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Reactions of Enolates with Vinyl Selenoxides and Vinyl Selenones. One-step Synthesis of Cyclopropylcarbonyl Compounds

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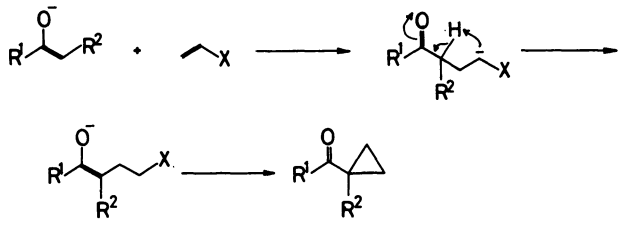
In the reactions with enolate anions, organoselenium moieties of aryl vinyl selenoxides and selenones have exhibited two important roles, *e.g.*, activation of C=C bonds for conjugate addition reaction and behaviors as excellent leaving groups. Owing to such characteristic features, ketone enolates react with *p*-chlorophenyl vinyl selenoxide to afford the corresponding cyclopropyl ketones through an initial conjugate addition followed by substitution processes. On the other hand, use of vinyl selenones usually gives much better results with anionic species of active methylene compounds. Vinyl selenones bearing hydroxyl, ketone, and ester groups can also be employed equally well for this type of transformation.

Cyclopropylcarbonyl compounds have recently received much attention because of their versatility in synthetic organic reactions.[1,2] Reactive conjugate receptors in which electron-withdrawing activator **X** also acts as a good leaving group may be used as versatile ethylene transfer reagents for enolates (dibasic nucleophiles) to yield the corresponding cyclopropyl ketones as shown in Scheme 1. Relatively few examples of reactions of this type are known. Gosselck and his collaborators reported the formation of cyclopropanes in the reaction of active methylene compounds with substituted dimethylvinylsulfonium salts.[3] Johnson and Lockard observed the cyclopropane ring formation in the reaction between [(dimethylamino)phenyl](2-phenylvinyl)oxosulfonium tetrafluoroborate and active methylene compounds.[4] More recently it was reported that the reaction of lithium enolate of acetophenone with dimethylvinylsulfonium perchlorate gave the corresponding cyclopropyl ketones.[5]



Scheme 1.

However, these procedures have only limited applicability due to the difficulty encountered for the preparation of vinylsulfonium salts and to the fact that only active methylene compounds are employable for the former two examples. In the latter case only acetophenone meets with success. It is, therefore, desirable to develop an easy and reliable ethylene transfer methodology to a variety of carbonyl compounds.

A few years ago, we began to study on use of vinyl selenoxide or vinyl selenones for such kind of organic transformations. In contrast to studies on the reactivities of vinyl sulfoxides,[6] those on vinyl selenoxides have limited numbers of investigation,[7] because alkyl aryl selenoxides are in usual quite unstable if they bear β-hydrogens. A well-documented *syn*-elimination of selenoxides always takes place at low temperature in such case, leading to the formation of olefins.[8,9] Selenoxides become relatively stable when there is no β-hydrogen available or areneseleninyl groups are attached to sp^2 or sp hybridized carbons.[7a,10] Further it has been reported that selenoxides are more polar and more basic than sulfoxides are.[11] In this regard, vinyl selenoxides appear to be more reactive than vinyl sulfoxides toward nucleophiles.

In this paper, we describe our results for the preparation of cyclopropylcarbonyl compound in full details by using organoselenium compounds.[12,13]

Results and Discussion

Although to date no reports deal with S_N2 type substitution of areneseleninyl groups, the weak C–Se bonds appear to make this type transformation feasible, which will lead to an introduction of a new functional group to the carbon bearing areneseleninyl group. In light of polar character of selenoxides[11] coupled with weak C–Se bonds, it is then expected that when **X** in Scheme 1 is displaced with areneseleninyl group, a cyclopropane ring may be formed through conjugate addition followed by substitution in the reaction between ketone enolates and aryl vinyl selenoxides.

Aryl vinyl selenoxides are readily prepared by oxidation of the corresponding aryl vinyl selenides with either 1 equiv of *m*-CPBA or sodium periodate.[7a] For the preparation of the starting materials, aryl vinyl selenides, two methods are now available[7a,14,15]: One involves an addition of an areneselenenyl halide to olefins followed by elimination of hydrogen halide with an appropriate base, and the other is the transformation from selenoacetals obtained from aldehydes and areneselenol.

Treatment of 1-dodecenyl phenyl selenoxide thus obtained with sodium diethyl malonate indeed gave rise to the 1,1-cyclopropanedicarboxylic ester in 47% yield.

It has been reported that the reaction of sodium diethyl malonate to tolyl vinyl sulfoxide proceeds in refluxing tetrahydrofuran (THF) to afford the addition product (not the cyclopropane derivative).[6] In strong contrast to the sulfoxide, vinyl selenoxides seem to be much more reactive toward this nucleophile, and the reaction proceeds at as low as −20°C.

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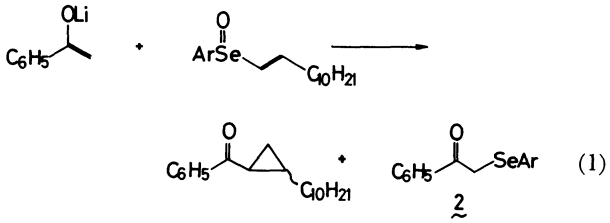
The reaction of the selenoxide with lithium enolate of acetophenone gave the cyclopropyl ketone **1** in much higher yield than the case with diethyl malonate. This conversion, however, is not free from side-reactions: Major by-product formed during the reaction is α-



(1)

phenylselenoacetophenone **2** arising from selenenylation of the enolate. To improve the procedure more precisely, effects of substituents on the benzene ring of areneseleninyl group as well as the reaction solvent were examined on the reaction of aryl 1-dodecenyl selenoxide with lithium enolate of acetophenone. Results are shown in Table 1.

