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Electrolyses of 2,2-Dichloro-3-phenylcyclopropanecarboxylic Acids in Hydroxylic Solvents with a Platinum Anode*

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Electrolysis of 2,2-dichloro-3-phenylcyclopropanecarboxylic acid (**1a**) in hydroxylic solvents such as methanol and acetic acid, or in aqueous methanol with acetic acid in excess, was carried out with a platinum anode. Solvolysis rather than coupling was found to occur yielding 3,3-dichloro-1-phenylallyl methyl ether (**4a**) or 3,3-dichloro-1-phenylallyl acetate (**5a**), or both, depending on the solvent. Electrolysis of 2,2-dichloro-3-methyl-3-phenylcyclopropanecarboxylic acid (**1b**) in aqueous methanol gave ether **4b**. Structural characterization of the products was also discussed.

In the Kolbe reaction of carboxylic acids, alkyl-substitution at the α-position of the carboxyl group causes a decrease in the yield of the coupled product.[1] Similarly, the α-phenyl-substitution of acetic acid hinders the normal Kolbe coupling reaction and favors anodic reactions such as methoxylation in methanol and acetoxylation in acetic acid.[2] Wladislaw and Ayres[3] have found that the electrolysis of α-methoxyphenylacetic acid and α-methoxydiphenylacetic acid in methanol produces benzaldehyde dimethyl acetal and benzophenone dimethyl acetal in good yield. For these anodic reactions, a two electron discharge mechanism to generate carbonium ion, which in turn undergoes solvolysis, has been postulated.[4a] Formation of allylic products in the electrolysis of cyclopropanecarboxylate has been presented as a proof.[4b] We investigated the behavior of 3-substituted 2,2-dichlorocyclopropanecarboxylic acids (**1a**, R=H; **1b**, R=CH_3) in the Kolbe anodic reaction in different hydroxylic solvents to obtain more chemical evidences concerning the reaction mechanism.

Electrolysis of 46 g of **1a** conducted in aqueous methanolic solution of acetic acid partly neutralized with potassium hydroxide, with two platinum foils (1.5 cm×2 cm) as an electrode, gave 44 g of neutral oily product, whose composition obtained by gas chromatography (glc) is shown in Table 1 (Electrolysis-1).

The principal product collected by fractional distillation of the neutral product (97—120°C/2 mmHg, see Experimental) was further purified by preparative thin layer chromatography (tlc). The results (C, 55.25; H, 4.80%), correspond to the formula $C_{10}H_{10}OCl_2$. We suspected that this might be 2,2-dichloro-3-methoxycyclopropylbenzene (**2a**) ($C_{10}H_{10}OCl_2$), since the primary step of the reaction would allow the existence of both 2,2-dichloro-3-phenylcyclopropyl radical and methoxy radical. Attempted synthesis of **2a** by the addition of dichlorocarbene to β-methoxystyrene gave only α-chlorocinnamal-

Table 1. Electrolytic products of 2,2-dichloro-3-phenylcyclopropanecarboxylic acid (**1a**)

Retention time[a] Min	Retention time[a] Sec	Neutral portion Peak area (%)	Constituent
2	18	7.7	Benzaldehyde
3	18	3.1	Methyl benzoate
3	54	0.9	Acetophenone
6	18	0.3	Benzyl alcohol
10	31	66.4	3,3-Dichloro-1-phenylallyl methyl ether (**4a**)
34	24	11.6	3,3-Dichloro-1-phenylallyl acetate (**5a**)
		10.0	Others

a) Hitachi F6-D gas chromatograph; column, 10% polyneopentyl glycol succinate, 4 m/m×1 m; column temp., 150°C; injection temp., 300°C; carrier gas, N_2 (0.5 kg/cm², 50 ml/min); detector, FID.

