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Hexacarbonylmolybdenum(0)-Induced Dechalcogenization of Allylic Sulfides, Sulfones, and Selenides: Nucleophilic Substitution and Reductive Dechalcogenization

Yoshiro MASUYAMA,* Kohji YAMADA, Soh-hei SHIMIZU, and Yasuhiko KURUSU
Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo 102
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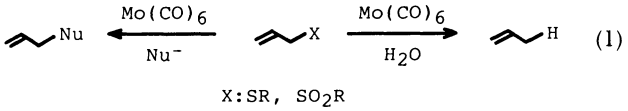
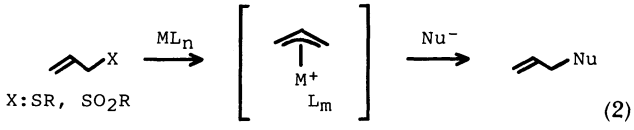
Hexacarbonylmolybdenum(0)-induced dechalcogenization of allylic sulfides **I**, sulfones **II**, and selenides **III** in refluxing dioxane, which led to nucleophilic substitutions with carbon nucleophiles. Attack of the relatively bulky nucleophile, 2-ethoxycarbonyl-2-sodiocyclopentanone occurred regioselectively at the less substituted end of the allyl unit after the dechalcogenization to give only one isomer. Attack of diethyl sodiomalonate to **I** and **III** occurred preferentially at γ-position, and that to **II** occurred preferentially at the more substituted end of the allyl unit after the desulfonylation. In the absence of the carbon nucleophiles, treatment of **I**, **II**, and **III** with $Mo(CO)_6$ in refluxing dioxane caused reductive dechalcogenization. Addition of H_2O accelerated the reductive dechalcogenization.

Organochalcogenides have made a great contribution to organic synthesis, due to the ability of the chalcogenide group to stabilize the adjacent carbanion.[1,2] In particular, allylic chalcogenides have been widely applied to the reactions with various electrophiles as reagents for three carbon homologation.[3] Since the chalcogenide-functional groups are rarely present in the final synthetic target, removal of the functional groups becomes an important subject. The representative removal methods are (1) β-elimination of the sulfide and selenide via oxidation[1,2] and of the sulfone under basic conditions[1,4] and (2) reductive defunctionalization of all groups with metal reagents.[1,5] The organochalcogen groups have not been generally utilized as the leaving groups in the nucleophilic substitutions with carbon nucleophiles. Use of a metal reagent, which has oxidizing-ability, may permit the nucleophilic substitution.[6] Hexacarbonylmolybdenum [$Mo(CO)_6$] seems to have both oxidizing and reducing abilities, since molybdenum has a variety of oxidation states between -2 and $+6$. In addition, molybdenum has thiophilicity. Thus, $Mo(CO)_6$ becomes an effective reagent for both the rare nucleophilic substitution (oxidation) and the reductive defunctionalization (reduction) of organosulfur compounds. The objective of our study is the development of an approach to this subject which has been achieved in allylic systems such as allylic sulfides and sulfones (Eq. 1).[7]



(1)

The early applications of the transition metal-promoted substitutions are represented by the nickel-catalyzed reaction of the allylic sulfides with Grignard reagents[8] and the palladium- or molybdenum-catalyzed reaction of the allylic sulfones with active methylene compounds.[9] These metal-promoted substitutions probably proceed via π-allylmetal complexes (Eq. 2).

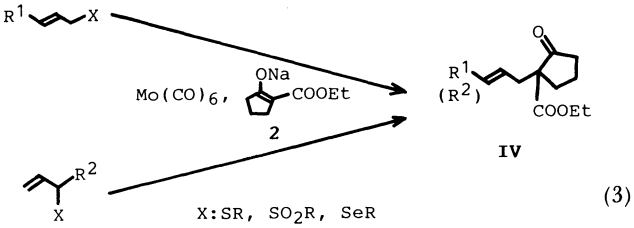


(2)

In both the nucleophilic substitutions and the reductive defunctionalizations of allylic sulfides, sulfones, and selenides with $Mo(CO)_6$, the properties of these organochalcogen groups should affect the coordination of olefins to molybdenum, namely the formation of π-allylmolybdenum complexes, to exhibit unique regiochemistry in the reaction of the allylic moieties.

