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ORGANOMETALLIC COMPOUNDS
3*. THE ACIDOLYSIS OF SOME SYMMETRICAL—AND UNSYMMETRICAL—DIALKYLZINCS BY PRIMARY AMINES**

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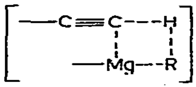
INTRODUCTION

Although one of the characteristic reactions of the more reactive organometallic compounds is their ready cleavage by weak acids, the number of investigations on this type of reaction is quite small. Ivanoff and Spassoff[2] showed that for the action of the chloromagnesium salt of phenylacetic acid on Grignard reagents in refluxing ether, (1), the Grignard reagents could be placed in a reactivity sequence iso-PrMgBr ~ EtMgBr > PrMgBr > sec-BuMgBr ~ MeMgI ~ iso-BuMgBr. A fuller sequence, iso-PrMgBr > EtMgBr > PrMgBr > sec-BuMgBr > BuMgBr ~ MeMgI > iso-BuMgBr, was later found by Ivanoff and Abdouloff[3] for the analogous reactions of Grignard reagents with indene, but with dibutyl ether as solvent.

$$\mathrm{RMgX + PhCH_2CO_2MgCl \rightarrow RH + PhCH(MgX)CO_2MgCl} \tag{1}$$

The first quantitative study was reported by Wotiz, Hollingsworth, and Dessy[4] who showed that the relative reactivities of alkylmagnesium bromides towards 1-hexyne were iso-Pr(210) > Et(100) > Pr(59) > Me(6) in refluxing ether as solvent. For the reaction of EtMgBr with BuC≡CH, and BuC≡CD, k_H/k_D was[5] 4.4, and in a series of 1-alkynes, there was no correlation[6] between the acidity of the alkyne and the rate of cleavage of EtMgBr. On the basis of these results, the four-centred transition states (I)[5] and (II)[7], in which the alkyl–magnesium bond of the Grignard reagent and the carbon–hydrogen bond of the alkyne are broken simultaneously, have been suggested. Wotiz and Proffitt[8] have argued, however, that co-ordination of alkyne to magnesium is the rate-determining step: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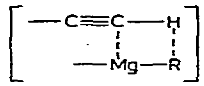
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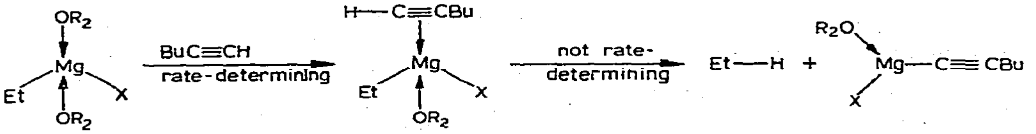

(2)

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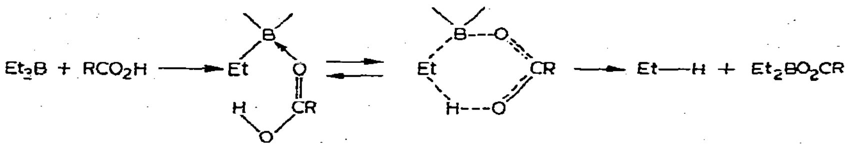
* Part 2, see ref. 1.

** A preliminary account of this work has appeared in *Proc. Chem. Soc.*, (1964) 175.

Hashimoto and his co-workers[9] have shown that in solvent ether, the reaction of ethylmagnesium bromide with 1-hexyne is first-order in each reactant and they suggest a simple mechanism in which the (dimeric) Grignard reagent reacts with 1-hexyne in a single, rate-determining step. They also observed that in solvent tetrahydrofuran (THF), in which[9] the Grignard was monomeric, the kinetic form was now second-order in Grignard and first-order in 1-hexyne, and they suggested a mechanism in which a complex between the alkyne and monomeric Grignard is subsequently attacked by a second molecule of Grignard. It is apparent that difficulties with the actual constitution of the reactants render interpretation of these results on the acidolyses of Grignard reagents far from easy.

