3-Chloro-2-chloromethyl-4-(4-chlorophenoxy)-1-butene as a Functionalized Isoprene Unit. An Electrochemical Preparation and Some Reactions

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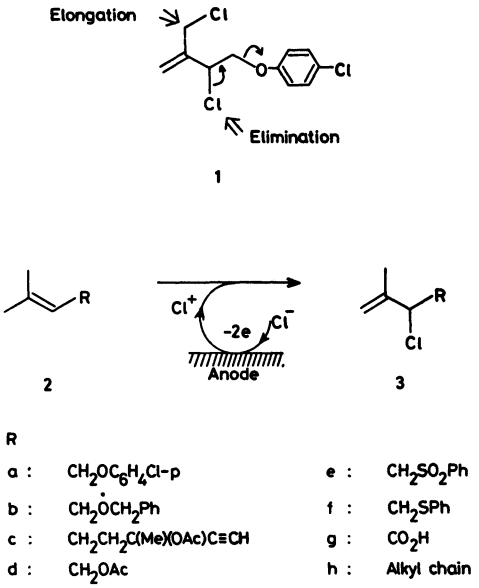
3-Chloro-2-chloromethyl-4-(4-chlorophenoxy)-1-butene (**1**) was prepared in 72% yield by electrooxidative double ene-type chlorination of 1-(4-chlorophenoxy)-3-methyl-2-butene. The electrolysis was conducted at room temperature in a two layer solvent system of dichloromethane and water in the presence of acids (HCl, H_2SO_4, H_3PO_4, *etc*). Either 3-chloro-2-methyl-4-(4-chlorophenoxy)-1-butene or **1** was selectively prepared, respectively after 4 or 10 F/mol of electricity were passed using platinum foils as electrodes in an undivided cell. The similar electrolysis of the related 3-methyl-2-butenyl derivatives **2b** and **2c** provided the ene-type products, 3-chloro-2-methyl-4-benzyloxy-1-butene and 4-chloro-1-ethynyl-1,5-dimethyl-5-hexenyl acetate, respectively. In contrast, 3-methyl-2-butenyl derivatives **2d**—**f** and 3-methyl-2-butenoic acid afforded a variety of products such as chlorohydrin, vinyl chloride, and sulfoxide other than ene-type products, suggesting that the functional group of R in **2** affects the reaction course. The elongation at 2-chloromethyl group and the subsequent dechlorophenoxylation convert **1** into 2-(phenylsulfonylmethyl)-1,3-butadiene and 2-(phenylthiomethyl)-1,3-butadiene.

Functionalization and subsequent elongation of isoprene derivatives are one of the effective approaches to the terpene synthesis.[1] Although there have been known various isoprene derivatives as a synthetic building block, 3-chloro-2-chloromethyl-4-(4-chlorophenoxy)-1-butene (**1**) has not been prepared. The compound **1** has two allylic chlorine atoms and can be elongated at the chloromethyl group and subsequently can be converted into a conjugated diene by reductive elimination of the another allylic chlorine atom. This paper describes an electrochemical preparation and some modifications of **1** along with the electrochemical chlorinative functionalization of the related isoprene derivatives **2a**—**g**.



R

a :	$CH_2OC_6H_4Cl$-p	e :	CH_2SO_2Ph
b :	CH_2OCH_2Ph	f :	CH_2SPh
c :	$CH_2CH_2C(Me)(OAc)C{\equiv}CH$	g :	CO_2H
d :	CH_2OAc	h :	Alkyl chain

Scheme 1.