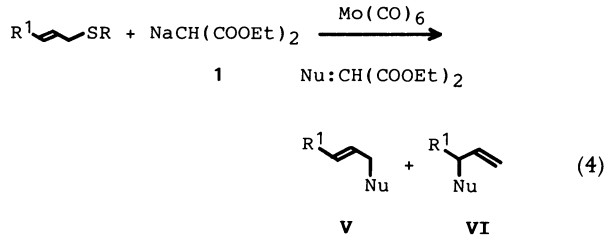
Results and Discussion

Nucleophilic Substitution. The $Mo(CO)_6$-induced nucleophilic substitution of allylic sulfides **I**, sulfones **II**, or selenides **III** with carbon nucleophiles, diethyl sodiomalonate (**1**) or 2-ethoxycarbonyl-2-sodiocyclopentanone (**2**) proceeded in refluxing dioxane under a nitrogen atmosphere to afford allylic alkylation products. The results are summarized in Table 1. In the reactions of **I** at 110 °C, use of dioxane as a solvent exhibited higher yield than that in solvents such as DMF and toluene, while the reaction did not occur in refluxing THF or benzene. Reactivity of **II** and **III** seems to be slightly higher than that of **I** in the nucleophilic substitution. Using any allylic compound mentioned above, the relatively bulky nucleophile **2** attacked regioselectively at the less substituted end of the allyl unit after the defunctionalization to produce only one isomer **IV** (Entries 4—7, 22—25, 35—38), as



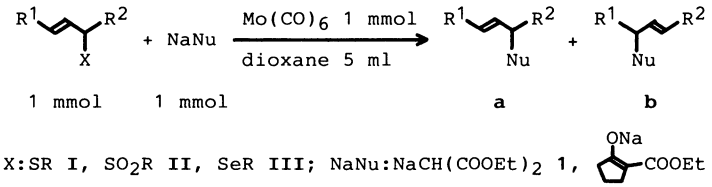
(3)

shown in Eq. 3. The attack of nucleophile **1** to **I** occurred at γ-position (product **VI**) in preference to



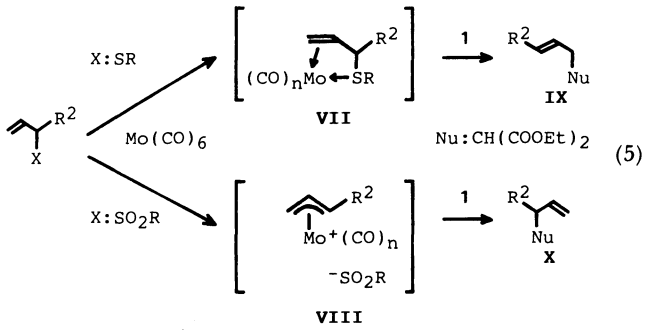
α-position (product **V**) even in γ-substituted allyl sulfides (Entries 9, 10, 12, 13, Eq. 4). However, any steric hindrance of bulky substituent on γ-carbon should reduce the regioselectivity. The low reactivity of α-substituted allyl sulfides toward **1** is presumably attributable to preferential complexation of **1** and $Mo(CO)_6$,[10] since the bulky α-substituent disturbs that of the allyl sulfides and $Mo(CO)_6$. Thus, the results demonstrate that the reaction proceeds not via π-allylmolybdenum intermediate but via coordination of

Table 1. Nucleophilic Substitutions



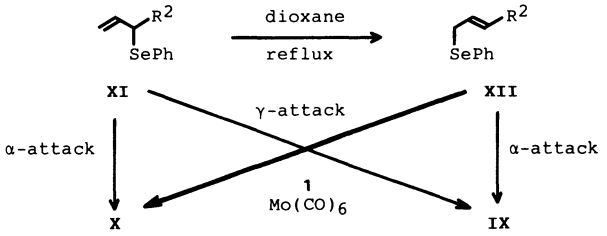
Entry	Allylic compound R¹	R²	X	NaNu	Time / h	Product	Yield[a] / %	Ratio[b] a : b
1	H	H	SPh	**2**	16	**3**	67	—
2	H	H	SPh	**2**	24	**3**	40[c]	—
3	H	H	SPh	**2**	67	**3**	23[d]	—
4	CH_3	H	SPh	**2**	40	**4**	75	100 0
5	Ph	H	SPh	**2**	47	**5**	52	100 0
6	H	PhCH=CHCH₂	SPh	**2**	41	**6**	48	0 100
7	H	$CH_3(CH_2)_3$	S-2-Py	**2**	63	**7**	47	0 100
8	-$(CH_2)_3$-		S-2-Py	**2**	34	**8**	22	—
9	CH_3	H	SPh	**1**	48	**9**	48	27 73
10	Ph	H	SPh	**1**	72	**10**	32	50 50
11	CH_3	CH_3	SPh	**1**	65	**11**	35	—
12	CH_3	$CH_3(CH_2)_3$	SPh	**1**	65	**12**	11	30 70
13	H	$CH_3(CH_2)_3$	SPh	**1**	72	**13**	6	0 100
14	H	H	SO_2Tol	**1**	20	**14**	29(14)[e]	—
15	H	H	SO_2Tol	**1**	24	**14**	12(30)[d,e]	—
16	H	H	SO_2Tol	**1**	68	**14**	36(35)[e,f]	—
17	CH_3	H	SO_2Tol	**1**	59	**9**	54	30 70
18	Ph	H	SO_2Tol	**1**	63	**10**	50	35 65
19	H	$CH_3(CH_2)_3$	SO_2Ph	**1**	66	**13**	32	100 0
20	H	$PhCH_2$	SO_2Ph	**1**	41	**15**	37	100 0
21	H	H	SO_2Tol	**2**	60	**3**	44	—
22	CH_3	H	SO_2Tol	**2**	60	**4**	48	100 0
23	Ph	H	SO_2Tol	**2**	45	**5**	24	100 0
24	H	$CH_3(CH_2)_3$	SO_2Ph	**2**	42	**7**	46	0 100
25	H	$PhCH_2$	SO_2Ph	**2**	45	**16**	41	0 100
26	H	H	SePh	**1**	41	**14**	53	—
27	H	H	SePh	**1**	96	**14**	19[g]	—
28	H	H	SePh	**1**	32	**14**	47[d]	—
29	CH_3	H	SePh	**1**	48	**9**	75	27 73
30	Ph	H	SePh	**1**	87	**10**	49	37 63
31	H	CH_3	SePh	**1**	62	**9**	36	58 42
32	H	$CH_3(CH_2)_3$	SePh	**1**	52	**13**	35	50 50
33	H	H	SePh	**2**	15	**3**	57	—
34	H	H	SePh	**2**	96	**3**	10[g]	—
35	CH_3	H	SePh	**2**	32	**4**	67	100 0
36	Ph	H	SePh	**2**	50	**5**	22	100 0
37	H	CH_3	SePh	**2**	62	**4**	60	0 100
38	H	$CH_3(CH_2)_3$	SePh	**2**	16	**7**	46	0 100

