

HIGH REACTIVITY OF THE ETHYL—ZINC GROUP IN “ETHYLZINC CARBOXYLATE” TOWARDS ACTIVE HYDROGEN COMPOUNDS

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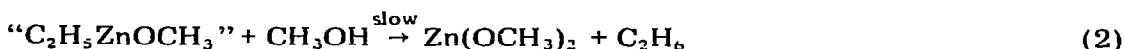
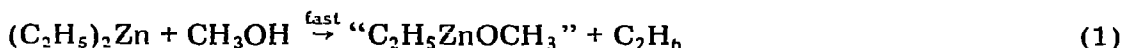
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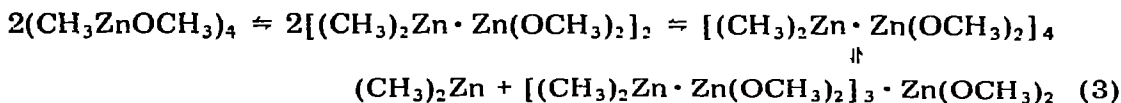
Summary

The reactivity of the ethyl—zinc group in “ethylzinc carboxylate”, formed by the equimolar reaction of diethylzinc and carboxylic acid, towards methanol and pyrrole is higher than that of diethylzinc. Electron withdrawing carboxyl groups are considered to be favorable for the coordination of the active hydrogen compounds with the zinc atom.

In the reaction of diethylzinc and two molar equivalents of methanol, the first ethyl—zinc group of diethylzinc reacts readily with methanol, but the reactivity of the second group is much diminished [1].



The product of a similar reaction to 1 of dimethylzinc may be isolated as a crystalline solid, which proved to be the tetramer $(\text{CH}_3\text{ZnOCH}_3)_4$ [2]. However, this compound in solution exists in equilibrium with a mixture of more complex species and dimethylzinc [3].

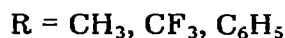
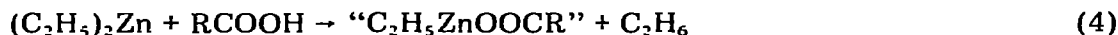


The low reactivity of the alkyl—zinc group in reaction 2, therefore, is considered to correspond to the low reactivity of the alkyl—zinc group in species like $(\text{RZnOR}')_x$ or $[\text{R}_2\text{Zn} \cdot \text{Zn}(\text{OR}')_2]_x$.

In contrast, as described in the present report, the reactivity of the ethyl—zinc group in the product of the equimolar reaction of diethylzinc and a carboxylic acid, “ethylzinc carboxylate”, is enhanced when compared with diethylzinc.

1. Reaction of diethylzinc and carboxylic acid

The equimolar reaction of diethylzinc and a carboxylic acid in benzene proceeds rapidly and quantitatively with the evolution of the stoichiometric amount of ethane (eqn. 4).



In the infrared spectra of the reaction mixtures no absorptions due to diethylzinc are observed, and in the NMR spectra no signals due to diethylzinc are apparent. These observations are considered to indicate the absence of free diethylzinc in the reaction mixture. Therefore, the product may be stoichiometrically represented as "ethylzinc carboxylate", $\text{C}_2\text{H}_5\text{ZnOOCR}$.

In the NMR spectrum of ethylzinc methoxide in benzene, two kinds of signals are observed for methoxy protons as well as for methylene(-zinc) protons. Similar observations have been made for "methylzinc methoxide" in benzene [3, 4] and for "ethylzinc methoxide" in cyclohexane [5]. On the other hand, in the NMR spectra of "ethylzinc acetate" and "ethylzinc trifluoroacetate" no clear splitting of signals for acetoxy and methylene(-zinc) protons is observed. However, a rapid interconversion between the species like $(\text{C}_2\text{H}_5\text{ZnOOCR})_x$ and $[(\text{C}_2\text{H}_5)_2\text{Zn} \cdot \text{Zn}(\text{OOCR})_2]_x$ may not be excluded. By cryoscopic measurements the "ethylzinc carboxylates" were found to be associated in benzene solution. These data are summarized in Table 1, together with characteristic IR and NMR absorption data.

