231. *Organometallic Compounds of Group II. Part III.*[1] *Unsolvated Organomagnesium Halides.*

By D. Bryce-Smith and G. F. Cox.

Organomagnesium halides have been prepared in hydrocarbon media by reactions between various alkyl and aryl halides and magnesium in the absence of the usual ethereal catalysts. The procedure has a narrower range of application than that used conventionally, but has given yields of up to 95% in certain cases. Frequently, but not invariably, the freshly prepared hydrocarbon-soluble products have an empirical formula close to R_3Mg_2Hal, and an apparently similar material has been obtained by desolvation of an ethereal Grignard reagent. Viscosity studies have suggested that these compounds are linearly associated, with a degree of association dependent on concentration. Changes of composition with time have also been observed. Unlike ethereal Grignard reagents, the present compounds react with titanium halides to provide catalysts effective for the polymerisation of ethylene and propene at 20° and atmospheric pressure.

In Parts I [2] and II,[1] respectively, reactions between alkyl halides and magnesium to produce free alkyl radicals and Friedel–Crafts-type alkylation of aromatic solvents were described. The present paper is concerned with conditions for the production of unsolvated organomagnesium halides by such reactions, and with some of their properties.

The excellence of Grignard's classical procedure seems largely to have discouraged attempts to prepare organomagnesium halides in the total absence of ethers and other donor catalysts (cf. Kharasch and Reinmuth [3]). Several workers have used hydrocarbon media which contained catalytic quantities of ether, dimethylaniline, etc.[3] Tschelinzeff [4] reported the preparation of Grignard reagents from some alkyl iodides in boiling xylene without added catalyst, but gave no yields or other details. Schlenk [5] obtained some high yields in benzene, but the reactions required two months for completion. König [6] obtained

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[1] Part II, Bryce-Smith and Owen, *J.*, 1960, 3319.

[2] Bryce-Smith and Cox, *J.*, 1958, 1050.

[3] Kharasch and Reinmuth, " Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954, p. 50.

[4] Tschelinzeff, *Ber.*, 1904, **37**, 4534.

[5] Schlenk, *Ber.*, 1931, **64**, 739.

[6] König, *Monatsh.*, 1955, **96**, 419.

a 42% yield of ethylmagnesium iodide in boiling benzene after three hours, and used aluminium chloride to catalyse some related preparations. Several workers [7,8] have prepared phenylmagnesium chloride by heating magnesium with an excess of chlorobenzene under pressure at *ca.* 160°, and Weissenborn [9] reports that freshly cut magnesium can be used at lower temperatures (cf. Shaw [10]), but Shoruigin *et al.*[11] found this technique to fail with various alkyl chlorides. No halogen analyses have been reported for the organomagnesium products of any of these reactions, and the formula RMgHal has been widely assumed. Little has been written of the general properties or constitution of unsolvated organomagnesium halides beyond statements that they are involatile and infusible solids, quite insoluble in hydrocarbons (but see below).[12]

An 85·5% yield of n-butylmagnesium iodide was reported in Part I [2] for a reaction between n-butyl iodide and magnesium powder in isopropylbenzene at 130°; but n-butyl chloride gave only 25% of n-butylmagnesium chloride under similar conditions. By substitution of tetrahydronaphthalene for isopropylbenzene, 85% yields of n-butylmagnesium chloride have now been readily obtained. A similar high yield of n-butylmagnesium bromide has been obtained in isopropylbenzene. These yields approximate to those reported for ethereal preparations.[13] Preliminary experiments with lower alkyl halides have given poor yields, but no attempt has been made to discover optimum conditions in these cases. No significant yields of organomagnesium products have been obtained by the use of various secondary and tertiary alkyl or benzyl halides, because of either failure to react with the metal or an excessive tendency for Wurtz-type reactions. On the other hand, phenyl halides have given good yields in deca- or tetrahydronaphthalene, or even the " paraffin oil " sold as a domestic fuel. There was no tendency for phenylation of aromatic media (cf. Part II [1]).

