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ORGANOMETALLIC COMPOUNDS
V*. ELECTROPHILIC SUBSTITUTION OF DIALKYLZINCS BY PHENYLMERCURIC CHLORIDE

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INTRODUCTION

The metal-for-metal exchange (1) is of considerable practical and theoretical interest, and several systems in which M and M′ are the same metal have been extensively studied (*e.g.* the alkyl mercury-for-mercury exchanges[2]).

$$R{-}M + M'{-}X \rightarrow R{-}M' + M{-}X \qquad (1)$$

Only few mechanistic investigations, however, have been made of systems in which M and M′ are different metals. Reid and Wilkins[3] observed second-order kinetics in the alkylation of trimethylhalosilanes by methylmagnesium halides ($M = Mg$, $M' = Si$), Hart and Ingold[4] have claimed that transfer of an ethyl and a sec-butyl group from thallium to mercury ($M = Tl$, $M' = Hg$) and transfer of a sec-butyl group from mercury to thallium ($M = Hg$, $M' = Tl$) were all examples of the S_E1 mechanism**, and Grant and Van Wazer[5] have discussed a number of transfers of methyl groups from tin to germanium ($M = Sn$, $M' = Ge$). No reports exist as to the (quantitative) effect of the alkyl group R (eqn. 1, $M \neq M'$) on the rate of such exchanges, and we hoped by choice of $M = Zn$ and $M' = Hg$ to observe the effect of various alkylzinc groups, and to relate, if possible, our observations to the well-documented alkyl mercury exchanges ($M = M' = Hg$).

DISCUSSION

To avoid the problem of consecutive alkylations of, say, a mercuric halide, we chose phenylmercuric chloride as a suitable electrophile and we selected diethylzinc as a representative zinc dialkyl. The expected reaction is (2), and this we were able to confirm. Exactly one hydrolysable ethyl group was lost per phenylmercuric chloride [in solvents ether and tetrahydrofuran (THF)] and the product contained both a phenylmercury group and an ethylmercury group.

$$Et_2Zn + PhHgCl \rightarrow PhHgEt + EtZnCl \qquad (2)$$

The only complication that might arise would involve the ethylzinc chloride in an

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* Part IV, see ref. 1.

** But Jensen and Heyman[15] have asserted that these transfers were not observed by Hart and Ingold (and hence, of course, that neither was the S_E1 mechanism).

equilibrium such as (3) ($X = Cl$):

$$2\,EtZnX \xrightleftharpoons{\text{solvent}} Et_2Zn + ZnX_2 \qquad (3)$$

Equilibrium (3), however, has been shown to lie well to the left for the cases $X = I$ in THF[1,6-8]; $X = I$ in ether[1,6]; $X = Br$ in THF[8]; $X = Br$ in ether[1]; $X = Cl$ in THF[8]. As Boersma and Noltes[9] have also shown that EtZnCl does not symmetrise in solvent ether, it is clear that we may disregard (3) (in ether, THF). Having ascertained the stoichiometry (2), we then attempted to follow the kinetics of (2) using solvent THF; unfortunately (2) is quite fast, and with initial concentrations of each reactant at 0.02 mole·l^{-1}, the half-life is about one minute at 0°. We were not able to reduce these initial concentrations very much, and so we were restricted to making a number of "one-point" determinations. These are given in the Table and show that the second-order rate constant, k_2^{ab}, is reasonably constant with an average value of 0.64 l·mole^{-1}·sec^{-1} at 0°. We also made some similar-type determinations using ether as the solvent. To our surprise (2) was even faster in ether, with $k_2^{ab} \sim 6$ l·mole^{-1}·sec^{-1} at 0°.

TABLE 1

THE SUBSTITUTION OF DIETHYLZINC BY PHENYLMERCURIC CHLORIDE IN TETRAHYDROFURAN

Reaction time (sec)	*Percent. reaction*	$[Et_2Zn]^\circ(a)$ *(mole·l^{-1})*	$[PhHgCl]^\circ(b)$ *(mole·l^{-1})*	k_1^a *(sec^{-1})*	k_1^b *(sec^{-1})*	k_2^{ab} *(l·mole^{-1}·sec^{-1})*
56	44	0.02071	0.01979	0.0097	0.010	0.67
78	65	0.02107	0.00300	0.0012	0.013	0.68
60	58	0.02107	0.00254	0.0012	0.014	0.71
60	56	0.02107	0.00254	0.0012	0.014	0.67
34	90	0.11980	0.01769	0.0042	0.068	0.62
66	93	0.09405	0.02205	0.0037	0.040	0.51
62	48	0.02288	0.02098	0.0094	0.011	0.62
56	44	0.02071	0.01979	0.0097	0.010	0.67

