Association Complexes of Aromatic Organometallic Halides in Solution.

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[Reprint Order No. 5646.]

Experiments are reported on the lowering of vapour pressure of solutions in diethyl ether of magnesium bromide or a Grignard compound, RMgX (R = *cyclo*hexyl, phenyl, *p*-tolyl, *o*-tolyl, or *p*-methoxyphenyl). Estimates have thus been obtained of the effect of the nature of R on the degree of association at different concentrations and temperatures. The bromine atom acts as a powerful centre promoting association of the Grignard compounds. Some associating power is also found in the organic groups, but any differences between the groups studied are small. Effects of traces of oxygen in promoting polymerisation are described.

THE formation of association complexes in solutions of Grignard reagents can influence the course of Grignard reactions (Mackle and Ubbelohde, *J.*, 1948, **1161**) in ways which may be important in syntheses and in the control of stoicheiometry required for calorimetric studies (Nichol and Ubbelohde, *J.*, 1952, 415). Complex formation may also be relevant for the interpretation of electron-deficient bonds involving organic groups, as in hexamethyldialuminium (Rundle, *J. Amer. Chem. Soc.*, 1947, **69**, 1327; *J. Chem. Phys.*, 1949, **17**, 671; Lewis and Rundle, *ibid.*, 1953, **21**, 986), and of polarisation bonds as in *p*-nitroaniline [McKeown, Ubbelohde, and (Miss) Woodward, *Acta Cryst.*, 1951, **4**, 391].

Published information on the molecular weights and association of Grignard compounds in solution is conflicting. Observations described on p. 111 suggest that part of the confusion may arise through the effects of oxygen in promoting polymerisation. Such effects may not have been completely excluded in all the results reported hitherto. From ebulliometric determination of the molecular weights Meisenheimer and Schlichenmaier (*Ber.*, 1928, **61**, 720) claimed that methylmagnesium iodide, ethylmagnesium bromide, and phenylmagnesium bromide exist in the monomeric form for concentrations less than 0·1M in diethyl ether. With increasing concentration the molecular weight increases, and it tends towards $(RMgX)_2$ for concentrations greater than 0·5M. On the other hand, Evans and Pearson (*J. Amer. Chem. Soc.*, 1933, **55**, 1474) claimed that phenylmagnesium bromide was colloidal and that the ions concerned were rapidly and completely transferred to anode and cathode during electrolysis. Other evidence suggests that any association complexes present in solutions of Grignard compounds appear to be ionic and dissociate into simpler species at higher temperatures. From solubility measurements, Stewart and Ubbelohde (*J.*, 1949, 2649) obtained evidence for equilibria involving complex formation, probably of the type:

$$n\mathrm{RMgX} \rightleftharpoons \mathrm{Mg}^{2+} + [\mathrm{R}_n\mathrm{Mg}_{n-1}\mathrm{X}_n]^{2-}$$

In the present work association has been studied in a range of Grignard compounds, chiefly aromatic, in diethyl ether solution, to obtain information about polarisation bonds. Lowering of vapour pressure was followed by means of a tensimeter of special design, to permit of observations on the change of association with time and with temperature. The results now obtained confirm the existence of limited association of the Grignard compounds. When magnesium bromide is added to the solutions there is a notable increase of association, confirming the conclusions from solubility measurements. Association also increases with increase of concentration, and decreases somewhat with rise in temperature, showing that no large heat changes are involved. Equilibrium depends on too many variables to permit of calculation of exact heats of dissociation. If allowance is made for for differences in the temperature of measurement the present findings agree much better with Meisenheimer and Schlichenmaier's at the boiling point of the solutions than with the conclusions based on electrolytic studies on phenylmagnesium bromide.

Because of the powerful influence of magnesium bromide in promoting association, it proved difficult to distinguish any major influence of the molecular structure of the different aromatic radicals on the degree of complex formation. So far as comparisons could be made under similar conditions relative tendencies to promote association appear to lie in the sequences Br > Cl; *cyclo*hexyl > phenyl > *p*-tolyl > *o*-tolyl > *p*-methoxyphenyl.