Results and Discussion

So far as the allylic chlorination of olefins is concerned, the selenium reagent-mediated NCS chlorination,[2] the action of hypochlorous acid[3] or calcium hypochlorite in dichloromethane[4] and the chlorination with *t*-butyl hypochlorite in the presence of silica gel[5] have been reported. Recently, we communicated an electrochemical chlorinative ene-type reaction of isoprenoids **2h** which offers a simple and highly regio- and chemoselective access to allylic chloride **3h**.[6] The electrolysis is conducted in a two layer solvent system where a chloronium ion or the corresponding active chlorinating reagent is electrooxidatively generated in an aqueous sodium chloride layer and the chlorination occurs subsequently in a dichloromethane layer.[6,7] The electrochemical chlorination, however, did not afford the doubly chlorinated products related to **1** presumably due to the deactivation of the double bond of **3h** by electronegative chlorine atom. On this basis, the acid-promoted activation of the electrochemically generated chlorinating reagent was devised to enable the double ene-type chlorination, and also the electrolysis of isoprene derivatives **2a**—**g** was examined in detail where substituents affect the reaction pathway markedly.

The electrolysis was conducted in a two layer solvent system of CH_2Cl_2–H_2O (2 : 1) using an undivided cell. Platinum electrodes were settled in an aqueous sodium chloride layer and a gentle stirring was preferable to avoid a complete mixing which induced chlorohydrination partially.[8] Upon no stirring the reaction solution, a current efficiency was extremely low. The complete mixing enhances the solubilization of the chlorinating reagent produced in a water layer into the dichloromethane layer to improve the current efficiency, meanwhile it induces chlorohydrination by the increased contact of the water layer with the organic layer. Thus, electrolysis of **2a** in the presence of a large excess amount of sodium chloride and hydrochloric acid in CH_2Cl_2–H_2O at room temperature afforded **3a** in 84% yield after 4 F/mol and **1** in 72% yield after 10 F/mol. Most of mineral acids (HCl, HNO_3, H_2SO_4, H_3PO_4) are effective for the double ene-type chlorination and likewise organic acids affect the reaction highly. However, formic acid is not effective since the current efficiency is unexpectedly low (Table 1). Although formic acid is known to activate *t*-butylhypochlorite for the chemical ene-type chlorination,[9] it is a reducing agent so that it would reduce the electrogenerated

chlorinating reagent. In fact, **1** was obtained in 63% yield by the reaction of **2a** with sodium hypochlorite in CH_2Cl_2–H_2O in the presence of hydrochloric acid. In contrast to this, none of **1** was detected in the presence of formic acid while only 7% of **3a** was isolated and 92% of **2a** was recovered.

The relation of the acid concentration and the yields is shown in Fig. 1. Excess use of hydrochloric acid accelerated dichlorination whereas in the absence of the acid, 57% of the starting substance **2a** was recovered, and 34% of **3a** was obtained but none of **1** was isolated even after 10 F/mol of electricity was passed. In fact, 40 F/mol of electricity was required in order to complete monochlorination of **2a** (89%) in the absence of acid.[10]

The yields of **1** and **3a** are dependent to electricity passed (F/mol) (Fig. 2). In the presence of excess amount of acid, the starting substance **2a** disappeared almost completely at around 4 F/mol where the yield of **3a** reached to an optimum, while the yield of **1** increased steadily in proportion to electricity. This result suggests that **2a** is more reactive toward the chlorinating reagent than **3a**.

The effect of the solvent is also noteworthy. The use of immiscible solvents in water such as dichloromethane, chloroform, 1,2-dichloroethane, and benzene all of which constitute a two-phase system leads to a selective formation of **1** and **3a**. In contrast, the use of miscible solvents such as methanol and acetonitrile induced predominantly chlorohydrination, chloromethoxylation, and chloroacetamidation, respectively. Ethyl acetate is immiscible but slightly soluble in water[11] so that it affected both ene-type chlorination and chlorohydrination. The transition state of the ene-type chlorination where chlorination to double bond and deprotonation from methyl group take place concertedly, is not cation-like,[12] and therefore it would be favored in less polar and water-immiscible solvents.

The mechanism of the acid-catalyzed ene-type chlorination is not clear yet at this stage. However, it is proposed that a protonated chlorinating reagent would be more reactive for the ene-type chlorination.[9] The electrochemically generated chlorinating reagent would be in equilibrium as shown in Eq. 1.[13]

$$2\,HOCl \rightleftharpoons Cl_2O + H_2O \quad (1)$$

Since chlorine monoxide (Cl_2O) is more soluble in

Table 1. Effect of acids on the electrochemical ene-type chlorination of **2a**[a] in dichloromethane–water.

