Synthesis and Acid-Catalyzed Ring Opening of 1-Alkenyl Cyclopropyl Ketones

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1-Alkenyl cyclopropyl ketones, when activated by cation-stabilizing substituents at the ring carbon or at the terminal carbon of the enone moiety, undergo polyphosphoric acid-catalyzed ring enlargement producing cyclopentanone or cyclohexenone derivatives. Similar acid-catalyzed ring opening of 1-alkenyl 2-phenoxycyclopropyl ketones offers a convenient and effective synthesis of 4-oxo-5-alkenals and their dioxolane-protected derivatives.

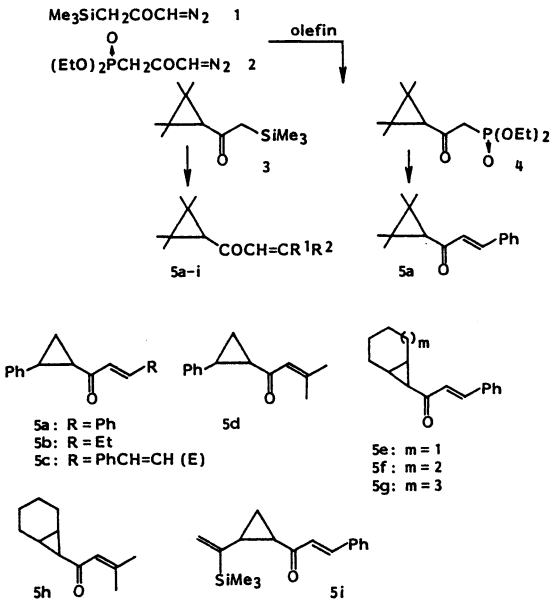
Our previous article described the simple synthesis of 1-alkenyl cyclopropyl ketones by a tandem cyclopropanation of 1-diazo-3-silyl-2-propanone and Peterson olefination sequence.[1] As a synthetic utilization and application of 1-alkenyl cyclopropyl ketones, homo-Nazarov type cyclization is expected since there are numerous examples known for ring opening reactions of cyclopropyl ketones[2] in the presence of acid catalysts such as protonic acids,[3] silylated acids,[4] Lewis acids,[5] and a pyridinium chloride.[6] Mostly the resulting carbonium ion intermediates are either quenched by nucleophiles present in the reaction mixture, e.g. conjugate bases arising from the acid catalysts or reaction solvents, or undergo β-elimination forming olefins.

To the best of our knowledge, no example of homo-Nazarov type ring enlargement of 1-alkenyl cyclopropyl ketones is known. Only a few examples for the related reactions have been reported previously. Aroyl cyclopropanes undergo acid-catalyzed ring enlargements to lead to tetralone derivatives,[7] or the cation intermediates involved in the acid-catalyzed ring opening were intramolecularly trapped by a separated aryl or olefin moiety.[8]

We wish to report here that 1-alkenyl cyclopropyl ketones undergo novel ring enlargements leading to cyclopentanones or cyclohexenones by action with polyphosphoric acid. Though the presence of an oxygen substituent on the cyclopropane ring of 1-alkenyl cyclopropyl ketones produces no ring-enlarged products, their ring openings are highly accelerated to furnish 4-oxo-5-alkenals or their dioxolane-protected derivatives.

Results and Discussion

1-Alkenyl cyclopropyl ketones **5a—h** used as substrates in the present work were previously prepared by a sequence of reactions including cyclopropanation of olefins with 1-diazo-3-trimethylsilyl-2-propanone (**1**), lithiation of the resulting cyclopropyl silylmethyl ketones **3**, and Peterson olefination using a variety of carbonyl compounds R^1COR^2 (Scheme 1).[1] Due to their susceptibility to moisture, silylmethyl ketones **3** were employed to the subsequent olefination without isolation and purification. As an additional example, the reaction of diazo ketone **1** with 2-(trimethylsilyl)-1,3-butadiene in the presence of a catalytic amount (1 mol%) of copper(II) acetylacetonate gave a mixture of two regioisomeric cyclopropanes. The mixture was then lithiated with lithium diisopropylamide (LDA) and allowed to react with benzaldehyde to afford **5i** and its regioisomer in 22% yield (2:1 by ^{1}H NMR, based on **1**).



Scheme 1.

It was expected that 1-diazo-3-[(diethoxyphosphoryl)-methyl]-2-propanone (**2**) could serve as a new synthetic equivalent of **1** and would lead to less moisture-sensitive cyclopropyl ketones such as **4**.[9] However cyclopropanations using diazo ketone **2** resulted in the formation of complex products. Only styrene furnished the corresponding cyclopropyl ketone **4** in a fair yield (44%).

Stable ketone **4** was converted into 1-alkenyl cyclopropyl ketone **5a** in 85% yield by the reaction with benzaldehyde in the presence of triethylamine and lithium bromide.[10]

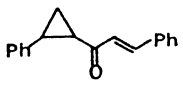
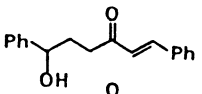
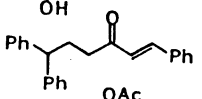
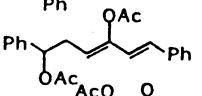
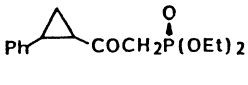
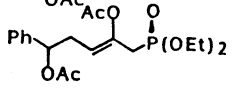
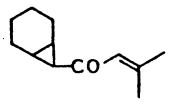
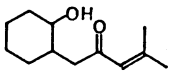
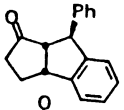
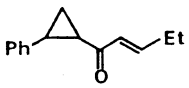
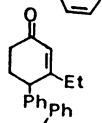
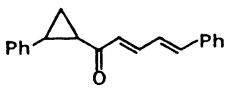
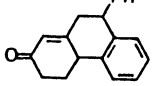
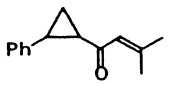
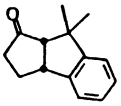
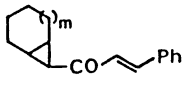
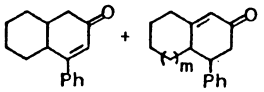
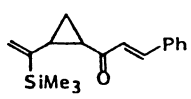
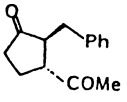
With an expectation of acid-catalysis for the ring opening, the 1-alkenyl cyclopropyl ketone **5a** was treated with a variety of Lewis or protonic acids. In many cases **5a** was either recovered intact ($Zn(OTf)_2$ in CH_2Cl_2, rt, 48 h; $Zn(OTf)_2$ in MeCN, rt, 48 h; $AlMe_3$ in CH_2Cl_2, rt, 19 h; LiOTf in CH_2Cl_2, rt, 9 d; $BF_3 \cdot OEt_2$ in CH_2Cl_2, rt, 7 h; PPSE[11] in $MeNO_2$, rt, 30 min) or decomposed into complex mixture ($TiCl_4$ in $MeNO_2$, rt, 10 min; $SnCl_4$ in CH_2Cl_2, rt, 22 h; PPSE in $MeNO_2$, reflux, 2 d; CF_3SO_3H in CH_2Cl_2, rt, 1 h).

Treatment of **5a** with trifluoromethanesulfonic acid in trifluoroacetic acid (TFA) at room temperature gave the expected ring-opened product **6** (Table 1, Entry 1). In this reaction water served as a nucleophile (Nu) to trap the resulting carbonium ion **A** (Scheme 2). Use of benzene as a solvent caused electrophilic substitution of **A** on the benzene to provide **7** (Entry 2). Boron trifluoride etherate also works as an effective catalyst (E^+) in a polar solvent, nitromethane which accelerates the ring opening of **5a**. Thus by action of boron trifluoride etherate and acetic anhydride, **5a** or **4** was readily converted into diacetate **8** or **9**, respectively (Entries 3 and 4). Polyphosphoric acid (PPA) is also able to open **5h** to give hydroxy ketone **10** (Entry 5).

Both diacetates **8** and **9** were obtained as single isomers. *Z*-Geometry of **8** with respect to the newly formed enol acetate was confirmed on the basis of the NOE difference ^1H NMR spectrum in which notable signal enhancement was observed between β-H of the enol acetate and the two styryl protons. Equally *Z*-selective formation of **8** was achieved regardless of the cis-trans ratio of the starting cyclopropyl ketones **5a**.

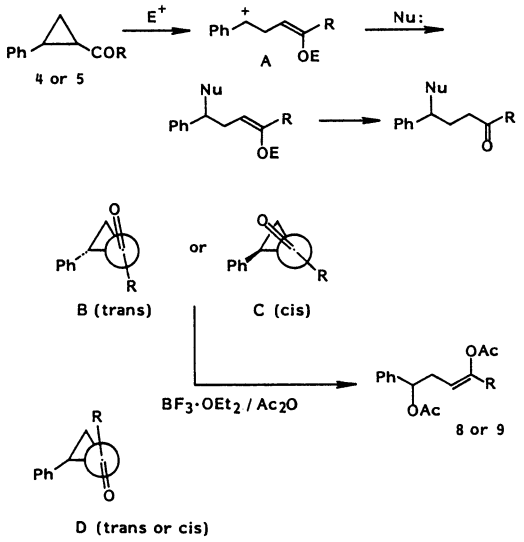
The above *Z*-selectivity seems to be a kinetical result on the basis of the following discussion: In the acid-

Table 1. Acid-Catalyzed Ring Opening of Cyclopropyl Ketones **4** and **5**

Entry	Ketone		Acid	Solvent	Condition	Product (yield/%)[a]	
1		**5a**	CF_3SO_3H	CF_3COOH	rt, 3h		**6** (66)
2	**5a**		CF_3SO_3H	Benzene	rt, 1.5 h		**7** (84)
3	**5a**		$BF_3 \cdot OEt_2/Ac_2O$	$MeNO_2$	rt, 10 min		**8** (59)
4		**4**	$BF_3 \cdot OEt_2/Ac_2O$	$MeNO_2$	rt, 18 h		**9** (78)
5		**5h**	PPA	Benzene	Reflux, 2.5 h		**10** (78)
6	**5a**		PPA	Benzene	Reflux, 40 h		**11** (71)
7		**5b**	PPA	Benzene	Reflux, 30 h		**12** (63)
8		**5c**	PPA	Benzene	Reflux, 10 d		**13** (43)
9		**5d**	PPA	Benzene	Reflux, 47 h		**14** (89)
							
10	**5e**: m=1		PPA	Benzene	Reflux, 55 h	**15** (57)	**16**: m=1 (18)
11	**5f**: m=2		PPA	Benzene	Reflux, 40 h		**17**: m=2 (15)
12	**5g**: m=3		PPA	Benzene	Reflux, 65 h		**18**: m=3 (26)
13		**5i**	PPA	Benzene	rt, 24 h		**19** (38)

a) Yield of isolated products.

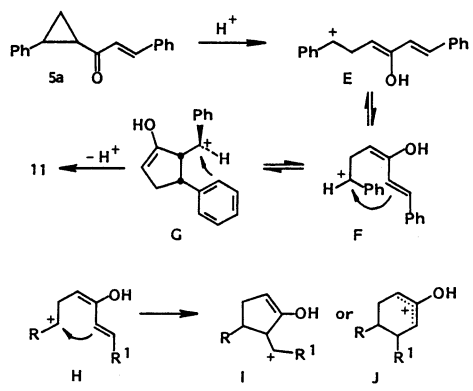
catalyzed ring opening of cyclopropyl ketones, the σ-bond to be cleaved must interact effectively with the carbonyl π-orbital.[12] So a concerted ring opening would occur in a stereospecific fashion if the bond to be cleaved is nearly perpendicular to the plane of the carbonyl. As the most stable conformations for *trans*-**5a** and for *cis*-**5a** are expected to bear the bulkier substituent R far from the unsubstituted methylene carbon (**B** for *trans*-**5a** and **C** for *cis*-**5a**),[13] their concerted ring opening would lead to *Z*-isomer **8**. This is the result actually observed. Conformation **D** may be less stable due to some serious steric hindrance between R and one of the ring methylene hydrogens.[14]



Scheme 2.

