THE CLEAVAGE OF ALKYL-ZINC BONDS BY METALLIC AND ORGANOMETALLIC HALIDES

by

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ABSTRACT

The possible mechanisms by which an alkyl group may transfer from one metal to another have been reviewed, together with evidence for these mechanisms. The nature and properties of the organic derivatives of the Group II metals have been reviewed, with particular reference to the alkylmetal halides.

In the present work the relative rates of reaction of dimethylzinc, diethylzinc and di-n-propylzinc with phenylmercuric chloride were found to be in the order

$$\begin{array}{ccccc} Me_2Zn & < & Et_2Zn & < & n\text{-}Pr_2Zn \\ (100) & & (450) & & (1660) \end{array}$$

in refluxing diethyl ether, by competition experiments in which mixtures of two dialkylzincs were allowed to react with a deficiency of phenylmercuric chloride. The mechanism of the reaction of a dialkylzinc with phenylmercuric chloride under these conditions is suggested as being an S_Ei one, involving a closed, four-membered, transition state. The same dialkylzincs reacted at the same rate with phenylmercuric chloride in tetrahydrofuran in similar competition experiments.

The reaction of diethylzinc with phenylmercuric chloride was too fast to be followed kinetically, in both solvents. Similarly the reactions of phenylmercuric iodide, ethylmercuric iodide and mercuric iodide with tetrahydrofuran solutions of "ethylzinc iodide" were too fast to follow kinetically.

Investigations into the nature of "ethylzinc iodide" solutions have shown that monomeric EtZnI does exist in both ethereal and tetrahydrofuran solutions. The existence of EtZnBr in tetrahydrofuran is suggested. In these studies use was made of both N.M.R. spectroscopy and the fact that it was found in the present work that N,N,N',N'-tetramethylethylenediamine forms 1 : 1 solid complexes with these ethylzinc halides.

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INTRODUCTION

CHAPTER I

THE MECHANISMS OF METAL TO METAL ALKYL EXCHANGE

The reactivity of organometallic compounds

A large range of properties is exhibited by organometallic compounds. For those in which a carbon atom is joined to a highly electropositive metal such as sodium or potassium a high degree of ionic character is shown. In the compounds of the Group II and III metals the ionic character gives way to a covalent one, and some of these compounds show association. Whilst the compounds of the Group I metals have, in general, high melting points, those of Groups II and III have low melting points. High chemical reactivity is a feature of most of these compounds. Many of them react with oxygen and molecules containing active hydrogen or halogen, with halogens themselves, and carbonyl groups. The exchange of alkyl groups from one alkylmetal to another, or to a metallic halide is also a feature of the chemistry of these compounds.

Scope

In this chapter it is proposed to review the possible mechanisms by which an alkyl group may transfer from one metal to another. The influence of various factors such as inductive and steric effects and solvent effects upon each mechanism will also be discussed. Evidence for each of these mechanisms in alkyl exchange gained from kinetic and stereochemical studies will then be examined in the second part of this chapter.

Part A: Possible mechanisms

The first four mechanisms are examples of electrophilic substitution at a saturated carbon atom, and several reviews have been published on this subject [1,2,3,4].

(i) Unimolecular electrophilic substitution. (S_E1)

The nature of a carbon to metal σ bond is such that to a greater or lesser extent it may be written as $\rangle C^{\delta-} - M^{\delta+}$. The S_E1 mechanism depends on this nature reaching its limit, and is written :

$$\left.\begin{array}{l} R-M_1 \xrightarrow{\text{slow}} R^- + M_1^+ \\ R^- + M_2^+ \xrightarrow{\text{fast}} R - M_2 \end{array}\right\} \text{———} \quad (1)$$

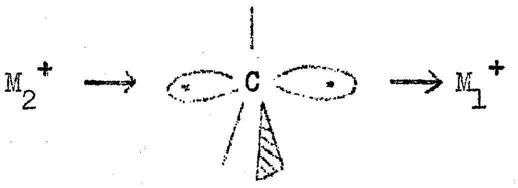
First order kinetics would be expected for a reaction proceeding by this mechanism. If the α-carbon atom of the group R were a centre of asymmetry it would also be expected that this would undergo racemisation in such a mechanism. However, this mechanism would be expected to be promoted by polar solvents, in which optical activity might be unstable anyway: although the carbanion would be stabilised if it contained a group which could accommodate the charge, e.g. by resonance. Added salts would accelerate the reaction by increasing the polarity of the medium. R groups having a +I effect would retard the mechanism and those having a -I effect would assist it. This mechanism is a perfect analogy to the S_N1 mechanism, apart from the last consideration, in which the converse would apply.

(ii) Bimolecular electrophilic substitution (S_E2)

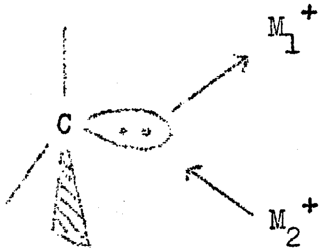
The S_E2 mechanism, written as :

$$M_2^+ + R - M_1 \longrightarrow R - M_2 + M_1^+ \qquad (2)$$

should show second order kinetics in dilute solution with the reactants in approximately equal concentrations. Two transition states are possible for this mechanism :



(I)

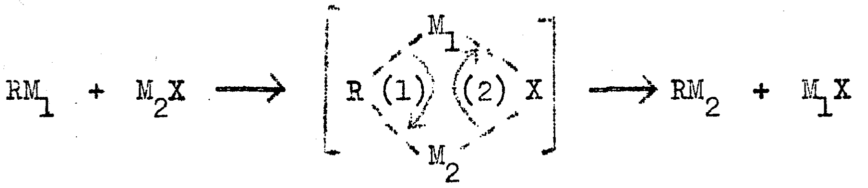


(II)

Unlike the S_N2 mechanism the attacking entity does not bring its bond electrons with it so there is no compulsion for a transition state similar to (I) to occur, leading to inversion of configuration at the α-carbon atom. Thus on theoretical grounds it is not possible to predict whether retention or inversion of configuration should be the rule for S_E2. However, it has been shown by wave mechanics [5] that the optimum angle between the entering and leaving groups is 76° 48', which would indicate that transition state (II) and hence retention of configuration might be favoured. The occurrence of the polar transition state would be enhanced in polar solvents, and added salts would also promote the mechanism. The presence of large groups on the attacked carbon atom might have an adverse effect upon the rate of reaction by this mechanism, particularly if it proceeded with inversion of configuration.

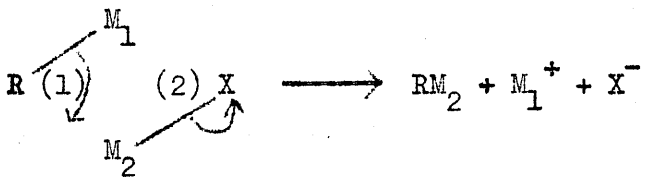
(iii) Internal electrophilic substitution (S_Ei)

The S_Ei mechanism may be written as :



$$RM_1 + M_2X \longrightarrow \left[R\,(1)\,\overset{M_1}{\underset{M_2}{\diamond}}\,(2)\,X \right] \longrightarrow RM_2 + M_1X \quad \text{—— (3)}$$

Second order kinetics would again be expected, but since the transition state is cyclic with at least electrostatic bonding, retention of configuration would be expected. Added salts should have no effect in the normal way since the transition state is not polar, but if the anion of the added salt should complex with the substrate it would assist nucleophilic attack on M_1. If the reaction between RM_1 and M_2X is written as an S_E2 mechanism :

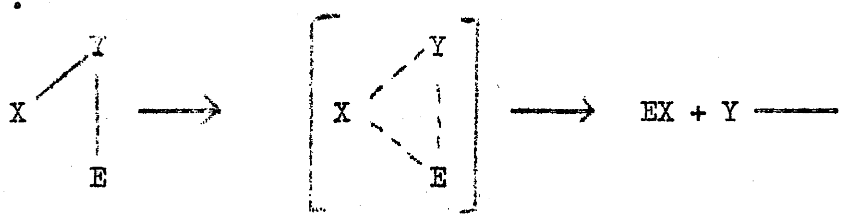


$$R\,(1)\,\overset{M_1}{\underset{M_2}{\ }}\,(2)\,X \longrightarrow RM_2 + M_1^+ + X^- \quad \text{—— (4)}$$

it becomes apparent that there is only a small difference between the S_E2 and the S_Ei mechanisms, and that one may well shade into the other. If an S_Ei mechanism proceeded in a polar solvent the metal salt produced might dissociate anyway.

(iv) Bimolecular four-centred substitution (S_F2)

This mechanism was named by Dessy [4], and as written by him is an alternative name for the S_Ei mechanism. Although it does illustrate the point that nucleophilic attack on M_1 could be the driving force behind reaction as well as, or in place of, electrophilic attack on R. Dessy prefers to reserve the symbol S_Ei for an intramolecular mechanism such as :

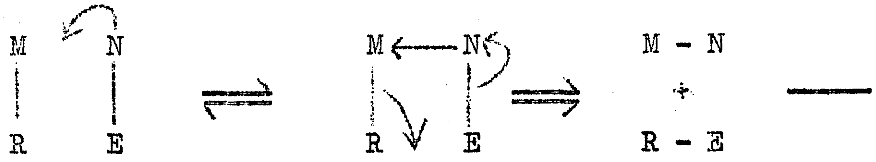


(5)

(E being an electrophilic group).

(v) The S_EC mechanism

The next logical step in progression from the last three mechanisms is one in which the first step is coordination onto the metal atom attached to the group R, followed by a 1,2 (or 1,3 or 1,4) shift of the group R onto an electrophilic centre in the coordinated group. The name S_EC has been suggested [6] for this mechanism, which in its simplest form may be written :

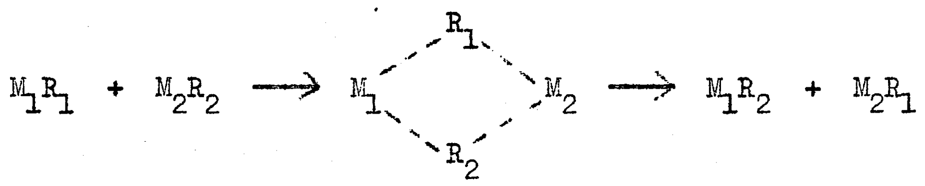


(6)

where N and E are groups with nucleophilic and electrophilic tendencies, respectively. The initial coordination step will be influenced by the tendency of N to coordinate and the electron deficient property of the metal atom, while the second step, the cleavage of R, will be promoted by an R group with a +I effect.

(vi) The alkyl bridge

This mechanism may be written as follows :



$$M_1R_1 + M_2R_2 \longrightarrow M_1 \genfrac{}{}{0pt}{}{R_1}{R_2} M_2 \longrightarrow M_1R_2 + M_2R_1 \quad \text{—— (7)}$$

where both steps may be reversible. At first sight this may appear to be similar to the S_Ei mechanism but the need for considering this as a separate mechanism arises from the fact that certain alkyl exchange reactions have been observed to proceed much faster than electrophilic exchanges with mercury compounds and alkyl exchanges are not considered to occur in the mercury systems other than through mechanisms involving mercury attached to an anion [7]. In other words in the alkyl bridge mechanism both bridging groups may be alkyl groups (although one may be a halide). The alkyl bridge mechanism would be assisted by hyperconjugative effects and retarded by steric effects, so an order of reactivity :

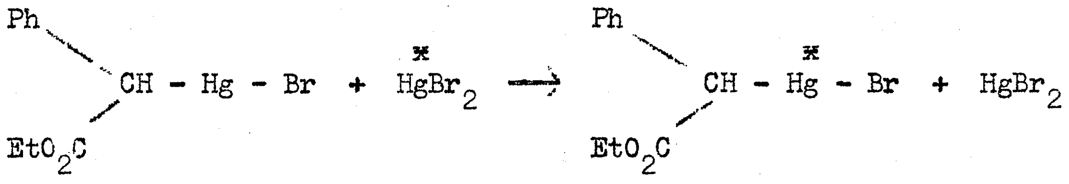
Me ≫ n-alkyl > 2ry alkyl > 3ry alkyl, might be expected.

Part B: Evidence for the possible mechanisms in alkyl exchange

(i) Unimolecular electrophilic substitution (S_E1)

A full study of the kinetic and stereochemical course of a reaction requires that one of the reactants be available in a stable, optically active form, with the optical activity associated with the carbon atom undergoing attack. The very reactive nature of most alkylmetal compounds presents difficulties in this respect. Using mercury compounds which are among the least reactive of the alkylmetal compounds, optically active organometallic compounds, with the asymmetric carbon atom next to the metal, have been resolved. It is for this reason, and the comparative ease with which organomercury compounds may be handled, that they feature so prominently in the following mechanistic work.

As already mentioned it would be expected that organic groups which aid the stability of a carbanion intermediate would promote the S_E1 mechanism. For this reason the one-alkyl exchange between α-carbethoxybenzylmercuric bromide and mercuric bromide was studied.



$$\mathrm{Ph(EtO_2C)CH-Hg-Br} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \longrightarrow \mathrm{Ph(EtO_2C)CH}-\overset{*}{\mathrm{Hg}}-\mathrm{Br} + \mathrm{HgBr_2}$$

Since the reactants and products are chemically the same it is necessary that one of the mercury atoms be radioactively labelled $(\overset{*}{\mathrm{Hg}})$. Optically active α-carbethoxybenzylmercuric bromide was used, but the fact that the reactants and the products are the same removes the problem of relating the sign of rotation to the configuration. In the first instance Reutov reported [8] that this reaction was first order in each reactant in 70% aqueous dioxan at 50°-70°. He later retracted this [9] and claimed the reaction was only first order in organomercuric halide. Ingold repeated this work [10] and found that the reaction was first order in each reactant. However, both Ingold [10] and Reutov [11] now agree that the reaction between α-carbethoxybenzylmercuric bromide and mercuric bromide in dimethyl sulphoxide at temperatures between 25°C and 60°C is first order in organomercuric halide and zeroth order in mercuric salt; thus identifying it as following an S_E1 mechanism, which can be written as :

$$\mathrm{EtO_2C.CHPh.HgBr} \xrightarrow{\text{slow}} \mathrm{EtO_2C.CHPh^-} + \mathrm{HgBr^+}$$

$$\mathrm{EtO_2C.CHPh^-} + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \xrightarrow{\text{fast}} \mathrm{EtO_2C.CHPh.}\overset{*}{\mathrm{Hg}}\mathrm{Br} + \mathrm{Br^-}$$

$$\mathrm{HgBr^+} + \mathrm{Br^-} \xrightarrow{\text{fast}} \mathrm{HgBr_2}.$$

In accord with the predicted inductive effects for this mechanism Reutov also found [11] that a p-nitro group substituent in the organommercuric halide increased the rate, and that a p-t-butyl substituent retarded the rate; whilst Ingold found [10] that substituting chloride for bromide in each reactant approximately halved the rate of reaction as might be expected from putting a more electronegative halide in the organomercuric halide whose ionisation is the rate controlling step. Studying the rates of racemisation of (−)-α-carbethoxybenzylmercuric bromide in dimethyl sulphoxide alone and in the presence of $^{203}\mathrm{HgBr_2}$, Ingold found that the two rates were almost identical, showing that the rate controlling step was the ionisation of the organomercuric salt, each carbanion produced having an equal probability of yielding either enantiomeric product. In addition Ingold found [10] that the addition of tetraethylammonium bromide had a catalytic effect dependent upon the square of the concentration of the added salt, showing that two bromide ions had been added to the organomercuric bromide before it ionised. This effect he termed two-anion catalysis and the mechanism $S_E1\text{-}2Br^-$. The bromide ions are added successively in a pre-equilibrium to yield a doubly-charged anion which is more ready to ionise than the normal organomercuric bromide. This process may be represented as :

$$\mathrm{RHgBr} \xrightleftharpoons[\text{fast}]{\mathrm{Br}^-} \mathrm{RHgBr_2}^- \xrightleftharpoons[\text{fast}]{\mathrm{Br}^-} \mathrm{RHgBr_3}^{2-}$$

$$\mathrm{RHgBr_3}^{2-} \xrightarrow{\text{slow}} \mathrm{R}^- + \mathrm{HgBr_3}^-$$

$$\mathrm{R}^- + \overset{*}{\mathrm{Hg}}\mathrm{Br_2} \xrightarrow{\text{fast}} \mathrm{R}\overset{*}{\mathrm{Hg}}\mathrm{Br} + \mathrm{Br}^-$$

The first order rate constants obtained by Ingold and Reutov for the reaction of α-carbethoxybenzylmercuric bromide with radiomercuric bromide in dimethyl sulphoxide are shown in Table 1.

TABLE 1

Reference	Temperature	$k_1 \times 10^3$ min.$^{-1}$
[11]	25°C	2.42
[10]	29.5°C	3.12
[11]	30°C	3.31
[11]	35°C	5.88
[11]	40°C	8.67
[10]	44.4°C	8.58
[10]	58.9°C	22.5

Reutov has also studied the reaction of p-substituted benzylmercuric bromides with radiomercuric bromide in dimethyl sulphoxide where the p-substituents were Cl, F, Me and i-Pr, and found these reactions to follow second order kinetics [12]. However, with a p-nitro substituent the reaction became first order in organomercuric bromide and zeroth order in radiomercuric bromide [13]. Obviously the introduction of the nitro group had caused sufficient delocalisation of charge to stabilise the carbanion. Reutov further found [14] that the addition of potassium bromide affected the rate. On adding increasing amounts of this salt he found that it had no effect until its concentration was nearly equal to that of the $^{203}HgBr_2$, when it accelerated the reaction. When the concentration of the added salt was greater than that of the mercuric bromide the rate of the reaction increased at a rate faster than before. This implies that the additional bromide ions add on to the mercuric bromide first of all, but that this addition is not quite quantitative for bromide ions add on to the organomercuric bromide just before the concentration of potassium bromide equals that of the mercuric bromide. After this point is reached the addition of further bromide ions has a catalytic effect similar to that observed by Ingold [10], except that only one extra anion is involved in the rate determining step.

The stabilisation of the α-carbethoxybenzyl carbanion due to its mesomeric nature could give it a longer life than an alkyl carbanion and thus make it more likely to racemise than an alkyl carbanion. Thus the S_E1 case studied stereochemically may not be a true guide to whether racemisation is the general rule for aliphatic electrophilic substitution. Accordingly Ingold looked for a reaction which proceeded by an S_E1 mechanism and which involved purely alkyl and not aryl groups [15]. He intended to study directly the reaction between diethylthallic bromide and triethylthallium but found it was too fast to follow kinetically. He was able to establish, however, that the reaction of di-s-butylmercury with diethylthallic bromide was first order in the organomercury compound and zeroth order in the organothallic halide, in dimethylformamide ($k_1 = 3.0 \pm 0.2 \times 10^{-5}$ sec.$^{-1}$, in DMF at 69.7°C, determined chemically). When the same reaction was done using optically active di-s-butylmercury it was found that the first order rate of racemisation was the same as the chemically determined first order rate constant for the thallium for mercury exchange ($k_1 = 3.1 \pm 0.3$ sec.$^{-1}$ at 69.7°C in DMF, determined polarimetrically); hence the reaction proceeds with total racemisation. It is written as :

$$\text{s-BuHgBu-s} \xrightarrow{\text{slow}} \text{s-Bu}^- + \text{s-BuHg}^+$$
$$\text{s-BuHg}^+ + \text{Br}^- \xrightarrow{\text{fast}} \text{s-BuHgBr}$$
$$\text{s-Bu}^- + \text{Et}_2\text{Tl}^+ \xrightarrow{\text{fast}} \text{s-BuTlEt}_2.$$

From these observations Ingold was able to deduce that the reverse reaction, that of s-butylmercuric bromide with diethyl-s-butylthallium to yield di-s-butylmercury and diethylthallium bromide, went also by an S_E1 mechanism :

$$\text{s-BuTlEt}_2 \xrightarrow{\text{fast}} \text{s-Bu}^- + \text{TlEt}_2^+$$
$$\text{s-BuHgBr} \xrightarrow{\text{slow}} \text{s-BuHg}^+ + \text{Br}^-$$
$$\text{s-BuHg}^+ + \text{s-Bu}^- \xrightarrow{\text{fast}} \text{s-BuHgBu-s}$$

with the slow stage as indicated. He then proceeded to deduce that the reaction between diethylthallic bromide and triethylthallium, the reaction he set out to study, is also an S_E1 process:

$$\mathrm{E\overset{\ddagger}{t}EtTlBr} + \mathrm{Et_3Tl} \rightleftharpoons \mathrm{E\overset{\ddagger}{t}Et_2T;} + \mathrm{Et_2TlBr}$$

and may be written in full as :

$$\mathrm{Et_3Tl} \xrightleftharpoons[\text{v.fast}]{\text{fast, rate-controlling}} \mathrm{Et^-} + \mathrm{Et_2Tl^+}$$

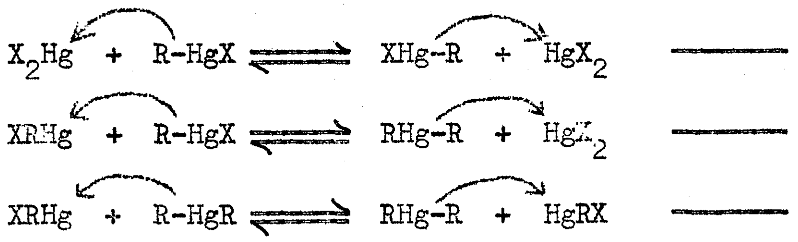
$$\overset{*}{\mathrm{E}}\mathrm{tEtTlBr} \xrightleftharpoons{\text{v. fast}} \overset{*}{\mathrm{E}}\mathrm{tEtTl^+} + \mathrm{Br^-}$$

$$\overset{*}{\mathrm{E}}\mathrm{tEtTl^+} + \mathrm{Et^-} \xrightleftharpoons[\text{fast, rate-controlling}]{\text{v. fast}} \overset{*}{\mathrm{E}}\mathrm{tEt_2Tl}$$

where $\overset{*}{\mathrm{E}}\mathrm{t}$ represents an ethyl group containing a ^{14}C label necessary to identify the products which are chemically the same as the reactants.

(ii) Bimolecular electrophilic substitution (S_E2)

Once again by far the greatest number of examples come from mercury chemistry. Alkyl exchange reactions between mercury compounds have been classified [1] and of the six possible reactions only three are considered to be independent :



$$\mathrm{X_2Hg} + \mathrm{R{-}HgX} \rightleftharpoons \mathrm{XHg{-}R} + \mathrm{HgX_2} \quad \text{———} \quad (1)$$

$$\mathrm{XRHg} + \mathrm{R{-}HgX} \rightleftharpoons \mathrm{RHg{-}R} + \mathrm{HgX_2} \quad \text{———} \quad (2)$$

$$\mathrm{XRHg} + \mathrm{R{-}HgR} \rightleftharpoons \mathrm{RHg{-}R} + \mathrm{HgRX} \quad \text{———} \quad (3)$$

These have been termed the one-alkyl, the two-alkyl and the three-alkyl exchanges respectively.

(a) The one-alkyl exchange for mercury

Ingold studied the reaction $\mathrm{RHgX} + \overset{**}{\mathrm{Hg}}\mathrm{X_2} \rightleftharpoons \mathrm{R}\overset{**}{\mathrm{Hg}}\,\mathrm{X} + \mathrm{HgX_2}$ where R = Me, X = Br, I, OAc, NO_3 and also R = s-butyl, X = OAc [16]. Since the reactants are chemically the same as the products a radioactive label is necessary, and $\overset{*}{Hg}$ refers to ^{203}Hg. This reaction had previously been assigned a two-stage mechanism for the case R = Me, X = Br [17] :

$$2\,MeHgBr \rightleftharpoons Me_2Hg + HgBr_2$$

$$Me_2Hg + \overset{*}{Hg}Br_2 \rightleftharpoons Me\overset{*}{Hg}Br + MeHgBr.$$

Ingold showed that in ethanol the reaction was first order with respect to each reactant, and in the case of R = (-)-s-butyl, that the reaction proceeded with retention of configuration. The rate of reaction increased along the series of the various mercury compounds in accord with the increasing ionicity of X :

$MeHgBr < MeHgI \ll MeHgOAc \ll MeHgNO_3$, showing that apart from solvation the transition state was of the open, polar, type. Therefore, the reaction proceeded by an S_E2 mechanism with retention of configuration. This work was extended to cover the cases R = Me, Et, neopentyl with X = Br and R = Me, s-Bu with X = OAc, in ethanol [18]. The relative rates showed that the steric retardations were in the order :

$$Me < 1\text{ ry alkyl} < 2\text{ ry alkyl}$$

[Me(100), Et(42), neopentyl(38), s-butyl(6)].

Reutov found that the one-alkyl exchanges of $R_1R_2R_3CHgBr$ with $\overset{*}{Hg}Br_2$, where R_1 = H, R_2 = CO_2Et, R_3 = Ph in pyridine [19] and dimethylformamide [20] and that of $Ph.CH_2HgBr$ in quinoline [21], were all catalysed by the basic solvents. This was explained by saying that the base complexed with the mercuric bromide before reaction; which agrees with other catalytic effects which will be discussed under the section on the S_Ei mechanism. In addition Reutov found [21] that the reaction between para substituted benzylmercuric chloride and mercuric chloride in quinoline was retarded by -I groups in the para position, and accelerated by +I groups. The rates of reaction for the following para substituents were in the order

$$F < Cl < H < Me < Me_2CH.$$

This again is additional evidence for either an S_E2 or an S_Ei mechanism. The anion-catalysed one-alkyl exchange studied by Ingold will be considered in the section on the S_Ei mechanism.

(b) The two-alkyl exchange for mercury

The two-alkyl exchange for mercury is written

$$RHgX + RHgX \rightleftharpoons R_2Hg + HgX_2.$$

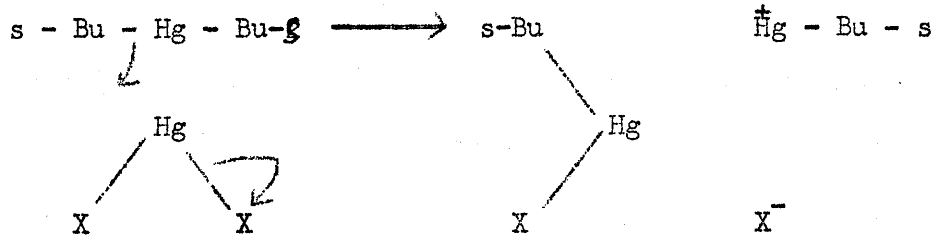
The reaction usually proceeds from the right to the left and is termed synproportionation. The reverse reaction is known as symmetrisation and may be induced by adding reagents which will complex with the mercuric halide. Ingold prepared di-s-butylmercury with one of the alkyl groups optically active, by reacting optically active s-butylmercuric bromide with a s-butyl Grignard reagent, and reacted it with mercuric bromide [7]. The optical activity of the s-butylmercuric bromide produced was compared with the activity of the s-butylmercuric bromide from which the dialkylmercury was prepared. The activity was half that of the standard, indicating that the reaction had proceeded with retention of configuration. This is obvious from the overall equation for the reaction :

$$\text{s-Bu}^{\circ}\text{HgBu-s} + \text{HgBr}_2 \longrightarrow \text{s-Bu}^{\circ}\text{HgBr} + \text{s-BuHgBr},$$

where the degree sign is used to indicate optical activity. This reaction was extended using a series of mercuric salts and the order of reactivity was :

$$\text{HgBr}_2 < \text{Hg(OAc)}_2 < \text{Hg(NO}_3)_2 < \text{Hg(ClO}_4)_2$$

in both ethanol and acetone. The reaction with mercuric nitrate was so fast that it had to be studied at -50°C and even at that low temperature the reaction with mercuric perchlorate was instantaneous. Those reactions whose kinetics could be studied were found to be first order in each reactant. That, and the fact that the reaction rate increased with the increasing ionicity of the mercuric salt used, indicated that the reaction was following an S_E2 mechanism :



The reaction between optically active di-s-butylmercury and mercuric bromide in ethanol :

$$(-)\text{-s-BuHgBu}(\pm)\text{-s} + \text{HgBr}_2 \longrightarrow (-)\text{-s-BuHgBr} + (\pm)\text{-s-BuHgBr}$$

has also been studied by Jensen [22]; who found also that the reaction proceeded with retention of configuration, although he undertook no kinetic studies of the reaction.

(c) The three-alkyl exchange for mercury

The three-alkyl exchange :

$$RHgX + R_2Hg \rightleftharpoons RHgX + R_2Hg$$

may proceed in three possible ways

(i) $R^\circ \overset{*}{Hg}X + R_2Hg \longrightarrow R^\circ \overset{*}{Hg}R + RHgX.$

(ii) $R^\circ \overset{*}{Hg}X + R_2Hg \longrightarrow R^\circ HgR + R\overset{*}{Hg}X.$

(iii) $2R^\circ \overset{*}{Hg}X \longrightarrow R^\circ{}_2Hg + \overset{*}{Hg}X_2$

$\overset{*}{Hg}X_2 + R_2Hg \longrightarrow R\overset{*}{Hg}X + RHgX.$

[the latter way being a two-alkyl exchange].

Double labelling, with a kinetic study of the exchange of both labels is necessary to distinguish these three possibilities. The three paths would give three different ratios for the rates of exchange of the optically active label (R°) and the radioactive label ($\overset{*}{Hg}$). (i) would give $\frac{R^\circ}{\overset{*}{Hg}} = 1:1$, (ii) would give $\frac{R^\circ}{\overset{*}{Hg}} = 1:0$, whilst (iii) would give $\frac{R^\circ}{\overset{*}{Hg}} = 2:1$. Using doubly labelled s-butylmercuric bromide and reacting it with di-s-butylmercury in ethanol at 35°C, Ingold [23] found that the ratio $\frac{R^\circ}{\overset{*}{Hg}} = 1:0.96$. He also found that the reaction was first order with respect to each reactant. Thus the reaction was a bimolecular electrophilic substitution. The rate of reaction increased with increasing ionicity of the alkylmercuric salt thus :

$$\text{s-BuHgBr} < \text{s-BuHgOAc} \ll \text{s-BuHgNO}_3,$$

and the addition of lithium salts caused an acceleration in the rate in the same order as the increasing ionicity of the salts :

$$LiOAc < LiNO_3 < LiBr < LiClO_4.$$

Thus an open, polar transition state is indicated, showing that the mechanism is S_E2 as opposed to S_Ei.