The signal due to methylene(-zinc) protons shows an upfield shift when the NMR spectrum is measured in 1,2-dimethoxyethane, perhaps due to breakdown of the associated structures into ether-solvated species. The relatively high extent of the upfield shift for "ethylzinc acetate" as compared with that of "ethylzinc methoxide" suggests that the solvation of the "carboxylate" takes place more strongly than that of the "alkoxide".

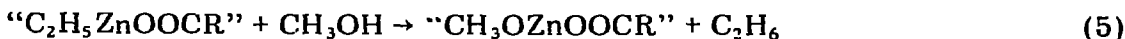
TABLE I
NMR AND IR CHARACTERISTIC ABSORPTIONS AND DEGREE OF ASSOCIATION OF "XZnEt"

"XZnEt"	NMR signals ^a		ν_{as} (C-Zn-X) ^b (cm^{-1})	Degree of association in benzene (0.1 mol/l) ^c
	$\delta(\text{CH}_3)$ (ppm)	$\delta(\text{CH}_2)$ (ppm)		
$\text{C}_2\text{H}_5\text{ZnEt}$	1.26 (1.19)	0.26 (0.10)	561	0.96
CH_3OZnEt	1.60 (1.33)	{ 0.70 { 0.72 (0.42)	552 (521)	4.2
$\text{CH}_3\text{COOZnEt}$	1.65 (1.20)	0.70 (0.18)	519 (514)	3.9
$\text{C}_6\text{H}_5\text{COOZnEt}$	1.39	0.55	(510)	2.9
$\text{CF}_3\text{COOZnEt}$	1.30	0.51		3.3

^a For $\text{CH}_3\text{-CH}_2\text{-Zn}$ in benzene (in 1,2-dimethoxyethane) $J(\text{CH}_2\text{-CH}_3) \sim 8\text{cps}$ ^b In benzene (in 1,2-dimethoxyethane) ^c Based on the assumed structure "XZnEt"

2. Reaction of "ethylzinc carboxylate" with methanol and pyrrole

The reactions of "ethylzinc carboxylates" with an equimolar amount of methanol were examined in toluene at 0°C. The volume of ethane evolved was determined to follow reaction 5.



R = CH₃, CF₃, C₆H₅

As shown in Fig. 1, the initial rates of the reactions of "ethylzinc carboxylates" and methanol are higher than that of diethylzinc. On the other hand, the reactivity of "ethylzinc methoxide" towards methanol is much lower. The reactivities of "ethylzinc phenoxide" and "ethylzinc thiophenoxide", formed by similar reactions to 1, are also lower than that of diethylzinc. The same observation is made in the reactions carried out in 1,2-dimethoxyethane at 0°C.

In the reactions of "ethylzinc carboxylate" and pyrrole in toluene at 50°C, higher reactivities of the ethyl-zinc groups in "ethylzinc trifluoroacetate" and "ethylzinc benzoate" than that in diethylzinc are observed. Although pyrrole possesses almost the same acidity as methanol (p*K*_a, methanol 16.6; pyrrole 16.5), the reactivity of the former towards the ethyl-zinc group is found to be much lower. This may be attributed to the absence of the lone pair electrons readily available for coordination with the zinc atom [6].

3. Discussion

As mentioned above, the ethyl-zinc group in the "ethylzinc carboxylate", formed by the equimolar reaction of diethylzinc and carboxylic acid, exhibits higher reactivity towards active hydrogen compounds than does diethylzinc.

Since "ethylzinc carboxylate" forms associated structures, the actual concentration of the reactive organozinc species would be lower than that of the

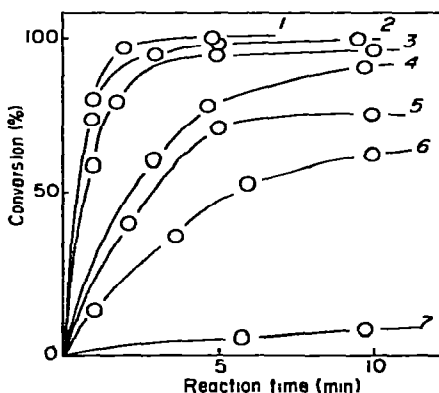
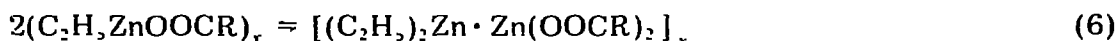