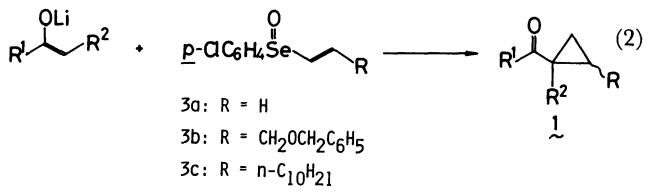
As shown in the Table 1, significant effects of substituents on aryl selenoxides together with those of solvents were observed. An electron-withdrawing substituent such as *m*-trifluoromethyl or *p*-chloro group facilitates the reaction remarkably (runs 6 and 9), whereas electron-donating *o*-methyl group decreased the product yield (run 5). In the *syn*-elimination reaction of selenoxides, *o*-nitro group has been known to facilitate the reaction.[16] In the present case, however, no detectable amount of the desired product was obtained (run 7). The use of ether as solvent proved to be most suitable because the undesired selenenylation of the enolate could be practically excluded. When THF is employed as the solvent, areneselenenylation of acetophenone usually accompanies up to 15% yield. It is likely that in ether the eliminated selenium species has poor solubility, which seems to make this species incapable of selenenylation.

Table 1. Effects of aryl substituents for cyclopropanation[a]

Run	Ar	Solvent	Yield/% of **1**
1	C_6H_5[b]	THF	65
2	C_6H_5[c]	THF	20
3	C_6H_5[d]	THF–HMPA	51
4	C_6H_5	Ether	63
5	*o*-$CH_3C_6H_4$	THF	17
6	*m*-$CF_3C_6H_4$	Ether	73
7	*o*-$NO_2C_6H_4$	Ether	Trace
8	*p*-ClC_6H_4	THF	69
9	*p*-ClC_6H_4	Ether	81
10	*p*-ClC_6H_4[e]	THF	91

a) A reactant ratio, ketone: selenoxide: LDA=1.2—1.25:1.0:1.5. b) Ketone: selenoxide :LDA=1.1:1.0:2.2. c) Sodium hexamethyldisilazide (1.4 equiv) was used. d) Ketone: selenoxide: LDA=1.1:1.0:1.4. e) An excess amount of enolate (1.7 equiv) was used.

A variety of lithium enolates were subjected to the reaction with three types of *p*-chlorophenyl vinyl selenoxides **3a**, **3b**, and **3c**. Table 2 lists the results.



(2)

3a: R = H
3b: R = $CH_2OCH_2C_6H_5$
3c: R = n-$C_{10}H_{21}$

Relatively hard nucleophiles such as ketone or α-phenylthio ester enolates gave better results, whereas the yields of cyclopropylcarbonyl compounds were decreased with soft nucleophiles such as α-phenylsulfinyl or α-phenylsulfonyl ester enolates and lithium diethyl malonate (runs 25, 26, 27, and 28).

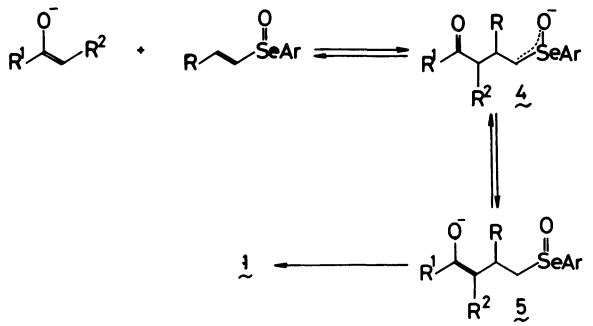
The present reaction proceeds most probably *via* conjugate addition of enolates to vinyl selenoxides followed by proton transfer from **4** to **5** and displacement of areneseleninyl group as outlined in Scheme 2.

The first conjugate addition step appears to be favored with relatively hard nucleophiles. With soft

Table 2. Reactions of vinyl selenoxides with ketone enolates[a]

Run	Ketone	Selenoxide		Yield/% of **1**
11	Acetophenone	**3a**	**1a**	72[b]
12	Acetophenone	**3b**	**1b**	70
13	Acetophenone	**3c**	**1c**	81
14	Propiophenone	**3a**	**1d**	59[b]
15	Propiophenone	**3b**	**1e**	84[b]
16	Propiophenone	**3c**	**1f**	62[b]
17	Ethyl (phenylthio)acetate	**3a**	**1g**	65[b]
18	Ethyl (phenylthio)acetate	**3b**	**1h**	72
19	Ethyl (phenylthio)acetate	**3c**	**1i**	71
20	Cyclododecanone	**3b**	**1j**	55
21	Cyclohexanone	**3c**	**1k**	51[b]
22	*t*-Buty methyl ketone	**3c**	**1l**	72
23	*t*-Butyl acetate	**3c**	**1m**	52
24	Isopropyl methyl ketone	**3c**	**1n**	56
25	1-Phenylthio-2-heptanone	**3c**	**1o**	47
26	Ethyl phenylsulfinylacetate	**3c**	**1p**	35
27	Ethyl phenylsulfonylacetate	**3c**	**1q**	13
28	Diethyl malonate	**3c**	**1r**	23

a) A reactant ratio, ketone: selenoxide: LDA=1.20—1.25:1.0:1.5. b) Ketone: selenoxide: LDA=1.0: 1.2:1.5.



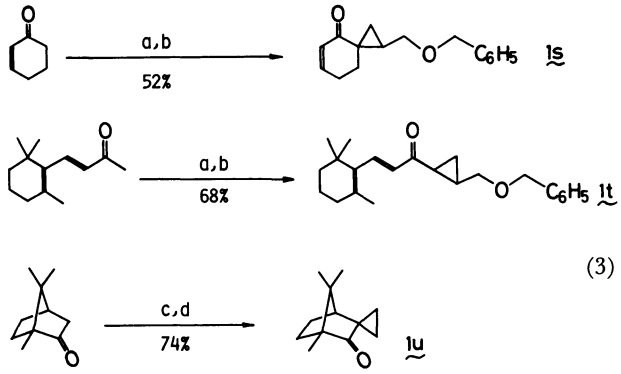
Scheme 2.

nucleophiles, the conjugate addition seems to proceed under equilibrium conditions. The equilibrium is usually favored on the left side (Scheme 2) and the other side reactions, *e.g.*, attack of enolates to areneseleninyl moiety or proton abstraction from vinyl selenoxide, may cause the low yield of the desired product.