In general, high yields in hydrocarbon media appear to require much greater attention to the experimental conditions than is required in conventional Grignard preparations. The optimum temperature seems to be a compromise between the need to ensure a sufficiently rapid reaction of the organic halide with magnesium, and the avoidance of Wurtz-type reactions, pyrolysis of the product, and magnesium halide-catalysed alkylation of aromatic solvents.[1] This temperature appears to vary from halide to halide, and tends to be somewhat higher with chlorides than with iodides. Wurtz-type reactions are minimised by slow addition of the halide, and the use of untarnished magnesium powder rather than turnings. n-Butylmagnesium iodide was reasonably stable at 130°, whereas the chloride had completely decomposed within three days at this temperature. It is not known whether this order of stability is general. With n-butyl chloride and bromide, the tendency to alkylate aromatic media was largely avoided by the use of a sufficiently high temperature (130° rather than *ca.* 100°).[1] Reduction in the proportion of magnesium was found to promote alkylation. Thus, although butylisopropylbenzenes were formed as minor side products in the preparation of n-butylmagnesium chloride from n-butyl chloride and a slight excess of magnesium in isopropylbenzene, and no hydrogen chloride was evolved,[1] the use of a catalytic quantity of magnesium gave butylisopropylbenzenes in 52% yield, and the evolution of 75·5% of the chlorine from the halide as free hydrogen chloride.

The solubilities of organomagnesium halides in hydrocarbons varied from case to case but, contrary to previous statements,[12] were normally appreciable and sometimes quite high. From limited data, they appeared to increase in the order Cl $<$ Br $<$ I, and with

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[7] Gilman and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 3330.

[8] Shoruigin, Issagulianz, Gusseewa, Ossipowa, and Poliakowa, *Ber.*, 1931, **64**, 2584.

[9] Weissenborn, G.P. 697,420/1940.

[10] Shaw, *J. Appl. Mechanics*, 1948, **15**, 37.

[11] Schoruigin, Issagulianz, and Gussewa, *Ber.*, 1933, **66**, 1426.

[12] Rochow, Hurd, and Lewis, " The Chemistry of Organometallic Compounds," Wiley, New York, 1957, p. 88.

[13] Houben, Boedler, and Fischer, *Ber.*, 1936, **69**, 1766.

the length of the alkyl chain (methylmagnesium iodide was almost completely insoluble in isopropylbenzene), and tended to be greater in aromatic than in aliphatic hydrocarbons.

No general chemical comparison with ethereal Grignard reagents has yet been made, although the normal reactions have been observed with carbon dioxide, chlorotriphenylsilane,[2] ethyl benzoate,[14] and Michler's ketone. Preliminary work (with Mr. E. T. Blues) has indicated that unsolvated organomagnesium compounds are more active than ethereal Grignard reagents as polymerisation catalysts for common vinyl monomers and have advantages in the synthesis of organo-aluminium, -boron, and -tin compounds. Unlike ethereal Grignard reagents, the unsolvated materials have been found to react with titanium(III) or (IV) chloride to give complexes which rapidly convert ethylene or propene at 20° and atmospheric pressure into essentially linear, solid polymers of high molecular weight: the polymerisation of propene was substantially stereospecific (cf. Erusalimski *et al.*,[15] and Ziegler [16]). The use of the insoluble organomagnesium reagents described previously,[16] in conjunction with insoluble titanium(III) halides, would presumably be impracticable.

Formulæ of Organomagnesium Halides.—These have been found from the ratios of hydroxide to halide ions produced by hydrolysis of aliquot parts of the hydrocarbon solutions (base/halide ratios). In many cases, and particularly with freshly prepared solutions, the ratio has been close to 3, indicative of the empirical formula R_3Mg_2Hal (or $R_2Mg,RMgHal$). Addition of isopropylbenzene to a conventionally prepared solution of n-butylmagnesium iodide in ether, followed by removal of the ether, gave a solution of n-butylmagnesium iodide in isopropylbenzene having a base/halide ratio of 3·0, and almost identical in this respect with a solution prepared directly in isopropylbenzene from n-butyl iodide and magnesium. The use of a catalytic quantity of ether in such a preparation gave a solution having a base/halide ratio of 3·3. Less frequently, and rather irreproducibly, especially with chlorides, solutions prepared by the direct method had base/halide ratios as low as 2 or as high as 6. The irreproducibility is probably connected with changes that have been found to occur in the reagents with time. Thus, a freshly prepared solution of n-butylmagnesium chloride in isopropylbenzene had an initial base/halide ratio of 2·0: after 19 and 50 hours at 25°, the ratios were 5·0 and 14·6 respectively. These changes in composition were accompanied by a slow precipitation of solid from solution, and the corresponding solution normalities with respect to C–Mg bonds were 0·235, 0·075, and 0·085.