Fig. 1 Equimolar reaction of "XZnC₂H₅" with methanol in toluene at 0°C initial conc., 2 mmol of "XZnC₂H₅" in 25 ml of toluene Conversion = evolved ethane/initial "XZnC₂H₅" 1, CF₃COOZnC₂H₅, 2, C₆H₅COOZnC₂H₅, 3, CH₃COOZnC₂H₅; 4, C₂H₅ZnC₂H₅, 5, C₆H₅SZnC₂H₅, 6, C₆H₅OZnC₂H₅, 7, CH₃OZnC₂H₅

zinc atom. The low reactivity of "ethylzinc methoxide" as compared with diethylzinc would be due, at least partly, to such association (eqn. 3). The higher reactivity of the "ethylzinc carboxylate" is noteworthy, since monomeric diethylzinc is considered more advantageous in this respect. As mentioned already, "ethylzinc carboxylate" would be an equilibrium mixture of associated species (eqn. 6) In such species the reactivity of the ethyl-zinc group should be higher than that of diethylzinc.



Among the factors governing the reactivity, the enhancement of the nucleophilicity of the ethyl-zinc group would be important. However, it should be noted that the reactivity of the ethyl-zinc group in "ethylzinc methoxide" is much lower, although an equilibrium similar to 6 is considered for this compound (eqn. 3). Since the carboxyl group is much less electron donating than the methoxy group, it is very unlikely that the former increases the nucleophilicity of the ethyl-zinc group more than the latter, either directly through the zinc atom (in $(\text{C}_2\text{H}_5\text{ZnOOCR})_x$) or via intermolecular coordination (in $[(\text{C}_2\text{H}_5)_2\text{Zn} \cdot \text{Zn}(\text{OOCR})_2]_x$).

Therefore, the coordination of active hydrogen compound with the zinc atom in the "ethylzinc carboxylate" is considered important for the enhanced reactivity. In this respect, the electron withdrawing carboxyl group is more favorable to increase relatively the electronegativity of the zinc atom than the methoxy group or the ethyl group (in diethylzinc), and the ability of the zinc atom to coordinate with methanol or pyrrole is enhanced. The higher reactivity of methanol than that of pyrrole also indicates the importance of such coordination.

4. Experimental

Reagents

Diethylzinc was purified by distillation under reduced pressure. Methanol and pyrrole were purified by the usual method. Acetic acid was dried over phosphorus pentoxide and then distilled over anhydrous copper sulfate. Trifluoroacetic acid was distilled over phosphorus pentoxide. Benzoic acid was purified by recrystallization from toluene.

Reaction of diethylzinc and carboxylic acid

Equimolar amounts of diethylzinc (2 mmol in 20 ml of solvent) and carboxylic acid (2 mmol in 5 ml of solvent) were allowed to react at 5°C (in benzene) or at 0°C (in 1,2-dimethoxyethane) with stirring for 5 min. The reaction was complete within the above reaction time as confirmed by volumetric measurement of the gas evolved, which was confirmed by gas chromatography to be ethane containing a negligible amount of ethylene.

No IR absorptions and NMR signals attributable to diethylzinc were observed in the reaction mixture. Therefore, if the formation of zinc dicarboxylate, $\text{Zn}(\text{OOCR})_2$, should occur because of the higher reactivity of "ethylzinc carboxylate" than diethylzinc, the dicarboxylate could not exist in its free form but should form a complex with diethylzinc or disproportionate to form ethylzinc carboxylate, which are considered to be in equilibrium with each other (eqn. 6).

Reaction of "ethylzinc carboxylate" with methanol or pyrrole

The above reaction mixture kept in a constant temperature bath was saturated with ethane, and 2 mmol of methanol or pyrrole were introduced into the solution by means of a syringe, followed by stirring. The volume of ethane evolved was measured with a gas burette.

Acknowledgement

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