a) Isolated yields of mixtures of **a** and **b**. b) Ratio of isomers was determined by ^1H NMR (FX-200 and GX-270). c) DMF was used as a solvent. d) Toluene was used as a solvent. e) Figures in parentheses are yields of diallylated product. f) Two equivalents of **II** were used. g) THF was used as a solvent.



(5)

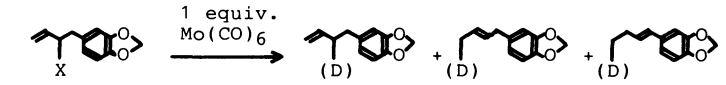
a sulfenyl group to molybdenum (chelate intermediate **VII**) (Eq. 5). Attack of **1** to α-substituted allyl sulfones occurred regioselectively at α-position, which is the more substituted end of the allyl unit, after the desulfonylation, contrary to the case of α-substituted allyl sulfides (Entries 19, 20, Eq. 5). Therefore, the intermediate derived from **II** and $Mo(CO)_6$ should be different from that derived from **I** and $Mo(CO)_6$. Since the nucleophilic substitution of π-allylmolybdenum complex, derived from allylic acetate and $Mo(CO)_6$, with dimethyl sodiomalonate has preferentially occurred at the more substituted end of the allyl unit,[10-12] π-allylmolybdenum intermediate **VIII** may be produced by the reaction of **II** with $Mo(CO)_6$, similarly to the case of π-allylpalladium complex prepared by that of **II** with $Pd(PPh_3)_4$ (Eq. 5).[9,13] In the case of γ-substituted allyl sulfones, the preparation of **VIII** may compete with that of the sulfide-like intermediate to afford the mixture of **a** and **b**, because bulky substituents on an olefin hindered π-coordination of the olefin (Entries 17, 18). γ-Substituted allyl selenides preferentially reacted with **1** at γ-position (Entries 29, 30). In contrast with α-substituted allyl sulfides, the γ-regioselective attack of **1** to α-substituted allyl selenides was not detected (Entries 31, 32). α-Substituted allyl selenides **XI** in refluxing dioxane easily caused [1,3] allylic shift of benzeneselenenyl group to produce γ-substituted allyl selenides **XII**.[14] In the reaction of **XI** with **1** in the presence of $Mo(CO)_6$, the [1,3] allylic shift should occur in preference to the nucleophilic substitution. Thus, the apparent attack of **1** at α-position of **XI** probably increased (Entries 31, 32, Eq. 6).