In order to examine the effect of the alkylzinc group on the rate of substitution by phenylmercuric chloride, we therefore resorted to competitive experiments to determine relative rate constants. A mixture of two symmetrical dialkylzincs was allowed to react with a deficiency of phenylmercuric chloride, and the resulting product hydrolysed to give the alkanes corresponding to the unreacted alkyl–zinc bonds. The amounts of unreacted dialkylzincs could thus be found (with due regard to the alkane evolved from the alkylzinc halides) and the relative rate constants obtained from the expression:

$$\frac{k}{k'} = \frac{\text{log of fraction of } R_2Zn \text{ unreacted}}{\text{log of fraction of } R'_2Zn \text{ unreacted}}.$$

The method is essentially that described[10] in detail by Abraham and Hill, except that in the present work the amounts of unreacted species were measured, whilst in the procedure of Abraham and Hill[10] the amounts of reacted species (*i.e.* products) were measured*.

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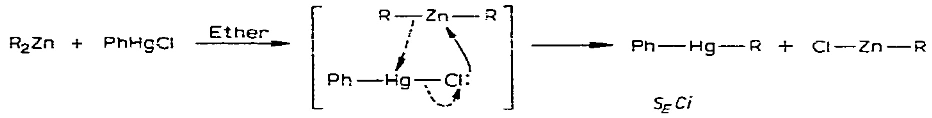
* Analysis of the reaction products is actually the preferred procedure, as it leads to a more accurate determination of the relative rate constants. In the present work, however, we were not able to analyse the products (PhHgR and PhHgR') by any convenient method.

We find, using solvent ether at 35°, that $k(\mathrm{Et})/k(\mathrm{Me}) = 4.5$, $k(\mathrm{Pr})/k(\mathrm{Et}) = 3.7$, and $k(\text{iso-Pr})/k(\mathrm{Et}) \sim 5$. The relative rate constants for substitution by phenylmercuric chloride are thus Me_2Zn (100), Et_2Zn (450), Pr_2Zn (1700), and iso-Pr_2Zn (~2200). In solvent THF at 25° all four dialkylzincs reacted at the same rate.

Now according to Abraham and Hill[11], substitutions proceeding via mechanism S_E2 are expected to give rise to the "steric" sequence of rate constants (which in the present case would be $Me_2Zn > Et_2Zn > Pr_2Zn >$ iso-Pr_2Zn), those proceeding via mechanism S_EC to the "polar" sequence of rate constants (in the present case $Me_2Zn < Et_2Zn \sim Pr_2Zn <$ iso-Pr_2Zn), and substitutions proceeding via mechanism S_Ei to give rise to combinations of these two extreme sequences. The sequence we have found using solvent ether is clearly the "polar" sequence and on the above hypothesis[11] the substitution reaction would be expected to involve mechanism S_EC or an internal substitution (S_Ei), in which co-ordination to the zinc atom by the reagent is rather more important than electrophilic attack—that is mechanism S_ECi[11]. We prefer the latter and hence write:



The sequence we have observed might be compared with a number of such sequences (see ref. 11) and especially with those found for two related reactions, the one-alkyl mercury exchange between alkylmercury halides and mercuric halides in solvent ethanol[12] (MeHgX > EtHgX > sec-BuHgX), and the two-alkyl mercury exchange between dialkylmercurys and mercuric iodide in solvent dioxane[13] ($Me_2Hg < Et_2Hg < Pr_2Hg >$ iso-Pr_2Hg). This latter sequence is almost the same as the one we find, although rather more compressed.

The similar rates of reaction of the four dialkylzincs with phenylmercuric chloride in solvent THF could be due to an exact balance between steric and polar effects of the alkyl groups, in mechanism S_Ei. Alternatively, the rate-determining stage (or at least a partly rate-determining stage) could be the displacement of THF, co-ordinated to the zinc atom, by phenylmercuric chloride. If this were followed by a fast shift of alkyl from zinc to mercury, constitutional influences of the alkyl group would be expected to be small. It is known[14] that THF is a much stronger Lewis base than is ether towards organometallics and thus displacement of co-ordinated THF should be much less facile than displacement of co-ordinated ether.