On treatment of cyclopropyl ketone **5a** with PPA under reflux in benzene in a two phase reaction, cyclopent[*a*]inden-1-one (**11**) was obtained in 71% yield as a single isomer (Table 1, Entry 6). The 3a,8a-cis-8,8a-trans stereochemistry was confirmed on the basis of the coupling constants ($J_{3a\text{-}8a}$=7.5 and $J_{8\text{-}8a}$=0.8 Hz).

Scheme 3 illustrates a possible mechanism for the stereoselective ring enlargement of 1-alkenyl cyclopropyl ketone **5a** leading to **11**. As discussed above (in Scheme 2), the acid-catalyzed ring opening of **5a** exclusively forms (*Z*)-enol cation intermediate **E** which can not undergo cyclization. Under the reaction conditions this enol **E** would equilibrate with (*E*)-enol cation **F** through a keto-enol tautomerization, presumably via a hydroxylated intermediate. Though olefin cyclization of **F** could lead to both cis benzyl cation intermediate **G** and its trans isomer, only **G** can undergo further cyclization. As a result, *cis*-selective cyclization into **G** takes place under equilibrating conditions. Intramolecular electrophilic substitution on the benzene ring as a substituent occurs again stereoselectively to give the isolated product **11**. As the cyclization of **G** should take place with the most stable

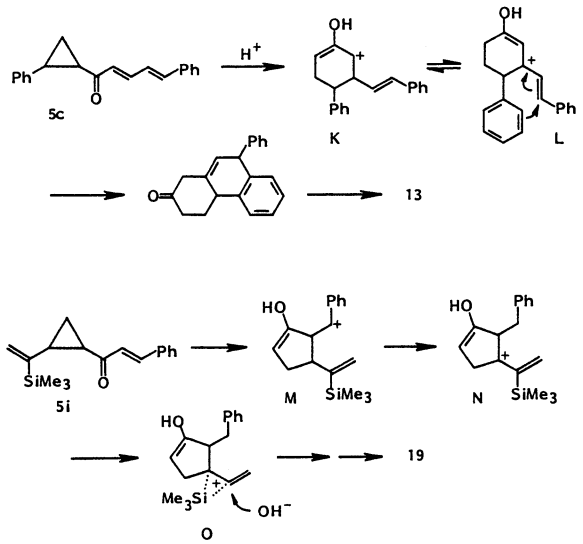


Scheme 3.

configuration where the bulkier phenyl group must be anti to the fused five-membered ring, it is now quite easy to understand the selective formation of **11**.

There are two possible cyclization patterns of intermediary cation **H** which is equivalent with the aforementioned intermediate **F**: One cyclization leads to five-membered ring **I** with an exo cation and the other six-membered ring **J** with an endo cation. It is expected that regiochemistry of the cyclization would depend upon the nature of cation stabilization by substituent R^1. Therefore some derivatives **5b—g** wearing a variety of substitution patterns were employed in PPA-catalyzed ring enlargement reactions.

Ketone **5d** bearing two methyl substituents on the β-carbon of enone showed a similar cyclization pattern, via intermediate **I**, to give **14** (Table 1, Entry 9). On the other hand, cyclizations of ketones **5b** and **5c** proceeded via six-membered intermediates **J** to furnish



Scheme 4.

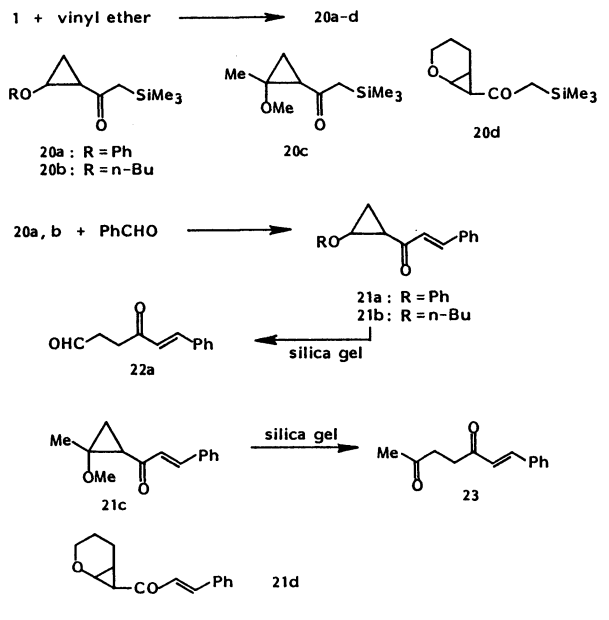
12 and **13** (Entries 7 and 8). Ring-fused cyclopropyl ketones **5e—g** are similarly isomerized into fused cyclohexenones **15—18** albeit in low yields (Entries 10—12).

In the isomerization of dienone **5c**, the direct cyclization of intermediate **K** is impossible due to the *E*-configuration of the styryl moiety (Scheme 4). This cation **K** can equilibrate with pentadienyl cation **L** through a deprotonation and reprotonation process, which is then transformed to the isolated product **13** via the step of making the second six-membered ring and the followed double-bond migration.

Ring enlargement of ketone **5i** bearing a 1-silylethenyl moiety on the cyclopropane ring occurred in a different way to produce desilylated cyclopentanone **19** as a single isomer. Structure of **19** was assigned to be *trans*-3-acetyl-2-benzylcyclopentanone mainly on the basis of the spectral data ($J_{2\text{-}3}$=9.7 Hz; ring CO: =210.03; MeCO: 1.88 and 200.70). This unusual reaction would involve the initial formation of intermediary benzyl cation **M** which then rearranges into equally stable tertiary 2-silyl-substituted allyl cation **N**. A 1,2-silyl migration[15] is followed by hydroxylation leading to the isolated product **19** after a spontaneous desilylation.

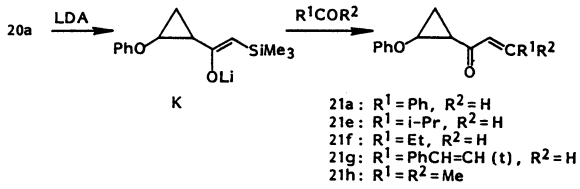
Though these PPA-catalyzed ring enlargements of 1-alkenyl cyclopropyl ketones are attractive as a new direct and stereoselective synthetic way to fused cyclopentanones and cyclohexenones, lack of the cation-stabilizing substituents in the substrates provides either only poor yields of ring-enlarged products or complex results.[16] An effective cation-stabilizing substituent is essential.

With an expectation that an alkoxy or aryloxy moiety would accelerate the ring enlargement, a variety of 1-alkenyl cyclopropyl ketones **21a—h** were prepared and their ring openings were studied.[17] Cyclopropanation of vinyl ethers with **1** in the presence of a catalytic amount (0.5—1 mol%) of copper(II) acetylacetonate or rhodium(II) acetate gives the corresponding cyclopropyl silylmethyl ketones **20a—d** in 46—79% yields (Scheme 5). As **20a—d** belong to moisture sensitive α-silyl ketones, vacuum distillation was the only practical separation method. Immediately after their separation **20a—d** were lithiated with LDA and then allowed to react with benzaldehyde to form 2-alkoxy enones **21a—d** in good yields (by ^{1}H NMR). Though in lower yields, these two steps of cyclopropanation and olefination can be performed in one flask (see Experimental).



Scheme 5.

Compared with the sufficient stability of the phenoxy derivative **21a** which can be separated and purified through column chromatography, the other three **21b—d** are all labile. Though their formation can be confirmed on the basis of ^{1}H and/or ^{13}C NMR spectra of the crude reaction mixtures, all attempts to isolate them by column chromatography resulted in their ring opening or decomposition. Thus crude **21b** and **21c** were chromatographed over silica gel to give 4-oxo-5-alkenal **22a** (60%) and 5-alkene-1,4-dione **23** (23% based on **1**), respectively, both as *E*-isomers (Scheme 5). The ring-fused enone **21d** decomposed to complex mixture by a similar procedure.



Scheme 6.

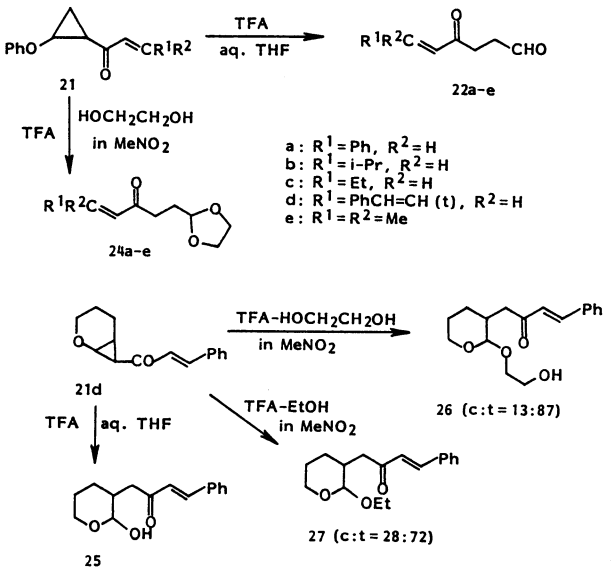
As the phenoxy-substituted enone **21a** proved to have higher stability, several derivatives **21e—h** were prepared from silylmethyl ketone **20a** by the same procedure applied for **21a** (Scheme 6). As a step-saving procedure, the following one-flask reactions can be employed: The reaction mixture containing crude **20a**, supplied from the cyclopropanation procedure using **1**, is immediately lithiated with LDA at −78 °C and then reacted with a variety of carbonyl compounds. The resulting mixtures are chromatographed over silica gel to give **21a** and **21e—h** in 20—40% total yields based upon **1**.

It was disappointing that treating **21a** with PPA under the same conditions applied in the conversion of **5a** into **11** gave no sign of formation of the expected cyclization product. However simple treatment of **5a** with TFA in aqueous tetrahydrofuran (THF) at room temperature gave (*E*)-4-oxo-6-phenyl-5-hexenal (**22a**) in 88% yield, which is identical with that obtained from **21b** (Scheme 7 and Table 2, Entry 1). Similarly a variety of 4-oxo-5-alkenals such as (*E*)-7-methyl-4-oxo-5-octenal (**22b**), (*E*)-4-oxo-5-octenal (**22c**), (*E,E*)-4-oxo-8-phenyl-5,7-octadienal (**22d**), and 6-methyl-4-oxo-5-heptenal (**22e**) were obtained in good yields (Entries 2—5). Although the ring opening of **21h** was so slug-

Table 2. Acid-Catalyzed Ring Opening of 1-Alkenyl 2-Phenyloxycyclopropyl Ketones **21a** and **21d—h**

Entry	Ketone	Reaction condition		Product (yield/%)[a]	
1	**21a**	TFA in wet THF	rt, 20.5 h	**22a** (88)	
2	**21e**	TFA in wet THF	rt, 24 h	**22b** (100)	
3	**21f**	TFA in wet THF	rt, 22 h	**22c** (71)	
4	**21g**	TFA in wet THF	rt, 63 h	**22d** (73)	
5	**21h**	TFA + LiCl[b] in wet THF	rt, 0.5 h	**22e** (71)	
6	**21a**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 20 min	**24a** (90)	
7	**21e**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 10 min	**24b** (58)	
8	**21f**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 10 min	**24c** (42)	
9	**21g**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 20 min	**24d** (58)	
10	**21h**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 30 min	**24e** (67)	
11	**21d**	TFA in wet THF	rt, 20 min	**25** (44)[c]	1 : 1[d]
12	**21d**	TFA + $HOCH_2CH_2OH$ in $MeNO_2$	0 °C, 1 h	**26** (60)[c]	8 : 52[e]
13	**21d**	TFA + EtOH in $MeNO_2$	0 °C, 15 min	**27** (46)[c]	13 : 33[e]

a) Yield of isolated products. b) Two equivalents of lithim chloride was used. c) Yield based on diazo ketone **1**. d) Inseparable mixture (NMR). e) Each isomer was isolated (cis : trans).