As the third step, the displacement of areneseleninyl group, this type of intramolecular substitution has closely related precedents in sulfone chemistry, where an approach to chrysanthemic acid represents an outstanding example.[17]

Although the formation of a cyclopentanone derivative might also be conceivable when the parent ketone is enolizable on both sides, such products were not obtained in any cases.

Further application to cyclohexenone, β-ionone, and camphor shows the utility of the present method.



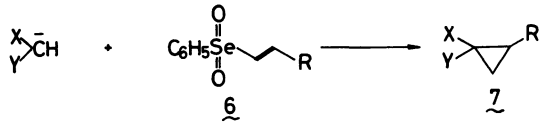
(3)

a) LDA (1.5 eq), ether. b) 3b (1.2 eq)
c) LDA (1.5 eq), DME. d) 3a (1.2 eq)

Cyclopropanation of camphor in THF gave rise to the desired ketone in only 38% yield along with concomitant formation of α-selenenylated ketone (18%). 1,2-Dimethoxyethane (DME) was proved to be a solvent of choice in that case.

Cory and his collaborators have reported the reaction of bicycloannulation of cyclohexenone derivatives with vinyltriphenylphosphonium salts[18] or vinyl sulfones.[19] In the present system, enolates of α,β-unsaturated ketones underwent cyclopropanation solely as indicated in the case with cyclohexenone. Relatively low efficacy of active methylene compounds as dibasic nucleophiles for this type of transformation may be attributable to insufficient activation of the neighboring C=C bonds with areneseleninyl group as well as its less efficient character as the leaving group.

Recently, we described preparation of vinyl selenones **6**: They can be easily prepared by oxidation of the corresponding vinyl selenides with 2—2.2 equiv of *m*-CPBA in an alcoholic media.[20] Further, in their reactions with alkoxides, *e.g.*, oxetane formation[20a] and fragmentation reactions,[20b] the selenonyl group has exhibited such similar characters as the seleninyl group described above, *e.g.*, activation of C=C bonds and as excellent leaving groups. By using such features of vinyl selenones, we have also examined the cyclopropanation reaction of enolate anions. Various examinations revealed that reactivity of a C=C bond to active methylene compounds has been greatly improved to form a cyclopropane ring on that linkage efficiently. For example, 1-hexenyl phenyl selenone was treated with an equimolar amount of sodium dimethyl malonate in THF at room temperature for 4 h, which gave the corresponding cyclopropanedicarboxylic ester in 92% yield. Various kinds of active methylene compounds can also be used equally well to give the corresponding cyclopropane **7** in good yields (see Table 3).



(4)

A transition metal-catalyzed reaction of olefins with diazo compounds has also been widely employed for

Table 3. Reactions of active methylene compounds with phenyl vinyl selenones **6**[a]

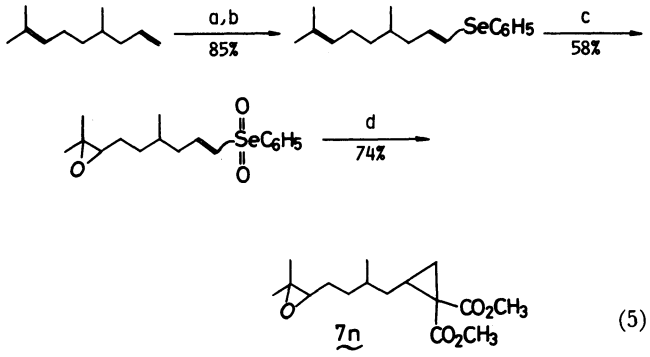
X	Y	R	Conditions	Yield/% of 7	
CO_2CH_3	CO_2CH_3	C_4H_9	r.t., 4 h	**7a**	92(87[b])
$COCH_3$	CO_2CH_3	C_4H_9	r.t., 1.5 h	**7b**	77
$COCH_3$	CONH-*t*-Bu	C_4H_9	r.t., 1.5 h	**7c**	98
CO_2CH_3	CN	C_4H_9	r.t., 1 h	**7d**	91
NO_2	H	C_4H_9	65 °C, 1 h	**7e**	75
$COCH_3$	C_6H_5S	C_4H_9	r.t., 1 h	**7f**	83
$CO_2C_2H_5$	C_6H_5S	C_4H_9	r.t., 2.5 h	**7g**	56
$CO_2C_2H_5$	$CO_2C_2H_5$	$(CH_2)_5C(OH)CH_2$	r.t., 4 h,	**7h**	72[b]
CO_2CH_3	CO_2CH_3	$C_5H_{11}CH(OH)$-$(CH_2)_3$-	r.t., 4 h	**7i**	80
CO_2CH_3	CO_2CH_3	$C_5H_{11}CO$-$(CH_2)_3$-	r.t., 2 h	**7j**	86
CO_2CH_3	CO_2CH_3	C_4H_9CO-$(CH_2)_8$-	r.t., 1.2 h	**7k**	91
CO_2CH_3	CO_2CH_3	CH_3O_2C-$(CH_2)_8$-	r.t., 2 h	**7l**	86
CO_2CH_3	CO_2CH_3	$CH_3O_2CCH(C_4H_9)$-$(CH_2)_3$-	r.t., 2 h,	**7m**	87

a) A reactant ratio, ketone:selenone=1.2:1.0. b) Lithium enolate was used.

this type of transformation,[20] but there exist serious drawbacks on the following two points; (i) use of an excess amount of olefin is usually required for moderate success, and (ii) a range of its application suffers from severe limitation because oxygen-containing functional groups prevent the cyclopropanation reaction.[21a]

Both of them have been overcome efficiently by the present method using vinyl selenones. First, olefins can be converted to the corresponding vinyl selenones effectively *via* vinyl selenides, and active methylene compounds undergo cyclopropanation with a stoichiometric amount of the vinyl selenones. In the second, various oxygen-containing functionalities do not disturb this olefin unit transfer to active methylene sites to give the corresponding cyclopropane in excellent yields as exemplified in formation of **7h—m**.