(iii) Internal electrophilic substitution (S_Ei)

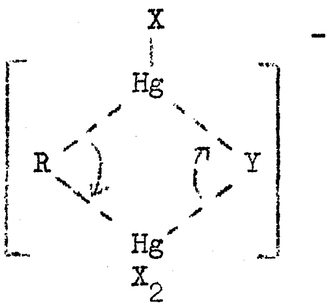
The one-alkyl mercury exchange studied by Ingold [16] was found to be catalysed by the addition of salts in a manner different from normal salt effects. The catalysed reaction :

$$RHgX + \overset{*}{Hg}X_2 \xrightleftharpoons{LiX} RH\overset{*}{g}X + HgX_2$$

had second order kinetics for R = Me, X = Br [24], and for R = neopentyl, X = Br [18], and to proceed with retention of configuration for R = s-butyl, X = I, Cl, Br, OAc [24], in acetone and ethanol. It was found [24] that the reaction was catalysed by the addition of anions such as I^-, Br^-, Cl^- or acetate which coordinate strongly with mercury. For example, in the reaction of methylmercuric bromide with radiomercuric bromide in ethanol at 60°C a plot of reaction rate against the concentration of added lithium bromide showed a straight line plot with a break at the point where the lithium bromide concentration and the mercuric bromide concentration were equal. Up to this point one-anion catalysis is considered to occur. One bromide anion is added to the mercuric bromide in a pre-equilibrium :

$$HgBr_2 + Br^- \rightleftharpoons HgBr_3^-$$

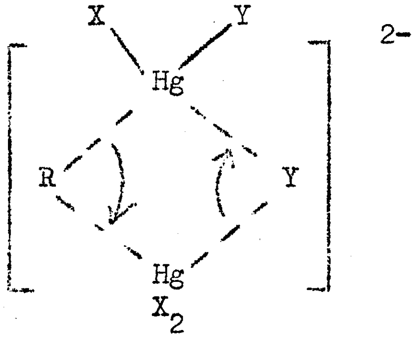
and is carried into the transition state where it bridges :



where the added anion is written as Y. This seems quite likely since Y must be carried out of the transition state by the upper of the two mercury atoms. When the concentration of the added anion is greater than that of the mercuric bromide the plot of rate against concentration of added salt changes its slope and two-anion catalysis is considered to occur. The break at the 1:1 equivalence point shows that up till then the addition of the added anion to the mercuric bromide had been stoichiometric. The two anion catalysis occurs by a further pre-equilibrium :

$$RHgBr + Br^- \rightleftharpoons RHgBr_2^-$$

The equilibrium is shown favouring the left hand side since the extent of addition can only be slight since plot continues in a straight line past the 2:1 equivalence point, i.e. no break in the plot is observed at this point. The further added anion is considered to be carried into the transition state on the mercury atom having the lowest co-ordination number.

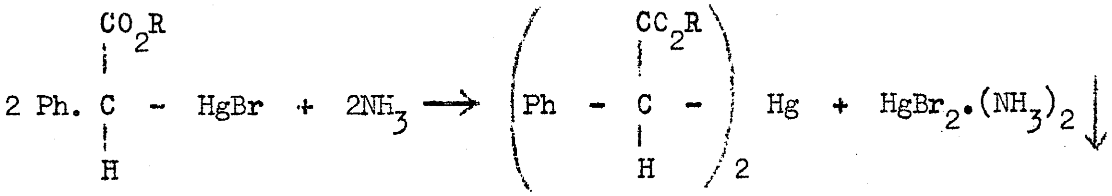


2-anion transition state.

Both of the transition states for the anion catalysed one-alkyl exchange are thus cyclic and considered to be examples of the S_Ei mechanism. As already mentioned in this section the catalysed reactions were studied using various R groups and when these results were compared with those found for the uncatalysed exchange it was found [18] that steric effects affected these mechanisms in the order :

$$S_E2 < S_Ei \text{ one-anion} < S_Ei \text{ two-anion.}$$

The symmetrisation reaction has been studied using ammonia to complex with the mercuric halide produced and so induce the reaction to proceed. Reutov has shown [25] that the esters of α-bromophenylmercury-acetic acid symmetrise in chloroform so :



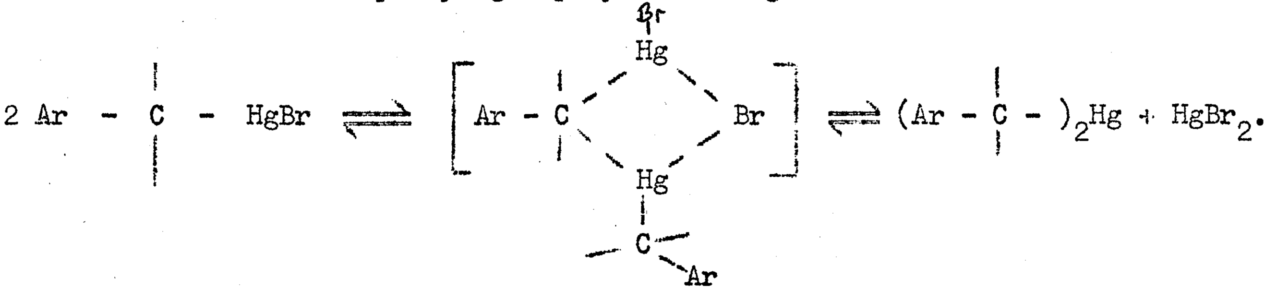
$$2\ Ph.\overset{CO_2R}{\underset{H}{C}} - HgBr + 2NH_3 \longrightarrow \left(Ph - \overset{CC_2R}{\underset{H}{C}} -\right)_2 Hg + HgBr_2\cdot(NH_3)_2\downarrow$$

and retention of configuration was observed [26]. The reaction was found to be second order in organomercury halide [25] and also second order in ammonia [27]; thus rate = $k[RHgBr]^2[NH_3]^2$. Reutov suggests the reaction may be written :

$$2RHgBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2Hg + HgBr_2$$

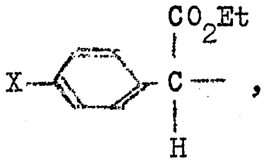
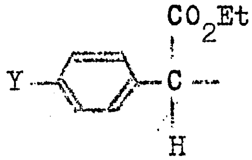
$$HgBr_2 + 2NH_3 \overset{k_2}{\rightleftharpoons} HgBr_2.(NH_3)_2\downarrow$$

but without saying which step is rate controlling. Doubt has been cast on this work by Jensen [28] who observes that Reutov explains rate effects of substituents in the phenyl group by referring to a transition state :

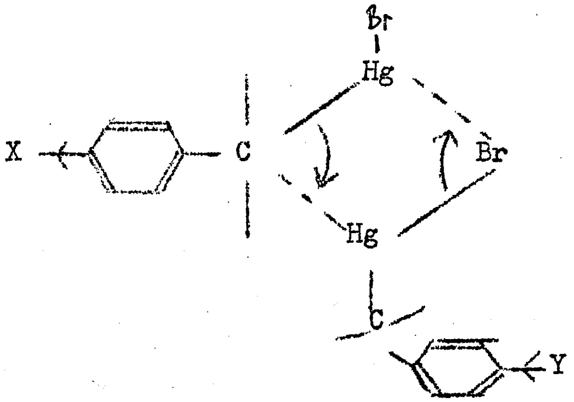


which blatantly ignores any dependence on ammonia. Jensen suggests that a more reasonable mechanism would involve the reaction of a complexed organomercuric halide. Reutov then studied the reaction [29] :

$$RHgBr + R'HgBr \xrightarrow{NH_3} RHgR' + HgBr_2$$

where R =  , and R' =  , in chloroform,

pointing out that if X were an electron withdrawing group and Y were an electron repelling group the first would assist the rupture of the old C – Hg bond and the second would assist the rupture of the old Hg – Br bond in the following transition state :



which he envisaged. He called this a co-symmetrisation reaction; and using X = Br, Y = H and X = H, Y = CH_3 and X = Br, Y = CH_3, found that the rates for these reactions were faster than the corresponding symmetrisation reactions. This effect was greatest when X and Y had the greatest difference in polarity (X = Br, Y = CH_3). Reutov then predicted that the mercury atom in the mercuric bromide formed should come from the organomercuric halide having the more electronegative substituent in the phenyl group. Using p-Br.Ph.CH($\overset{*}{\mathrm{Hg}}$Br)CO_2Et and p-Me.Ph.CH(HgBr)CO_2Et he was able to confirm this. Thus Reutov was able to deduce that the transition state he envisaged was correct and the reaction followed an S_Ei mechanism. However, he acknowledges that there is a possibility of the reactants symmetrising as well as co-symmetrising.

Reutov considers that the mercury to mercury alkyl exchanges he has studied proceed via a closed transition state; an S_Ei mechanism. He suggests [3] that the difference between the S_Ei mechanism and the S_E2 mechanism is very small and implies that it is not worth bothering about. He suggests that all bimolecular electrophilic substitutions proceed with retention of configuration and that they proceed even in only slightly polar solvents, where the existence of ions is unlikely, whereas Ingold's studies have been done in polar solvents where an open transition state would be favoured anyway.

It seems profitable at this stage to consider some of the work of Gielen and Nasielski who have studied bimolecular aliphatic electrophilic substitution reactions, although not metal to metal alkyl exchanges. By considering their work [30,31,32] on the halogenation of tetraalkyl tin compounds (which they showed to be bimolecular electrophilic substitutions) with the work of other authors they have tried to correlate the results to form an overall picture. The table of results they used [36] is shown in Table 2.

TABLE 2

Relative rates of reaction

Reaction	R_2Hg + HCl in DMSO/ Dioxan	RHgI + $HClO_4$ in H_2O	RHgBr + $HgBr_2$ in EtOH	R_4Sn + HCl in PhH	R_4Sn + HCl in Dioxan	R_4Sn + Br_2 in C_6H_5Cl	R_4Sn + I_2 in MeOH	R_4Sn + I_2 in AcOH	R_4Sn + Br_2 in DMF	R_4Sn + Br_2 in AcOH
ref. / R	33	34	18	35	35	36	30	31	31	31
Me	100	100	100	100	100	100	100	100	100	100
Et	770	44	42	750	300	~~300~~ 1200	~~1200~~ 11·8	~~11.8~~ 37	~~37~~ 46	84
n-Pr	460	22	-	300	-	450	~~450~~ 1·5	~~1.5~~ 4·3	~~4.3~~ 6·1	12
i-Pr	510	13	-	300	-	1300	~~1300~~	- 0·04	~~0.04~~	2.5

They observe two overall effects :

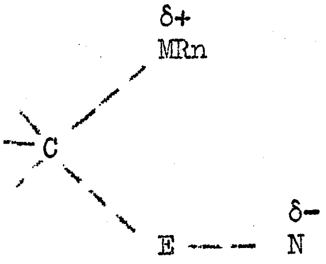
(i) A steric sequence is observed in polar solvents :-

$\mathrm{Me} > \mathrm{Et} > \mathrm{n\text{-}Pr} > \mathrm{i\text{-}Pr}$,

(ii) An inductive sequence is observed in non-polar solvents :-

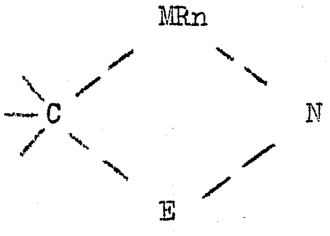
$\mathrm{Me} < \mathrm{Et} > \mathrm{nPr} \leqslant \mathrm{i\text{-}Pr}$.

They argue that in a polar solvent a transition complex of the type S_E2 is energetically more favoured than one of the type S_F2 (which is the name by which they refer to S_Ei), and thus steric effects will preponderate and lead to the sequence of reactivity as in (i). In a less polar medium the partial charges of the open S_E2 transition state are not so stable and an S_F2 mechanism becomes more favourable. Attack by the nucleophilic part of the reagent on the metal of the substrate makes the transition complex less sensitive to variations in the steric effect due to altering R, and the repulsion between the entering and leaving groups becomes the same order of magnitude as the inductive effects; leading to sequence (ii). Thus the two possible transition states are :



S_E2

(polar solvents)



S_F2

(non-polar solvents)

However, if an even large range of results is considered [6] the "solvent rule" of Gielen and Nasielski appears to have less general applicability. The range considered is shown in Table 3. In the first six cases considered a strict order of steric effects is observed; conforming to the views of Gielen and Nasielski that an S_E2 mechanism is operative. Cases seven to seventeen show an interplay of steric and inductive effects indicative of an S_Ei mechanism. In the last four cases in this table an inductive order is observed in polar solvents, and it is difficult to account for this by either an S_E2 or S_Ei mechanism. In the case of reaction 20 it has been shown [42] that coordination of a nucleophile onto the metal is the initial stage of the mechanism, and it seems probable that the other three cases (18, 19, 21) follow a similar course. As already explained, this mechanism in which the motivating force is a coordination step has been named the S_EC mechanism, although the mechanism itself was proposed [43] a few years before. Thus in reading down Table 3 there is a natural progression from the S_E2 mechanism in which the motivating force is an electrophilic attack on an alkyl group, to the S_Ei mechanism with its cyclic transition state in which nucleophilic attack on the metal assumes equal (or nearly equal) importance with the electrophilic attack, finally to the S_EC mechanism (which may or may not have an open transition state) in which the motivating force is coordination onto the metal.

TABLE 3

Relative rates of electrophilic substitutions

No.	R=Me	Et	n-Pr	i-Pr	t-Bu	Reactants	Solvent	Ref.
1	100	11	4	-	-	$R_4Pb + HClO_4$	AcOH	37
2	100	12	1.5	-	-	$R_4Sn + I_2$	MeOH	30
3	100	41	44	0.04	-	$R_4Sn + I_2$	AcOH	31
4	100	40	22	13	0.81	$RHgI + HClO_4$	H_2O	34
5	100	42	-	6a	-	$RHgX + HgX_2$	EtOH	18
6	100	46	6.1	-	-	$R_4Sn + Br_2$	DMF	31
7	100	79	19	-	-	R_4Pb + AcOH	AcOH	37
8	100	83	12	2.6	-	$R_4Sn + Br_2$	AcOH	31
9	100	146	18	-	-	$R_3SnBr + Br_2$	AcOH	31
10	100	244	102	149	-	R_2Zn + p-toluidine	Et_2O	38
11	100	630	390	430	-	R_2Hg + HCl	DMSO/Diox	33a
12	100	600	78	560	-	$R_4Sn + I_2$	PhCl	32
13	100	750	300	300	-	R_4Sn + HCl	Benzene	35
14	100	1200	450	1300	-	$R_4Sn + Br_2$	PhCl	36
15	100	1670	980	3500	-	RMgBr + hex-1-yne	Et_2O	39
16	100	2080	2260	1920	-	$R_2Hg + HgI_2$	Dioxan	40
17	100	9300	4500	80000	-	$R_4Sn + Br_2$	CCl_4	32
18	100	13500	9000	20200	-	$R_4Sn + CrO_3$	AcOH	41
19c	100	-	3020 b	-	39200	$RB(OH)_2 + H_2O_2$	H_2O	42
20c	100	-	3900 b	18400 a	56500	$RB(OH)_2 + HOO^-$	H_2O	42
21c	100	3×10^5	-	-	3×10^7	$RB(OH)_2 + HCrO_4^-$	H_2O	42

a Bu^s , b Bu^n ,c Overall relative rates .

The conclusion that one may draw from these attempts at correlation by the several workers mentioned, is that they are all correct as far as they go; since no two workers have studied the same reaction in the same solvent and arrived at greatly differing results. Reutov's observations that all the bimolecular electrophilic substitutions he has studied proceed by an S_Ei mechanism cannot be challenged on the evidence he has presented, although his observations that these reactions proceed in non-polar solvents are derived in the main from his studies of halogenation of organomercuric halides; reactions which are not metal to metal alkyl exchanges. Ingold's differentiations between the S_E2 and the S_Ei mechanism are most explicit but to test them further it would be necessary to perform the reactions in non-polar solvents. In such solvents, however, it is doubtful whether the reactants would be sufficiently soluble. Thus one is left with the individual results which have been presented, and each one must be argued on its merits. To attempt to draw them into an overall picture larger than those that have already been drawn might be unwise.

(iv) The bimolecular four-centred mechanism (S_F2)

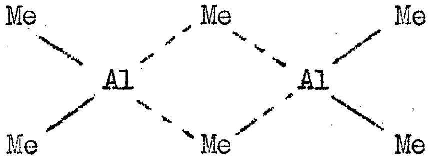
This appears merely to be an alternative name for the S_Ei mechanism. As defined by Dessy [4] it appears similar to the S_Ei mechanism, and the term as used by Gielen and Nasielski [36] is applied to a reaction scheme that could equally well be called an S_Ei mechanism.

(v) The S_EC mechanism

This name has only recently been suggested and there are no metal to metal alkyl exchanges to which it may be applied.

(vi) The alkyl bridge mechanism

An alkyl bridge has been shown to be present in the dimer Me_6Al_2 in the solid state, by x-ray crystallography [44].

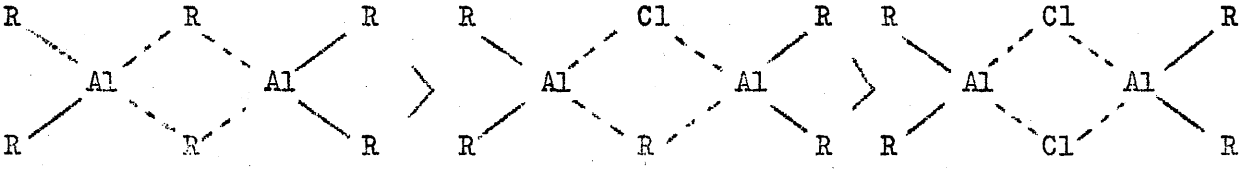


The N.M.R. spectrum of a solution of Me_6Al_2 in cyclopentane at room temperature shows only one peak [45], indicating that all the protons are equivalent or that a rapid exchange of methyl groups is occurring. As the temperature is lowered down to -75°C the spectrum changes to two peaks (one for each of the different types of methyl group present in the bridged structure), indicating that an exchange is occurring. By the same method it has been shown [46] that for neat triethylaluminium a rapid exchange of ethyl groups occurs at room temperature, but the rate diminishes at -60°C so that it is hardly discernible. The successive introduction of chlorine into the Me_6Al_2 molecule has an adverse effect upon the alkyl exchange [47]. Rapid exchange occurs between Me_6Al_2 and $Me_4Al_2Cl_2$, but the spectra of $Me_4Al_2Cl_2$ alone and of

$Me_2Al_2Cl_4$ alone, show the presence of only one type of methyl group, even at low temperatures. This implies the presence of a chloride bridge structure as opposed to the methyl bridge structure in cases where exchange occurs. Thus the comparative rates of exchange for the systems mentioned are :

$$R_3Al/R_3Al > R_3Al/R_2AlCl > R_2AlCl/R_2AlCl = 0.$$

i.e.



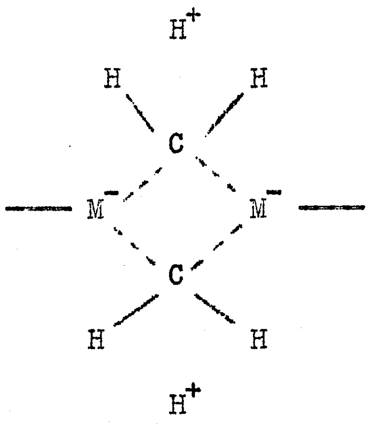
= 0.

Exactly the reverse order would be expected if these exchanges occurred by an S_E2 or S_Ei mechanism; the successive introduction of a chloride (a potential nucleophile) into the molecules would increase the rate of exchange by an S_E2 or S_Ei mechanism. For the system trimethylaluminium and dimethylaluminium methoxide if exchange occurs at all it is much slower than in the case of trimethylaluminium alone [48]. This indicates that a methoxy group bridges preferentially to a methyl group.

Prior coordination of the aluminium also has an adverse effect upon alkyl exchange. For the system trimethylaluminium and trimethylaluminium-triethylamine complex if exchange of methyl groups occurs at all it is slower than in the case of trimethylaluminium alone [48]; showing that the Al - N bond is strong compared to the association bond of the bridged dimer. Similarly it was found that methyl groups exchanged in trimethylthallium in toluene, but if this exchange was studied in ether or trimethylamine the exchange was much slower, due to complex formation [49].

Alkyl exchange by the bridge mechanism is not limited to aluminium compounds. Exchange occurs between R_3Al and $R_3{}^1B$ rapidly at room temperature, and traces of trialkylaluminium catalyse exchange between two different trialkylborons [50,51]. In exchanging systems where the products and reactants are not identical N.M.R. is not essential to demonstrate exchange, and in some cases of such systems exchange may be demonstrated by distilling off the more volatile products. This was done for the systems $R_3Al/R_3{}^1B$ ($R = Me,Et$; $R^1 = Bu,i\text{-}Bu$); $R_3Al/R_2{}^1Zn$ ($R = Me$; $R^1 = Et,Pr$ and $R = Et$; $R^1 = n\text{-}Bu$); $R_3B/R_2{}^1Zn$ ($R = Et$; $R^1 = Me$) [52].

Overall the results of alkyl exchanges studied, which proceed by a bridge mechanism, show that these reactions occur more easily for methyl compounds, and some resonance stabilisation of the methyl bridge might be expected :



It might also be predicted that exchange would occur more readily the more easily the metal could accept electrons. An order : Al $>$ Zn $>$ Cd $>$ Hg would be expected and this is borne out in the results of McCoy and Allred [53] who found that exchange between Me_3Al and Me_2Cd is twelve times faster than between Me_2Zn and Me_2Cd, whilst Me_2Zn and Me_2Hg, and Me_2Cd and Me_2Hg exchange even more slowly if at all. This work is interesting from the point that it, and similar work by Dessy [54], represent the only detailed work on alkyl exchange reactions of dialkylzincs that has ever been done. The parameter obtained from these studies is the average life-time of a carbon-metal bond before it is broken and the methyl group is exchanged. Some of these results are shown in Table 4.

TABLE 4

A (m/1.)	B (m/1.)	solvent	t secs.	ref.
Me_3Al (0.062)	Me_2Cd (0.097)	benzene	< 0.09	[53]
Me_2Mg (0.33)	Me_2Zn (0.33)	THF	< 0.009	[54]
Me_2Mg (0.60)	Me_2Cd (0.60)	THF	< 0.007	[54]
Me_2Mg (0.60)	Me_2Hg (0.60)	THF	> 0.040	[54]
Me_2Hg (0.60	Me_2Zn (0.60)	THF	> 0.058	[54]
Me_2Hg (0.60)	Me_2Cd (0.60)	THF	> 0.073	[54]

where t is the average lifetime of the bonds.

The proviso must be made that in the last two cases the N.M.R. spectra showed no exchange phenomena and so the upper limit of t in these two cases could be infinity. However, the rate of exchange between dimethylzinc and dimethylcadmium proved amenable to kinetic studies in various solvents. The results are shown in Table 5.

TABLE 5

Rate constants for the reaction Me_2Zn and Me_2Cd

Solvent	$[Me_2Zn] = [Me_2Cd]$ m/l.	Apparent order, n	k(moles/l.)$^{1-n}$sec^{-1}
nitrobenzene	0.247	1.6	8.9
	0.375		9.1
	0.492		9.1
	0.619		9.0
pyridine	0.185	2.0	11.4
	0.240		12.2
	0.305		11.6
benzene	0.79	1.8	5.2
	1.35		5.7
	2.23		5.0
cyclohexane	2.36	1.4	5.7
	2.80		5.5
	3.40		5.7

Little can be deduced from the results in Table 5, except that there is no appreciable solvent effect.

Dessy's study [55] of exchange between mercury and magnesium compounds provides an example of steric hindrance of an alkyl bridge. It was found that reactions in which the bridging groups were phenyl and ethyl, phenyl and i-propyl, and ethyl and i-propyl proceeded, but exchanges which would have involved a t-butyl group in a bridging position did not proceed.

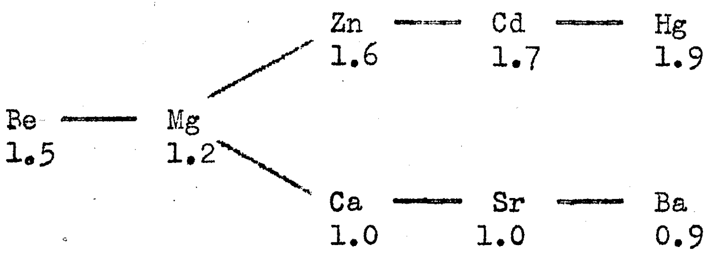
CHAPTER II

THE GROUP II ORGANO-METAL COMPOUNDS

1. General

In this chapter the general nature and properties of the Group II alkyl and aryl metal compounds will be reviewed, with particular reference to the organometallic halides.

The gradation of properties of the organometals of this group follows very closely the gradation of electronegativities [56] of the parent metals.



Derivatives of calcium, strontium and barium have properties similar to those of the alkali metals, in that they have a large amount of polar character; reacting with carbon-carbon double bonds, and replacing hydrogen in metalation reactions. Derivatives of magnesium and beryllium are more covalent in nature and generally less reactive than those of calcium, strontium and barium. Some beryllium compounds show a polymeric nature and to a lesser extent so do magnesium compounds. The increasing electronegativity of the elements zinc, cadmium and mercury is reflected in the falling off of chemical reactivity along this series. Their dialkyls and diaryls are all covalent and monomeric in structure.

2. Calcium, Strontium and Barium

Relatively little is known of the organo derivatives of these metals. It has been claimed [57] that the dimethyl derivatives of these three metals have been prepared by reacting the metals with methyl iodide in pyridine. The products showed their chemical similarity to the alkali metal compounds by adding [58] across ethylenic double bonds and by metalating aromatic compounds. Ethereal solutions which have been claimed to contain phenylbarium iodide [59] and phenylcalcium iodide [60] have been prepared from the reaction of those metals with iodobenzene in ether. More recently it has been claimed that solutions containing some alkyl and aryl calcium iodides and bromides have been obtained [61] by the action of organic halides on calcium and calcium alloys, in ether. The contents of these solutions showed their chemical similarity to the organo-alkali metal compounds (the lithium ones in particular); e.g. "phenylcalcium iodide" metalated anisole in the ortho position, but failed to metalate toluene, and they reacted with carbon dioxide to give not only the corresponding carboxylic acids but some ketones and tertiary alcohols, also.

3. Magnesium

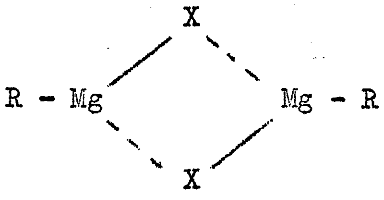
Diorganomagnesiums have been sparsely studied in comparison to the organomagnesium halides. Their preparation may be effected by the action of diorganomercury compounds on magnesium in ether, or by the action of olefins on magnesium in the presence of hydrogen, at elevated temperatures. Dimethylmagnesium is polymeric in nature and forms a complex with trimethylamine.

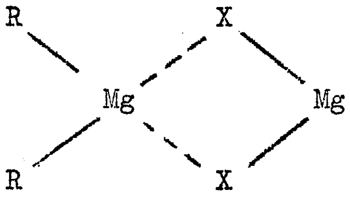
The Grignard reagents formed by the action of alkyl and aryl halides on magnesium in ether and other solvents have been the object of much study, directed towards elucidating their structure. The use of Grignard reagents in synthetic chemistry is widespread and their reactions and high reactivity well known; (e.g. [62]) their addition to multiple bonds such as $>C=O$, $-C\equiv N$, $-N=O$, and their reactivity towards compounds containing an active hydrogen, and halogen. Here it is proposed to review only some of the more recent work directed towards discovering the nature of the Grignard reagent. The equilibria (1) and (2) have been suggested to account for the properties of the Grignard reagents; some workers favour only one of these equilibria and others favour both equilibria together.

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad \text{——— (1)}$$

$$R_2Mg + MgX_2 \rightleftharpoons R_2Mg.MgX_2 \qquad \text{——— (2)}$$

Dessy found [63] that there was no exchange of label between diethylmagnesium and $^{28}MgBr_2$ in ether, and concluded that equilibrium (1) did not exist. He also found that equimolar mixtures of diethylmagnesium and magnesium bromide in ether had the same properties as the Grignard reagent made from magnesium and ethyl bromide in ether; their conductances [64] and dielectric constants [65] he claimed were similar, and the kinetics of their reactions with hex - 1 - yne [66] were similar. Thus Dessy believes the only equilibrium to be operating is (2) and that the Grignard reagent in ether is best represented as $R_2Mg.MgX_2$, and that of the two logical structures I and II, his work favours II.


I


II

However, in another paper [67], in which he found no exchange of label between diphenylmagnesium and $^{28}MgBr_2$, Dessy also found that exchange did occur between diethylmagnesium and $^{25}MgBr_2$ in ether; which he ascribed to "some impurity in the ^{25}Mg". He later reported [68] a series of experiments using diethylmagnesium and $^{28}MgBr_2$ in both ether and tetrahydrogen in which duplicate experiments gave conflicting results. Later, Roberts, using high purity materials, found [69] that exchange took place between $^{25}MgBr_2$ and the Grignard reagent made from ethyl bromide and magnesium, in ether.

Doubt has also been cast on some of Dessy's work by the recent, meticulous, work of Vreugdenhil and Blomberg. They did molecular weight measurements in the range $10^{-3} - 10^{-2}M$ in solvent ether, using very pure materials, and rigorously excluding oxygen. Their measurements were on the Grignard reagent made from ethyl bromide and magnesium, on magnesium bromide and diethylmagnesium and on mixtures of the latter two, all in solvent ether. Their observations were [70]:

(a) the association number for magnesium bromide was 1.15,

(b) the association number for the Grignard reagent was 1.00,

(c) mixtures of diethylmagnesium and magnesium bromide showed no association.

From (c) equilibrium (1) may be excluded. From (b) the Grignard reagent may be formulated as EtMgBr or $Et_2Mg + MgBr_2$. However, the second of these formulations would give an association number of 1.07 (since the value for magnesium bromide is 1.15); hence EtMgBr is the only formulation that holds in ether in the concentration range studied. They also found [71] the same Grignard reagent to be monomeric in tetrahydrofuran. But in this solvent magnesium bromide was also unassociated. When they investigated [72] the electrical conductivities of the same systems in solvent ether, under the same rigorous conditions as before, they obtained values considerably lower than those obtained by previous workers, and then demonstrated that by opening their apparatus to the atmosphere they got higher values of electrical conductivities compatible with those values obtained by previous workers. Their measurements were made in the range 0.05 - 3.0M, and they found significant differences between the conductivities of equimolar mixtures of diethylmagnesium and magnesium bromide, and the corresponding Grignard reagent, in solvent ether, only up to 0.4M.

They found, in this range 0 - 0.4M, that the molar conductivity increased with increasing concentration for both systems, but that the conductivity of the Grignard reagent was lower. They concluded that associates having a higher conductance than the monomeric molecules must be formed at higher concentrations, and that at low concentrations these associates were already present in the mixtures, but not in the Grignard reagent. When investigating the influence of added oxygen upon molecular weight determinations on the ethylmagnesium bromide Grignard reagent they found [73] that the addition of three atoms of oxygen caused the disappearance of two molecules of the magnesium compound; i.e. a trimer was formed. Finally, seeking to prove that there was no equilibrium between the Grignard reagent made from ethyl bromide and magnesium, and diethylmagnesium, by using a ^{14}C label in the ethyl group in the Grignard reagent, they found [74] that exchange of the label did occur. This, unfortunately, may be interpreted in either of two ways: that an equilibrium does exist, or that a transmetalation reaction

$$\overset{*}{Et}MgBr + EtMgEt \rightleftharpoons EtMgBr + \overset{*}{Et}MgEt$$

has occurred.