Scheme 7.

gish under these conditions that most of **21h** was recovered after a week at room temperature, the addition of lithium chloride accelerated this reaction to such an extent that the reaction was complete in 30 min to give 71% yield of **22e**.

When the ring opening reactions of **21** are carried out in the presence of 1,2-ethanediol in nitromethane, dioxolane-protected derivatives **24a—e** are directly obtained (Scheme 7 and Entries 6—10 in Table 2). The reactions proceed smoothly and are complete at 0 °C in less than 30 min.

The ring-fused cyclopropyl ketone **21d** is very susceptible to acid. Thus TFA in THF or nitromethane opens the cyclopropane ring of **21d** to give hemiacetals **25—27** through an addition of the nucleophiles employed (Scheme 7 and Entries 11—13 in Table 2).

Experimental

General. Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^1H NMR spectra were recorded on a Hitachi R-40 (90 MHz), a JEOL FX-100 (100 MHz), or a JEOL GSX-270 instrument (270 MHz), and ^{13}C NMR on a JEOL FX-100 (25.05 MHz) or a JEOL GSX-270 spectrometer (67.94 MHz). Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL-01SG-2 spectrometer at 70 eV of ionization energy. High-resolution mass spectra were obtained on the same instrument. Elemental analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), and silica gel 60 (Merck) were employed. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with silica gel 60 (Merck, size: 0.04—0.063 mm). Preparative high-performance liquid chromatography (HPLC) was performed on a Kusano KHLC-201 apparatus with a UV-detector Uvilog-III using a column (22×300 mm) packed with silica gel (Wakogel LC-50H). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatograph (Yanagimoto) with an ionization flame detector using a glass column (SE-30, 3×2000 mm) or a glass capillary column (Silicone GE, SE-30, 0.25×50000 mm). Micro vacuum distillation was carried out on a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Materials. 1-Diazo-3-trimethylsilyl-2-propanone (**1**),[1] 1-diazo-3-(diethoxyphosphoryl)-2-propanone (**2**),[9] (diethoxyphosphoryl)methyl 2-phenylcyclopropyl ketone,[9] 2-trimethylsilyl-1,3-butadiene,[18] phenyl vinyl ether[19] were prepared according to the reported methods. Butyl vinyl ether, 2-methoxypropene, and 3,4-dihydro-2*H*-pyran are all commercially available and used without further purification. Trifluoromethanesulfonic acid and polyphosphoric acid (PPA, H_3PO_4 content; 105%, Katayanma Kagaku Co., Ltd.) are also commercially available. 1-Alkenyl cyclopropyl ketones **5a—h** were previously prepared by one-pot proce-

dure for a sequence of cyclopropanation using diazo ketone **1** and Peterson olefination with a variety of carbonyl compounds.[1,9]

(*E*)-2-Phenylethenyl 2-[(1-Trimethylsilyl)ethenyl]cyclopropyl Ketone (5i): To the mixture of copper(II) acetylacetonate (3 mg, 0.01 mmol) and 2-trimethylsilyl-1,3-butadiene (1 g, 8 mmol) preheated at 75 °C was added slowly under nitrogen 1-diazo-3-trimethylsilyl-2-propanone (**1**, 0.156 g, 1 mmol) in a period of 0.5 h. After cooled to room temperature, the reaction mixture was diluted with dry THF (1 ml). This solution was added dropwise at −78 °C to lithium diisopropylamide (LDA, 1.61 mmol) freshly prepared in THF (1.5 ml). After 45 min at the same temperature, benzaldehyde (0.16 ml, 1.61 mmol) was added. The resulting mixture was stirred at −78 °C for 2 h and then at room temperature for 0.5 h. Saturated aqueous ammonium chloride was added and extraction procedure with dichloromethane (20 ml×2) was followed. The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-ethyl acetate (20 : 1 v/v) to give **5i** (0.04 g, 15% based on **1**) and then (*E*)-2-phenylethenyl 2-trimethylsilyl-2-vinylcyclopropyl ketone (0.02 g, 7% based on **1**). **5i:** Colorless liquid; IR (neat) 1690, 1246, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.12 (9H, s, $SiMe_3$), 1.23 (1H, ddd, J=8.6, 8.0, and 3.8 Hz, ring CH_2), 1.55 (1H, ddd, J=8.6, 5.0, and 3.8 Hz, ring CH_2), 2.1—2.3 (2H, m, ring CH), 5.36 (1H, d, J=2.6 Hz, $=CH_2$), 5.49 (1H, dd, J=2.6 and 2.0 Hz, $=CH_2$), 6.88 (1H, d, J=16.1 Hz, =CH), 7.3—7.6 (5H, m, Ph), and 7.60 (1H, d, J=16.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=−1.71 ($SiMe_3$), 17.67 (ring CH_2), 29.43, 30.11 (ring CH), 121.97 ($=CH_2$), 126.55, 128.29, 128.91, 130.35, 134.35, 142.11, 150.97, and 198.45 (CO); MS m/z (rel intensity, %) 270 (M^+, 31), 139 (20), 131 (62), and 73 (base peak). HRMS Found: m/z 270.1444. Calcd for $C_{17}H_{23}OSi$: M, 270.1439.

(*E*)-6-Hydroxy-1,6-diphenyl-1-hexen-3-one (6). To a solution of **5a** (0.037 g, 0.15 mmol) in trifluoroacetic acid (TFA, 1 ml) was added trifluoromethanesulfonic acid (0.01 ml). After 3 h at room temperature, the mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane-ethyl acetate (2 : 1 v/v) to provide **6** (0.026 g, 66%): Yellow liquid; IR (neat) 3430 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.58 (1H, br s, OH), 2.14 (2H, dt, J=7.0 and 6.2 Hz, 5-H), 2.80 (2H, t, J=7.0 Hz, 4-H), 4.79 (1H, t, J=6.2 Hz, 6-H), 6.70 (1H, d, J=16.5 Hz, 2-H), 6.9—7.6 (10H, m, Ph), and 7.54 (1H, d, J=16.5 Hz, 1-H); ^{13}C NMR ($CDCl_3$) δ=33.36, 37.18 (each t, 4- and 5-C), 73.77 (d, 6-C), 126.13, 126.48, 127.83, 128.65, 128.83, 129.30, 130.89, 134.83, 143.24, 144.85, and 201.07 (s, CO); MS m/z (rel intensity, %) 266 (M^+, 15), 248 (82), 157 (22), 146 (44), 144 (20), 131 (base peak), 116 (33), 103 (58), 91 (24), and 77 (57). Found: C, 80.49; H, 6.81%. Calcd for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81%.

(*E*)-1,6,6-Triphenyl-1-hexen-3-one (7). To a solution of **5a** (0.15 g, 0.6 mmol) in benzene (6 ml) was added trifluoromethanesulfonic acid (0.265 ml, 3 mmol). After stirred at room temperature for 1.5 h, the mixture was poured into aqueous sodium hydrogencarbonate and extracted with diethyl ether (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.197 g) was subjected to column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) to give **7** (0.165 g, 84%). Colorless needles; mp 124—125 °C (diethyl ether-hexane); IR (KBr) 1687 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.3—2.7 (4H, m, 4- and 5-H), 3.95 (1H, t, J=8.0 Hz, 6-H), 6.64 (1H, d, J=16.0 Hz, 2-H), 7.0—7.6 (15H, m, Ph), and 7.40 (1H, d, J=16.0 Hz, 1-H); ^{13}C NMR ($CDCl_3$) δ=29.77, 39.06 (each t, 4- and 5-C), 50.47 (d, 6-C), 126.42, 127.95, 128.30, 128.65, 128.95, 130.48, 134.54, 142.36, 144.54 (d, 1-C), and 199.89 (s, CO). Found: C, 88.43; H, 6.87%. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%.

(*E*)-3,6-Diacetoxy-1,6-diphenyl-1,3-hexadiene (8). A mixture of **5a** (0.05 g, 0.2 mmol), boron trifluoride etherate (0.024 ml, 0.2 mmol), acetic anhydride (0.038 ml, 0.4 mmol), and nitromethane (1 ml) was stirred at room temperature for 10 min. Treatment with saturated aqueous sodium hydrogencarbonate was followed by extraction with dichloromethane (10 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.073 g) was subjected to column chromatography over silica gel by using hexane-ethyl acetate (4 : 1 v/v) to give **8** (0.042 g, 59%): Pale yellow liquid; IR (neat) 1760 and 1739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08, 2.30 (each 3H, s, COMe), 2.4—2.9 (2H, m, 5-H), 5.32 (1H, t, J=7.5 Hz, 4-H), 5.80 (1H, t, J=7.0 Hz, 6-H), 6.40 (1H, d, J=15.9 Hz, 2-H), 6.60 (1H, d, J=15.9 Hz, 1-H), and 7.2—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=20.47, 21.18 (each q, COMe), 33.18 (t, 5-H), 74.59 (d, 6-C), 117.12 (d, 4-C), 123.07 (d, 4-C), 126.60, 126.83, 128.13, 128.36, 128.71 (each d), 136.36, 139.89 (each s), 148.01 (d, 1-C), 168.30, and 170.37 (each s, COMe); MS m/z (rel intensity, %) 350 (M^+, 1), 290 (34), 248 (36), 159 (87), 131 (51), 107 (39), 103 (26), 91 (24), 77 (31), and 43 (base peak). HRMS Found: m/z 350.1518. Calcd for $C_{22}H_{22}O_4$: M, 350.1517.

(*E*)-2,5-Diacetoxy-1-(diethoxyphosphoryl)-5-phenyl-2-pentene (9). To a solution of **4** (0.101 g, 0.34 mmol) in dry nitromethane (2 ml) were added at 0°C boron trifluoride etherate (0.041 ml, 0.34 mmol) and acetic anhydride (0.065 ml, 0.68 mmol). The mixture was stirred at room temperature under nitrogen for 18 h, poured into saturated aqueous sodium hydrogencarbonate, and extracted with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.18 g) was subjected to column chromatography over silica gel with ethyl acetate to give **9** (0.105 g, 78%): Pale yellow liquid; IR (neat) 1753, 1240, 1051, and 1025 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (6H, t, J=7.0 Hz, OEt), 2.06, 2.16 (each 3H, s, COMe), 2.4—2.7 (2H, m, 4-H), 2.84 (2H, d, $J_{H\text{-}P}$=21.5 Hz, PCH_2), 4.07 (4H, qd, J=8.4 and 7.0 Hz, OEt), 5.11 (1H, td, J=7.0 and $J_{H\text{-}P}$=4.5 Hz, 3-H), 5.74 (1H, t, J=7.0 Hz, 5-H), and 7.31 (5H, s, Ph); MS m/z (rel intensity, %) 398 (M^+, 0.5), 296 (50), 207 (67), 179 (24), 151 (24), and 43 (base peak). HRMS Found: m/z 398.1500. Calcd for $C_{19}H_{27}O_7P$: M, 398.1493.

2-(3-Methyl-1-oxo-2-butenyl)cyclohexanol (10). A mixture of **5h** (0.13 g, 0.73 mmol), polyphosphoric acid (PPA, P_2O_5 content, 75%, 1.3 g) in benzene (1 ml) was heated under reflux for 2.5 h. The mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with diethyl ether (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was subjected to column chromatography over silica gel with hexane-ethyl acetate (20 : 1 v/v) to afford **10** (0.079 g, 55%) as a single isomer: Colorless liquid; IR (neat) 3440, 1680, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.0—3.0 (11H, m,

CH_2 and CH), 1.84, 2.08 (each 3H, s, Me), 3.7—3.8 (1H, m, CHOH), and 6.00 (1H, s, =CH); ^{13}C NMR ($CDCl_3$) δ=20.82 (q and t, Me and CH_2), 24.65, 27.47 (each t), 27.76 (q, Me), 32.53 (t), 37.65 (d), 46.53 (t), 69.42 (d, CHOH), 124.48 (d, =CH), 155.83 (s, $=CMe_2$), and 201.95 (s, CO); MS *m/z* (rel intensity, %) 196 (M^+, 12), 178 (11), 99 (36), 98 (38), 83 (base peak), 82 (13), and 55 (49). HRMS Found: *m/z* 196.1462. Calcd for $C_{12}H_{20}O_2$: M, 196.1461.

