Polymeric Alkoxyalkylaluminum Compounds by Novel Reductive Cleavage of Saturated Cyclic Ethers. A New Organometallic Reagent in Organic Synthesis

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(Received November 10, 1977)

Insertion of aluminum to the C–O–C bond of saturated cyclic ethers by the $HgCl_2$–$ZnCl_2$–MeI catalyst system led to the reductive cleavage of 5, 6, and 7 membered ring ethers to give polymeric alkoxyalkylaluminum compounds. The relative rate of the reaction was increased in the order of tetrahydrofuran, 3-methyltetrahydrofuran, 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, tetrahydropyran, oxepane, 7-oxabicyclo[2.2.1]-heptane, and 2-methyltetrahydropyran. The cleaved cyclic ethers are bonded with aluminum atoms bifunctionally and the resulting polymeric aluminum compound gave dideuterio alcohols upon deuterolysis. Addition reaction of allyl halides and reduction of chloral with the aluminum compound provided a novel route for the preparation of unsaturated alcohols.

A number of methods for the cleavage of saturated cyclic ethers have been reported and summarized in several reviews.[1–4] Both acid[5–8] and base[9–11] catalyzed cleavages are known and the ring opening mechanism,[12,13] ring size effects[14] and influences of the group substituted on the ring[15,16] have been extensively studied. Most of the studies reported so far are concerned with the stoichiometric reactions between cyclic ethers and ring cleaving agent. We present here a novel direct reaction of saturated cyclic ethers with aluminum which led to the reductive cleavage of 5, 6, and 7 membered cyclic ethers. Remarkable points of this reaction lie in the following points; 1) metallic aluminum, a neutral reactant, can undergo the stoichiometric reaction with cyclic ethers to give a new type of aluminum compounds, 2) the order in reactivity of the cyclic ethers follows that of the steric effects of the alkyl group on the ring and of the carbon chain consisting the ring, and 3) this method has the advantages of experimental simplicity and broad applicability for the preparation of unsaturated alcohols with elongated carbon chain from allyl halides.

Results and Discussion

Reductive Cleavage of Cyclic Ethers by Aluminum. In our search for the new method for activating main group metals, we found an unusual reductive cleavage of tetrahydrofuran(THF) with aluminum to give polymeric alkoxyalkylaluminum compounds. The reaction proceeded by employing the aluminum turnings activated not only with mercury(II) halides, in accordance with the general procedure,[17] but also with a minute quantity of organic halides. All of the mercury(II) or mercury(I) halides, $HgBr_2$, Hg_2Br_2, $HgCl_2$, Hg_2Cl_2, HgI_2, and Hg_2I_2, were effective as catalysts in various concentrations from 0.1 to 0.4 mol% when it was used simultaneously with an organic halide in concentrations of 4.0—8.0 mol% to aluminum turnings. Iodine, alkyl iodides and bromides were preferred over chloro compounds. The addition of zinc chloride to the HgX_2–RX catalyst system brought about a remarkable acceleration of the reaction. The use of the catalyst system composed of $HgCl_2$(2 mol%)–MeI(4.0 mol%)–$ZnCl_2$(4.0 mol%) resulted in the formation of the tetrahydrofuran-aluminum compound **1** in 93% yield as listed in Table 1. When an excess of THF(10 equivalent mole) reacted at 80 °C for 70 h, aluminum was consumed completely and a liquid amalgam was precipitated. The hydrolysis of the amalgam with 10 M HCl and the chemical analysis of the hydrolyzate by the 8-quinolinol method showed that 99% of mercury and 68% of zinc added to the system were reduced to metals as amalgam. As the promotors, $FeCl_3$ and $TiCl_4$ were also effective, but the use of zinc chloride was more favorable with respect to the reproducibility of the reaction. No reaction occurred when boron, magnesium, calcium or alkali metals were used in place of aluminum. It

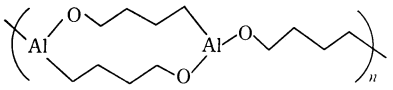
TABLE 1. YIELDS OF THE ALUMINUM-THF COMPOUND **1** WITH VARIOUS CATALYST SYSTEMS[a]