These observations seem not to be explained adequately by the assumption implied in Part I [2] that the solutions contain mixtures of R_2Mg and RMgHal. The presence of R_2Mg is inconsistent with the solubility data. Thus, Strohmeier [17] reported the solubilities of diphenylmagnesium and diethylmagnesium in benzene at 25° to be 0·006 and 0·016 mole per l. respectively. We found that a saturated solution of di-n-butylmagnesium in boiling isopropylbenzene at 151° contained the equivalent of 0·008 mole of $Bu^n{}_2Mg$ per l., and the solubilities of anhydrous magnesium halides were too low to be measured. The present, freshly prepared n-butyl- and phenyl-magnesium halides had a much higher order of solubility, and the solutions can therefore have contained little if any free R_2Mg or $MgHal_2$. A slight uncertainty arises from a possible variation of solubility of R_2Mg with the degree of association; but this variation seems likely to be small in comparison with the observed differences, and would not readily account for the marked dependence of the solubility of freshly prepared n-butylmagnesium halides on the nature of the halogen. Further, Ph_3Mg_2Cl crystallised from tetrahydronaphthalene unchanged in its empirical composition. This behaviour would not be expected from a mixture of complexes

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[14] Bryce-Smith and Skinner, unpublished work.

[15] Erusalimski, Fo-Sun, and Kabonenko, paper presented at the Symposium on Macromolecular Chemistry, Moscow, 1960.

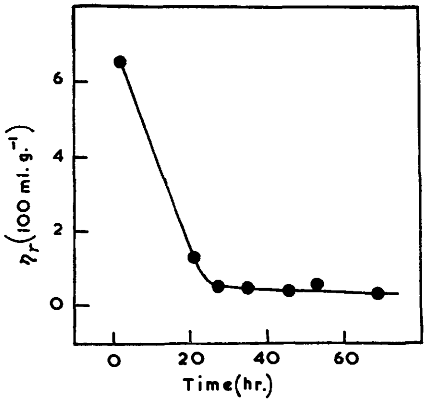
[16] Ziegler, B.P. 801,031/1958.

[17] Strohmeier, *Ber.*, 1955, **88**, 1218.

differing in their halogen content, but rather suggests either the presence of a single solute species or, more probably, a range of associated species $(Ph_3Mg_2Cl)_n$.

We suggest that the changes that can occur in these reagents with time result from a tendency for slow elimination of insoluble magnesium halide to give species which contain progressively less halogen and become correspondingly less soluble until the almost insoluble R_2Mg compound is attained. An example of this extreme production of di-n-butylmagnesium, when n-butyl bromide was heated under prolonged reflux with magnesium in benzene, was given in Part II.[1] It is noteworthy that Gilman and Brown [18] obtained dimethylmagnesium by heating methylmagnesium chloride at 190°.

Viscosity Studies.—The present solutions in hydrocarbons were normally markedly more viscous than are ethereal Grignard reagents, these being often about two-fold associated, depending on the concentration.[19] The association of $Bu^n{}_3Mg_2I$ has been investigated by measurements of the reduced viscosity, η_r, of a solution in isopropylbenzene. For molecular weights, M_1, up to *ca.* 8000, the intrinsic viscosity $[\eta] = k_1 + k_2M_1$. At higher molecular weights, M_2, the relation $[\eta] = k_3M_2{}^{\alpha}$ is generally considered to hold. k_1, k_2, k_3, and α are constants which depend only on the solvent and the chemical and physical nature of the solute. The reduced viscosity is related to the intrinsic viscosity by the empirical equation $\eta_r = [\eta] + k_1[\eta]^2c + k_2[\eta]^3c^2 + \ldots$, where c is the concentration of the solute, and k_1, k_2, etc., are constants independent of the molecular weight of the solute. Thus, although the reduced viscosity is normally a function of the molecular weight of the solute, only relative rather than absolute values of molecular weights have been obtained owing to the difficulty of assigning values for the constants which would be applicable to a system of the present unusual type, and the unavailability of structurally analogous reference solutes of known molecular weight.



Variation, with time, of the reduced viscosity at 25° *of* 0·26N-*n-butylmagnesium iodide in isopropylbenzene after dilution from* 0·52N.