EXPERIMENTAL

Preparation of the Aryl- and Alkyl-magnesium Bromides.—Methods described by Mackle and Ubbelohde (*J.*, 1948, 1161) and Stewart and Ubbelohde (*J.*, 1949, 2649) were used, the amounts of organic halide being adjusted to give the desired concentrations of Grignard solutions. Dry, oxygen-free nitrogen was used to protect all the ethereal solutions at every stage during preparation, transfer, and storage. In view of previous experience on the photosensitivity of Grignard compounds all work was carried out in the dark or in diffused light.

Magnesium bromide was prepared by reaction of magnesium and bromine under dry ether. The reaction was moderated by a cold-water bath. Pure nitrogen was then passed over the solution until only white crystals remained. The issuing nitrogen was passed into alcoholic silver nitrate solution; no precipitate resulted, indicating the absence of volatile organic bromo-compounds which might have resulted from attack on the ether. The crystals were redissolved in pure ether and this solution was filtered through glass wool. As previously reported (Menschutkin, *Z. anorg. Chem.*, 1906—1909, **49**—**62**) the concentrated solution separates into two layers. The upper, water-white layer was used for vapour-pressure measurements and for addition of magnesium bromide to the other solutions studied. Estimation of bromide by Volhard's method and of magnesium gravimetrically as pyrophosphate gave a ratio of Mg : Br = 1·00 : 1·94 ± 0·03 (Calc. for $MgBr_2$, 1·00 : 2·00). This confirmed the conclusion obtained by the silver nitrate method that there was little or no attack on the ether, since reactions of the type

$$Mg + Br_2 + Et_2O \longrightarrow BrMg{\cdot}OEt + EtBr$$

would have increased the Mg : Br ratio above the theoretical value.

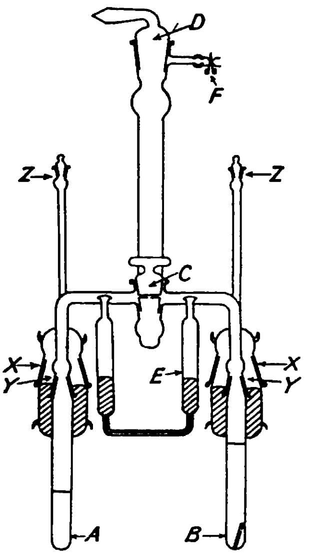


FIG. 1. *Tensimetric vapour-pressure apparatus.*

Differential Tensimetry.—In view of many difficulties encountered in obtaining reliable results with these labile ethereal solutions, the tensimeter is described in some detail (Fig. 1). All joints and taps except the B34 external joints *X* were well lubricated with starch–glycerol paste (Allen, Everett, and Penney, *Proc. Roy. Soc.*, 1952, *A*, **212**, 164) made by heating 8·25 g. of starch with 22 g. of glycerol under vacuum until a paste of the appropriate consistency resulted. The internal B14 joints *Y* on both tubes *A* and *B* were mercury-sealed by pouring dry mercury through the A7 joints Z, fused to the cups. The B34 joints, isolating the mercury from the water of the thermostat, were well lubricated with silicone high-vacuum grease. The diameter (1 cm.) of the tubing of the manometer E was chosen to minimise surface tension effects, yet avoiding the use of exceptionally large quantities of mercury.

Pressure differences were measured with a travelling microscope, mounted on a fixed steel plate which had been grooved to form a geometrical clamp, giving the necessary degree of freedom.

About 5 ml. of pure, dry ether were distilled off from 10 ml. of the Grignard solution into tube A, under vacuum. Tube A was then transferred to the tensimeter, and 10 ml. of Grignard solution were transferred to tube B. Tubes A and B were then further protected from light by metal-foil coverings, and their contents were frozen in liquid air. The apparatus was then evacuated through tap D to a pressure of approximately 10^{-3} mm. Tap D was then closed, the screw clip F tightened, and the apparatus removed from the vacuum-train and allowed to warm to room temperature.