Acid	Products (%) 4 F/mol			10 F/mol		
	2a	**3a**	**1**	**2a**	**3a**	**1**
HCl	0	84	4	0	0	72
H_2SO_4[c]	0	80	4	0	2	65
HNO_3	0	80	6	0	2	66
H_3PO_4[d]	0	75	4	0	1	63
AcOH	0	76	12	0	1	66
$CH_3(CH_2)_2CO_2H$	0	85	2	0	46	36
$C_{10}H_{16}O_4S$[b]	0	79	4	0	2	71
HCO_2H	73	19	0	49	42	0

a) CH_2Cl_2 (8 ml)–H_2O (4 ml)–3 mol dm^{-3} acid (1ml). b) *dl*-10-Camphorsulfonic acid. c) 1.5 mol dm^{-3} of H_2SO_4 (1 ml). d) 1 mol dm^{-3} of H_3PO_4 (1 ml).

Table 2. Effect of solvents on the electrochemical ene-type chlorination of **2a**[a]

Solvent[b]	Products (%) **2a**	**3a**	**1**	Others
CH_2Cl_2–H_2O	0	84	3	—
$CHCl_3$–H_2O	3	84	0	—
$ClCH_2CH_2Cl$–H_2O	13	75	0	—
C_6H_6–H_2O	11	79	0	—
AcOEt–H_2O	0	0[c]	51	**4a**(32), **4d**(15)
MeOH–H_2O	18	0	0	**4a**(41), **4b**(24)
MeCN–H_2O	0	0	0	**4a**(31), **4c**(60)
$(C_2H_5)_2O$–H_2O	47	40	1	**4a**(11)

a) A constant current (20 mA/cm^2, 4 F/mol) was applied. b) Organic solvent (8 ml)–water (4 ml)–3.2 mol dm^{-3} HCl (1 ml). c) At 3 F/mol, **3a** (36%) and **1** (21%) were obtained.

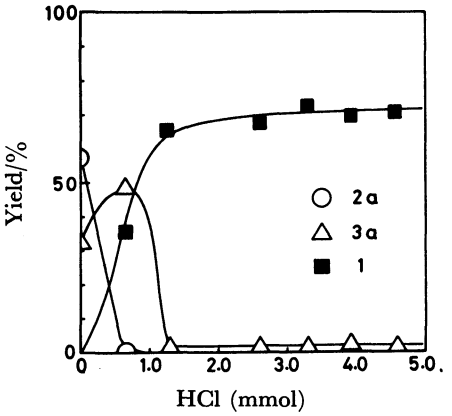


Fig. 1. The relation of the yields of **1** and **3a** with the concentration of HCl in the electrochemical ene-type chlorination of **2a** in CH_2Cl_2 (8 ml)–H_2O (4 ml) containing **2a** (50 mg, 0.25 mmol) and NaCl (500 mg, 8.6 mmol). The constant current (20 mA/cm^2, 10 F/mol) was applied at room temperature.

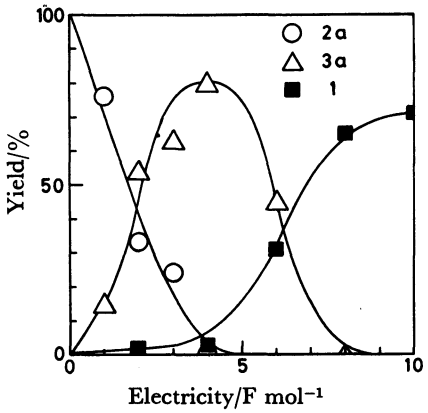


Fig. 2. The relation of the yields of **1** and **3a** with electricity (F/mol) in the electrochemical ene-type chlorination of **2a** in CH_2Cl_2 (8 ml)–H_2O (4 ml)–3.2 mol dm^{-3} HCl (1 ml) containing **2a** (50 mg) and NaCl (500 mg).