The variation in reduced viscosity with time of a 0·26N-solution of $Bu^n{}_3Mg_2I$ in isopropylbenzene is shown in the Figure. This solution was prepared by dilution of a 70-hours-old 0·52N-solution at zero time on the graph. It may be seen that the reduced viscosity decreased markedly over a period of about 25 hours and thereafter became almost constant. There were only slight variations in the base/halide ratio during the experiment, and no solid matter separated in the viscometer. The simplest explanation for this is that slow dissociation of an associated solute occurred after dilution, until the mean molecular weight became characteristic of the lower concentration. Changes in density with time were also observed (Table 2), but their structural implications are uncertain (particular care was taken to exclude all oxygen during this experiment in view of Slough and Ubbelohde's report of its effect in promoting the association of ethereal

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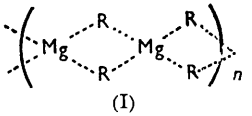
[18] Gilman and Brown, *Rec. Trav. chim.*, 1929, **48**, 1133.
[19] Slough and Ubbelohde, *J.*, 1955, 108.

Grignard reagents [19]). Experiments with more concentrated solutions of n-butylmagnesium iodide were unsatisfactory owing to a tendency for separation of solid solute; this may have been a supersaturation phenomenon, or may perhaps have involved the production of less soluble material by association. The variation of molecular weight with concentration, inferred from the Figure, and found also with ethereal Grignard reagents,[19] has a parallel in Coates, Glockling, and Huck's observation [20] that the degree of association of dimethylberyllium vapour is pressure-dependent.

It thus appears from the available data that hydrocarbon solutions of organomagnesium halides are liable to suffer spontaneous change both through disproportionation and through changes in the degree of association, and that the relative importance of these two processes varies with the nature of the groups involved.

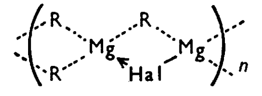
Structure.—Dimethylberyllium is known to have a linear polymeric structure,[21,20] and an analogous structure (I) has often been inferred for dialkylmagnesium compounds (electron-deficient bonds are denoted by dotted lines). For unsolvated organomagnesium halides, the present results are consistent with a range of similar structures in which there is partial replacement of R by halogen atoms. Stoicheiometry suggests that the *initial* product of reaction between magnesium and alkyl halides should be RMgHal; and in the absence of donor solvents fairly rapid association of this hypothetical intermediate is to be expected.* Since products where R/Hal $\approx$ 1 have not yet been obtained, we assume that $MgHal_2$ is readily lost under the experimental conditions. It seems that structures having R/Hal $\approx$ 3 provide a somewhat preferred arrangement, although the reasons for this, and for the evident instability of the initial product, remain obscure. The final product, only attained on a single occasion, appears to be a mixture of MgR_2 and $MgHal_2$. Formulæ (II) and (III) represent the repeating units in two possible structural alternatives when R/Hal = 3.

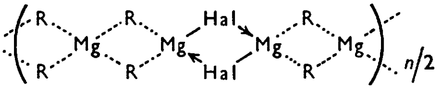


(I)

No clear decision between (II) and (III) is yet possible. No examples of " mixed " bridges of the type shown in (II) have been established although their existence has been occasionally suggested.[24] Moreover, it seems likely that the orbital overlap involved in such bridges would be a compromise resulting from differing geometric needs of R and Hal, and less than in symmetrical bridges. In the case of dimeric methylaluminium halides, $MeAlHal_2$ and Me_2AlHal, where " mixed " bridges might in principle be possible, van der Kelen and Herman [25] have obtained evidence from Raman spectra that bridging occurs only *via* the methyl groups. Further, the suggested disproportionation by elimination of magnesium halide can be more readily envisaged on the basis of (III) than of (II). Formula (III) is therefore slightly preferred.

(II)





(III)

EXPERIMENTAL

Oxygen-free nitrogen (B.O.C. " White Spot ") was used in all preparations, and for the viscosity experiments was further purified over heated copper. Hydrocarbon solvents were

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* In view of the long-established usage of " RMgHal " as a shorthand term for Grignard reagents, it is noteworthy that no unsolvated compound of this empirical formula has yet been shown to exist. The closest approach is found in BrMg·C≡C·MgBr which, remarkably, is reported not to form an ether complex under the usual conditions.[22] Alkylmercuric halides appear to provide the only monomeric examples of this structural type in Group II.[23]

[20] Coates, Glockling, and Huck, *J.*, 1952, 4496.

[21] Snow and Rundle, *Acta Cryst.*, 1957, **4**, 348.