On the other hand, Dessy and his co-workers[10] have shown that there is an inverse correlation between the acid strengths of a number of carboxylic acids and the rates of their cleavages of triethylboron. A small kinetic isotope effect, $k(CH_3CO_2H)/k(CH_3CO_2D) = 3.3$, was found, and a mechanism in which the acid first co-ordinates to boron thus elegantly explains[10] these observations:



(3)

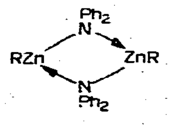
As we have previously shown[1], mechanisms of electrophilic substitution in which each of the reactants is involved in the transition state may be conveniently classified as S_E2, S_Ei, and S_EC, and we have correlated[1] the relative rates of electrophilic substitution of a large number of series of metal alkyls with these mechanisms of substitution. It thus seemed of interest to attempt a study of the acidolysis of a series of reactive organometallics by weak acids, without the constitutional problems associated with the use of Grignard reagents. We chose dialkylzincs as they are simple, monomeric substances[11], easily isolated and purified, and we selected primary amines as suitable weak acids.

No mechanistic studies have been reported on such reactions, although some preparative work has been described. Frankland[12] showed that a number of amines reacted with diethylzinc, primary ones much more readily than secondary ones:

$$2\,PhNH_2 + Et_2Zn \xrightarrow{\text{ether}} (PhNH)_2Zn + 2\,EtH \tag{4}$$

$$2\,Et_2NH + Et_2Zn \xrightarrow{\text{heat}} (Et_2N)_2Zn + 2\,EtH \tag{5}$$

Noltes[13] has prepared compounds of type $RZnNR''_2$ by action of secondary amines on dialkylzincs at 80–110°, and Coates and Ridley[14] have shown that $EtZnNPh_2$ and $MeZnNPh_2$, prepared as by Noltes, are dimeric in solvent benzene with structures of type (III) (R = Me, Et).



(III)

DISCUSSION

The symmetrical dialkyls were prepared by standard procedures and analysed for zinc and for hydrolysable alkyl: the latter analysis provides a convenient check on the purity of sealed-off samples of dialkylzincs. Details of these analyses are given in Table 1.

TABLE 1

ANALYSES OF DIALKYLZINCS

Dialkylzinc	*B.p.* (°*C/mm*)	*Zn calcd.* (%)	*Zn found* (%)	*Hydrolysable alkyl* (*moles/mole*)
Me_2Zn	44.4°/768	67.5	67.7	
Et_2Zn	51–52°/75	52.9	53.0	2.04
Pr_2Zn	48.5–49°/15	43.1	42.8	2.01
Bu_2Zn	61°/4	36.4	36.5	1.95
iso-Pr_2Zn[a]	40°/12	43.1	42.8	1.97
EtZnPr	42–44°/20	47.5	47.2	1.97[b]
PrZnBu	38–43°/3	39.5	39.8	1.89[c]

[a] The diisopropylzinc was kindly prepared and analysed by Dr. P. H. Rolfe. [b] The ethane/propane ratio found was 1/1. [c] The propane/butane ratio found was 1.08/1.

Unsymmetrical dialkylzincs have been prepared previously[15,16] by the action of ethereal solutions of Grignard reagents on alkylzinc halides. Krause and Fromm, in a careful investigation, showed[16] that the unsymmetrical dialkyls gradually rearranged to the symmetrical compounds on standing at room temperature. They were able to distinguish an unsymmetrical dialkyl from an equimolar mixture of the two corresponding symmetrical compounds only by fractional distillation, but we have checked that this is a valid procedure. We have found that, for example, a 1 : 1 mixture of di-n-propylzinc and di-n-butylzinc did not co-distil, but gave two clean fractions corresponding to Pr_2Zn and Bu_2Zn, whereas PrZnBu gave only one main fraction on distillation, with a boiling point intermediate between those of the symmetrical dialkyls (*cf.* ref. 15). We conclude that PrZnBu and the other unsymmetrical dialkyl that we have prepared, EtZnPr, are, indeed, isolatable chemical compounds. Analyses of these compounds are also given in Table 1; from these analyses we estimate that our sample of PrZnBu was only 96% pure and was contaminated with 4% of Pr_2Zn. We have corrected for this where necessary.