From molecular weight measurements, Ashby found [75] that the Grignard reagent made from ethyl chloride and magnesium was monomeric in tetrahydrofuran, and also he isolated diethylmagnesium and a compound analysing for $EtMg_2Cl_3$ from a solution of the same Grignard reagent. He took the latter observations as indicating that alkyl exchange had occurred. He also found that mixtures of diethylmagnesium and magnesium chloride showed no association in tetrahydrofuran. In addition a 2M solution of the ethylmagnesium chloride Grignard reagent in tetrahydrofuran did not precipitate magnesium chloride on standing although this salt is only 0.5M soluble in this solvent. He concluded that the situation was covered by equilibrium (1), and that it lay far to the left. Later, from molecular weight studies in solvent ether, Ashby found [76] that alkyl and aryl magnesium bromides and iodides were monomeric up to 0.05M and dimeric in the range 0.5 - 0.1M, whilst alkylmagnesium chlorides were dimeric even in the low concentration ranges. Thus for Grignard reagents in general, an expanded form of equilibria (1) and (2) was necessary; viz.

$$(RMgX)_2 \rightleftharpoons 2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons R_2Mg.MgX_2.$$

A summary of the results obtained by Ashby is shown in Table 6. A summary of the molecular weight determinations made by Vreugdenhil and Blomberg is given in Table 7.

TABLE 6

Molecular weight determinations on Grignard reagents in ether [76]

Compound	Concn. m/l. based on RMgX.	i*	Compound	Conc. m/l.	i
EtMgBr	0.035	1.00	i-PrMgCl	0.042	1.85
	0.102	1.04		0.080	1.90
	0.150	1.16		0.144	1.93
	0.200	1.26		0.201	2.00
	0.249	1.37		0.260	2.02
EtMgI	0.055	1.00	PhMgBr	0.042	1.07
	0.108	1.12		0.111	1.17
	0.158	1.27		0.179	1.31
	0.204	1.36		0.241	1.50
EtMgCl	0.086	1.87		0.326	1.70
	0.143	1.86	MesitylMgBr	0.059	1.06
	0.196	1.92		0.172	1.41
MeMgI	0.037	1.09		0.275	1.77
	0.084	1.17			
	0.140	1.36			
	0.245	1.59			

* i, the association constant = $\frac{\text{molecular wt.}}{\text{formula wt.}}$

TABLE 7

Molecular weight determinations in ether [70]

Compound	Conc. range (m/l.)	i [*]
$MgBr_2$	.00066 - .00399	1.10 ± .02
Et_2Mg	.0025 - .0050	0.99 ± .02
$MgBr_2$	.01059	1.17
EtMgBr	.00419	0.99
$MgBr_2$	.0005 - .0035	1.15 ± .02
EtMgBr	.0838	1.01
Et_2Mg	.00264 - .00528	0.97 ± .04
$MgBr_2$	.00053 - .00371	1.15 ± .02
Et_2Mg	.00792	0.98

[*] i, the association constant = $\frac{\text{molecular wt.}}{\text{formula wt.}}$

Single crystal X-ray studies by Rundle have shown both phenylmagnesium bromide [77] and ethylmagnesium bromide [78] dietherates to be monomeric, with their structures as distorted tetrahedra based around magnesium. Proton magnetic resonance studies [79,80] on Grignard reagents and dialkylmagnesiums and mixtures of dialkylmagnesiums and magnesium halides in both ether and tetrahydrofuran have shown remarkable similarities, which suggested to these workers that Grignard reagents were best written as $R_2Mg.MgX_2$. Infra-red spectra of both Grignard reagents and mixtures of dialkylmagnesiums and magnesium halides are also identical. However, these authors [81] considered that equilibrium (1) was more applicable than (2), in both ether and tetrahydrofuran.

In summarising the latest knowledge on the structure of the Grignard reagent, it becomes apparent that no great generalisations can be made. What is true for one Grignard reagent in one solvent may not be true for another Grignard reagent in a different solvent or even the same solvent. What can be stated with some certainty is that from the work of Vreugdenhil and Blomberg, the Grignard reagent made from ethyl bromide and magnesium may be written as EtMgBr when considered in ethereal solution at low concentrations and that the same is true in tetrahydrofuran. While Ashby has shown that for some alkyl and aryl magnesium bromides and iodides their degree of association in ether rises with increasing concentration, whilst some alkylmagnesium chlorides are almost dimeric even at low concentrations.

4. Beryllium

Diorganoberylliums may be prepared by reacting an ethereal solution of the appropriate Grignard reagent with beryllium chloride dietherate, and in some cases by the prolonged heating of beryllium with a diorganomercury. Dimethylberyllium is a sublimable polymeric, solid, and in accord with its electron deficiency it forms coordination complexes with donor molecules such as trimethylamine. Its reactivity is displayed by its vigorous reactions with water and air and even carbon dioxide. Both diethyl and diisopropyl beryllium show some association. The former reacts vigorously with water, and it is interesting to note that the latter slowly decomposes.

Gilman claimed to have prepared [82] ethereal solutions of methyl, ethyl, n-butyl and phenyl beryllium iodides and ethylberyllium bromide by prolonged heating of beryllium with organic halides in ether with added mercuric chloride, at 80-90°C. All these solutions reacted vigorously with water but did not fume in air. The solution of "methylberyllium iodide" did not react with carbon dioxide, unlike its magnesium counterpart, but gave acetanilide with phenyl isocyanate. Gilman also found that on concentrating an ethereal solution of "methylberyllium iodide", a liquid residue which fumed in air was produced, and which, on further heating yielded dimethylberyllium. This led him to believe that the equilibrium : $2RBeX \rightleftharpoons BeX_2 + R_2Be$, existed; particularly since he found that an ethereal solution of diethylberyllium and beryllium chloride "had the same characteristics" as a solution of "ethylberyllium chloride" made directly from a Grignard reagent and beryllium chloride. Gilman isolated no solid beryllium compounds nor did he present any analytical data.

More recently, Dessy has found that [83] there was no exchange of radioactively labelled beryllium between diphenylberyllium and $^7BeBr_2$, in ether; thus excluding the equilibrium proposed by Gilman. Instead Dessy proposes that the equilibrium

$$R_2Be + BeX_2 \rightleftharpoons R_2Be.BeX_2$$

represents the true state of affairs. Later it was found [84] that beryllium would react with alkyl halides in the absence of ether or any catalyst to give alkylberyllium halides. By heating the reactants at 130°C for 12 - 60 hrs. these authors obtained ethyl, pentyl and octyl beryllium iodides and butylberyllium bromide as solids, insoluble in their respective alkyl halides.

5. Zinc

Dialkylzincs, which have been known [85] since 1849, are stable, covalent, monomeric liquids. Despite their spontaneous inflammability in air and their vigorous hydrolysis by water, they are chemically less reactive than magnesium compounds. They will not react with carbon dioxide, except under pressure, and they do not react with ketones, but they will react with molecules containing active hydrogen. The most general method of preparation of dialkylzincs is that due to Noller [86], in which the product of the reaction between an alkyl halide and a zinc-copper couple, is heated under vacuum and the dialkylzinc distilled off.

Until about 13 years ago it was tacitly assumed that the intermediate in this preparation was an alkylzinc halide. This was supported by the fact that unsymmetrical dialkylzincs could be prepared from the interaction of a Grignard reagent with this intermediate. This preparation could then be written :

$$RZnX + R'MgX \longrightarrow RZnR' + MgX_2.$$

Solutions of alkylzinc halides made by dissolving the product of the reaction of an alkyl halide (usually an iodide) with zinc, were widely used as reagents in synthetic chemistry until they were replaced by the more convenient Grignard reagents. Such solutions were known as Blaise [87] reagents. Even recently the reactions of such solutions of alkyl compounds were described [88], and the reacting species referred to simply as "a solvated organo-zinc compound". Blaise also prepared solutions of "arylzinc halides" by reacting zinc halides with solutions of Grignard reagents. When he attempted to isolate a solid product from these solutions he obtained compounds containing both zinc and magnesium. He did not attempt this isolation for aliphatic compounds.

Three routes are apparent for the possible preparation of organozinc halides :

$$Zn + RX \longrightarrow RZnX \qquad \text{———} \quad (a)$$
$$R_2Zn + ZnX_2 \longrightarrow 2RZnX \qquad \text{———} \quad (b)$$
$$RMgX + ZnX_2 \longrightarrow RZnX + MgX_2 \qquad \text{———} \quad (c)$$

Jander and Fischer [89] obtained identical solid products, both analysing for ethylzinc iodide, from reaction schemes (a) and (b). However, the same analytical figures would have been given by another possible reaction product, $(EtZnI)_2$, which is apparent if it is assumed that there is a possibility of the Schlenk equilibrium being applicable to zinc as it is to magnesium :

$$2RZnX \rightleftharpoons R_2Zn + ZnX_2 \rightleftharpoons R_2Zn.ZnX_2 \qquad \text{———} \quad (3)$$

Kocheshkov and Sheverdina have described in a series of papers [90,91,92,93] the preparation of alkyl and aryl zinc halide dioxanates, by the addition of dioxan to the reaction mixtures from scheme (b), in ether. In the case of R = Et, X = I, they obtained identical dioxanates from all three schemes. Previously it had been suggested [94] that for R = Et, X = Br, the righthand part of equilibrium (3), only, was applicable, on the basis of some solubility measurements on mixtures of diethylzinc and zinc bromide in heptane. Dessy found [95] that statistical exchange of radioactively labelled zinc occurred between diethylzinc and $^{65}ZnCl_2$ in both ether and tetrahydrofuran, thus showing that either ethylzinc chloride existed or that a non-ionic exchange had taken place. He separated the species present in solution by the differing solubilities of their 2,2'dipyridyl complexes, yet did not obtain an ethylzinc chloride complex, which would indicate that the lefthand part of equilibrium (3) lay well to the right, or that the addition of the dipyridyl had pushed it to the right. As with magnesium the proton magnetic resonance spectra of "ethylzinc iodide" and diethylzinc in ether, have been found [80] to be identical.

On the purely preparative side, it is known that in the presence of highly solvating solvents such as dimethylformamide [96,97] and dimethyl sulphoxide [96], alkyl iodides and bromides will react with zinc alone, although alkyl bromides react more readily [96] with a zinc-copper couple than with zinc alone, even in such solvents.

6. Cadmium

The easiest method of preparation of diorganocadmiums is by the action of cadmium halides on the appropriate Grignard reagent in ether; from which mixture the product may be distilled off. The cadmium dialkyls are monomeric, covalent liquids which decompose readily above 150°C. They are chemically less reactive than dialkylzincs; not igniting so readily in air, but still reacting with molecules containing active hydrogen. Their ease of handling as compared to the dialkylzincs suits them better for the preparation of ketones (with which they do not react) from acid chlorides.

Alkylcadmium halides have been prepared [93,98], only recently, by the addition of dialkylcadmiums to suspensions of cadmium halides in ether. Filtration, followed by removal of the ether under reduced pressure yields powders analysing for RCdX. In this way ethylcadmium chloride, bromide and iodide, and n-butylcadmium bromide have been made. Chemically they behave similarly to their parent dialkyls; oxidising in air but not igniting, and being rapidly decomposed by water and ethanol, and also yielding ketones with acid chlorides. The authors make the reservation that their products could equally well be written as $R_2Cd.CdX_2$. This formulation has been suggested [94] for the species present in a tetrahydrofuran solution of diethylcadmium and cadmium bromide.

7. Mercury

Dialkylmercury compounds may be prepared from a mercuric halide, and a Grignard reagent or lithium alkyl, and diarylmercury compounds from the reduction of arylmercuric halides. Both dialkyl and diaryl mercury compounds can be made from the action of a sodium amalgam on the appropriate halide, in toluene. Unsymmetrical diorganomercury compounds can be made from an organomercury halide and a Grignard reagent. Large numbers of diorganomercury compounds are known. Their chemical reactivity compared to the other compounds mentioned in this chapter is very low; they are unaffected by water and the atmosphere and even dilute mineral acids, and give few of the reactions typical of the compounds already mentioned. The dialkyls are monomeric liquids and the diaryls mostly solids.

Alkyl and aryl mercuric halides are known on as large a scale as the diorganomercury compounds. They are well characterised as stable monomeric solids, as inert chemically as their parent diorganomercury compounds. They behave as covalent compounds, sometimes steam volatile. RHgX compounds where X is nitrate, sulphate, acetate, cyanide, etc., are also known; their degree of polarity depending on the tendency to ionise as $RHg^{+}X^{-}$. Organomercury halides may be prepared by the interaction of a Grignard reagent and a mercuric halide, or by the action of a halogen on a diorganomercury. The relationship between organomercury halides and diorganomercury compounds, represented by the equilibrium :

$$R_2Hg + HgX_2 \rightleftharpoons 2RHgX,$$

which normally lies far to the right, has been discussed earlier.

DISCUSSION

SECTION I

THE PURPOSE OF THE WORK

The mechanisms of the alkyl exchange reactions of organomercury compounds have been the object of much study recently and the purpose of the present work was to extend these studies by identifying and studying alkyl exchange reactions which involved transfer of an alkyl group from zinc to mercury.

Dialkylzincs were chosen since they are stable, monomeric liquids, easily prepared and purified, and they undergo the reactions typical of organometallic compounds. In addition they have recently been shown to be amenable to kinetic studies in the form of comparative rate studies at least [38]. In the present work studies of both the absolute rates and the comparative rates of reaction of dialkylzincs with organomercury halides were attempted. Since the results obtained were not completely satisfactory "ethylzinc iodide" solutions were used in similar studies of absolute rates of reaction in the hope that these reactions might be slower. This led to a study of the precise nature of "ethylzinc iodide" and, in particular, its relation to diethylzinc and zinc iodide as shown by the equation :

$$Et_2Zn + ZnI_2 \rightleftharpoons 2EtZnI,$$

which is an alkyl exchange reaction involving transfer of an alkyl group from zinc to zinc. Similar studies of the corresponding bromide system were also undertaken, and in both the iodide and bromide systems use was made of complexes of N,N,N',N'-tetramethylethylenediamine (TMED) and N.M.R. studies of these complexes.

SECTION II

KINETIC STUDIES

1. The identification of the reaction between diethylzinc and phenylmercuric chloride

The identification of the reaction between a dialkylzinc and an organomercuric halide would be made easier if the organic groups on the zinc and the mercury were different. Diethylzinc was chosen as one reactant since it is a typical member of the homologous series of symmetrical dialkylzincs and easier to handle than dimethylzinc. Phenylmercuric chloride was chosen as the other reactant since out of a wide range of organomercuric halides available it is one of the least objectionable. The choice of solvents in which to study the reaction was limited to those which would not react with dialkylzincs and yet would dissolve phenylmercuric chloride in sufficient quantities. Tetrahydrofuran and diethyl ether were chosen as solvents.

The main reaction between diethylzinc and phenylmercuric chloride was envisaged as being : $Et_2Zn + PhHgCl \longrightarrow EtHgPh + EtZnCl$ ... (1)

perhaps followed by

$$EtHgPh + EtZnCl \longrightarrow Et_2Hg + PhZnCl \quad \ldots \quad (2)$$

Possible side-reactions, no matter how unlikely some of them may be, are :

$$EtHgPh + Et_2Zn \longrightarrow Et_2Hg + EtZnPh \qquad \ldots \qquad (3)$$

$$PhHgCl + EtZnCl \longrightarrow EtHgPh + ZnCl_2 \qquad \ldots \qquad (4)$$

$$EtHgPh + PhZnCl \longrightarrow Ph_2Hg + EtZnCl \qquad \ldots \qquad (5)$$

$$Et_2Hg + EtZnCl \longrightarrow EtHgCl + Et_2Zn \qquad \ldots \qquad (6)$$

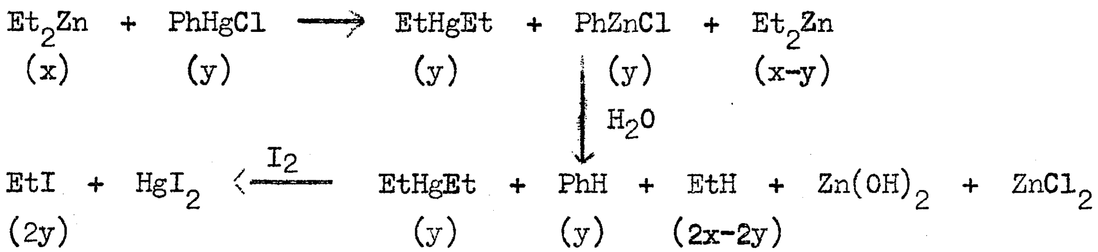
At this point it is necessary to note that EtZnCl and PhZnCl may not exist as such but as equimolar mixtures of $Et_2Zn + ZnCl_2$ and $Ph_2Zn + ZnCl_2$ respectively. The reasoning given below, which is based on quantitative observations, is unaffected by this possibility since the number of bonds on each side of the equations will still balance. In addition side-reaction (4) would become the same as reaction (1).

In the first instance the occurrence of side-reactions was guarded against by always having diethylzinc present in excess of the phenylmercuric chloride based on equation (1). The occurrence of reactions (5) and (6) depends on the initial occurrence of reaction (2). Hydrolysis of the final reaction mixture with careful measurement of the volume of gas produced and then iodination of the mixture followed by analysis of V.P.C. to determine which organic iodides are present would distinguish between the occurrence of reactions (1) and (2) or a mixture of both. This is made clear by the following reaction schemes:

Scheme A (reaction (1)):

$$\begin{array}{lcccccl}
Et_2Zn + PhHgCl & \longrightarrow & EtHgPh & + & EtZnCl & + & Et_2Zn \\
(x\text{ moles})+(y\text{ moles}) & & (y) & & (y) & & (x-y) \\
 & & & & \Big\downarrow H_2O & & \\
EtI + PhI + HgI_2 & \xleftarrow{I_2} & EtHgPh & + & EtH & + & Zn(HO)_2 + ZnCl_2 \\
(y)\quad (y) & & (y) & & (2x-y) & &
\end{array}$$

Scheme B (reactions (1) + (2)):



$$\underset{(x)}{\mathrm{Et_2Zn}} + \underset{(y)}{\mathrm{PhHgCl}} \longrightarrow \underset{(y)}{\mathrm{EtHgEt}} + \underset{(y)}{\mathrm{PhZnCl}} + \underset{(x-y)}{\mathrm{Et_2Zn}}$$

$$\Big\downarrow \mathrm{H_2O}$$

$$\underset{(2y)}{\mathrm{EtI}} + \mathrm{HgI_2} \xleftarrow{I_2} \underset{(y)}{\mathrm{EtHgEt}} + \underset{(y)}{\mathrm{PhH}} + \underset{(2x-2y)}{\mathrm{EtH}} + \mathrm{Zn(OH)_2} + \mathrm{ZnCl_2}$$

Scheme A represents the transfer of one ethyl group from zinc to mercury and would lead, on hydrolysis, to the evolution of 2x-y moles of ethane, and after iodination would show the presence of ethyl iodide and iodobenzene only. Scheme B represents the transfer of both ethyl groups from zinc to mercury and would lead, on hydrolysis, to the evolution of 2x -2y moles of ethane, and after iodination would show the presence of ethyl iodide and benzene only, when analysed by V.P.C. A mixture of the two schemes A and B would lead to intermediate volumes of ethane and mixtures of ethyl iodide, iodobenzene and benzene. The results of experiments such as these are shown in Tables 11 and 12. (In the tables the term "Vol. of gas expected" refers to the volume of ethane expected if reaction (1) [Scheme A], only occurred.) The volumes of ethane evolved from experiments in both tetrahydrofuran and ether corresponded to reaction (1) only. For comparison the volumes of ethane that would be expected if no reaction occurred, for reaction (1) only [Scheme A] and for reaction (1) and (2) [Scheme B] are given in Table 8.

TABLE 8

Run No.	Vol.of gas for no reaction	Vol.of gas for reaction (1)[A]	Vol. of gas for reaction (1) + (2) [B]	Vol.of gas observed	Solvent
12	148 ml.	109 ml.	72 ml.	106 ml.	THF
15	170	128	86	129	THF
16	147	103	59	104	THF
17	150	111	72	112	THF
18	206	183	161	175	ether
19	246	226	207	220	ether
20	129	104	78	99	ether

Analysis of the iodinated reaction residue showed the presence of ethyl iodide and iodobenzene only, when the reaction mixture had been hydrolysed by water. This result augmented the results obtained from the measurements of gas volumes and confirmed that reaction (1) only was occurring. In cases where dilute mineral acid was used to hydrolyse the reaction mixture, ethyl iodide and benzene only were detected in the iodinated residue. This is interpreted as being due to hydrolysis of the phenylmercury bond of ethylmercuric phenyl produced by reaction (1), under the conditions used, i.e. in refluxing tetrahydrofuran.

The exclusion of the occurrence of reaction (2) automatically excludes reactions (5) and (6). Reaction (3) would lead to the evolution of less ethane than that expected for reaction (1) and to the presence of benzene in the reaction residue, even in cases where hydrolysis had been done using water (from the EtZnPh). Reaction (4) is unlikely since the diethylzinc was present in an excess. Analysis of the iodinated reaction residues was only possible for those experiments performed in tetrahydrofuran, but since the volumes of ethane evolved from experiments done in ether corresponded to reaction (1) it is concluded that reaction (1) is the only reaction occurring in both ether and tetrahydrofuran, under the conditions of these experiments.

2. An attempted study of the kinetics of the reaction between diethylzinc and phenylmercuric chloride and between diethylzinc and ethylmercuric chloride

The identified reaction, $Et_2Zn + PhHgCl \longrightarrow EtHgPh + EtZnCl$ was studied in both tetrahydrofuran and ether at 0°C. The reaction between diethylzinc and ethylmercuric chloride was taken, by analogy, to be $Et_2Zn + EtHgCl \longrightarrow Et_2Hg + EtZnCl$, and was studied in the same solvents, also at 0°C. The reactions were stopped by pipetting samples into saturated aqueous potassium hydrogen phthalate at 0°C, which was found, in check experiments, a sufficiently strong acid to dissolve any zinc hydroxide that might be produced, and yet not to hydrolyse the organomercury compounds present. The quenched reaction samples were then shaken with benzene, which extracted the organomercury compounds. The chloride content of the aqueous layer was then determined. This represented the amount of chloride transferred from mercury to zinc, i.e. the extent to which reaction had occurred. Check experiments showed that this analytical procedure (including the benzene extraction) would produce results consistent to within 3%. One point only was taken in each experiment to give some idea of the time scale of these reactions. The results, shown in Table 13, show that the reactions were too fast to follow kinetically, and hence nothing can be deduced about their mechanisms. Slight inconsistencies in this table are due to the fact that with the organomercuric halide concentration less than about 0.005M the end-points of the titrations become more difficult to determine. The reagents were only used in such low concentrations in an attempt to gain a rough idea of the time scale of the reactions.

3. An attempted study of the kinetics of the reaction between ethylzinc iodide and phenylmercuric iodide in tetrahydrofuran at 0°C.

The reaction to be studied was envisaged as

$$\mathrm{EtZnI} + \mathrm{PhHgI} \longrightarrow \mathrm{EtHgPh} + \mathrm{ZnI_2}$$

and hence the same analytical procedure as before could be used. The amount of iodide found in the aqueous layer (allowing for the iodide due to the EtZnI), would be a measure of the extent to which reaction had occurred. Ethylzinc iodide was used in the hope that the reaction would be slower than that using diethylzinc, and the phenylmercuric halide was changed from chloride to iodide to prevent halide exchange reactions. The results, which are given in Table 14, show that after an initial burst of activity the reaction rapidly tails off and was never found to have proceeded beyond 65.9%. The results would not fit second order kinetics (first order with respect to each reactant) nor would they fit first order kinetics with respect to either reactant. This reaction was not investigated any further.

4. An attempted study of the kinetics of the reaction of ethylzinc iodide with mercuric iodide in tetrahydrofuran at 25°C.

The reaction studied $EtZnI + HgI_2 \longrightarrow EtHgI + ZnI_2$ was followed by determining the concentration of ethylzinc iodide by acid/alkali titrations. The reaction was followed using a flow apparatus (see Fig.5 for apparatus and page 115 for details of its operation). The reaction was not followed by titrating for iodide as in previous kinetic experiments since the partition of the mercuric iodide in the solvent extraction process might be affected by both the tetrahydrofuran and by other species containing iodide ion.

It was confirmed in check experiments that ethylmercuric iodide would not interfere in the acid/alkali titrations. Bromocresol purple was used as the indicator in these titrations, in which the kinetic sample was mixed with an excess of acid and the acid back-titrated with sodium hydroxide, since its colour change from yellow to purple occurred before the precipitation of zinc hydroxide, and also since its colour change was not greatly affected by the presence of tetrahydrofuran. The results of these experiments are given in Table 15, and show that this reaction was too fast to follow kinetically. Over the range of reaction in which it was possible to follow the kinetics the data would not fit second order kinetics, and the reaction appeared to be tailing-off rapidly, as might be expected in the range 80-90% reaction. Again no conclusions regarding the mechanism of the reaction may be drawn.

One run was performed between ethylzinc iodide and potassium mercury tri-iodide. In this case the presumed electrophilic attack on the zinc compound would be by HgI_3^- and would be expected to be slower than attack by HgI_2. However this reaction was again too fast to follow.

5. An attempted study of the kinetics of the reaction between ethylzinc iodide and ethylmercuric iodide in tetrahydrofuran at 25°C.

The reaction studied was $EtZnI + EtHgI \longrightarrow Et_2Hg + ZnI_2$. The same apparatus and techniques were used in following this reaction as for the previous reaction. The results, shown in Table 16, were calculated on the assumption that the quenching acid was consumed by ethylzinc iodide only. The results obtained are explained by a slow hydrolysis of the diethylmercury produced in the reaction. This was not verified in check experiments because of the toxicity of diethylmercury. Thus the analytical method used was inappropriate and the initial reaction it was intended to follow must have been very fast.

6. Conclusions

The rates of the following three alkyl exchange processes, where (X = I)

$$R_2Hg + HgX_2 \longrightarrow 2RHgX \quad \ldots \quad (a)$$

$$R_2Zn + ZnX_2 \longrightarrow 2RZnX \quad \ldots \quad (b)$$

$$R_2Zn + HgX_2 \longrightarrow RZnX + RHgX \quad \ldots \quad (c),$$

may be summarised as: (a) slow; (b) slow (c.f. Section IV of this discussion); and (c) fast. These differences may be due to the order of the electrophilicity of the attacking metal halides being in the order $HgX_2 > ZnX_2$, and the nucleophilicity of the α-carbon atom of the dialkyl metals being in the order $R_2Zn > R_2Hg$. Thus, in order to find a metal to unlike metal alkyl exchange which proceeds at a measurable rate involving either zinc or mercury, it would seem necessary to react either a mercuric halide with an alkyl metal compound in which the α-carbon atom has a less nucleophilic character than that in a zinc compound (e.g. the reaction of a tetraalkyltin with a mercuric halide), or to react a dialkylzinc with a metal halide less electrophilic in character than a mercuric halide (e.g. the reaction of a dialkylzinc with a cadmium halide).

SECTION III

COMPETITIVE STUDIES

The method of reacting approximately equimolar mixtures of dialkylzincs with a deficiency of reagent to determine the relative rates of reaction of the two dialkylzincs with that reagent has been used successfully before [38,99]. The reaction of phenylmercuric chloride; with a mixture of dimethyl and diethyl zinc in tetrahydrofuran at 25°C and in ether at reflux temperature; with a mixture of diethyl and di-n-propyl zinc in tetrahydrofuran both at 25°C and at reflux temperature and in ether at reflux temperature; and with a mixture of diethyl and di-i-propyl zinc in tetrahydrofuran at 25°C and reflux temperature and in ether at reflux temperature, was studied. Since the boiling point of dimethylzinc is 44°C it was not possible to study the reaction of phenylmercuric chloride with a mixture of dimethyl and diethyl zinc in refluxing tetrahydrofuran.

The results of the competitive experiments are shown in Tables 17, 18 and 19, on pages 121,123-4. In these tables the first three columns give the amounts of reactants used. The phenylmercuric chloride was weighed out. The amounts of dialkylzincs used were known since capsules containing known weights of dialkylzinc mixtures were used. The percentage composition of these mixtures was checked from time to time during each series of runs but no significant variations were found. The column headed "$\frac{RH}{RH_{orig'l}}$" refers to the composition of the gaseous mixtures evolved upon hydrolysis of samples of the mixtures of dialkylzincs used; and so gives a value for the percentage composition of the mixture of dialkylzincs used. The column headed "Vol. of gas expected" refers to the volume of gas that would be expected after hydrolysis if only one alkyl group is transferred from zinc to mercury. The column headed "$\frac{R'H}{RH}$ found" refers to the composition of the gaseous mixture evolved upon hydrolysis. The final column gives the relative rates of reaction of the two dialkylzincs used in the experiment.

The reaction was followed by hydrolysing the reaction mixture after reaction had occurred (10 minutes was found to be an adequate time to ensure complete reaction) and measuring the volume of the hydrocarbon mixture produced and analysing it by V.P.C. to determine the ratio $\frac{RH}{R'H}$. $\frac{k}{k'}$ is given by : [100]

$$\frac{k}{k'} = \frac{\text{log.(mole fraction of } R_2\text{Zn remaining)}}{\text{log.(mole fraction of } R_2\text{'Zn remaining)}}$$

and for this purpose a deficiency of phenylmercuric chloride was always used, also the initial ratio of $\frac{R_2Zn}{R'_2Zn}$ was kept as close to 1 as possible. A sample calculation is given below :

in general terms the reactions occuring are :

$$\begin{array}{ccccccccc} Me_2Zn & + & PhHgCl & \longrightarrow & MeHgPh & + & MeZnCl & + & Me_2Zn \\ (a)\text{moles} & & (x)\text{moles} & & (x) & & (x) & & (a-x) \end{array}$$

$$\begin{array}{ccccccccc} Et_2Zn & + & PhHgCl & \longrightarrow & EtHgPh & + & EtZnCl & + & Et_2Zn \\ (b) & & (y) & & (y) & & (y) & & (b-y) \end{array}$$

which on hydrolysis would yield 2a-x moles of methane and 2b-y moles of ethane.

The expression for the relative rates becomes :

$$\frac{k_{Et}}{k_{Me}} = \frac{\log \frac{b-y}{b}}{\log \frac{a-x}{a}}$$

This expression for the relative rates of reaction is only applicable to the reaction scheme shown above, which is based on the assumption that alkylzinc chlorides exist as distinct species. If this is not so, the expression used for the relative rates will not hold, but since the reacting dialkylzincs were always present in excess over the phenylmercuric chloride the differences between the relative rates found using the expression for relative rates given above and the true relative rates will not be large.

