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Silicon-Assisted Ring Opening of Cyclopropyl Ketones with Boron Trifluoride–Acetic Acid Complex[1)]

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2-(Trimethylsilylmethyl)cyclopropyl ketones were smoothly cleaved with boron trifluoride–acetic acid complex under mild reaction conditions with the assistance of the trimethylsilyl group to give γ,δ-enones in good yields. The major effect of the trimethylsilyl group in the ring opening of the cyclopropyl ketones was unambiguously confirmed in the dicyclopropyl ketone **15**: one of its two cyclopropyl rings, which has a trimethylsilylmethyl group, was selectively cleaved. Furthermore, the reaction was applied to the formal total synthesis of *cis*-jasmone.

Keywords——ring opening of cyclopropyl ketone; trimethylsilyl group; γ,δ-enone; *cis*-jasmone; allylsilane; boron trifluoride–acetic acid

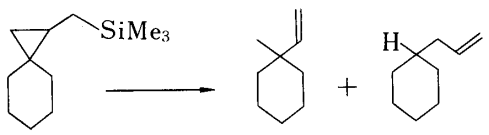
Cyclopropanes are attractive synthetic intermediates because of their ready availability and reactivity.[2)] Cyclopropyl ketones, when reduced with metals in ammonia, undergo reductive cleavage of the cyclopropane ring.[3)] It is also well-known that cyclopropyl ketones are cleaved by a variety of nucleophiles including RS^-, RO^-, R_2CuLi, *etc.*[4)] For the acid-catalyzed cleavage of cyclopropyl ketones, drastic reaction conditions have usually been employed.[4,5)] Our interest in organosilicon chemistry led us to study the effect of a trimethylsilyl group on the ring opening of cyclopropyl ketones.

In a previous communication[6)] we reported that cyclobutyl ketones **2** obtained by the cycloaddition of allylsilanes to photoactivated double bonds, on treatment with boron trifluoride etherate at 0 °C in dichloromethane, gave unsaturated ketones **4** by smooth cleavage of the cyclobutyl ring with the assistance of the trimethylsilyl group. In this report, we describe an extension of this ring opening reaction to the cyclopropyl ketones **1**, providing useful synthetic intermediates, γ,δ-enones **3**, as the products (see Chart 1).

1 : $n=1$, **2** : $n=2$ — **3** : $n=1$, **4** : $n=2$

Chart 1

The zinc chloride-catalyzed elimination of trimethylchlorosilane from trimethylsilylmethyl-substituted *gem*-dihalocyclopropane has been reported to give halogen-substituted 1,3-diene.[7)] A spirocyclopropane derivative **5** has been shown to give a mixture of olefins **6** and **7** on treatment with boron trifluoride and acetic acid.[8)]

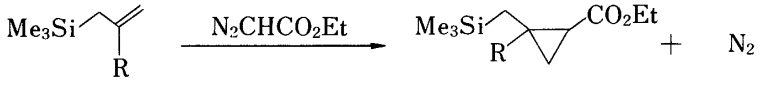


5 **6** **7**

Chart 2

Results and Discussion

Transition metal-catalyzed cyclopropanation of olefins with diazo compounds is one of the most important methods for the synthesis of cyclopropanes.[9] Dyakonov and co-workers[10] reported that allyltrimethylsilane (**8**) on treatment with ethyl diazoacetate in the presence of $CuSO_4$ afforded a mixture of *cis*- and *trans*-isomers (2:3 ratio) of ethyl 2-(trimethylsilylmethyl)cyclopropanecarboxylate (**10**) in 66% yield. For the synthesis of various kinds of cyclopropyl ketones, we have employed the ester **10** as the starting compound.



8 : R=H
9 : R=Me

10 : R=H
11 : R=Me

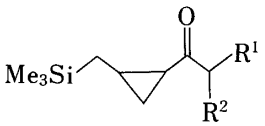
Chart 3

Synthesis of Cyclopropyl Ketones

The ester **10** (a 2:3 mixture of *cis*- and *trans*-isomers) on treatment with 2 eq of the sodium salt[11] of methyl phenyl sulfone gave the β-keto sulfone **12a** in 91% yield. The corresponding methyl sulfone **12b** was prepared by the reaction with the sodium salt of dimethyl sulfone in 43% yield in a similar manner. The ester **10** on treatment with the dilithio derivative of benzyl phenyl sulfone, which was prepared according to the procedure developed by Kondo and Tunemoto,[12] gave the β-keto sulfone **12g** in 56% yield. The sulfone **12a** on methylation with sodium hydride and methyl iodide in dimethyl sulfoxide (DMSO) gave **12c** in 89% yield; **12a** on similar treatment with *n*-amyl iodide afforded the sulfone **12d** in 90% yield. The reductive cleavage[13] of the carbon–sulfur bond of **12d** or **12g** using sodium amalgam gave rise to the ketone **12e** or **12f**, respectively, in good yield.