The acidolysis of dialkylzincs

In preliminary experiments we found that the rates of acidolysis of di-n-propylzinc by various weak acids in solvent diisopropyl ether at reflux temperature were in the order: benzoic acid, ethanol, 2-naphthol, all very fast $\gg$ *p*-toluidine > cyclohexylamine $\gg$ 1-hexyne, diphenylamine, acetanilide, all very slow. We hence selected *p*-toluidine and cyclohexylamine and measured the alkane evolved on addition of the amine to di-n-propyl- and to diethyl-zinc in ether or diisopropyl ether at reflux temperature. In all cases one mole of alkane per mole of amine was evolved, *e.g.* the following results for *p*-toluidine in diisopropyl ether:

Moles *p*-toluidine/mole Pr_2Zn:	0.47	0.54	0.57	0.96	1.21	1.61
Moles propane/mole Pr_2Zn:	0.45	0.57	0.56	0.93	1.29	1.55

The amines both behave as monobasic acids, and the stoichiometry of the acidolysis is consistent with eqns. (6) and (7).

$$R_2Zn + H_2NR'' \rightarrow RH + RZnNHR'' \tag{6}$$
$$R_2Zn + 2\ H_2NR'' \rightarrow 2\ RH + Zn(NHR'')_2 \tag{7}$$

Such a stoichiometry can obviously lead to the two consecutive reactions (8) and (9).

$$R_2Zn + H_2NR'' \rightarrow RH + RZnNHR'' \tag{8}$$
$$RZnNHR'' + H_2NR'' \rightarrow RH + Zn(NHR'')_2 \tag{9}$$

The kinetics of acidolysis may thus be expected to be complicated, as indeed we found, and we decided to use competitive experiments to ascertain the relative reactivities of the various dialkylzincs. We have, however, carried out a number of kinetic experiments using a large excess of amine in order to reduce (8) and (9) to two consecutive first-order reactions, rather than two consecutive second-order reactions [assuming that (8) and (9) are first order in R_2Zn, as indeed we found]. In a series of runs, with varying concentrations of the primary amine, the total amine concentration was kept constant by addition of 2,6-lutidine. Only the first 50% or so of reaction (8) could be treated as a first-order reaction, owing to incursion of (9), and in Table 2 are given the first-order rate constants for (8), obtained from the expression, rate of evolution of propane = $k_1[Pr_2Zn]$. It can be seen that whilst k_1 varies with the primary amine concentration, the second-order rate constant, k_2, ($k_2 = k_1/[\text{primary amine}]$) is essentially constant, and hence the kinetic form of (8) is first-order in di-n-propylzinc and first-order in primary amine. No other dialkylzinc has been studied, but in view of the small fluctuations in relative rates of reaction amongst the dialkylzincs, it is most probable that the same kinetic form obtains. We have considered the situation that would arise if the product, PrZnNHR″, rapidly disproportionated to Pr_2Zn

TABLE 2

KINETICS OF ACIDOLYSIS OF DI-n-PROPYLZINC BY CYCLOHEXYLAMINE AND BY *p*-TOLUIDINE IN DIISOPROPYL ETHER AT 76°

Concentration (mole l^{-1})				
Pr_2Zn	*Cyclohexylamine*	*2,6-Lutidine*	*k_1 (sec^{-1})*	*k_2 ($l\cdot mole^{-1}\cdot sec^{-1}$)*
0.060	1.74	0	35×10^{-4}	20×10^{-4}
0.053	0.87	0.87	14×10^{-4}	16×10^{-4}
0.060	0.64	1.10	11×10^{-4}	17×10^{-4}
0.057	0.50	1.24	9×10^{-4}	18×10^{-4}
Pr_2Zn	*p-Toluidine*	*2,6-Lutidine*		
0.060	1.00	0	21×10^{-3}	21×10^{-3}
0.040	0.81	0.19	19×10^{-3}	23×10^{-3}
0.058	0.62	0.38	12×10^{-3}	19×10^{-3}

and $Zn(NHR'')_2$ but the kinetics of propane evolution are more compatible with the set of consecutive reactions (8) and (9) in which the rate constant for the second step is about one sixth that of the first step. The work of Coates and Ridley[14] also suggests that a product PrZnNHR″ would not disproportionate under our conditions.

