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REACTIONS OF ORGANOZINC COORDINATION COMPOUNDS
III*. REACTIVITY TOWARDS ACIDIC HYDROCARBONS

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SUMMARY

The reaction of diethylzinc and of the diethylzinc/*N,N,N′,N′*-tetramethylethylene-1,2-diamine complex with cyclopentadiene, indene and fluorene is very slow. The diethylzinc/bipyridine complex shows a slightly enhanced reactivity towards cyclopentadiene. In view of the high reactivity of nitrogen acids such as pyrrole towards the above complexes, π-coordination of the acidic hydrocarbons and the nitrogen acids to the organozinc complex is not thought to play much part in the reaction.

INTRODUCTION

As we have reported[1,2], in comparison with diethylzinc itself, the equimolar complex of diethylzinc with 2,2′-bipyridine (Bipy) or *N,N,N′,N′*-tetramethylethylene-1,2-diamine (TMEDA) shows a much enhanced reactivity towards secondary amines such as diphenylamine, pyrrole, indole and carbazole. In the reaction with secondary amines, the Bipy complex exhibits a much higher reactivity than the TMEDA complex. On the basis of this and other findings we suggested that coordination of the amine to the organozinc complex plays an important part in this reaction. Usually, the lone pair of amine nitrogen is considered responsible for the coordination, but in pyrrole and the derivatives, the possibility of π-coordination must also be considered.

In order to clarify the nature of the interaction between organozinc complexes and active hydrogen compounds, the reaction of diethylzinc–Bipy and diethylzinc–TMEDA complexes with some acidic hydrocarbons such as cyclopentadiene, indene and fluorene has been studied, and the results are discussed in relation to those obtained with nitrogen acids (amines).

RESULTS AND DISCUSSION

1. *Reaction of diethylzinc with acidic hydrocarbons*

The progress of the reaction of diethylzinc with acidic hydrocarbons was

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* For Part II see ref. 2.

followed by measuring the amount of ethane evolved by the reaction.

$$\gtrdot\mathrm{C{-}H} + \mathrm{Et_2Zn} \longrightarrow \gtrdot\mathrm{C{-}ZnEt} + \mathrm{EtH} \tag{1}$$

The reaction with cyclopentadiene (p*K*a 15), indene (p*K*a 19.9) and fluorene (p*K*a 22.9) was examined, and the results are given in Fig. 1, along with those for ethanol (p*K*a 18)[2] and pyrrole (p*K*a 16.5)[2] for comparison. Cyclopentadiene is much less reactive than expected from its p*K*a, being similar to pyrrole in this respect.

These results clearly demonstrate the importance of σ-coordination through the oxygen lone-pair, which is possible for ethanol but not for acidic hydrocarbons. All the acidic hydrocarbons examined showed low reactivity, and among them reactivity was in the order of p*K*a, that is, cyclopentadiene > indene > fluorene.

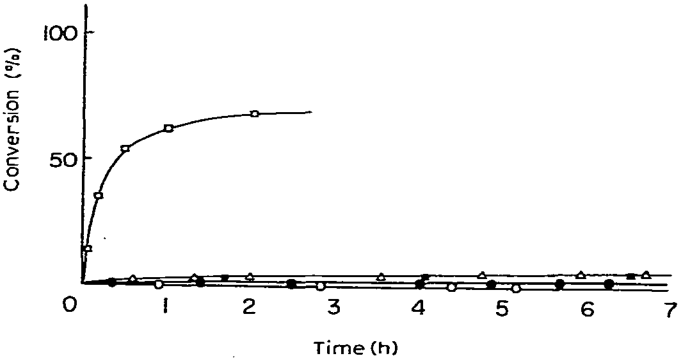

Fig. 1. Reaction of diethylzinc with acidic hydrocarbons, ethanol and pyrrole. Equimolar reaction in toluene at 40°. Initial conc.: 0.3 *M*. △ cyclopentadiene (at 30°), ● indene, ○ fluorene, □ ethanol (initial conc.: 0.075 *M*), ■ pyrrole.

2. *Reaction of diethylzinc complex*

In Fig. 2 are presented the results of the reaction of diethylzinc–TMEDA complex with acidic hydrocarbons, along with those for pyrrole[2] and ethanol. Although complex formation with TMEDA markedly increased the rate of reaction

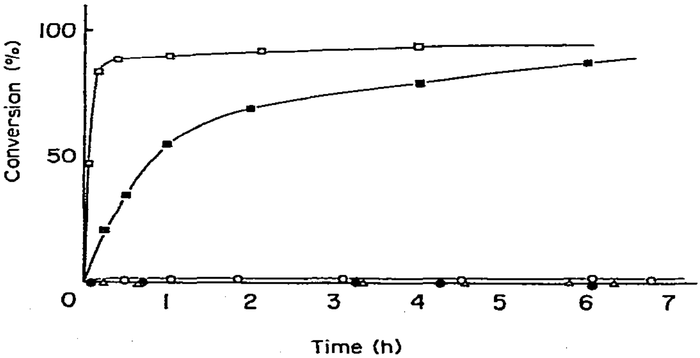

Fig. 2. Reaction of diethylzinc–TMEDA complex with acidic hydrocarbons, ethanol and pyrrole. Equimolar reaction in toluene at 40°. Initial conc.: 0.3 *M*. ○ cyclopentadiene (at 30°), ● indene, △ fluorene, □ ethanol (initial conc.: 0.075 *M*), ■ pyrrole.

of diethylzinc with pyrrole or ethanol (see Fig. 1), the acceleration was very small or non-existent in the reactions with acidic hydrocarbons. *N,N,N',N'*-tetramethyl-*o*-phenylenediamine (TMOPDA) did not accelerate the reaction of diethylzinc with acidic hydrocarbons.