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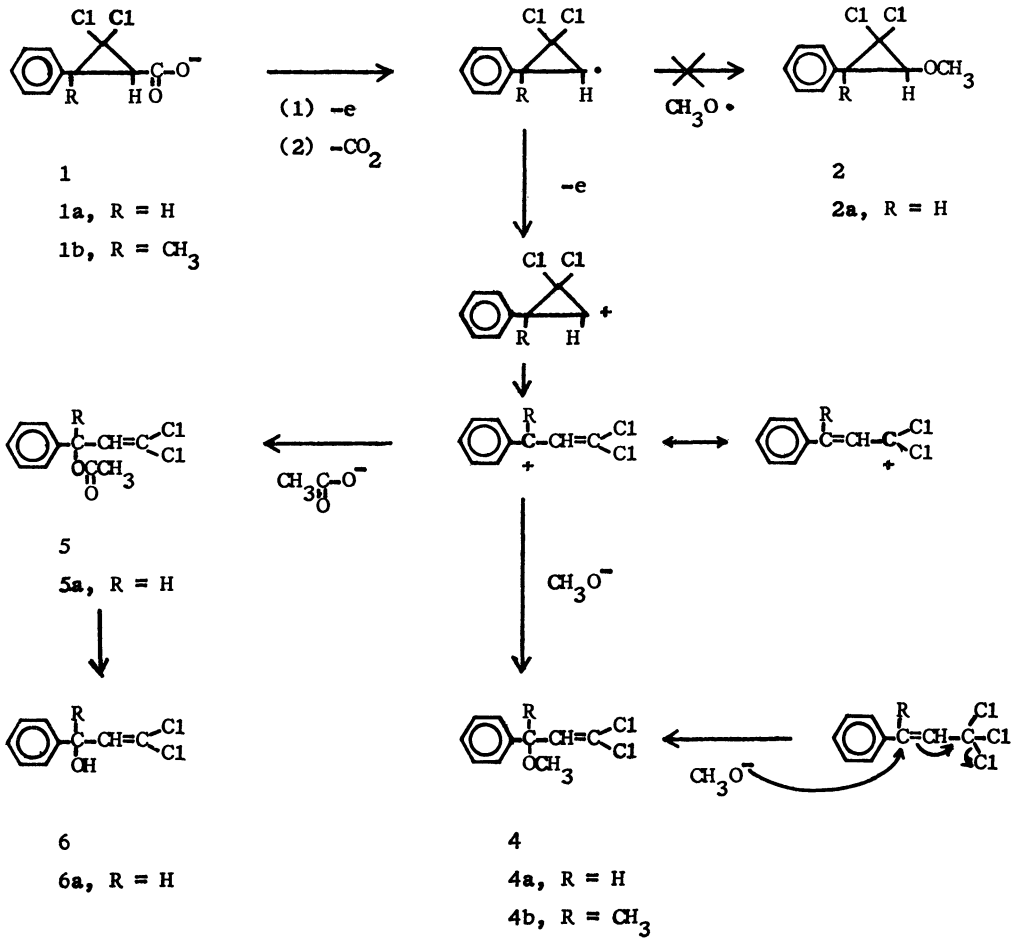
1) B. C. L. Weedon "Advances in Organic Chemistry", Vol. 1, ed. by R. A. Raphael, E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1960), p. 1.

2) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, **1952**, 3624.

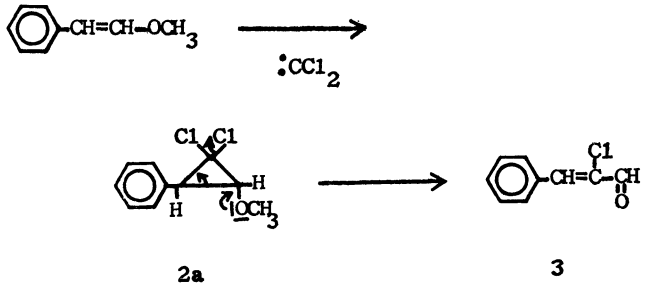
3) B. Wladislaw and A. M. J. Ayres, *J. Org. Chem.*, **27**, 281 (1962).

4) a) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960). b) T. Shono, I. Nishiguchi, S. Yamane, and R. Oda, *Tetrahedron Lett.*, **1969**, 1965.