This freezing of the Grignard solutions and of the pure ether led to the squeezing out of much dissolved gas from the crystal lattices; bubbles were visible on melting. This degassing was considerably assisted by a few glass helices, previously placed in the two tubes. The two solutions were then again frozen and the apparatus re-evacuated, isolated as before from the vacuum train, and allowed to warm to about 15°. The Grignard solution was agitated thoroughly by a piece of soft iron enclosed in Pyrex glass, by use of a small strong magnet externally, and the apparatus was placed in a thermostat ($\pm 0{\cdot}01°$) with the three-way tap C closed. The water level was adjusted to be just below C. After the solutions had reached equilibrium the pressure difference was then noted. As check, solutions of naphthalene in ether gave a lowering of vapour pressure (which was steady) within $\pm 0{\cdot}5\%$ of the value calculated for ideal 0·15M-solutions. In the complete absence of oxygen, vapour-pressure lowering due to the Grignard compounds likewise showed practically no drift at constant temperature. Drifts observed when oxygen was present are discussed below.

Analysis.—The content of Grignard reagent in the ethereal solutions was estimated by Gilman's acid titration. For this purpose a 10 ml. aliquot portion was pipetted out at the same time as filling of the tensimeter. To make sure changes of association were not due to decomposition, an aliquot portion was withdrawn from tube A at the end of a run and analysed in the same way. Total halide was also estimated by Volhard's method. Results are given in the second column of Table 1.

TABLE 1. *Association of Grignard reagents* (*complete absence of oxygen*).

R in RMgBr	Ratio, Halogen/Basicity	[RMgX] per 10 ml. ether (from basic titres) (milliequiv.)	Temp.	*i* uncorrected for side reactions	*i* corrected for side reactions
Phenyl	1·06 : 1·00	3·31	15·0°	1·85	1·97
	,,	,,	20·0	1·67	1·77
o-Tolyl	1·06 : 1·00	4·13	15·0	1·32	1·38
	,,	,,	20·0	1·33	1·39
p-Tolyl	1·20 : 1·00	2·10	15·0	1·27	1·58
	1·04 : 1·00	3·68	15·0	1·56	1·80
	,,	5·66	15·0	1·71	2·03
	—	,,	20·0	1·65	1·82
p-Methoxyphenyl ...	1·13 : 1·00	3·27	15·0	1·08	1·10
	—	—	20·0	1·00	1·03
*cyclo*Hexyl	1·21 : 1·00	1·89	15·0	1·76	2·29
	1·25 : 1·00	3·24	15·0	2·09	2·93
	—	,,	20·0	2·05	2·94
	1·25 : 1·00	6·69	15·0	2·60	4·14
	,,	,,	20·0	2·19	3·33
*cyclo*Hexyl (chloride)	1·09 : 1·00	5·51	15·0	1·20	1·28
	,,	,,	20·0	1·20	1·29
$\mathrm{MgBr_2}$	—	0·71	20·0	1·05	—

Departure of the ratio halogen/basic titre from 1·00 indicates that in addition to the normal Grignard reaction $\mathrm{Mg} + \mathrm{RX} \longrightarrow \mathrm{RMgX}$ side reactions (cf. Meisenheimer and Schlichenmaier, *Ber.*, 1928, **61**, 720) of the type

$$\mathrm{Mg} + 2\mathrm{RX} \longrightarrow \mathrm{R_2} + \mathrm{MgX_2} \qquad \text{(Würtz)}$$

and

$$\mathrm{Mg} + 2\mathrm{RX} \longrightarrow \mathrm{RH} + \mathrm{R''} + \mathrm{MgX_2} \ \text{(disproportionation)}$$

had occurred to some extent. When it was necessary to correct for these side reactions in subsequent molecular-weight determinations, the Würtz reaction was assumed to predominate, in accordance with general experience. As a result of solubility measurements (Stewart and Ubbelohde, *loc. cit.*) and other experiments quoted below, the MgX_2 in excess of the ratio 1·00 was taken to be incorporated into the association complex. Any uncertainty arising from these assumptions is serious only for *cyclo*hexylmagnesium bromide.