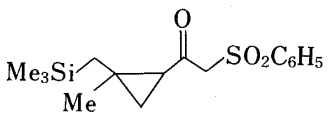
The 2,2-disubstituted cyclopropanecarboxylate **11** (a 1:1 mixture of *cis*- and *trans*-isomers) was prepared quantitatively by the rhodium(II) acetate-catalyzed cyclopropanation[14] of the allylsilane **9** with ethyl diazoacetate, and treated with the sodium salt of methyl phenyl sulfone to give the β-keto sulfone **13**, which was very unstable and was used without further purification.

The biscyclopropyl ketone **15** was prepared by the reductive desulfurization of the sulfone **14**, with sodium amalgam. Compound **14** was derived from **12a** through treatment



12a–g

a : R^1=H, R^2=$SO_2C_6H_5$
b : R^1=H, R^2=SO_2Me
c : R^1=Me, R^2=$SO_2C_6H_5$
d : R^1=n-C_5H_{11}, R^2=$SO_2C_6H_5$
e : R^1=n-C_5H_{11}, R^2=H
f : R^1=C_6H_5, R^2=H
g : R^1=C_6H_5, R^2=$SO_2C_6H_5$



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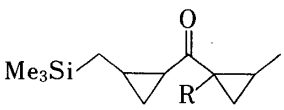
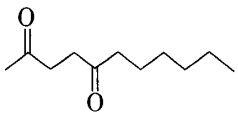


14 : R=$SO_2C_6H_5$
15 : R=H



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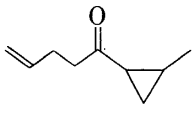


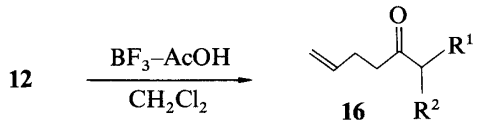
22

with potassium carbonate and 1,2-dibromopropane in dimethylformamide (DMF)[15] (overall yield of **15** from **12a**: 24%).

Ring Opening of Cyclopropyl Ketones

As expected, the acid-catalyzed ring opening of 2-(trimethylsilylmethyl)cyclopropyl ketones proceeded smoothly under mild reaction conditions. On treatment with 3.5 eq of boron trifluoride–acetic acid complex in dichloromethane at 0 °C for 20 min, the ketone **12e** gave the γ,δ-enone **16e** in 79% yield. The structure of **16e** was confirmed by its conversion into the known 1,4-diketone **17**,[16] a precursor of dihydrojasmone, by palladium-catalyzed oxidation.[17] In a similar manner, various kinds of cyclopropyl ketones **12** were cleaved smoothly with the assistance of the trimethylsilyl group. The results are summarized in Table I. The reaction was also shown to proceed by using a catalytic amount of boron trifluoride–acetic acid complex (Table I, Run 2).

TABLE I. Ring Opening of Cyclopropyl Ketones **12** Using Boron Trifluoride–Acetic Acid in Dichloromethane



Run	Cyclopropyl ketone **12**	Reaction conditions[a]	γ,δ-Enone	**16**	Yield[b] %
1	**12a**	0 °C, 20 min	$R^1=H$, $R^2=SO_2C_6H_5$	**16a**	67
2	**12a**	0 °C, 12 h[c]	**16a**		92
3	**12b**	0 °C, 20 min	$R^1=H$, $R^2=SO_2Me$	**16b**	72
4	**12c**	0 °C, 20 min	$R^1=Me$, $R^2=SO_2C_6H_5$	**16c**	84
5	**12d**	0 °C, 20 min	$R^1=n\text{-}C_5H_{11}$, $R^2=SO_2C_6H_5$	**16d**	97
6	**12e**	0 °C, 20 min	$R^1=n\text{-}C_5H_{11}$, $R^2=H$	**16e**	79
7	**12f**	0 °C, 20 min[d]	$R^1=C_6H_5$, $R^2=H$	**16f**	81

a) 3.5 eq of boron trifluoride–acetic acid complex were used unless otherwise noted.
b) Isolated yield.
c) 0.3 eq of boron trifluoride–acetic acid complex was used.
d) Chloroform was used as the solvent.