Scheme 1

dehyde (**3**).[14] Compound **3** was identified by its IR spectra, the IR spectra, melting point, and elementary analysis of its 2,4-dinitrophenylhydrazone. This suggests that compound **2a**, if its formation was possible in electrolysis, is so unstable to rearrange to **3** immediately. Actually, the presence of **3** in the electrolyte could not be detected. Thus, 3,3-dichloro-1-phenylallyl methyl ether (**4a**) was considered to be the possible structure of the principal product in Electrolysis-1. The structure has been verified by identity of its spectral data with those of the authentic sample, prepared in a different way. Preparation of 1,1-dichloro-3-methoxy-1-butene by the action of sodium methoxide to 1,1,1-trichloro-2-butene has been reported by Nesmeyanov *et al.*[5] The reaction



Scheme 2

of sodium methoxide with 1-phenyl-3,3,3-trichloropropene[6] afforded **4a** in 77% yield; IR (cm^{-1}, liquid) 2840 (OCH_3), 1615 (C=C), 765, and 705; NMR(τ, $CDCl_3$) 6.62 (s, 3H, $-OCH_3$), 4.95 (d, 1H, J= 8.2 Hz, C_6H_5-CH-OCH_3), 3.96(d, 1H, J=8.2 Hz, =CH–), and 2.63(s, 5H, C_6H_5–).

Identification of benzaldehyde, acetophenone, benzyl alcohol, methyl benzoate, and 3,3-dichloro-1-phenylallyl acetate (**5a**) present in the electrolyte was made by a comparison of the retention time in glc with that of the authentic sample. We failed to isolate **5a** either by preparative glc (TCD) or by tlc. However, its existence in the neutral product has been confirmed by the retention time of glc (FID), which was determined for the acetate **5a** obtained in Electrolysis-4 (see Experimental).

The anodic reaction of 2,2-dichloro-3-methyl-3-phenylcyclopropanecarboxylic acid (**1b**) carried out in a similar condition, gave products such as acetophenone, α-methylbenzyl alcohol, α-methylbenzyl acetate, and 3,3-dichloro-1-methyl-1-phenylallyl

5) A. N. Nesmeyanov, R. Kh. Fre idlina, L. I. Zakharkin, and A. B. Belyavskiĭ, *Zh. Obshch. Khim.*, **26**, 107 (1956); *Chem. Abstr.*, **50**, 16658 (1956).

6) M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1105 (1947).

methyl ether (**4b**) (Electrolysis-2). Compound **4b** was isolated by means of preparative tlc, and its structure has been elucidated by IR spectra, NMR spectra, and elementary analyses. Table 2 summarizes the compositions of the neutral product in Electrolysis-2, which were analyzed by glc (FID) at different reaction times (12 hr and 30 hr).

Table 2. Electrolytic products of 2,2-dichloro-3-methyl-3-phenylcyclopropanecarboxylic acid (**1b**)

Retention time[a] Min	Sec	Neutral portion Peak area (%) 12 hr	30 hr	Constituent
4	6	27.7	48.2	Acetophenone
4	42	0.9	2.1	α-Methylbenzyl acetate
5	45	0.6	4.5	α-Methylbenzyl alcohol
13	48	56.2	22.3	3,3-Dichloro-1-methyl-1-phenylallyl methyl ether (**4b**)
		14.6	22.9	Others

a) Hitachi F6-D gas chromatograph; column, 10% polyneopentyl glycol succinate, 4 m/m×1 m; column temp., 160°C; injection temp., 290°C; carrier gas, N_2 (0.5 kg/cm², 50 ml/min); detector, FID.

Formation of ether **4** and acetate **5** can be interpreted by assuming a two electron discharge mechanism of **1** to generate cyclopropyl cation as an intermediate, which undergoes ring opening followed by solvolysis to **4** and **5**. The reaction sequence is shown in Schemes 1 and 2. The pathway in which the carbonyl compounds such as benzaldehyde and acetophenone were formed could not be ascertained in detail. However, the fact that the content ratio of acetophenone to ether **4b** in the product of Electrolysis-2 was upset between the 12th hr and 30th hr of the reaction strongly supports the assumption that **4b** primarily produced is transformed to acetophenone during electrolysis. Accordingly, it seems reasonable to consider that methyl benzoate, acetophenone, and benzyl alcohol in Electrolysis-1 and α-methylbenzyl acetate and α-methylbenzyl alcohol in Electrolysis-2 are the secondary products from benzaldehyde in the former and from acetophenone in the latter.[7]

Electrolysis of **1a** in methanol gave **4a** in 81% yield, together with benzaldehyde in 5% yield. On the other hand, electrolysis of **1a** in acetic acid containing anhydrous sodium acetate afforded **5a** in 94% yield and benzaldehyde in 4% yield. Compound **5a** tends to be decomposed during distillation or by treatment with either tlc or glc. Therefore, the acetate **5a** was hydrolyzed to α-(2,2-dichlorovinyl) benzyl alcohol (**6a**)[8] with 1 N aqueous sodium hydroxide for structural confirmation.