Mean Molecular Weights.—Observed lowerings of the vapour pressure by Δp (mm.) can conveniently be combined with the known vapour pressures p of pure diethyl ether at the same temperatures (taken from the International Critical Tables) by assuming the formal relation

$$\Delta p/p = n/(N + n) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where n is the number of moles of solute and N the number of moles of ether.

If n = number of moles of complex per 10 ml. of ether calculated from (1) and n_E = number of moles expected on the basis of the Gilman analyses, the formula weight being assumed to be the same as the molecular weight, then

$$i = n_E/n \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

Values of i uncorrected for any side reactions are given in Table 1. Values found by assuming Würtz side reactions and incorporation of the MgX_2 into the association complex are calculated by subtracting the lowering of vapour pressure $\Delta p'$ due to the R_2 molecules, from the total, and then calculating the number of moles n' from the equation

$$(\Delta p - \Delta p')/p = n'/(N + n') \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

and

$$i_{\text{corr.}} = n_T/n' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where n_T = number of moles of complex expected on the basis of the Gilman titration plus number of moles of magnesium bromide produced by Würtz reaction. The following is a typical calculation for the extreme case of *cyclo*hexylmagnesium bromide.

The concentrations (per 10 ml.) of the Grignard reagent (6·69 milliequiv.) and of magnesium bromide (8·36 milliequiv.) found differ by 1·67 milliequiv. or 0·84 mmoles. Thus $n_T = 6{\cdot}69 + 0{\cdot}84 = 7{\cdot}53$ mmoles, and the Würtz reaction has produced 0·84 mmoles of both di*cyclo*hexyl and magnesium bromide. The vapour pressure of diethyl ether being 360·7 mm. and the number of moles of ether, N, in 10 ml. of this solution being 0·0991, at 15°, the di*cyclo*hexyl will, by Raoult's law, produce a lowering of the vapour pressure, $\Delta p'$, given by

$$\Delta p' = 360{\cdot}7 \times 0{\cdot}84 \times 10^{-3}/(0{\cdot}84 \times 10^{-3} + 0{\cdot}0991) = 3{\cdot}01 \text{ mm.}$$

The lowering due to the Grignard complex is thus $\Delta p - \Delta p'$, corresponding to n' moles of complex and N of ether, and Δp is found experimentally to be 9·49. Equation (3), therefore, becomes $(9{\cdot}49 - 3{\cdot}01)/360{\cdot}7 = n'/(n' + 0{\cdot}0991)$, from which $n' = 1{\cdot}81$ mmoles per 10 ml. and, from equation (4), $i_{\text{corr.}} = 7{\cdot}53/1{\cdot}81 = 4{\cdot}14$. This correction leads to somewhat higher values of i, as shown in Table 1.

Addition of Excess of Magnesium Bromide.—Because of the marked effect of the magnesium bromide produced in side reactions on the degree of association, it was desirable to obtain some quantitative measure of changes due to variations in concentration of magnesium bromide.

TABLE 2. *Effect of magnesium bromide on the association of Grignard compounds at* 15°.

R in RMgBr	Concn. (mmoles/ per 10 ml. of ether)	Halogen/ basicity	i uncorr.	R in RMgBr	Concn. (mmoles/ per 10 ml. of ether)	Halogen/ basicity	i uncorr.
Phenyl	3·31	1·06	1·90	*p*-Methoxyphenyl	3·27	1·00	1·10
	2·69	1·20	2·22		2·10	1·20	1·30

The two systems selected had quite different concentrations of magnesium bromide originally, and were brought to approximately the same halogen/basicity titre by the addition of pure magnesium bromide dissolved in ether. Results were as in Table 2; the upper line gives the parameters of the solution as prepared in the formation of the Grignard compound, the lower the solution after addition of magnesium bromide.