The competitive experiments consisted in allowing a mixture of two symmetrical dialkylzincs to react with a deficiency of *p*-toluidine. From analyses of the evolved alkanes, the amounts of the two dialkylzincs remaining could be determined. For a pair of homocompetitive reactions (10) and (10′) (where HA = *p*-toluidine):

$$R_2Zn + HA \xrightarrow{k_{10}} RH + RZnA \tag{10}$$

$$R'_2Zn + HA \xrightarrow{k_{10'}} R'H + R'ZnA \tag{10'}$$

it can be shown[17] that

$$r = \frac{k_{10}}{k_{10'}} = \frac{\text{log of fraction of } R_2Zn \text{ remaining}}{\text{log of fraction of } R'_2Zn \text{ remaining}}$$

provided that (10) and (10′) are each first-order in dialkylzinc and that the order in HA is the same in (10) as in (10′). These conditions we have assumed. Furthermore, the most accurate values of r are obtained[17] if $[R_2Zn]_0 = [R'_2Zn]_0$, this being our usual initial state, and if $[HA]_0/([R_2Zn]_0 + [R'_2Zn]_0) = 0.63$ when $r = 1.2$ or 0.83, and $= 0.61$ when $r = 4$ or 0.25. We have generally used amounts of *p*-toluidine less than these figures require, in order to prevent reaction (9) from taking place, but where we have determined the influence of these ratios on r, there has been but little effect:

$[HA]_0/([Me_2Zn]_0+[Et_2Zn]_0)$:	0.49	0.57	0.63	0.65	Ether,	35°
$r = k(Me)/k(Et)$:	0.36	0.46	0.41	0.42		
$[HA]_0/([Et_2Zn]_0+[\text{iso-}Pr_2Zn]_0)$:	0.19	0.24	0.29		Ether,	35°
$r = k(\text{iso-}Pr)/k(Et)$:	0.61	0.60	0.55			
$[HA]_0/([Et_2Zn]_0+[\text{iso-}Pr_2Zn]_0)$:	0.19	0.22	0.51		iso-Pr_2O,	68°
$r = k(\text{iso-}Pr)/k(Et)$:	0.66	0.67	0.69			

Two main series of experiments have been carried out, using refluxing ether and refluxing diisopropyl ether as solvents, as well as a study of the Et_2Zn/iso-Pr_2Zn system in solvents hexane and tetrahydrofuran (THF). Ratios, r, found are:

System	Ether, 35°	iso-Pr_2O, 68°	Hexane, 69°	THF, 66°
Me_2Zn/Et_2Zn	0.41			
Pr_2Zn/Et_2Zn	0.42	0.33		
Bu_2Zn/Pr_2Zn	0.64	1.05		
iso-Pr_2Zn/Et_2Zn	0.61	0.67	0.71	0.82

We can now determine relative second-order rate constants, and we have used Et_2Zn as a standard (244) such that the value for Me_2Zn is 100. Results are in Table 3.

Competitive experiments on the unsymmetrical dialkyls require another

TABLE 3

RELATIVE SECOND-ORDER RATE CONSTANTS FOR THE ACIDOLYSIS OF DIALKYLZINCS BY *p*-TOLUIDINE (REACTION 8).