[22] Kleinfeller, *Ber.*, 1929, **62**, 2736.

[23] Dessy and Lee, *J. Amer. Chem. Soc.*, 1960, **82**, 689.

[24] Ref. 12, p. 92.

[25] van der Kelen and Herman, *Bull. Soc. chim. belges*, 1956, **65**, 362.

dry (CaH_2) and peroxide-free, and were redistilled immediately before use. Magnesium was used in the form of bright powder (*ca.* 150 mesh) and this was found much superior to the usual turnings. Turnings were used where indicated when suitable powder was temporarily unavailable, but not from choice. Mixtures were vigorously stirred. Initiation by a trace of

TABLE 1. *Preparation and analyses of n-butyl- and phenyl-magnesium halides in hydrocarbons.*

Experiment no.	1	2					3	4
Organic halide	n-BuI	n-BuI					n-BuI	n-BuBr
Amount of halide (mole)	0·071	0·080					0·070	0·080
Solvent	C [a]	C [a]					C [a]	C [a]
Amount of solvent (mole)	0·30	0·59					0·31 [c]	0·58
Amount of magnesium (g.-atom)	0·123	0·278					0·123	0·276
Reaction temperature	130°	130°					20—25°	130°
Time of addition of halide (min.)	29	45					20	70
Time of stirring (min.)	120	120					200	150
Amount of solvent added at end of reaction (mole)	0·298	0					0	0·29
Temperature at which 1-ml. portion was taken for analysis	20°	25°	25°	25°	25°	25°	20°	20°
Time after which aliquot portion was taken for analysis (hr.)	—	3	50	314	362	458	48	4
Base titre (ml. of 0·1N-H_2SO_4)	6·1	9·75	9·9	8·2	8·45	8·4	23·0 [g]	5·6
Yield of C–Mg material (%)	73	83·5	—	—	—	—	37	83·5
Halide titre (ml. of 0·1N-$AgNO_3$)	2·1	4·95	1·95	2·15	2·2	2·1	6·9 [g]	1·75
Base/halide ratio	2·9	2·0	5·1	3·8	3·8	4·0	3·3	3·2

Experiment no.	5			6		7		8		
Organic halide	n-BuCl			n-BuCl		PhCl		PhCl		
Amount of halide (mole)	0·080			0·080		0·084		0·082		
Solvent	C [a]			T [b]		T [b]		T [b]		
Amount of solvent (mole)	0·58			0·59		0·60		0·66		
Amount of magnesium (g.-atom)	0·284			0·273		0·266 [f]		0·146		
Reaction temperature	135°			130°		180—185°		180—185°		
Time of addition of halide (min.)	35			50		20		25		
Time of stirring (min.)	120			120		120		45		
Amount of solvent added at end of reaction (mole)	0			0		1·51		1·07		
Temperature at which 1-ml. portion was taken for analysis	25°	25°	25°	130°	130°	180—185°	23°	170°	22°	170°
Time after which aliquot portion was taken for analysis (hr.)	3	22	72	3·5	28·5	1	20	1	27	31·5
Base titre (ml. of 0·1N-H_2SO_4)	2·35	0·75	4·4 [g]	7·65	3·58	1·85	5·15 [g]	11·9 [g]	5·8 [g]	12·2 [g]
Yield of C–Mg material (%)	26·4	—	—	85	—	*ca.* 70	—	—	—	*ca* 75 [h]
Halide titre (ml. of 0·1N-$AgNO_3$)	1·15	0·15	0·3 [g]	2·0	0·7	0·6	1·6 [g]	2·1 [g]	1·45 [g]	2·2 [g]
Base/halide ratio	2·0	5·0	14·6	3·8	5·1	3·1	3·2	5·65	4·5	5·6

[a] C = Isopropylbenzene. [b] T = Tetrahydronaphthalene. Decahydronaphthalene, "Novasol" (Shell), and "Aladdin Pink paraffin" (purified with oleum and redistilled) also proved to be suitable solvents. [c] Diethyl ether (0·003 mole) was added. [d] Magnesium coarser than 40 mesh was used. [e] A similar experiment in which the proportion of magnesium was reduced to 4% of this figure (0·0114 g.-atom) gave no organomagnesium compounds. Instead, butylisopropylbenzene (52%), of unknown isomeric composition, was obtained, having b. p. 206—230°, n_D^{20} 1·4886 (Found: C, 88·7; H, 11·4. Calc. for $C_{13}H_{20}$: C, 88·5; H, 11·5%), together with n-octane (5%). Of the halogen in the n-butyl chloride, 75·5% appeared as free hydrogen chloride, and 7% as magnesium chloride. The total reaction period was 7 hr. [f] Magnesium was activated by heating it with *ca.* 2% by weight of iodine to *ca.* 300° in a stream of oxygen-free nitrogen. [g] 5-ml. aliquot parts were taken. [h] Carboxylation of a portion of the product gave benzoic acid, m. p. 120—121° and mixed m. p. 121°.

iodine was usually unnecessary, even with chlorides, but was occasionally resorted to in obstinate cases.

