Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

THE PREPARATION AND PROPERTIES OF ETHYLZINC 2,2,2-TRICHLOROETHOXIDE

TAKEO SAEGUSA AND TAKASHI UESHIMA
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto (Japan)

(Received November 27th, 1967)

INTRODUCTION

In a series of studies upon the catalytic behavior of metal alkyls and metal alcoholates in the polymerization of cyclic ethers and vinyl compounds, several haloalcoholates of aluminum were prepared and their properties were studied[1-3]. It was found that aluminum haloalcoholates are stronger Lewis acids than the usual aluminum alcoholates of unsubstituted alcohols[1,2]. In the present study, ethylzinc 2,2,2-trichloroethoxide, $CH_3CH_2ZnOCH_2CCl_3$, (I), was prepared and its properties were compared with those of the usual alkylzinc alcoholates.

EXPERIMENTAL

Synthesis of (I)

Under nitrogen, 0.1 mole of 2,2,2-trichloroethanol diluted in 20 ml of ethyl ether was added with stirring to 0.12 mole of diethylzinc dissolved in 30 ml of ethyl ether at $-10°$ to $-20°$. Then the mixture was allowed to warm to room temperature and finally heated at reflux for 2 h. The product separated as a white precipitate, which was washed repeatedly with cold ether and dried *in vacuo*. Attempted further purification by means of recrystallization or sublimation *in vacuo* was not successful. (I) decomposed at 90° without melting or subliming even *in vacuo*. The yield of (I) was about 50% (Found: Zn, 26.38. $C_4H_7Cl_3OZn$ calcd.: Zn, 26.92%.)

The ratio of CCl_3CH_2O-group to Zn in the product (1.01) was determined from the GLC analysis of trichloroethanol in the reaction mixture obtained upon acid hydrolysis. The ratio of ethyl group to Zn in the product was 1.00, which was determined from the amount of ethane gas evolved in the acid hydrolysis of the product.

Isolation of (I)–donor (1 : 1) *complexes*

Volatile components were removed below 0.1 mm at room temperature from a solution of 5 mmoles of (I) and 20 mmoles of pyridine in benzene, leaving a white solid, which was shown to be (I)–pyridine (1 : 1) complex by means of its elemental analysis and NMR spectrum. (Found: Zn, 20.06. $C_9H_{12}Cl_3NOZn$ calcd.: Zn, 20.31%.)

The pyridine complex was soluble in n-heptane, benzene and methylene chloride and was crystallized from methylene chloride. The (I)–dioxane (1 : 1) complex, prepared similarly, was insoluble in the above mentioned solvents, but soluble in systems containing dioxane.

RESULTS AND DISCUSSION

(I) differs from the usual ethylzinc alcoholates of unsubstituted alcohols in solubility and accepting power for donor. First, (I) is soluble only in donor solvents such as dioxane, tetrahydrofuran and pyridine, whereas the usual ethylzinc alcoholates are known to be easily soluble in various solvents including aliphatic hydrocarbons, benzene, methylene chloride, diethyl ether and dioxane[4–6].

Secondly, the accepting power of (I) for donor molecules, *i.e.*, the Lewis acid strength, is much stronger than that of usual alkylzinc alcoholates. Coates *et al.*[5,7] reported that pyridine was removed completely *in vacuo* at room temperature from a mixture of methylzinc methoxide and pyridine and that the IR spectrum of methylzinc methoxide was not changed substantially by admixing with pyridine. On the other hand, the 1 : 1 complexes of (I) with pyridine and with dioxane were isolated by removing volatiles *in vacuo* from (I)–pyridine and (I)–dioxane mixtures (see experimental section).

Strong interaction between (I) and pyridine was manifested also in IR spectrum, *i.e.*, the ν(C=N) band of pyridine shifted from 1580 cm^{-1} to 1600 cm^{-1} by complexization with (I) (Fig. 1). Ethylzinc ethoxide, an example of the usual alkylzinc alcoholates, did not cause any shift of ν(C=N) band of pyridine. The cryoscopic molecular weight of (I) in dioxane was 496, the calculated value for dimer being 486. This value corre-

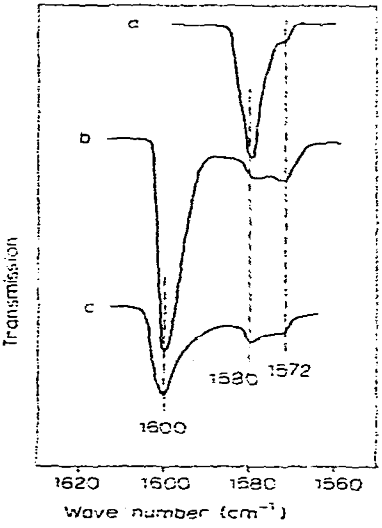
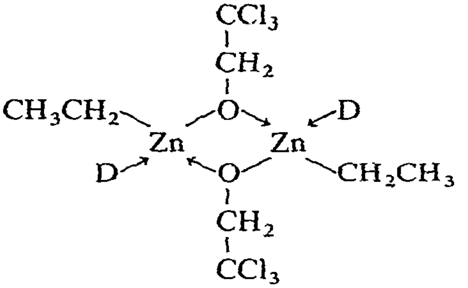


Fig. 1. The infrared spectra of the $CH_3CH_2ZnOCH_2CCl_3$–pyridine (1 : 1) complex in methylene chloride; (a) free pyridine; (b) (1 : 1) complex (5 wt. %); (c) (1 : 1) complex (1.5 wt. %).

sponds to the degree of association of 2.04. The NMR spectrum of a solution of (I) in dioxane has a quartet at τ 9.82 (a), a triplet at τ 8.85 (b) and a singlet at τ 5.77 (c), which are assigned to Zn–CH_2 (a), Zn–CH_2–$C\underline{H}_3$ (b) and Zn–OCH_2CCl_3 (c), respectively. The peak area ratio of a : b : c = 2.0 : 3.0 : 2.0 is consistent with the formula of $CH_3CH_2ZnOCH_2CCl_3$. The NMR spectrum indicates that all ethyl and trichloroethoxy groups are equivalent in dioxane. A dimeric form [(II), D = dioxane] is presented for the complex of (I) with dioxane.