(6)

Reductive Dechalcogenization. The results of reductive dechalcogenization of 1-(3,4-methylenedioxybenzyl)allyl derivatives **17**, **18**, and **19** with $Mo(CO)_6$ are summarized in Table 2. These results demonstrated that reductive deselenenylation of allylic selenides with $Mo(CO)_6$ was easier than the corresponding reductive desulfenylation or desulfonylation. The addition of H_2O (or D_2O) accelerated the reductive dechalcogenization. Product **20c** was probably produced by the isomerization of **20b** with $Mo(CO)_6$, because elongation of the reaction time led to the increase of **20c**. Both the results of regioselectivity in deuteration with D_2O and the ratios of deuteration to protonation suggested that reaction mechanism of the reductive desulfonylation was different from that of

Table 2. Reductive Dechalcogenization of **17**, **18**, and **19**



X:SPh **17**
SO_2Tol **18**
SePh **19**

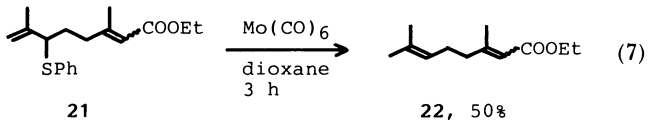
20a **20b** **20c**

Entry	Substrate	Additive	Equiv.	Time / h	Yield[a] / %	Ratio[b] a : b[c] : c
1	**17**	—		40	34	10 : 90
2	**17**	D_2O	5	20	56[d]	50 : 50
3	**17**		5	35	48	11 : 89
4	**18**	—		40	38	27 : 43 : 30
5	**18**	D_2O	5	19	65[e]	22 : 43 : 35
6	**19**	—		21	81	6 : 32 : 62
7	**19**	D_2O	5	19	80[f]	4 : 61 : 35

a) Isolated yields of a mixture of **20a**, **20b**, and **20c**. b) Ratio of isomers was determined by ^1H NMR (FX-200 or GX-270). c) The *E*/*Z* ratio of **20b** was ca 3/1 in every case. d) Complete deuteration occurred. e) The ratios of deuteration to protonation in every isomer were 13—15%. f) The ratios of deuteration to protonation in every isomer were 35—40%.

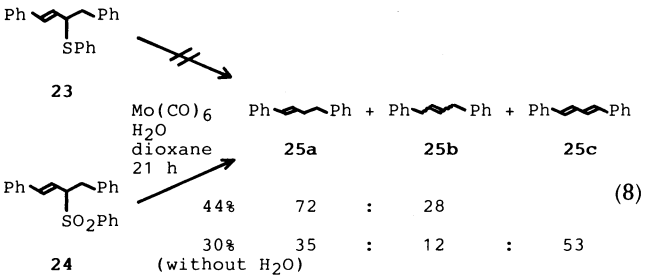
the reductive desulfenylation. The intermediates in the reductive dechalcogenizations seem to be the same as those in the corresponding nucleophilic substitutions. Deuteration scarcely occurred in the desulfenylation of **17** without H_2O in refluxing dioxane-d_8.[15]

The reductive desulfenylation of substrate **21**[16] proceeded more rapidly to give only one regioisomer **22** (Eq. 7). Even in the presence of nucleophile **1**, **21**



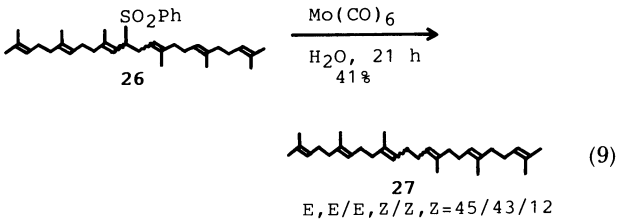
21 **22**, 50% (7)

did not cause nucleophilic substitution but did cause reductive desulfenylation. 1-Benzyl-3-phenylallyl sulfide **23** did not react with $Mo(CO)_6$, but the corresponding sulfone **24** caused reductive desulfonylation in the presence of H_2O to give **25a** and **25b** (Eq. 8). In



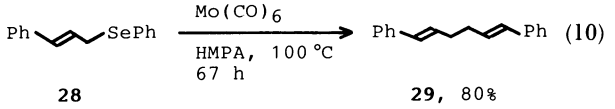
(8)

absence of H_2O, main product of the reaction was diene **25c**. Considering the ease of alkylation of allylic sulfones, the reductive desulfonylation could be applied to organic synthesis of alkene derivatives. This desulfonylation was applied to the synthesis of squalene (**27**) from allylic sulfone **26**[17] (Eq. 9).[18]



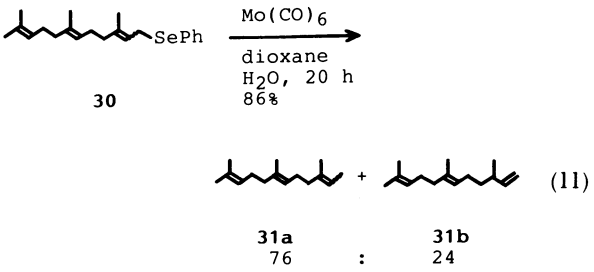
(9)

Cinnamyl phenyl selenide (**28**) did not cause the reductive deselenenylation in refluxing dioxane, but caused reductive allylic homocoupling at 100 °C in HMPA (Eq. 10). The reductive deselenenylation of



28 **29**, 80% (10)

allylic selenide having trisubstituted olefin, farnesyl phenyl selenide (**30**), easily occurred in refluxing dioxane to give triene isomers **31a** and **31b** (Eq. 11).