Me_2Zn	Et_2Zn	Pr_2Zn	Bu_2Zn	iso-Pr_2Zn	*Solvent*
100	244	102	65	149	Ether, 35°
	244	81	85	163	iso-Pr_2O, 68°
	244			173	Hexane, 69°
	244			200	THF, 66°

treatment, and it can be shown[17] that in the set of reactions (11) and (12), $r = k(R)/k(R') = [RH]/[R'H]$ at any time during the reaction provided[17] that the orders of reactions (11) and (12) are the same in [RZnR'] and in [HA]. This we have assumed, and results are given in Table 4 for the two compounds we have studied.

$$RZnR' + HA \begin{cases} \xrightarrow{k_R} RH + R'ZnA & (11) \\ \xrightarrow{k_{R'}} R'H + RZnA & (12) \end{cases}$$

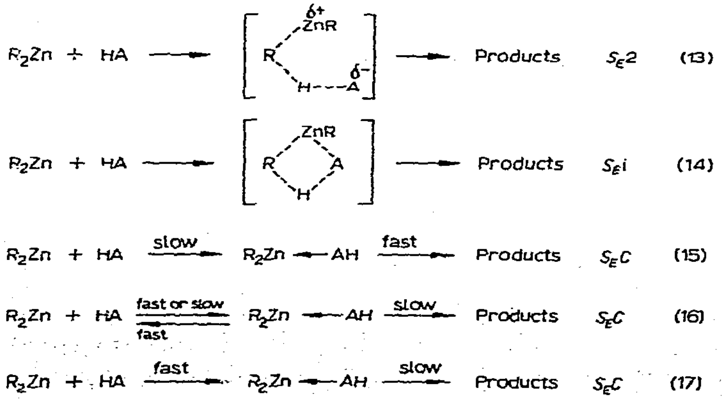
TABLE 4

RELATIVE RATE CONSTANTS FOR THE ACIDOLYSIS OF UNSYMMETRICAL DIALKYLZINCS BY *p*-TOLUIDINE

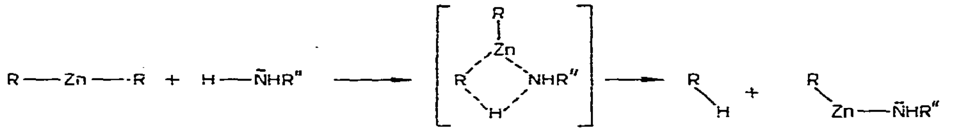
EtZnPr	k(Et) 244	to	k(Pr) 127	in	iso-Pr_2O	at	68°
PrZnBu	k(Pr) 127	to	k(Bu) 100	in	iso-Pr_2O	at	68°

Possible mechanisms of acidolysis of dialkylzincs

The observation of second-order kinetics for the reaction of di-n-propylzinc with either cyclohexylamine or *p*-toluidine in solvent diisopropyl ether excludes an S_E1 mechanism in these two particular cases. The spread of reactivities amongst the dialkyls is quite small, the observed sequences of relative rate-constants are not in accord with those expected[1] for reactions following S_E1 mechanisms, and we will consider this mechanism no further. There remains the S_E2, S_Ei, and a number of variants of the S_EC mechanism (HA = *p*-toluidine):



Reaction (17) can be excluded, as it would lead to overall first-order kinetics of alkane evolution. Although complexes of aliphatic and heterocyclic amines with dialkylzincs are known, analogous complexes of aromatic amines have not hitherto been described, no doubt due to the comparatively weak Lewis base properties of the aromatic amines. Hence, if a complex $R_2Zn \leftarrow :NH_2Ar$ is formed between a dialkylzinc and *p*-toluidine, it is extremely probable that such a complex would be in equilibrium with its components, *i.e.* we regard (16) as a possible mechanism, but tend to exclude (15). The non-polar character of the solvents used, ether and diisopropyl ether, will favour mechanisms proceeding via uncharged transition states (S_Ei) rather than those giving rise to transition states in which separation of charge takes place (S_E2), and so we reduce the probable mechanisms to the S_Ei (14) and the S_EC (16) for acidolysis by *p*-toluidine. Now Dessy and his co-workers[10] have shown that in the acidolysis of triethylboron by carboxylic acids, proceeding by an S_EC mechanism, the stronger is the acid the slower is the acidolysis. Similarly we might expect that *p*-toluidine (stronger acid, weaker base) would lead to a much slower acidolysis than cyclohexylamine (weaker acid, stronger base) if the mechanism of acidolysis involved an S_EC mechanism. The converse, however, is true; *p*-toluidine is about ten times as reactive as cyclohexylamine towards di-n-propylzinc (Table 2). Although the two acids could be reacting by different mechanisms, we feel that these reactivities may be explained more concisely on the basis of an S_Ei mechanism in both cases. Naturally, we would expect the mechanism of acidolysis by *p*-toluidine to be somewhat nearer the S_E2 end of the "spectrum" than that of acidolysis by cyclohexylamine (see ref. 1), but for both of the acids we write:



S_Ei

We have previously[1] argued that in alkyls of type R_nM, the sequences of relative rate constants observed as the group R is varied may be correlated with the mechanism of electrophilic substitution, and that in reactions proceeding by S_E2 mechanism steric effects in R dominate and lead to a sequence of rate constants in the order R = Me > Et > Pr > iso-Pr > tert-Bu. On the other hand, if the mechanism of substitution is S_EC the sequence is the polar one, R = Me < Et ~ Pr < iso-Pr < tert-Bu. Intermediate between the S_E2 and S_EC mechanisms is the S_Ei which can lead to sequences of rate constants which are combinations of the two extreme sequences. In the present work the observed (Table 3) sequences Me < Et > Pr > Bu and Me < Et > Pr < iso-Pr show just this combination of steric and polar effects that we have previously suggested[1] might be observed when both electrophilic attack at saturated carbon, and nucleophilic attack at the metal atom were important features of the transition state, and thus nicely reinforce our above arguments for mechanism S_Ei.

In the unsymmetrical dialkyls the pattern of reactivity is quite close to that of the corresponding symmetrical compounds (Tables 3 and 4). Steric effects are somewhat smaller in the unsymmetrical dialkyls, but this is to be expected as in EtZnPr, for example, we are comparing substitution at Et, which involves the leaving-group ZnPr, with substitution at Pr, which involves the leaving-group ZnEt. If the steric effect of the leaving-group alkyl is less than that of the substituted alkyl (a reasonable assumption) then it follows that cleavage from EtZnPr will be in the same order as from Et_2Zn/Pr_2Zn, as observed, but the ratio of reactivities of the alkyl groups will be closer in the unsymmetrical dialkyl than in the two symmetrical dialkylzincs.

Finally, although limited to very few solvents by our experimental method and by the nature of dialkylzincs, the results on the acidolysis of the Et_2Zn/iso-Pr_2Zn system by *p*-toluidine in hexane, diisopropyl ether and THF (Table 3) show that there is little change in relative reactivity in going from the least solvating solvent, hexane, to the most solvating solvent, THF; it seems quite probable that the mechanism of acidolysis is the same in all three solvents and that an S_Ei mechanism operates.

Our sequences of relative reactivity are quite close to that[4] for the cleavage of Grignard reagents by 1-hexyne; the latter set is rather more polar in character (Me < Et < iso-Pr) than is our comparable sequence (Me < Et > iso-Pr). The sequences found by Ivanoff and his co-workers[2,3] also reflect a combination of steric and polar influences, so that the only four investigations of the acidolysis of the more reactive metal alkyls have all produced comparable sequences of reactivity in the alkyl groups studied.

EXPERIMENTAL

All operations involving dialkylzincs were carried out in an atmosphere of dry, oxygen-free nitrogen or carbon dioxide. Solvents were re-distilled and dried over sodium, except for THF which was distilled from $LiAlH_4$ in a stream of nitrogen immediately before use. Cyclohexylamine and 2,6-lutidine were dried over KOH pellets and distilled just before use; *p*-toluidine was recrystallised twice from A.R. benzene.

Preparation of dialkylzincs

Dimethylzinc was prepared by refluxing methyl iodide with an excess of Zn/Cu couple for 12 h, followed by fractional distillation. After a small fore-run of slightly impure dimethylzinc, b.p. 44.0–44.4°/768 mm, the main fraction was collected at 44.4°/768 mm. The other dialkylzincs were prepared by Noller's method[18] and then fractionally distilled. All of the dialkyls, including the unsymmetrical ones, were stored in sealed ampoules under solid CO_2. Diisopropylzinc was much less stable thermally than the other dialkyls and was always redistilled just before use. Analyses and b.p.'s of the dialkyls are given in Table 1.