Experimenal[9]

The melting points and boiling points are uncorrected. Thin layer chromatography was carried out on silica gel G (E. Merck AG, Darmstadt), where the spots of materials were detected by spraying with sulfuric acid solution of potassium permanganate (7 : 3 in wt.). Infrared spectra was determined on a Hitachi IR EPI-S2 spectrophotometer. The electrolysis was carried out using the apparatus described previously.[7b] Standard conditions of electrolysis are as follows [code number of electrolysis experiment, terminal voltage (V), current density (A/cm²), current efficiency (%)]: 1, 6—8, 0.8, 8; 2, 9—12, 0.8, 3; 3, 15, 0.4, 9; 4, 15, 0.2, 3.

Materials. Ethyl ester of **1a** was prepared from ethyl cinnamate and sodium trichloroacetate, bp 135—140°C/4 mmHg (lit. bp 103—106°C/0.3 mmHg).[10] Acid **1a** was obtained from the ester by hydrolysis, mp 101°C (lit. mp 101°C).[10] Ethyl ester of **1b** was prepared from ethyl β-methylcinnamate[11] and sodium trichloroacetate in 57% yield, bp 126—130°C/2 mmHg. Found: C, 57.05; H, 5.13%. Calcd for $C_{13}H_{14}O_2Cl_2$: C, 57.16; H, 5.17%. The acid **1b** was prepared from the ethyl ester by treatment with a mixture of fuming hydrochloric acid and acetic acid (1 : 1 V/V) in 53% yield, mp 136.5°C. Found: C, 53.67; H, 4.17%. Calcd for $C_{11}H_{10}O_2Cl_2$: C, 53.90; H, 4.11%.

Commercially available compounds were used as reference samples for tlc and glc. α-Methylbenzyl acetate was prepared, bp 103—104°C/17 mmHg.[12]

Electrolysis of 2,2-Dichloro-3-phenylcyclopropanecarboxylic Acid (1a) in Aqueous Acetic Acid-Methanol-Potassium Hydroxide Solution (Electrolysis-1). A mixture of **1a** (46.2 g, 0.2 mol) with acetic acid (120 g, 2 mol), methanol (60 ml), water (120 ml), and potassium hydroxide (16.8 g, 0.3 mol) was charged to the cell. Electrolysis was carried out for 58 hr at 30—33°C with magnetic stirring with terminal voltage 6—8 V and a current of 2.0—2.4 A. Platinum electrodes were cleaned every 5 hr to avoid deposition of resinous material on the surface until the electrolyte became weakly acidic (pH 5—6). The reaction mixture was diluted with 300 ml of water and taken up in ether. The extract was separated in the usual manner giving neutral component (43.7 g) and acidic component (0.8 g). The glc analysis of the neutral portion has been summarized in Table 1. It was fractionally distilled under reduced pressure as follows.

Fraction	Bp, °C/mmHg	Weight, g
1	50—97/2	3.5
2	97—110/2	7.9
3	110—120/2	2.1
4	120—145/2	1.3
5	Residue	5.7

By glc analysis each fraction was found to be a mixture but the principal constituent was present in fractions 2 and 3. Product identification was achieved by comparing retention times with those of authentic samples. The analytical sample of the principal constituent (**4a**) was isolated by preparative tlc,[13] bp 110—114°C (bath temp.)/4 mmHg, R_f 0.85, IR

7) a) A. Takeda, S. Torii, and H. Oka, *Tetrahedron Lett.*, **1968**, 1781. b) A. Takeda, S. Wada, S. Torii, and Y. Matui, This Bulletin, **42**, 1047 (1969).

8) D. S. Matteson and R. W. H. Mah, *J. Org. Chem.*, **28**, 2174 (1963).

9) Elementary analyses were carried out by Mr. Eiichiro Amano of our laboratory. We are indebted to Dr. Akira Suzuki, and Mr. Sigezo Simokawa, both of Hokkaido University, Sapporo, for NMR measurements.