Association in the Presence of Small Amounts of Oxygen.—The experimental evidence to be described differs from that on the more extensive attack by this gas on Grignard solutions

(Meisenheimer, *Ber.*, **1928**, **61**, 708), in that much less oxygen was involved in our experiments. The influence of oxygen now observed may even be catalytic. Two principal types of observation were made: (i) If the solutions of aromatic Grignard compounds were prepared and handled throughout under nitrogen rigorously freed from oxygen, they could be frozen to give white crystals and remelted to give identical products. But if the nitrogen contained as little as 2% of oxygen, even when the solutions were exposed to this gas for only a few minutes, a heavy yellow oil separated on freezing. After warming, this could only be redispersed after considerable agitation. Separate analyses of the two layers showed an enhancement of the halogen/basicity ratio in the oil. This would hardly be the case if this polymer incorporated Mg–OR linkages (Meisenheimer). Further discussion of this polymerisation is deferred. Comparisons of the vapour pressures before and after freezing out of the oil showed very little change due to its removal, showing that its molecular weight was very considerably higher than that of the ordinary association complex.

TABLE 3*A*. *Effects of oxygen on the composition of the association complexes.*

R in RMgBr	Halogen/basicity		R in RMgBr	Halogen/basicity	
o-Tolyl	Original overall	1·03 : 1·00	*p*-Tolyl	Original overall	1·04 : 1·00
	In upper layer after freezing	0·92 : 1·00		In upper layer after freezing	1·00 : 1·00
	In oil after freezing	1·25 : 1·00		In oil after freezing	1·19 : 1·00

Storage of Grignard solutions for 24 hr. under nitrogen in flasks fitted with ungreased standard ground stoppers led to the separation of oil after freezing. When a positive pressure of nitrogen was maintained, with ungreased stoppers, no oil was formed. *cyclo*Hexylmagnesium bromide (and magnesium dibromide) showed no tendency to polymerise in this way. *cyclo*Hexylmagnesium bromide solutions froze to a clear glass whether exposed to oxygen or not.

(ii) If solutions of Grignard compounds were exposed for a brief time to diluted oxygen, and were then examined in the tensimeter, the vapour pressure was much less steady and tended to drift for as much as 100 hr. *cyclo*Hexylmagnesium bromide showed no drift. Ultimately a markedly higher degree of overall association was observed than in the absence of oxygen. This can be seen from Table 3*B*, which should be compared with Table 1.

TABLE 3*B*. *Association in the presence of small quantities of oxygen.*

R in RMgBr	Concn., mmoles/ per 10 ml.	Temp.	$i_{\text{uncorr.}}$	R in RMgBr	Concn., mmoles/ per 10 ml.	Temp.	$i_{\text{uncorr.}}$
Phenyl	4·20	15·0°	5·98	*p*-Tolyl	1·87	15·0°	3·88
						20·0	

DISCUSSION

Inspection of the i values in Table 1 makes it evident that these Grignard compounds are associated to a moderate extent in ether. There is an increase in association with increase of concentration for example in the *cyclo*hexyl or *p*-tolyl compounds; an overall picture is obtainable from Fig. 2. Increase of temperature decreases association to some extent for *cyclo*hexyl-, phenyl-, *p*-tolyl-, and *p*-methoxyphenyl-magnesium bromide, but has little effect on *o*-tolylmagnesium bromide or on *cyclo*hexylmagnesium chloride. Heats of dissociation appear to be small. Exact calculation from the van't Hoff isochore is hampered by the number of variables which influence the degree of association. A large number of experiments would be required to establish the precise equilibrium constants at different temperatures.

