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SHORT COMMUNICATION

The reaction of aluminum 2,2,2-trichloroethoxide with diazomethane

Introduction

In the course of studies of the catalytic behavior of aluminum alkoxides in the polymerization of aldehydes and cyclic ethers[1-3], we prepared aluminum 2,2,2-trichloroethoxide, $Al(OCH_2CCl_3)_3$ (I), and investigated its catalytic properties[4]. In comparison with the usual aluminum alkoxides, (I) is characterized by a stronger electron accepting power of aluminum (Lewis acid strength) and by a marked tendency to dissociate to solvated monomer in donor solvents[4].

The present communication describes our finding that (I) reacts with diazomethane to produce the linkage of $>Al{-}CH_2OCH_2CCl_3$ by methylene insertion into the Al–O bond, along with polymethylene formation.

$$\underset{\text{(I)}}{>AlOCH_2CCl_3} \xrightarrow[-N_2]{CH_2N_2} >AlCH_2OCH_2CCl_3 \qquad (1)$$

Reactions of simple, non-halogenated aluminum alkoxides with diazomethane resulted only in polymethylene formation. This different behavior of (I) can be understood in terms of its properties mentioned above.

Experimental

The aluminum alkoxides employed in the present study were (I), $Al[OCH(CH_3)_2]_3$ and $Al[OC(CH_3)_3]_3$. (I) was prepared by the reaction of triethylaluminum with 2,2,2-trichloroethanol[4]. A toluene solution of diazomethane was prepared by treating N-nitroso-N-methylurea with aqueous KOH solution[5]. This then was added dropwise to an equimolar amount of solid aluminum alkoxide at 0°. The reaction system was kept at 0° until the yellow color of the diazomethane faded away, and then was decomposed with dilute aqueous HCl. The acid hydrolyzate was extracted with toluene, and the toluene extract was subjected to VPC analysis with Model GC-2C (Shimazu Seisakusho Co., Japan) using hydrogen as carrier gas. Methyl ethers were searched in the toluene extract and identified by comparisons of retention time with the authentic samples in two columns, Silicone DC 550 and PEG 20,000. The quantitative determination was made by the peak area method using calibration curves.

The solid, insoluble residue was extracted with hot xylene to isolate polymethylene.

The reaction mixture of (I) with diazomethane was hydrolyzed with heavy water. The deuterated methyl ether, $DCH_2OCH_2CCl_3$, was isolated by means of preparative VPC, and was identified by means of its NMR spectrum with Varian A-60 Spectrometer. In CCl_4, a singlet at 3.97 ppm downfield from TMS (Cl_3CCH_2-, area 1.00) and a triplet with components of equal intensity centered at 3.60 ppm (DCH_2-, area 1.06) were observed. The chemical shifts of these absorptions were almost the same as those of non-deuterated methyl ether, $CH_3OCH_2CCl_3$. Experimental details are summarized in Table 1.

TABLE 1

REACTION OF ALUMINUM TRIALKOXIDES WITH DIAZOMETHANE

$Al(OR)_3$	*Mmoles*	CH_2N_2 (*mmoles/toluene ml*)	*Polymethylene yield*[a]	*Methyl ether yield*[a]
$Al[OCH(CH_3)_2]_3$[b]	34.0	34.0/80.0	20%	$CH_3OCH(CH_3)_2$ 0%
$Al[OC(CH_3)_3]_3$[b]	43.7	40.0/94.0	36%	$CH_3OC(CH_3)_3$ 0%
$Al[OCH_2CCl_3]_3$[c]	46.3	46.3/133.5	13%	$DCH_2OCH_2CCl_3$ 17%

[a] Based upon diazomethane. [b] Reaction 5 days, 0°. [c] Reaction 30 min, 0°.

Discussion

In the reactions of $Al[OCH(CH_3)_2]_3$ and $Al[OC(CH_3)_3]_3$ with diazomethane, polymethylene formation was observed, but methylene insertion into the Al–O bond was not. The methyl ethers, $CH_3OCH(CH_3)_2$ or $CH_3OC(CH_3)_3$, respectively, should have been found in the acid hydrolyzate of the reaction system if the methylene insertion had occurred, but they were not detected by VPC analysis. On the other hand, (I) underwent the methylene insertion reaction. The hydrolysis with heavy water of the reaction mixture of (I) and diazomethane gave $DCH_2OCH_2CCl_3$ in a yield of about 17% along with polymethylene in a yield of 13%.

$$\underset{\text{(I)}}{>\text{Al-OCH}_2\text{CCl}_3} \xrightarrow[-N_2]{CH_2N_2} \underset{\text{(II)}}{>\text{Al-CH}_2\text{OCH}_2\text{CCl}_3} \xrightarrow{D_2O} \text{DCH}_2\text{OCH}_2\text{CCl}_3 \qquad (2)$$

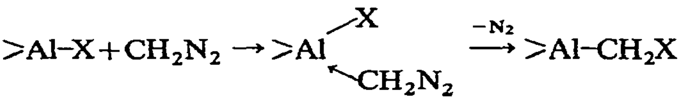
The formation of an organoaluminum compound (II) is the most reasonable explanation for the formation of $DCH_2OCH_2CCl_3$.

Hoberg[6,7] has shown that the reactions of trialkylaluminums, alkylaluminum hydrides and alkylaluminum halides with diazomethane result in insertion of the methylene group into the >Al–alkyl, >Al–hydrogen and >Al–halogen linkages, respectively.

$$>\text{Al-X} \xrightarrow[-N_2]{CH_2N_2} >\text{AlCH}_2\text{X} \qquad (\text{X} = \text{alkyl, hydrogen and halogen}) \qquad (3)$$

Alkylaluminum alkoxides, [X = alkoxy in eqn. (3)], on the other hand, did not undergo methylene insertion, but only caused the polymerization of diazomethane to polymethylene. In the present study, aluminum isopropoxide and tert-butoxide have been shown to resemble alkylaluminum alkoxides in their reactions with diazomethane.

It has been assumed by Hoberg[7] that coordination of diazomethane to aluminum is needed for the methylene insertion reaction.



$$>\text{Al-X}+\text{CH}_2\text{N}_2 \rightarrow >\text{Al}\begin{smallmatrix}\nearrow \text{X} \\ \nwarrow \text{CH}_2\text{N}_2\end{smallmatrix} \xrightarrow{-N_2} >\text{Al-CH}_2\text{X} \qquad (4)$$

On this basis, the diazomethane CH_2 insertion into the usual aluminum alkoxides does not take place probably because of the weak acid strength of the usual aluminum alkoxides[4,7-9] and because of their association to higher aggregates[4,9]. The stronger acceptor power and the decreased tendency of association of (I)[4], on the other hand, make the coordination of diazomethane to (I) more favorable, and thus the methylene insertion reaction is observed.

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