Taking for example run number 47 from Table 17, then $a = 1.570 \times 10^{-3}$ moles and $b = 1.707 \times 10^{-3}$ moles. The volume of gas collected was 129 ml. but the volume expected for the reaction indicated was 127 (.9) ml.; in all calculations the volume of gas expected was the figure used in calculating the comparative rates. The analysis of the mixture of hydrocarbons evolved showed

$$\text{MeH/EtH} = 1/0.913(4) \text{ or } \frac{\text{EtH}}{\text{MeH}} = 0.913(4).$$

Hence 1.913(4) ml. contain 1 ml. of MeH and 0.913(4) ml. of EtH,

$$\therefore 127.(9) \text{ ml. contain } \frac{127.(9)}{1.913(4) \times 22400} \text{ moles of MeH and}$$

$$\frac{127.(9) \times 0.913(4)}{1.913(4) \times 22400} \text{ moles of EtH,}$$

i.e. 127.(9) ml. contain 2.986×10^{-3} moles of MeH and 2.727×10^{-3} moles of EtH.

Hence $2a - x = 2.986 \times 10^{-3} \quad \therefore \quad x = 0.154 \times 10^{-3}$ moles

and $2b - y = 2.727 \times 10^{-3} \quad \therefore \quad y = 0.687 \times 10^{-3}$ moles.

$$\therefore \quad \frac{k_{Et}}{k_{Me}} = \frac{\log\left(\frac{1.707 - 0.687}{1.707}\right)}{\log\left(\frac{1.570 - 0.154}{1.570}\right)} = 4.9(78)$$

The figures for the analyses of the hydrocarbon mixtures produced on hydrolysis of all the reactions performed in tetrahydrofuran, whether at 25°C or at reflux temperature, were considered to be within experimental error of the original values of $\frac{R'H}{RH}$ before the experiments were performed, and in these cases the two dialkylzincs were considered to have reacted at the same rate. Taking an average of the values for the comparative rate of reaction of dimethylzinc and diethylzinc with phenylmercuric chloride in ether (Table 17) it is found that diethylzinc reacts 4.5 times faster than dimethylzinc. Again, taking an average of the values in Table 18, it is found that di-n-propylzinc reacts 3.7 times faster than diethylzinc in refluxing ether. The values for the comparative rate of reaction of diethylzinc and di-i-propylzinc in refluxing ether are too scattered to have any meaning, and reactions involving di-i-propylzinc will not be considered now.

The results obtained may be presented in table form on the style of Tables 2 and 3.

TABLE 9

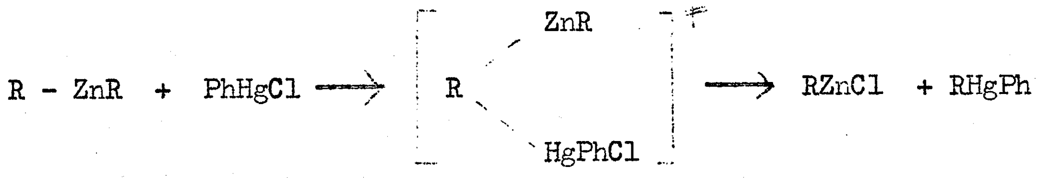
Relative rates of reaction of R_2Zn with PhHgCl

R	R_2Zn + PhHgCl in Et_2O at 35°C	R_2Zn + PhHgCl in THF at 25°C	R_2Zn + PhHgCl in THF at 65°C
Me	100	100	100
Et	450	100	100
n-Pr	1,665	100	100

The comparative rates of reactions performed in ether are not in very good agreement and this may be due to the fact that the experimental method used depends not upon analysing the products of the reaction, but upon analysis of the products of hydrolysis of the products of reaction together with reactants remaining. However, even if the absolute values of the comparative rates are of slightly dubious validity the experiments certainly showed that the order of reactivity was Me $<$ Et $<$ n-Pr, in ether, and that the orders of magnitude involved are very small. The results of the competitive studies in ethereal solution will be considered in detail first.

Since the absolute kinetics of these reactions could not be studied the molecularity of these reactions could not be determined, but it seems unreasonable that they should be other than either first order with respect to one reactant and zeroth order with respect to the other, or first order with respect to each reactant. Considering the possible mechanisms listed in Part A of Chapter I, some of these may be eliminated straight away. The possibility of the reaction proceeding by an alkyl bridge mechanism may be rejected since in that case it would be expected that when $R_2Zn = Me_2Zn$, the reaction should proceed very much faster than cases in which R is ethyl and n-propyl. The S_EC mechanism may be rejected due to the absence of any notable coordinating group in either reactant. A mechanism in which the rate determining step depends upon an ionisation of the phenylmercuric chloride may be excluded since then all the dialkylzincs used would react at the same rate with phenylmercuric chloride. An S_E1 mechanism in which the rate determining step is an ionisation of the dialkylzinc; $R_2Zn \rightleftharpoons R^- + RZn^+$, may also be excluded since the +I effects of the n-alkyl groups are in the order Me $<$ Et $<$ n-Pr and hence (since +I effects would retard such an ionisation) an order of reactivity Me $>$ Et $>$ n-Pr would be expected in such a case. The mechanisms left are S_E2 and S_Ei.

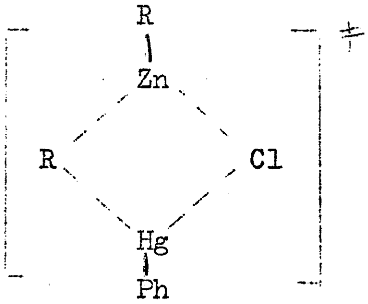
It would be expected [6,36] that an open S_E2 mechanism



$$R-ZnR + PhHgCl \longrightarrow \left[R \begin{matrix} ZnR \\ \\ HgPhCl \end{matrix} \right]^{\ddagger} \longrightarrow RZnCl + RHgPh$$

would lead to a steric sequence of reactivity, i.e.,

$Me_2Zn > Et_2Zn > n\text{-}Pr_2Zn$. However a closed transition state mechanism, S_Ei,

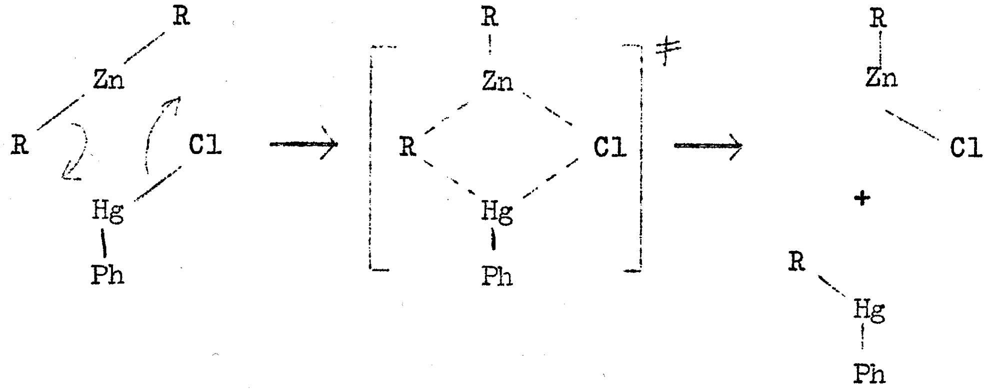


would be expected to lead to a "mixed sequence" with an interplay of steric and inductive effects. Table 2 on page 27 shows a number of reactions involving metal alkyls of the type R_2M in which just such a sequence is observed:

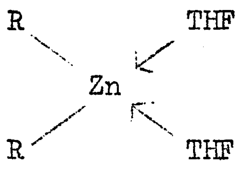
No.	R = Me	Et	n - Pr	Reaction
10	100	244	102	R_2Zn + p-toluidine in Et_2O
11	100	630	390	R_2Hg + HCl in DMSO/Dioxan
16	100	2080	2260	R_2Hg + HgI_2 in Dioxan
This work	100	450	1660	R_2Zn + PhHgCl in Et_2O

In a solvent such as ether a transition state such as an S_E2 one carrying a charge separation is not expected to be favoured, and the sequence found in this work, although polar in nature, is less pronounced than a wholly polar sequence such as is found in an S_EC reaction (c.f. Table 3).

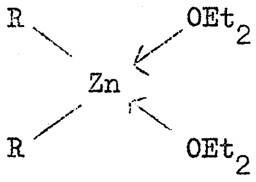
Thus the sequence found in this work is suggested as indicating an S_Ei-type transition state :



Considering now the competitive studies performed in tetrahydrofuran in which all the dialkylzincs appeared to react at the same rate, it is suggested that in these cases the reactions were so fast that no difference in rates was discernible. It is known that dimethylzinc will form a complex with tetrahydrofuran [101] and it is not unreasonable to expect that other dialkylzincs will also show a similar tendency. Complex formation of this type would tend to weaken the carbon to zinc bonds in the dialkylzinc. (It has been shown that the carbon to metal bonds in Et_3Al and Et_3Ga are weaker in ethereal solution than in the neat liquids [102].) Thus weakened, the bonds would break more readily and the reaction would be expected to occur very rapidly. An increased reactivity of organomagnesium compounds in such strongly solvating media as tetrahydrofuran and dimethoxyethane has been observed in the alkylation of metallic halides [102a]. Although the alkylation of phenylmercuric chloride is fast both in ether and in tetrahydrofuran it is suggested that complexing such as :



would be stronger than



and that the alkylation in tetrahydrofuran would be much faster than in ether. Hence the discrimination by the phenylmercuric chloride in reacting with either of the dialkylzincs present in the mixture will become less, and in the limit the two dialkylzincs present will react at the same rate with the phenylmercuric chloride.

Finally, considering the competitive studies between diethylzinc and di-i-propylzinc, mention must be made of difficulties encountered in the handling of di-i-propylzinc. During the fractional distillation of di-i-propylzinc in the final stage of its preparation it showed a ready tendency to decompose, depositing metallic zinc; much more so than diethylzinc and di-n-propylzinc. Also whilst being handled in the nitrogen box it readily decomposed depositing metallic zinc when exposed to an atmosphere in which diethylzinc scarcely fumed at all.

These observations, together with the scattered results of the competitive studies in ethereal solution, preclude experiments involving di-i-propylzinc from the discussion on mechanisms.

SECTION IV

THE NATURE OF ALKYLZINC HALIDES

The use of solutions thought to contain ethylzinc iodide in some of the kinetic studies prompted an investigation of the precise nature of ethylzinc iodide, particularly since conflicting reports were to be found in the literature [80,89,94,95]. This work was also extended to a study of ethylzinc bromide. The crux of the problem is which side of the equilibrium :

$$2RZnX \rightleftharpoons R_2Zn + ZnX_2 \qquad \ldots \quad (1)$$

is favoured and under what conditions.

The work done will be dealt with in two parts. Part A is concerned with isolating solid N,N,N',N'-tetramethylethylenediamine (TMED) complexes. Part B concerns the use of N.M.R. to investigate the species present in solution, and also some observations made during these studies, but which are not directly concerned with investigating the nature of alkylzinc halides, will be included in it for the sake of convenience.

PART A - Isolation of complexes

1. Ethylzinc iodide

Addition of TMED to solutions of ethylzinc iodide (prepared as on page 106) in both ether and tetrahydrofuran yielded a 1 : 1 complex of ethylzinc iodide and TMED. Identical products were obtained from solutions of ethylzinc iodide that had been freshly prepared and from solutions that had been kept for several weeks. A 1 : 1 zinc iodide complex was prepared from both THF and methanolic solutions for use as a reference compound. Both the ethylzinc iodide and the zinc iodide complexes are new compounds. Attempts to isolate a diethylzinc complex were unsuccessful. Addition of TMED to an equimolar mixture of diethylzinc and zinc iodide in THF - kept at room temperature - yielded the zinc iodide complex only, when the addition was made after the mixture had been made only two hours. Addition of TMED to a similar mixture that had been kept for seven days at 25°C, yielded the ethylzinc iodide complex only. The possibility that the addition of TMED had pushed equilibrium (1) [X = I, R = Et] to the right, in the first experiment, is removed by the isolation of a different complex in the second experiment. It is concluded that the natural position of equilibrium (1) for R = Et, X = I in tetrahydrofuran, is to the left but that some time is necessary for the system to reach equilibrium at the concentrations used. The possibility that ethylzinc iodide exists as a dimer $(EtZnI)_2$ as some Grignard reagents do [76] was removed by molecular weight determinations. The molecular weight of the species present in ethylzinc iodide solutions in both THF and ether was determined by ebullioscopy. The results are shown in Table 22. The degree of association found was never greater than 1.37 over the range of concentrations used. (0.03 - 0.4M in THF and 0.019 - 0.10M in ether.) More significantly, the degree of association found showed no trend with varying concentration. It is known that traces of moisture and oxygen can greatly increase the observed molecular weights in determinations on alkylmagnesium halides and trialkylgalliums [73,103], and so it is concluded that ethylzinc iodide is present mainly in a monomeric form in THF and ether in the concentrations used.

In one instance when the complex-forming experiments in tetrahydrofuran were being repeated, the solution of diethylzinc and zinc iodide was inadvertently allowed to become warm on being made up. In this case a material with analysis figures intermediate to those of zinc iodide complex and ethylzinc iodide complex was obtained when TMED was added to the mixture after it had been made up for two hours, which demonstrates that the syn-proportionation reaction :

$$Et_2Zn + ZnI_2 \xrightarrow{THF} 2EtZnI$$

proceeds quite readily under these conditions.

Unfortunately zinc iodide was not sufficiently soluble in ether to allow the complex-forming experiments performed in tetrahydrofuran solution to be repeated in ethereal solution.

2. Ethylzinc bromide

Attempts to prepare ethylzinc bromide by the direct reaction of ethyl bromide on zinc were unsuccessful, except when ethyl bromide in dimethylformamide was refluxed in the presence of a zinc-copper couple, when a reactive solution was obtained. However, attempts to isolate a TMED complex of the species present in solution were unsuccessful. It may have been that a competition for the species present in solution occurred between TMED and dimethylformamide.

Addition of TMED to an equimolar mixture of diethylzinc and zinc bromide in tetrahydrofuran yielded the zinc bromide complex when the addition was made both two hours after the mixture had been made up and after it had been kept for seven days at 25°C.

Addition of TMED to an equimolar mixture of diethylzinc and zinc bromide in diethyl ether after the mixture had been made up for fifteen minutes yielded a complex whose analysis corresponded to EtZnBr.TMED. The melting point of this material was 46°C, but it was not prepared in sufficient quantity to allow it to be recrystallised to a constant melting point. The ethylzinc bromide complex is also a new compound.

Thus ethylzinc bromide appears to be more labile than ethylzinc iodide in tetrahydrofuran and equilibrium (1) (R = Et, X = Br) lies to the right. Whilst in diethyl ether the equilibrium lies to the left. This difference in behaviour in the two solvents may be due to the greater solvating (or complexing) ability of tetrahydrofuran as compared to ether, causing the right-hand side of equilibrium (1) to be more favoured in tetrahydrofuran.

Conclusions

This work has shown that an identical product, ethylzinc iodide is obtained from the following two reactions :

$$\mathrm{EtI} + \mathrm{Zn} \longrightarrow$$

$$\mathrm{Et_2Zn} + \mathrm{ZnI_2} \longrightarrow$$

which is in agreement with the work of Jander and Fischer [89] although these latter workers did not characterise their product. Furthermore, the identification of ethylzinc iodide in ether and tetrahydrofuran now explains the preparation of unsymmetrical dialkylzincs as mentioned on p. 47.

$$EtI + Zn \longrightarrow EtZnI \xrightarrow{RMgX/Et_2O} EtZnR.$$

Previously only one set of work on the ethylzinc bromide system had been reported [94], in heptane solution, and then in a manner which renders interpretation of the results difficult. Work in which mixtures of Et_2Zn and $^{65}ZnCl_2$ in ether and tetrahydrofuran were treated with 2,2'-dipyridyl to precipitate a zinc chloride-dipyridyl complex [95] made no mention of interference by ethylzinc chloride. Thus, from chemical evidence, the main species existing in solutions of ethylzinc halides may be summarised as :

Solvent	Ether	THF	Ref.
X = I	EtZnI	EtZnI	This work
X = Br	EtZnBr	$Et_2Zn + ZnBr_2$	This work
X = Cl	$Et_2Zn + ZnCl_2$	$Et_2Zn + ZnCl_2$	[95]

A possible explanation of these results is that tetrahydrofuran forms a very strong complex with zinc halides compared with ethylzinc halides and diethylzinc. Hence in the equilibrium

$$Et_2Zn + ZnX_2 \rightleftharpoons 2EtZnX ,$$

the side containing the zinc halide is more favoured in tetrahydrofuran.

PART B - N.M.R. Studies

The N.M.R. spectra of the ethylzinc groups in ethylzinc iodide (prepared as on page 106) and diethylzinc in tetrahydrofuran were found to be identical, and also identical with the spectrum of a mixture of the two compounds (Figs.6 and 7). The fact that these two compounds should have the same N.M.R. spectrum is unusual. The possibility of a rapid exchange in the system diethylzinc plus ethylzinc iodide cannot, however, be excluded. In view of the previous results found in this work this similarity of spectra is interpreted as showing that N.M.R. cannot distinguish the two compounds and not as showing that the same species were present (as concluded by Evans and Maher from studies in ethereal solution [80]). For comparison the τ values obtained in this work and those obtained by Evans and Maher are shown in Table 10.

TABLE 10

τ values for the ethylzinc group

Solvent	EtZnI		Et_2Zn	
	τ CH_2	τ CH_3	τ CH_2	τ CH_3
-	-	-	9.698	8.854
Et_2O	9.651	~ 8.78	9.778	8.874
dioxan	9.740	8.897	-	-
CH_2Cl_2	-	-	9.744	8.87
C_6H_6	-	-	9.851	9.064
THF *	9.92	8.95	9.92	8.95

* This work (average of several spectral values)

The spectrum of a THF solution of TMED showed two peaks due to the amine; one at 7.74 τ whose area was one third of the area of the second peak at 7.90 τ. The first peak is due to the protons of the methylene groups in the amine and the second is due to the protons on the methyl groups. Considering the formula of the amine; $(CH_3)_2.N.CH_2.CH_2.N(CH_3)_2$, it is seen that there are 12 methyl protons and 4 methylene protons per molecule, hence the areas of the peaks due to these should be in the ratio 3 : 1.

1. The system ZnI_2 + TMED

The τ values of the amine peaks of spectra of solutions of zinc iodide with varying amounts of TMED (Table 20) are lower than those of the uncomplexed amine as might be expected due to electron withdrawal from the amine in complex formation. When the amine is present in excess over the zinc iodide the peaks due to the amine broaden and shift to high magnetic field towards the position of the peaks due to uncomplexed amine (Fig.8). It is suggested that equilibrium (a) lies well to the right :

$$\mathrm{TMED} + ZnI_2 \rightleftharpoons ZnI_2.\mathrm{TMED} \qquad \ldots \quad (a)$$

and so when the amine is present in deficiency it is all coordinated onto the zinc iodide. When the amine is present in excess an equilibrium as in (b) begins to operate

$$\mathrm{TMED}^* + ZnI_2.\mathrm{TMED} \rightleftharpoons ZnI_2.\mathrm{TMED}^* + \mathrm{TMED} \qquad \ldots \quad (b)$$

which leads to a merging of the peaks due to free and complexed amine.

Purely as a guide to the rate of this exchange process if the difference in frequency in c.p.s. for the peaks due to complexed amine and uncomplexed amine (40 c.p.s.) is substituted in the formula for the half-life of a species in an exchange process with equal populations at each site, in which the exchange process causes the peaks to just merge,

$$t = \frac{\sqrt{2}}{2\pi(\Delta\nu)} \quad [104];$$

a value for t, the half-life of a species at one site, of 0.0056 secs. is obtained. However it was found that the separation and positions of the two amine peaks varied with concentration; diluting a mixture of zinc iodide and a deficiency of amine caused the two amine peaks to move further apart and to low magnetic field (G, H and I of Fig.9), whilst diluting a solution of solid zinc iodide complex caused the two amine peaks to move closer together and to high magnetic field (J and K of Fig.9).

2. The system Et_2Zn + TMED

The spectrum of an equimolar mixture of diethylzinc and TMED (Fig.10) showed two amine peaks at 7.72 τ and 7.83 τ very close to the position of the peaks for uncomplexed amine, which suggests that diethylzinc may be considered as maintly uncoordinated, i.e. equilibrium (c) lies mainly to the left.

$$\text{TMED} + Et_2Zn \rightleftharpoons Et_2Zn.\,\text{TMED} \qquad \ldots \qquad (c).$$

3. The system EtZnI + TMED

Typical spectra of mixtures of ethylzinc iodide solutions (prepared as on page 106) with varying amounts of TMED are shown in Figs. 11 and 12, and the results are shown in Table 21. These spectra cannot be considered as spectra of mixtures of diethylzinc, zinc iodide and TMED, since in this case, with a deficiency of amine, only two amine peaks, both sharp, in the region 7.35 and 7.49 τ would be expected due to zinc iodide complex, and with an excess of amine over zinc iodide (i.e. at EtZnI : TMED ratios less than 1 : 0.5) two broad peaks upfield due to the exchange as in equilibrium (b) would be expected.

Considering first the spectrum of a mixture of ethylzinc iodide and TMED in the molar ratio of 1/0.225 (line one of Table 21), two pairs of amine resonances occur. The pair at 7.39 and 7.52 τ are considered to be due to zinc iodide complex present and the pair at 7.51 and 7.62 τ are due to ethylzinc iodide complex. From the relative areas of these peaks (the figures in brackets under the τ values in Table 21), it is seen that 44.4% of the amine is present as zinc iodide complex. Similarly in line two of Table 21, the pair of peaks at 7.41 and 7.53 τ are due to zinc iodide complex and the pair at 7.52 and 7.64 τ are due to ethylzinc iodide complex and 46.5% of the amine is present as zinc iodide complex. Again in line three of Table 21, the pair of peaks at 7.33 and 7.50 τ are due to zinc iodide complex and the pair at 7.45 and 7.59 τ are due to ethylzinc iodide complex, and 16.4% of the amine is present as zinc iodide complex. In these three cases all the amine peaks are sharp and since the amine is present in a deficiency, equilibrium (b) ($\text{TMED}^{*} + \text{ZnI}_2.\text{TMED} \rightleftharpoons \text{ZnI}_2.\text{TMED}^{*} + \text{TMED}$) and equilibrium (d)

$$\text{TMED}^{*} + \text{EtZnI.TMED} \rightleftharpoons \text{EtZnI.TMED}^{*} + \text{TMED} \quad \ldots \quad (d)$$

do not occur. However, the ethylzinc iodide is present in excess over the amine and it was found that the peaks due to the methylene groups of the ethylzinc group were broadened (Fig.11). This is suggested as being due to an exchange process in which the environment of the methylene group is altering. Equilibrium (e) represents the only possibility :

$$\text{EtZnI.TMED} + \text{Et}\overset{*}{\text{Zn}}\text{I} \rightleftharpoons \text{Et}\overset{*}{\text{Zn}}\text{I.TMED} + \text{EtZnI} \quad \ldots \quad (e)$$

and since the environment of the amine is unchanged its spectrum is not affected. Assuming that Fig.12 represents the case where the peaks due to methylene groups of complexed and uncomplexed ethylzinc iodide are just merged and taking the difference in c.p.s. between the methylene group of an uncomplexed ethylzinc iodide molecule and the methylene of a complexed ethylzinc iodide molecule as 5 c.p.s., substituting again in the formula

$$t = \frac{\sqrt{2}}{2\pi(\Delta\nu)} \quad [104]$$

a value of t, the half-life of a species before it exchanges, of 0.045 secs. is obtained. It is realised that this formula only applies to cases where the exchanging species are present in equal concentrations, but it is used merely to give a guide to the rate of the exchange process.

In cases where the EtZnI : TMED ratio becomes $1 \leqslant 1.0$ (lines 4 and five of Table 21) uncomplexed amine is present and equilibria (b) and (d) can operate leading to a broadening of amine peaks. Since there is no longer an excess of ethylzinc iodide over amine, equilibrium (e) can no longer operate and the peaks due to the methylene groups of the ethylzinc group are sharp.

To confirm that the assignment of all four amine peaks in lines 1 - 3 of Table 21 was correct, a spectrum of a solution of solid ethylzinc iodide complex was run and then again with successive additions of zinc iodide. The spectra are shown in Fig.14. The spectrum of 1.0M solution of ethylzinc iodide complex showed four amine peaks at 7.40, 7.57, 7.60 and 7.67 τ. Addition of zinc iodide so that the molar ratio of ethylzinc iodide complex to zinc iodide was 1 : 0.25 caused the two peaks at 7.40 and 7.52 τ to increase in size, and a further addition so that the molar ratio was 1 : 0.5 caused a further increase in size of these two peaks. Hence in this case the peaks due to complexed zinc iodide were the two adjacent low-field peaks at 7.40 and 7.52 τ. Yet in the assignment of the peaks in Table 21, clearly alternate peaks should be paired since the ratios of their areas must be 1 : 3. The middle two peaks in Fig.14 are very close (separation 0.03 τ or 3 c/s), and since it was found that the position of the peaks due to amine complexed to zinc iodide varied with concentration, it is suggested that both interpretations are correct. In Fig.14 the pairs of amine peaks due to the two complexed species are just separated and in the cases quoted in Table 21, the two sets of amine peaks due to the two different complexed species have just overlapped. This being so it would be expected that the peak due to the methyl protons of amine complexed to zinc iodide would coincide with the peak due to the methylene protons of amine complexed to ethylzinc iodide at a certain concentration. Figs. 15A and B show two such cases.

4. The system $Et_2Zn + ZnI_2$ + TMED

The spectrum of a mixture of diethylzinc, zinc iodide and TMED with the components in 1.0M, 1.0M and 1.4M concentrations respectively in tetrahydrofuran was run after the mixture had been kept in solid carbon dioxide since being made up, and again after being kept at room temperature for one week. The two spectra were identical and one of them is shown in Fig.13. The amine peaks occurred at 7.31, 7.44, 7.49 and 7.58 τ and their areas were in the ratios 1 : 5.2 : 3.2 : 15.3, and so the peaks at 7.31 and 7.49 τ are due to amine complexed to zinc iodide and those at 7.44 and 7.58 τ are due to amine complexed to ethylzinc iodide. Considering the ratios of the areas of the amine peaks 23.8% of the amine was present as zinc iodide complex. The concentrations of the components correspond to EtZnI : TMED in the ratio 1 : 0.7 and referring again to Table 21 it is seen that in all respects this spectrum is intermediate to those recorded on lines two and three. Since the concentrations of the components correspond to an EtZnI : TMED ratio of 1 : 0.7 it would be expected that equilibrium (e)

$$(\mathrm{EtZnI.TMED} + \mathrm{Et\overset{*}{Z}nI} \rightleftharpoons \mathrm{Et\overset{*}{Z}nI.TMED} + \mathrm{EtZnI})$$

would again operate. This was found to be the case and the spectrum of the methylene group of the ethylzinc group was broadened. Thus the mixture reacted to give ethylzinc iodide in between the time it was made up and the time its spectrum was first run, even though it was stored at -80°C during this time. It may be that one week at -80°C was sufficient time for the syn-proportionation reaction to proceed since in the case of the complex isolation experiments the reaction took some time between two hours and one week at 25°C to occur, or it may be that the continuous presence of the amine had some effect on the rate of syn-proportionation. It has already been shown that the reaction between diethylzinc and phenylmercuric chloride is probably faster in tetrahydrofuran than in ether, and so the presence of another coordinating reagent such as TMED might also be expected to accelerate a reaction :

$$R_2Zn + ZnX_2 \longrightarrow 2RZnX,$$

even though the amount of TMED coordinated to the dialkylzinc at any time may be quite low.

5. The system $ZnBr_2$ + TMED

This sytem was not investigated as fully as the zinc iodide plus TMED system, but a solution of zinc bromide with a deficiency of TMED showed two amine peaks at slightly higher τ values than in the zinc iodide case. Dilution of a solution of zinc bromide and a deficiency of TMED and dilution of a solution of zinc bromide complex had exactly the same effects as in the zinc iodide cases. (These spectra are shown in Fig.9, spectra A, B and C showing the effect of successive dilution of a solution of zinc bromide with a deficiency of amine and spectra D, E and F showing the effect of successive dilution upon a solution of zinc bromide complex.)

6. The system $Et_2Zn + ZnBr_2 + TMED$

The spectrum of a mixture of diethylzinc, zinc bromide and TMED in 1.0M, 1.0M and 0.5M concentrations in tetrahydrofuran respectively was run after the mixture had been stored under solid carbon dioxide since being made up, and again after the mixture had stood for one week at room temperature. The spectra were identical; one of them is shown in Fig.16. The spectrum which showed three peaks due to amine at 7.56, 7.66 and 7.72 τ would appear to be a case in which two amine peaks have coincided since the ratios of the areas of the peaks is 1 : 4.6 : 2.9. The spectrum obtained is not that which would be expected for a mixture of diethylzinc and zinc bromide complexes alone. The concentrations of the components correspond to a molar ratio of EtZnBr : TMED of 1 : 0.25 and by analogy to the ethylzinc iodide case the amine peaks would be expected to be sharp, but the spectrum of the methylene group of the ethylzinc group would be expected to be broadened. The spectrum of this latter group is only very slightly broadened but then if an exchange such as

$$Et\overset{*}{Zn}Br + EtZnBr.TMED \rightleftharpoons Et\overset{*}{Zn}Br.TMED + EtZnBr \quad \ldots \quad (f)$$

did occur, it would be unlikely to occur at the same rate as the corresponding ethylzinc iodide case. The effect of adding an excess of zinc bromide to this sample is shown in the upper spectrum in the same Fig. (Fig.16). The spectrum of the ethylzinc methylene group is slightly sharper and the amine peaks are now two in number, from which it is concluded that the original spectrum was that of a mixture containing some ethylzinc bromide complex. The added zinc bromide stripped the amine from the weak ethylzinc bromide complex and so destroyed equilibrium (f), forming more zinc bromide complex with the amine from it. Thus ethylzinc bromide complex exists and the failure to isolate it in the preparative work may be explained by its labile nature.

Zinc bromide was not sufficiently soluble in ether to allow N.M.R. studies of the same zinc bromide systems in ether.

7. Conclusions

From the chemical studies it was concluded that ethylzinc iodide exists in ether and tetrahydrofuran and that ethylzinc bromide exists in ether, but that "ethylzinc bromide" in tetrahydrofuran and "ethylzinc chloride" in both ether and tetrahydrofuran exist as diethylzinc plus zinc halide. The N.M.R. studies have shown that in tetrahydrofuran the complex EtZnI.TMED exists. However, it appears to be in an equilibrium with zinc iodide complex (and also diethylzinc) :

$$2EtZnI.TMED \rightleftharpoons ZnI_2.TMED + Et_2Zn + TMED$$

since both EtZnI.TMED and ZnI_2.TMED were observed in tetrahydrofuran solution.