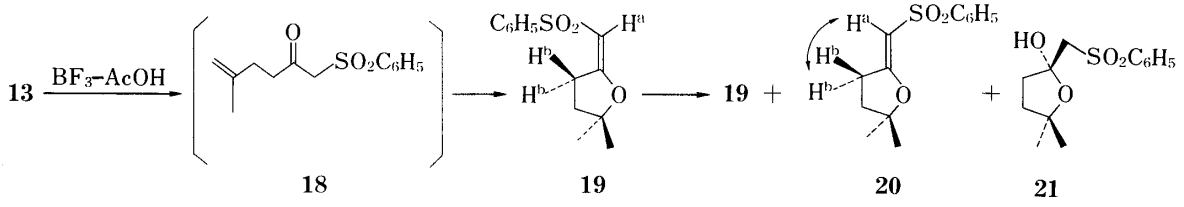


Chart 4

Acid-catalyzed ring opening of a crude mixture of stereoisomers of the ketone **13**, which is very unstable because of serious steric strain between the acyl substituent and the methyl or trimethylsilylmethyl group in the *cis* relationship, afforded the cyclic enol ether **19** in 54% overall yield from the ester **11**. The formation of the ether **19** can be reasonably explained by the reaction sequence shown in Chart 4: recyclization of the ring opening product **18** occurs *via* the oxygen atom of the enolic form of the β-keto sulfone in a fashion similar to the selenium-mediated cyclization of alkenyl-substituted β-ketoesters.[18] On standing in a refrigerator for about 2 months, the cyclic ether **19** was partially isomerized to yield a mixture of compounds **19**, **20**, and **21**. The stereochemistry of the cyclic ethers **19** and **20** was deduced

from the differences of the chemical shifts of their H^a and H^b protons (see the experimental section) and confirmed by comparison of the nuclear Overhauser effect (NOE): a 13% NOE of the vinylic proton H^a of **20** was observed on irradiation of the H^b protons, while no such NOE was observed in compound **19**.

The large contribution of the trimethylsilyl group to ring opening of the cyclopropyl ketones was unambiguously confirmed by the following evidence. The biscyclopropyl ketone **15** on treatment with boron trifluoride–acetic acid at 0 °C gave a 1 : 1 epimeric mixture of the unsaturated ketone **22** in good yield; a selective cleavage of the cyclopropyl ring bearing the trimethylsilyl group was observed.

In contrast to the facile ring opening of the ketones **12**, the ester **10** was recovered unchanged after treatment with boron trifluoride–acetic acid in dichloromethane at room temperature, but isomerization to the thermodynamically more stable *trans*-**10** was observed in dichloromethane under reflux. On the other hand, the cyclopropyl ring of the ester **11** was smoothly cleaved on treatment with boron trifluoride–acetic acid in refluxing dichloromethane to afford a γ-lactone **25** in good yield. The lactone **25** was presumably produced *via* formation of the ring opening product **23** followed by its conversion to an oxonium ion such as **24** (Chart 5).

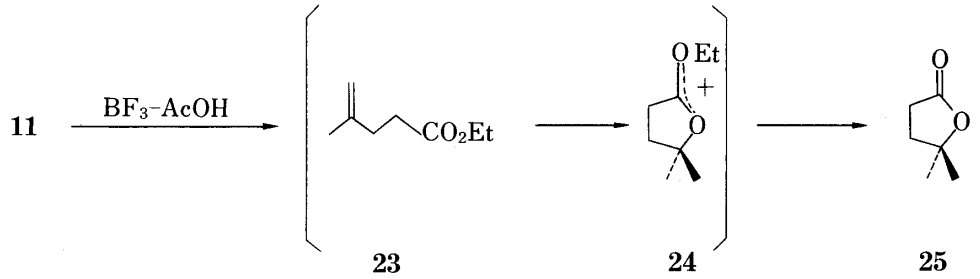


Chart 5

Formal Total Synthesis of *cis*-Jasmone

As a synthetic application of the ring cleavage reaction assisted by the trimethylsilyl group, the diketone **28**, which has been converted to *cis*-jasmone,[19] was synthesized. Compound **10** on treatment with the dilithio derivative of *cis*-3-hexen-1-yl phenyl sulfone[19] in tetrahydrofuran afforded the β-keto sulfone **26** in 68% yield, the ring opening of which was easily achieved to give the unsaturated ketone **27** in 97% yield. Palladium-catalyzed oxidation of **27** afforded the desired diketone **28** in good yield (Chart 6).

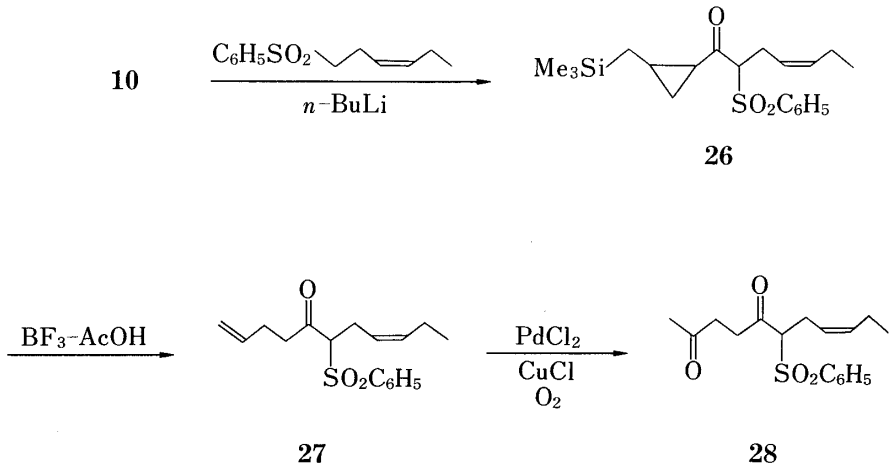


Chart 6

Experimental

Infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer. ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) and ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectra were obtained with a JEOL JNM-FX100 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a JEOL JMS-0ISG double-focusing mass spectrometer. Analytical gas chromatography was performed on a Shimadzu GC-4CM gas chromatograph with a column of 20% Silicone DC-200 on Celite 545 or 20% Silicone GE SF-96 on Chromosorb W. Preparative gas chromatography was performed on a Varian Aerograph model 920 gas chromatograph with a column of 10% Silicone DC-200 on Chromosorb W. Silica gel column chromatography was performed on Kieselgel 60 (Merck). Preparative thin-layer chromatography (TLC) was carried out on Kieselgel 60 F254 (Merck).