(11)

Conclusion

Hexacarbonylmolybdenum-induced dechalcogenization of allylic sulfides, sulfones, and selenides, which led to nucleophilic substitution with carbon nucleophiles and reduction without the carbon nucleophiles. Yields in the nucleophilic substitution were not so high, since reductive dechalcogenization presumably occurred even in the presence of the carbon nucleophiles. $Mo(CO)_6$ could thus be used as both an oxidizing agent and a reducing agent in the dechalcogenization. The reactivity of sulfonyl and selenenyl groups with $Mo(CO)_6$ seems to be higher than that of sulfenyl groups with $Mo(CO)_6$. The regiochemistry in both the nucleophilic substitution and the reduction of allylic sulfones was different from that in reactions of both allylic sulfides and selenides. The intermediate should hence be different for allylic sulfones and for allylic sulfides and selenides. Both reactions of allylic sulfones probably proceeded via π-allylmolybdenum intermediates. In contrast with allylic sulfones, allylic sulfides and selenides should not form the corresponding π-allylmolybdenum intermediates, since the coordination of sulfenyl and selenenyl groups to molybdenum center was stronger than that of olefinic moiety.

Experimental

General. $Mo(CO)_6$ was purchased from Strem Chemicals, Inc. Benzenethiol, 2-pyridinethiol, sodium benzenesulfinate, sodium *p*-toluenesulfinate, 3-bromo-1-propene, 3-chloro-1-phenyl-1-propene, 1-chloro-2-butene, 3-chloro-2-methyl-1-propene, 1-iodobutane, iodomethane, benzyl bromide, diethyl malonate, methyl vinyl ketone, and ethyl diethoxyphosphinylacetate were purchased from Tokyo Chemical Industry Co., Ltd. Diphenyl diselenide was prepared by the reaction of phenylmagnesium bromide with selenium, followed by oxidation. 2-(Ethoxycarbonyl)-cyclopentanone was prepared by the Dieckmann condensation. Allyl and γ-substituted allyl sulfides, sulfones, and selenides were prepared by reactions of allylic halides with sodium thiolates, sulfinates, and selenolates, respectively. α-Substituted allyl sulfides and selenides were prepared by alkylation of the anion of the corresponding allylic compounds with alkyl halides.[3] α-Substituted allyl sulfones were prepared by molybdenum-catalyzed oxidation of the corresponding allylic sulfides with H_2O_2. Sodium hydride and potassium hydride were employed after removal of mineral oil from 60 wt.% dispersion NaH and 35 wt.% dispersion KH, respectively (Wako Pure Chemical Industries,

Ltd.). Sodium borohydride was purchased from Wako Pure Chemical Industries, Ltd. Dioxane, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl. Purification of products was carried out by means of column chromatography (E. Merck, Silica gel 60). IR spectra were recorded on a Hitachi 260-50 spectrophotometer, ^{1}H NMR spectra on Hitachi R-22 and Jeolco FX-200 and GX-270 spectrometers, and mass spectra on a Jeolco JMS-D300 spectrometer.

General Procedure of Nucleophilic Substitution. To a solution of carbanion derived from diethyl malonate (0.16 g, 1.0 mmol) or 2-(ethoxycarbonyl)cyclopentanone (0.16 g, 1.0 mmol) with sodium hydride (29 mg, 1.2 mmol) in dry dioxane (5 ml) were added allylic compounds **I**, **II**, or **III** (1 mmol) and Mo(CO)$_6$ (1.1 mmol). This mixture was refluxed for 16—87 h under nitrogen atmosphere. The reaction mixture was diluted with chloroform (30 ml) and a precipitate was removed from the mixture by filtration. Evaporation of solvents and purification by column chromatography on silica gel using hexane/ethyl acetate (7/1) as eluent gave the product.