This observation is not in direct conflict with the observations from chemical studies, but suggests that the presence of TMED modifies the equilibrium and tends to shift it to the side of the strongest complex ($ZnI_2 \cdot TMED$).

Thus :

$$Et_2Zn + ZnI_2 \xrightleftharpoons{THF} 2EtZnI$$

$$Et_2Zn + ZnI_2 \xrightleftharpoons[TMED]{THF} 2EtZnI$$

The ethylzinc bromide system appears to be more complicated in that the chemical studies yielded only zinc bromide complex from a tetrahydrofuran solution of diethylzinc and zinc bromide, and yet the N.M.R. studies showed the presence of a zinc bromide complex and an ethylzinc bromide complex in a tetrahydrofuran solution of diethylzinc and zinc bromide plus TMED. This result from the chemical studies may be due, not to the absence of ethylzinc bromide in tetrahydrofuran, but due to a disturbance of the equilibrium by TMED, or even by the preferential precipitation of the least soluble of all the possible complexes ($ZnBr_2 \cdot TMED$). From both the chemical and the N.M.R. studies it is concluded that ethylzinc bromide does exist in tetrahydrofuran solution as the TMED complex, and that in the absence of the amine it is also possible that ethylzinc bromide exists.

The observations of Dessy [95] may be explained by similar reasoning. In both ether and tetrahydrofuran the equilibrium

$$Et_2Zn + ZnCl_2 \rightleftharpoons 2EtZnCl$$

may lie either to the left or right; but Dessy only isolated a zinc chloride-dipyridyl complex. This may be due either to the fact that the equilibrium lies naturally to the left, or that the equilibrium lies naturally to the right, and the addition of the 2,2'-dipyridyl shifted it to the left.

Finally, from both chemical and N.M.R. studies the following conclusions on the nature of the ethylzinc halides may be drawn :

(i) "ethylzinc iodide" in tetrahydrofuran definitely exists as EtZnI.

(ii) "ethylzinc iodide" in ether definitely exists as EtZnI.

(iii) "ethylzinc bromide" in tetrahydrofuran probably takes part in a labile equilibrium : $Et_2Zn + ZnBr_2 \rightleftharpoons 2EtZnBr$.

(iv) "ethylzinc bromide" in ether probably exists as EtZnBr.

(v) "ethylzinc chloride" in both ether and tetrahydrofuran either exists as a mixture of diethylzinc and zinc chloride or takes part in a labile equilibrium : $Et_2Zn + ZnCl_2 \rightleftharpoons 2EtZnCl$.

From the N.M.R. spectra the TMED complexes prepared may be deduced to be chelate compounds. Chemical analysis showed them to be 1 : 1 complexes, and retention of the characteristic TMED N.M.R. spectrum in the complexed amine showed that the amine part of the molecule was symmetrical. Attachment of the amine to zinc by only one nitrogen atom would have removed the equibalence of the methyl and methylene groups attached to each nitrogen and produced further splitting of the amine spectrum.

Considering the alkylmetal halides of Group II in general it is known that alkylmercury halides (X = Cl, Br, I) exist, and are identifiable crystalline solids. Furthermore, the equilibrium in solution lies far on the side of the RHgX compounds :

$$R_2Hg + HgX_2 \rightleftharpoons 2RHgX$$

Very recently, in spite of previous reports to the contrary, it has become clear that Grignard reagents in dilute solution in ether and in tetrahydrofuran may exist in some cases as monomeric RMgX (e.g. R = Et, X = Br). In the present work, in at least one case, an alkylzinc halide (EtZnI) has been identified in ether and tetrahydrofuran. Thus for magnesium, zinc and mercury the existence of the species RMX is known.

SECTION V

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

1. Kinetic studies

The following reactions have been studied :

(a) $Et_2Zn + PhHgCl \longrightarrow EtHgPh + EtZnCl$ in ether and tetrahydrofuran at °C.

(b) $Et_2Zn + EtHgCl \longrightarrow Et_2Hg + EtZnCl$ in ether and tetrahydrofuran at °C.

(c) $EtZnI + HgI_2 \longrightarrow EtHgI + ZnI_2$ in tetrahydrofuran at 25°C.

(d) $EtZnI + EtHgI \longrightarrow Et_2Hg + ZnI_2$ in tetrahydrofuran at 25°C,

and all were found too fast to follow.

The reaction $EtZnI + PhHgI \longrightarrow EtHgPh + ZnI_2$ goes very rapidly at first and then tails off rapidly in tetrahydrofuran at 0°C. None of these reactions is worth any further investigation since the problems of dealing with oxygen and moisture sensitive materials and using rapid reaction kinetic methods are difficult to combine. No information concerning the mechanisms of these reactions could be deduced.

2. Comparative studies

The order of reactivity of dimethylzinc, diethylzinc and di-n-propylzinc with phenylmercuric chloride in refluxing ether was found to be

$$\begin{array}{ccccc} Me & < & Et & < & n\text{-}Pr \\ (1) & & (4.5) & & (16.6) \end{array}$$

and it is suggested that these reactions proceed by an S_Ei mechanism. The same dialkylzincs were found to react at the same rate with phenylmercuric chloride in tetrahydrofuran at 25°C and diethylzinc and di-n-propylzinc were found to react at the same rate in refluxing tetrahydrofuran. It is suggested that all these reactions are very fast.

The applicability of the method used is limited and the results produced from it are also of limited usefulness. In general, the field of alkyl exchange reactions between zinc and mercury compounds appears to be populated with numbers of very fast reactions and unless this extreme reactivity can be curbed in some way mechanistic studies in this field may not be worthwhile.

3. The nature of alkylzinc halides

It has been shown that ethylzinc iodide exists in ethereal and tetrahydrofuran solution as the monomeric species EtZnI.

The new compounds ZnI_2.TMED, EtZnI.TMED and EtZnBr.TMED have been prepared. The existence of ethylzinc bromide in ethereal solution as EtZnBr is suggested. The method of identifying the various TMED complexes in tetrahydrofuran by N.M.R. spectroscopy was quite successful, but as addition of TMED may alter equilibria present in solution extrapolation to deduce the species present in solution is not justified unless check experiments are carried out. The method might conveniently be extended to study the higher alkylzinc halides about which very little is known, and may even be of use in determining the nature of the alkylcadmium halides, together with molecular weight determinations. The N.M.R. studies revealed a number of interesting phenomena, all of which might be worth further study. The exchanges involving zinc halides and TMED would present little difficulty, particularly in the handling of the reagents.

EXPERIMENTAL

SECTION I

GENERAL TECHNIQUES

1. Introduction

The melting points and boiling points recorded are uncorrected. With regard to the purity of the dialkylzincs prepared the term "moles of active alkane" refers to the number of g.moles of alkane produced by the hydrolysis of a sample of dialkylzinc, divided by the number of g.moles of dialkylzinc hydrolysed. The diethyl ether used was distilled, dried over calcium chloride, redistilled and stored over sodium wire. The tetrahydrofuran used was distilled and stored over sodium. Immediately prior to use it was distilled from lithium aluminium hydride under nitrogen. The nitrogen used in this and other operations was British Oxygen "white-spot" nitrogen, and was purified by passing it through a gas-train consisting of chromous chloride and concentrated sulphuric acid bubblers and phosphorous pentoxide drying towers. The carbon dioxide used was purified by passing it through a similar gas-train. All the dialkylzincs used were stored under solid carbon dioxide to minimise their thermal decomposition.

2. The handling of dialkylzincs

Reactions with dialkylzincs were carried out by either crushing or snapping a capsule containing dialkylzinc in the presence of the appropriate reagent. Crushing capsules were blown from soda glass tubing of 2.5 mm. diameter. The length of the neck of each capsule was approximately

4 cm. and the diameter of the bulb 1 cm. They each held approximately 0.1 g. of dialkylzinc and were used in determining the purity of the dialkylzincs. The snapping capsules were made from 7 mm. o.diameter soda glass tubing and were approximately 7 cm. long, and held up to 1 g. of dialkylzinc. Both types of capsule were oven dried and then flushed with nitrogen. To make the snapping capsules the glass tubing was sealed at one end and pulled out into a neck about two thirds of the way along its length. Both types of capsule were filled with dialkylzinc in a nitrogen box using a syringe. The crushing capsules were then sealed at the open end and the snapping capsules sealed at the neck. Both types of capsule were weighed before and after filling so that the weight of the contents were known. Mixtures of dialkylzincs were made by syringing the appropriate quantities of the two dialkylzincs into a flask in a nitrogen box. After thorough mixing the mixture was syringed into the capsules in the normal way.

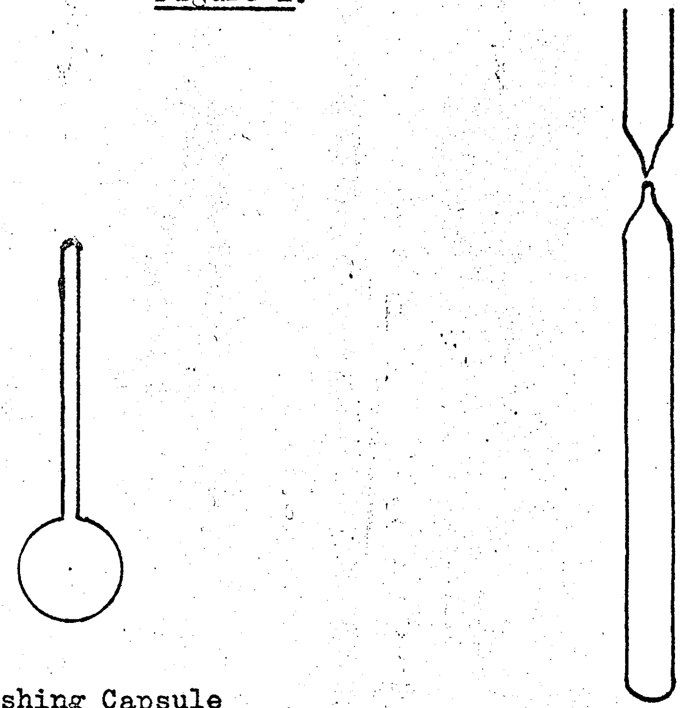
When using ethylzinc iodide solutions in kinetic experiments it was necessary to use a larger version of the snapping-type capsule capable of holding 10 ml. of solution. All three types of capsule are shown in Fig. 1. These larger capsules were not filled in a nitrogen box, but by using a multiple pig technique; the apparatus is shown in Fig. 2.

3. Analytical techniques

(a) The determination of zinc.

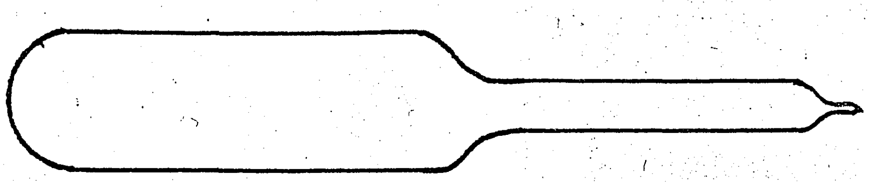
The zinc content of dialkylzincs and zinc complexes prepared was determined by titration with E.D.T.A. at pH 10. A stock solution of 0.01M

Figure 1.

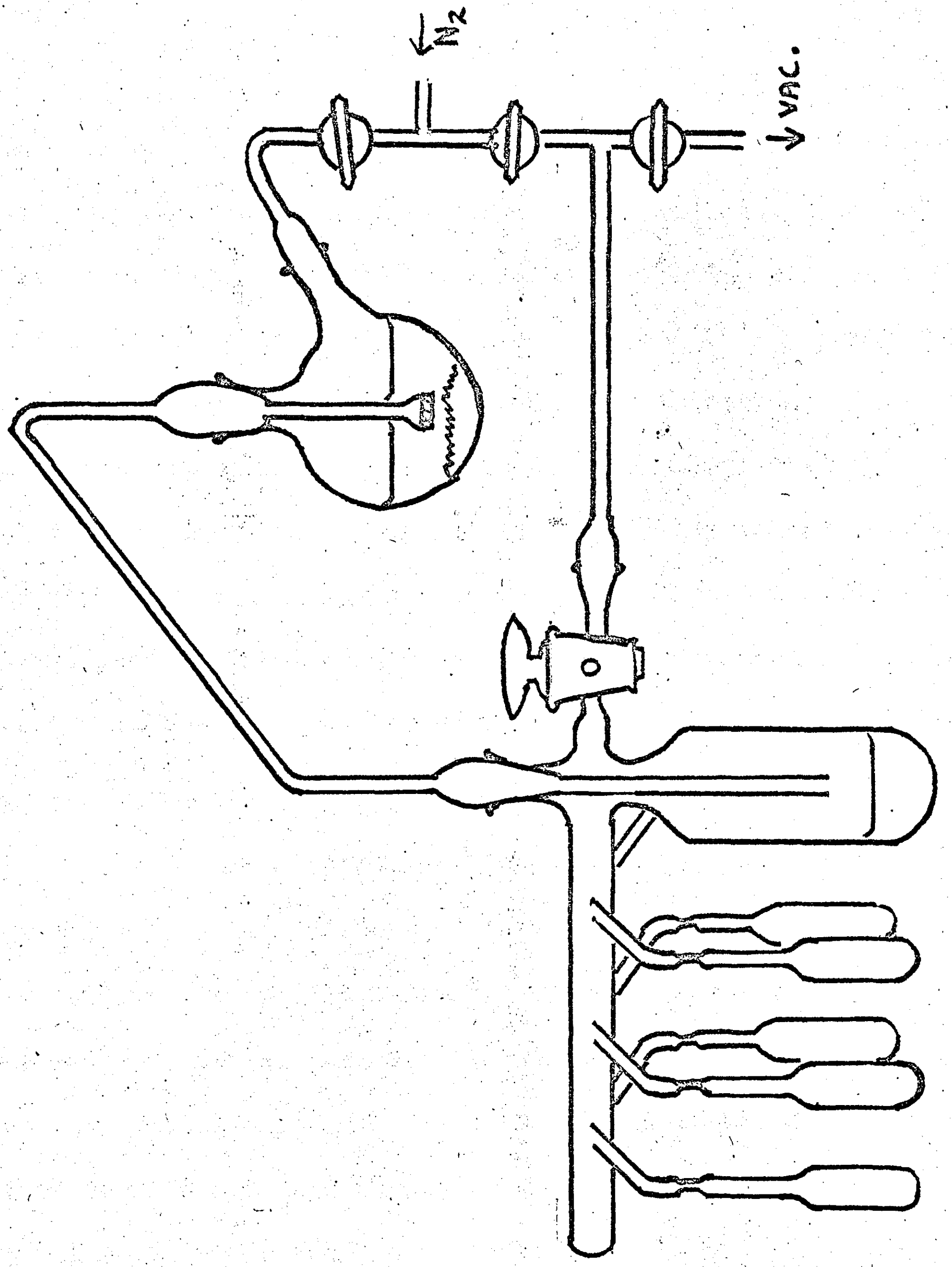


Crushing Capsule

Small Snapping Capsule



Large Snapping Capsule



Capsuling EtZnI solutions

Figure 2.

E.D.T.A. was prepared by dissolving disodium ethylenediaminetetra-acetic acid in distilled water, and was standardised each time before use against a standard magnesium solution made by dissolving pure magnesium raspings in dilute hydrochloric acid. A 1% solution of eriochrome black T in triethanolamine was used as the indicator throughout. The dialkylzinc to be determined was dissolved in 0.1N sulphuric acid by crushing a capsule of it under the acid. The resulting solution was neutralised to methyl red with ammonium hydroxide, buffered and then titrated. Complexes to be analysed for zinc were dissolved in 0.1N sulphuric acid and the solution treated in the same way as above.

(b) The determination of halide.

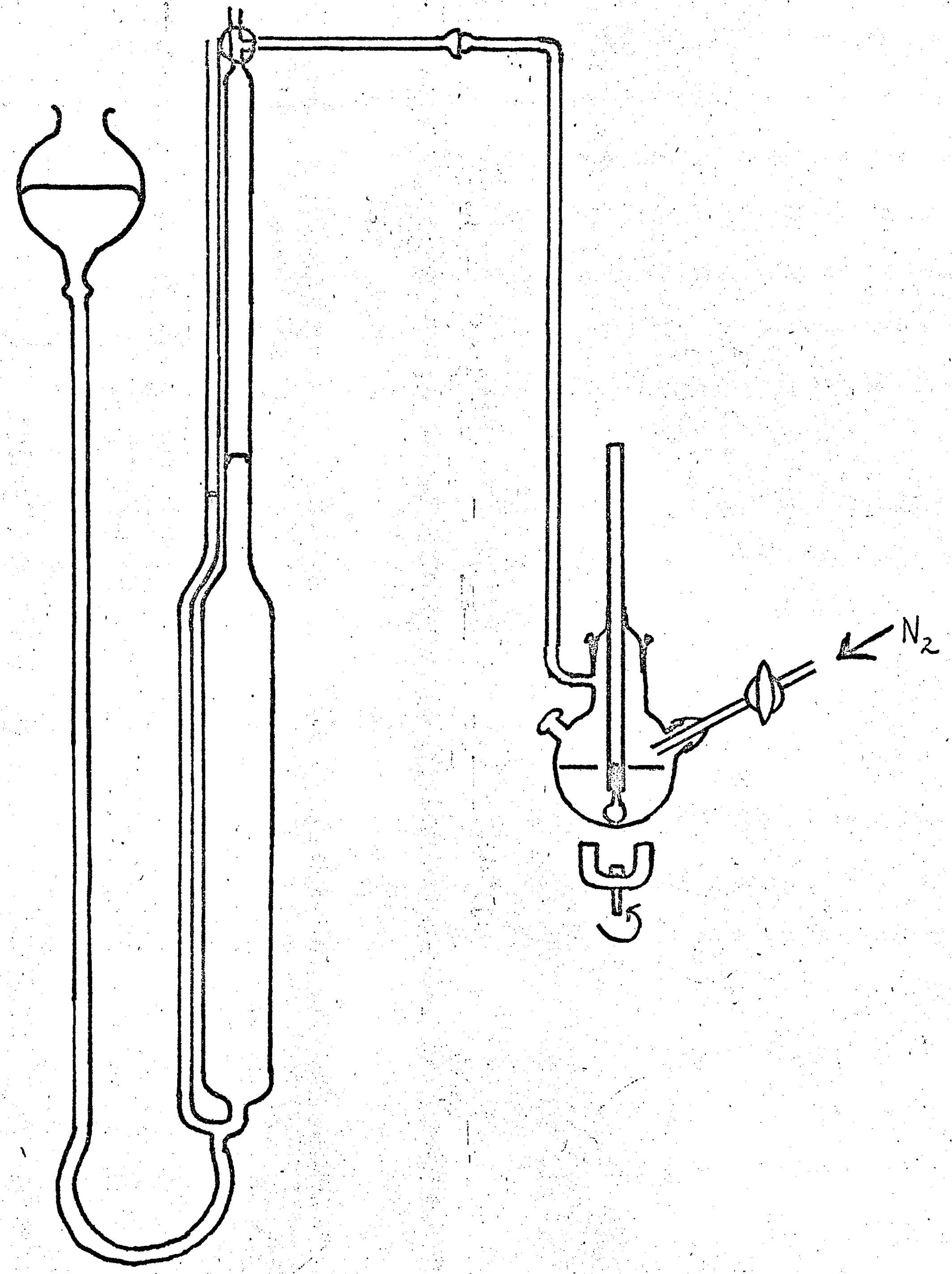
Chloride and iodide in kinetic samples and bromide and iodide in complexes were determined by Volhard's method. The solution to be analysed was acidified with dilute nitric acid and excess silver nitrate solution was added. In the case of chloride determinations a few ml. of nitrobenzene were also added. The excess silver nitrate solution was back-titrated with standard potassium thiocyanate solution using a saturated solution of ferric alum as indicator.

(c) The determination of active alkane in dialkylzincs.

The apparatus used is depicted in Fig. 3. The sample (1-2×10^{-3} moles), in a crushing capsule was placed in the crusher. 0.1N sulphuric acid (100 ml.) was poured into the flask, and the gas inlet tube

Figure 3.

Apparatus for hydrolysis of dialkylzincs



connected to the nitrogen supply to flush out the flask and the gas burette. After ½ hour the gas inlet was closed and the gas burette connected to the reaction flask alone. The pressure in the apparatus was set at about 10 cm. of mercury below atmospheric pressure so that when hydrolysis occurred the sudden surge of pressure did not damage the apparatus. The apparatus was then left for another ½ hour to equilibrate before crushing the capsule by a smart tap on top of the crushing rod, and allowing hydrolysis to take place. The aqueous solution produced was analysed for zinc to determine the amount of dialkylzinc which had been hydrolysed, and measurement of the volume of alkane produced, corrected to S.T.P., allowed the moles of active alkane to be calculated.

In the case of hydrolysis of mixtures of dialkylzincs, samples of the alkane produced were withdrawn through a rubber serum cap with a syringe, to be analysed by vapour phase chromatography.

4. Vapour Phase Chromatography

(a) Chromatography of gaseous mixtures.

The apparatus used was a Shandon chromatograph with a thermocouple detector unit. The column used was a four foot long copper tube, of 4 mm. internal diameter, packed with alumina (100-125 mesh) with 2% squalane added. The gaseous mixtures to be analysed were binary and were methane/ethane and ethane/propane. In the case of the first mixture it was necessary to immerse one foot of the column's length in an acetone-solid carbon dioxide mixture to effect a separation of methane and any air present.

These mixtures could be determined quantitatively since the response of the instrument was proportional to the mass of the component causing the response and its heat of combustion. Thus :

$$\frac{\text{moles of alkane A}}{\text{moles of alkane B}} = \frac{\text{Peak area of A}}{\text{Peak area of B}} \times \frac{\text{Heat of combustion of B(Kcal/mole)}}{\text{Heat of combustion of A(Kcal/mole)}}$$

for a mixture of alkanes A and B.

The areas of the peaks were determined by carefully cutting them out and weighing them. The mean of at least six determinations was taken for each binary alkane mixture. The reproducibility of results was within 4%.

(b) Chromatography of liquid mixtures.

The apparatus used was a Pye argon chromatograph with an ionisation detector. The column was a glass one, five feet long, internal diameter 0.4 cm, packed with celite with 2% added tritolyl phosphate.

This apparatus was used for identifying the components in ethereal and tetrahydrofuran solutions of reaction products. This was done by comparing the chromatograms of the samples with the chromatograms of the pure possible products run under the same conditions.

5. Nuclear magnetic resonance studies

These studies will be dealt with in a later separate section.

SECTION II

PREPARATION OF REAGENTS

1. The preparation of dialkylzincs by Noller's method [86]

(a) The general method

An active zinc-copper couple was prepared by heating a finely ground mixture of zinc dust and cupric oxide (13/1 by weight) to just below red heat, under a vigorous stream of hydrogen, in a three-necked flask. After cooling, the couple was broken up into small lumps using a glass rod, whilst protected by a vigorous stream of nitrogen. The flask was then fitted with a tap funnel, a mercury-seal stirrer and a double surface reflux condenser. The nitrogen supply was connected through two T pieces to a bubbler and the T pieces connected to the tops of the tap funnel and the condenser.

An equimolecular mixture of the alkyl iodide and bromide were added, slowly, with stirring. It was found easiest to initiate the reaction by adding some of the alkyl iodide first, and warming gently. When the reaction started it was controlled by alternately adding the alkyl halide mixture and the application of an ice bath. After the addition the stirrer was removed and the flask left overnight.

The next morning the tap funnel and condenser were replaced by stoppers and the centre neck of the flask connected via glass tubing to a two-necked flask which was connected to a trap and a vacuum line. Any unreacted alkyl halide and any dialkylzinc already present were removed by pumping, with the trap immersed in a "Drikold"-acetone mixture. The reaction vessel was heated slowly in an oil bath. When the temperature of this had risen to 90°C a "Drikold"-acetone mixture was put around the two-necked receiving flask to collect the dialkylzinc which was beginning to distil over. The temperature of the oil bath was raised to 180°C over a period of $1\frac{1}{2}$ hours. The dialkylzinc collected was purified by fractional distillation.

(b) The preparation of diethylzinc

A mixture of ethyl iodide (78 g., 0.5 moles) and ethyl bromide (54.5 g., 0.5 moles) was added to a zinc-copper couple (Zn 130 g., CuO 10 g.) over $1\frac{1}{2}$ hours, in a 500 ml. three-necked flask. The reaction had initiated 10 minutes after the addition of some of the ethyl iodide (20 g.) alone, and gentle warming. Next day, distillation of the reaction mixture yielded diethylzinc (55.8 g., 90.9% yield) over the range 90°C/0.25 mm. - 180°C/0.2mm. The receiving flask contained glass wool, which aided regular boiling of the crude yield when it was fractionally distilled to give pure diethylzinc (38.5 g.), b.p. 50-52°C/74 mm. (lit.Et_2Zn 117.7°C/760 mm., 16°C/9.5 mm) [100a][105] in 61% yield. (Found: Zn 52.78%; $C_4H_{10}Zn$ requires 52.94%. Moles of active alkane, 1.98).

(c) The preparation of di-n-propylzinc

A mixture of n-propyl iodide (85.0 g., 0.5 moles) and n-propyl bromide (66.5 g., 0.5 moles) was added to a zinc-copper couple (Zn 130 g., CuO 10 g.) over 2 hours. Distillation of the reaction mixture gave di-n-propylzinc (60 g., 80% yield) over the range 140°C/0.5 mm. - 170°C/0.5 mm. The product was fractionally distilled to give di-n-propylzinc (51 g., b.p. 50°C/15 mm.)(lit. 48°C/10 mm. 39-40°C/9 mm.) [86] in 68% yield. (Found: Zn 42.13%; $C_6H_{14}Zn$ requires 43.15%. Moles of active alkane, 1.95).

(d) The preparation of di-i-propylzinc

This was made by Noller's general method, with modifications due to Sorcos and Morgana [106]. The mixture of i-propyl iodide (85.0 g., 0.5 moles) and i-propyl bromide (66.5 g., 0.5 moles) was added to the zinc-copper couple (Zn 130 g., CuO 10 g.) over 5 hours, after the reaction had been initiated. The reaction mixture was maintained at 40°C, and stirred, for ½ hour after the addition of the alkyl halides. When the reaction mixture was distilled, the next day, a mercury diffusion pump was used so that the di-i-propylzinc produced would distil at the lowest possible temperature. The product was obtained over the temperature range 95 - 180°C, in a 67% yield (63.7 g.). The fractional distillation of the crude product was attempted at 22 mm., but before it would boil a thick deposit of zinc was observed in the distilland. The distillation was stopped. A pure product (27 g.) was finally obtained b.p. 40.0°C/12 mm. in 35.6% yield, but the residue contained a large deposit of zinc (lit. b.p. 40.3°C/13 mm.)[106] (Found: Zn 42.84%, $C_6H_{14}Zn$ requires 43.15%. Moles of active alkane, 1.97).

2. The preparation of ethylzinc iodide solutions

These solutions were made in small batches so that they could be used up as soon as possible. The general method of preparation was the same as the first stage of the preparation of diethylzinc by Noller's method. Ethyl iodide (15.5 g., 0.1 moles) was added in one portion to a zinc-copper couple (Zn 13 g., CuO 1 g.) in a 100 ml. two-necked flask and stirred magnetically from underneath. The reaction was initiated after $\frac{1}{4}$ hour by gentle warming and then controlled by the occasional application of an ice bath. The next day the reaction flask was connected to a trap immersed in a "Drikold"-acetone mixture and pumped down to 0.2 mm. to remove unreacted ethyl iodide and any diethylzinc formed. Under a nitrogen guard either diethyl ether (40 ml.) or tetrahydrofuran (40 ml.) was added to the reaction mixture, which was then stirred magnetically again until the solid reaction mixture had been broken up, and all but the excess couple had dissolved. During this solvation, heat was evolved. The mixture was left to settle for 2 days and then the supernatant liquid filtered off through a glass sinter, under nitrogen, into the capsuling apparatus (Fig. 2).

3. The preparation of mercuric compounds

The mercuric iodide used was B.D.H. Laboratory Reagent grade material that had been recrystallised twice from methanol. The ethylmercuric chloride and phenylmercuric chloride used were also B.D.H. Laboratory

Reagent grade materials and were recrystallised from benzene. Ethylmercuric iodide and phenylmercuric iodide were both made from the corresponding chlorides by a simple double decomposition reaction with sodium iodide in acetone. Both were recrystallised from benzene, after preparation. As an example the preparation of phenylmercuric iodide on a 1/40 molar scale is described.

Phenylmercuric chloride (7.82 g.) was dissolved in acetone (600 ml.) with heating. The cold solution was added to a solution of sodium iodide (7.48 g., a two molar ratio) in acetone (50 ml.). The mixture was boiled for ten minutes and then allowed to cool. The precipitate of sodium chloride was filtered off at the pump and the filtrate evaporated to dryness. The solid residue was boiled with distilled water (500 ml.) for ten minutes and the slurry filtered. Sodium chloride and sodium iodide were carried away in the filtrate. The residue of phenylmercuric iodide was dried at the pump and then recrystallised from benzene. Yield 9.83 g., 97.1% of the theoretical yield.