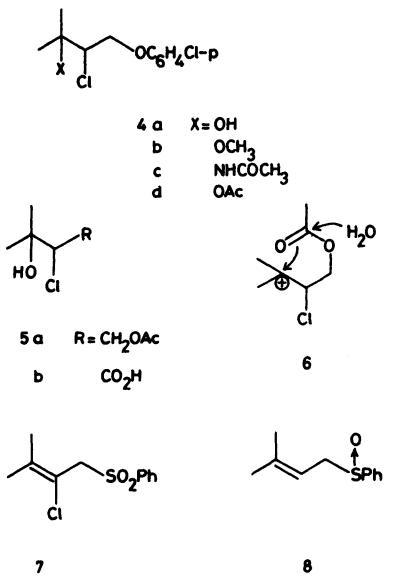
TABLE 3. THE ELECTROCHEMICAL ENE-TYPE CHLORINATION OF **2a**—**g** IN DICHLOROMETHANE–WATER[a)]

Substrate **2** R	F/mol[b)]	Product (%)		
		3	**5**	Others
2a $CH_2OC_6H_4Cl$-*p*	4.0	84	0	0
2b $CH_2OCH_2C_6H_5$	4.0	81	0	0
2c $CH_2CH_2C(OAc)(CH_3)C{\equiv}CH$	5.0	86	0	0
2d CH_2OAc[c)]	3.2	0	85	0
2e $CH_2SO_2C_6H_5$[e)]	4.0	23	0	**7**(68)
2f $CH_2SC_6H_5$[d,e)]	4.0	0	0	**8**(77)[f)]
2g CO_2H	4.0	0	55	0

a) CH_2Cl_2 (8 ml)–H_2O (4 ml)–3.2 mol dm^{-3} HCl (1 ml). b) Current density 20 mA/cm^2. c) 1,2-dichloroethane was employed as a solvent. d) Current density 7 mA/cm^2. e) 3.2 mol dm^{-3} (1.5 ml) was used. f) **2f** (7%) was recovered.

organic solvents than in water,[14)] the electrogenerated chlorinating reagent would preferentially migrate as chlorine monoxide into the organic phase where the acid-catalyzed ene-type chlorination proceeds. The fact that the use of organic acids (Table 1) highly facilitates the ene-type reaction suggests the hypothesis.

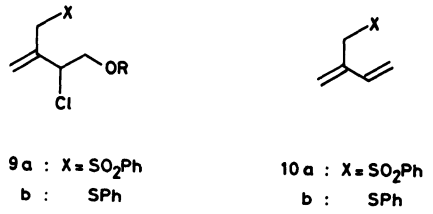
The electrolyses of **2b**—**g** were carried out in similar conditions and the result is shown in Table 3. The result suggests that the reaction pathways of **2** with the electrogenerated chlorinating reagent are extensively affected by the nature of the substituents on the prenyl moiety. The desired chlorination of **2a**, **2b**, and **2c**, proceeds smoothly to give **3a** (84%), **3b** (81%), and **3c** (86%), respectively. However, the electrolyses of **2d**, **2e**, **2f**, and **2g**, are quite dissimilar to the ene-type chlorination. Both **2d** and **2g** provided chlorohydrins **5a** and **5b**. The chlorohydrination of **2d** would proceed *via* intramolecular trapping of the carbocation **6** by acetoxyl group.[15)] Sulfone **2e** gave preferentially a vinyl chloride derivative **7** (68%) along with **3d** (23%). Deprotonation of H-2 would compete with the normal ene-type deprotonation because of the higher acidity



Scheme 2.

of H-2 than H-4 by the electron-withdrawing nature of benzenesulfonyl group. Sulfide **2f** is oxidized at the divalent sulfur atom to give sulfoxide **8**. The exclusive sulfoxidation can be rationalized by the fact that the divalent sulfur atom is more readily oxidized both by electrode process and by chemical reagents like NBS.[16)]

Substitution reaction of **1** with sodium benzenesulfinate in DMF proceeded smoothly at chloromethyl group providing **9a** in 72% yield. Likewise, reaction of **1** with sodium benzene thiolate in DMF at −20 °C yielded **9b** (92%). Dechlorophenoxylation of both **9a** and **9b** were performed in 87 and 74% yields, respectively by reduction with zinc in ethanol.[17)]



Scheme 3.