Ethylpropylzinc. An equimolar mixture of ethyl iodide and ethyl bromide was added slowly to a Zn/Cu couple. After the vigorous reaction had subsided, the product was left overnight and then pumped down to 2 mm at room temperature to remove traces of unreacted halides. An ethereal solution of n-propylmagnesium chloride was added to the ethylzinc halide at a rate sufficient to maintain a gentle reflux. The ether was then carefully removed at room temperature at the pump, and the residue distilled into a liquid air trap at 0.05 mm and room temperature. Fractional distillation of this material gave the unsymmetrical dialkyl.

Propylbutylzinc. By a similar procedure from n-propylzinc halide and nbutylmagnesium chloride, the hitherto unknown PrZnBu was obtained. Analyses of the unsymmetrical dialkyls are in Table 1.

Methylethylzinc, attempted preparation. An ethereal solution of methylmagnesium iodide was added to ethylzinc halide in the usual manner. The resulting product was then distilled from a bath no higher than 40°, first on the water pump and then at 0.05 mm. The distillate (ether plus dialkylzinc) was fractionated at atmospheric pressure to give a fore-run of ether/Me_2Zn, followed by pure Me_2Zn. No fraction corresponding to MeZnEt was obtained, and after all the dimethylzinc had distilled over, the temperature rose sharply to 117°, when diethylzinc was collected.

Distillation of dipropylzinc and dibutylzinc. A 1:1 mixture of the two dialkyls on distillation gave two distinct fractions, b.p. 30°/4 mm and 60°/3.5 mm, corresponding to Pr_2Zn and Bu_2Zn respectively. The temperature rose sharply between 30° and 60°, indicating that no detectable amount of a 1:1 co-distillate or of PrZnBu (b.p. 38–43°/3 mm) could have been formed.

Handling of the dialkyls. The dialkylzincs, either singly, or as mixtures, were sealed into capsules: (*i*) thin-walled small bulbs holding about 0.1 to 0.2 g, and (*ii*) cylindrical capsules 7 mm o.d. and about 70 mm long, in which up to 1 g of dialkyl could be contained. The small bulbs were crushed, the cylindrical capsules were broken by the device due to Larkworthy[19].

Analyses

Dialkylzincs were analysed for zinc by the method of Abraham[20]. Hydrolysable-alkyl analyses were performed by crushing a bulb containing about 0.1–0.2 g of dialkyl under 100 ml of 0.1 N sulphuric acid in a flask attached to a gas-burette. Alkane evolution was measured by volume, and samples of the gas could be withdrawn via a serum cap for analysis by gas chromatography. Dimethylzinc could not be analysed by this method owing to the violence of the methane evolution.

Gas chromatographic analyses of alkanes, either from hydrolysable alkyl determinations, or from competitive experiments, were performed on a "Shandon" flame thermocouple chromatograph with H_2/N_2 carrier gas and a 120 cm column of 2% squalane on 100–120 mesh alumina. In the analysis of any given gaseous mixture, some 8 to 11 separate gas chromatographic analyses were made. It has been shown[21] that with a flame thermocouple detector, amounts of hydrocarbons are inversely proportional to their heats of combustion:

$$\frac{\text{Mole of component A}}{\text{Mole of component B}} = \frac{\text{Peak area of A} \times \text{heat of combustion of B (per mole)}}{\text{Peak area of B} \times \text{heat of combustion of A (per mole)}}$$

For the particular chromatograph we have used, and for the same hydrocarbons we have analysed, this relationship has been verified[22] by the analysis of a mixture of hydrocarbons of known composition.