Further, the following example has demonstrated site-selective activation of terminal olefins. When started from a diene, selenenylation takes place selectively on the terminal C=C bond.[14,22] Although an internal one also undergoes oxidation to the oxirane during conversion of a selenide to the selenone, selective formation of cyclopropane ring has been executed on the parent terminal C=C bond under the reaction conditions where the oxirane survives as shown in Eq. 5.



(5)

a) C_6H_5SeBr. b) t-BuOK. c) m-CPBA (2.2 eq). d) $NaCH(CO_2CH_3)_2$

Conclusion

As shown above, various kinds of enolate anions behave as dibasic nucleophiles toward vinyl selenoxides and vinyl selenones due to characteristic features of seleninyl and selenonyl groups. Difference between vinyl selenoxides and vinyl selenones should be noted here. As described earlier, the formers in general give much better results with usual enolates than with anionic species of active methylene compounds. On the contrary, vinyl selenones has exhibited slight different behavior toward enolate nucleophiles. Thus, in addition to activation of a neighboring C=C bond to nucleophiles, a selenonyl group appears to enhance the acidity of vinyl proton, which sometimes results in undesired side-reactions such as decomposition to the corresponding acetylene[23] when anionic species of less acidic substrates are used as nucleophiles. For example, treatment of 1-dodecenyl phenyl selenone with lithium enolate of acetophenone led to the formation of the cyclopropane in 41% yield together with 1-dodecyne (19%). Such a feature clearly disfavors use of vinyl selenones for the preparation of cyclopropyl ketones, and use of vinyl selenoxides should be recommended.

There have been developed several types of procedures for cyclopropanation of olefins, *e.g.*, use of oxosulfonium,[24] phosphonium[25] selenium ylides,[26] or Simmons-Smith reagent.[27] In regard to the accessibility of the starting material, the present procedure, complementary to these methods, offers a simple and useful approach to cyclopropylcarbonyl compounds.

Experimental

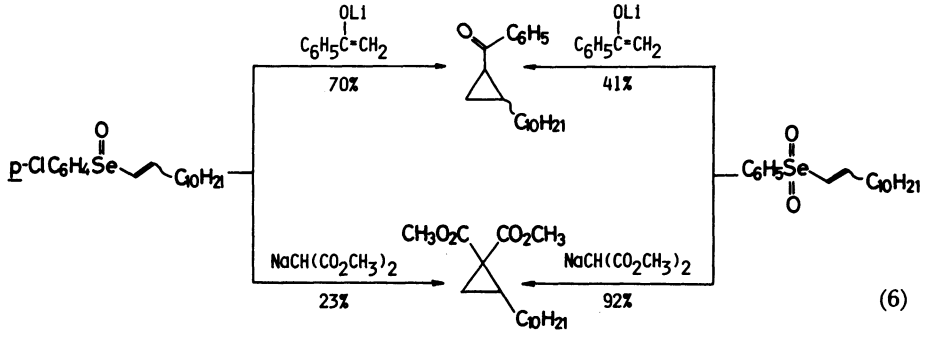
General Methods. Boiling points and melting points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G3 spectrometer; absorptions are given in reciprocal centimeters. Proton nuclear magnetic resonance spectra (^1H NMR) were obtained on a Hitachi R-24B spectrometer; chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra (70 eV) were determined on a Hitachi RMU-6C or RMU-7M spectrometer. Microanalysis were performed with a Perkin Elmer 240 at the Microanalysis Laboratory, Tokyo Institute of Technology.

Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks with magnetic stirring bars under nitrogen or argon. Bulb-to-bulb distillation was performed with a Büchi Kügelrohr apparatus.

Preparative thin-layer chromatography (TLC) was carried out on glass plates (20×20 cm) coated with Merck silica gel PF 254 (1 mm thick). Column chromatography was performed on Merck Kieselgel or Wakogel C-200.

Ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane were distilled from sodium–benzophenone ketyl in a recycling still immediately before use. *m*-Chloroperbenzoic acid (*m*-CPBA, 85% pure), purchased from Aldrich Chemical Co., was used directly without purification.

Preparation of Aryl Vinyl Selenides. The preparation



(6)

of 1-dodecenyl *p*-chlorophenyl selenide, which was prepared by a similar method developed by Raucher *et al*,[14a] represents a typical procedure. To a solution of *p*-chlorobenzeneselenenyl bromide prepared from bis(*p*-chlorophenyl) diselenide (2.29 g, 6.0 mmol) and bromine (6 mL of 1 M (1 M=1 mol dm^{-3}) carbon tetrachloride solution, 6.0 mmol) in 5 mL of acetonitrile was added a solution of 1-dodecene (2.02 g, 12 mmol) in 35 mL of acetonitrile, and the reaction mixture was stirred for 2.5 h at room temperature. After all the solvent was removed, potassium *t*-butoxide (2.7 g, 24 mmol) and THF (50 mL) were added to the crude mixture, and the resulting brown-colored mixture was stirred for 1 h at room temperature. Then, it was washed with satd aq NaCl, and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried and concentrated to give an oil, which was distilled to afford a mixture of (*E*)- and (*Z*)-1-dodecenyl *p*-chlorophenyl selenide (2.98 g, 69%); bp 105 °C/0.08 mmHg**; IR (neat) 2900, 1600, 1470, 1380, 1090, 1010, 950, 810, 725; NMR (CCl_4) 0.80—1.70 (m, 19H), 1.90—2.33 (m, 2H), 5.73—6.50 (m, 2H), 7.03—7.60 (m, 4H). Calcd for $C_{18}H_{27}SeCl$: C, 64.42; H, 7.61%. Found: C, 64.72; H, 7.79%.

1-Dodecenyl Phenyl Selenide. IR (neat) 2919, 1580, 1480, 1440, 1075, 1025, 1000, 955, 740, 690; NMR (CCl_4) 0.70—1.60 (m, 19H), 1.90—2.63 (m, 2H), 5.70—6.50 (m, 2H), 7.00—7.50 (m, 5H). Calcd for $C_{18}H_{28}Se$: C, 66.86; H, 8.73%. Found: C, 66.82; H, 8.67%.