Experimental

All boiling and melting points are uncorrected. IR spectra were determined with a JASCO IRA-I infrared spectrometer. ^1H NMR spectra were obtained with a Hitachi R-24 (60 MHz) or a JEOL FX-100 (100 MHz) spectrometer and the chemical shifts are expressed in ppm (δ) downfield from TMS as an internal standard.

Electrolysis. Electrolysis was carried out in a beaker (3 cm in diameter and 10 cm in height) fitted with two platinum foil electrodes (1.5×2 cm^2) in 7—10 mm apart. A constant current (20 mA/cm^2) was applied by a regulated DC powder instrument (Metronix 543B). The electrodes were settled in a water layer and the reaction solution was gently stirred by a magnetic stirrer so that the water layer can well contact with the organic layer but drops of the water layer do not disperse into the organic layer.

Electrolysis of 2a; 3-Chloro-2-chloromethyl-4-(4-chlorophenoxy)-1-butene (1) and 3-chloro-2-methyl-4-(4-chlorophenoxy)-1-butene (3a). A mixture of **2a** (50 mg, 0.25 mmol, NaCl (500 mg, 8.5 mmol) and 3.2 mol dm^{-3} HCl (1 ml) in CH_2Cl_2 (8 ml) –H_2O (4 ml) was electrolyzed at room temperature for 27.3 min (4 F/mol). The mixture was neutralized with saturated $NaHCO_3$ and the organic substances were extracted with ether. The organic layer was washed two times with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako-gel C-200, *n*-hexane) to give a colorless oil (54 mg) whose HPLC analysis (μ-porasil, hexane–AcOEt=20 : 1) showed purity of **3a** was over 90%. Thus, yield of **3a** was 84%. Other products were **1** (3%), 3-chloro-2-methyl-4-(3,4-dichlorophenoxy)-1-butene (2—3%) and the unidentified product (2—3%) by HPLC analysis: **1**: Bp 118 °C/0.02 mmHg (1 mmHg≈133.322 Pa); IR: 1630, 1595, 1580, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.18 (s, 2H, CH_2Cl), 4.21 (d, J=7 Hz, 2H, CH_2), 4.80 (*t*, J=7 Hz, 1H, CHCl), 5.42 (br. s, 2H, CH_2=), 6.7—7.3 (m, 4H, ArH). Found: C, 49.92; H, 4.33%. Calcd for $C_{11}H_{11}Cl_3O$: C, 49.75; H, 4.15%. **3a**: Bp 105 °C/0.33 mmHg; IR: 1650 (C=C), 1595, 1580, 1240 cm^{-1}; ^1H NMR (CCl_4) δ=1.84 (s, 3H, CH_3), 4.08 (d, J=6 Hz, 2H, CH_2), 4.55 (dd, J_1=6 Hz, J_2=5 Hz, 1H, CHCl), 4.9—5.3 (m,

2H, CH_2=), 6.5—7.2 (m, 4H, ArH). Found: C, 57.36; H, 5.11%. Calcd for $C_{11}H_{12}Cl_2O$: C, 57.17; H, 5.20%.

*3-Chloro-2-methyl-4-benzyloxy-1-butene (**3b**)*: Bp 65 °C/0.03 mmHg; IR: 1645 (C=C), 1600, 1580, 1120 cm^{-1}; ^1H NMR (CCl_4) δ=1.75 (br. s, 3H, CH_3), 3.55 (d, J=7 Hz, 2H, CH_2), 4.42 (t, J=7 Hz, 1H, CHCl), 4.45 (s, 2H, CH_2), 4.8—5.1 (m, 2H, CH_2=), 7.20 (br. s, 5H, ArH). Found: C, 68.53; H, 7.35%. Calcd for $C_{12}H_{15}ClO$: C, 68.42; H, 7.13%.