2-Ethoxycarbonyl-2-(2-propenyl)cyclopentanone (**3**): IR and ^{1}H NMR spectra corresponded with those of the authentic sample.[19]

2-[(*E*)-2-Butenyl]-2-(ethoxycarbonyl)cyclopentanone (**4**): IR and ^{1}H NMR spectra corresponded with those of the authentic sample.[19]

2-Ethoxycarbonyl-2-[(*E*)-3-phenyl-2-propenyl]cyclopentanone (**5**): IR (neat) 1750, 1715, 1220, 1150, 1020, 740, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.25 (t, J=7.18 Hz, 3H), 1.85—2.87 (m, 8H), 4.16 (q, J=7.18 Hz, 2H), 6.09 (dt, J=15.7, 7.53 Hz, 1H), 6.45 (d, J=15.7 Hz, 1H), 7.15—7.36 (m, 5H). The IR and ^{1}H NMR spectra corresponded with those of one regioisomer of the authentic sample.[19]

2-Ethoxycarbonyl-2-(6-phenyl-2,5-hexadienyl)cyclopentanone (**6**): IR (neat) 1750, 1720, 1220, 1150, 1020, 740, 690 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.21 (t, J=7.0 Hz, 3H), 1.74—2.70 (m, 8H), 2.84 (br. t, J=5.4 Hz, 2H), 4.06 (q, J=7.0 Hz, 2H), 5.16—5.68 (m, 2H), 6.01 (dt, J=15.4, 5.4 Hz, 1H), 6.28 (d, J=15.4 Hz, 1H), 7.02—7.32 (m, 5H). MS (70 eV) m/z (rel intensity) 312 (M^+; 0.4), 199 (39), 198 (48), 156 (100), 141 (32), 117 (79), 115 (41), 104 (54), 91 (76). Calcd for $C_{20}H_{24}O_3$: M, 312.1724. Found: m/z 312.1717.

2-Ethoxycarbonyl-2-(2-heptenyl)cyclopentanone (**7**): IR (neat) 1750, 1720, 1220, 1155 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.89 (br. t, J=6.5 Hz, 3H), 1.24 (t, J=7.0 Hz, 3H), 1.22—1.42 (m, 4H), 1.75—2.70 (m, 10H), 4.15 (q, J=7.0 Hz, 2H), 5.06—5.70 (m, 2H). MS (70 eV) m/z (rel intensity) 252 (M^+; 6.8), 179 (41), 156 (91), 121 (100), 110 (44), 55 (43). Calcd for $C_{15}H_{24}O_3$: M, 252.1724. Found: m/z 252.1727.

2-(2-Cyclohexenyl)-2-(ethoxycarbonyl)cyclopentanone (**8**): IR (neat) 1750, 1720, 1220, 1155 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.21 (t, J=7.0 Hz, 3H), 1.42—2.54 (m, 12H), 2.84—3.22 (br, 1H), 4.08 (q, J=7.0 Hz, 2H), 4.97—5.41 (m, 1H), 5.52—5.78 (m, 1H).

A mixture of diethyl 2-butenylmalonate and diethyl 1-methyl-2-propenylmalonate (**9**) (Entry 9 in Table 1): IR (neat) 1740, 1635, 1260, 1220, 1175, 1145, 1030 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.11 (d, J=6.84 Hz, 2.19H), 1.25, 1.27 (2t, J=7.18 Hz, 6H), 1.64 (d, J=6.22 Hz, 0.81H), 2.54—2.69 (m, 0.54H), 2.88—3.00 (m, 0.73H), 3.27 (d, J=8.89 Hz, 0.73H), 3.36 (t, J=7.70 Hz, 0.27H), 4.17, 4.22 (2q, J=7.18 Hz, 4H), 5.01 (dd, J=10.2, 2.60 Hz, 0.73H), 5.09 (dd, J=17.5, 2.60 Hz, 0.73H), 5.20—5.62 (m, 0.54H), 5.79 (ddd, J=17.5, 10.2, 7.86 Hz, 0.73H). MS (70 eV) m/z (rel intensity) 214 (M^+; 5.6), 141 (100), 140 (35), 123 (44), 113 (32), 112 (53), 95 (30), 55 (47). Calcd for $C_{11}H_{18}O_3$: M, 214.1204. Found: m/z 214.1198.

A mixture of diethyl 3-phenyl-2-propenylmalonate and diethyl 1-phenyl-2-propenylmalonate (**10**) (Entry 10 in Table 1): IR (neat) 1745, 1730, 1255, 1225, 1170, 1150 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.25 (t, J=7.18 Hz, 6H), 2.80 (dd, J=7.52, 7.18 Hz, 1H), 3.49 (t, J=7.52 Hz, 0.5H), 3.83 (d, J=10.9 Hz, 0.5H), 4.06—4.15 (m, 0.5H), 4.20 (q, J=7.18 Hz, 4H), 5.07 (d, J=10.2 Hz, 0.5H), 5.12 (d, J=17.0 Hz, 0.5H), 6.00 (ddd, J=17.0, 10.2, 8.12 Hz, 0.5H), 6.15 (dt, J=15.7, 7.18 Hz, 0.5H), 6.47 (d, J=15.7 Hz, 0.5H), 7.15—7.35 (m, 5H). MS (70 eV) m/z (rel intensity) 276 (M^+; 5.9), 203 (100), 175 (21), 129 (48), 117 (92), 115 (29). Calcd for $C_{16}H_{20}O_4$: M, 276.1360. Found: m/z 276.1358.