Catalyst component			Reaction conditions		Yields (%)
HgX_2 (mol%)	RX (mol%)	Promotor (mol%)	Time (h)	Temp (°C)	
8.0($HgCl_2$)	0.0	0.0	240	80	0
2.0($HgCl_2$)	4.0(MeI)	0.0	170	80	22
2.0($HgCl_2$)	4.0(MeI)	4.0($ZnCl_2$)	70	80	93
2.0($HgCl_2$)	4.0(MeI)	4.0($ZnCl_2$)	240	40	0
0.0	4.0(MeI)	4.0($ZnCl_2$)	240	80	0
2.0(HgI_2)	4.0(MeI)	4.0($ZnCl_2$)	70	80	95
2.0(HgI_2)	4.0(BuCl)	4.0($ZnCl_2$)	70	80	15
2.0(HgI_2)	4.0(MeI)	4.0($FeCl_3$)	70	80	85

a) The g-atom/mol ratio of aluminum to THF was 1 : 4.

may be noted that the present reaction is characteristic to cyclic ethers and, hence, acyclic ethers such as diethyl or dipropyl ether can be used as a solvent.

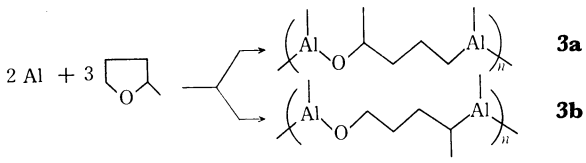
Characterization of the Aluminum Compoumds. The aluminum compound **1** thus obtained was soluble in benzene or ether. It gave terminally dideuterated 1-butanol C_4H_8DOD quantitatively upon deuterolysis and produced no detectable amount of by-product as evidenced by GC and TLC. The molecular weight of **1** determined cryoscopically in benzene corresponded to that of $(Al_2C_{12}H_{24}O_3)_n$ where $n=2$. The ratio of aluminum to 1-butanol analyzed with the 8-quinolinol method and GC was 2:3. PMR spectral data taken in benzene also agreed with the following structure. Proton signals assigned to CH_2 adjacent



1

to Al, internal CH_2, and CH_2 bonded with oxygen atoms appeared at δ 0.54, 1.84, and 3.92 ppm in 1:2:1 peak area ratio. When 4 mol% of $FeCl_3$ or $TiCl_4$ was used as a promotor instead of zinc chloride, the molecular weight of the aluminum compound increased to 1050—1105 which corresponds to $(Al_2C_{12}H_{24}O_3)_4$, but the NMR data coincided in chemical shift and peak area ratio with that of **1**. In the similar manner, 3-methyltetrahydrofuran-aluminum **2**, 2-methyltetrahydrofuran-aluminum **3**, 2,5-dimethyltetrahydrofuran-aluminum **4**, tetrahydropyran-aluminum **5**, oxepane-aluminum **6** and 7-oxabicyclo[2.2.1]-heptane-aluminum **7** compounds could be prepared individually by using the $HgCl_2$–$ZnCl_2$–MeI catalyst system. All of these aluminum compounds gave the corresponding dideuterio alcohols upon deuterolysis and have oligomeric structures similar to **1** where $n=2$ (Table 2). PMR spectral data of **5** and **6** were in accord in chemical shift with that of **1** within 10 Hz.