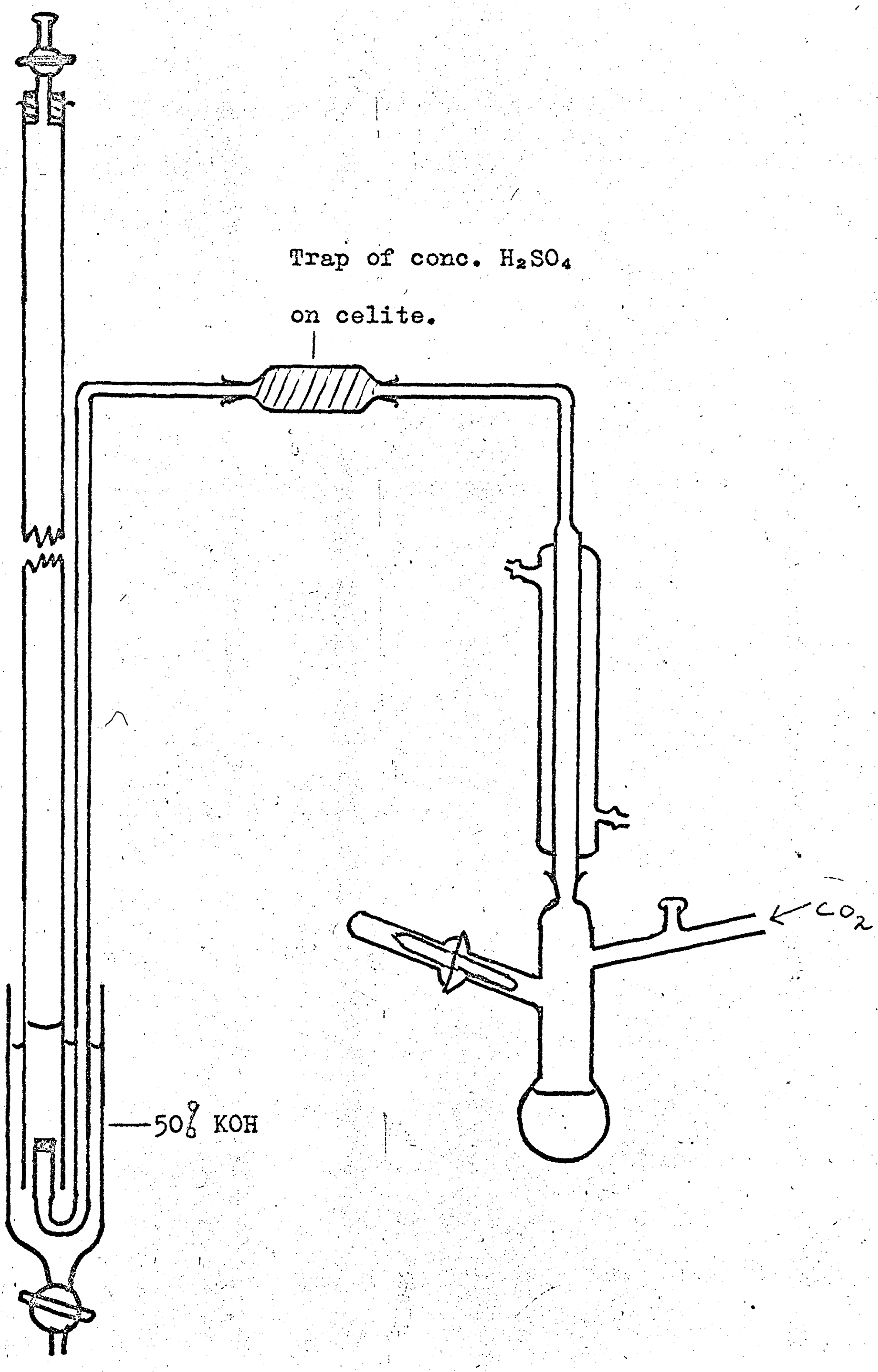
SECTION III

KINETIC STUDIES

1. The identification of the reaction between diethyl zinc and phenylmercuric chloride

(a) In tetrahydrofuran

Phenylmercuric chloride (1.6 - 1.9 m.moles) was placed in the reaction vessel (Fig. 4) and tetrahydrofuran (25 ml.) was added. The apparatus was flushed with carbon dioxide until only carbon dioxide was issuing into the gas collection tube. (As indicated by the appearance of small bubbles which dissolved in the 50% potassium hydroxide immediately, only). A snapping-type capsule of diethylzinc was then placed in the ball and socket side arm. The tetrahydrofuran was refluxed by a refluxing methylated spirit vapour jacket around the reaction vessel. When all the phenylmercuric chloride had dissolved and the tetrahydrofuran was refluxing at a steady rate the ball and socket side arm was flexed and the capsule of diethylzinc broken, allowing it and its contents to fall into the reaction vessel. The mixture was allowed to react for ten minutes and then hydrolysed by the careful addition of 2 ml. of either dilute mineral acid or water. After fifteen minutes when the evolution of gas had ceased and only carbon dioxide was issuing from the apparatus, the reaction residue was iodinated by the addition of excess solid iodine. The mixture was then extracted with ether (10 ml.) and the extract analysed by vapour phase



Apparatus for competitive experiments
Figure 4.

chromatography. The volume of hydrocarbon that had been produced in the hydrolysis was measured and corrected to S.T.P. The results of these experiments are shown in Table 11.

TABLE 11

Run No.	Moles of $Et_2Zn \times 10^3$	Moles of $PhHgCl \times 10^3$	Vol. of gas produced	Vol. of gas expected (c.f.p.)
12	3.301	1.692	106 ml.	109 ml.
15	3.808	1.877	129 ml.	128 ml.
16	3.295	1.950	104 ml.	103 ml.
17	3.368	1.760	112 ml.	111 ml.

Run No.	Contents of ethereal extract	Hydrolysed by
15	Et_2O, THF, EtI, C_6H_6	dil. HCl
16	Et_2O, THF, EtI, C_6H_6	dil. H_2SO_4
17	Et_2O, THF, EtI, C_6H_5I	H_2O

(b) <u>In ether</u>

These experiments were performed in the same way as in tetrahydrofuran except that it was necessary to use 200 ml. of ether, in a larger reaction vessel, which was placed in a water-bath at 40°C. It was also necessary to stir the contents of the reaction vessel magnetically from underneath to aid the dissolving of the phenylmercuric chloride. The ethereal residue was too dilute to be examined immediately by V.P.C., but after concentration it gave negative results; the small amount of organic iodides present must have been lost in the concentration process. The results of these experiments are shown in Table 12.

TABLE 12

Run No.	Moles of EtZn x 10^3	Moles of PhHgCl x 10^3	Vol. of gas produced	Vol of gas expected (c.f. p.)
18	4.609	1.011	175 ml.	183 ml.
19	5.495	0.8613	220 ml.	226 ml.
20	2.884	1.125	99 ml.	104 ml.

2. An attempted study of the kinetics of the reactions between diethylzinc and phenylmercuric chloride and between diethylzinc and ethylmercuric chloride

Separate solutions of the reactants were pipetted into the two arms of a nitrogen filled reaction vessel, which was immersed in an ice-water bath. After allowing 30 minutes for the solutions to attain the temperature of their surroundings the reaction vessel was tilted, allowing the two solutions to mix. Zero reaction time was taken as this moment. The reaction mixture was stirred magnetically from underneath. In these experiments one point only was taken to determine the time-scale of the reaction. The samples were taken by pipette whilst the reaction mixture was protected by a stream of nitrogen. The sample was pipetted into an ice-cold solution of potassium hydrogen phthalate in water to quench it. This solution was then carefully extracted with benzene (2 x 15 ml.) to remove organomercury compounds, and the aqueous layer titrated for chloride by Volhard's method. The results, in terms of percentage reaction, which had occurred when each point was taken, are shown in Table 13.

TABLE 13

Reaction of Et_2Zn with PhHgCl and EtHgCl at 0°C

Run No.	[Et_2Zn] m/l.	[PhHgCl] m/l.	Solvent	Reaction Time (secs.)	% Reaction
1	.05478	.01756	THF	1800	98
2	.11980	.01769	"	34	90
3	.09405	.02205	"	66	93
4	.02071	.01979	"	56	44
5	.02288	.02098	"	62	48
6	.02107	.00300	"	78	65
7	.02107	.00254	"	60	58
8	.02107	.00254	"	60	56
12	.00718	.00071	Et_2O	180	95
13	.00588	.00064	"	60	89
		[EtHgCl] m/l.			
9	.02107	.00288	THF	60	55
10	.02107	.00288	"	60	41
11	.02107	.00288	"	120	63
14	.00643	.00118	Et_2O	30	54
15	.00643	.00117	"	30	49

3. An attempted study of the kinetics of the reaction between ethylzinc iodide and phenylmercuric iodide in tetrahydrofuran at 0°C.

The solutions of the reactants were put into two arms of a reaction vessel and could be mixed by tilting the vessel. The concentration of the ethylzinc iodide solution was determined by both acid/alkali and iodide titrations. The reaction was followed by determining the iodide liberated from the phenylmercuric iodide by Volhard's method as described in the previous section. For convenience the results are again shown in the form of percentage reaction which had occurred when each point was taken and are shown in Table 14.

TABLE 14

The reaction of EtZnI + PhHgI in THF at 0°C

Run No.

2		3		4		5	
[EtZnI] = .01886m/l. [PhHgI] = .00491m/l.		[EtZnI] = .01784m/l. [PhHgI] = .00585m/l.		[EtZnI] = .01382m/l. [PhHgI] = .00467m/l.		[EtZnI] = .01675m/l. [PhHgI] = .00153m/l.	
T mins.	% reaction	T mins.	% reaction	T mins.	% reaction	T mins.	% reaction
8	5.1	2	1.5	5	42.1	2	14.9
16	7.2	8	23.6	10	43.7	10	26.2
50	11.5	16	32.0	15	44.8	20	44.3
120	18.5	30	41.4	20	46.2	40	54.6
		79	43.6	90	48.8	60	54.6
		305	44.0			155	65.9

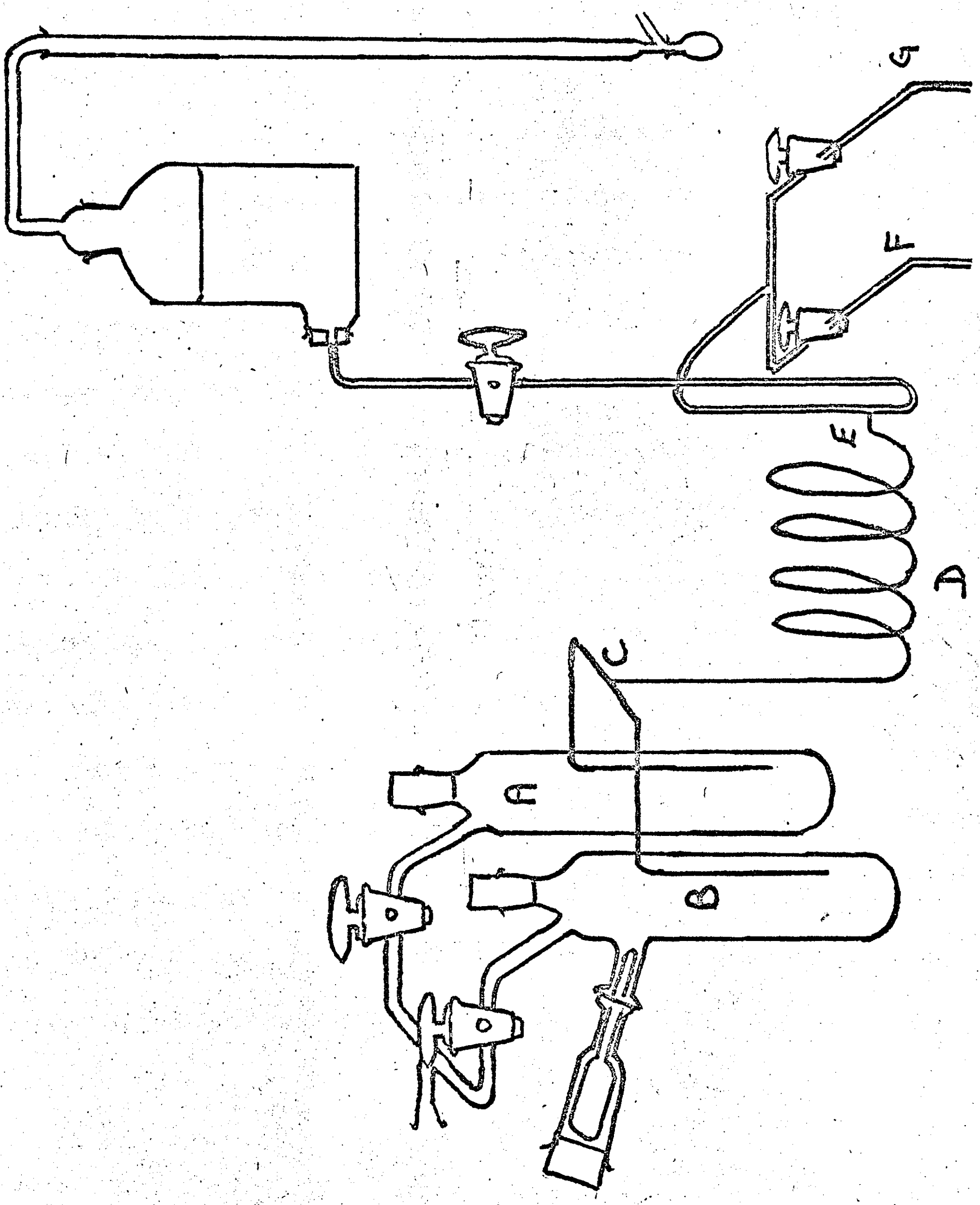
The results would fit neither second order kinetics nor first order kinetics with respect to either reactant.

4. An attempted study of the reaction of ethylzinc iodide with mercuric iodide in tetrahydrofuran at 25°C.

In anticipation of this reaction being very fast a flow apparatus was constructed for following its kinetics. The apparatus is shown in Fig. 5. The capillary spiral was of glass tubing of internal diameter 0.0858 cm. The length of the spiral between the T-pieces C and E was 282 cm. for runs 1 - 3, and 81 cm. for the following runs. The mercuric iodide solution was put in storage vessel A, and tetrahydrofuran was put in vessel B. (The entire apparatus having been flushed with nitrogen). The volume of both vessels was approximately 300 ml. A large snapping-type capsule containing approximately 10 ml. of a 30% solution of ethylzinc iodide in tetrahydrofuran was placed in the ball and socket side arm of vessel B. By flexing the ball and socket joint the end of the capsule was broken off and the contents poured into vessel B, which was stirred magnetically from underneath for five minutes before the whole apparatus was lowered into a water bath at 25°C. The concentration of the ethylzinc iodide solution was then determined by withdrawing a sample with a pipette and pipetting it into excess dilute sulphuric acid, which was then back-titrated with sodium hydroxide, using bromocresol purple as indicator. By applying a few cm. of mercury pressure to both storage vessels the reactant solutions were forced up to the T-piece C where they mixed. As the solution passed along the spiral, reaction

Figure 5.

Flow apparatus



proceeded. At T-piece E the reaction was stopped when the reaction mixture met a flow of dilute sulphuric acid (in 50% water/ethanol). The effluent was collected at either of the exits F and G. By varying the applied nitrogen pressure the flow rate and hence the time of reaction could be varied. The flow rate of the quenching solution was measured by means of a bubble flow-meter attached to the top of its reservoir. For each kinetic point two samples of effluent were collected for the same time. One sample was titrated for zinc by E.D.T.A. (using excess potassium iodide to mask the mercury), so that the flow rate and hence the reaction time could be determined. The sulphuric acid in the other sample was titrated with sodium hydroxide to determine the amount of reaction that had proceeded. The relative volumes of solution delivered by each storage vessel under the same nitrogen pressure were determined in a check experiment. It was found that vessel B delivered 1.095 ml. whilst vessel A delivered 1.000 ml. over the whole range of pressures used. This was corrected for in the calculations. Reaction times of 1.04 secs. could be obtained by applying a pressure of 30 cm. of mercury. The results which are shown in Table 15 are again given in the form of percentage reaction that had occurred when each point was taken.

TABLE 15

EtZnI + HgI_2 in THF at 25°C.

Run No.

4		5		6	
[EtZnI] = .05338 m/l. [HgI_2] = .02842 m/l.		[EtZnI] = .04820 m/l. [HgI_2] = .05881 m/l.		[EtZnI] = .01667 m/l. [HgI_2] = .01849 m/l.	
T secs.	% reaction	T secs.	% reaction	T secs.	% reaction
7.23	100	1.09	87.1	1.04	80.4
		1.28	88.43	1.29	82.1
		1.56	89.28	1.90	83.1
		1.96	89.56	2.59	83.8
		2.62	90.07	3.02	85.3

In addition one run was performed using an equimolar mixture of mercuric iodide and potassium iodide instead of mercuric iodide. With the ethylzinc iodide concentration at 0.05811 moles per litre and the $KHgI_3$ concentration of 0.02864 moles per litre, the reaction had gone to 100% by the time the first point was taken at 1.81 secs.

5. An attempted study of the kinetics of the reaction between ethylzinc iodide and ethylmercuric iodide in tetrahydrofuran at 25°C.

Using the same apparatus and the same techniques as in the previous section the kinetics of the reaction between ethylzinc iodide and ethylmercuric iodide were studied. The whole operation was performed in a fume-cupboard. The results are shown in Table 16.

TABLE 16

The reaction between EtZnI and EtHgI in THF at 25°C.

Run No.			
1		2	
[EtZnI] = .05885 m/l. [EtHgI] = .03797 m/l.		[EtZnI] = .03440 m/l. [EtHgI] = .02746 m/l.	
T secs.	% reaction	T secs.	% reaction *
1.15	87.4	1.21	57.2
1.69	79.8	1.41	45.4
1.95	68.5	2.04	19.0
2.99	44.7	2.65	17.4
7.18	22.5	3.41	14.7

---

* The percentage reaction was calculated on the assumption that the quenching acid was used up by C - Zn bonds only.

SECTION IV

COMPETITIVE STUDIES

The relative rates of reaction of dialkylzincs with phenylmercuric chloride were determined by the same technique as used in identifying the reaction between diethylzinc and phenylmercuric chloride (page 108) and using the same apparatus (Fig. 4).

1. With a mixture of dimethylzinc and diethylzinc

The mixture of dimethylzinc and diethylzinc contained approximately equimolar quantities of the two dialkyls in the form of a 30% solution in cyclohexane, and had been prepared previously [99]. The purity and percentage composition of the mixture was determined at intervals during the course of the experiments by hydrolysing samples of it as described on page 99. The results of these periodic determinations were used to correct the values for the percentage composition of the capsules of the mixture used in the competitive studies. The relative rate of reaction of dimethylzinc and diethylzinc with phenylmercuric chloride was determined in refluxing ether and in tetrahydrofuran at 25°C. In the latter case, after hydrolysis of the reaction mixture, it was brought to the boil for fifteen minutes and then allowed to cool, under a flow of carbon dioxide, to ensure that all the hydrocarbon produced was driven off and collected. The results of these experiments are shown in Table 17.

TABLE 17

Reaction of Me_2Zn + Et_2Zn with PhHgCl, in 25 ml. of THF at 25°C being allowed to react for fifteen minutes

<table>
<tr><th>Run No.</th><th>Moles of Me_2Zn x 10^3</th><th>Moles of Et_2Zn x 10^3</th><th>Moles of PhHgCl x 10^3</th><th>Vol. of gas produced (ml.)</th><th>Vol. of gas expected (ml.)</th><th>$\frac{MeH}{EtH}$ orig'l</th><th>$\frac{MeH}{EtH}$ found</th><th>$\frac{k_{Et}}{k_{Me}}$</th></tr>
<tr><td>36</td><td>2.613</td><td>2.841</td><td>1.146</td><td>146</td><td>218</td><td>1/1.087</td><td>1/1.008</td><td>1</td></tr>
<tr><td>37</td><td>2.099</td><td>2.283</td><td>1.500</td><td>128</td><td>162</td><td>"</td><td>1/1.018</td><td>1</td></tr>
<tr><td>38</td><td>2.196</td><td>2.388</td><td>1.343</td><td>142</td><td>175</td><td>"</td><td>1/1.010</td><td>1</td></tr>
<tr><td>39</td><td>2.352</td><td>2.559</td><td>1.854</td><td>141</td><td>178</td><td>"</td><td>1/1.034</td><td>1</td></tr>
<tr><td>41</td><td>2.004</td><td>2.178</td><td>1.663</td><td>119</td><td>140</td><td>"</td><td>1/1.027</td><td>1</td></tr>
<tr><td></td><td colspan="8">Reaction of Me_2Zn + Et_2Zn with PhHgCl, in 200 ml. of refluxing ether, being allowed to react for fifteen minutes.</td></tr>
<tr><td>46</td><td>2.386</td><td>2.595</td><td>1.054</td><td>219</td><td>199</td><td>1/1.087</td><td>1/0.933</td><td>5.8</td></tr>
<tr><td>47</td><td>1.570</td><td>1.707</td><td>0.8448</td><td>129</td><td>127</td><td>"</td><td>1/0.913</td><td>4.9</td></tr>
<tr><td>48</td><td>1.507</td><td>1.638</td><td>0.9923</td><td>130</td><td>128</td><td>"</td><td>1/0.940</td><td>2.7</td></tr>
<tr><td>50</td><td>1.330</td><td>1.446</td><td>0.6029</td><td>147</td><td>110</td><td>"</td><td>1/0.928</td><td>5.9</td></tr>
<tr><td>51</td><td>1.688</td><td>1.794</td><td>0.8300</td><td>140</td><td>137</td><td>"</td><td>1/0.946</td><td>3.1</td></tr>
</table>

2. With a mixture of diethylzinc and di-n-propylzinc

The mixture used contained only neat diethylzinc and di-n-propylzinc. Its purity was periodically checked as previously mentioned. The relative rate of reaction of diethylzinc and di-n-propylzinc with phenylmercuric chloride was determined in refluxing ether, refluxing tetrahydrofuran and tetrahydrofuran at 25°C. The results are shown in Table 18.

3. With a mixture of diethylzinc and di-i-propylzinc

The mixture used contained only neat diethylzinc and di-i-propylzinc and its purity was periodically checked. The relative rate of reaction of the two dialkylzincs with phenylmercuric chloride was determined in refluxing ether, refluxing tetrahydrofuran and tetrahydrofuran at 25°C. The results are shown in Table 19.

TABLE 18

Reaction of Et_2Zn + n-Pr_2Zn with PhHgCl in 25 ml. THF at 25°C being allowed to react for ten minutes

Run No.	Moles of Et_2Zn x 10^{-3}	Moles of nPr_2Zn x 10^3	Moles of PhHgCl x 10^3	Vol. of gas produced (ml.)	Vol. of gas expected (ml.)	$\frac{EtH}{PrH}$ orig'l	$\frac{EtH}{PrH}$ found	$\frac{k_{Pr}}{k_{Et}}$
28	1.514	1.493	2.165	85	86	1/0.986	1/.999	1
29	1.648	1.625	0.8263	140	128	"	1/1.002	1
30	1.543	1.522	1.472	103	104	"	1/.986	1
	Reaction of Et_2Zn + nPr_2Zn with PhHgCl in 25 ml. THF at reflux (65°C) being allowed to react for ten minutes.							
32	1.507	1.486	1.082	108	109	"	1/0.984	1
33	1.731	1.708	0.8708	129	134	"	1/0.988	1
35	1.615	1.593	0.9970	127	121	"	1/1.043	1
	Reaction of Et_2Zn + n-Pr_2Zn with PhHgCl in 200 ml. Et_2O at reflux (35°C) being allowed to react for ten minutes.							
22	1.685	1.685	0.8408	132	133	1/1.000	1/0.775	8.1
23	1.517	1.517	1.249	134	91	"	1/0.843	2.2
24	1.254	1.254	0.7493	87	95	"	1/0.888	2.3
25	1.391	1.391	0.5596	150	112	"	1/0.858	6.2
26	1.575	1.575	0.6662	200	126	"	1/0.811	1.9
27	1.994	1.994	0.7907	163	161	"	1/0.918	1.2

TABLE 19

Reaction of Et_2Zn + i-Pr_2Zn with PhHgCl in 25 ml. THF at 25°C, being allowed to react for ten minutes

Run No.	Moles of Et_2Zn x 10^3	Moles of i-Pr_2Zn x 10^3	Moles of PhHgCl x 10^3	Vol. of gas produced (ml.)	Vol of gas expected (ml.)	$\frac{EtH}{PrH}$ orig'l	$\frac{EtH}{PrH}$ found	$\frac{k_{iPr}}{k_{Et}}$
69	3.462	3.462	1.128	270	285	1/1.000	1/1.061	1
70	3.583	3.583	1.250	279	294	"	1/1.097	1
72	3.340	3.340	1.397	261	268	"	1/1.057	1
Reaction of Et_2Zn + i-Pr_2Zn with PhHgCl in 25 ml. THF at 65°C being allowed to react for ten minutes								
64	4.083	4.083	0.6873		350	1/1.000	1/1.023	1
67	3.549	3.549	1.123	285	292	"	1/1.067	1
68	3.986	3.986	1.258	319	329	"	1/1.138	1
Reaction of Et_2Zn + i-Pr_2Zn with PhHgCl in 200 ml. of Et_2O at 35°C being allowed to react for ten minutes								
58	3.259	3.259	0.9560	232	270	1/1.000	1/0.881	9.7
59	2.210	2.210	0.6387	172	183	"	1/1.032	1
60	2.949	2.949	0.7731	242	247	"	1/0.898	5.0
61	3.607	3.607	0.7661	285	305	"	1/1.004	1
62	2.044	2.044	0.6905	163	167	"	1/1.118	0.22
63	3.110	3.110	0.6456	243	264	"	1/0.954	7.2

SECTION V

THE SYN-PROPORTIONATION OF DIETHYLZINC AND ZINC HALIDES

1. The preparation of zinc halide - N,N,N'N'-tetramethylethylenediamine complexes

(a) Zinc iodide complex

N,N,N'N'-tetramethylethylenediamine (TMED) (4.5 m.moles) was added to a solution of zinc iodide (1.5 m.moles) in methanol (10 ml.). On cooling, and after reduction of the volume under vacuum, colourless crystals were deposited. After recrystallisation from methanol these crystals had m.p. 201-202°C.

(Found: Zn 15.09%, I 58.00%; $C_6H_{16}N_2ZnI_2$ requires Zn 15.01%, I 58.29%).
An identical material was prepared from tetrahydrofuran (5 ml.), using the same quantities as above. After recrystallisation from tetrahydrofuran the crystals had m.p. 201°C.

(Found: Zn 15.07%, I 58.30%).

(b) Zinc bromide complex

TMED (4.5 m.moles) was added to a solution of zinc bromide (1.5 m.moles) in methanol (10 ml.). The product, which was isolated in the same manner as the zinc iodide complex was recrystallised from methanol, when it had m.p. 179°C. (lit 178°C [107]).

(Found: Zn 19.06, Br 46.63%; $C_6H_{16}ZnBr_2$ requires Zn 19.15%, Br 46.81%).
An identical material was prepared from tetrahydrofuran (5 ml.), using

the same quantities as above. After recrystallisation from tetrahydrofuran it had m.p. 178°C.

(Found: Zn 19.01%, Br 46.44%).

2. The ethylzinc iodide complex

TMED (12.0 m.moles) was added to an ethereal solution of ethylzinc iodide (30%, 4.5 m.moles) under nitrogen, and the mixture stirred magnetically. Heat was evolved, and as the solution cooled colourless crystals were deposited. After recrystallisation from ether, under nitrogen, these had m.p. 103°C.

(Found: Zn 19.94%, I 37.64%; $C_8H_{21}N_2ZnI$ requires Zn 19.37%, 37.60%).

An identical material was prepared from tetrahydrofuran, using the same quantities as above. After recrystallisation from tetrahydrofuran it had m.p. 102°C.

(Found: Zn 19.53%, I 37.98%).

3. The system diethylzinc plus zinc iodide in tetrahydrofuran

A solution of diethylzinc (9.8 m.moles) and zinc iodide (10.0 m.moles) in tetrahydrofuran (3.0 ml.), was divided into two equal parts and each portion used as follows :

(i) TMED (7 m.moles) dissolved in petroleum ether (60-80°C, 10 ml.) was added to one portion of the solution after it had been made for two hours. This was done under nitrogen, and the mixture stirred magnetically. The colourless crystalline product was filtered off and washed with pet.

ether (10 ml.) then dried under vacuum and capsuled off. It had m.p.164°C. (Found: Zn ~~18.97~~ 15.97%, I 58.50%).

(ii) The other half of the solution was kept for seven days at 25°C and then treated as above. The product had m.p. 105°C. (Found: Zn 18.97%, I 38.43%).

4. The system diethylzinc plus zinc bromide in tetrahydrofuran

A solution of diethylzinc (0.053 moles) and zinc bromide (0.053 moles) in tetrahydrofuran (25 ml.) was divided into two halves.

(i) After it had been made up for two hours, one half of the solution was treated with TMED (0.027 moles) dissolved in hexane (10 ml.), under nitrogen, and stirred magnetically for fifteen minutes. After reduction of the volume of the solution under vacuum a colourless crystalline precipitate was produced, which was filtered off, washed with hexane (10 ml.), vacuum dried and capsuled off. This crude product had m.p.175°C. (Found: Zn 20.33%, Br 44.71%; $C_6H_{16}N_2ZnBr_2$ requires Zn 19.15%, Br 46.81% and $C_8H_{21}N_2ZnBr$ requires Zn 22.50%, Br 27.51%).
After recrystallisation from tetrahydrofuran the product had m.p.178°C.
(mixed m.p. with $ZnBr_2$.TMED 178°C)
(Found Zn 20.05%, Br 45.25%).

(ii) The second half of the solution was kept for seven days at 25°C and then treated in the same way as the first half to yield a crude product which had m.p. 173°C.

(Found: Zn 20.14%, Br 42.35%).

After recrystallisation from tetrahydrofuran the product had m.p. 178°C.

(mixed m.p. with $ZnBr_2$.TMED 178°C).

(Found: Zn 19.72%, Br 45.31%).

5. The system diethylzinc plus zinc bromide in diethyl ether

A solution of diethylzinc (0.019 moles) and zinc bromide (0.0186 moles) in diethyl ether (30 ml.) was treated with TMED (0.039 moles) fifteen minutes after it had been prepared. After stirring for one hour a dense crystalline deposit appeared. This was filtered off, washed twice with hexane (2 x 15 ml.), and then vacuum dried and capsuled off. The product had m.p. 46°C.

(Found: Zn 21.92%, Br 28.32%).

A quantitative hydrolysis of a portion of the product with dilute sulphuric acid yielded 79.9% of the ethane that would be expected if it were EtZnBr.TMED.

6. Attempted preparation of ethylzinc bromide complex by the action of ethyl bromide on a zinc-copper couple

Ethyl bromide failed to react with a zinc-copper couple under conditions similar to those used for the preparation of ethylzinc iodide. Also no reaction would occur when ethyl bromide in tetrahydrofuran was refluxed in the presence of a zinc-copper couple. However, ethyl bromide reacted with a zinc-copper couple when refluxed in dimethylformamide; the solution produced reacted violently with water, producing ethane. On the addition of TMED, however, no complex could be isolated.

SECTION VI

N.M.R. STUDIES

The spectrometer used was a Varian HA 100 model with a field-frequency internal lock. Benzene was used as the internal standard throughout and its τ value was taken as 2.73. All samples were in tetrahydrofuran solution. Due to difficulties in handling organozinc compounds quantitatively on a small scale the concentration of some of the solutions whose spectra have been investigated is not known exactly.

The spectra of approximately 30% solutions of diethylzinc and ethylzinc iodide in tetrahydrofuran proved to be identical; a triplet (J, 8 cps) at 8.95 τ and a quartet (J, 8 cps) at 9.92 τ due to the methyl and methylene groups of the ethyl group respectively. Fig. 6 shows the spectrum of a 30% solution of ethylzinc iodide. In addition the spectrum of an approximately equimolar mixture of the two organozinc compounds was identical to that of either of the two individual compounds (Fig. 7).

The spectrum of TMED showed two single peaks at 7.74 τ and 7.90 τ whose areas were in the ratio 1:3, due to the methylene and methyl groups respectively. The position of these peaks was independent of the concentration of TMED in tetrahydrofuran.