3a,8a-*cis*-8,8a-*trans*-8-Phenyl-3,3a,8,8a-tetrahydrocyclopent[*a*]inden-1(2*H*)-one (11). A mixture of **5a** (0.15 g, 0.6 mmol) and PPA (P_2O_5 content, 75%, 1.5 g) in benzene (1.5 ml) was heated at 80—85 °C for 40 h during which time the reaction was monitored by GLC. The reaction mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with diethyl ether (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel by using hexane-ethyl acetate (50 : 1 v/v) to give **11** (0.106 g, 71%) as a single isomer: Colorless needles (ethyl acetate-hexane); mp 97—98 °C; IR (KBr) 1725, 1490, 1445, 1130, 795, 750 and 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.0—2.5 (4H, m, 2- and 3-H), 2.82 (1H, dd, *J*=7.5 and 0.8 Hz, 8a-H), 4.1—4.2 (1H, m, 3a-H), 4.75 (1H, d, *J*=0.8 Hz, 8-H), and 6.8—7.3 (9H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=26.26 (t, 2-C), 36.74 (t, 3-C), 46.00, 54.36, 61.06 (each d, 3a-, 8-, and 8a-C), 124.07, 125.66, 126.60, 127.48, 127.78, 127.90, 128.01, 128.78, and 221.31 (s, CO); MS *m/z* (rel intensity, %) 248 (M^+, 31), 220 (26), 204 (52), 192 (base peak), 191 (66), 189 (38), 165 (42), 115 (39), and 42 (21); Found: C, 87.27; H, 6.57%. Calcd for $C_{18}H_{16}O$: C, 87.06, 6.49%.

3-Ethyl-4-phenyl-2-cyclohexen-1-one (12). A similar procedure using **5b** (0.105 g, 0.53 mmol), PPA (P_2O_5 content, 75%, 1 g), and benzene (1 ml) under reflux for 30 h and subsequent chromatographic operation (silica gel, hexane-ethyl acetate (50 : 1 v/v)) gave **12** (0.066 g, 63%): Colorless liquid; IR (neat) 1660, 1445, 1245, 880, 760, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (3H, t, *J*=6.5 Hz, Et), 1.1—2.4 (4H, m, CH_2), 2.09 (2H, q, *J*=6.5 Hz, Et), 3.60 (1H, t, *J*=4.0 Hz, 4-H), 6.0—6.1 (1H, m, 2-H), and 7.0—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=11.35 (q, Et), 29.36, 31.65, 34.00 (each t, CH_2), 45.47 (d, 4-C), 126.48, 127.24, 128.36, 129.01 (each d), 140.95 (s), 167.95 (s, 3-C), and 200.13 (s, CO); MS *m/z* (rel intensity, %) 200 (M^+, 63), 172 (53), 158 (38), 157 (42), 143 (39), 129 (base peak), 128 (41), 115 (51), 91 (25), and 43 (28). HRMS Found: *m/z* 200.2794. Calcd for $C_{14}H_{16}O$: M, 200.2794.

9-Phenyl-4,4a,9,10-tetrahydro-2(3*H*)-phenanthrenone (13). A similar procedure using **5c** (0.14 g, 0.5 mmol), PPA (P_2O_5 content, 75%, 1.4 g), and benzene (1 m) at 80—85 °C for 10 d and subsequent chromatographic separation (silica gel, hexane-ethyl acetate (30 : 1 v/v)) afforded **13** (0.06 g, 43%) as a single isomer: Colorless prisms (ethyl acetate-hexane); mp 114—115 °C; IR (KBr) 1670, 1430, 1370, 1290, 750, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.0—3.2 (7H, m, CH_2 and CH), 4.2—4.4 (1H, m, 9-H), and 6.8—7.8 (10H, m, Ar and 1-H); ^{13}C NMR ($CDCl_3$) δ=23.35, 29.30, 31.00, 33.59 (each t, CH_2), 50.42 (d, 9-C), 126.48, 126.83, 128.13, 128.30, 128.60, 130.13, 130.48, (each d), 134.36 (d, 1-C), 141.42, 143.13, 145.71 (each s), 163.83 (s, 10a-C), and 209.72 (CO); MS *m/z* (rel intensity, %) 274 (M^+, base peak), 246 (53), 218 (71), 217 (42), 215 (28), 204 (20), and 202 (22). HRMS Found: *m/z* 274.1357. Calcd for $C_{20}H_{18}O$: M, 274.1368.

8,8-Dimethyl-3,3a,8,8a-tetrahydrocyclopent[*a*]inden-1(2*H*)-one (14). A similar procedure using **5d** (0.14 g, 0.62 mmol), PPA (P_2O_5 content, 75%, 1.4 g), and benzene (1.5 ml) at 80—85 °C for 47 h and subsequent chromatography (silica gel, hexane-ethyl acetate (50 : 1 v/v)) gave **14** (0.075 g, 89%): Colorless liquid; IR (neat) 1730, 1680, 1485, 1455, 1280, 1160, 805, and 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.27, 1.34 (each 3H, s, Me), 2.0—2.3 (4H, m, CH_2), 2.56 (1H, d, *J*=8.0 Hz, 8a-H), 3.9—4.1 (1H, m, 3a-H), and 7.0—7.2 (4H, m Ar); ^{13}C NMR ($CDCl_3$) δ=24.77 (q, Me), 27.07 (t, 3-C), 33.30 (q, Me), 38.71 (t, 2-C), 45.42 (d, 8a-C), 47.53 (s, 8-C), 61.95 (d, 3a-C), 122.18, 124.01, 127.54, 127.77 (each d), 143.36, 152.07 (each s), and 220.02 (s, CO); MS *m/z* (rel intensity, %) 200 (M^+, 17), 185 (56), 157 (39), 143 (52), 142 (23), 141 (28), 129 (base peak), 128 (87), 127 (30), and 115 (43). HRMS Found: *m/z* 200.1200. Calcd for $C_{14}H_{16}O$: M, 200.1213.

4-Phenyl-4a,5,6,7,8,8a-hexahydro-2(1*H*)-naphthalenone (15) and 4-Phenyl-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (16). A mixture of **5e** (0.14 g, 0.62 mmol), PPA (P_2O_5 content, 75%, 1.4 g), and benzene (1.5 ml) was heated at 80—85°C for 55 h during which time the reaction was monitored by GLC. The mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with diethyl ether (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel; the elution with hexane-ethyl acetate (50 : 1 v/v) gave **15** (0.08 g, 57%) and with hexane-ethyl acetate (20 : 1 v/v) **16** (0.025 g, 18%), both as single isomers. **15**: Colorless viscous liquid; IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—3.0 (12H, m, CH_2 and CH), 6.24 (1H, s, 6-H), and 7.1—7.6 (5H, m Ph); ^{13}C NMR ($CDCl_3$) δ=20.47, 25.83, 27.17, 30.41 (each t, CH_2), 33.77 (d, 8a-C), 37.77 (t, 8-C), 39.71 (d, 4a-C), 124.95, 126.83, 129.01 (each d), 130.07, 138.18 (each s), 165.36 (s, 5-C), and 200.89 (s, CO); MS *m/z* (rel intensity, %) 226 (M^+, 26), 184 (33), 169 (26), 157 (23), 156 (29), 155 (26), 142 (34), 141 (76), 131 (30), 129 (59), 128 (87), 127 (37), 116 (25), 115 (base peak), 103 (33), 102 (42), 91 (41), and 77 (55). HRMS Found: *m/z* 226.1357. Calcd for $C_{16}H_{18}O$: M, 226.1363. **16**: Colorless prisms (ethyl acetate-hexane); mp 61—63 °C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—3.1 (12H, m, CH_2 and CH), 5.90 (1H, s, 8-H), and 7.1—7.6 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=25.47, 26.59, 32.41, 35.71 (each t, CH_2), 44.06 (t, 2-C), 44.89, 47.77 (each d, 4a- and 5-C), 124.72, 127.13, 127.71, 128.89 (each d, Ph and 8-C), 142.83 (s, Ph), 166.30 (s, 8a-C), and 199.31 (s, CO); MS *m/z* (rel intensity, %) 226 (M^+, 16), 128 (24), 122 (base peak), 115 (41), 107 (21), 104 (60), 103 (34), 94 (65), 91 (65), 79 (63), 78 (59), and 77 (75). HRMS Found: *m/z* 226.1357. Calcd for $C_{16}H_{18}O$: M, 226.1351.

4-Phenyl-3,4,4a,5,6,7,8,9-octahydro-2*H*-benzocyclohepten-2-one (17). A similar procedure using **5f** (0.153 g, 0.64 mmol), PPA (P_2O_5 content, 75%, 0.85 g), and benzene (1.5 ml) at 80—85 °C for 40 h and subsequent chromatography over silica gel (hexane-ethyl acetate (50 : 1 v/v)) gave **17** (0.023 g, 15%) as a single isomer: Colorless viscous liquid; IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.9—3.2 (14H, CH_2 and CH), 5.89 (1H, m, 4-H), and 7.0—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=26.18, 29.00, 29.18, 30.36, 37.06 (each t, CH_2), 44.42 (t, 2-C), 46.00, 47.53 (each d, CH), 127.07, 127.48, 127.71, 129.01 (each d), 143.42 (s), 171.07 (s, 4a-C), and 199.01 (s, CO); MS *m/z* (rel intensity, %) 240 (M^+, 31), 136 (base peak), 108 (52), 93 (24), 91 (34), 79 (37), 78 (21), 77 (35), 41 (25), and 39. HRMS Found: *m/z* 240.1513. Calcd for $C_{17}H_{20}O$: M, 240.1509.

4-Phenyl-3,4,4a,5,6,7,8,9,10-octahydrobenzocycloocten-2-(3*H*)-one (18). A similar procedure using **5g** (0.15 g, 0.6 mmol), PPA (P_2O_5 content, 75%, 1.5 g), and benzene (1.5 ml) at 80—85 °C for 65 h and subsequent chromatographic separation (silica gel, hexane-ethyl acetate (50 : 1 v/v)) gave **18** (0.039 g, 26%) as a single isomer: Colorless viscous liquid; IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.1—3.4 (16H, m, CH_2 and CH), 5.93 (1H, m, 4-H), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=24.35, 24.83, 25.06, 26.65, 31.94, 34.36 (each t, CH_2), 44.42 (t, 2-C), 44.77, 45.47 (each d, 1- and 10a-C), 127.07, 127.48, 129.01 (each d), 143.24 (s), 172.83 (s, 4a-C), and 198.48 (s, CO); MS *m/z* (rel intensity, %) 254 (M^+, 40), 150 (86), 122 (base peak), 91 (33), 77 (27), and 43 (20). Found: C, 84.99; H, 2.54%. Calcd for $C_{18}H_{22}O$: C, 85.12; H, 8.85%.

***trans*-3-Acetyl-2-benzylcyclopentanone (19).** A mixture of **5i** (0.026 g, 0.1 mmol) and PPA (P_2O_5 content, 75%, 0.3 g) in benzene (1 ml) was stirred at room temperature for 23 h during which time the reaction was monitored by GLC. The mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with diethyl ether (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane-ethyl acetate (2 : 1 v/v) to give **19** as a single isomer: Yellow liquid; IR (neat) 1725 and 1715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88 (3H, s, COMe), 1.9—2.0 (1H, m, CH_2), 2.1—2.3 (1H, m, CH_2), 2.4—2.7 (4H, m, CH_2), 3.16 (1H, dt, *J*=9.7 and 3.8 Hz, CH), 3.27 (1H, dt, *J*=9.7 and 6.5 Hz, CH), and 7.2—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=28.11 (t, 4-C), 30.24 (q, COMe), 39.88 (t, 5-C), 46.41 (d, 3-C), 47.82 (t, $PhCH_2$), 55.35 (d, 2-C), 127.07, 127.32, 128.98 (each d, Ph), 141.81 (s, Ph), 200.70 (s, COMe), and 210.03 (s, CO); MS *m/z* (rel intensity, %) 216 (M^+, 48), 156 (28), 146 (22), 145 (20), 117 (27), 104 (27), 103 (21), 91 (48), 83 (28), 76 (23), 55 (24), and 43 (base peak). HRMS Found: *m/z* 216.1143. Calcd for $C_{14}H_{16}O_2$: M, 216.1149.