Steric and Ring Size Effect of the Cyclic Ethers. The reactions mentioned above were of the second order and the relative rate of reactions is listed in Table 3. A higher homologue, 2-methyltetrahydropyran, had no reactivity and was recovered quantitatively. The order in reactivity of cyclic ethers which form **1**, **2**, **3** and **4** is consistent with the half-lives for the nucleophilic cleavage of those ethers with organolithium compounds[18,19] but not consistent with the order in reactivity of cyclic ethers toward electrophiles[20] or their basicities against various acids,[21,22] nevertheless this reaction was initiated with a Lewis acid catalyst system. The substitution of THF with methyl group in α position caused to the remarkable decrease in reactivity. In case of 7-oxabicyclo[2.2.1]heptane, which may be considered as *cis*-2,5-dimethyltetrahydrofuran with methyl group bound together in a bridge, the reactivity was significantly small compared to 2,5-dimethyltetrahydrofuran. This should be ascribed to the cage effect derived from the bulky bicyclic ring.[21] In the reaction of 2-methyltetrahydrofuran, the substituted carbon atom is known to be attacked preferentially by both nucleophilic[18,19] and electrophilic[23] reagents. However, the ring cleavage of 2-methyltetrahydrofuran by the present method afforded **3a** stereoselectively (99%). The yield of **3b** was only 1%. The compound **2** also gave the abnormal product predomonantly; *i.e.*, the ratio of 2-methyl- to 3-methylbutanol was 74 : 26. These results are concordant with the reductive cleavage of 2-methyltetrahydrofuran by a bulky nucleophile, $LiAlH(OtBu)_3$-BH_3,[24] which gave only 2-methylbutanol. Thus the ring opening of cyclic ethers with aluminum was oriented mainly by the steric effect of subsituents rather than the ionic or inductive effects. The ratio of **3a** to **3b**(99 : 1) was proportional to that of relative rates of reaction between THF and 2,5-dimethyltetrahydrofuran, 92 : 8. The orientation of the ring opening of 2-methyltetrahydrofuran was, therfore, interpreted in terms of the steric effect of substituents.



3a

3b

To elucidate the ring size effect, the reaction of 3, 4, 5, 6, and 7 membered ring ethers bearing no methyl substituents was examined. Comparison of these ethers showed that the rate of reaction increased in the order of 5>6>7 membered ring. Three and four membered ring ethers are unfortunately too sensitive to the catalyst to permit the comparative studies(polymerization occurred preferentially). This order varies inversely as the order of inductive effect, 7>6>5, and is not consistent with that of pK_a values[21] of cyclic ethers or the strain energies, ΔG,[25] which

TABLE 2. CHARACTERIZATION OF ALUMINUM-CYCLIC ETHER COMPOUNDS

Compound	Mol wt Found(Calcd)	Al (%) Found(Calcd)	Hydrolysis product
1	520 (270)	19.8 (20.0)	1-butanol
2	605 (312)	17.3 (17.3)	2-methyl-1-butanol 3-methyl-1-butanol
3	620 (312)	17.1 (17.3)	2-pentanol
4	690 (354)	15.2 (15.2)	2-hexanol
5	590 (312)	16.8 (17.3)	1-pentanol
6	701 (354)	15.3 (15.2)	1-hexanol
7	705 (348)	15.7 (15.5)	cyclohexanol

TABLE 3. COMPARATIVE RATES OF REACTION OF CYCLIC ETHERS

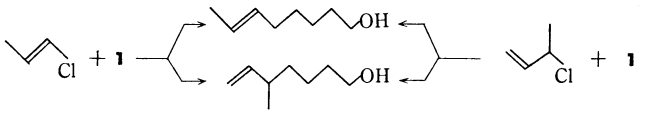
Cyclic ethers	Initial rate const $10^4 k$ (l/mol h)
Tetrahydrofuran	378.4
3-Methyltetrahydrofuran	154.5
2-Methyltetrahydrofuran	67.4
2,5-Dimethyltetrahydrofuran	15.4
Tetrahydropyran	9.1
Oxepane	8.1
7-Oxabicyclo[2.2.1]heptane	2.2

increased in order of 7>6>5. Although systematic data about the steric effect of cyclic ethers are lacking, those of linear ethers[26] clearly showed that the steric effect was reversed by the inductive effect. The order in reactivity of 5, 6, and 7 membered ring ethers should be, therfore, ascribed to the steric effect of the methylene chain on the ring.