The spectrum of a 0.9M solution of zinc iodide with added TMED again showed only two peaks, whose areas were in the ratio 1:3. Varying the amine concentration affected the spectrum: as the amine changed from being

Figure 6.

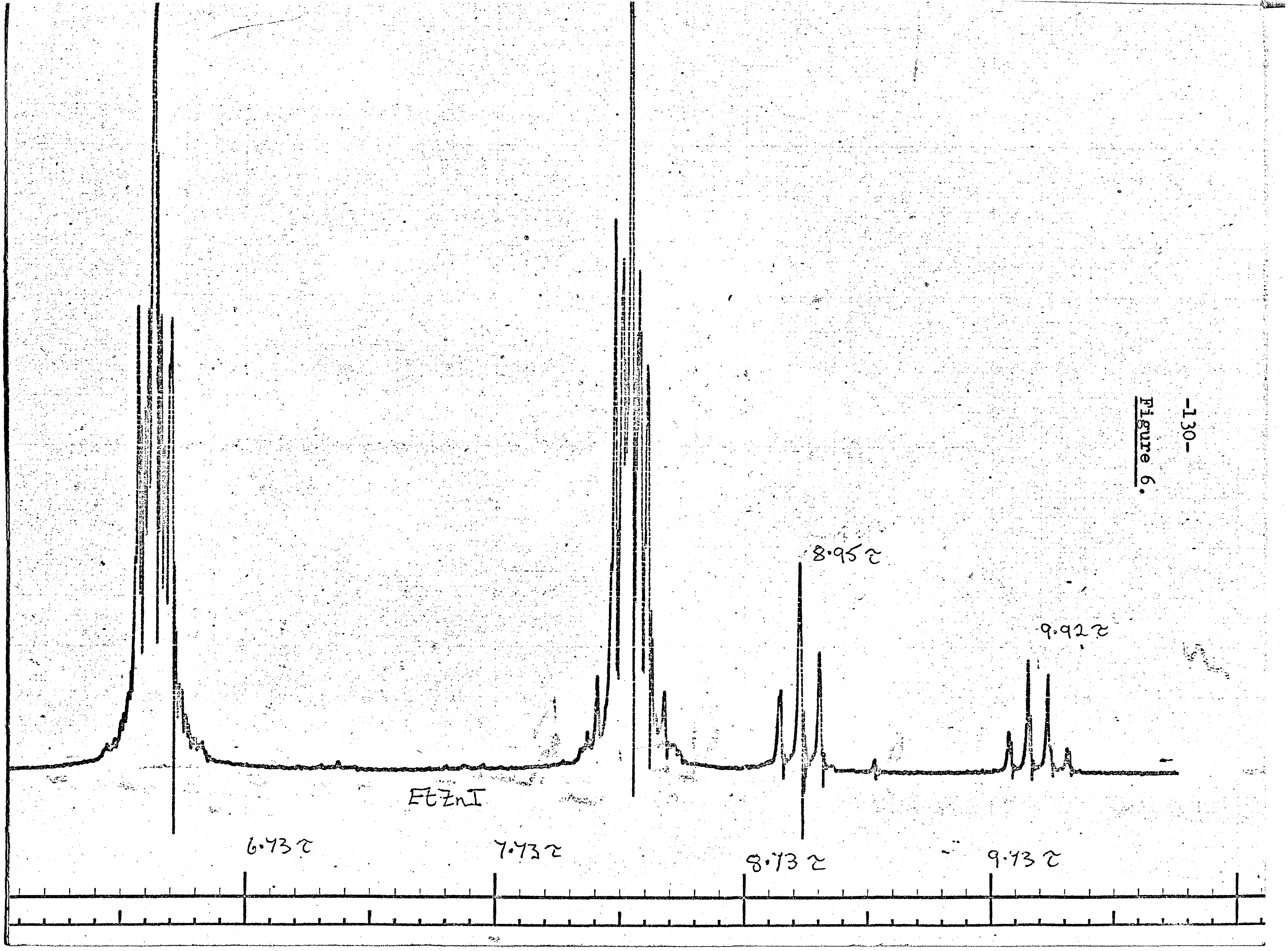
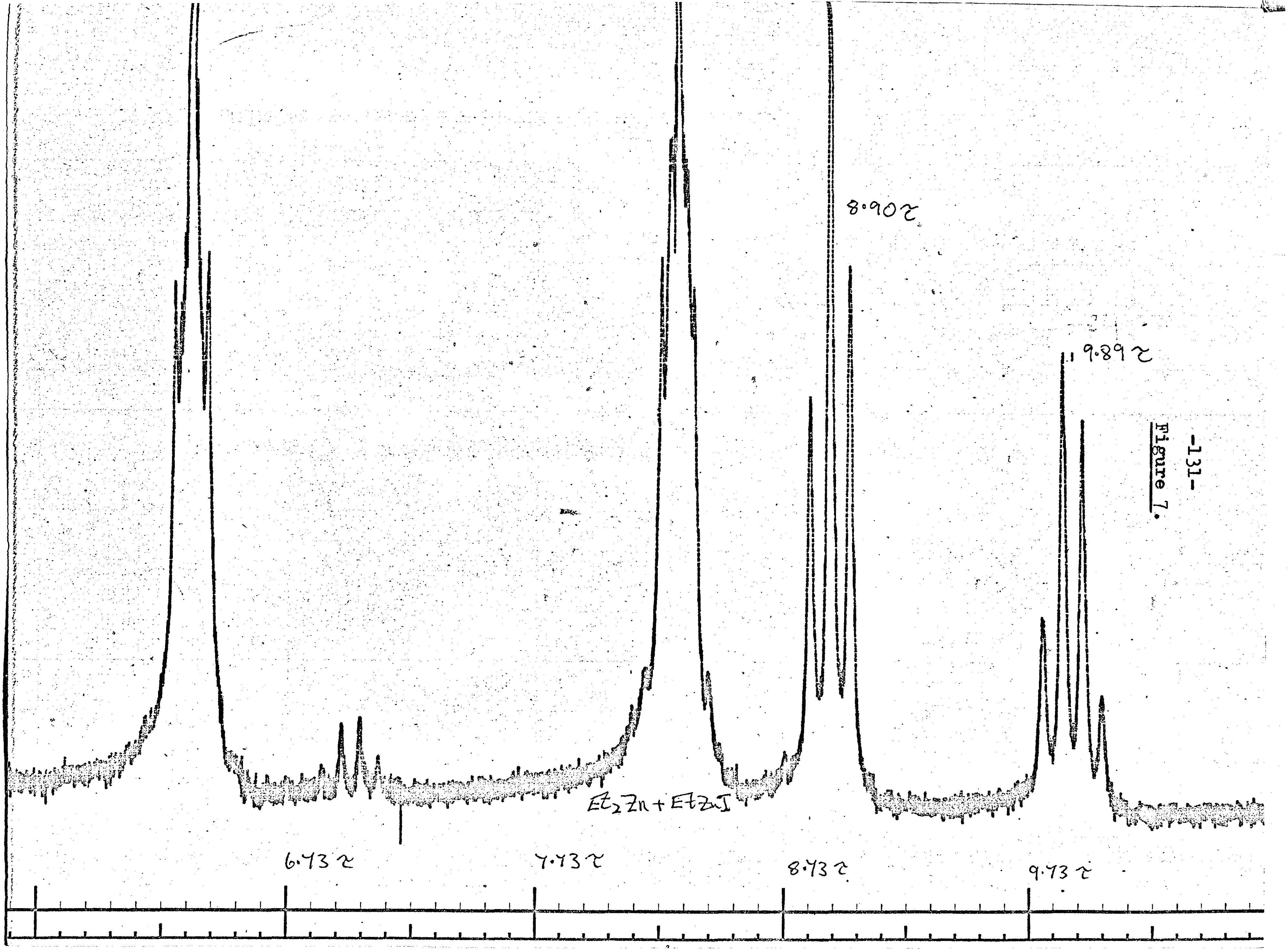


Figure 7.



in deficiency to being in excess the peaks broadened and moved to high magnetic field. τ values are shown in Table 20. The figures in brackets refer to the molar ratios of zinc iodide and TMED.

TABLE 20

ZnI_2	TMED	τ	τ
A(1)	($\frac{1}{2}$)	7.35	7.49
B(1)	(1)	7.34	7.49
C(1)	($1\frac{1}{2}$)	7.48	7.64

The spectra for this are shown in Fig.8. In addition it was found that on diluting a sample of zinc iodide plus a deficiency of TMED, the pair of peaks due to complexed amine moved further apart and to low magnetic field; i.e. from 7.43 and 7.53 τ (G) through 7.41 and 7.52 τ (H), to 7.37 and 7.50 τ (I). The opposite effect was observed on diluting a solution of zinc iodide complex; the peaks moved closer together and up-field [(J) and (K)]. Spectra of both these effects are shown in Fig. 9. Similar effects were observed with zinc bromide. On diluting a sample of zinc bromide plus a deficiency of amine with tetrahydrofuran, the pair of amine peaks moved from 7.48 and 7.60 τ (A) to 7.41 and 7.54 τ (C). On diluting a solution of zinc bromide complex the amine peaks moved from

Figure 8.

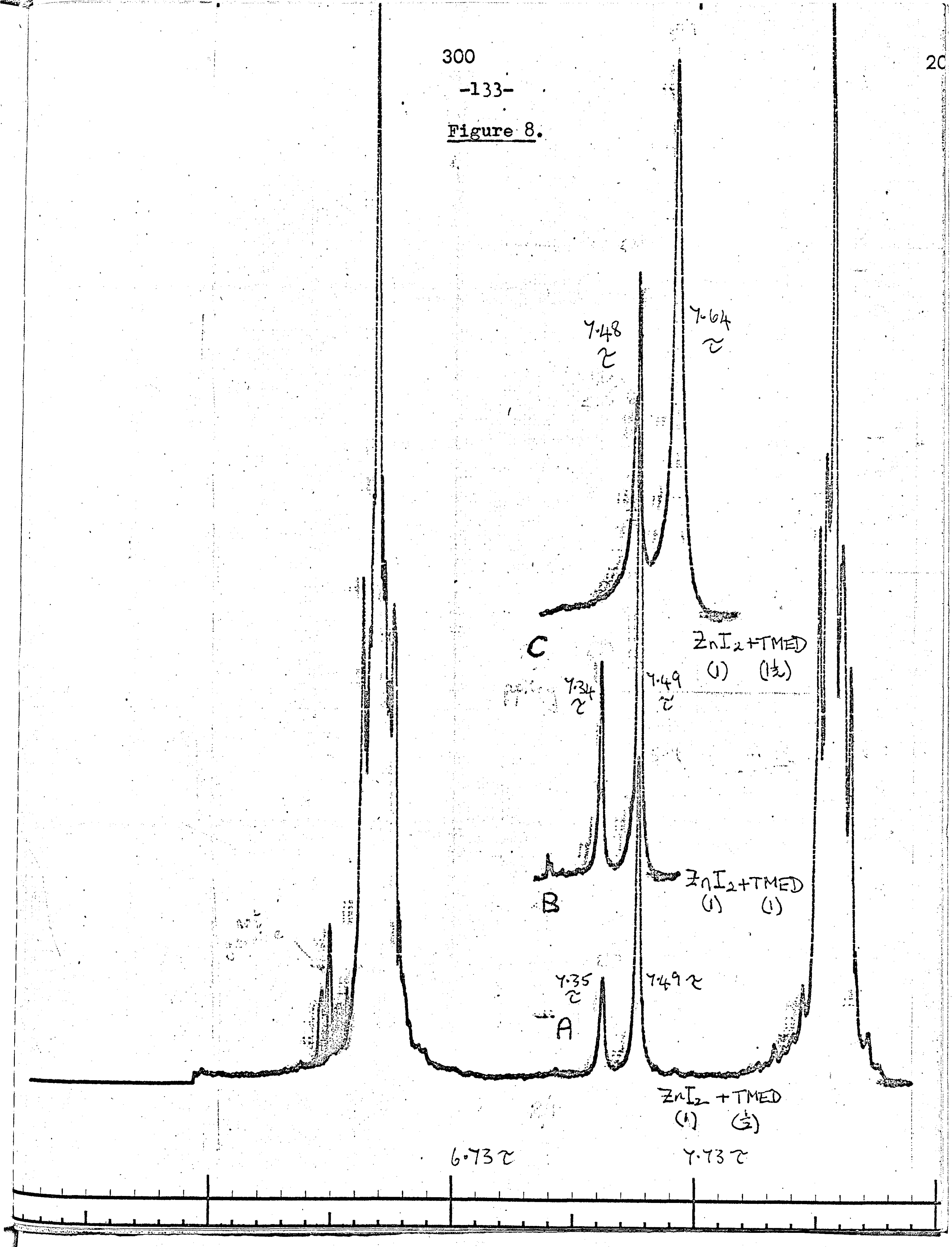
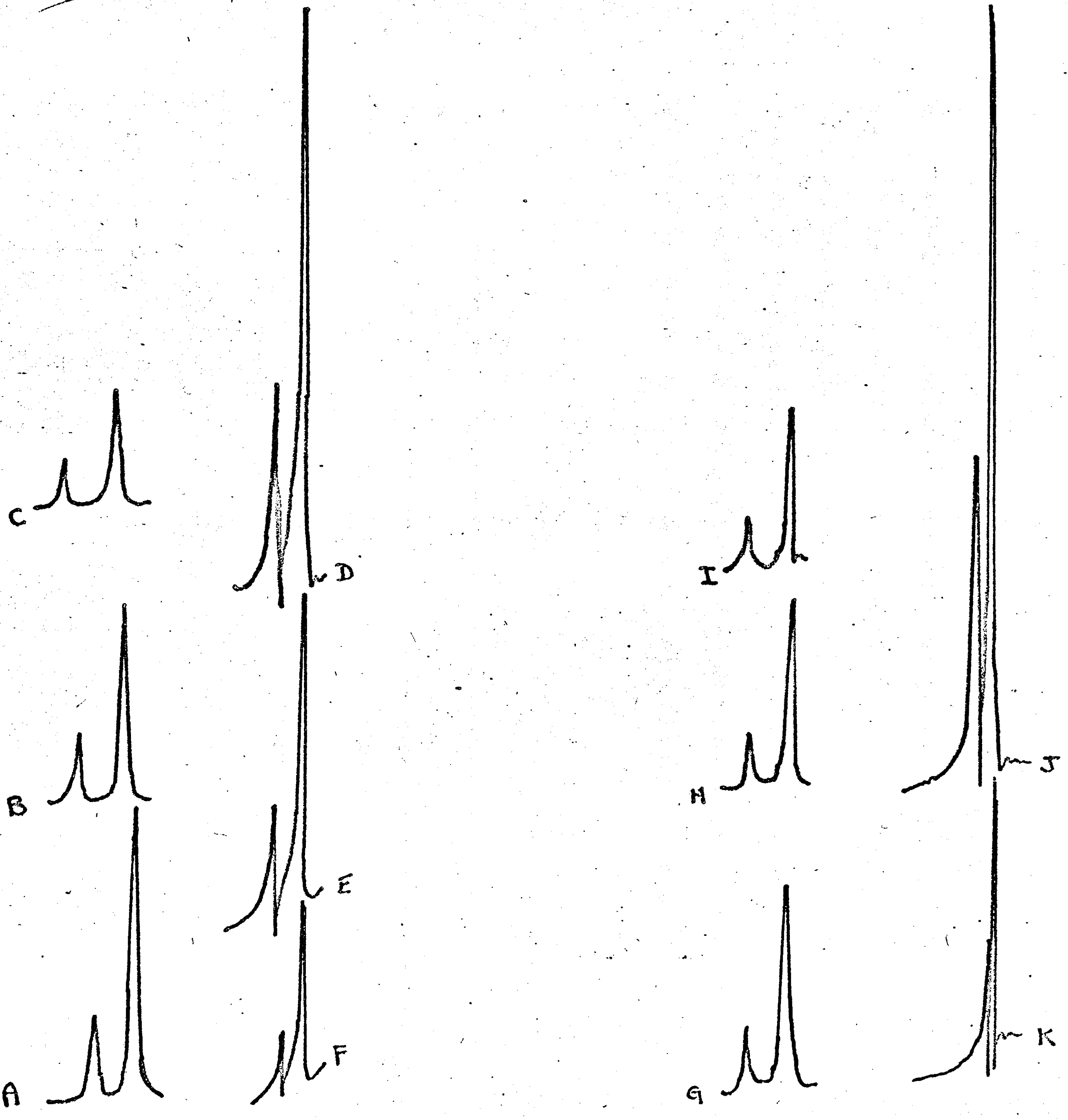

300
20
7·48 τ
7·64 τ
C
ZnI₂+TMED
(1) (1½)
7·34 τ
7·49 τ
B
ZnI₂+TMED
(1) (1)
7·35 τ
7·49 τ
A
ZnI₂ +TMED
(1) (½)
6·73 τ
7·73 τ

Figure 9.



7.49 and 7.57 τ (D) to 7.54 and 7.61 τ (F). Both of these effects for zinc bromide are also shown in Fig. 9.

The spectrum of an equimolar mixture of diethylzinc and TMED, both approximately in 3M concentrations shows two peaks due to the amine at 7.72 and 7.83 τ, whose areas are in the ratio 1:3. Whilst the ethyl group shows a triplet at 8.84 τ and a quartet at 10.08 τ. The spectrum of this mixture is shown in Fig. 10.

The spectra of 30% solutions of ethylzinc iodide in tetrahydrofuran with varying amounts of amine were also investigated; the results are shown in Table 21.

TABLE 21

EtZnI/TMED	Amine peaks τ	τ Methylene	Fig.
1/0.225	7.39, 7.51, 7.52, 7.62 (1) (1.2) (3.0) (3.7)	broad 9.81	—
1/0.23	7.41, 7.52, 7.53, 7.64 (1) (1.15) (3.0) (3.5)	broad 9.89	—
1/0.92	7.33, 7.45, 7.50, 7.59 (1) (5.1) (2.6) (14.2)	broad 10.05	11
1/1.0	7.50, 7.65 (broad) (1) (2.9)	sharp 10.08	—
1/1.5	7.57, 7.72 (broad) (1) (3.0)	sharp 10.07	12

Figure 10.

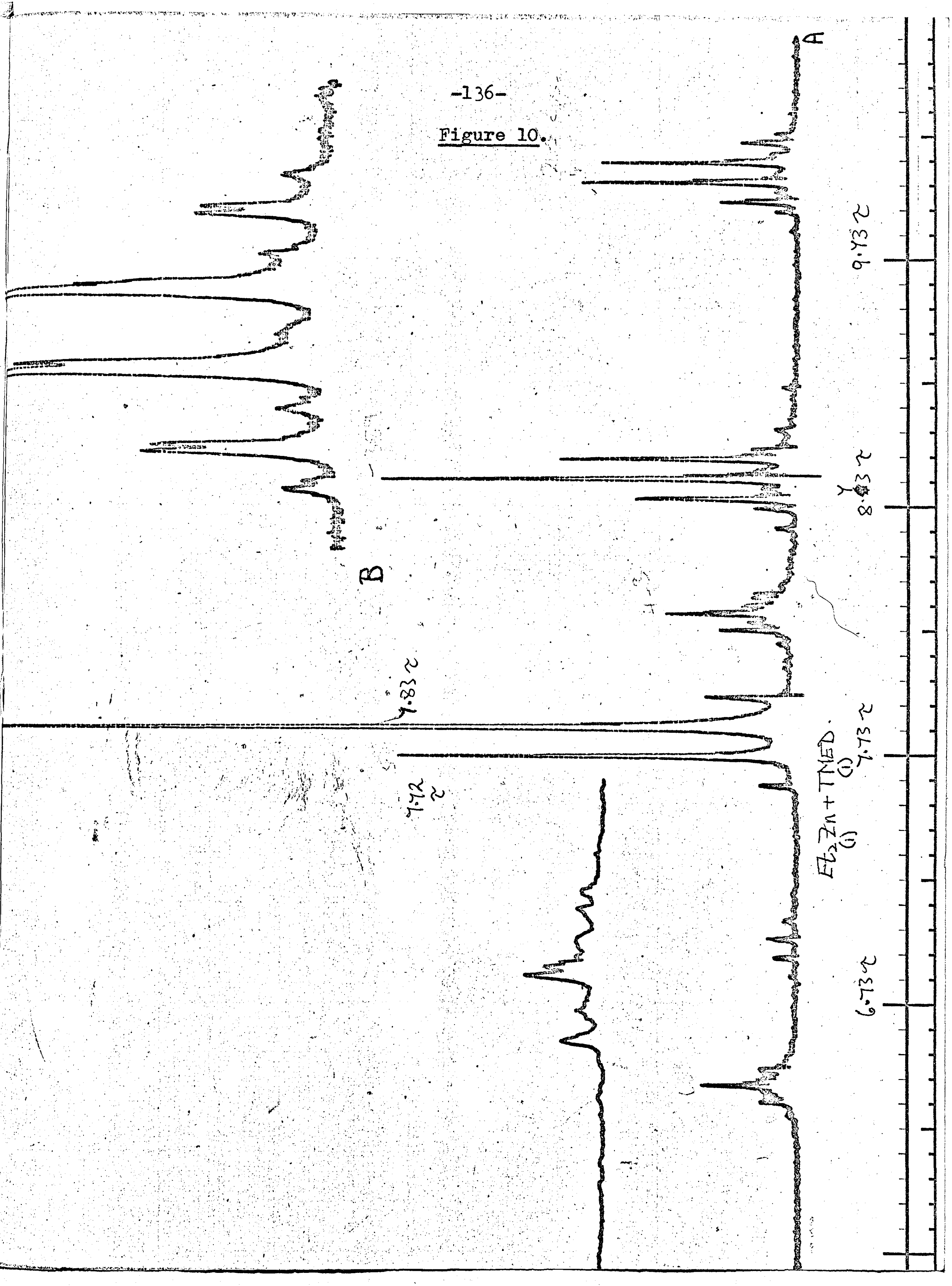


Figure 11.

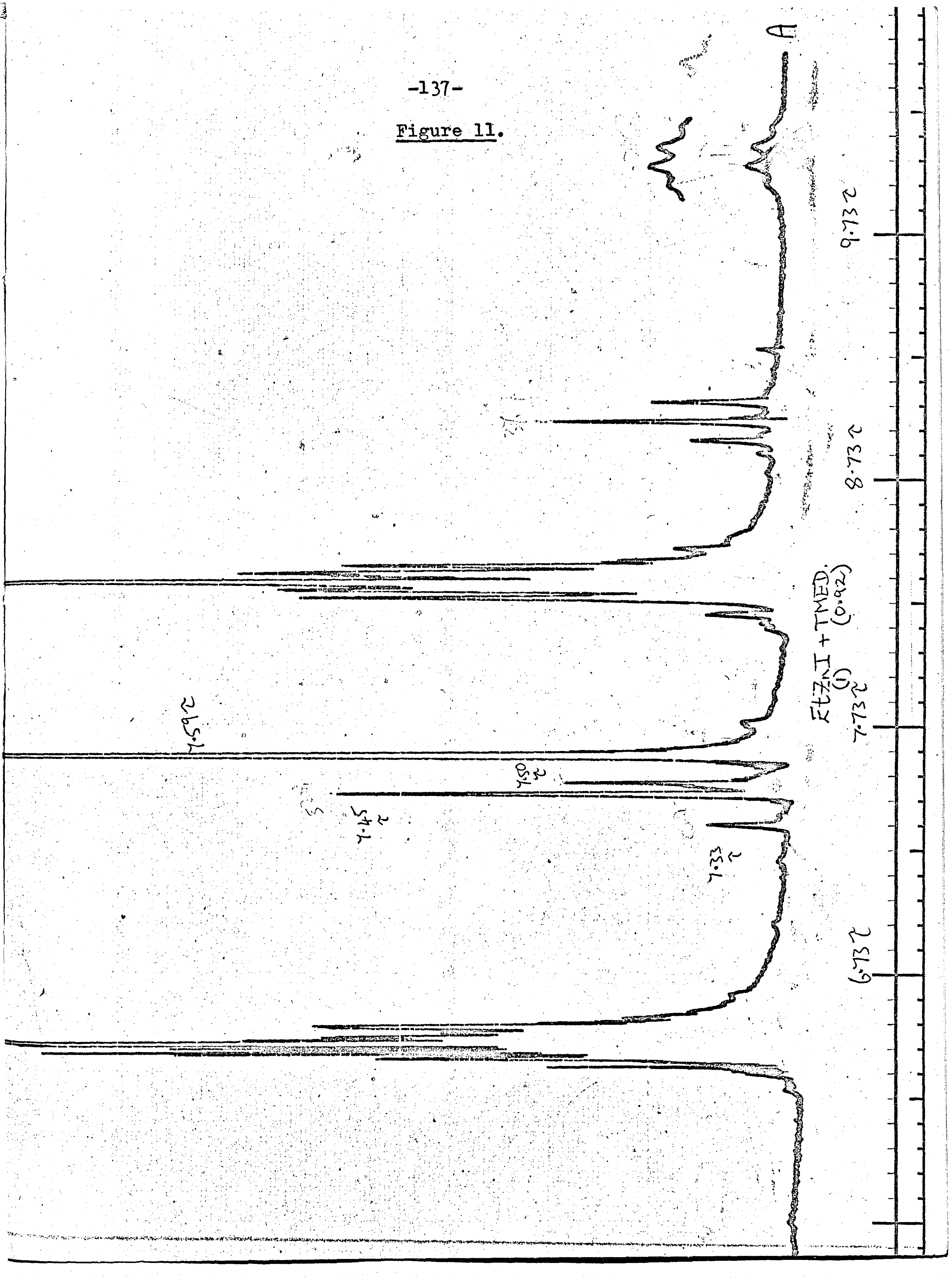
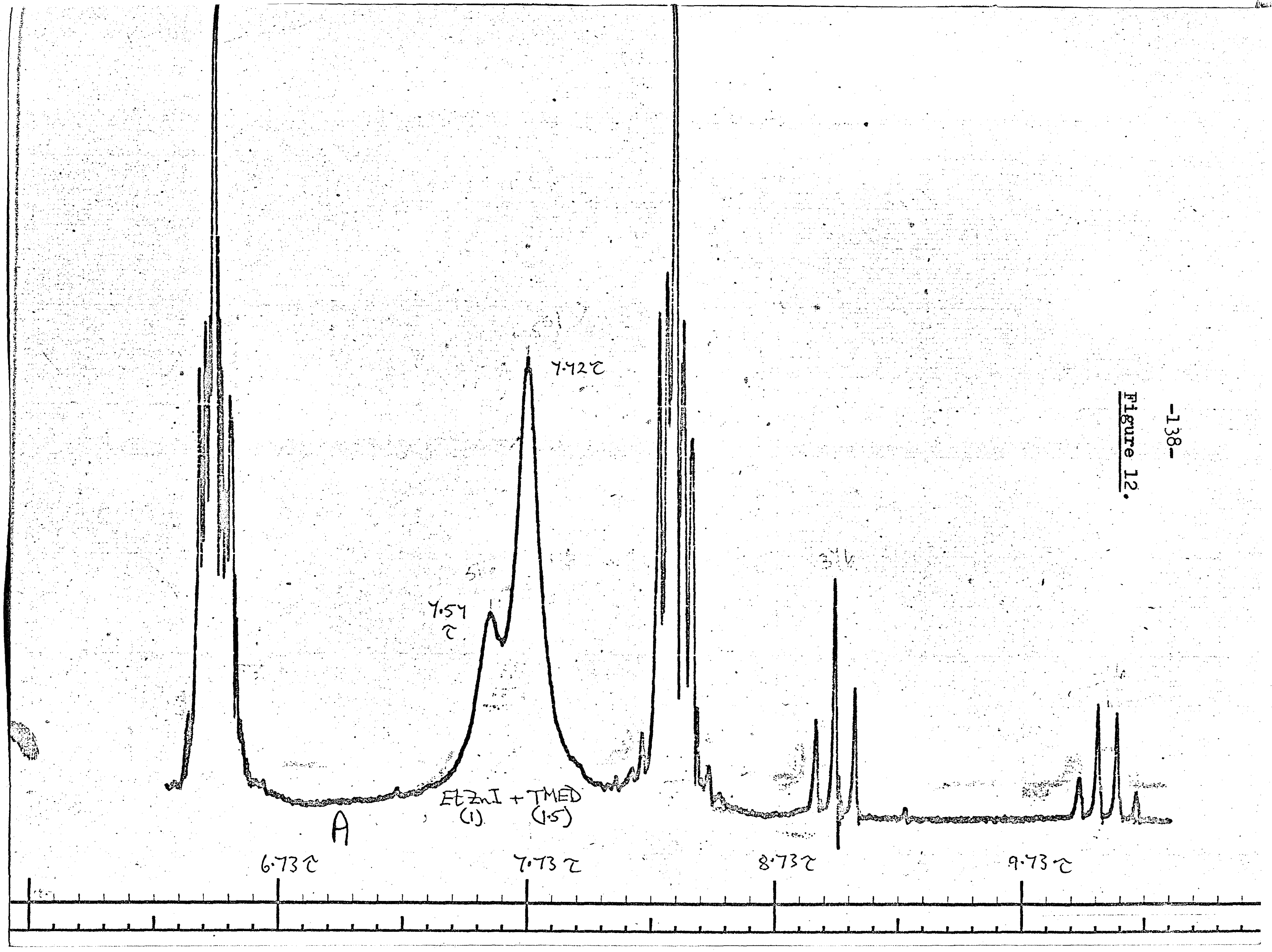


Figure 12.



The first column refers to the molar ratios of ethylzinc iodide to TMED; the second column gives the τ values for the amine peaks observed, the figures in brackets under the τ values give the relative areas of those peaks; the third column refers to the spectrum of the methylene of the ethylzinc group and describes its shape and gives its τ value.

The spectrum of a mixture of diethylzinc, zinc iodide and TMED, with the components in 1.0M, 1.0M and 1.4M concentrations respectively, was run after the mixture had been stored in solid carbon dioxide since being made up. The spectrum was also run after the mixture had been left to stand for one week at room temperature. The spectrum showed no change. The amine peaks occurred at 7.31, 7.44, 7.49 and 7.58 τ and their areas were in the ratios, 1 : 5.2 : 3.2 : 15.3 respectively. The methylene group occurred at 10.02 τ and was broadened. The spectrum is shown in Fig. 13.

To assist in the assignment of the four amine peaks observed, a spectrum of a 1.0M solution of ethylzinc iodide complex was run and repeated with added zinc iodide. As the concentration of added zinc iodide was increased from zero to 0.25M to 0.5M the two low field peaks increased in intensity. This is shown in Fig. 14.

It was found in some of the spectra that the four amine peaks were not fully resolved. Fig. 15 A, shows a spectrum of ethylzinc iodide plus TMED in which the middle two peaks are only just resolved, and Fig. 15 B, a spectrum of a mixture of diethylzinc plus zinc iodide plus TMED shows that the two middle peaks have merged.