1-Dodecenyl o-Tolyl Selenide. IR (neat) 2900, 1605, 1585, 1565, 1460, 1375, 1050, 1035, 950, 740; NMR (CCl_4) 0.70—1.70 (m, 19H), 1.57—2.50 (m, 2H), 2.37 (s, 3H), 5.73—6.50 (m, 2H), 6.83—7.50 (m, 4H). Calcd for $C_{19}H_{30}Se$: C, 67.63; H, 8.96%. Found: C, 67.72; H, 9.04%.

1-Dodecenyl o-Nitrophenyl Selenide. IR (neat) 2890, 1580, 1465, 1445, 1330, 1300, 1100, 1040, 970, 860, 790, 735; NMR (CCl_4) 0.70—1.70 (m, 19H), 2.00—2.50 (m, 2H), 6.20—6.50 (m, 2H), 7.00—7.57 (m, 3H), 8.03—8.90 (m, 1H). Calcd for $C_{18}H_{27}NO_2Se$: C, 58.69; H, 7.39; N, 3.80%. Found: C, 58.99; H, 7.55; N, 3.95%.

1-Decenyl m-Trifluoromethylphenyl Selenide. IR (neat) 2905, 1575, 1465, 1420, 1315, 1270, 1160, 1125, 1095, 1080, 1065, 995, 960, 890, 790, 690; NMR (CCl_4) 0.50—1.70 (19H), 2.00—2.67 (m, 2H), 6.13—6.23 (m, 1H), 6.50—6.70 (m, 1H), 7.50—8.10 (m, 4H). Calcd for $C_{19}H_{27}F_3Se$: C, 58.31; H, 6.95%. Found: C, 58.59; H, 7.29%.

3-Benzyloxy-1-propenyl p-Chlorophenyl Selenide. To a solution of sodium *p*-chlorobenzeneselenolate prepared by reduction of bis(*p*-chlorophenyl) diselenide (7.6 g, 20 mmol) with sodium borohydride (1.5 g, 40 mmol) in ethanol (100 mL) was added a solution of epichlorohydrin (11.1 g, 120 mmol) in ethanol (20 mL) at −78 °C and the reaction mixture was allowed to stand at room temperature for 20 h. Then all the solvent was removed *in vacuo*. The resulting residue was washed with satd aq NaCl, and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried and concentrated to give an oil. To a suspension of sodium hydride (45 mmol) in THF (10 mL) was added a solution of the crude oil obtained above in 40 mL of THF, and the mixture was stirred under refluxing for 1.5 h. Then a solution of benzyl bromide (6.7 g, 39.2 mmol) in THF (20 mL) was added to the ice-cooled mixture. After allowed to stand for 16 h at room temperature, the reaction mixture was washed with satd aq NaCl and dried. Removal of the solvent gave an oil, which was distilled to yield the title compound (8.8 g, 67%) as a mixture of (*E*)- and (*Z*)-isomers: bp 122 °C (bath temp)/0.08 mmHg; IR (neat) 3000, 2900, 2830, 1605, 1475, 1450, 1390, 1360, 1305, 1210, 1095, 1015, 950, 820, 740, 700; NMR (CCl_4) 3.93, 3.96 (unresolved dd, *J*=5 and 6 Hz, 2H), 4.47 (unresolved, s, 2H), 5.70—6.80 (m, 2H), 7.00—7.60 (m, 4H). Calcd for $C_{16}H_{15}OSeCl$: C, 56.91; H, 4.48%. Found: C, 56.67; H, 4.32%.

** 1 mmHg=133.322 Pa

p-Chlorophenyl Vinyl Selenide. To a solution of sodium *p*-chlorobenzeneselenolate prepared from bis(*p*-chlorophenyl) diselenide (3.81 g, 10 mmol) and sodium borohydride (758 mg, 20 mmol) in ethanol (29 mL) was added 1,2-dichloroethane (78 mL) at room temperature, and the mixture was allowed to stand for 24 h at that temperature. After usual work-up, potassium *t*-butoxide (3.36 g, 30 mmol) was added to a THF (50 mL) solution of the crude oil obtained above, and it was stirred for 1 h at room temperature. Usual work-up of the reaction mixture followed by distillation gave the title compound (2.6 g, 60%) as a colorless oil: bp 115 °C (bath temp)/0.2 mmHg; IR(neat) 2910, 1585, 1475, 1390, 1250, 1100, 1020, 965, 895, 870, 820, 795, 770; NMR (CCl_4) 5.12 (dd, *J*=16 and 2Hz, 1H), 5.40 (dd, *J*=10 and 2 Hz, 1H), 6.30 (dd, *J*=16 and 10 Hz, 1H), 6.87—7.10 (m, 4H). Calcd for C_8H_7SeCl; C, 44.17; H, 3.24%. Found: C, 43.95; H, 3.18%.

Preparation of 1-Dodecenyl p-Chlorophenyl Selenoxide **3c**. *General Procedure for the Preparation of Vinyl Selenoxide.* A solution of 1-dodecenyl *p*-chlorophenyl selenide (179 mg, 0.5 mmol) in dichloromethane (4 mL) was added to a solution of *m*-CPBA (152 mg of 85% pure material, 0.75 mmol) in 1 mL of dichloromethane. After allowed to stand for 30 min at room temperature, the reaction mixture was washed with satd aq $NaHCO_3$ and dried. Removal of the solvent from organic layer gave the title compound as a colorless oil (176 mg, 94%) which was homogeneous in tlc; IR (neat) 2905, 1980, 1470, 1090, 1015, 820, 730; NMR (CCl_4) 0.70—1.70 (m, 19H), 2.23—2.56 (m, 2H), 6.17—6.30 (m, 1H), 6.33—6.80 (m, 1H), 7.10—7.70 (m, 4H).

p-Chlorophenyl Vinyl Selenoxide **3a**. IR (neat) 2890, 2830, 1590, 1570, 1470, 1390, 1360, 1175, 1090, 1020, 970, 940, 890, 830, 735; NMR(CCl_4) 6.03 (dd, *J*=9 and 1 Hz, 1H), 6.27 (dd, *J*=17 and 1 Hz, 1H), 6.93 (dd, *J*=17 and 9 Hz, 1H), 7.30—7.67 (m, 4H).