The steric effect observed in the present system is unusually large. This unique behavior may be interpreted with the concept that the real catalyst is formed on the aluminum surface to proceed a kind of template reaction. The following examination supports this assumption; *i.e.*, aluminum turnings activated with the above mentioned catalyst at 40 °C in THF was washed thoroughly with excess of anhydrous ether to remove unreacted catalyst components. Although no ring opening had occurred at this temperature, the aluminum turnings thus treated were already activated and they maintained the activity to give **1** by the reaction with freshly introduced THF at 80 °C. In addition, aluminum chloride, methylalminum dichloride, and dimethylaluminum chloride, candidates of the real catalyst which could be formed[27,28] from the mixture of aluminum, mercury(II) chloride, zinc chloride, and methyl iodide, had no catalytic activity. The stoichiometric reaction of the catalyst, $HgCl_2$–$ZnCl_2$–MeI, with THF gave no ring opening products, unless aluminum was present in the system. On the bases of these results, we can reasonably conclude that the ring cleavage occrured certainly on the aluminum surface and the large steric effect observed in this system was caused by the metal surface reaction.

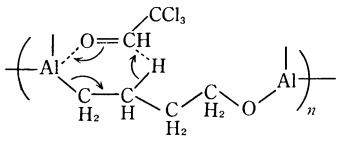
This method was less applicable to the cleavage of aromatic cyclic ethers whose ring were stabilized by the conjugation effect.[29] The reaction of 2,3-dihydrobenzofuran and 1,3-benzodioxole with aluminum resulted in the formation of 2-ethylphenol and catechol, respectively, in 10—20% yield. Desired *o*-methoxyphenol was not obtained from 1,3-benzodioxole.

Preparation of Unsaturated Alcohols from Cyclic Ethers. The cleaved cyclic ether is bonded with aluminum atoms bifunctionally, differing from the alkoxy group of the aluminum alkoxide. By taking advantage of the bifunctional nature of the cleaved cyclic ether, the addition of allyl group to the terminal methylene of the cleaved tetrahydrofuran was attempted. The addition of 2 mol. of 3-bromopropene to **1** at 80 °C resulted in the formation of 6-hepten-1-ol in only 5% yield upon hydrolysis, but the addition of cupric or cuprous compounds($CuBr_2$ or CuBr, 1 mol% to the aluminum compound) as catalyst brought about the increase of the yield to 70%. They were more effective as catalyst than Cd, Zn, Ni(II), Co(II), Pd(II), or Fe(III) compound as the latter was reduced immediately to the metal. In a similar manner, the reaction of **2** with 3-bromopropene gave 2-methyl-6-hepten-1-ol(75%) and 3-methyl-6-hepten-1-ol(25%) in 62% yield and **3** gave 7-octen-2-ol in 65% yield. The reaction of **1** with *trans*-1-chloro-2-butene in the presence of $CuBr_2$(1.0 mol%) gave 5-methyl-6-hepten-1-ol and 6-octen-1-ol with 1 : 1 ratio in 60% yield. The isomer, 3-chloro-1-butene also gave the same alcohols with 1 : 1 ratio in 63% yield under the same



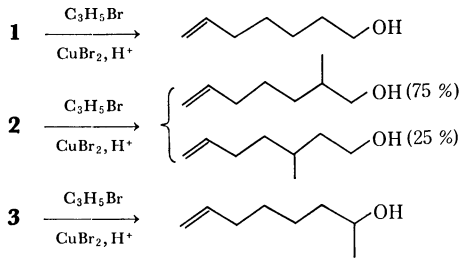
reaction conditions(80 °C for 10 h). This suggests that the ratio of two isomeric butenyl cations formed in both reactions are identical with each other. Thus the polymeric alkoxyalkylaluminum reagents are preferred for the preparation of unsaturated alcohols with elongated carbon chain from allyl halides. Elongation of the carbon chain with diiodomethane was also possible. For example, the reaction of **1** with diiodomethane at 80 °C for 20 h gave 5-iodopentanol in 49% yield upon hydrolysis.

In order to explore the reducing ability of **1**—**3**, reduction of chloral was examined. Two moles of **1** reduced three moles of chloral resulting in the formation of 2,2,2-trichloroethanol and 3-buten-1-ol in 77% yield. The following intermediate can be considered for this reaction. The reducing ability of **1** is similar



to that of triethylaluminum.[30] Acetaldehyde and acetone were not reduced with **1**. Similarly, **2** gave 2-methyl-3-buten-1-ol and 3-methyl-3-buten-1-ol in 7 : 3 ratio and **3** gave 4-penten-2-ol by the reaction with chloral.