Materials——Allyltrimethylsilane (**8**) is commercially available (Shin-Etsu Silicon Chem.). 2-Methyl-2-propenyltrimethylsilane (**9**) was prepared from 2-methyl-2-propenylmagnesium chloride and trimethylchlorosilane in tetrahydrofuran (THF).

Ethyl 2-(Trimethylsilylmethyl)cyclopropanecarboxylate (10)——According to the procedure described in the literature,[10] a 2 : 3 mixture of *cis*- and *trans*-isomers of the ester **10** was prepared. The ratio was determined from the methyl signals of the trimethylsilyl groups in the ^{1}H-NMR spectrum ($CDCl_3$): they appeared at δ 0.02 for *cis*-**10** and 0.04 for *trans*-**10**. *cis*-**10**: ^{13}C-NMR ($CDCl_3$) δ: 172.5 (s), 60.1 (t), 19.0, 18.0 (each d), 14.9 (t), 14.3, 13.9, −1.5 (q). *trans*-**10**: ^{13}C-NMR ($CDCl_3$) δ: 174.1 (s), 60.1 (t), 22.0 (d), 21.0 (t), 19.0 (d), 17.2 (t), 14.3, −1.5 (each q).

2-(Trimethylsilylmethyl)-1-(1-oxo-2-phenylsulfonylethyl)cyclopropane (12a)——A solution of methyl phenyl sulfone (1.56 g, 10 mmol) in DMSO (2.5 ml) and 1,2-dimethoxyethane (DME) (5 ml) was added to sodium hydride (0.24 g, 10 mmol) under nitrogen and the mixture was heated at 65 °C for 1 h. Then a solution of the ester **10** (1 g, 5 mmol) in DME (4 ml) was added. The mixture was heated at 65 °C for 1.5 h. The reaction mixture was quenched with aqueous ammonium chloride solution and extracted with dichloromethane. The organic layer was washed with water and dried. Evaporation left an oil, which was chromatographed on a silica gel column (Merck, Silica-gel 60) using hexane–ethyl acetate (8 : 2) to give a mixture of stereoisomers of the β-keto sulfone **12a** (1.4 g, 91%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1330, 1160, 1070, 840. MS *m/e*: 310 (M^+), 295, 199, 168, 153, 135, 75 (base peak), 73. High resolution MS: Found 310.1035. Calcd for $C_{15}H_{22}O_3SSi$ (M^+) 310.1058. ^{1}H-NMR ($CDCl_3$) δ: 0.0, 0.03 (total 9H, each s), 0.2—1.8 (5H, m), 1.9—2.5 (1H, m), 4.26 (2H), 7.4—7.7 (3H, m), 7.8—8.0 (2H, m). ^{13}C-NMR ($CDCl_3$) δ: 196.8, 195.3, 138.8, 138.6 (each s), 133.8, 128.9, 127.9 (each d), 68.5, 68.0 (each t), 32.1, 28.5, 26.1, 25.3 (each d), 22.3, 21.4, 18.6, 13.2 (each t), 1.6 (q).

2-(Trimethylsilylmethyl)-1-(1-oxo-2-methylsulfonylethyl)cyclopropane (12b)——The ester **10** (400 mg, 2 mmol) was converted to a mixture of stereoisomers of the β-keto sulfone **12b** (211 mg, 43%) using sodium hydride (96 mg, 4 mmol), dimethyl sulfone (376 mg, 4 mmol), and DMSO (1.3 ml) by the same method as described for the synthesis of **12a**. **12b**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1320, 1040, 840. MS *m/e*: 233, 168, 153, 137, 75 (base peak), 73. ^{1}H-NMR ($CDCl_3$) δ: 0.04 (9H, s), 0.3—1.8 (5H, m), 1.8—2.5 (1H, m), 3.0 (3H, s), 4.13 (2H, s). ^{13}C-NMR ($CDCl_3$) δ: 198.1, 196.6 (each s), 66.4, 65.4 (each t), 41.5 (q), 32.5, 28.9, 26.0, 25.5 (each d), 22.1, 21.4, 18.5, 13.3 (each t), 1.6 (q). *Anal.* Calcd for $C_{10}H_{20}O_3SSi$: C, 48.35; H, 8.12. Found: C, 48.01; H, 8.29.

