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Reaction of Aluminum Haloalkoxide with Diazomethane

Takeo SAEGUSA, Shimpei TOMITA and Takashi UESHIMA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku Kyoto

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In the reaction of diazomethane with four aluminum haloalkoxides, $Al(OCH_2CF_3)_3$ (I), $Al(OCH_2CCl_3)_3$ (II), $Al(OCH_2CBr_3)_3$ (III), and $Al[OCH(CH_2Cl)_2]_3$ (IV), a methylene insertion into the aluminum-alkoxyl linkage was observed along with the polymethylene formation. By the methylene insertion, an organoaluminum compound with a haloalkoxymethyl-aluminum linkage is formed. Among aluminum alkoxides, these four haloalkoxides are distinguished by this methylene insertion. The usual aluminum alkoxides of unsubstituted alcohols do not undergo a methylene insertion reaction, but only the polymethylene formation. The difference in the reactivity towards diazomethane between the four haloalkoxides and usual alkoxides has been explained by the difference in acid strength.

In the course of our studies of the catalytic behavior of aluminum alkoxide in the polymerization of cyclic ethers,[1,2] we prepared five aluminum haloalkoxides,[3] $Al(OCH_2CF_3)_3$ (I), $Al(OCH_2CCl_3)_3$[4] (II), $Al(OCH_2CBr_3)_3$ (III), $Al[OCH(CH_2Cl)_2]_3$ (IV) and $Al(OCH_2CHCl_2)_3$ (V). In comparison with usual aluminum alkoxides, four haloalkoxides (I to IV) are characterized by a strong electron-accepting power of aluminum (Lewis acid strength), and by a marked tendency to dissociate to solvated monomers in a donor solvent.[3,4]

In the present study, we have found that four aluminum haloalkoxides of I to IV react with diazomethane to produce the linkage of al-CH_2OR by the insertion of a methylene group into the al-OR bond:

$$\text{al-OR} + CH_2N_2 \xrightarrow{-N_2} \text{al-}CH_2OR \qquad (1)$$

$$(R = \text{-}CH_2CF_3,\ \text{-}CH_2CCl_3,\ \text{-}CH_2CBr_3,\ \text{-}CH(CH_2Cl)_2)$$

In the reaction of diazomethane with the usual aluminum alkoxides of unsubstituted alcohols, the above insertion reaction was not observed. The difference in reactivity between the haloalkoxides and usual alkoxides has been explained by the difference in acid strength.

The reactions of the methylene insertion into aluminum-alkyl, -halide and, -hydrogen bonds by diazomethane have been known.[5-7] The present paper will describe a finding of the methylene insertion into the aluminum-alkoxyl bond.

Experimental

Reagents. Five aluminum haloalkoxides, I to V, were prepared and purified by the procedures given in previous papers.[3,4] Aluminum isopropoxide was a commercial reagent which was purified by distillation. Aluminum *t*-butoxide was prepared by the reaction of aluminum turning and *t*-butanol, and was purified by recrystallization from diethyl ether.

A toluene solution of diazomethane was prepared by treating *N*-nitroso-*N*-methylurea with an aqueous solution of KOH in toluene.[8]

The Reaction of Aluminum Alkoxide with Diazomethane. A toluene solution of diazomethane was added, drop by drop, into a toluene suspension or solution of an equimolar amount of aluminum alkoxide

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[1] H. Imai, T. Saegusa and J. Furukawa, *Makromol. Chem.*, **81**, 92 (1965).

[2] T. Saegusa, T. Ueshima and S. Tomita, *Makromol. Chem.*, **107**, 131 (1967).

[3] T. Ueshima, S. Tomita and T. Saegusa, to be published in This Bulletin,

[4] T. Saegusa and T. Ueshima, *Inorg. Chem.*, **6**, 1679 (1967).

[5] H. Hoberg, *Ann.*, **656**, 1, 15 (1956).

[6] H. Hoberg, *Angew. Chem.*, **77**, 1084 (1965).

[7] H. Hoberg, *Ann.*, **695**, 1 (1966).

[8] F. Arndt, "Organic Synthesis," Coll. Vol. II, p. 165 (1943).