*4-Chloro-1-ethynyl-1,5-dimethyl-5-hexenyl Acetate (**3c**)*: Bp 80 −82 °C/0.03 mmHg; IR: 3300 (≡CH), 2100 (C≡C), 1740 (AcO) cm^{-1}; ^1H NMR ($CDCl_3$) δ=5.13 (br. s, 1H, =CH_2), 5.00 (br. s, 1H, =CH_2), 4.46 (t, J=6.6 Hz, 1H, CHCl), 2.62 (s, 1H, ≡CH), 2.08 (s, 3H, Ac), 2.2—1.9 (m, 4H, CH_2), 1.86 (br. s, 3H, CH_3), 1.74 (s, 3H, CH_3). Found: C, 63.06; H, 7.55%. Calcd for $C_{12}H_{17}O_2Cl$: C, 63.01; H, 7.49%.

*3-Chloro-2-methyl-4-phenylsulfonyl-1-butene (**3e**)*: Bp 117 °C/0.02 mmHg; IR: 1640 (C=C), 1580, 1310 (SO_2), 1140 (SO_2) cm^{-1}; ^1H NMR (CCl_4) δ=1.75 (br. s, 3H, CH_3), 1.77 (s, 3H, CH_3), 3.55 (d, J=7 Hz, 2H, CH_2), 4.80 (t, J=7 Hz, 1H, CHCl), 4.92 (br. s, 1H, CH=), 5.10 (br. s, 1H, CH=), 7.3—8.0 (m, 5H, ArH). Found: C, 53.93; H, 5.32%. Calcd for $C_{11}H_{13}O_2ClS$: C, 54.00; H, 5.32%.

*3-Chloro-2-methyl-4-(4-chlorophenoxy)-2-butanol (**4a**)*: Bp 113 °C/0.02 mmHg; IR: 3400 (OH), 1590, 1580, 1250 cm^{-1}; ^1H NMR (CCl_4) δ=1.36 (s, 6H, CH_3), 2.4 (br. s, 1H, OH), 4.0—4.5 (m, 3H, $CHClCH_2O$), 6.7—7.4 (m, 4H, ArH). Found: C, 53.15; H, 5.85%. Calcd for $C_{11}H_{14}O_2Cl_2$: C, 53.03; H, 5.62%.

*2-Chloro-3-methyl-3-methoxybutyl 4-Chlorophenyl Ether (**4b**)*: Bp 91 °C/0.015 mmHg; IR: 2830, 1605, 1250 cm^{-1}; ^1H NMR (CCl_4) δ=1.27 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 3.23 (s, 3H, CH_3O), 3.9—4.6 (m, 3H, $CHClCH_2O$), 6.7—7.3 (m, 4H, ArH). Found: C, 54.63; H, 6.13%. Calcd for $C_{12}H_{16}O_2Cl_2$: C, 54.77; H, 6.09%.

N-[*2-Chloro-1,1-dimethyl-3-(4-chlorophenoxy)propyl*] *Acetamide (**4c**)*: Bp 110 °C/0.035 mmHg; IR: 3260 (NH), 1650 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.49 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 4.0—4.4 (m, 2H, CH_2O), 4.94 (dd, J_1=6 Hz, J_2=4 Hz, 1H, CHCl), 6.31 (br. s, 1H, NH), 6.6—7.3 (m, 4H, ArH). Found: C, 53.74; H, 5.79%. Calcd for $C_{13}H_{17}O_2NCl_2$: C, 53.81; H, 5.86%.

*2-Chloro-1,1-dimethyl-3-(4-chlorophenoxy)propyl Acetate (**4d**)*: Bp 120 °C/0.03 mmHg; IR: 1740 (C=O), 1595, 1580, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.67 (s, 6H, CH_3), 2.06 (s, 3H, Ac), 4.14 (dd, J_1=7.2 Hz, J_2=10.5 Hz, 1H, CH_2O), 4.37 (dd, J_1=4.2 Hz, J_2=10.5 Hz, 1H, CH_2O), 4.80 (dd, J_1=4.2 Hz, J_2=7.2 Hz, CHCl), 6.80—7.44 (m, 4H, ArH). Found: C, 53.76; H, 5.59%. Calcd for $C_{13}H_{16}O_3Cl_2$: C, 53.62; H, 5.55%.