10) J. J. K. Novak, J. Farkas and F. Sorm, *Collect. Czech. Chem. Commun.*, **26**, 2090 (1961); *Chem. Abstr.*, **55**, 27125 (1961).

11) S. Lindenbaum, *Ber.*, **50**, 1279 (1917).

12) J. Steigman and L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 2536 (1937).

13) Conditions of the preparative tlc: support, silica gel G (E. Merck AG, Darmstadt), 0.8 mm; developer, *n*-hexane-acetone (5 : 1 V/V); eluent, acetone.

(cm^{-1}, liquid) 2840 (-OCH_3), 1615 (C=C), 765, and 705; NMR (τ, $CDCl_3$) 6.62 (s, 3H, -OCH_3), 4.95 (d, 1H, J= 8.2 Hz, C_6H_5-CH-OCH_3), 3.96 (d, 1H, J=8.2 Hz, =CH-), and 2.68 (s, 1H, C_6H_5-).

Found: C, 55.25; H, 4.80%. Calcd for $C_{10}H_{10}OCl_2$: C, 55.32; H, 4.64%.

Alternative Synthesis of 3,3-Dichloro-1-phenylallyl Methyl Ether (4a). This compound was prepared in the same manner as in the synthesis of 1,1-dichloro-3-methoxy-1-butene.[5] To a sodium methoxide solution prepared by dissolving sodium (0.07 g, 0.003 g-atom) in methanol (5 m*l*) was added 1-phenyl-3,3,3-trichloropropene[6] (0.7 g, 0.003 mol). After refluxing for 150 min, the mixture was allowed to stand overnight. Water was added and the organic layer was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. Removal of the solvent gave 0.5 g (77%) of the oily product, which was purified by preparative tlc; bp 110—115°C (bath temp.)/4 mmHg; IR (cm^{-1}, liquid) 2840 (-OCH_3), 1615 (C=C), 765, and 705.

Found: C, 55.51; H, 4.63%. Calcd for $C_{10}H_{10}OCl_2$: C, 55.32; H, 4.64%.

Attempted Reaction[14] of β-Methoxystyrene with Dichlorocarbene (α-Chlorocinnamaldehyde). To a stirred solution of β-methoxystyrene[15] (9.4 g, 0.07 mol) and chloroform (56.9 g, 0.48 mol) in petroleum ether (500 m*l*) was added powdered potassium *t*-butoxide (17.4 g, 0.18 mol) in small portions at −35——40°C. Stirring was continued for additional 5 hr at room temperature. After being allowed to stand overnight, the reaction mixture was diluted with water. The organic layer was separated and washed with water several times, dried over anhydrous sodium sulfate, and concentrated. Distillation of the residue *in vacuo* gave 6.4 g (43%) of oily product boiling at 107—108°C/3 mmHg, which exhibited one large spot at R_f 0.41 and one very small spot at R_f 0.66. The constituent with the R_f value of 0.41 was purified by preparative tlc; IR (cm^{-1}, liquid) 1690 (C=O) and 1610 (C=C).

The oily product gave 2,4-dinitrophenylhydrazone quantitatively; mp 269—270°C (lit. mp 272—273°C);[16] IR (cm^{-1}, Nujol) 1620 (C=N), 1510 (NO_2), and 1340 (NO_2).

Found: C, 52.20; H, 3.44; N, 15.78%. Calcd for $C_{15}H_{11}O_4ClN_4$; C, 51.96; H, 3.20; N, 16.16%.

Electrolysis of 2,2-Dichloro-3-methyl-3-phenylcyclopropanecarboxylic Acid (1b) in Aqueous Acetic Acid-Methanol-Potassium Hydroxide Solution (Electrolysis-2). A mixture of **1b** (9.6 g, 0.04 mol) with acetic acid (24.0 g, 0.4 mol), methanol (40 m*l*), water (40 m*l*), and potassium hydroxide (3.4 g, 0.06 mol) was electrolyzed for 30 hr at 20—26°C with magnetic stirring, with terminal voltage 9—12 V and a current of 2.0—2.4 A. During the electrolysis, a 20 m*l* portion of acetic acid was added every 5 hr to the reaction mixture. It was worked up in a manner similar to that in Electrolysis-1, giving 5.4 g of the neutral portion and 0.3 g of the acidic portion. Glc analysis of the product is summarized in Table 2. Isolation of 3,3-dichloro-1-methyl-1-phenylallyl methyl ether (**4b**) from the non-ketone and non-aldehyde portion was achieved by preparative tlc;[13] bp 103—108°C (bath temp.)/2 mmHg; R_f 0.73; IR (cm^{-1}, liquid) 2840 (-OCH_3), 1610 (C=C), 767, and 705; NMR (τ, $CDCl_3$) 8.30 (s, 3H, CH_3-), 6.93 (s, 3H, -OCH_3), 3.76 (s, 1H, =CH-), and 2.75 (s, 5H, C_6H_5-).