Thus, a series of polymeric alkoxyalkylalumunum compounds obtained here has a large utility in the novel synthesis of unsaturated alcohols with or without elongated carbon chain.



Experimental

All the cyclic ethers obtained commercially were dried over sodium/potassium alloy and distilled. Aluminum foil (99.99% in purity, thickness 0.025 mm, 2.0×2.0 mm width, Nakarai Chem.), aluminum powder(99% purity, Alfa Chem.) and aluminum foil for kitchen use (97% purity, Toyo Aluminum Tech.) were used as the Aluminum turnings. Anhydrous metal halides were prepared by heating the hydrates in vacuum at the prescribed temperature. Reactions were carried out under nitrogen using the two-necked glass tube(30×150 mm, thickness 2.0 mm). GC analysis and the separation of the reaction products were made with Yanagimoto Model G-80 and Varian-Aerograph

Model 700 gas chromatographs. PMR spectra were taken with a Varian Model A-60 instrument and MS with a Hitachi RMU-7HR spectrometer. IR spectra were recorded on a Hitachi Model EPI-2 spectrometer.

*Preparation of **1** from THF.* To the aluminum turnings (2.7 g, 0.1 g-atom) in THF(40 ml, 0.4 mol), a mixture of mercury(II) chloride(0.54 g, 2.0 mol% to aluminum), zinc chloride(0.54 g, 4.0 mol%), and methyl iodide(0.25 ml, 4.0 mol%) was added as catalyst. After the tube was sealed and shaken for 70 h at 80 °C in a temperature controlled water bath equipped with a vibrator, benzene(120 ml) was added to the product. The colorless benzene solution was transferred with a hypodermic syringe to remove the residual aluminum amalgam and was evaporated to dryness to give **1** as a semi-solid substance. Any differences in reactivity were not observed among the three brands of aluminum turnings used in this experiment.

*Preparation of Aluminum Compounds **2**—**6**.* In essentially the same way as described above, the reaction of 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, tetrahydropyran, and oxepane(0.4 mol) with aluminum turnings(2.7 g, 0.1 g-atom) were carried out at 80 °C for 150 h. The resulting products were dissolved in benzene (120 ml) and poured into hexane(300 ml) to precipitate the compound. After decantation, the precipitates **2**—**6** were dried *in vacuo* to give semi-solid materials.

*Deuterolysis of the Compound **1**—**7**.* The aluminum compounds **1**—**7**(50 mmol) were deuterolyzed at 0 °C with deuterium oxide(5 ml) in ether(50 ml). Isomeric alcohols were separated with a preparative GC using a column(4 m) packed with 15% Silicone DC-500 on 40/60 mesh Celite 545. The position of deuteriums in the resulting alcohols was determined with IR, PMR, and MS, by reference to alcohols obtained by hydrolysis.

*Butan-4-*d*-1-ol-*d *from **1***: IR(neat) 2490(ν OD), 2180 cm^{-1} (ν CD). PMR($CDCl_3$) δ 3.68(2H, q, CH_2O), 1.52(4H, m, CH_2), 0.99(2H, m, CH_2D). MS *m/e* 76(M^+), 74, 57, 32.

*2-Methylbutan-4-*d*-1-ol-*d *from **2***: IR(neat) 2483(ν OD), 2182 cm^{-1}(ν CD). PMR($CDCl_3$) δ 3.62(2H, t, CH_2O), 1.50 (3H, m, CH_2CH), 0.93(5H, m, CH_3 and CH_2D). MS *m/e* 90(M^+), 88, 71, 32.

*3-Methylbutan-4-*d*-1-ol-*d *from **2***: IR(neat) 2485(ν OD), 2180 cm^{-1}(ν CD). PMR($CDCl_3$) δ 3.68(2H, t, CH_2O), 1.51 (3H, m, CH_2CH), 0.93(5H, d, CH_3 and CH_2D). MS *m/e* 90(M^+), 88.

*Pentan-5-*d*-2-ol-*d *from **3***: IR(neat) 2489(ν OD), 2179 cm^{-1} (ν CD). PMR($CDCl_3$) δ 3.80(1H, m, CH), 1.48(4H, m, CH_2), 1.18(3H, d, CH_3), 0.93(2H, m, CH_2D). MS *m/e* 90(M^+), 88, 75, 71, 32.