Figure 13.

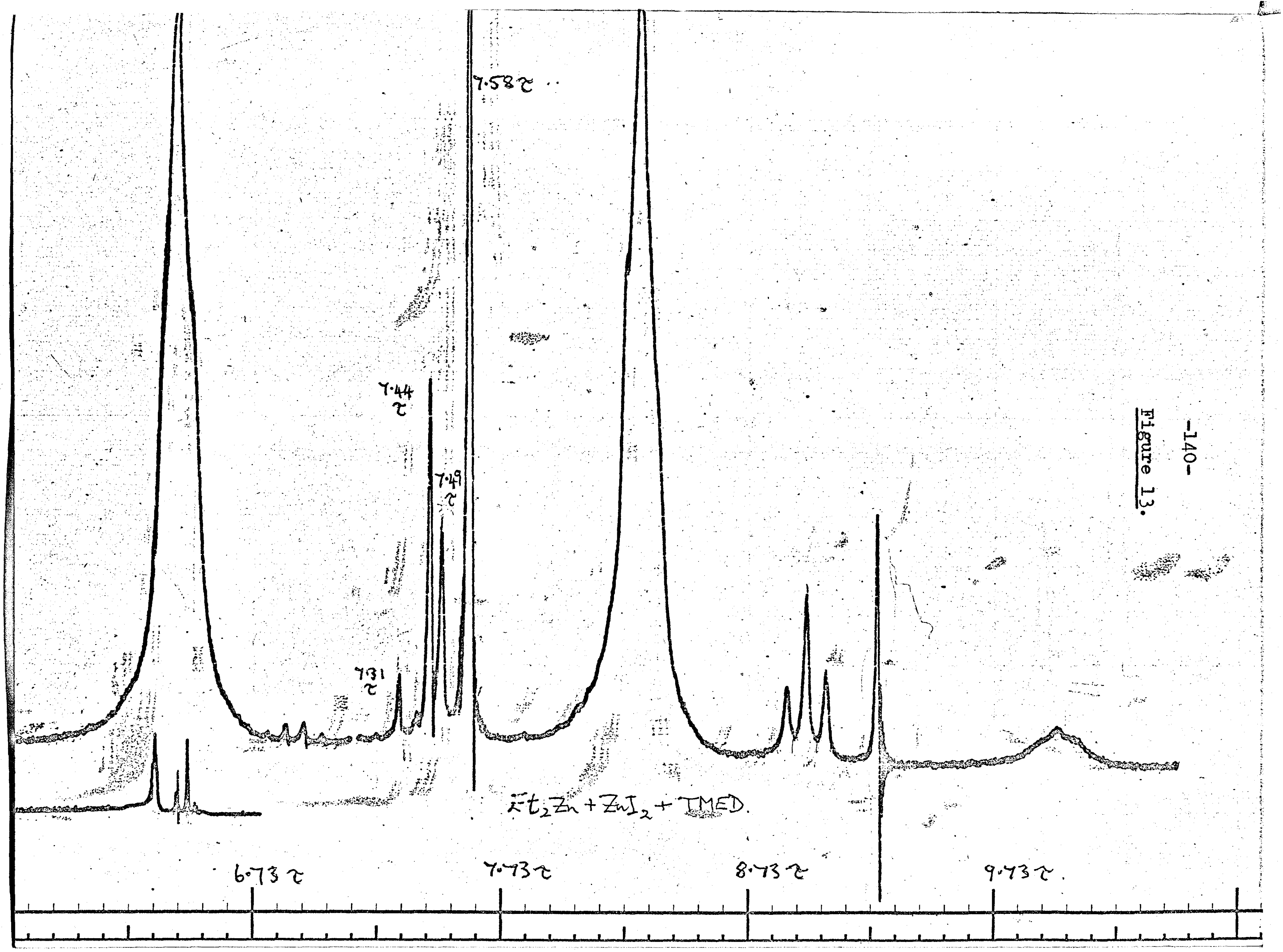
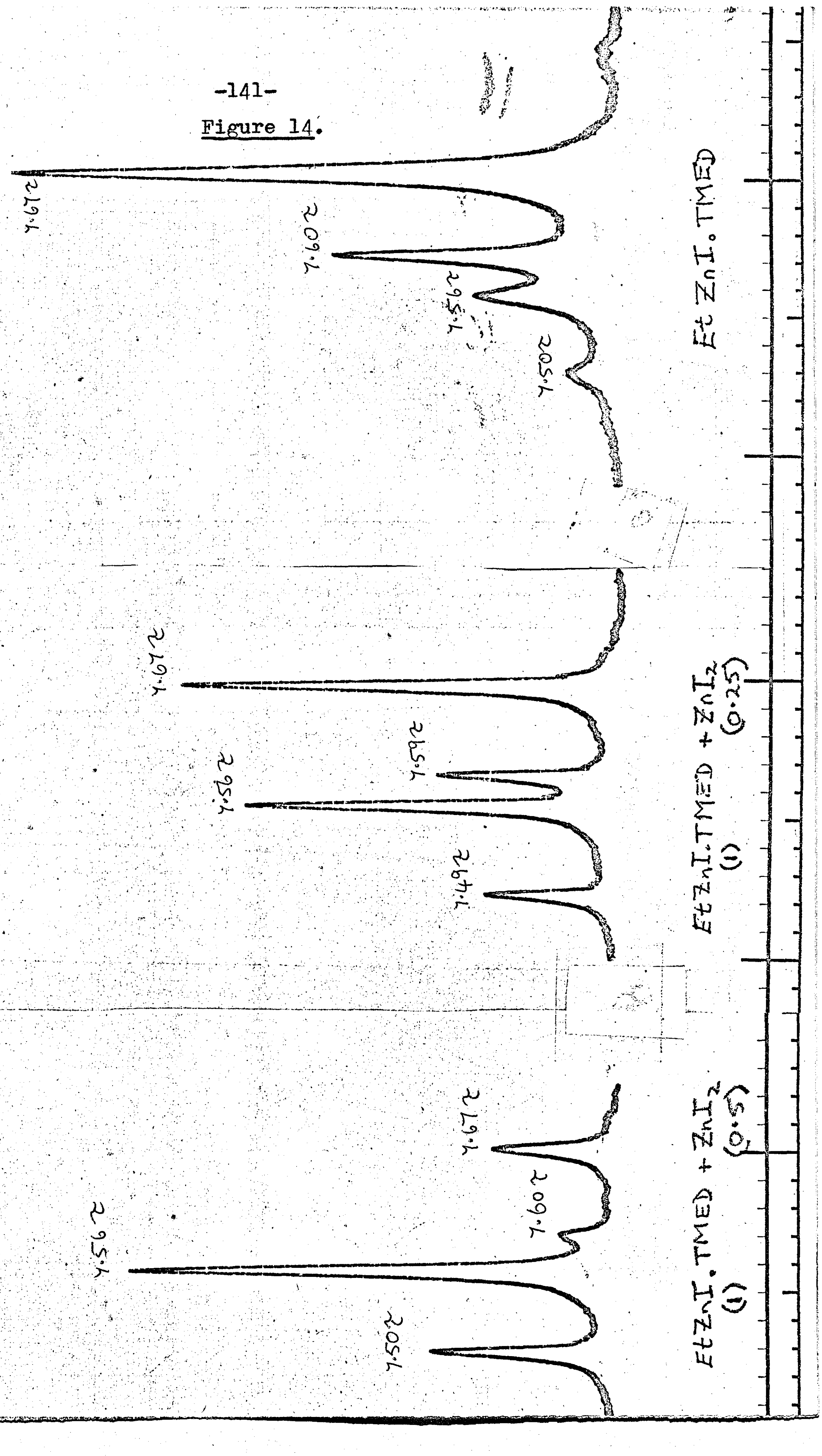


Figure 14.


EtZnI.TMED
7.67τ
7.60τ
7.56τ
7.50τ
EtZnI.TMED + ZnI2
(1) (0.25)
7.67τ
7.56τ
7.59τ
7.49τ
EtZnI.TMED + ZnI2
(1) (0.5)
7.67τ
7.60τ
7.56τ
7.50τ

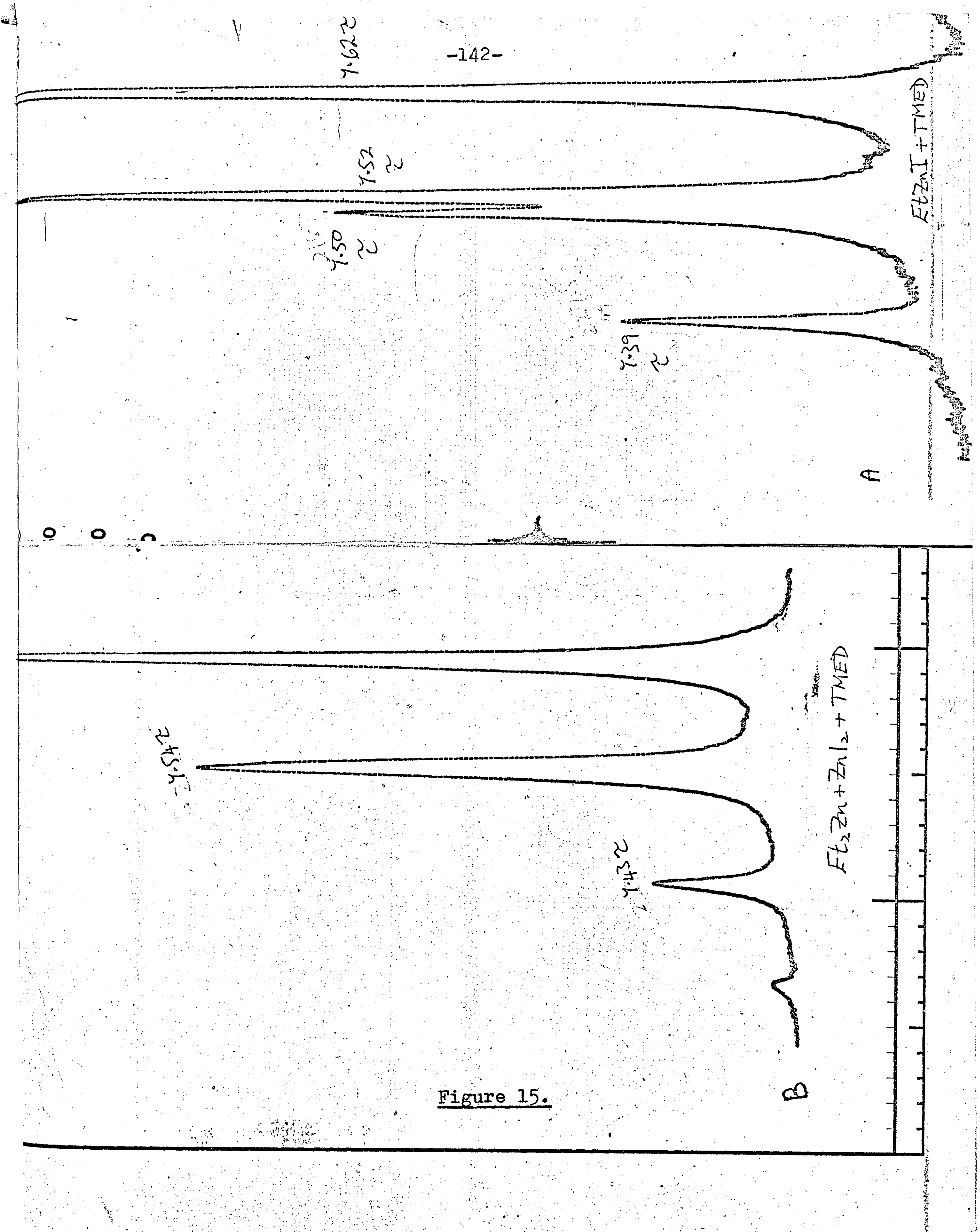
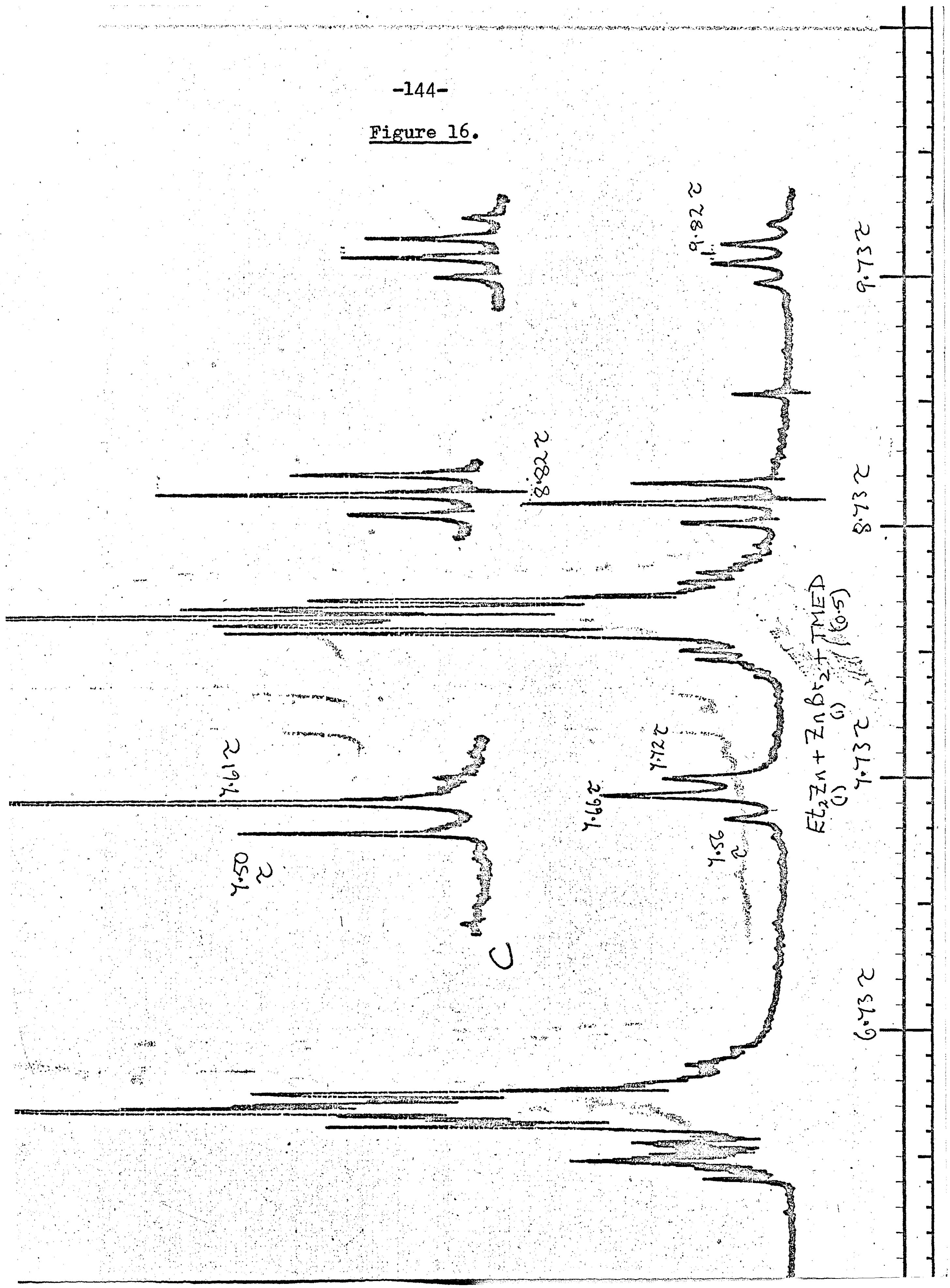


Figure 15.

Finally, a spectrum of a mixture of diethylzinc plus zinc bromide plus TMED in 1.0M, 1.0M and 0.5M concentrations respectively was run after the mixture had been stored under solid carbon dioxide since being made up, and again after standing for one week at room temperature; the spectra were identical. Three amine peaks were observed at 7.56, 7.66 and 7.72 τ: their areas were in the ratios 1 : 4.6 : 2.9. The methyl triplet occurred at 8.82 τ and the methylene quartet at 9.82 and was sharp. The addition of zinc bromide to this sample broke up the three amine peaks and gave two amine peaks at 7.50 and 7.61 τ whose areas were in the ratio 1 : 3. These two spectra are shown in Fig. 16.

Figure 16.


9.73τ
8.73τ
7.73τ
6.73τ
9.82τ
8.82τ
7.61τ
7.50τ
7.66τ
7.72τ
7.56τ
C
$Et_2Zn + ZnBr_2 + TMED$
(1) (1) (0.5)

SECTION VII

MOLECULAR WEIGHT DETERMINATIONS

The molecular weight of ethylzinc iodide as prepared in Section II, in both tetrahydrofuran and diethyl ether at various concentrations was determined by the elevation of boiling point method, under nitrogen. The relationship used was :

$$M = \frac{K_b . 1000. W_2}{\Delta T. W_1}$$

where M = the molecular weight of the species present in solution; K_b is the ebullioscopic constant for the solvent used; W_2 is the weight of the solute; ΔT is the elevation of the boiling point; and W_1 is the weight of the solvent. A value of $K_b = 2.292$ for tetrahydrofuran was used; this was determined using phenanthrene. For diethyl ether the literature value of $K_b = 2.02$ was used [108]. The molecular weights found are listed in Table 22. The results are expressed in terms of an association constant.

$\left(\frac{\text{Found M.W.}}{\text{Formula M.W.}}\right.$; c.f. page 43)

TABLE 22

Molecular weight determinations on ethylzinc iodide

	[EtZnI] m/l.	M.W. found	Assocn. Const.
In THF	0.03070	278.7	1.259
	0.03860	290.4	1.312
	0.06529	255.4	1.155
	0.12010	275.7	1.246
	0.40700	238.4	1.077
In Et_2O	0.01967	256.4	1.158
	0.03473	295.0	1.332
	0.05636	303.8	1.374
	0.06229	256.3	1.158
	0.10560	300.1	1.356

REFERENCES

[1] C. K. Ingold, Ann.Rep.Chem.Soc., 1961, LVIII, 167.

[2] G. Kobrich, Angew.Chem.(International Edn.), 1962, I, 382.

[3] O. A. Reutov, Journal of the D.I.Mendeleev All-Union Chemical Society, 1962, VII, 290.

[4] R. E. Dessy, F. Paulik, J. Chem. Ed., 1963, 40, 185.

[5] M. Gielen, J. Nasielski, Ind.Chim.Belg., 1961, 28, 1393.

[6] M. H. Abraham, J. A. Hill, Chem. and Ind., 1965, 561.

[7] H. B. Charman, E. D. Hughes, C. K. Ingold, Chem. and Ind., 1958, 1517. J. Chem. Soc., 1959, 2523.

[8] O. A. Reutov, I. P. Beletskaya, J. Yin-Tsei, Izvest.Akad. Nauk. S.S.S.R., 1960, 43.

[9] O. A. Reutov, V. I. Sokolov, I. P. Beletskaya, Doklady. Akad. Nauk. S.S.S.R., 1961, 136, 631.

[10] E. D. Hughes, C. K. Ingold, R. M. G. Roberts, J. Chem. Soc., 1964, 743.

[11] O. A. Reutov, B. Praisner, I. P. Beletskaya, V. I. Sokolov, Izvest. Akad. Nauk. S.S.S.R., 1963, 970.

[12] V. A. Kalyavin, T. A. Smolina, O. A. Reutov, Doklady. Akad. Nauk. S.S.S.R., 1964, 155, 596. Proc. Acad. Sci. U.S.S.R., 1964, 155, 273.

[13] idem, ibid., 1964, 156, 95. Proc. Acad. Sci. U.S.S.R., 1964, 156, 460.

[14] idem, ibid., 1964, 157, 919. Proc. Acad. Sci. U.S.S.R., 1964, 157, 762.

[15] C. R. Hart, C. K. Ingold, J. Chem. Soc., 1964, 4372.

[16] E. D. Hughes, C. K. Ingold, G. Thorpe, H. C. Volger, ibid., 1961, 1133.

[17] V. D. Nefedov, E. N. Sintova, N. Ya. Frolov, Zhur.fiz.khim., 1956, 30, 2356.

[18] E. D. Hughes, H. C. Volger, J. Chem. Soc., 1961, 2359.

[19] O. A. Reutov, V. I. Sokolov, I. P. Beletskaya, Izvest. Akad. Nauk S.S.S.R., 1961, 1213. Bull. Acad. Sci. U.S.S.R., 1961, 1123.

[20] idem, ibid., 1961, 1561. Bull. Acad. Sci. U.S.S.R., 1961, 1458.

[21] O. A. Reutov, T. A. Smolina, V.A.Kalyavin, Doklady. Akad. Nauk. S.S.S.R., 1961, 139, 389. Proc. Acad. Sci. U.S.S.R., 1961, 139, 697.

[22] F. R. Jensen, J.Amer.Chem.Soc., 1960, 82, 2468.

[23] H. B. Charman, E. D. Hughes, C. K. Ingold, G. Thorpe, J. Chem. Soc., 1961, 1121.

[24] H. B. Charman, E. D. Hughes, C. K. Ingold, H. C. Volger, ibid., 1961, 1142.

[25] O. A. Reutov, I. P. Beletskaya, R. E. Mardaleishvili, Proc. Acad. Sci. U.S.S.R., 1957, 116, 901.

[26] A. N. Nesmayanov, O. A. Reutov, W. Yang-Chieh, L. Ching-Chu, Bull. Acad. Sci. U.S.S.R., 1958, 1250.

[27] O. A. Reutov, I. P. Beletskaya, R. E. Mardaleishvili, Russ. J. Phys. Chem., 1959, 33, 240.

[28] F. R. Jensen, B. Rickborn, J.Amer.Chem.Soc., 1964, 86, 3784.

[29] I. P. Beletskaya, G. A. Artamkina, O. A. Reutov, Doklady. Akad. Nauk. S.S.S.R., 1963, 149, 90.

[30] M. Gielen, J. Nasielski, Bull.Soc.Chim.Belg., 1962, 71, 32.

[31] idem, ibid., 1962, 71, 601.

[32] idem, J. Organometallic Chem., 1963, 1, 173.

[33] R. E. Dessy et al., J.Amer.Chem.Soc. (a) 1959, 81, 2683, (b) 1961, 83, 1163, (c) 1962, 84, 1172.

[34] M. M. Kreevoy, R. L. Hansen, J.Amer.Chem.Soc., 1961, 83, 826.

[35] R. Walreavens, quoted in [36].

[36] M. Gielen, J. Nasielski, Rec.Trav.chim., 1963, 82, 228.

[37] G. C. Robinson, J.Org.Chem., 1963, 28, 843.

[38] M. H. Abraham, J. A. Hill, Proc.Chem.Soc., 1964, 175.

[39] J. H. Wotiz, C. A. Hollingsworth, R. E. Dessy, J.Org.Chem., 1955, 17, 103.

[40] M. D. Rausch, J. R. Van Wazer, Inorg.Chem., 1964, 3, 761.
R. E. Dessy, J. K. Lee, J.Amer.Chem.Soc., 1960, 82, 689.

[41] C. Deblandre, M. Gielen, J. Nasielski, Bull.Soc.Chim.Belg., 1964, 73, 214.

[42] H. Minato, J. C. Ware, T. G. Traylor, J.Amer.Chem.Soc., 1963, 85, 3024.

J. C. Ware, T. G. Traylor, ibid., p.3026.

[43] A. G. Davies, "Organic Peroxides", Butterworths, London, 1961, pp.124-127.

[44] P. H. Lewis, R. E. Rundle, J.Chem.Phys., 1953, 21, 986.

[45] N. Muller, D. E. Pritchard, J.Amer.Chem.Soc., 1960, 82, 248.

[46] J. Smidt, M. P. Groenewege, H. de Vries, Rec.Trav.chim., 1962, 81, 729.

[47] M. P. Groenewege, J. Smidt, H. de Vries, J.Amer.Chem.Soc., 1960, 82, 4425.

[48] E. G. Hoffman, Trans.Farad.Soc., 1962, 58, 642.

[49] J. P. Maher, D. F. Evans, J. Chem. Soc., 1963, 5534.

[50] G. E. Coates, "Organo-metallic compounds", Methuen and Co.Ltd., London, 1960, p.133.

[51] K. Ziegler, Annalen, 1960, 629.

[52] L. I. Zakharkin, O. Yu. Okhlobystin, Zhur. Obshchei, Khim., 1960, 30, 2134. J. Gen. Chem. U.S.S.R., 1960, 30, 2109.

[53] C. R. McCoy, A. L. Allred, J.Amer.Chem.Soc., 1962, 84, 912.

[54] R. E. Dessy, F. Kaplan, G. R. Coe, R. M. Salinger, ibid., 1963, 85, 1191.

[55] R. M. Salinger, R. E. Dessy, Tet. Letters, 1963, 11, 729.

[56] L. Pauling, "College Chemistry", W. H. Freeman and Co., 3rd Edn., 1964, p.278.

[57] D. A. Payne, R. T. Sanderson, J.Amer.Chem.Soc., 1958, 80, 5324.

[58] H. Gilman, R. N. Meals, G. O'Donnell, ibid., 1943, 65, 268.

[59] H. Gilman, F. Schulze, Bull.Soc.Chim.France, 1927, 41, 1333.

[60] H. Gilman, R. H. Kirby, M. Lichtenwalter, Rec.Trav.chim., 1936, 55, 79.

[61] D. Bryce-Smith, A. C. Skinner, J.Chem.Soc., 1963, 577.

[62] I. L. Finar, "Organic Chemistry, Vol.I", Longmans, Green and Co., London, 1959, p.331.

[63] R. E. Dessy, G. S. Handler, J. H. Wotiz, C. A. Hollingsworth, J.Amer.Chem.Soc., 1957, 79, 3476.

[64] R. E. Dessy, R. M. Jones, J.Org.Chem., 1959, 24, 1685.

[65] R. E. Dessy, ibid., 1960, 25, 2260.

[66] R. E. Dessy, J. H. Wotiz, C. A. Hollingsworth, J.Amer.Chem.Soc., 1957, 79, 358.

[67] R. E. Dessy, G. S. Handler, ibid., 1958, 80, 5824.

[68] R. E. Dessy, S. E. I. Green, R. M. Salinger, Tet. Letters, 1964, 21, 1369.

[69] D. O. Cowan, J. Hsu, J. D. Roberts, J.Org.Chem., 1964, 29, 3688.

[70] A. D. Vreugdenhil, C. Blomberg, Rec.Trav.chim., 1963, 82, 453.

[71] idem, ibid., 1963, 82, 461.

[72] idem, ibid., 1964, 83, 1096.

[73] idem, ibid., 1965, 84, 39.

[74] C. Blomberg, A. D. Vreugdenhil, B. Van Zanten, P. Vink, ibid., 1965, 84, 828.

[75] E. C. Ashby, W. E. Becker, J.Amer.Chem.Soc., 1963, 85, 118.

[76] E. C. Ashby, M. B. Smith, ibid., 1964, 86, 4363.

[77] G. Stucky, R. E. Rundle, ibid., 1964, 86, 4825.

[78] L. J. Guggenberger, R. E. Rundle, ibid., 1964, 86, 5344.

[79] H. Roos, W. Zeil, Chem. Ber., 1963, 67, 28.

[80] D. F. Evans, J. P. Maher, J. Chem. Soc., 1962, 5125.

[81] R. M. Salinger, H. S. Masher, J.Amer.Chem.Soc., 1964, 86, 1782.

[82] H. Gilman, F. Schulze, ibid., 1927, 49, 2904.

[83] R. E. Dessy, ibid., 1960, 82, 1580.

[84] L. I. Zakharkin, O. Yu. Okhlobystin, B. N. Strunik, Izvest. Akad. Nauk. S.S.S.R., 1961, 2254. Bull. Acad. Sci. U.S.S.R., 1961, 2114.

[85] E. E. Frankland, Annalen, 1849, 71, 171.

[86] C. R. Noller, "Organic Syntheses", Coll. Vol.II, 1950, p.184. J.Amer.Chem.Soc., 1929, 51, 594.

[87] E. E. Blaise, Bull.Soc.Chim.France, 1911, 9, 1.

[88] M. Gaudemar, ibid., 1962, 974.

[89] G. Jander, L. Fischer, Z.Elektrochem., 1958, 62, 971.

[90] N. I. Sheverdina, L. V. Abramova, K. A. Kocheshkov, Doklady, Akad. Sci. U.S.S.R., 1959, 124, 65.

[91] idem, ibid., 1960, 134, 853.

[92] K. A. Kocheshkov, N. I. Sheverdina, J.E.Paleeva, Bull.Soc.Chim. France, 1963, 1472.

[93] J. E. Paleeva, N. I. Sheverdina, L. V. Abramova, K. A. Kocheskov, Doklady. Akad. Nauk. S.S.S.R., 1964, 159, 609.

[94] A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley, A. Touma, Rec.Chem.Progress, 1952, 13, 155.

[95] R. E. Dessy, G. R. Coe, J. Org. Chem., 1963, 28, 3592.

[96] L. I. Zakharkin, O. Yu. Okhlobystin, Izvest. Akad.Nauk. S.S.S.R.,1963, 193. Bull. Acad. Sci. U.S.S.R., 1963, 176.

[97] R. Joly, R. Bucourt, U.S.Pat.3,040,079, 19th June, 1962. C.A., 1963, 58, 10238.

[98] N. I. Sheverdina, J. E. Paleeva, E. D. Delinskaya, K. A. Kocheshkov, Doklady. Akad. Nauk, S.S.S.R., 1959, 125, 348. Proc. Acad. Sci. U.S.S.R., 1959, 125, 222.

[99] J. A. Hill. Ph.D. Thesis, London, 1963.

[100] T. S. Lee, "Rates and Mechanisms of Reactions", Chapt.III, part 2, Interscience Publishers Inc., N.Y., 1953, Edited by S. L. Friess and A. Weissberger.

[100a] A. S. Carson, K. Hartley, H. A. Skinner, Trans.Farad. Soc., 1949, 45, 1159.

[101] K -H. Thiele, Z.Anorg.Chem., 1962, 319, 183.

[102] S. Brownstein, B. C. Smith, G. Ehrlich, A. W. Laubengayer, J.Amer.Chem.Soc., 1959, 81, 3826.

[102a] L. I. Zakharkin, O. Yu. Okhlobystin, K. A. Bilevitch, Tetrahedron, 1965, Vol.21, 881.

[103] N. Muller, A. L. Otermatt, Inorg.Chem., 1965, 4, 296.

[104] J. A. Pople, W. G. Schneider, H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance", McGraw-Hill, London, 1959, p.223.

[105] E. Krause, W. Fromm, Chem. Ber., 1926, 59, 931.

[106] H. Soroos, M. Morgana, J.Amer.Chem.Soc., 1944, 66, 893.

[107] G. E. Coates, D. Ridley, J.Chem.Soc., 1964, 166.

[108] "Handbook of Chemistry and Physics", Editor-in-Chief C. D. Hodgman. The Chemical Rubber Publishing Co., Ohio, 1962, p.2392.