone (0.24 g, 2 mmol) and LDA (1 mmol). After similar treatment, **20a, 22a,** and **22b** were obtained in 0.12 g (51%), 0.07 g (37%), and 0.04 g (21%) yields, respectively.

*1,5-Diphenyl-2,4-pentadien-1-one (20a)*: Oil; IR (neat): 1650 $cm^{-1}$; $^1H$ NMR $\delta$=6.70—8.10 (14H, m, aromatic and olefinic H); MS Found: *m/z* 234.1035. Calcd for $C_{17}H_{14}O$: 234.1044 ($M^+$).

*(E)-1-Ethoxycarbonyl-2-phenyl-1-propene (22a)*: Oil; IR (neat): 1720 $cm^{-1}$; $^1H$ NMR $\delta$=1.07 (3H, t, *J*=7.14 Hz, $CH_2CH_3$), 2.17 (3H, d, *J*=1.47 Hz,  ), 3.99 (2H, q, *J*=7.14 Hz, $OCH_2CH_3$), 5.90 (1H, q, *J*=1.47 Hz,  ), 6.90—7.50 (5H, m, phenyl H); MS Found: *m/z* 190.1013. Calcd for $C_{12}H_{14}O_2$: 190.0994 ($M^+$). This compound was consistent with an authentic sample prepared from **1a** and acetophenone.

*(Z)-1-Ethoxycarbonyl-2-phenyl-1-propene (22b)*: Oil; IR (neat): 1710 $cm^{-1}$; $^1H$ NMR $\delta$=1.30 (3H, t, *J*=7.18 Hz, $CH_2CH_3$), 2.57 (3H, d, *J*=1.17 Hz,  ), 4.42 (2H, q, *J*=7.18 Hz, $OCH_2CH_3$), 6.13 (1H, q, *J*=1.17 Hz,  ), 7.10—7.60 (5H, m, phenyl H); MS *m/z* 190 ($M^+$). This compound was consistent with an authentic sample prepared from **1a** and acetophenone.

We are grateful for support of this work by a Grant-in-Aid for Scientific Research (No 58550548) from the Ministry of Education, Science and Culture.

## References

1) a) T. Minami, H. Suganuma, and T. Agawa, *Chem. Lett.*, **1978**, 285; b) W. A. Kleschick and C. H. Heathcock, *J. Org. Chem.*, **43**, 1256 (1978); c) M. A. Semmelhack, J. C. Tomesch, M. Czarny, and S. Boettger, *ibid.*, **43**, 1259 (1978); d) J. Ide, R. Endo and S. Muramatsu, *Chem. Lett.*, **1978**, 401; e) M. Mikolajczyk, S. Grzejszczak, and K. Korbacz, *Tetrahedron Lett.*, **22**, 3097 (1981); f) B. Venugopalan, A. B. Hamlet, and T. Durst, *ibid.*, **22**, 191 (1981); g) T. Minami, K. Nishimura, I. Hirao, H. Suganuma, and T. Agawa, *J. Org. Chem.*, **47**, 2360 (1982) and references cited therein.

2) T. Minami, T. Yamanouchi, S. Takenaka, and I. Hirao, *Tetrahedron Lett.*, **24**, 767 (1983).

3) a) J. Newham, *Chem. Rev.*, **63**, 123 (1963); b) C. Gröger and H. Musso, *Angew. Chem.,Int. Ed. Engl.*, **15**, 373 (1976); c) M. Charton, "The Chemistry of Alkenes", ed. by J. Zabicky, Interscience, New York (1970), Vol. 2, p 588.

4) S. D. Darling, F. N. Muralidharan, and V. B. Muralidharan, *Tetrahedron Lett.*, **1979**, 2757, 2761.

5) S. F. Martin and P. J. Garrison, *Synthesis*, **1982**, 394.