*Hexan-6-*d*-2-ol-*d *from **4***: IR(neat) 2490(ν OD), 2175 cm^{-1} (ν CD). PMR($CDCl_3$) δ 3.80(1H, m, CH), 1.31(6H, m, CH_2), 1.18(3H, d, CH_3), 0.92(2H, q, CH_2D). MS *m/e* 104 (M^+), 85, 57, 32.

*Pentan-5-*d*-1-ol-*d *from **5***: IR(neat) 2490(ν OD), 2182 cm^{-1} (ν CD). PMR($CDCl_3$) δ 3.62(2H, t, CH_2O), 1.40(6H, m, CH_2), 0.90(2H, m, CH_2D). MS *m/e* 88(M^+-2), 71, 55, 32.

*Hexan-6-*d*-1-ol-*d *from **6***: IR(neat) 2485(ν OD), 2170 cm^{-1} (ν CD). PMR($CDCl_3$) δ 3.67(2H, m, CH_2O), 1.38(8H, m, CH_2), 0.90(2H, m, CH_2D). MS *m/e* 102(M^+-2), 85, 67, 32.

*Cyclohexan-4-*d*-ol-*d *from **7***: IR(neat) 2489(ν OD), 2208, 2109 cm^{-1}(ν CD). PMR($CDCl_3$) δ 3.63(1H, m, CH), 1.78—1.32(9H, m, CH_2 and CHD). MS *m/e* 102(M^+), 83, 32.

Reaction of Aromatic Cyclic Ethers with Aluminum. To a mixture of 2,3-dihydrobenzofuran(5.7 ml, 50 mmol) and aluminum(1.4 g, 50 mg-atom) in benzene(15 ml) was added the catalyst, $HgCl_2$–$ZnCl_2$–MeI(4, 8, and 8 mol%, respectively). The mixture was heated at 80 °C for 100 h, hydrolyzed at 0 °C and then distilled. Deuterolysis of the product gave 2-ethyl-phenol-d_2 in 15% yield. IR(neat) 2558(ν OD), 2447 cm^{-1}(ν CD). PMR($CDCl_3$) δ 6.82(4H, m, CH), 2.59 (2H, q, CH_2), 1.20(2H, t, CH_2D). MS *m/e* 124(M^+). Phthalan had no reactivity toward aluminum even carrying out the reaction at 120 °C for 150 h. The reaction of 1,3-benzodioxole(6.1 g, 50 mmol) with aluminum(1.4 g) at 100 °C for 150 h resulted in the formation of catechol in 20% yield.

*Allylation of **1**—**3** with 3-Bromopropene.* To a stirred mixture of anhydrous 3-bromopropene(10.4 ml, 120 mmol) and $CuBr_2$(0.18 g, 0.8 mmol) was added compounds **1**—**3** (40 mmol) in benzene(30 ml). After the reaction was allowed to proceed at 80 °C for 20 h, products were hydrolyzed, filtered and distilled. Yields, 65—75%.

*6-Hepten-1-ol from **1***: IR(neat) 3340, 915 cm^{-1}. PMR ($CDCl_3$) δ 5.71, 4.90(3H, m, CH_2=CH), 3.65(2H, t, CH_2), 2.01(2H, m, CH_2), 1.87(1H, s, OH), 1.38(6H, m, CH_2). MS *m/e* 114(M^+).

*3-Methyl-6-hepten-1-ol from **2***. IR(neat) 3340, 915 cm^{-1}. PMR($CDCl_3$) δ 5.69, 4.95(3H, m, CH_2=CH), 3.63 (2H, t, CH_2), 2.02(2H, m, CH_2), 1.83(1H, s, OH), 1.63(1H, m, CH), 1.38(4H, m, CH_2), 0.94(3H, d, CH_3). MS *m/e* 127(M^+-1).