TABLE 1. REACTION OF ALUMINUM ALKOXIDE WITH DIAZOMETHANE

$Al(OR)_3$				CH_2N_2 mmol/ml of toluene	Reaction time hr	Poly-methylene yield,a) %	Methyl ethers	Yielda) %
		mmol	(ml of toluene)					
$Al(OCH_2CF_3)_3$	(I)	29.2	(10)	30.0/ 64	1/4	88	$CH_3OCH_2CF_3$	2.4
$Al(OCH_2CCl_3)_3$	(II)	46.3	(—)b)	46.3/134	1/2	13	$DCH_2OCH_2CCl_3$	17.0
$Al(OCH_2CBr_3)_3$	(III)	5.9	(5)	5.9/ 15	1/6	79.5	$CH_3OCH_2CBr_3$	5.5
$Al[OCH(CH_2Cl)_2]_3$	(IV)	7.3	(5)	7.3/ 10	1/3	52.5	$CH_3OCH(CH_2Cl)_2$	4.0
$Al(OCH_2CHCl_2)_3$	(V)	16.3	(7)	16.3/ 22	7/6	96.5	$CH_3OCH_2CHCl_2$	0
$Al[OCH(CH_3)_2]_3$		34.0	(—)b)	34.0/ 80	120	20	$CH_3OCH(CH_3)_2$	0
$Al[OC(CH_3)_3]_3$		43.7	(—)b)	40.0/ 94	120	36	$CH_3OC(CH_3)_3$	0

a) Based on diazomethane.
b) Diazomethane solution was added to the solid aluminum alkoxide.

under a nitrogen atmosphere at 0°C. The reaction system was kept at 0°C until the gas evolution ceased and the yellow color of diazomethane faded away. Then the reaction mixture was subjected to evaporation at 50—60°C under 0.1 mmHg for 7—10 hr. The residue of the vacuum evaporation was treated with a dilute aqueous solution of HCl. The acid hydrolysis mixture was then extracted with diethyl ether or with toluene, and the extract was examined by v.p.c. analysis for the haloalkyl methyl ether, which should have been formed by the acid hydrolysis of the product of the methylene insertion reaction if the insertion had occurred. Haloalkyl methyl ethers were identified by a comparison of the retention time of the v.p.c. with those of the corresponding authentic samples. Two columns, silicone DC 550 and PEG 20000, were employed in the v.p.c. analysis. The solid insoluble residue of acid hydrolysis was extracted with hot xylene to isolate polymethylene.

In the case of $Al(OCH_2CCl_3)_3$ (II), the reaction with diazomethane was carried out by the same procedure, and the residue of vacuum evaporation was hydrolyzed with heavy water. Deutrated methyl ether, $DCH_2OCH_2CCl_3$, was isolated by means of a preparative v.p.c. technique, and was identified by means of its NMR spectrum using Varian A-60 Spectrometer. In the NMR spectrum of a CCl_4 solution, a singlet at 3.97 ppm downfield from TMS ($CCl_3\underline{CH_2}$-, area 1.00) and a triplet with components of an equal intensity centered at 3.60 ppm ($D\underline{CH_2}$- area 1.06) were observed. The chemical shifts of these absorptions were almost the same as those of the nondeutrated methyl ether, $CH_3OCH_2CCl_3$.

Results and Discussion

The results are summarized in Table 1.

The methylene insertion reaction produces an aluminum-alkyl bond, which was examined by the formation of the corresponding methyl ether (VI) in the acid hydrolysis of the reaction mixture.

$$\text{al-OR} + CH_2N_2 \xrightarrow{-N_2} \text{al-}CH_2OR \xrightarrow{H^+} \underset{\text{(VI)}}{CH_3OR} \quad (2)$$

As to the methyl ether formation, it has been established9) that alcohol reacts with diazomethane, in the presence of aluminum alkoxide as the catalyst, to produce alkyl methyl ether. Therefore, the formation of haloalkyl methyl ether in the present study might be ascribed to the reaction of alcohol, which was possibly produced by the partial hydrolysis of aluminum haloalkoxide with impure moisture. This reaction route does not lead to the formation of the aluminum-alkyl bond. This possibility, however, has been definitely eliminated by the following two observations:

a. The hydrolysis of the reaction mixture with heavy water produced the deutrated methyl ether (VII):

$$\text{al-}OCH_2CCl_3 + CH_2N_2 \xrightarrow{-N_2}$$

$$\text{al-}CH_2OCH_2CCl_3 \xrightarrow{D_2O} \underset{\text{(VII)}}{DCH_2OCH_2CCl_3}$$

b. A reference experiment has shown that the vacuum evaporation of the reaction mixture before acid hydrolysis is quite effective in removing ether almost completely if it is present before the acid hydrolysis.