Diethyl 1-methyl-2-butenylmalonate (**11**): IR (neat) 1730, 1240, 1150 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.00 (d, J=7.0 Hz, 3H), 1.21 (br. t, J=7.0 Hz, 6H), 1.58 (d, J=4.5 Hz, 3H), 2.64—2.86 (m, 1H), 3.02 (d, J=7.5 Hz, 1H), 4.05, 4.08 (2d, J=7.0 Hz, 4H), 5.00—5.67 (m, 2H).

A mixture of diethyl 1-butyl-2-butenylmalonate (**12**): IR (neat) 1730, 1240, 1150 cm^{-1}. ^{1}H NMR (CCl_4) δ=0.70—1.08 (br, 3H) 1.03 (d, J=6.0 Hz, 2.1H), 1.15—1.74 (m, 10.6H), 1.61 (d, J=5.6 Hz, 0.9H), 1.74—2.14 (m, 1.4H), 2.44—3.02 (m, 1H), 3.02—3.21 (m, 1H), 3.92—4.26 (m, 4H), 5.00—5.56 (m, 2H).

A mixture of diethyl 1-butyl-2-propenylmalonate and diethyl 2-heptenylmalonate (**13**) (Entry 32 in Table 1): IR (neat) 1750, 1725, 1240, 1150 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.80—0.95 (br, 3H), 1.15—1.45 (m, 11H), 1.95—2.03 (m, 1H), 2.57 (dd, J=6.60, 6.30 Hz, 1H), 2.83—2.90 (m, 0.5H), 3.30—3.42 (m, 1H), 4.18 (q, J=7.18 Hz, 4H), 5.03—5.14 (m, 1H), 5.25—5.74 (m, 1.5H). MS (70 eV) m/z (rel intensity) 256 (M^+; 6.5), 199 (81), 183 (83), 165 (42), 161 (30), 160 (100), 155 (30), 153 (38), 140 (34), 133 (36), 127 (39), 125 (43), 115 (31), 81 (37), 67 (34), 55 (87). Calcd for $C_{14}H_{24}O_4$: M, 256.1673. Found: m/z 256.1677.

Diethyl 2-propenylmalonate (**14**): IR (neat) 1725, 1270, 1115 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.27 (t, J=7.18 Hz, 6H), 2.61—2.67 (m, 2H), 3.42 (t, J=7.52 Hz, 1H), 4.20 (q, J=7.18 Hz, 4H), 5.06 (dd, J=10.3, 2.60 Hz, 1H), 5.12 (dd, J=17.1, 2.60 Hz, 1H), 5.78 (ddt, J=17.1, 10.3, 6.83 Hz, 1H). MS (70 eV) m/z (rel intensity) 200 (M^+; 3.0), 182 (30), 153 (39), 127 (40), 109 (36), 105 (100), 98 (32), 93 (29), 81 (27), 77 (53). Calcd for $C_{10}H_{16}O_4$: M, 200.1048. Found: m/z 200.1045.

Diethyl 1-benzyl-2-propenylmalonate (**15**): IR (neat) 1730, 1230, 1150 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.21 (t, J=6.8 Hz, 6H), 2.43—2.92 (m, 3H), 3.25 (d, J=6.0 Hz, 1H), 4.09 (2q, J=6.8 Hz, 4H), 4.72—4.95 (m, 2H), 5.46—5.90 (m, 1H), 6.93—7.24 (m, 5H).

2-Ethoxycarbonyl-2-(4-phenyl-2-butenyl)cyclopentanone (**16**): IR (neat) 1745, 1720, 1220, 1150, 750, 700 cm^{-1}. ^{1}H NMR (CCl_4) δ=1.17 (t, J=7.2 Hz, 3H), 1.63—2.70 (m, 8H), 3.24 (d, J=6.4 Hz, 2H), 4.03 (q, J=7.2 Hz, 2H), 5.10—5.75 (m, 2H), 6.90—7.25 (m, 5H). MS (70 eV) m/z (rel intensity) 286 (M^+; 0.1), 131 (16), 130 (100), 129 (13), 121 (11), 91 (20). Calcd for $C_{18}H_{22}O_3$: M, 286.1568. Found: m/z 286.1565.

General Procedure of Reductive Dechalcogenization. A solution of allylic compound **I**, **II**, or **III** (1 mmol), Mo(CO)$_6$ (1.1 mmol), and H_2O (5 mmol) in dioxane (7 ml) was refluxed for 3—40 h under nitrogen atmosphere. The reaction mixture was diluted with chloroform (40 ml) and

precipitate material was removed from the mixture by filtration. Evaporation of solvents and purification by column chromatography on silica gel using hexane or hexane/ethyl acetate as eluent gave the product.