EXPERIMENTAL

All operations involving dialkylzincs were carried out in an atmosphere of dry, oxygen-free nitrogen or carbon dioxide. The dialkylzincs were prepared and analysed as described previously[1,10]. Phenylmercuric chloride was recrystallised from benzene. Ether was distilled, dried over $CaCl_2$, redistilled and stored over sodium. THF was distilled, stored over sodium, and redistilled from $LiAlH_4$ under nitrogen immediately prior to use.

Action of diethylzinc on phenylmercuric chloride

An excess of diethylzinc was added to a solution of phenylmercuric chloride in THF under carbon dioxide. After 10 min the mixture was hydrolysed by the addition of water, and the evolved ethane collected over 50% aq. KOH. From the volume of ethane evolved, we calculated that exactly one hydrolysable ethyl group had been consumed per phenylmercuric chloride. Addition of iodine to the hydrolysed mixture, followed by an ether extraction, yielded ethyl iodide and iodobenzene—no benzene could be detected—as found by gas chromatography. Using ether as the solvent, again we calculated that one hydrolysable ethyl group was consumed per phenylmercuric chloride.

Kinetic studies

Solutions of phenylmercuric chloride and diethylzinc in THF (10 ml of each) were placed in the two arms of a reaction vessel, under nitrogen, and the vessel then immersed in an ice-water bath. After equilibration, the vessel was tilted, thus allowing the two solutions to mix rapidly; zero time was taken from the first instant of mixing. The reaction mixture was quenched by the rapid addition of a saturated solution of aq. potassium hydrogen phthalate; reaction time was taken to the start of this addition. The quenched mixture was washed into a separating funnel, using THF (10 ml) and water (10 ml), and extracted with benzene (40 ml) to remove unchanged PhHgCl and the formed EtHgPh. The benzene extract was washed with water (20 ml) and the combined aq. extract and washings were analysed for chloride ion by Volhard's method, thus giving directly the amount of Cl transferred from mercury to zinc. Check experiments showed that neither PhHgCl nor Ph_2Hg interfered, and, on reaction mixtures run to infinity, the chloride ion found in this way agreed with the original quantity of PhHgCl. For reactions in solvent ether, the two reactants were in 200 ml ether (PhHgCl) and 20 ml ether (Et_2Zn), the mixture quenched as before, and the quenched mixture merely shaken with water (50 ml). The PhHgCl and EtHgPh were retained in the ethereal layer, and the aq. layer was again analysed for chloride ion by Volhard's method.

Competitive studies

The apparatus and general procedure were as described[10] before. A mixture of two (symmetrical) dialkylzincs was allowed to react with a deficiency of phenylmercuric chloride in solvent ether or THF in an atmosphere of carbon dioxide. The resulting product was hydrolysed by addition of dilute H_2SO_4, the evolved alkanes collected over 50% aq. KOH, and their volume and proportions determined—the latter by gas chromatography[10]. Results from experiments involving diisopropylzinc were somewhat erratic, due, we believe, to the thermal instability of this dialkyl, although the samples of diisopropylzinc in these experiments were always redistilled just before use. Five runs were carried out on each pair of dialkylzincs.

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SUMMARY

The substitution of diethylzinc by phenylmercuric chloride is first order in each reactant, with $k_2 = 0.64$ l·mole^{-1}·sec^{-1} in solvent tetrahydrofuran, and with $k_2 \sim 6$ l·mole^{-1}·sec^{-1} in solvent ether, both at 0°. The relative rate constants for substitution by phenylmercuric chloride in ether at 35° are Me_2Zn (100), Et_2Zn (450), Pr_2Zn (1700), and iso-Pr_2Zn (~2200); this sequence is interpreted as arising from an $S_Ei(S_ECi)$ mechanism of electrophilic substitution at saturated carbon. In solvent tetrahydrofuran at 25° the four dialkylzincs undergo substitution at approximately the same rate; this may be due to an exact balance of steric and polar effects in mechanism S_Ei, or to the displacement of co-ordinated tetrahydrofuran from the zinc atom by phenylmercuric chloride being, at least partly, rate-determining.

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