*2-Methyl-6-hepten-1-ol from **2***. IR(neat) 3350, 915 cm^{-1}. PMR($CDCl_3$) δ 5.68, 4.89(3H, m, CH_2=CH), 3.44(2H, d, CH_2), 2.05(2H, m, CH_2), 1.80(1H, s, OH), 1.65(1H, m, CH), 1.33(4H, m, CH_2), 0.98(3H, d, CH_3). MS *m/e* 127(M^+-1).

*7-Octen-2-ol from **3***. IR(neat) 3380, 915 cm^{-1}. PMR ($CDCl_3$) δ 5.78, 4.79(3H, m, CH_2=CH), 3.76(1H, m, CH), 1.99(2H, t, CH_2), 1.91(1H, s, OH), 1.38(6H, m, CH_2), 1.18 (3H, d, CH_3). MS *m/e* 127(M^+-1).

*Reaction of **1** with 1-Chloro-2-butene and 3-Chloro-1-butene.* A solution of **1**(5.4 g, 40 mmol) in benzene(30 ml) was added to a stirred mixture of anhydrous *trans*-1-chloro-2-butene (11.8 ml, 120 mmol) and $CuBr_2$(0.18 g, 0.8 mmol). The mixture was heated to 80 °C for 20 h and then hydrolyzed. Resulting two alcohols(with 1:1 ratio) were separated with GC. Typical yield, 63% based on **3**.

a) trans-*6-Octen-1-ol*: IR(neat) 3340(ν OH), 967(ν *trans* C=C). PMR($CDCl_3$) δ 5.42(2H, m, CH), 3.60(2H, t, CH_2O), 1.96(2H, m, CH_2), 1.82(1H, s, OH), 1.61(3H, m, CH_3), 1.38(6H, m, CH_2). MS *m/e* 128(M^+).

b) 5-Methyl-6-hepten-1-ol: IR(neat) 3370(ν OH), 920 cm^{-1}(ν C=C). PMR($CDCl_3$) δ 5.60, 4.95(3H, m, CH_2=CH), 3.63(2H, t, CH_2O), 2.05(1H, m, CH), 1.39(6H, m, CH_2), 0.99(3H, d, CH_3). MS *m/e* 128(M^+).

The same alcohols were obtained also from the reaction of 3-chloro-1-butene(12.7 ml, 120 mmol) with **1**(5.4 g) in 63% yield with 1:1 ratio.

*Addition of Methylene Iodide to **1**.* To a solution of **1** prepared from aluminum(1.4 g) and excess of tetrahydrofuran(40 ml) was added directly methylene iodide(16.1 ml, 0.2 mol) and the mixture was heated to 80° for 20 h. Distillation of the hydrolyzate gave 5-iodo-1-pentanol in 49% yield based on **1**. IR(neat) 3390(ν OH), 722 cm^{-1}(ν CI). PMR($CDCl_3$) δ 3.61(2H, t, CH_2O), 3.18(2H, t, CH_2I), 1.89 (1H, s, OH), 1.56(6H, m, CH_2). MS *m/e* 213(M^+-1).

*Reduction of Chloral with **1**—**3**.* To a solution of **1** (5.4 g, 40 mmol) in benzene(30 ml) was added dropwisely anhydrous chloral(11.8 g, 80 mmol) dried over calcium hydride with vigourous stirring at 20 °C. The mixture was heated at 60° for 3 h and then hydrolyzed. The resulting 2,2,2-trichloroethanol and 3-buten-1-ol obtained from the benzene fraction were identified with authentic samples. The yield of 3-buten-1-ol was 77% based on **1**. In the similar

manner, reduction of chloral with **2** gave 3-methyl-3-buten-1-ol(30%). Which was identified with the commercial sample, and also 2-methyl-3-buten-1-ol(70%). IR(neat) 3330 (ν OH), 905 cm^{-1}(ν CH_2=CH). PMR($CDCl_3$) δ 5.8—5.1 (3H, m, CH_2=CH), 3.68(2H, d, CH_2O), 2.01(1H, m, CH), 1.95(1H, s, OH), 1.33(3H, d, CH_3). MS *m/e* 86(M^+), 85. Typical yield was 70%. Reduction of chloral with **3** under the same reaction condition gave 4-penten-2-ol in 70% yield and it was identified with the authentic sample.

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