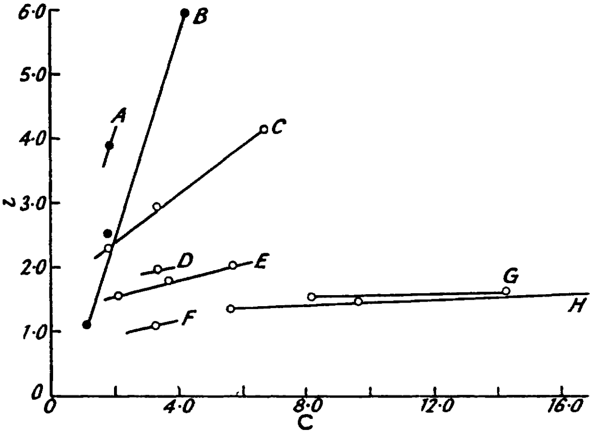
As shown in Table 2, i for phenylmagnesium bromide is raised from 1·90 to 2·22 by adding magnesium bromide equivalent to the amount present in *cyclo*hexylmagnesium bromide. At corresponding concentrations of magnesium bromide the i value for the *cyclo*hexyl compound is still appreciably greater (2·70), while *p*-methoxyphenylmagnesium bromide even with a halogen/basic titre ratio raised to 1·20 is still the least associated bromide. Differences between the organic radicals discussed below are thus somewhat reduced but are not wiped out when allowance is made for the magnesium bromide present. Magnesium bromide has $i = 1·05$ referred to undissociated magnesium bromide. Apart from the possibility that it exists very largely in undissociated form in ethereal solution, it could also be present mainly as $[\mathrm{Mg},n\mathrm{Et_2O}]^{2+}[{}^{\mathrm{Br}}_{\mathrm{Br}}{>}\mathrm{Mg}{<}^{\mathrm{Br}}_{\mathrm{Br}}]^{2-}$ (cf. Meisenheimer and Schlichenmeier, *loc. cit.*) but in the presence of excess of Grignard compound which forms complexes with magnesium bromide any correction for this effect may be neglected.

Detailed Effects of the Structure of R *on the Degree of Association.*—Further interpretation of the results requires additional assumptions which seem reasonable but are not yet fully substantiated. On the basis of the work of Evans and his colleagues, it seems likely that the Grignard compounds must be written in the form $\mathrm{Mg^{2+}[Mg_{\mathit{r}-1}R_{\mathit{r}}X_{\mathit{r}}]^{2-}}$, possibly with some ether co-ordinated with the ions. At present the values of *r* are not known. Indeed, it seems likely that a cascade of equilibria is present, of the type

$$[\mathrm{Mg}_{r+1}\mathrm{R}_r\mathrm{X}_r]^{2-} \rightleftharpoons \mathrm{RMgX} + [\mathrm{Mg}_r\mathrm{R}_{r-1}\mathrm{X}_{r-1}]^{2-}$$
$$[\mathrm{Mg}_r\mathrm{R}_{r-1}\mathrm{X}_{r-1}]^{2-} \rightleftharpoons \mathrm{RMgX} + [\mathrm{Mg}_{r-1}\mathrm{R}_{r-2}\mathrm{X}_{r-2}]^{2-}$$

Furthermore, when excess of magnesium bromide is added it is readily incorporated into the complexes, facilitating the building-up of larger values of *r*. If, as a simplifying approximation, only a single species of complex anion is assumed to be present, the calculated values of *r* change with concentration, and with the nature of R, as shown in Table 4. The series refer to the same experiments as in Table 1. $r = 2i_{\mathrm{corr.}}$.

FIG. 2. *Variation of association with concentration for* RMgBr.



i = observed molecular weight/formula weight.

c = concn. in mmoles per 10 ml. of solution.

Small amounts of oxygen present (15°).

A = *p*-tolylmagnesium bromide.
B = phenylmagnesium bromide.

Rigorous exclusion of oxygen (15°).

C = *cyclo*hexylmagnesium bromide.
D = phenylmagnesium bromide.
E = *p*-tolylmagnesium bromide.
F = *p*-methoxyphenylmagnesium bromide.

In boiling ether (35°).

G = phenylmagnesium bromide.
H = ethylmagnesium bromide.

TABLE 4. *Apparent size,* r, *of complex anions in Grignard compounds,* RMgBr.

R	*r*	Temp.	R	*r*	Temp.	R	*r*	Temp.
Phenyl	3·94	15·0°	*p*-Tolyl	3·16	15·0°	*cyclo*Hexyl	4·58	15·0°
	3·54	20·0		3·60	15·0		5·86	15·0
				4·06	15·0		5·88	20·0
o-Tolyl	2·76	15·0		3·64	20·0		8·28	15·0
	2·78	20·0					6·66	20·0
			p-Methoxyphenyl	2·20	15·0		2·56	15·0
				2·06	20·0		2·58	20·0

Except in the extreme case of *cyclo*hexylmagnesium bromide, differences in the halogen/basicity ratio are not sufficiently large (cf. Table 2) to have major influence on the values of *r*, and may provisionally be disregarded. When values of *r* for the different R radicals are compared, it seems safe to say that these promote association in the sequence *cyclo*hexyl > phenyl > *p*-tolyl > *o*-tolyl > *p*-methoxyphenyl. The origin of the association forces present is not definitely known, so that only brief reference will be made to some of the possibilities.