A mixture of 4-(3,4-methylenedioxyphenyl)-1-butene (**20a**), 1-(3,4-methylenedioxyphenyl)-2-butene (**20b**), and 1-(3,4-methylenedioxyphenyl)-1-butene (**20c**): ^{1}H NMR ($CDCl_3$) **20a**: δ=2.33 (m, 2H), 2.62 (t, J=7.42 Hz, 2H), 4.97 (br. d, J=10.9 Hz, 1H), 5.02 (br. d, J=18.0 Hz, 1H), 5.76—5.88 (m, 1H), 5.91 (s, 2H), 6.60 (br, 1H), 6.63 (br, 2H), **20b**: δ=1.67 (br. d, J=5.10 Hz, 3H), 3.22, 3.31 (E/Z=81/19, 2d, J=5.10, 5.79 Hz, 2H), 5.49—5.56 (m, 2H), 5.92 (s, 2H), 6.67 (br, 2H), 6.71 (s, 1H), **20c**: δ=1.07 (t, J=7.52 Hz, 3H), 2.19 (m, 2H), 5.90 (s, 2H), 6.08 (dt, J=15.6, 6.33 Hz, 1H), 6.28 (d, J=15.6 Hz, 1H), 6.73 (br, 2H), 6.89 (br, 1H). MS (70 eV) m/z (rel intensity) 176 (M^+, 93), 161 (29), 131 (100), 103 (46), 77 (22). Calcd for $C_{11}H_{12}O_2$: M, 176.0836. Found: m/z 176.0836.

Ethyl 3,7-dimethyl-2,6-octadienoate (**22**): ^{1}H NMR (CCl_4) δ=1.21 (t, J=7.2 Hz, 3H), 1.56 (s, 3H), 1.64 (s, 3H), 1.90—2.30 (m, 4H), 2.09 (s, 3H), 4.02 (q, J=7.2 Hz, 2H), 5.00 (m, 1H), 5.51 (br, 1H). The NMR spectrum corresponded with that of the authentic sample derived from 6-methyl-5-hepten-2-one and ethyl diethoxyphosphinylacetate with t-BuOK.

A mixture of stereoisomers of squalene (**27**): ^{1}H NMR ($CDCl_3$) δ=1.60, 1.68 (2s, 24H), 1.90—2.15 (m, 20H), 5.03—5.19 (m, 6H). The NMR spectrum corresponded with that of an authentic sample.[20] The isomer ratio was determined by GLPC [5% OV-17/Chromosorb W (AW-DMCS), 60—80 mesh, 2 m, He, 200 °C].[20]

1,6-Diphenyl-1,5-hexadiene (**29**): IR (KBr) 1590, 1480, 1180, 1065, 1015, 735 cm^{-1}. ^{1}H NMR (CCl_4) δ=2.23—2.38 (br, 4H), 6.07 (dt, J=16.0, 5.8 Hz, 2H), 6.35 (t, J=16.0 Hz, 2H), 6.90—7.25 (m, 10H). The IR and NMR spectra and retention time of GLPC [5% OV-17/Chromosorb W (AW-DMCS), 60—80 mesh, 2 m, He, 230 °C] corresponded with those of an authentic sample.[20]

A mixture of 2,6,10-trimethyl-2,6,10-dodecatriene (**31a**) and 3,7,11-trimethyl-1,6,10-dodecatriene (**31b**): IR (neat) 2960, 2920, 970 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=0.95 (d, J=6.96 Hz, 0.72H), 1.53—1.75 (m, 14.0H), 1.90—2.20 (br, 7.8H), 4.90 (dd, J=9.60, 2.20 Hz, 0.24H), 4.95 (d, J=16.0 Hz, 0.24H), 5.11 (t, J=5.38 Hz, 2H), 5.20 (q, J=6.70 Hz, 0.76H), 5.68 (ddd, J=16.0, 9.60, 7.80 Hz, 0.24H). MS (70 eV) m/z (rel intensity) 206 (M^+, 6), 137 (14), 123 (14), 81 (62), 69 (100), 55 (18). Calcd for $C_{15}H_{26}$: M, 206.2033. Found: m/z 206.2033.

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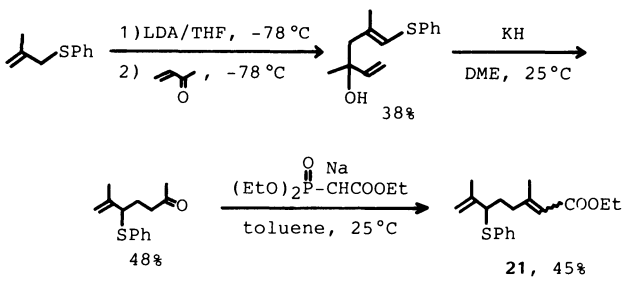

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