Competitive experiments

The solvent to be used (about 25 ml) was refluxed with a known weight of *p*-toluidine in an apparatus contained in a vapour jacket of boiling cyclohexane (with iso-Pr_2O as solvent) or boiling methylene chloride (with ether as solvent). A slow stream of CO_2 was passed through the apparatus until all air or nitrogen had been expelled, as shown by the complete absorption of the exit gases in 50% aq. KOH. A cylindrical capsule of the dialkylzinc mixture was cracked in a side arm of the apparatus, the dialkyls washed into the solvent body by the refluxing solvent, and the evolved alkanes collected over 50% aq. KOH, well shaken, and analysed. Check experiments showed that in the absence of *p*-toluidine no alkane at all was evolved on passing CO_2 through the apparatus containing the dialkylzincs in the refluxing solvents.

Kinetic experiments

A standard solution of amine and 2,6-lutidine in diisopropyl ether was refluxed in an apparatus connected to a gas-burette. A bulb containing a known weight of di-n-propylzinc, immersed in the refluxing amine solution, was crushed when equilibrium had been reached, and the volume of evolved alkane measured at set intervals of time.

Results of a representative run are given below: Run R5; $[Pr_2Zn] = 0.053$ mol·l^{-1}, [cyclohexylamine] = [2,6-lutidine] = 0.87 mol·l^{-1}. As two moles of propane are evolved per mole of dipropylzinc, $[Pr_2Zn]_0 \equiv$ 25.85 ml propane.

Time, t, in min:	Volume evolved, V, in ml:
0	0
1	1.8
2	4.5
3	5.4
4	7.55
5	9.0
6	10.2
7	11.35
8	12.45
9	13.45
10	14.35
11	15.3
12	16.3
13	17.2
14	17.9
15	18.75
16	19.55
17	20.35
18	21.05
19	21.75
20	22.65
22	24.05
24	25.2
26	26.2
28	27.4
30	28.8
34	31.0
36	32.05
38	33.1
40	34.1
42	35.15
44	35.95
46	36.9
48	37.6
50	38.5
58	41.3
60	41.6
65	43.1
75	45.25
80	46.1
85	46.8
90	47.3
95	47.75
100	48.05
105	48.35
110	48.65
115	49.0
120	49.2
125	49.5
130	49.75
135	49.9
140	50.05
∞	51.7

A plot of $\log(25.85 - V)$ *vs.* t gives a straight line, over the interval $t = 0$ to $t = 10$ min, of slope 0.0355 min^{-1}, whence the first-order rate constant for reaction (8) is 0.0014 sec^{-1}. A plot of $\log(51.7 - V)$ *vs.* t converges to a straight line at about $t = 80$ min and from the slope over the interval $t = 80$ to $t = 140$ min, 0.0086 min^{-1}, an approximate value can be obtained for the first-order rate constant for reaction (9) of 0.0003 sec^{-1}. If the product from reactions (8) rapidly disproportioned to Pr_2Zn and $Zn(NHC_6H_{11})_2$ the plot of $\log(51.7 - V)$ *vs.* t should give a straight line from $t = 0$ to $t = 140$ min, but a marked deviation is observed as early as $t = 6$ min.

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SUMMARY

The acidolysis of di-n-propylzinc by both *p*-toluidine and cyclohexylamine,

which function as monobasic acids, in solvent diisopropyl ether is first-order in dialkylzinc and first-order in amine. Competitive experiments have established the following relative rate constants for acidolysis by *p*-toluidine: Me_2Zn(100), Et_2Zn (244), Pr_2Zn(102), Bu_2Zn(65), and iso-Pr_2Zn(149) in solvent ether at 35°, and Et_2Zn(244), Pr_2Zn(81), Bu_2Zn(85), and iso-Pr_2Zn(163) in solvent diisopropyl ether at 68°. For acidolysis by *p*-toluidine, in diisopropyl ether at 68°, of unsymmetrical dialkylzincs, the relative rate constants are Et(244) to Pr(127) from EtZnPr and Pr(127) to Bu(100) from PrZnBu.

These acidolyses are considered to proceed by mechanism S_Ei, with both electrophilic attack at the α-carbon atom, and nucleophilic attack at the zinc atom being important features of the transition state.

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