*2-Chloro-3-hydroxy-3-methylbutyl Acetate (**5a**)*: Bp 93 °C/0.03 mmHg; IR: 3440 (OH), 1740 (C=O), 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (s, 6H, CH_3), 2.05 (s, 3H, Ac), 2.73 (s, 1H, OH), 3.8—4.6 (m, 3H, $CHClCH_2O$). Found: C, 46.53; H, 7.26%. Calcd for $C_7H_{13}O_3Cl$: C, 46.55; H, 7.20%.

*2-Chloro-3-hydroxy-3-methylbutanoic Acid (**5b**)*: The carboxylic acid **5b** was esterified with diazomethane in ether and the analytical data were measured as its methyl ester. Bp 92 °C/0.02 mmHg; IR: 3460 (OH), 1740 (C=O), 1170 cm^{-1}; ^1H NMR (CCl_4) δ=1.34 (s, 6H, CH_3), 2.3—2.8 (m, 1H, OH), 3.79 (s, CH_3O), 4.16 (s, 1H, CHCl). Found: C, 43.32; H, 6.57%. Calcd for $C_6H_{11}O_3Cl$: C, 43.37; H, 6.63%.

*2-Chloro-3-methyl-1-phenylsulfonyl-2-butene (**7**)*: Bp 120 °C/0.02 mmHg; IR: 1640 (C=C), 1585, 1305 (SO_2), 1140 (SO_2) cm^{-1}; ^1H NMR (CCl_4) δ=1.65 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 4.08 (s, 2H, CH_2), 7.3—8.0 (m, 5H, ArH). Found: C, 54.17; H, 5.55%. Calcd for $C_{11}H_{13}O_2ClS$: C, 54.00; H, 5.32%.

*3-Methyl-2-butenylphenylsulfoxide (**8**)*: Bp 88 °C/0.03 mmHg; IR: 1665 (C=C), 1580, 1045 (SO) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.43 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 3.56 (d, J=8 Hz, 2H, CH_2), 5.12 (t, J=8 Hz, 1H, =CH), 7.31—7.90 (m, 5H, ArH), Found: C, 68.05; H, 7.29%. Calcd for $C_{11}H_{14}OS$: C, 67.99; H, 7.27%.

*3-Chloro-4-(4-chlorophenoxy)-2-(phenylsulfonylmethyl)-1-butene (**9a**)*: Mp: 49—51 °C; IR: 1640 (C=C), 1320 (SO_2), 1230. 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.03 (s, 2H, CH_2SO_2), 4.26 (d, J=6.3 Hz, 2H, CH_2O), 4.91 (t, J=6.3 Hz, 1H, CHCl), 5.60 (s, 1H, CH=), 5.25 (s, 1H, CH=), 6.7—7.4 (m, 4H, ArH), 7.5—8.1 (m, 5H, ArH). Found: C, 55.06; H, 4.17%. Calcd for $C_{17}H_{16}O_3Cl_2S$: C, 55.00; H, 4.31%.

*3-Chloro-4-(4-chlorophenoxy)-2-(phenylthiomethyl)-1-butene(**9b**)*: Bp 136 °C/0.025 mmHg; IR: 1600, 1580, 1495, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.66 (s, 2H, CH_2S), 4.18 (d, J=6 Hz, 2H, CH_2O), 4.86 (t, J=6 Hz, 1H, CHCl), 5.15 (br. s, 1H, CH_2=), 5.22 (br. s, 1H, CH_2=), 6.5—7.4 (m, 9H, ArH). Found: C, 60.17; H, 4.69%. Calcd for $C_{17}H_{16}OSCl_2$: C, 60.19; H, 4.72%.