3-Benzyloxy-1-propenyl p-Chlorophenyl Selenoxide **3b**. IR (neat) 2880, 1465, 1380, 1085, 1010, 820, 730, 695; NMR (CCl_4) 4.00 (unresolved s, $CH_2C_6H_5$), 4.13 (unresolved s, $CH_2C_6H_5$), 4.36—4.57 (m, 2H), 6.20 (unresolved s, 1H), 6.70 (unresolved s, 1H), 6.80—7.70 (m, 4H).

2-Decylcyclopropyl Phenyl Ketone **1c**. *General Procedure for the Reactions in Tables 1 and 2.* A solution of acetophenone (66 mg, 0.55 mmol) in ether (3 mL) was added to a solution of lithium diisopropylamide (LDA) (0.75 mmol) in ether (2 mL) at −30 °C, and the mixture was stirred for 30 min at that temperature. An ethereal solution (5 mL) of 1-dodecenyl *p*-chlorophenyl selenoxide (164 mg, 0.44 mmol) was added to the solution of enolate, and it was stirred for 1 h at the same temperature. Then, after allowed to stand at room temperature for 5 h, the reaction mixture was washed with satd aq NaCl and dried. Removal of the solvent from organic layer followed by purification by preparative tlc gave the title compound (102 mg, 81%) as a colorless oil; bp 114 °C (bath temp)/0.04 mmHg; IR (neat) 1655; NMR (CCl_4) 0.60—1.80 (m, 24H), 2.10—2.50 (m, 1H), 7.25—7.50 (m, 3H), 7.65—8.00 (m, 2H). Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%. Found: C, 83.57; H, 10.47%.

Cyclopropyl Phenyl Ketone **1a**. IR (neat) 1660; NMR (CCl_4) 0.50—1.70 (m, 4H), 2.35—2.85 (m, 1H), 7.00—7.60 (m, 5H). These spectroscopic properties were identical with those of the commercially available sample from Aldrich Chemical Co.

2-Benzyloxymethylcyclopropyl Phenyl Ketone **1b**. IR (neat) 1660; NMR (CCl_4) 0.70—2.00 (m, 3H), 2.35—2.70 (m, 1H), 3.20—3.50 (m, 2H), 4.43 (s, 2H), 6.90—7.60 (m, 8H), 7.60—8.10 (m, 2H); mass spectrum *m/z* (relative %) 266 (M^+, 1), 234 (1), 160 (10), 145 (9), 115 (5), 105 (100), 91 (93), 77 (64), 65 (29), 51 (36).

1-Methylcyclopropyl Phenyl Ketone **1d**. Bp 55 °C (bath temp)/0.2 mmHg; IR (neat) 1670; NMR (CCl_4) 0.50—1.70 (m, 7H including a singlet (3H) at 1.40), 7.10—7.55 (m, 3H), 7.55—7.90 (m, 2H). Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.54%. Found: C, 82.84; H, 7.55%.

2-Benzyloxymethyl-1-methylcyclopropyl Phenyl Ketone **1e**. IR (neat) 1670; NMR (CCl_4) 0.70—2.00 (m, 6H including a singlet (3H) at 1.40), 3.10—3.55 (m, 1H), 3.70—4.00 (m, 1H), 4.50 (s, 2H), 7.00—7.50 (m, 8H), 7.70—8.50 (m, 2H).

2-Decyl-1-methylcyclopropyl Phenyl Ketone **1f**. IR (neat) 1670; NMR (CCl_4) 0.70—1.80 (m, 27H), 7.20—7.50 (m, 3H), 7.50—7.80 (m, 2H); mass spectrum *m/z* (relative %) 300 (M^+, 12), 285 (2), 215 (2), 201 (9), 173 (14), 145 (4), 134 (12), 105 (100), 91 (9), 77 (27).

Ethyl 1-(Phenylthio)cyclopropanecarboxylate **1g**. Bp 85 °C (bath temp)/0.1 mmHg; IR (neat) 1705; NMR (CCl_4) 0.70—2.00 (m, 7H), 4.03 (q, J=9 Hz, 2H), 6.85—7.50 (m, 5H); Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.85; H, 6.35; S, 14.43%. Found: C, 65.18; H, 6.21; S, 14.43%.

Ethyl 2-Benzyloxymethyl-1-(phenylthio)cyclopropanecarboxylate. **1h**. Bp 135 °C (bath temp)/0.04 mmHg; IR (neat) 1705; NMR (CCl_4) 0.75—1.30 (m, 4H including a triplet (J=7 Hz, 3H) at 1.33), 1.55—2.50 (m, 2H), 3.40—3.80 (m, 2H), 4.00 (q, J=7 Hz, 2H), 4.30 (s, 2H), 6.70—7.40 (m, 10H). Calcd for $C_{20}H_{22}O_3S$: C, 70.16; H, 6.48; S, 9.37%. Found: C, 70.20; H, 6.43; S, 9.39%.

Ethyl 2-Decyl-1-(phenylthio)cyclopropanecarboxylate **1i**. IR (neat) 1705; NMR (CCl_4) 0.70—2.00 (m, 27H), 4.05 (q, J=7 Hz, 2H), 7.13 (s, 5H).

1-(Benzyloxymethyl)spiro[2.11]pentadecan-4-one **1j**. IR (neat) 1670; NMR (CCl_4) 0.70—2.70 (m, 13H), 3.15—3.75 (m, 2H), 4.43 (unresolved s, 2H), 7.23 (unresolved s, 5H).