Reactions of n-Butyl Chloride, Bromide, and Iodide, and of Chlorobenzene with Magnesium in Hydrocarbon Media.—The procedures and principal results are summarised in Table 1.

Formation of $Bu^n_3Mg_2I$ *by Desolvation of Ethereal n-Butylmagnesium Iodide.*—n-Butylmagnesium iodide was prepared in the usual manner from n-butyl iodide (42·3 g., 0·23 mole) and magnesium turnings (6·2 g., 0·258 g.-atom) in diethyl ether (86 g.). The resulting solution was slowly sucked into isopropylbenzene (58 g.) which was refluxing under a reduced pressure of nitrogen at 130°. A white precipitate was formed immediately, and ether was driven off, through a Dufton column, with stirring. Distillation at 130° was continued until the refractive index of the distillate was that of isopropylbenzene (isopropylbenzene, n_D^{20} 1·4927; diethyl ether, n_D^{20} 1·3530). More (total 90 g.) isopropylbenzene was added at intervals during this process to maintain the liquid volume in the distillation flask.

After the mixture (volume 52 ml.) had been kept under nitrogen for 12 hr. at *ca.* 18°, the titres of the hydrolysis products of a 1-ml. aliquot part of the rather viscous clear supernatant liquid were 12·05 ml. of 0·1N-sulphuric acid, and 4·0 ml. of 0·1N-silver nitrate. Thus, the base/halide ratio was 3·0 After a further 72 hr., the corresponding figures were 12·4 ml., 4·0 ml., and 3·1. After the mixture had been heated for 4 hr. at 130°, and then set aside for 12 hr. at *ca.* 18°, the corresponding figures were 12·75 ml., 4·25 ml., and 3·0. In order to determine whether these figures referred to a saturated solution in contact with undissolved solute, isopropylbenzene (47 ml.) was then added, and the mixture stirred at 130° for 30 min. and then left for 12 hr. at *ca.* 18°, the analytical figures changing to 9·05 ml., 3·0 ml., and 3·0 respectively. Thus the base/halide ratio remained essentially constant, and the initial isopropylbenzene solution was saturated. The dissolution of solid phase after dilution gave an unsaturated solution, and did not modify the apparent empirical formula of the solute, *viz.*, $Bu^n_3Mg_2I$.

Reaction of Methyl Iodide with Magnesium.—Magnesium was activated as in Table 1, note *f*. The reaction conditions were similar to those in Table 1, experiment 1, except that the medium was a mixture of a petroleum fraction, b. p. 200—240° (30 ml.; from B.D.H.), and light petroleum, of b. p. 100—120° (8 ml.), the mixture refluxing at 130°. The product was insoluble and was brought into solution by the addition of ether. The yield of methylmagnesium compounds, estimated by the usual titration, was 10%. The use of isopropylbenzene as medium also gave an insoluble methylmagnesium product. Reactions were very difficult to initiate with unactivated magnesium, even by the subsequent addition of iodine.

Reaction of Ethyl Iodide with Magnesium.—The reaction conditions were similar to those in experiment 1, Table 1, except that magnesium turnings were employed and the medium was decahydronaphthalene. The product (7% yield) was very sparingly soluble, and the resulting saturated solution was 0·0035N at 20° with respect to C–Mg. Ethylmagnesium bromide with a base/halide ratio of 2·8 has been similarly obtained by Mr. E. T. Blues in *ca.* 6% yield.

Reaction of n-Propyl Bromide with Magnesium.—Under conditions similar to those in the previous experiment, the yield of n-propylmagnesium bromide was 15%. The saturated solution was 0·20N at 20°.