2-(Trimethylsilylmethyl)-1-(1-oxo-2-phenylsulfonylpropyl)cyclopropane (12c)——A mixture of the sulfone **12a** (80 mg, 0.258 mmol) and sodium hydride (6.2 mg, 0.258 mmol) in DMSO (1.5 ml) was stirred at room temperature for 1 h under nitrogen. After the addition of methyl iodide (40 mg, 0.283 mmol) to the resulting yellow solution, the mixture was stirred at room temperature for 1 h, quenched with aqueous ammonium chloride solution, and then extracted with dichloromethane. The organic layer was washed with water and dried. Evaporation left an oil, which was purified by preparative TLC (hexane–ethyl acetate (3 : 1)) to afford a mixture of stereoisomers of the sulfone **12c** (75 mg, 89%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1315, 1150, 1050, 840. MS *m/e*: 324 (M^+), 309, 260, 183, 73 (base peak). High resolution MS: Found 324.1219. Calcd for $C_{16}H_{24}O_3SSi$ (M^+) 324.1214. ^{1}H-NMR ($CDCl_3$) δ: 0.0, 0.04, 0.06 (total 9H, each s), 0.2—1.6 (8H, m), 1.9—2.7 (1H, m), 4.0—4.5 (1H, m), 7.4—7.7 (3H, m), 7.7—8.0 (2H, m).

2-(Trimethylsilylmethyl)-1-(1-oxo-2-phenylsulfonylheptyl)cyclopropane (12d)——The sulfone **12a** (150 mg, 0.483 mmol) was converted to a mixture of stereoisomers of **12d** (166 mg, 90%) using sodium hydride (12 mg, 0.5 mmol), pentyl iodide (105 mg, 0.53 mmol), and DMSO (3 ml) by the same method as described for the synthesis of **12c**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1310, 1150, 840. MS *m/e*: 380 (M^+), 365, 239, 73 (base peak). High resolution MS: Found 380.1834. Calcd for $C_{20}H_{32}O_3SSi$ (M^+) 380.1839. ^{1}H-NMR ($CDCl_3$) δ: 0.01, 0.03, 0.04, (total 9H, each s), 0.2—2.5 (17H, m), 3.9—4.4 (1H, m), 7.4—8.0 (5H, m).

2-(Trimethylsilylmethyl)-1-(1-oxoheptyl)cyclopropane (12e)——Sodium amalgam (5%, 323 mg) was added at 0 °C to a solution of the sulfone **12d** (82 mg, 0.215 mmol) and anhydrous disodium hydrogen phosphate (122 mg, 0.862 mmol) in dry methanol (5 ml), and the mixture was stirred at 0 °C for 1 h and then at room temperature for 16 h. The mixture was poured into water and extracted with ether. After the usual work-up, a crude product was purified by preparative TLC (hexane–ethyl acetate (4 : 1)) to give the ketone **12e** (48 mg, 92%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1210, 845. MS *m/e*: 240 (M^+), 225, 183, 170, 155, 73 (base peak). High resolution MS: Found 240.1899. Calcd for $C_{14}H_{28}OSi$ (M^+) 240.1906. ^{1}H-NMR ($CDCl_3$) δ: 0.02, 0.03 (total 9H, each s), 0.2—2.2 (17H, m), 2.5 (2H, t, J = 7 Hz).

2-(Trimethylsilylmethyl)-1-(1-oxo-2-phenylethyl)cyclopropane (12f)——Butyllithium (1.6 M in hexane) (0.625 ml, 1 mmol) was added to a stirred solution of benzyl phenyl sulfone (116 mg, 0.5 mmol) in THF (1 ml) containing tetramethylethylenediamine (TMEDA) (116 mg, 1 mmol) at −78 °C under nitrogen, and the solution was stirred for 1 h at the same temperature. The resulting dianion solution was added to a cooled (−78 °C) solution of **10** (100 mg, 0.5 mmol) in THF (1 ml) and hexamethylphosphoric triamide (HMPA) (0.2 ml). After being stirred for 1 h at −78 °C and for an additional 5 h at room temperature, the reaction mixture was quenched with an aqueous solution of ammonium chloride and extracted with ether. A usual work-up left an oil, which was separated by preparative TLC (hexane–ethyl acetate (8 : 2)) to afford the desired sulfone **12g** (108 mg, 56%) (with recovery of 43 mg of the ester **10**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1320, 1310, 1150, 1070, 850. MS *m/e*: 386 (M^+), 371, 304, 295, 245, 155, 110, 91, 75 (base peak), 73. High resolution MS: Found 371.1098. Calcd for $C_{20}H_{23}O_3SSi$ (M^+ − Me) 371.1126. ^{1}H-NMR ($CDCl_3$) δ: −0.09, 0.01 (total 9H, each s), 0.2—2.0 (6H, m), 5.32 (1H, s), 7.2—7.8 (10H, m). The sulfone **12g** (8 mg, 0.02 mmol) was converted to the ketone **12f** (4.7 mg, 96%) using sodium amalgam (5%, 30 mg) and anhydrous disodium hydrogen phosphate (11.3 mg, 0.08 mmol) by a method similar to that described for the synthesis of **12e**. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680, 1040, 850. MS *m/e*: 246 (M^+), 231, 217, 177, 155, 73 (base peak). High resolution MS: Found 246.1475. Calcd for $C_{15}H_{22}OSi$ (M^+) 246.1440. ^{1}H-NMR ($CDCl_3$) δ: −0.01 (9H, s), 0.2—1.8 (6H, m), 3.80 (2H, s), 7.0—7.5 (5H, m).

