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Investigations on organozinc compounds
VI*. NMR study of unsolvated organozinc halides

Alkyl group exchange between alkyl derivatives of different Group II metals has been previously reported[1]. Using NMR spectroscopy we have been unable to detect this phenomenon in mixtures of different dialkylzincs (*e.g.* Et_2Zn with Me_2Zn or tert-Bu_2Zn). This is in accordance with the existence of relatively stable mixed dialkylzinc compounds[2]. However, our NMR results demonstrate that alkyl group exchange between alkylzinc compounds does occur, if at least one of these is of the mono-alkyl type RZnX. Exchange takes place between Et_2Zn and EtZnX for compounds in which X is halogen or a group bound to zinc via O, N and S, the rate of exchange depending on the nature of X[3].

The purpose of the present communication is to report some details of our NMR study of unsolvated organozinc halides[4] and, in particular, to draw attention to the unusual behaviour of EtZnI in non-solvating solvents. A number of recent reports have dealt with ether-solvated EtZnI[5].

Only one set of ethyl group absorptions—one triplet and one quartet—is present in the NMR spectrum of a mixture of EtZnX (X = Cl, Br, I) and Et_2Zn in aprotic, non-polar solvents. We have determined the chemical shift of the methylene protons of the ethylzinc group, $\delta(CH_2)$, in mixtures of EtZnX and Et_2Zn dissolved in toluene as a function of the fraction of ethyl groups bound to EtZnX, x(EtZnX). Solutions were made up to constant ethyl group concentration. The results are graphically shown in Fig. 1.

An excellent linear relationship between $\delta(CH_2)$ and x(EtZnX) is observed in each case, proving the occurrence of exchange[6]. Exchange is extremely fast ($\tau < 0.004$ sec), only very slight broadening of the resonance signals being observed at $-60°$. No exchange takes place at room temperature between R_2Hg and RHgX (X = Cl, Br), whereas slow exchange occurs if X = I[7].

Organozinc halides may be subject to disproportionation according to (1) (Schlenk equilibrium):

$$2\,RZnX \rightleftharpoons R_2Zn + ZnX_2 \rightleftharpoons R_2Zn \cdot ZnX_2 \qquad (1)$$

Therefore, the reported $\delta(CH_2)$ values for EtZnX in toluene[4] might actually represent $\delta(CH_2)$ for the equilibrium mixture. The "true" value of $\delta(CH_2)$ for EtZnX may be obtained by extrapolating $\delta(CH_2)$ to $x(EtZnX) = 1$.

For EtZnCl the reported value of $\delta(CH_2)$ (0.65 ppm) and $\delta(CH_2)$ obtained from the graph are identical, indicating that in toluene the Schlenk equilibrium for EtZnCl lies completely to the left. Similarly, for EtZnBr there is only a slight difference ($\delta_{rep.}$ 0.69 ppm; $\delta_{graph.}$ 0.73 ppm) pointing out that (1) lies to the left also if X = Br.

However, for EtZnI the difference between $\delta_{rep.}$ and $\delta_{graph.}$ is considerable: 0.34 and 0.80 ppm. As appears from Fig. 1 $\delta(CH_2)$ remains fairly constant for values of $x(EtZnI) > \sim 0.19$. Apparently in this region the Et_2Zn/EtZnI ratio in solution is

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* For Part V see ref. 4.

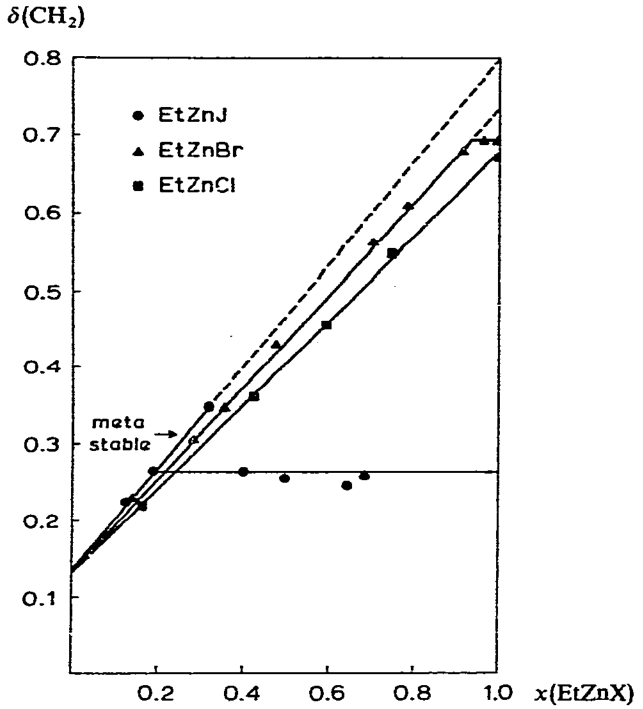

Fig. 1. $\delta(CH_2)$ as a function of x(EtZnX) for mixtures of EtZnX and Et_2Zn (total concentration ~ 1.0 *M*) in toluene (Varian Model HR-100 NMR spectrometer; δ in ppm downfield from tetramethylsilane)

constant. When solutions of EtZnI with $x(\text{EtZnI}) > 0.19$ were made up a colourless solid analyzing for ZnI_2 settled out of solution. It would seem that EtZnI disproportionates according to (1) to such an extent that enough Et_2Zn is present to solvate the remaining EtZnI. In other words, EtZnI only dissolves in non-coordinating solvents, if a sufficient quantity of Et_2Zn is present. From the NMR data a ratio EtZnI/Et_2Zn = ~0.47 may be calculated.

A constant Zn/I ratio (~3.0) was found when the supernatants obtained by "dissolving" varying amounts of EtZnI in toluene were analyzed for Zn and I. This again points to a constant EtZnI/Et_2Zn ratio in solution, whatever may be the nature of the dissolved species. The values obtained from the analytical data (~0.50) and from the NMR data (~0.47) are in good agreement.

In benzene EtZnI displays the same solution behaviour. Determination of the Zn and I content in a number of supernatants revealed the same Zn/I ratio of 3.0 (EtZnI/Et_2Zn = 0.50) in solution (the insoluble residue analyzed for ZnI_2). The molarity of these supernatants was determined cryoscopically (EtZnCl and EtZnBr are tetrameric in benzene[4].). Surprisingly, in each case the molarity found could be accounted for by the quantity of Et_2Zn calculated from the analytical data. Thus, it would seem that EtZnI does not measurably contribute to the molarity of these solutions.

These data leave unanswered questions concerning the nature of the dissolved EtZnI species, in particular the role played by Et_2Zn.

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