Thus, the production of haloalkyl methyl ethers in the acid hydrolysis of the reaction mixture is taken to indicate the occurrence of the methylene insertion.

Table 1 shows that the four aluminum haloalkoxides, I to IV, differ from others in their reactivity toward diazomethane. The former alkoxides react with diazomethane to form the linkages of alkoxymethylaluminum along with the formation of polymethylene. The alkoxide of V and the usual alkoxides of unsubstituted alcohols cause only the polymerization of methylene carbene from diazomethane.

Hoberg5-7) has reported that, in the reactions of diazomethane with trialkylaluminums, alkylaluminum hydrides and alkylaluminum halides underwent the methylene insertion into aluminum-alkyl, -hydrogen, and -halogen bonds:

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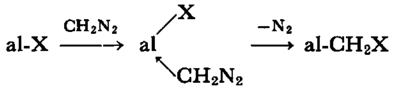
9) H. Meerwein and G. Hinz, *Ann.*, **484**, 1 (1930).



$$\text{al-X} \xrightarrow{CH_2N_2} \text{al}\begin{matrix} \nearrow X \\ \searrow CH_2N_2 \end{matrix} \xrightarrow{-N_2} \text{al-}CH_2X$$

(X=alkyl, hydrogen, halogen)

It was also shown, however, that, in the reaction of alkylaluminum alkoxide with diazomethane, the methylene insertion into the aluminum-alkoxyl or the aluminum-alkyl bond did not take place. Only the formation of polymethylene occurred. The present study has indicated that $Al[OCH(CH_3)_2]_3$, $Al[OC(CH_3)_3]_3$, and V behave in almost the same manner as alkylaluminum alkoxide in their reaction with diazomethane, although $Al[OCH(CH_3)_2]_3$ and $Al[OC(CH_3)_3]_3$ have depressed catalytic activities for the polymethylene formation in comparison with Hoberg's alkylaluminum alkoxide and V. The present study is the first to observe the methylene insertion into the aluminum-alkoxyl bond, which is limited to haloalkoxides of aluminum.

The difference in the reactivity toward diazomethane between haloalkoxides and usual akloxides may reasonably be ascribed to the difference in acid strength. Hoberg[7] has suggested that the coordination of diazomethane onto aluminum was necessary prior to the methylene insertion. In this process, the aluminum compound acts as a Lewis acid.

Table 2. Shift of carbonyl band of xanthone caused by aluminum alkoxides

$Al(OR)_3$	$\Delta\nu_{C-O}$ of xanthone
$Al(OCH_2CF_3)_3$	91
$Al(OCH_2CCl_3)_3$	90
$Al(OCH_2CBr_3)_3$	89
$Al[OCH(CH_2Cl)_2]_3$	91
$Al(OCH_2CHCl_2)_3$	0
$Al[OCH(CH_3)_2]_3$	0
$Al[OC(CH_3)_3]_3$	0
$AlEt_3$	88

By means of the Hammett indicator method as well as the extent of the shift of the infrared absorption of the xanthone carbonyl group, we have already shown that usual aluminum alkoxides and alkylaluminum alkoxides of unsubstituted alcohols are weaker acids than trialkylaluminums and alkylaluminum halides.[1] The four haloalkoxides, on the other hand, are shown to be stronger Lewis acids by the extent of the shift of the xanthone carbonyl band (Table 2). They are as strong as $AlEt_3$. Diazomethane coordinates onto haloalkoxides of strong acid, and hence the methylene insertion takes place. Unlike the four haloalkoxides, the haloalkoxide (V) does not undergo the methylene insertion reaction; this is explained by the finding that the alkoxide (V) is a much weaker acid than I—IV.