The diethylzinc–Bipy complex was slightly more reactive towards acidic hydrocarbons, than diethylzinc itself, as shown in Fig. 3 for the reaction with cyclopentadiene. On the other hand, the diethylzinc–Bipy complex reacted with pyrrole 5000 times as fast as diethylzinc[2].

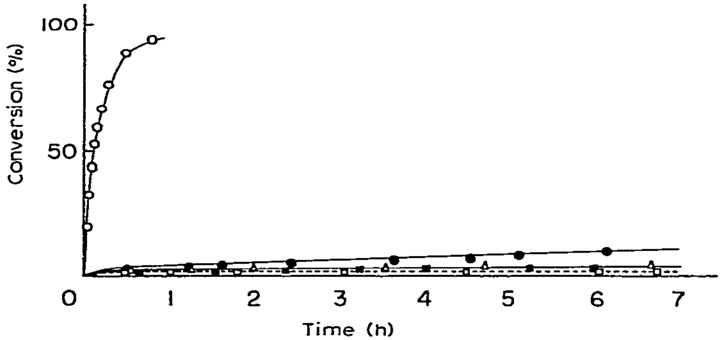

Fig. 3. Reaction of diethylzinc complex with cyclopentadiene. Equimolar reaction in toluene at 30°. Initial conc.: 0.3 *M*. Complexing agent: ● Bipyridine, □ TMEDA, ■ TMOPDA, △ none, ○ Reaction of Bipy complex with pyrrole.

The effect of complex formation of diethylzinc with Bipy was even less in the reaction with indene and fluorene than in the reaction with cyclopentadiene.

3. *Comparison of acidic hydrocarbons and nitrogen acids*

The reactivity of diethylzinc complexes towards active hydrogen compounds (acids) is considered to be governed by (*i*) the acidity of the acid, (*ii*) the nucleophilicity of the ethyl group bound to zinc, and (*iii*) the ability of the acid to coordinate to zinc. As described above, the difference in the reactivities of acidic hydrocarbon and acidic nitrogen compounds with similar acidity, cyclopentadiene and pyrrole, is very remarkable in the reaction with the diethylzinc–TMEDA or diethylzinc–Bipy complex. Such a large difference is thought to reflect the difference in coordination ability of the acidic nitrogen compounds and acidic hydrocarbon. Thus, the coordination which is of primary importance is σ-coordination. However, the slightly higher reactivity of the diethylzinc–Bipy complex than of the diethylzinc–TMEDA complex towards cyclopentadiene indicates that there is some contribution from π-coordination by acidic hydrocarbon, though not much. Back donation from zinc to Bipy in the Bipy complex[2,3] may favour π-coordination of the reacting cyclopentadiene.

It is relevant to note that acceleration of the reaction of diethylzinc with phenylacetylene and fluorene by polar solvents such as dimethylformamide, dimethyl sulfoxide and hexamethylphosphoric triamide has been reported, but this was thought to be due to the increase of the nucleophilicity of the organozinc compound caused by solvation[4].

EXPFRIMENTAL

Reagents

Purification of reagents was carried out under nitrogen.

Diethylzinc was purified by distillation, b.p. 50°/64 mm. Indene was refluxed over calcium hydride and distilled, b.p. 103°/64 mm. Fluorene was recrystallized twice from ethanol, m.p. 118–119°. Cyclopentadiene was prepared by thermal decomposition of dicyclopentadiene[5], b.p. 41°. Ethanol was refluxed over barium oxide and distilled.

N,N,N',N'-Tetramethylethylene-1,2-diamine (TMEDA) was refluxed over calcium hydride and distilled, b.p. 121°. 2,2'-Bipyridine (Bipy) was recrystallized twice from n-hexane, m.p. 70°. *N,N,N',N'*-Tetramethyl-*o*-phenylenediamine (TMOPDA) was prepared from *o*-phenylenediamine and trimethyl phosphate[2].

Organozinc complex

The complexes of diethylzinc with TMEDA and Bipy were prepared by dissolving equimolar amounts of the components in toluene, since the complexes are reported to be very stable in benzene[3].

Reaction

The progress of the reaction was followed by measurement of the volume of ethane evolved, as previously described[2]. The reaction was usually carried out at 40° in toluene. The reaction with cyclopentadiene was carried out at 30° because of the low boiling point of cyclopentadiene.

The fact that no reaction other than hydrogen abstraction (eqn. (1)) occurred was confirmed in the reaction of diethylzinc with cyclopentadiene as follows. After the reaction, the mixture was treated with an excess of acetic acid and the volume of evolved ethane was determined. The total ethane evolution (in the reaction and after the acidification) corresponded with quantitative protolyses of the Et–Zn linkages in the diethylzinc taken, indicating that no addition reaction was occurring.

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