1-Decylspiro[2.4]octan-4-one **1k**. IR (neat) 1675; NMR (CCl_4) 0.70—2.10 (m, 32H).

t-Butyl 2-Decylcyclopropyl Ketone **1l**. Bp 87 °C (bath temp)/0.08 mmHg; IR (neat) 1680; NMR (CCl_4) 0.70—2.00 (m, 34H including a singlet (9H) at 1.10). Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86%. Found: C, 81.10; H, 12.72%.

t-Butyl 2-Decylcyclopropanecarboxylate **1m**. Bp 86 °C (bath temp)/0.01 mmHg; IR (neat) 1715; NMR (CCl_4) 0.50—1.90 (m, 34H including a singlet (9H) at 1.30). Calcd for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13%. Found: C, 76.29; H, 12.09%.

2-Decylcyclopropyl Isopropyl Ketone **1n**. IR (neat) 1680; NMR (CCl_4) 0.50—1.85 (m, 30H), 1.85—2.30 (m, 1H), 2.30—3.00 (m, 1H).

2-Decyl-1-(phenylthio)cyclopropyl Hexyl Ketone **1o**. IR (neat) 1680; NMR (CCl_4) 0.50—2.10 (m, 33H), 2.80 (t, J=6 Hz, 2H), 7.10 (s, 5H); mass spectrum *m/z* (relative %) 388 (M^+, 15), 217 (12), 208 (6), 154 (18), 148 (12), 110 (65), 109 (41), 105 (29), 91 (59), 85 (32), 77 (35), 71 (53), 69 (53), 57 (100), 55 (82).

Ethyl 2-Decyl-1-(phenylsulfinyl)cyclopropanecarboxylate **1p**. IR (neat) 1725, 1710; NMR (CCl_4) 0.50—2.00 (m, 27H), 4.03 (q, J=6 Hz, 2H), 7.00—7.83 (m, 5H).

Ethyl 2-Decyl-1-(phenylsulfonyl)cyclopropanecarboxylate **1q**. IR (neat) 1720; NMR (CCl_4) 0.50—2.20 (m, 27H), 4.07 (q, J=6 Hz, 2H), 7.17—8.00 (m, 5H).

Diethyl 2-Decyl-1,1-cyclopropanedicarboxylate **1r**. Bp 110 ° C (bath temp)/0.03 mmHg; IR (neat) 1720; NMR (CCl_4) 0.67—1.83 (m, 30H), 4.13 (q, J=6 Hz, 4H); mass spectrum *m/z* (relative %) 281 (M^+—45, 13), 253 (17), 235 (7), 173 (73), 160 (100), 127 (93), 108 (27), 99 (33), 95 (27), 81 (23), 74 (40), 59 (73), 55 (53). Calcd for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50%. Found: C, 69.67; H, 10.41%.

1-(Benzyloxymethyl)spiro[2.5]oct-5-en-4-one **1s**. IR (neat) 1665; NMR (CCl_4) 0.70—2.70 (m, 7H), 3.15—3.80 (m, 2H), 4.35—4.70 (m, 2H), 5.80—6.25 (m, 1H), 6.70—7.60 (m, 6H).

1-(2-Benzyloxymethylcyclopropyl)-3-(2,6,6-trimethyl-1-cyclohexenyl)-2-propen-1-one **1t**. IR (neat) 1670; NMR (CCl_4) 0.70—2.25 (m, 19H including singlets at 1.03 and 1.76), 3.35 (m, 2H), 4.17 (s, 2H), 4.13 (d, J=16 Hz, 1H), 7.17 (s, 5H), 7.23 (d, J=16 Hz, 1H).

4,7,7-Trimethylspiro[bicyclo[2.2.1]heptan-2,1'-cyclopropan]-3-one **1u**. IR (neat) 1720; NMR (CCl_4) 0.50—2.33 (m, 18H including three methyl singlets at 0.83, 0.87, and 0.97); mass spectrum *m/z* (relative %) 178 (M^+, 13), 162 (17), 135 (25), 109 (29), 95 (100), 83 (33), 74 (33), 69 (42), 59 (54), 55 (42).

1-Hexenyl Phenyl Selenone. General Procedure for the Preparation of Vinyl Selenones **6**. To a solution of 1-phenylseleno-1-hexene (1.50 g, 6.3 mmol) in methanol (20 mL) was added *m*-CPBA (2.8 g, 14 mmol) at 0 °C, and it was stirred overnight at room temperature. After the solvent was removed *in vacuo*, satd aq $NaHCO_3$ was added and it was extracted with chloroform. The combined extracts were dried and concentrated to give an oil, which was purified by column chromatography (hexane:ethyl acetate=1:1) to afford the title compound (1.30 g, 76%); IR (neat) 935, 885; NMR (CCl_4) 0.60—1.85 (m, 7H), 2.05—3.00 (m, 2H), 6.30—7.30 (m, 2H), 7.35—8.15 (m, 5H).

Dimethyl 2-Butyl-1,1-cyclopropanedicarboxylate **7a**. *General Procedure for an Olefin Unit Transfer to Active Methylene Compounds in Table 3.* To a suspension of NaH (0.33 mmol) in THF (0.5 mL) was added dimethyl malonate (48 mg, 0.37 mmol) at 0 °C and it was stirred for 10 min at that temperature. Then, a THF (1.0 mL) solution of 1-hexenyl phenyl selenone (83 mg, 0.30 mmol) was added to the resulting mixture, and it kept stirring 4 h at room temperature. The reaction mixture was quenched with water and the aqueous layer was extracted with ether. The combined extracts were washed with satd aq NaCl, dried over anhyd $MgSO_4$, and then concentrated to give an oil, which was purified by column chromatography to afford the title compound (60.0 mg, 92%); bp 62—64 °C (bath temp)/0.012 mmHg; IR (neat) 1710; NMR (CCl_4) 0.65—2.10 (m, 12H), 3.62 (s, 6H). Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%. Found: C, 61.40; H, 8.54%.

Methyl 1-Acetyl-2-butylcyclopropanecarboxylate **7b**. Bp 85 °C (bath temp)/9 mmHg; IR (neat) 1710; NMR (CCl_4) 0.60—2.15 (m, 12H), 2.26 (s, 3H), 3.69 (s, 3H). Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%. Found: C, 66.57; H, 9.11%.