2-Phenoxycyclopropyl Trimethylsilylmethyl Ketone (20a). Under nitrogen, a mixture of phenyl vinyl ether (0.6 g, 5 mmol) and copper(II) acetylacetonate (0.006 g, 0.02 mmol) was heated at 75 °C. A solution of **1** (0.312 g, 2 mmol) in dry diethyl ether (0.5 ml) was added dropwise in a period of 1 h. The reaction mixture was subjected to micro vacuum distillation on a Kugelrohr distilling apparatus to provide **20a** (0.28 g, 46%): Pale yellow liquid; bp 130 °C/26 Pa (bulb-to-bulb); IR (neat) 1660, 1245, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (9H, s, $SiMe_3$), 1.38 (1H, ddd, *J*=9.7, 5.4, and 3.8 Hz, ring CH_2), 1.54 (1H, dt, *J*=5.9 and 5.4 Hz, ring CH_2), 2.15 (1H, ddd, *J*=9.7, 5.4, and 2.2 Hz, ring CH), 2.37, 2.53 (each 1H, d, *J*=10.3 Hz, CH_2CO), 4.05 (1H, ddd, *J*=5.9, 3.8, and 2.2 Hz, ring CH), 6.9—7.1 (3H, m, Ph), and 7.2—7.4 (2H, m Ph); ^{13}C NMR ($CDCl_3$) δ=−0.07 ($SiMe_3$), 17.98 (ring CH_2), 30.17 (ring CH), 40.21 (CH_2CO), 59.23 (ring CH), 115.08, 121.63, 129.71, 158.26 (each Ph), and 206.55 (CO); MS *m/z* (rel intensity, %) 248 (M^+, 1), 155 (23), 153 (36), 94 (33), 82 (49), 81 (84), 76 (26), 72 (base peak), and 43(26). HRMS Found: *m/z* 248.1240. Calcd for $C_{14}H_{20}O_2Si$: M, 248.1231.

2-Butoxycyclopropyl Trimethylsilylmethyl Ketone (20b). Butyl vinyl ether (3 ml, 23 mmol) was heated at 75 °C under nitrogen together with copper(II) acetylacetonate (0.003 g, 0.01 mmol). Diazo ketone **1** (0.312 g, 2 mmol) was added dropwise in a period of 1 h. The reaction mixture was distilled under vacuum on a Kugelrohr distilling apparatus to give **20b** (0.29 g, 64%): Pale yellow liquid; bp 110 °C/106 Pa (bulb-to-bulb); IR (neat) 1670, 1250, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.15 (9H, s, $SiMe_3$), 0.91 (3H, t, *J*=7.3 Hz, *n*-Bu), 1.1—1.2 (1H, m, ring CH_2), 1.3—1.7 (4H, m, *n*-Bu), 1.9—2.0 (1H, m, ring CH_2), 2.2—2.5 (3H, m, ring CH and CH_2CO), and 3.3—3.6 (3H, m, *n*-Bu and ring CH); ^{13}C NMR ($CDCl_3$) δ=−0.83 (q, $SiMe_3$), 14.02 (q, *n*-Bu), 18.02 (t, ring CH_2), 19.46 (t, *n*-Bu), 30.41 (d, ring CH), 32.06 (t, *n*-Bu), 39.76 (t, CH_2CO), 63.29 (d, ring CH), 71.25 (t, *n*-Bu), and 206.97 (s, CO); MS *m/z* (rel intensity, %) 228 (M^+, 2), 80 (20), 73 (base peak), 57 (30), and 45 (25). HRMS Found: *m/z* 228.1542. Calcd for $C_{12}H_{24}O_2Si$: M, 228.1544.

2-Methoxy-2-methylcyclopropyl Trimethylsilylmethyl Ketone (20c). Under nitrogen, a mixture of 2-methoxypropene (2 ml, 20 mmol) and rhodium(II) acetate (0.002 g, 0.005 mmol) was heated at 75 °C. Diazo ketone **1** (0.312 g, 2 mmol) was added dropwise in a period of 1 h. The resulting mixture was distilled under vacuum on a Kugelrohr distilling apparatus to give **20c** (0.25 g, 63%) as a mixture of two stereoisomers: Colorless liquid; bp 80 °C/266 Pa (bulb-to-bulb); ^{13}C NMR ($CDCl_3$) δ=−1.28, −0.88 (each $SiMe_3$), 13.44, 18.39 (each ring CH_2), 22.54, 25.42 (each Me), 36.19 (ring CH), 40.45, 40.54 (each CH_2CO), 49.52, 54.22 (each MeO), 68.04 (ring CH), and 205.88 (CO). This mixture was directly used in the reaction with benzaldehyde leading to **21c**.

5-[(Trimethylsilyl)acetyl]perhydrocyclopropa[*b*]pyran (20d). A mixture of 3,4-dihydro-2*H*-pyran (3 ml, 33 mmol) and copper(II) acetylacetonate (0.003 g, 0.01 mmol) was heated under nitrogen at 75 °C. Diazo ketone **1** (0.312 g, 2 mmol) was added dropwise in a period of 1 h. The reaction mixture was distilled on a Kugelrohr distilling apparatus to give **20d** (0.335 g, 79%): Colorless liquid; bp 110 °C/80 Pa (bulb-to-bulb); IR (neat) 1665, 1250, and 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.08 (9H, s, $SiMe_3$), 1.3—1.5 (2H, m, 4-H), 1.7—2.0 (4H, m, 3-, 4a-, and 5-H), 2.28 (2H, s, CH_2CO), 3.2—3.4 (1H, m, 2-H), 3.5—3.6 (1H, m, 2-H), and 3.77 (1H, d, *J*=7.0 Hz, 5a-H); ^{13}C NMR ($CDCl_3$) δ=−0.90 (q, $SiMe_3$), 19.25 (t, 4-C), 22.17 (t, 3-C), 24.36 (d, 4a-C), 36.31 (t, 5-C), 40.01 (t, CH_2CO), 63.02 (d, 5a-C), 64.62 (t, 2-C), and 206.18 (s, CO); MS *m/z* (rel intensity, %) 212 (M^+, 42), 122 (47), 75 (38), and 73 (base peak). HRMS Found: *m/z* 212.1197. Calcd for $C_{11}H_{20}O_2Si$: M, 212.1231.

(*E*)-2-Phenoxycyclopropyl 2-Phenylethenyl Ketone (21a): Reaction of diazo ketone **1** (0.312 g, 2 mmol) with phenyl vinyl ether (1.2 g, 10 mmol) in the presence of a catalytic amount of copper(II) acetylacetonate (0.003 g, 0.01 mmol) was carried out according to the procedure mentioned above. The reaction mixture was diluted with dry THF (2 ml). This solution was added dropwise, at −78 °C under nitrogen, to LDA (1.8 mmol) freshly prepared in THF (2 ml). After 1 h, benzaldehyde (0.18 mmol) was added. The mixture was stirred at −78 °C for 1 h and at room temperature for 0.5 h. Quench with saturated aqueous ammonium chloride was followed by extraction with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (1.02 g) was chromatographed over silica gel with hexane-ethyl acetate (50 : 1 v/v) to give **21a** (0.223 g, 42% based on **1**): Colorless needles (diethyl ether-hexane); mp 75—78 °C; IR (KBr) 1675, 1645, and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.58 (1H, ddd, *J*=9.5, 5.5, and 4.4 Hz, ring CH_2), 1.76 (1H, ddd, *J*=6.6, 6.2, and 5.5 Hz, ring CH_2), 2.57 (1H, ddd, *J*=9.5, 6.2, and 2.2 Hz, ring CH), 4.12 (1H, ddd, *J*=6.6, 4.4, and 2.2 Hz, ring CH), 6.92 (1H, d, *J*=16.1 Hz, =CHCO), 6.9—7.6 (10H, m, Ph), and 7.65

(1H, d, J=16.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=17.98 (ring CH_2), 28.08 (ring CH), 60.13 (ring CH), 114.80, 121.65, 126.27, 128.40, 128.95, 129.57, 130.62, 134.39, 143.19, 157.99 (=CH), and 197.07 (CO); MS m/z (rel intensity, %) 171 (34), 170 (base peak), 143 (24), 141 (23), 131 (27), 128 (40), 115 (22), 103 (32), and 77 (55). Found: C, 81.86; H: 6.13%. Calcd for $C_{18}H_{16}O_2$: C, 81:80; H, 6.10%.

(*E*)-2-Butoxycyclopropyl 2-Phenylethenyl Ketone (21b). A solution of silylmethyl ketone **20b** (0.272 g, 1.19 mmol) in dry THF (1 ml) was added dropwise at −78 °C to LDA (1.43 mmol) freshly prepared in THF (1 ml). After 1 h, benzaldehyde (0.12 ml, 1.19 mmol) was added and the mixture was stirred at −78 °C for 1 h and then at room temperature for 1 h. Quench with saturated aqueous ammonium chloride was followed by extraction with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo to give **20b** which decomposed to **22a** (0.134 g, 60% based on **20b**) on column chromatography over silica gel (hexane-ethyl acetate (9:1 v/v)). **20b**: Yellow liquid; ^{13}C NMR ($CDCl_3$) δ=13.92 (*n*-Bu), 19.37 (*n*-Bu), 28.65 (ring CH_2), 31.60 (ring CH), 64.45 (*n*-Bu), 71.30 (*n*-Bu), 126.53, 128.41, 129.44, 130.51, 134.75, 142.43 (=CH), and 197.57 (CO). Purification of **21b** by chromatography over silica gel gave **22a**.

(*E*)-2-Methyl-2-methoxycyclopropyl 2-Phenylethenyl Ketone (21c). A similar one-flask procedure using **1** (0.156 g, 1 mmol in dry diethyl ether (1 ml)), rhodium(II) acetate (0.002 g, 0.005 mmol), and 2-methoxypropene (0.48 ml, 5 mmol) for cyclopropanation (80 °C, 1 h) and then LDA (1.61 mmol in THF (1.5 ml)) and benzaldehyde (0.16 ml, 1.61 mmol) for olefination (1 h at −78 °C and 0.5 h at room temperature) gave **21c** as unstable product. Column chromatography of **21c** gave **23** in 23% yield based on **1**.

(*E*)-5-(1-Oxo-3-phenyl-2-propenyl)perhydrocyclopropa[*b*]pyran (21d). To freshly prepared LDA (1.74 mmol) in dry THF (1 ml) was added at −78 °C a solution of silylmethyl ketone **20d** (0.307 g, 1.45 mmol). After 1 h at −78 °C under nitrogen, benzaldehyde (0.14 ml, 1.45 mmol) was added. Stirring was continued at the same temperature for 1.5 h and at room temperature for 0.5 h. The mixture was poured into saturated aqueous ammonium chloride and extracted with dichloromethane (15 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo to give **21d** as a labile product. This compound **21d** decomposed to complex mixture when chromatographed over silica gel. **21d**: ^{13}C NMR ($CDCl_3$) δ=19.19 (ring CH_2), 22.02 (ring CH_2), 25.72 (ring CH), 34.55 (ring CH), 64.09, 64.68 (ring CH_2 and CH), 126.75, 128.26, 128.91, 130.29, 134.74, 141.82 (=CH), and 196.95 (CO). Column chromatography of **21d** over silica gel led to complex mixture.