*2-(Phenylsulfonylmethyl)-1,3-butadiene (**10a**)*: Mp 41—42 °C IR: 1595, 1320 (SO_2), 1310, 1150 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.03 (s, 2H, CH_2), 5.04—5.37 (m, 4H, CH_2), 6.32 (dd, J_1=11 Hz, J_2=18 Hz, 1H, CH=), 7.5—8.0 (m, 5H, ArH). Found: C, 63.39; H, 5.64%. Calcd for $C_{11}H_{12}O_2S$: C, 63.46; H, 5.77%.

*2-(Phenylthiomethyl)-1,3-butadiene (**10a**)*: Bp 70 °C/0.03 mmHg; IR: 1630 (C=C), 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 3.75 (s, 2H, CH_2), 5.18 (s, 2H, CH_2=), 5.22 (d, J=11.5 Hz, 1H, CH_2=), 5.41 (d, J=17.5 Hz, 1H, CH_2=), 6.46 (dd, J_1= 11.5 Hz, J_2=17.5 Hz, 1H, CH=), 7.2—7.5 (m, 5H, ArH). Found: C, 74.89; H, 6.87%. Calcd for $C_{11}H_{12}S$: C, 75.00; H, 6.82%.

References

1) K. Takabe, T. Katagiri, J. Tanaka, *Koryo*, **108**, 27 (1974); Y. Fujita, Y. Ninagawa, T. Nishida, and K. Itoi, *Yuki Gosei Kagaku Kyokai Shi*, **37**, 244 (1979); S. Torii, K. Uneyama, and T. Inokuchi, *Koryo*, **125**, 47 (1979).

2) T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44**, 4202, 4208 (1979).

3) S. Marmor and J. G. Maroski, *J. Org. Chem.*, **31**, 4278 (1966).

4) S. G. Hedge, M. K. Vogel, J. Saddler, T. Hrinyo, N. Rockwell, R. Haynes, M. Oliver, and J. Wolinski, *Tetrahedron Lett.*, **21**, 441 (1980); S. G. Hedge, and J. Wolinsky, *ibid.*, **22**, 5019 (1981).

5) W. Sato, N. Ikeda, and H. Yamamoto, *Chem. Lett.*, **1982**, 141.

6) S. Torii, K. Uneyama, T. Nakai, and T. Yasuda, *Tetrahedron Lett.*, **22**, 2291 (1981).

7) S. Torii, H. Tanaka, N. Saitoh, T. Siroi, M. Sasaoka, and J. Nokami, *Tetrahedron Lett.*, **22**, 3193 (1981).

8) Chlorohydrin **4a** (11%) was obtained as one of by-product.

9) R. D. G. Cooper, *Tetrahedron Lett.*, **21**, 781 (1980); L. A. Paquette, L. W. Hertel, R. Gleiter, M. C. Bohm, M. A. Beno, and G. G. Christoph, *J. Am. Chem. Soc.*, **103**, 7106 (1981).

10) **1** (6%) was obtained as a byproduct.

11) Solubility (g/100 g of water) of the solvents employed is as follows; CH_2Cl_2 (2), $CHCl_3$ (0.8), $ClCH_2CH_2Cl$ (0.9), C_6H_6 (0), AcOEt (7.9), MeOH (∞), MeCN (∞).

12) M. Yoshioka, T. Tsuji, S. Uyeo, S. Yamamoto, T. Aoki, Y. Nishitani, S. Mori, H. Satoh, Y. Hamada, H. Ishitobi, and W. Nagata, *Tetrahedron Lett.*, **21**, 351 (1980).

13) The chemistry of chlorine monoxide is reviewed. J. J.

Renard and H. I. Bolker, *Chem. Rev.*, **76**, 487 (1976).
14) S. Goldschmidt, *Chem. Ber.*, **52B**, 753 (1919).
15) S. Winstein, C. R. Lindegren, H. Marshall, and L. L, Ingraham, *J. Am. Chem. Soc.*, **75**, 147 (1953); The acetoxyl group participation toward selenirenium type cation has been proposed. K. Uneyama, K. Takano, and S. Torii, *Tetrahedron Lett.*, **23**, 1161 (1982).
16) S. Torii, K. Uneyama, K. Iida, and K. Sasaki, *Tetrahedron Lett.*, **1972**, 4513.
17) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 182 (1958).