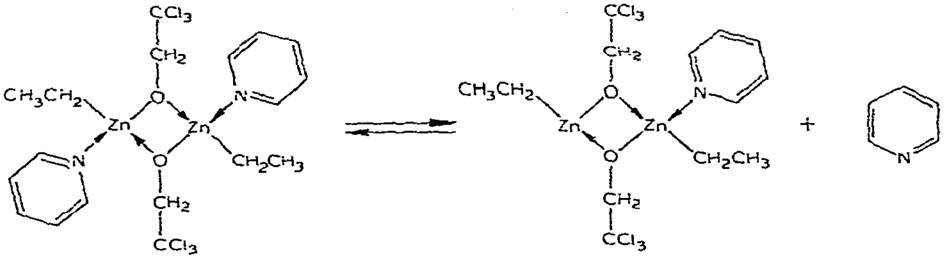


(D = dioxane, pyridine)

(II)

Also in the NMR spectrum of (I) in pyridine all ethyl and trichloroethoxy groups are equivalent. As discussed in the following section, the cryoscopic molecular weight of the 1 : 1 complex with pyridine in benzene, was not contradictory to dimer. The structure (II) may be proposed also for the 1 : 1 complex of (I) with pyridine.

The 1 : 1 complex with pyridine may dissociate in solution. In the NMR spectra of the solutions in methylene chloride there observed two singlets attributed to Zn–OCH_2CCl_3 at τ 5.75 (d) (strong) and τ 5.53 (e) (weak) besides a quartet at τ 9.18 (f), a triplet at τ 8.24 (g) and a set of multiplets (h) in a region of 2.5～1.0 τ which are assigned respectively to the protons of Zn–CH_2 (f), Zn–CH_2–$C\underline{H}_3$ (g) and hydrogens of pyridine (h). The peak area ratio was (d+e) : f : g : h = 2.1 : 2.0 : 3.1 : 4.9. The (e)/(d) peak ratio is increased by the dilution of solution. The ratio of (e)/(d) was 0.049, 0.077, 0.129 and 0.134, respectively, at four concentrations of 20, 10, 5 and 2.5 wt. %.



(1)

(III) (IV)

The system of the 1 : 1 pyridine complex in benzene was then examined by cryoscopy. The apparent molecular weight of the complex was 609 and 605 at the concentrations of 5 and 1.3 wt. %, respectively. These values were slightly lower than the calculated value for dimer (III) (644). Dissociation increases the number of particles in the solution to decrease average molecular weight.

The above observations in NMR spectrum and cryoscopy suggest the dissociation of the complex in solution according to the equation (1). The peak (d) at τ 5.75 will be assigned to Zn–OCH_2CCl_3 in (III) and the peak at τ 5.53 to that in (IV). It is reasonably assumed that the protons of Zn–OCH_2CCl_3 in (III) is highly shielded by two pyridine ligands compared with that in (III) by one pyridine ligand. The IR spectrum studies gave further support for dissociation (Fig. 1). Three absorptions of ν(C=N) of pyridine were observed at 1600 (strong), 1580 (weak) and 1572 cm^{-1} (weak). The absorption at 1600 cm^{-1} may be assigned to the pyridine ring coordinated to zinc atom[1,8]. The ν(C=N) of free pyridine [Fig. 1, (a)] appears only at 1580 (strong) and 1572 cm^{-1} (weak). The absorption at 1580 cm^{-1} of the solution of pyridine complex indicates the presence of free pyridine. Increase in the degree of dissociation by dilution is indicated by the decrease of the intensity ratio of $D(1600)/D(1580)$. The degree of dissociation calculated from the NMR spectrum was *ca.* 6.5% at the concentration of 5 wt. % in benzene at room temperature.

REFERENCES

1 T. SAEGUSA AND T. UESHIMA, *Inorg. Chem.*, 6 (1967) 1679.
2 T. UESHIMA AND T. SAEGUSA, *Bull. Chem. Soc. Jap.*, in press.
3 T. SAEGUSA, S. TOMITA AND T. UESHIMA, *J. Organometal. Chem.*, 10 (1967) 360.
4 H. M. SHEARER AND C. B. SPENCER, *Chem. Commun.*, (1966) 194.
5 G. E. COATES AND D. RIDLEY, *J. Chem. Soc.*, (1965) 1870.
6 G. ALLEN, J. M. BRUCE, D. W. FARREN AND E. G. HUTCHINSON, *J. Chem. Soc.*, *B*, (1966) 799.
7 G. E. COATES AND D. BRADLEY, *J. Chem. Soc.*, *A*, (1966) 1064.
8 M. R. BASILA, T. R. KANTER AND K. H. RHEE, *J. Phys. Chem.*, 68 (1964) 3197.