(*E*)-4-Methyl-1-oxo-2-pentenyl 2-Phenoxycyclopropyl Ketone (21e). A similar one-flask procedure using **1** (0.312 g, 2 mmol), copper(II) acetylacetonate (0.003 g, 0.01 mmol), and phenyl vinyl ether (1.2 g, 10 mmol) for cyclopropanation (1 h at 70 °C) and then LDA (3.2 mmol in THF (2 ml)) and 2-methylpropanal (0.3 g, 3.2 mmol) for olefination (1h at −78 °C and 0.5 h at room temperature) gave **21e** (0.179 g, 39% based on **1**) after column chromatography over silica gel with hexane-ethyl acetate (50:1 v/v). **21e**: Colorless liquid; IR (neat) 1677 and 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.08 (6H, d, J=6.6 Hz, *i*-Pr), 1.46 (1H, ddd, J=9.5, 5.2, and 5.1 Hz, ring CH_2), 1.66 (1H, dt, J=6.2 and 5.2 Hz, ring CH_2), 2.4—2.6 (2H, m, ring CH and *i*-Pr), 4.02 (1H, ddd, J=6.2, 4.0, and 1.8 Hz, ring CH), 6.21 (1H, d, J=16.1 Hz, =CHCO), and 6.9—7.3 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=17.66 (ring CH_2), 21.42, 21.45 (each *i*-Pr), 27.25 (ring CH), 31.40 (*i*-Pr), 59.96 (ring CH), 114.95, 121.73, 127.93, 129.64, 154.52, 158.16 (=CH), and 197.67 (CO); MS m/z (rel intensity, %) 137 (20), 136 (45), 121 (40), 105 (20), 97 (42), 95 (20), 94 (31), 93 (20), 91 (29), 81 (30), 79 (28), 77 (96), 75 (19), and 73 (base peak). Found: C, 77.67; H, 8.01%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

(*E*)-1-Oxo-2-pentenyl 2-Phenoxycyclopropyl Ketone (21f). A similar one-flask procedure using **1** (0.312 g, 2 mmol), copper(II) acetylacetonate (0.003 g, 0.01 mmol), and phenyl vinyl ether (1.2 g, 10 mmol) for cyclopropanation (1 h at 70 °C) and then LDA (2 mmol in THF (2 ml)) and propanal (0.22 ml, 2.4 mmol) for olefination (1 h at −78 °C and 0.5 h at room temperature) gave **21f** (0.128 g, 29% based on **1**) after column chromatography over silica gel with hexane-ethyl acetate (50:1 v/v). **21f**: Colorless liquid; IR (neat) 1677 and 1655 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, t, J=7.7 Hz, Et), 1.48 (1H, ddd, J=9.1, 6.2, and 4.0 Hz, ring CH_2), 1.67 (1H, dt, J=6.2 and 5.8 Hz, ring CH_2), 2.2—2.4 (2H, m, Et), 2.45 (1H, ddd, J=9.1, 5.8, and 2.2 Hz, ring CH), 4.03 (1H, ddd, J=6.2, 4.0, and 2.2 Hz, ring CH), 6.25 (1H, d, J=16.1 Hz, =CHCO), and 6.9—7.3 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=12.45 (Et), 17.81 (ring CH_2), 25.27 (Et), 27.31 (ring CH), 60.01 (ring CH), 115.02, 121.81, 129.72, 149.93, 158.23 (=CH), and 197.60 (CO); MS m/z (rel intensity, %) 123 (38), 122 (base peak), 107 (36), 105 (19), 95 (46), 94 (18), 93 (15), 83 (40), 79 (27), and 77 (66). Found: C, 77.19; H, 7.48%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

(2*Z*,4*E*)-1-Oxo-5-phenyl-2,4-pentadienyl 2-Phenoxycyclopropyl Ketone ((*Z*,*E*)-21g) and (*E*,*E*)-1-Oxo-5-phenyl-2,4-pentadienyl 2-(Phenyloxy)cyclopropyl Ketone ((*E*,*E*)-21g). A similar one-flask procedure using **1** (0.312 g, 2 mmol), copper(II) acetylacetonate (0.003 g, 0.01 mmol), and phenyl vinyl ether (1.2 g, 10 mmol) for cyclopropanation (1 h at 70 °C) and then LDA (2 mmol in THF (2 ml)) and cinnamaldehyde (0.23 ml, 1.8 mmol) for olefination (1 h at −78 °C and 0.5 h at room temperature) gave (*Z*,*E*)-**21g** (0.051 g, 8% based on **1**) and then (*E*,*E*)-**21g** (0.288 g, 50% based on **1**) after column chromatography over silica gel with hexane-ethyl acetate (50:1 v/v). (*Z*,*E*)-**21g**: Yellow liquid; IR (neat) 1660, 1600, and 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.52 (1H, ddd, J=8.6, 6.0, and 4.0 Hz, ring CH_2), 1.73 (1H, q, J=6.0 Hz, ring CH_2), 2.33 (1H, ddd, J=8.6, 6.0, and 2.0 Hz, ring CH), 4.07 (1H, ddd, J=6.0, 4.0, and 2.0 Hz, ring CH), 6.27 (1H, d, J=11.0 Hz, =CHCO), 6.66 (1H, t, J=11.0 Hz, =CH), 6.8—7.6 (11H, m, Ph and =CH), and 8.24 (1H, dd, J=15.8 and 12.5 Hz, =CH); MS m/z (rel intensity, %) 290 (M^+, 4), 225 (21), 205 (23), 94 (53), 76 (35), 75 (46), 73 (base peak), and 43 (27). (*E*,*E*)-**21g**: Colorless plates (hexane); mp 91—93 °C; IR (KBr) 1637 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.52 (1H, ddd, J=9.1, 5.1, and 4.0 Hz, ring CH_2), 1.72 (1H, dt, J=6.2 and 5.1 Hz, ring CH_2), 2.47 (1H, ddd, J=9.1, 6.2, and 2.2 Hz, ring CH), 4.08 (1H, ddd, J=6.2, 4.0, and 2.2 Hz, ring CH), 6.44 (1H, d, J=15.4 Hz, =CHCO), and 6.8—7.5 (13H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=17.85 (ring CH_2), 28.01 (ring CH), 60.06 (ring CH), 114.83, 121.64, 126.62, 127.31, 128.86, 129.31, 129.56, 135.96, 141.94, 143.18, 158.04, and 197.03 (CO); MS m/z (rel intensity, %) 290 (M^+, 14), 196 (36), 94 (29), and 32 (base peak); Found: C, 82.91; H, 6.30%. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%.

3-Methyl-1-oxo-2-butenyl 2-Phenoxycyclopropyl Ketone

(21h). A similar one-flask procedure using **1** (0.312 g, 2 mmol), copper(II) acetylacetonate (0.003 g, 0.01 mmol), and phenyl vinyl ether (1.2 g, 10 mmol) for cyclopropanation (1 h at 70 °C) and then LDA (1.8 mmol in THF (2 ml)) and acetone (0.15 ml, 2 mmol) for olefination (2 h at −78 °C and 1 h at room temperature) gave **21h** (0.082 g, 19% based on **1**) after column chromatography over silica gel with hexane-ethyl acetate (50 : 1 v/v): Colorless liquid; IR (neat) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.42 (1H, ddd, J=9.5, 5.1, and 4.0 Hz, ring CH_2), 1.62 (1H, dt, J=6.2 and 5.5 Hz, ring CH_2), 1.92, 2.18 (each 3H, d, J=1.1 Hz, Me), 2.2—2.3 (1H, m, ring CH), 4.00 (1H, ddd, J=6.2, 4.0, and 2.2 Hz, ring CH), 6.28 (1H, dd, J=2.6 and 1.1 Hz, =CHCO), and 7.0—7.3 (5H, m Ph); ^{13}C NMR ($CDCl_3$) δ=17.45 (ring CH_2), 20.94 (Me), 27.72 (ring CH), 30.71 (Me), 59.72 (ring CH), 114.80, 121.51, 124.16, 156.01, 158.12 (=CH), and 197.46 (CO); MS m/z (rel intensity, %) 123 (33), 122 (base peak), 95 (63), 93 (21), and 82 (52). Found: C, 77.11; H, 7.56%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

***(E)*-4-Oxo-6-phenyl-5-hexenal (22a).** A mixture of **21a** (0.223 g, 0.84 mmol), water (0.03 ml, 1.68 mmol), and trifluoroacetic acid (TFA, 0.064 ml, 0.84 mmol) in dry THF (2 ml) was stirred at room temperature for 20.5 h. The mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.195 g) was chromatographed over silica gel with hexane-ethyl acetate (9 : 1 v/v) to afford **22a** (0.139 g, 88%): Colorless liquid; IR (neat) 1715, 1680, 1653, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.87 (2H, t, J=6.5 Hz, CH_2), 3.03 (2H, t, J=6.5 Hz, CH_2), 6.77 (1H, d, J=16.1 Hz, 5-H), 7.3—7.6 (5H, m, Ph), 7.60 (1H, d, J=16.1 Hz, 6-H), and 9.87 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) δ=32.37, 37.58 (2- and 3-C), 125.74, 128.32, 128.97, 130.59 (each Ph), 135.17 (5-C), 143.06 (6-C), 197.45 (4-C), and 200.61 (CHO); MS m/z (rel intensity, %), 188 (M^+, 1), 160 (30), 131 (55), 103 (78), 102 (30), 91 (51), 76 (85), 51 (48), 42 (26), and 30 (base peak). HRMS Found: m/z 188.0838. Calcd for $C_{12}H_{12}O_2$: M, 188.0837.

***(E)*-7-Methyl-4-oxo-5-octenal (22b).** A similar procedure using **21e** (0.044 g, 0.19 mmol), water (0.004 ml, 0.19 mmol), and TFA (0.015 ml, 0.19 mmol) in THF (0.5 ml) at room temperature for 24 h and subsequent silica-gel chromatography (hexane-ethyl acetate (9 : 1 v/v)) gave **22b** (0.029 g, 100%): Colorless liquid; IR (neat) 1720 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (6H, d, J=6.6 Hz, Me), 2.4—2.6 (1H, m, 7-H), 2.7—2.9 (4H, m, 2- and 3-H), 6.08 (1H, dd, J=16.1 and 1.5 Hz, 5-H), 6.86 (1H, dd, J=16.1 and 6.6 Hz, 6-H), and 9.84 (1H, s, CHO); MS m/z (rel intensity, %) 154 (M^+, 15), 126 (21), 97 (base peak), 84 (49), 82 (26), 69 (33), 41 (58), and 30 (22). HRMS Found: m/z 154.0990. Calcd for $C_9H_{14}O_2$: M, 154.0993.

***(E)*-4-Oxo-5-octenal (22c).** A similar procedure employing **21f** (0.063 mg, 0.29 mmol), water (0.005 ml, 0.29 mmol), and TFA (0.022 ml, 0.29 mmol) in THF (1 ml) at room temperature for 22 h and subsequent column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) provided **22c** (0.029 g, 71%): Colorless liquid; IR (neat) 1725 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.09 (3H, t, J=7.7 Hz, Et), 2.26 (2H, dq, J=7.7 and 1.4 Hz, 7-H), 2.79, 2.90 (each 2H, t, J=5.5 Hz, 2- and 3-H), 6.14 (1H, dt, J=16.1 and 1.4 Hz, 5-H), 6.95 (1H, dt, J=16.1 and 6.6 Hz, 6-H), and 9.83 (1H, s, CHO); MS m/z (rel intensity, %) 140 (M^+, 1), 82 (base peak), 55 (76), 41 (20), and 39 (38). HRMS Found: m/z 140.0794. Calcd for $C_8H_{12}O_2$: M, 140.0837.

