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PROPERTIES OF UNSOLVATED ORGANOZINC HALIDES

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Several recent papers have dealt with the interaction of diethylzinc and zinc halides(1, 2) with special emphasis on the nature of the species present in ether solvents(3-6). In the present communication we wish to report on some aspects of the chemistry of unsolvated alkylzinc halides.

The title compounds are obtained according to (I) by heating the appropriate zinc halide and dialkylzinc (100 % excess) at 70° till the first has completely dissolved (10-20 min.), removing the excess of dialkylzinc _in vacuo_ and recrystallizing the solid residue from _n_-pentane*.

$$R_2Zn + ZnX_2 \rightleftharpoons 2\ RZnX \qquad (I)$$

Ethylzinc halides so obtained (Table I) are colourless, crystalline solids. EtZnCl and EtZnBr show a sharp melting point and give perfectly clear solutions in aprotic, apolar solvents such as _n_-hexane or toluene.

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* Satisfactory analyses have been obtained for all compounds reported.

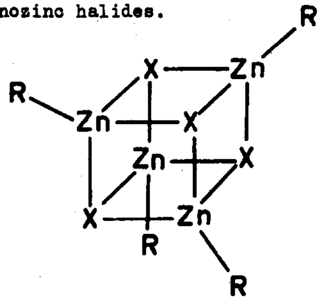
EtZnI, however, melts with decomposition and deposits a residue of ZnI_2 upon redissolution in apolar solvents, making an accurate molecular weight determination impossible.

TABLE I

Compound	M.p.	Mol.wt.	δ_{CH_2}[b]	δ_{CH_2}[c]
EtZnCl	68°	491 (517)[a]	0.65	0.22
EtZnBr	81°	658 (697)[a]	0.69	0.28
EtZnI	96-99 (dec)	-	0.34	0.35
Et_2Zn	-	-	0.13	0.21

[a] Calculated for tetramer; [b] 10 % solution in toluene (δ in p.p.m. downfield from tetramethylsilane; Varian Model HR-100 N.M.R. spectrometer); [c] 10 % solution in Et_2O.

Interestingly, EtZnCl and EtZnBr are tetrameric in benzene solution as appears from cryoscopic molecular weight determinations (Table I). Whereas organozinc diphenylamides $RZnNPh_2$ are dimeric in benzene[7, 8], alkylzinc alkoxides RZnOR'[7] and $MeZnOSiMe_3$[9] have recently been reported to be tetrameric. A cubic arrangement of the zinc and halogen atoms (structure I) similar to the cubic structure of tetrameric trimethylplatinum chloride $(Me_3PtCl)_4$[10] may be considered for the unsolvated organozinc halides.



X = Cl, Br, I

I

Such a structure has recently been proposed by Coates and Ridley for $(RZnOR')_4$[7].

In unsolvated EtZnX the electronegative halogen would be expected to cause the CH_2-protons to be deshielded as compared with in Et_2Zn. Coordinate covalent bonding from X to Zn as occurring in I will counteract this effect*. In view of the weak nature of this bonding (see below) the net effect must be expected to be a down-field shift for the CH_2-protons as compared with in Et_2Zn. The data in Table I agree with this picture. The low value of δ_{CH_2} for EtZnI is caused by the presence of Et_2Zn in the sample (see below).

Coordinate bonding is weaker in tetrameric organozinc halides than in the corresponding alkoxides as appears from their complex-forming behaviour. Whereas compounds RZnOR' do not form complexes with pyridine[7] or 2,2-bipyridine (Bipy)[11], ethylzinc halides dissolved in _n_-pentane form stable, monomeric 1:2 complexes with pyridine (_e.g._ EtZnCl.2 Py, colourless crystals with m.p. 63° from _n_-pentane). Addition of TMED or Bipy to EtZnCl in _n_-pentane does not result in complete breakdown of the tetrameric structure. Due to insolubility of the primary chelated species formed complexes precipitate which, as appears from analytical and molecular weight data, have the composition $(EtZnCl)_n$. TMED and $(EtZnCl)_n$. Bipy, the value of n being > 1, ~ 2-3 depending on the method of preparation. In Et_2O monomeric, colourless EtZnCl. TMED (m.p. 115°) and light-yellow EtZnCl.Bipy (dec. > 240°) are obtained (cf. ref. 5).

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* The value of δ_{CH_2} for Et_2Zn shifts upfield from $\delta = 0.13$ p.p.m. to $\delta = -0.07$ p.p.m. upon complexation with N,N,N',N'-tetramethylethylenediamine (TMED).

A high-field shift of δ_{CH_2} is observed, if the N.M.R. spectrum of the ethylzinc halides is recorded in Et_2O instead of in toluene (Table I). Breakdown of the tetrameric structure I to Et_2O-solvated species (replacement of weak Zn-Cl by stronger Zn-O coordinate bonds) would be expected to result in increased shielding of the methylene protons. Because no such shift is observed for Et_2Zn, the N.M.R. spectra of ethylzinc halides and Et_2Zn in Et_2O-solution are rather similar (Table I) and thus cannot serve to distinguish between these compounds (cf. refs. 3 and 5). Unexpectedly, δ_{CH_2} decreases with increasing electronegativity of the halogen. This might be explained on the basis of long-range deshielding caused by the magnetically anisotropic Zn-X bond (cf. ref. 12). Similar observations made by Evans and Maher for ethylmercuric halides were explained on the same basis[3].

The Schlenk equilibrium (I) for EtZnCl and EtZnBr dissolved in n-pentane or toluene lies essentially on the right at roomtemperature: $ZnCl_2$ or $ZnBr_2$ do not precipitate from solution and upon addition of Bipy the orange-red colour of Et_2Zn.Bipy[13] is barely perceptible. This does not hold true for EtZnI as appears from the presence of insoluble ZnI_2 in a pentane or toluene solution of EtZnI and the formation of Et_2Zn.Bipy upon addition of Bipy.

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