2-Methyl-2-(trimethylsilylmethyl)-1-(1-oxo-2-phenylsulfonylethyl)cyclopropane (13)——According to the procedure of Doyle,[14] 2-methyl-2-propenyltrimethylsilane (**9**) (2.1 g, 16.4 mmol) was converted to the ester **11** in quantitative yield using ethyl diazoacetate (3.74 g, 32.8 mmol) and rhodium(II) acetate (73 mg, 0.164 mmol). Analytical gas chromatography showed the presence of stereoisomers in a ratio of 1 : 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1170, 840, 720. MS *m/e*: 214 (M^+), 199, 96, 73 (base peak). High resolution MS: Found 214.1391. Calcd for $C_{11}H_{22}O_2Si$ (M^+) 214.1390. ^{1}H-NMR ($CDCl_3$) δ: 0.04, 0.06 (total 9H, each s), 0.7—1.7 (11H), 4.14 (2H, q, J=4 Hz). The ester **11** (500 mg, 2.33 mmol) was condensed with the sodium salt of methyl phenyl sulfone (4.66 mmol) by a method similar to that described for the synthesis of **12a**, giving a crude β-keto sulfone **13** (1.283 g). The compound was found to be very unstable and was used without further purification.

2-Methylcyclopropyl 2′-Trimethylsilylmethylcyclopropyl Ketone (15)——1,2-Dibromopropane (1.73 g, 8.56 mmol) was added to a stirred mixture of the sulfone **12a** (1.33 g, 4.28 mmol) and potassium carbonate (1.42 g, 10.27 mmol) in DMF (15 ml) under nitrogen and the mixture was heated at 100 °C for 31 h. The reaction mixture was poured into an aqueous ammonium chloride solution and extracted with ether. After the usual work-up, the crude product was chromatographed on silica gel with hexane–ethyl acetate (8 : 2) to give a mixture of stereoisomers of **14** (792 mg), which was contaminated with a small amount of impurity. **14**: MS *m/e*: 350 (M^+), 335, 271, 208, 181, 73 (base peak). High resolution MS: Found 335.1130. Calcd for $C_{17}H_{23}O_3SSi$ (M^+ − Me) 335.1136. The reductive desulfonylation of **14** (600 mg) afforded the ketone **15** (166 mg) by a method similar to that described for the synthesis of **12e**. **15**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1675, 1250, 1100, 840. MS *m/e*: 210 (M^+), 195, 181, 105, 75, 73, 55, 45 (base peak). High resolution MS: Found 210.1427. Calcd for $C_{12}H_{22}OSi$ (M^+) 210.1439. ^{1}H-NMR ($CDCl_3$) δ: 0.03 (9H, s), 0.4—2.3 (13H, m).

General Procedure for Ring Opening of Cyclopropyl Ketones 12——Boron trifluoride–acetic acid complex (0.35 mmol) was added dropwise to a stirred solution of **12** (0.1 mmol) in dry dichloromethane (2 ml) at 0 °C under nitrogen. The mixture was stirred under the conditions described in Table I. After the addition of an aqueous solution of ammonium chloride, the reaction mixture was extracted with ether. The organic layer was washed with water and dried. Evaporation left an oil, which was purified by silica gel column chromatography or by preparative TLC to afford the γ,δ-enone **16**.

1-Phenylsulfonyl-5-hexen-2-one (16a)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1325, 1155, 1050. MS *m/e*: 238 (M^+), 183, 141, 96 (base peak), 77. High resolution MS: Found 238.0656. Calcd for $C_{12}H_{14}O_3S$ (M^+) 238.0661. ^{1}H-NMR ($CDCl_3$) δ: 2.3 (2H, q, J=7 Hz), 2.81 (2H, t, J=7 Hz), 4.12 (2H, s), 4.8—5.2 (2H, m), 5.5—6.0 (1H, m), 7.4—7.7 (3H, m), 7.7—8.0 (2H, m).

1-Methylsulfonyl-5-hexen-2-one (16b)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1640, 1320, 1150, 970, 920. MS *m/e*: 176 (M^+), 121, 96 (base peak), 79. High resolution MS: Found 177.0547. Calcd for $C_7H_{13}O_3S$ (M^+ + 1) 177.0585. ^{1}H-NMR ($CDCl_3$) δ: 2.37 (2H, q, J=7 Hz), 2.83 (2H, t, J=7 Hz), 3.05 (3H, s), 4.05 (2H, s), 4.9—5.2 (2H, m), 5.6—6.1 (1H, m).