***(E,E)*-4-Oxo-8-phenyl-5,7-octadienal (22d).** A similar procedure using **21g** (0.045 g, 0.16 mmol), water (0.005 ml, 0.29 mmol), TFA (0.012 ml, 0.15 mmol) in THF (1 ml) at room temperature for 63 h and subsequent chromatography over silica gel with hexane-ethyl acetate (4 : 1 v/v)) gave **22d** (0.025 g, 73%): Colorless crystals; mp 71—73 °C; IR (KBr) 1718 and 1673 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.83, 2.96 (each 2H, t, J=6.6 Hz, 2- and 3-H), 6.31 (1H, d, J=15.4 Hz, 5-H), 6.8—7.0 (2H, m, 6- and 7-H), 7.3—7.5 (6H, m, Ph and 8-H), and 9.85 (1H, s, CHO); MS m/z (rel intensity, %) 214 (M^+, 31), 186 (20), 157 (41), 129 (25), 128 (35), and 32 (base peak). HRMS Found: m/z 214.0986. Calcd for $C_{14}H_{14}O_2$: M, 214.0993.

6-Methyl-4-oxo-5-heptenal (22e). To a mixture of **21h** (0.035 g, 0.16 mmol) and lithium chloride (0.013 g, 0.32 mmol) in THF (1 ml) were added water (0.006 ml, 0.32 mmol) and TFA (0.012 ml, 0.16 mmol). This mixture was stirred at room temperature for 30 min, poured into saturated aqueous sodium hydrogencarbonate, and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.039 g) was chromatographed over silica gel with hexane-ethyl acetate (9 : 1 v/v) to give **22e** (0.016 g, 71%): Colorless liquid; IR (neat) 1720 and 1687 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.90, 2.14 (each 3H, s, Me), 2.76 (4H, s, 2- and 3-H), 6.12 (1H, s, 5-H), and 9.83 (1H, s, CHO); MS m/z (rel intensity, %) 140 (M^+, 12), 83 (base peak), 55 (50), and 39 (21). HRMS Found: m/z 140.0838. Calcd for $C_8H_{12}O_2$: M, 140.0837.

***(E)*-7-Phenyl-6-heptene-2,5-dione (23).** Crude **21c** prepared from **1** (0.156 g, 1 mmol) according to the above method was chromatographed twice over silica gel with hexane-ethyl acetate (9 : 1 v/v) to give **23** (0.046 g, 23%): Yellow liquid; IR (neat) 1715, 1690, and 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (3H, s, COMe), 2.81, 2.97 (each 2H, t, J=5.9 Hz, CH_2), 6.75 (1H, d, J=16.5 Hz, =CHCO), 7.3—7.5 (5H, m, Ph), and 7.58 (1H, d, J=16.5 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=30.00 (MeCO), 34.24, 37.06 (each CH_2), 126.00, 128.30, 128.94, 130.49, 134.47, 142.82 (=CH), 198.48 (CO), and 207.32 (COMe); MS m/z (rel intensity, %) 202 (M^+, 13), 144 (22), 131 (base peak), 108 (37), 107 (34), 103 (41), 83 (29), 78 (48), and 76 (51). HRMS Found: m/z 202.0990. Calcd for $C_{13}H_{14}O_2$: M, 202.0993.

***(E)*-2-(3-Oxo-5-phenyl-4-pentenyl)-1,3-dioxolane (24a).** To a solution of **21a** (0.1 g, 0.37 mmol) and 1,2-ethanediol (0.05 ml, 0.82 mmol) in nitromethane (2.5 ml) was added TFA (0.03 ml, 0.39 mmol) at 0 °C. After stirring at the same temperature for 20 min, the mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with diethyl ether (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.119 g) was chromatographed over silica gel with hexane-ethyl acetate (9 : 1 v/v) to give **24a** (0.078 g, 90%): Pale yellow liquid; IR (neat) 1685 and 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (2H, dt, J=7.3 and 4.4 Hz, CH_2), 2.82 (2H, t, J=7.3 Hz, CH_2), 3.8—4.0 (4H, m, OCH_2CH_2O), 4.97 (1H, t, J=4.4 Hz, CH), 6.74 (1H, d, J=16.1 Hz, =CHCO), and 7.3—7.6 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=27.98, 34.56 (each CH_2), 64.89 (OCH_2CH_2O), 103.44 (CH), 126.20, 128.25, 128.94, 130.42 (each Ph), 134.54, 142.52 (each =CH), and 199.32 (CO); MS m/z (rel intensity, %) 232 (M^+, 14), 146 (35), 131 (74), 103 (74), 103 (56), 99 (47), 87 (59), 77 (40), 73 (base peak), and 44 (28). HRMS Found: m/z 232.1096. Calcd for $C_{14}H_{16}O_3$: M, 232.1099.

(*E*)-2-(6-Methyl-3-oxo-4-heptenyl)-1,3-dioxolane (24b). A similar procedure using **21e** (0.12 g, 0.52 mmol), 1,2-ethanediol (0.05 ml, 1.04 mmol), TFA (0.04 ml, 0.52 mmol) in nitromethane (2 ml) at 0 °C for 10 min and subsequent column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) gave **24b** (0.06 g, 58%): Colorless liquid; IR (neat) 1695, 1670, and 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.06 (6H, d, J=6.6 Hz, *i*-Pr), 2.00 (2H, dt, J=7.7 and 4.4 Hz, CH_2), 2.46 (1H, dq, J=6.6 and 1.5 Hz, *i*-Pr), 2.70 (2H, t, J=7.7 Hz, CH_2), 3.8—4.0 (4H, m, OCH_2CH_2O), 4.94 (1H, t, J=4.4 Hz, CH), 6.05 (1H, dd, J=16.1 and 1.5 Hz, =CHCO), and 6.81 (1H, dd, J=16.1 and 6.6 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=21.32 (*i*-Pr), 27.90 (CH_2), 31.13 (*i*-Pr), 33.84 (CH_2), 64.97 (OCH_2CH_2O), 103.52 (CH), 127.48, 153.56 (each =CH), and 199.92 (CO); MS m/z (rel intensity, %) 198 (M^+, 3), 155 (25), 97 (25), 85 (22), and 73 (base peak). HRMS Found: m/z 198.1253. Calcd for $C_{11}H_{18}O_3$: M, 198.1255.

(*E*)-2-(3-Oxo-4-heptenyl)-1,3-dioxolane (24c). A similar procedure using **21f** (0.12 g, 0.56 mmol), 1,2-ethanediol (0.06 ml, 1.12 mmol), TFA (0.042 ml, 0.56 mmol) in nitromethane (2 ml) at 0 °C for 10 min and subsequent column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) gave **24c** (0.043 g, 42%): Colorless liquid; IR (neat) 1670 and 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (3H, t, J=7.3 Hz, Et), 2.00 (2H, dt, J=7.3 and 4.4 Hz, CH_2), 2.24 (2H, m, Et), 2.69 (2H, t, J=7.3 Hz, CH_2), 3.8—4.0 (4H, m, OCH_2CH_2O), 4.93 (1H, t, J=4.4 Hz, CH), 6.09 (1H, dt, J=16.2 and 1.5 Hz, =CHCO), and 6.90 (1H, dt, J=16.2 and 6.2 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=12.27 (Et), 25.54, (Et), 27.92, 33.81 (each CH_2), 64.98 (OCH_2CH_2O), 103.52 (CH), 129.37, 148.79 (each =CH), and 199.65 (CO); MS m/z (rel intensity, %) 184 (M^+, 11), 85 (23), 82 (32), and 73 (base peak). HRMS Found: m/z 184.1104. Calcd for $C_{10}H_{16}O_3$: M, 184.1099.

(*E,E*)-2-(3-Oxo-7-phenyl-4,6-heptadienyl)-1,3-dioxolane (24d). A similar procedure using **21g** (0.089 g, 0.31 mmol), 1,2-ethanediol (0.033 ml, 0.6 mmol), TFA (0.023 ml, 0.3 mmol) in nitromethane (1.5 ml) at 0 °C for 20 min and subsequent column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) gave **24d** (0.046 g, 58%): Colorless crystals; mp 66—70 °C; IR (KBr) 1654 and 1621 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.05 (2H, dt, J=7.3 and 4.4 Hz, CH_2), 2.74 (2H, t, J=7.3 Hz, CH_2), 3.8—4.1 (4H, m, OCH_2CH_2O), 4.95 (1H, t, J=4.4 Hz, CH), 6.28 (1H, d, J=15.7 Hz, =CHCO), and 6.8—7.5 (8H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=28.02, 34.41 (each CH_2), 64.97 (OCH_2CH_2O), 103.47 (CH), 126.72, 128.82, 129.14, 129.56, 136.02, 141.20, 142.52, and 199.33 (CO); MS m/z (rel intensity, %) 258 (M^+, 12) and 32 (base peak). HRMS Found: m/z 258.1254. Calcd for $C_{16}H_{18}O_3$: M, 258.1254.

2-(5-Methyl-3-oxo-4-hexenyl)-1,3-dioxolane (24e). A similar procedure employing **21h** (0.065 g, 0.3 mmol), 1,2-ethanediol (0.033 ml, 0.6 mmol), TFA (0.023 ml, 0.3 mmol) in nitromethane (1 ml) at 0 °C for 30 min and subsequent column chromatography over silica gel with hexane-ethyl acetate (9 : 1 v/v) provided **24e** (0.037 g, 67%): Colorless liquid; IR (neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88 (3H, d, J=1.1 Hz, Me), 1.97 (2H, dt, J=7.7 and 4.4 Hz, CH_2), 2.14 (3H, d, J=1.1 Hz, Me), 2.55 (2H, t, J=7.7 Hz, CH_2), 3.8—4.0 (4H, m, OCH_2CH_2O), 4.92 (1H, t, J=4.4 Hz, CH), and 6.08 (1H, t, J=1.1 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ=20.71, 27.65 (each Me), 27.98, 38.07 (each CH_2), 64.97 (OCH_2CH_2O), 103.63 (CH), 123.70 (=CH), 155.03 (=CMe_2), and 199.76 (CO); MS m/z (rel intensity, %) 184 (M^+, 8), 86 (23), 82 (base peak), 73 (78), 55 (60), and 53 (20). HRMS Found: m/z 184.1097. Calcd for $C_{10}H_{16}O_3$: M, 184.1099.

(*E*)-3-(2-Oxo-4-phenyl-3-butenyl)-3,4,5,6-tetrahydro-2*H*-pyran-2-ol (25). To a solution of crude **21d** (0.257 g), which had been prepared from **20d** (0.184 g, 0.87 mmol) according to the method mentioned above, were added water (0.031 ml, 1.74 mmol) and TFA (0.066 ml, 0.87 mmol). After 20 min at room temperature, this mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.219 g) was subjected to column chromatography over silica gel with hexane-ethyl acetate (1 : 1 v/v) to provide **25** (0.095 g, 44% based on **20d**) as a 1 : 1 mixture of two inseparable stereoisomers: Colorless liquid; IR (neat) 3400 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.3—1.9 (4H, m), 2.1—2.4 (1H m), 2.64 (1H, dd, J=17.8 and 6.5 Hz), 2.88 (1H, dd, J=17.3 and 6.5 Hz), 2.98 (1H, dd, J=17.3 and 6.5 Hz), 3.5—3.7 (1H, m), 3.9—4.1 (1H, m), 4.45 (0.5H, J=7.7 Hz), 5.11 (0.5H, d, J=2.6 Hz), 6.74 (1H, d, J=16.1 Hz), 6.75 (1H, d, J=16.1 Hz), and 7.2—7.6 (6H, m); ^{13}C NMR ($CDCl_3$) δ=24.42, 24.58, 24.97, 28.49 (each ring CH_2), 35.76, 38.44 (each ring CH), 41.93, 43.02 (each CH_2CO), 60.62, 65.84 (each ring CH_2), 93.77, 99.50 (each ring CH), 126.07, 126.56 (each =CHCO), 128.35, 128.39, 128.96, 130.55, 130.65, 134.35, 134.46, 143.02 (=CH), 143.28 (=CH), 200.06, and 200.12 (each CO); MS m/z (rel intensity, %) 246 (M^+, 23), 159 (28), 147 (41), 146 (20), 131 (base peak), 129 (21), 113 (31), 103 (61), 100 (32), 97 (27), 76 (41), 73 (74), and 43 (41). Found: C, 73.02; H, 7.45. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