N-t-Butyl-1-acetyl-2-butyl-1-cyclopropanecarboxamide **7c**. Two stereoisomers (**A** and **B**) were isolated. **A**; IR (neat) 3280, 1650; NMR (CCl_4) 0.65—1.65 (m, 12H), 1.30 (s, 9H), 2.14 (s, 3H), 6.70 (br s, 1H); Anal. Calcd for $C_{14}H_{25}NO_2$: C, 70.25; H, 10.53; N, 5.85. Found: C, 70.17; H, 10.43; N, 6.03. **B**; IR (neat) 3280, 1650; NMR (CCl_4) 0.60—1.70 (m, 12H), 1.33 (s, 9H), 2.01 (s, 3H), 7.38 (br s, 1H).

Methyl 2-Butyl-1-cyanocyclopropanecarboxylate **7d**. Bp 53—57 °C (bath temp)/0.012 mmHg; IR (neat) 2230, 1730; NMR (CCl_4) 0.70—2.10 (m, 12H), 3.74 (s, 3H). Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73%. Found: C, 65.94; H, 8.31; N, 7.52%.

1-Butyl-2-nitrocyclopropane **7e**. Bp 80 °C (bath temp)/9 mmHg; IR (neat) 1530; NMR (CCl_4) 0.60—2.05 (m, 12H), 3.87 (m, 1H). Calcd for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78%. Found: C, 58.94; H, 9.34; N, 9.72%.

2-Butyl-1-(phenylthio)cyclopropyl Methyl Ketone **7f**. Bp 110 °C (bath temp)/3 mmHg; IR (neat) 1685; NMR (CCl_4) 0.65—2.15 (m, 12H), 2.31 (s, 3H), 6.85—7.20 (m, 5H). Calcd for $C_{15}H_{20}OS$: C, 72.54; H, 8.12; S, 12.91%. Found: C, 72.45; H, 7.88; S, 12.96%.

Ethyl 2-Butyl-1-(phenylthio)cyclopropanecarboxylate **7g**. Bp 140 °C (bath temp)/3 mmHg; IR (neat) 1708; NMR (CCl_4) 0.68—2.10 (m, 15H), 4.06 (q, J=7 Hz, 2H), 6.87—7.50 (m, 5H). Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96; S, 11.52%. Found: C, 68.80; H, 7.92; S, 11.07%.

Diethyl 2-[(1-Hydroxycyclohexyl)methyl]-1,1-cyclopropanedicarboxylate **7h**. To a THF (0.3 mL) solution of lithio

diethyl malonate prepared from diethyl malonate (26.4 mg, 0.17 mmol) and butyllithium (0.11 mL of 1.57 M hexane solution, 0.17 mmol) was added a THF (0.3 mL) solution of 1-(3-phenylselenonyl-1-propenyl)-1-cyclohexanol (45.1 mg, 0.14 mmol), and it was stirred for 4 h at room temperature. Then, the reaction mixture was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined extracts were washed with satd aq NaCl and were dried over anhyd $MgSO_4$. Removal of the solvent followed by purification with column chromatography afforded the title compound (29.6 mg, 72%); bp 114 °C (bath temp)/0.08 mmHg; IR (neat) 3475, 1724; NMR (CCl_4) 1.0—2.2 (m, 22H), 4.07 (q, J=7.0 Hz, 4H). Calcd for $C_{16}H_{26}O_5$: C, 64.40; H, 8.76%. Found: C, 64.23; H, 8.81%.

Dimethyl 2-(4-Hydroxynonyl)-1,1-cyclopropanedicarboxylate **7i**. Bp 120 °C (bath temp)/0.019 mmHg; IR (neat) 3350, 1710; NMR (CCl_4) 0.65—1.95 (m, 21H), 3.20—3.55 (br s, 1H), 3.59 (s, 6H). Calcd for $C_{16}H_{28}O_5$: C, 63.97; H, 9.39%. Found: C, 63.90; H, 9.47%.

Dimethyl 2-(4-Oxononyl)-1,1-cyclopropanedicarboxylate **7j**. Bp 114 °C (bath temp)/0.013 mmHg; IR (neat) 1705; NMR (CCl_4) 0.65—1.90 (m, 16H), 2.10—2.50 (m, 4H), 3.58 (s, 3H), 3.61 (s, 3H). Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78%. Found: C, 64.28; H, 8.75%.

Dimethyl 2-(9-Oxotridecyl)-1,1-cyclopropanedicarboxylate **7k**. Bp 134 °C (bath temp)/0.024 mmHg; IR (neat) 1720, 1705; NMR (CCl_4) 0.70—1.85 (m, 24H), 2.10—2.45 (m, 4H), 3.60 (s, 6H). Calcd for $C_{20}H_{34}O_5$: C, 67.77; H, 9.67%. Found: C, 67.83; H, 9.96%.

Dimethyl 2-(8-Methoxycarbonyloctyl)-1,1-cyclopropanedicarboxylate **7l**. Bp 116 °C/0.015 mmHg; IR (neat) 1725; NMR (CCl_4) 1.05—2.35 (18H), 2.83 (s, 3H), 2.93 (s, 6H). Calcd for $C_{17}H_{28}O_6$: C, 62.18; H, 8.59%. Found: C, 62.36; H, 8.45%.

Dimethyl 2-(4-Methoxycarbonyloctyl)-1,1-cyclopropanedicarboxylate **7m**. Bp 138 °C/0.14 mmHg; IR (neat) 1725; NMR (CCl_4) 0.70—2.30 (m, 22H), 3.62 (s, 6H), 3.98 (q, J=7.0 Hz, 2H). Calcd for $C_{18}H_{30}O_6$: C, 63.14; H, 8.83%. Found: C, 63.00; H, 8.75%.

Dimethyl 2-(5,6-Epoxy-2,6-dimethylheptyl)-1,1-cyclopropanedicarboxylate **7n**. Bp 96 °C (bath temp)/0.02 mmHg; IR (neat) 1735; NMR (CCl_4) 0.75—1.95 (m, 18H), 2.30—2.50 (m, 1H), 3.58 (s, 6H). Calcd for $C_{16}H_{26}O_5$: C, 64.41; H, 8.78%. Found: C, 64.63; H, 8.84%.

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