Found: C, 56.87; H, 5.17%. Calcd for $C_{11}H_{12}OCl_2$: C, 57.16; H, 5.23%.

Electrolysis of 1a in Methanol (Electrolysis-3). To a solution of sodium methoxide (0.012 mol) in absolute methanol (200 m*l*) was added 13.8 g (0.06 mol) of **1a**. The mixture was electrolyzed at 30—31°C for 31 hr with magnetic stirring, with terminal voltage 15 V and a current of 0.9—1.2 A. After removal of the solvent under reduced pressure, the residue was dissolved in ether and separated into the neutral portion (12.4 g) and acidic portion (2.5 g) as usual. Glc analysis (FID) of the constituents of the neutral material indicated the presence of 3,3-dichloro-1-phenylallyl methyl ether (**4a**) (81.4%), benzaldehyde (4.9%), and unidentified materials (13.7%).

Electrolysis of 1a in Acetic Acid (Electrolysis-4). A solution of **1a** (4.6 g, 0.02 mol) and anhydrous sodium acetate (9.8 g, 0.12 mol) in acetic acid (144 g, 2.4 mol) was electrolyzed at 27—30°C for 55 hr with magnetic stirring, with terminal voltage 15 V and a current of 0.5—0.6 A. After working up in the usual manner, 3.3 g of neutral portion and 0.1 g of acidic portion were obtained. By glc analysis the neutral portion was found to contain **5a** (93.5%), benzaldehyde (4.3%), and a small amount (2.2%) of unidentified materials. Purification of **5a** by means of preparative tlc or glc was unsuccessful because of decomposition under such treatment. A crude sample of **5a** obtained by preparative tlc gave no correct analysis; IR (cm^{-1}, liquid) 1745 (acetate C=O), 1625 (C=C), and 1235 (ester C-O).

A mixture of 7.4 g (0.03 mol) of the crude ester and 60m*l* of 1 N aqueous sodium hydroxide was heated at 50°C for 42 hr. The hydrolysate was acidified and extracted with ether. The ethereal extract, after being washed with water, dried over anhydrous sodium sulfate, and removal of the solvent, gave 4.0 g (58%) of the crude product, which was distilled under reduced pressure to yield the following fractions.

Fraction	Bp, °C/mmHg	Weight, g
1	50—118/2.5	1.0
2	118—122/2.5	1.8
3	122—150/2.5	0.3
4	Residue	0.9

α-(2,2-Dichlorovinyl)benzyl alcohol (**6a**) was isolated from fraction 2 by preparative tlc;[13] mp 53—55°C (lit. mp 53—54°C);[8] R_f 0.58; IR (cm^{-1}, Nujol) 3200 (OH), 1615 (C=C), 1025, 760, and 705 (lit. IR 1621, 1026, 901, 895, 763, and 699);[8] NMR (τ, $CDCl_3$) 7.55 (s, 1H, -OH), 4.50 (d, 1H, J=8.2 Hz, C_6H_5-CH-OH), and 3.90 (d, 1H, J=8.2 Hz, =CH-).

Found: C, 53.13; H, 3.94%. Calcd for $C_9H_8OCl_2$: C, 53.23; H, 3.97%.

14) The synthesis of alkyl-substituted *gem*-dichlorocyclopropyl ethers has been reported by Skattebøl [L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1965)]. These ethers, when heated under reflux with an alcohol in the presence of a base, undergo ring opening with formation of acetals.

15) K. Auwers, *Ber.*, **44**, 3514 (1911).

16) G. Märkl, *Chem. Ber.*, **95**, 3003 (1962).