2-Phenylsulfonyl-6-hepten-3-one (16c)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1640, 1310, 1150, 995, 915. MS *m/e*: 252 (M^+), 197, 184, 170, 141, 110, 77 (base peak). High resolution MS: Found 252.0813. Calcd for $C_{13}H_{16}O_3S$ (M^+) 252.0818. ^{1}H-NMR ($CDCl_3$) δ: 1.40 (3H, d, J=7 Hz), 2.34 (2H, q, J=7 Hz), 2.5—3.3 (2H, m), 4.22 (1H, q, J=7 Hz), 4.9—5.2 (2H, m), 5.6—6.1 (1H, m), 7.5—8.0 (5H, m).

6-Phenylsulfonyl-1-undecen-5-one (16d)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1645, 1310, 1125, 915. MS *m/e*: 308 (M^+), 253, 225, 166, 83, 77, 55 (base peak). High resolution MS: Found 308.1448. Calcd for $C_{17}H_{24}O_3S$ (M^+) 308.1447. ^{1}H-NMR ($CDCl_3$) δ: 0.7—1.0 (3H), 1.0—1.4 (6H), 1.7—2.1 (2H, m), 2.1—2.5 (2H, m), 2.5—3.2 (2H, m), 4.08 (1H, t, J=7 Hz), 4.8—5.2 (2H, m), 5.5—6.0 (1H, m), 7.3—7.9 (5H, m).

1-Undecen-5-one (16e)[20]——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705, 1640, 1200, 910. MS *m/e*: 168 (M^+), 167, 71, 57, 44 (base peak). ^{1}H-NMR ($CDCl_3$) δ: 0.7—1.0 (3H), 1.0—2.0 (8H), 2.1—2.6 (6H, m), 4.8—5.2 (2H, m), 5.5—6.1 (1H, m).

1-Phenyl-5-hexen-2-one (16f)——IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1640, 1050, 915. MS *m/e*: 174 (M^+), 155, 119, 91, 83, 55 (base peak). High resolution MS: Found 174.1077. Calcd for $C_{12}H_{14}O$ (M^+) 174.1045. ^{1}H-NMR ($CDCl_3$) δ: 2.1—2.4

(2H, m), 2.4—2.7 (2H, m), 3.67 (2H, s), 4.8—5.2 (2H, m), 5.5—6.0 (1H, m), 7.1—7.5 (5H, m).

Undecan-2,5-dione (17)[16]——According to the procedure developed by Tsuji,[17] the γ,δ-enone **16e** (8 mg, 0.048 mmol) was converted to the diketone **17** in quantitative yield by the palladium-catalyzed oxidation reaction. **17**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710. MS *m/e*: 184 (M^+), 141., 127, 114 (base peak), 99, 71. High resolution MS: Found 184.1470. Calcd for $C_{11}H_{20}O_2$ (M^+) 184.1464. ^{1}H-NMR ($CDCl_3$) δ: 2.2 (3H, s), 2.46 (2H, t, J=7 Hz), 2.69 (4H, s).

Ring Opening of the Ketone 13——Boron trifluoride–acetic acid complex (491 mg, 3 mmol) was added dropwise to a solution of the crude ketone **13** (448 mg) in dry dichloromethane (3 ml) at −78 °C under nitrogen, and the mixture was warmed to 0 °C. After being stirred for 20 min at 0 °C, the mixture was poured into an aqueous solution of sodium hydrogen carbonate, and extracted with ether. After the usual work-up, preparative TLC (hexane–ethyl acetate (7 : 3)) afforded the ether **19** (110 mg, 54% overall yield from **11**). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1615, 1605, 1310, 1135, 1085. MS *m/e*: 252 (M^+), 183, 141, 111, 93, 77 (base peak). High resolution MS: Found 252.0815. Calcd for $C_{13}H_{16}O_3S$ (M^+) 252.0820. ^{1}H-NMR ($CDCl_3$) δ: 1.35 (6H, s), 1.91 (2H, t, J=8 Hz), 3.22 (2H, dt, J=2, 8 Hz), 5.64 (1H, t, J=2 Hz), 7.3—7.6 (3H, m), 7.7—7.9 (2H, m). The ether **19** was found to be an unstable compound: on standing in a refrigerator for about 2 months, **19** (35 mg) was partially isomerized to give **19** (7 mg), **20** (4 mg), and **21** (22 mg), **20**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1625, 1305, 1135, 1085, 960, 850. MS *m/e*: 252 (M^+), 183, 141, 111, 93, 77 (base peak). High resolution MS: Found 252.0790. Calcd for $C_{13}H_{16}O_3S$ (M^+) 252.0820. ^{1}H-NMR ($CDCl_3$) δ: 1.28 (6H, s), 1.81 (2H, t, J=8 Hz), 2.75 (2H, dt, J=1.5, 8 Hz), 5.38 (1H, t, J=1.5 Hz), 7.3—7.6 (3H, m), 7.7—8.0 (2H, m). **21**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3520, 1310, 1130, 1040, 990. MS *m/e*: 270 (M^+), 255, 252, 237, 156, 141, 99, 94, 77 (base peak), 51. High resolution MS: Found 270.0904. Calcd for $C_{13}H_{18}O_4S$ (M^+) 270.0926. ^{1}H-NMR ($CDCl_3$) δ: 0.79 (3H, s), 1.23 (3H, s), 1.5—2.3 (4H, m), 3.48 (2H, s), 7.4—7.7 (3H, m), 7.8—8.0 (2H, m).