(*E*)-2-(2-Hydroxyethoxy)-3-(2-oxo-4-phenyl-3-butenyl)-3,4,5,6-tetrahydro-2*H*-pyran (26). A mixture of crude **21d**, which had been similarly prepared as above from **20d** (0.324 g, 1.52 mmol), 1,2-ethanediol (0.11 ml, 2.4 mmol), and TFA (0.09 ml, 1.2 mmol) in dry nitromethane (6 ml) was stirred at 0 °C for 1 h. This mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.334 g) was chromatographed over silica gel with hexane-ethyl acetate (1 : 1 v/v) to provide *cis*-**26** (0.028 g, 8% based on **20d**) and then *trans*-**26** (0.182 g, 52% based on **20d**). *cis*-**26**: Pale yellow liquid; IR (neat) 3450 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.5—1.8 (4H, m, ring CH_2), 2.3—2.4 (1H, m, ring CH), 2.58 (1H, dd, J=15.8 and 6.6 Hz, $COCH_2$), 2.79 (1H, dd, J=15.8 and 7.7 Hz, $COCH_2$), 2.89 (1H, br s, OH), 3.5—3.9 (6H, m, OCH_2), 4.71 (1H, d, J=3.3 Hz, ring CH), 6.75 (1H, d, J=16.5 Hz, =CHCO), and 7.3—7.6 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=24.79, 24.94 (each ring CH_2), 36.20 (ring CH), 42.71 (CH_2CO), 60.32, 62.14 (OCH_2), 70.16 (ring CH_2), 99.29 (ring CH), 126.30 (=CHCO), 128.36, 128.98, 130.61, 134.42, 143.02 (=CHPh), and 199.65 (CO); MS m/z (rel intensity, %) 290 (M^+, 3), 144 (35), 131 (base peak), 103 (83), 77 (56), and 73 (22). HRMS Found: m/z 290.1525. Calcd for $C_{17}H_{22}O_4$: M, 290.1517. *trans*-**26**: Pale yellow liquid; IR (neat) 3450 and 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—2.3 (5H, m, ring CH_2 and CH), 2.54 (1H, dt, J=15.8 and 6.6 Hz, $COCH_2$), 2.87 (1H, dd, J=15.8 and 7.0 Hz, $COCH_2$), 3.12 (1H, br s, OH), 3.5—4.1 (6H, m, OCH_2 and ring CH_2), 4.25 (1H, d, J=7.0 Hz, ring CH), 6.76 (1H, d, J=16.1 Hz, =CHCO), and 7.4—7.6 (6H, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=24.43, 27.80 (each ring CH_2), 37.52 (ring CH), 43.27 (CH_2CO), 62.11, 65.17 (CH_2O), 71.66 (ring CH_2), 104.85 (ring

CH), 126.06, 128.33, 128.95, 130.54, 134.44, 142.77 (=CH), and 199.49 (CO); MS *m/z* (rel intensity, %) 290 (M^+, 5), 157 (24), 144 (59), 131 (base peak), 103 (52), 101 (25), and 77 (28). HRMS Found: *m/z* 290.1520. Calcd for $C_{17}H_{22}O_4$: M, 290.1517.

(*E*)-2-Ethoxy-3-(2-oxo-4-phenyl-3-butenyl)-3,4,5,6-tetrahydro-2*H*-pyran (27). To a solution of crude **21d**, which had been prepared from **20d** (0.286 g, 1.35 mmol) according to the method mentioned above, and ethanol (0.08 ml, 1.36 mmol) in nitromethane (3 ml) was added TFA (0.052 ml, 0.68 mmol) at 0 °C. After stirring at the same temperature for 15 min, the reaction mixture was poured into saturated aqueous sodium hydrogencarbonate and extracted with dichloromethane (20 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue (0.134 g) was chromatographed over silica gel with hexane-ethyl acetate (20 : 1 v/v) to give *cis*-**27** (0.026 g, 13% based on **20d**) and *trans*-**27** (0.06 g, 33% based on **20d**). *cis*-**27**: Pale yellow crystals; mp 67—71 °C; IR (KBr) 1691 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (3H, t, *J*=7.0 Hz, OEt), 1.5—1.8 (5H, m, ring CH_2 and CH), 2.53 (1H, dd, *J*=16.5 and 7.0 Hz, CH_2CO), 2.79 (1H, dd, *J*=16.5 and 7.0 Hz, CH_2CO), 3.3—3.6 (2H, m, OEt), 3.7—3.8 (2H, m, ring CH_2), 4.68 (1H, d, *J*=2.9 Hz, ring CH), 6.73 (1H, d, *J*=16.1 Hz, =CHCO), and 7.3—7.6 (6H, m, Ph and =CH); MS *m/z* (rel intensity, %) 274 (M^+, 8), 131 (base peak), 128 (91), 103 (53), and 77 (26). HRMS Found: *m/z* 274.1566. Calcd for $C_{17}H_{22}O_3$: M, 274.1568. *trans*-**27**: Pale yellow liquid; IR (neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (3H, t, *J*=7.0 Hz, OEt), 1.2—2.2 (5H, m, ring CH_2 and CH), 2.48 (1H, dd, *J*=15.4 and 8.1 Hz, CH_2CO), 2.98 (1H, dd, *J*=15.4 and 5.5 Hz, CH_2CO), 3.4—3.6 (2H, m, OEt), 3.8—4.0 (2H, m, ring CH_2), 4.25 (1H, d, *J*=6.6 Hz, ring CH), 6.75 (1H, d, *J*=16.1 Hz, =CHCO), and 7.3—7.6 (6H, m, Ph and =CH); ^{13}C NMR ($CDCl_3$) δ=15.16 (OEt), 24.13, 27.03 (each ring CH_2), 36.89 (ring CH), 42.63 (CH_2CO), 63.86, 64.39 (each OCH_2), 103.35 (ring CH), 126.36 (=CHCO), 128.26, 128.92, 130.41, 134.57 (each Ph), 142.50 (=CH), and 199.22 (CO); MS *m/z* (rel intensity, %) 274 (M^+, 7), 141 (24), 131 (63), 128 (base peak), 103 (25), and 77 (25). HRMS Found: *m/z* 274.1564. Calcd for $C_{17}H_{22}O_3$: M, 274.1568.

References

1) O. Tsuge, S. Kanemasa, T. Suzuki, and K. Matsuda, *Bull. Chem. Soc. Jpn.*, **59**, 2851 (1986).

2) As reviews: M. Murakami and S. Nishida, *Yuki Gosei Kagaku Kyokai Shi*, **41**, 22 (1983); D. Tunemoto and K. Kondo, *ibid.*, **35**, 1070 (1977).

3) E. Wenkert and D. A. Berges, *J. Am. Chem. Soc.*, **89**, 2507 (1967); C. U. Pittman, Jr., *ibid.*, **91**, 5915 (1969); F. Sakan, H. Hashimoto, A. Ichihara, H. Shirahama, and T. Matsumoto, *Tetrahedron Lett.*, **1971**, 3703; T. Nakai, E. Wada, and M. Okawara, *ibid.*, **1975**, 1531; D. Caine, A. A. Boucugnani, and W. R. Pennington, *J. Org. Chem.*, **41**, 3632 (1976); J. Yovell, D. Hirsch, and S. Sarel, *ibid.*, **42**, 850 (1977); A. Murai, K. Kato, and T. Masamune, *Tetrahedron Lett.*, **23**, 2887 (1982); W. S. Murphy and K. Hantawong, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 817.

4) T. Hiyama, H. Saimoto, K. Nishio, M. Shinoda, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, **1979**, 2043; Y. Morizawa, T. Hiyama, and H. Nozaki, *ibid.*, **22**, 2297 (1981); R. D. Miller and D. R. McKean, *J. Org. Chem.*, **46**, 2412 (1981); S. P. Brown, B. S. Bal, and H. W. Pinnick, *Tetrahedron Lett.*, **22**, 4891 (1981); R. K. Dieter and S. Pounds, *J. Org. Chem.*, **47**, 3174 (1982).

5) H. W. Pinnick, S. P. Brown, E. A. McLean, and L. W. Zoller, III, *J. Org. Chem.*, **46**, 3760 (1981); T. Nakajima, H. Miyaji, M. Segi, and S. Suga, *Chem. Lett.*, **1986**, 181.

6) L. Pellacani, P. A. Tardella, and M. A. Loreto, *J. Org. Chem.*, **41**, 1282 (1976).

7) W. S. Murphy and S. Wattanasin, *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2920 and references cited therein.

8) P. A. Grieco and R. S. Finkelhor, *Tetrahedron Lett.*, **1974**, 527 and references cited therein.

9) Diazo ketone **2** was prepared in the reaction of (diethoxyphosphoryl) acetyl chloride with dry diazomethane in diethyl ether (O. Tsuge, S. Kanemasa, and T. Otsuka, unpublished results).

10) M. A. Blanchette, W. Choy, J. T. Davis, A. P. Essenfeld, S. Masamune, W. R. Roush, and T. Sakai, *Tetrahedron Lett.*, **25**, 2183 (1984); M. W. Rathke and M. Nowak, *J. Org. Chem.*, **50**, 2624 (1985); T. Rosen and C. H. Heathcock, *J. Am. Chem. Soc.*, **107**, 3731 (1985); O. Tsuge, S. Kanemasa, N. Nakagawa, and H. Suga, *Bull. Chem. Soc. Jpn.*, **60**, 4091 (1987).

11) Polyphosphoric acid trimethylsilyl ester (PPSE) has been used as a strong dehydrating agent which is soluble in most of organic solvent (S. Ogata, A. Mochizuki, M. Kakimoto, and Y. Imai, *Bull. Chem. Soc. Jpn.*, **59**, 2171 (1986) and references cited therein).

12) M. Julia, S. Julia, and R. Guegan, *Bull. Soc. Chim. Fr.*, **1960**, 1072; M. Julia, S. Julia, and S. Y. Tchen, *ibid.*, **1961**, 1849.

13) The MM2 calculation of 2-phenylcyclopropyl ethyl ketone as a model compound of **5a** shows the following total energy for each conformer (R=Et in all cases): For *trans*-2-phenylcyclopropyl ethyl ketone: conformer **B**: 114.2982 kcal mol^{-1} (1 cal=4.184 J); conformer **D**: 114.4617 kcal mol^{-1}. For *cis*-2-phenylcyclopropyl ethyl ketone: conformer **C**: 115.7168 kcal mol^{-1}; conformer **D**: 117.6096 kcal mol^{-1}.

14) Another explanation is possible with a bisected structure model preferred for the resulting cyclopropylcarbinyl cation (D. S. Kabakoff and E. Namanworth, *J. Am. Chem. Soc.*, **92**, 3234 (1970); L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380 (1970)).

15) As similar silyl migrations: R. L. Danheiser, D. J. Carini, and A. Basak, *J. Am. Chem. Soc.*, **103**, 1604 (1981); A. Jellal and M. Santelli, *Tetrahedron Lett.*, **21**, 4487 (1980); A. W. P. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, **1969**, 852.

16) Replacement of the phenyl group on the ring of **5a—d** with an alkyl substituent led to no ring-enlarged product, but mixture of complex products.

17) E. Wenkert, B. L. Buckwalter, A. A. Craveiro, E. L. Sanchez, and S. S. Sathe, *J. Am. Chem. Soc.*, **100**, 1267 (1978); Y. Morizawa, A. Kanakura, H. Yamamoto, T. Hiyama, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **57**, 1935 (1984).

18) S. Kyushin, A. Hosomi, Y. Nakadaira, and H. Sakurai, unpublished results (presented at the 7th International Symposium on Organo Silicon Chemistry (Kyoto), 1984, PT19, preprint p. 221).

19) U. L. Tweedie and B. G. Barron, *J. Org. Chem.*, **25**, 2027 (1960).