Reaction of Bromobenzene with Magnesium in Decahydronaphthalene.—Bromobenzene (*ca.* 1 ml. from 11·8 g.) was added to magnesium turnings (3·5 g.) in decahydronaphthalene (30 g.) at the reflux temperature (188°). Reaction commenced after 5 minutes' stirring, and the remainder of the bromobenzene was then added dropwise in 20 min. Refluxing was continued for a further 20 min., by which time the exothermic reaction had ceased. The product was sparingly soluble in the cold reaction medium, but dissolved on addition of ether. The yield of phenylmagnesium bromide was 95%.

The yield in a similar experiment performed at 170° was 40·5%.

The use of *m*- and *p*-bromotoluene as above at 188° gave yields of 87 and 64·5% respectively; but *o*-bromotoluene proved inert to magnesium under these conditions. Iodobenzene gave an 80·5% yield at 170° with a total reaction period of 90 min.

Polymerisation of Ethylene.—Phenylmagnesium chloride was prepared essentially as in experiment 7, Table 1, except that the solvent was a largely aliphatic petroleum fraction, b. p. 190—240°, obtained by treatment of " Aladdin Pink paraffin " with oleum. Benzene (300 ml.) was added to the cooled product. Titanium tetrachloride (14 ml. of a 10% solution in benzene) was added at intervals during 14 hr. After the addition of the first 2 ml., ethylene (dry, and free from oxygen and carbon dioxide) was passed into the well-stirred dark brown suspension at 20°. Heat was evolved, and the temperature was maintained below 30° by cooling. After 15 hr., 36 g. of a polymer were obtained as a fine powder. The infrared spectrum was typical of a polyethylene. There was no significant chain-branching, as indicated by the absence of a peak at 7·25 μ. A small peak at 6·1 μ may have been attributable to the presence of phenyl residues.

Similar results were obtained when n-butylmagnesium chloride or iodide was used in place of phenylmagnesium chloride.

TABLE 2. *Variation with time of the viscosity and density at 25° of* 0·26N-*n-butylmagnesium iodide in isopropylbenzene after dilution from* 0·52N.

Time after dilution (hr.)	1	20	26	34	45	55	68
Time of flow (solution) (sec.)	1751	379	166	152	114	99	83
Time of flow (solvent) (sec.)	79	79	79	79	79	79	79
Density of solution	0·98	0·92	0·91	0·92	0·86	0·86	0·86
Reduced viscosity (100 ml. $g.^{-1}$)	6·53	1·19	0·52	0·49	0·40	0·55	0·31
Titre of 0·1N-acid * (ml.)	2·6	2·9	2·85	2·8	2·45	1·9	2·25
Base/halide ratio	3·0	3·4	3·3	3·3	3·5	3·4	3·4

* Ml. of 0·1N-hydrochloric acid required to neutralise the hydrolysis products of a 1-ml. sample.

Polymerisation of Propene.—Phenylmagnesium chloride was prepared as in experiment 8, Table 1, with chlorobenzene (11·5 g.), magnesium (7·5 g.), and tetrahydronaphthalene (80 g.). Dry benzene was then added, followed by titanium tetrachloride (1·2 g.), with vigorous stirring. Propene (dry, and free from oxygen and carbon dioxide) was passed slowly through the brown suspension for 14 hr. at 20—25°. The reaction was mildly exothermic. The resulting polymer was extracted successively with ether and light petroleum (b. p. 80—100°), to give a residue (20 g.) of isotactic polypropene (infrared spectrum).

Catalysts of lower reactivity but higher stereospecificity were obtained by substitution of titanium trichloride (brown or violet modifications) for the tetrachloride in the above experiment.

Ether was found to act as a catalyst poison.

Viscosity of a Solution of n-Butylmagnesium Iodide in Isopropylbenzene.—An Ostwald viscometer was adapted for use in an inert atmosphere, and all manipulations and measurements were made at 25° ± 0·01°. The solution was prepared essentially as in experiment 2, Table 1, and was left at 25° for 70 hr. A portion of the clear supernatant liquid was diluted from 0·52N to 0·26N with isopropylbenzene. Samples (vol. 9·91 ml.) used for a viscosity measurement were not returned to the main solution, but were removed for weighing to determine the density. The main results are given in Table 2. The erratic variation in the acid titres is unexplained; but we are inclined to attribute it to sampling errors, as similar solutions on other occasions gave no such variation. The base/halide ratios, which would be independent of sampling errors, were essentially constant. Density as well as viscosity decreased with time, and the values of both eventually became almost identical with those for the pure solvent.

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