(i) In principle, all the aromatic radicals can act as acceptor groups and form polarisation bonds with the halogens. The direction of the electron displacement in the dotted polarisation bond is shown by the arrow in Fig. 3. For this kind of association, which resembles that in potassium graphite (McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191) and in potassium anthracene (Holmes-Walker, and Ubbelohde, *J.*, 1954, 720), substituents in the aromatic group which are electron donors should reduce the tendency to form association bonds between the bromide ion and the acceptor aromatic group. Roughly speaking, this is what is found, though steric effects probably also operate. This polarisation bonding would be stronger for Br^- than for Cl^- which is again as found. Recently a crystalline compound between bromine and perylene has been described (Akamatu, Inokuchi, and Matsunaga, *Nature*, 1954, **173**, 168) in which perylene appears to be the electron acceptor.

(ii) The aromatic groups might act as donor groups, through an overlap of their π-orbitals with empty orbitals of the magnesium, such as an sp^3-hybridised tetrahedral set (Fig. 4). Overlap of this kind could be stabilised by the formation of a complex anion which increases

FIG. 3. *Phenylmagnesium bromide complex with possible polarisation bonding.*

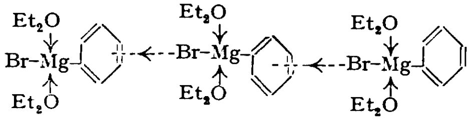
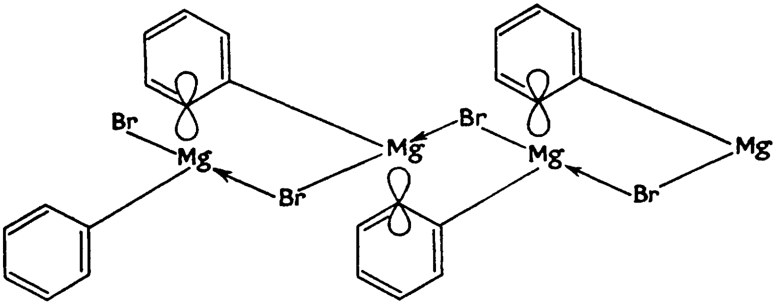


FIG. 4. *Phenylmagnesium bromide, showing possible π-orbital overlap.*



the symmetry of the system. This type of bonding would have certain analogies with the complexes between the silver ion and aromatic groups (Rundle and Goring, *J. Amer. Chem. Soc.*, 1950, **72**, 5337; Andrews and Keefer, *ibid.*, 1949, **71**, 3644; 1950, **72**, 3113, 5034).

Bonding in benzene complexes such as C_6H_6,Al_2Br_6, C_6H_6,Al_2I_6, which are stated to exist in solution (Eley and King, *J.*, 1952, 4972) has been represented by the two canonical structures :

(I) C_6H_6,Al_2Br_6 $\qquad\qquad$ $C_6H_6^+,Al_2Br_6^-$ (II)

The bonding in (I) and (II) may involve aromatic donor groups with electron interaction with the aluminium. Or there may be donation of *d*-electrons from bromine to the anti-bonding orbitals of the aromatic group acting as electron acceptor (Dewar, *Bull. Soc. chim.*, 1951, **18**, 79C; Eley and King, *loc. cit.*). These alternative suggestions have analogies with possibilities (i) and (ii) above.

(iii) The *cyclo*hexyl group which shows tendencies to promote association is incapable of forming either type of bonding described above for aromatic systems. Unless the association is to be entirely attributed to the halogen groups, *cyclo*hexyl must form overlap bonds of some kind with empty orbitals of the magnesium atoms, but their nature is as yet obscure.

Acknowledgement is made by one of us (W. S.) to Imperial Chemical Industries Limited for a research grant.

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[*Received, August* 16*th*, 1954.]