Selective Ring Opening of the Ketone 15——According to the general procedure for ring opening of **12**, the dicyclopropyl ketone **15** (18 mg, 0.086 mmol) was treated with boron trifluoride–acetic acid complex (38 mg, 0.25 mmol) at 0 °C for 30 min. Analytical gas chromatography showed the formation of the γ,δ-enone **22** in quantitative yield. A pure sample of **22** was obtained by preparative TLC (hexane–ethyl acetate (7 : 3)). **22**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1640, 1080, 915. MS *m/e*: 138 (M^+), 123, 110, 109, 83, 55, 32, 28 (base peak). High resolution MS: Found 138.1033. Calcd for $C_9H_{14}O$ (M^+) 138.1044. ^{1}H-NMR ($CDCl_3$) δ: 1.06, 1.11, (total 3H, each d, J=5 Hz) 2.2—2.5 (2H, m), 2.5—2.8 (2H, m), 4.9—5.2 (2H, m), 5.6—6.1 (1H, m). The signals of δ 1.06 and 1.11 were assigned to the methyl groups of *cis*- and *trans*-isomers of **22** respectively, by comparison with the ^{1}H-NMR data for the saturated counterpart of **22**.[21]

Ring Opening of the Ester 11——According to the general procedure for ring opening, **11** (94 mg, 0.44 mmol) was treated with boron trifluoride–acetic acid complex (189 mg, 1.24 mmol) in dichloromethane (2 ml) for 3 h at room temperature, then for 9 h at reflux. Analytical gas chromatography indicated an 84% yield of isocaprolactone (**25**).[22] A pure sample was isolated by preparative gas chromatography. **25**: ^{1}H-NMR ($CDCl_3$) δ: 1.44 (6H, s), 2.08 (2H, t, J=8 Hz), 2.64 (2H, t, J=8 Hz).

The Unsaturated β-Keto Sulfone 26——The ester **10** (150 mg, 0.75 mmol) was converted to the sulfone **26** (211 mg, 68%) by using *cis*-3-hexen-1-yl phenyl sulfone (184 mg, 0.825 mmol),[19] butyllithium (1.6 M in hexane) (1.03 ml, 1.65 mmol), TMEDA (191 mg, 1.65 mmol), and HMPA (0.3 ml) by the same method as described for the synthesis of **12f**. **26**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690, 1310, 1150, 1080, 845. MS *m/e*: 378 (M^+), 363, 311, 295, 279, 237, 73 (base peak). High resolution MS: Found 363.1445. Calcd for $C_{19}H_{27}O_3SSi$ (M^+ − Me) 363.1450. ^{1}H-NMR ($CDCl_3$) δ: 0.0, 0.02, 0.03, 0.04 (total 9H, each s), 0.90 (3H, t, J=8 Hz), 2.5—2.9 (2H, m), 4.0—4.3 (1H, m), 4.9—5.6 (2H, m), 7.4—7.7 (3H, m), 7.7—7.9 (2H, m).

***cis*-6-Phenylsulfonylundeca-1,8-dien-5-one (27)**——Ring opening of **26** (129 mg, 0.34 mmol) afforded the diene **27** (102 mg, 97%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1640, 1310, 1145, 915. MS *m/e*: 306 (M^+), 239, 165, 135, 109, 77, 55 (base peak). High resolution MS: Found 306.1245. Calcd for $C_{17}H_{22}O_3S$ (M^+) 306.1289. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=8 Hz), 1.7—3.1 (8H), 4.08 (1H, dd, J=7, 8 Hz), 4.9—5.2 (3H, m), 5.3—6.0 (2H, m), 7.4—7.9 (5H, m).

***cis*-6-Phenylsulfonyl-8-undecen-2,5-dione (28)**——According to the procedure of Tsuji,[17] the diene **27** (86 mg, 0.28 mmol) was converted to the diketone **28** (70mg, 77%) by the palladium-catalyzed oxidation reaction. **28**: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1625, 1310, 1145, 1075. MS *m/e*: 322 (M^+), 304, 291, 279, 255, 237, 181, 151, 99 (base peak). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=8 Hz), 1.7—2.1 (2H), 2.12 (3H, s), 2.4—3.2 (6H, m), 4.13 (1H, dd, J=7, 8 Hz), 4.9—5.7 (2H, m), 7.4—8.0 (5H, m).

References and Notes

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