209. *Formation of Free Radicals during the Preparation of Organomagnesium Compounds in a Hydrocarbon Solvent.*

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Reactions of *n*-butyl chloride and *n*-butyl iodide (separately and mixed) with magnesium in *iso*propylbenzene have been examined. Evidence has been obtained for the intermediate production of free *n*-butyl radicals, mainly in reactions of the type $R_2Mg + 2RHal \longrightarrow 4R\cdot + MgHal_2$, analogous to those found previously with alkali-metal alkyls. High yields (85%) of *n*-butylmagnesium compounds have been obtained under certain conditions. With *n*-butyl iodide, the organometallic product is mainly di-*n*-butylmagnesium, with a small proportion of *n*-butylmagnesium iodide.

n-Butyltriphenylsilane has been prepared in high yield by the reaction of the di-*n*-butylmagnesium–*n*-butylmagnesium iodide reagent with chlorotriphenylsilane.

In previous work on the mechanism of the Wurtz reaction,[1, 2] it was shown that free alkyl radicals are produced during the reactions between alkyl halides and alkali metals in benzene and in *iso*propylbenzene under certain conditions. The tendency for the metals to produce free *n*-butyl radicals from *n*-butyl iodide was found to increase in the order K < Na < Li. The present work concerns analogous experiments with magnesium.

Experimental

*iso*Propylbenzene and alkyl halides were purified and dried by the methods previously described.[1] Reactions were carried out under oxygen-free nitrogen. Butane–butene mixtures were analysed by absorption of the butene in a saturated solution of nickel sulphate in concentrated sulphuric acid.

A typical experiment is described below. Other experiments given in Tables 1 and 2 were performed with the same weights of *iso*propylbenzene and *n*-butyl iodide (or the equivalent of *n*-butyl chloride), and the proportion of magnesium was varied.

Table 1. *Reactions between* n-*butyl iodide and magnesium in* iso*propylbenzene at* 130°.

Expt. no.	1	2	3	4	5	6	7
Equivs. of Mg [a]	1·0	1·2	1·5	3·5	3·5	3·5	3·5 [b]
Heating period (hr.)	20 [c]	20 [c]	2	2	2	2	12
Yield (%) of n-Bu_2Mg	0	9·5	40·5	55·5	*d*	*d*	57·0
,, n-BuMgI	0	2·5	4·5	17·5	*d*	*d*	13·5
,, total C–Mg material	0 [e]	12·0	45·0	73·0	72·5	85·5	70·5
,, n-C_4H_{10} [f]	47·5	34·5	18·0	8·5	4·5	*d*	6·5
,, n-C_4H_8	24·0	25·0	7·0	0·5	0·5	*d*	1·0
,, n-C_8H_{18}	29·0	*d*	15·0	16·0	13·5	*d*	21·0
Yield $C_{18}H_{22}$ [g]	18·5	11·0	7·5	3·0	3·6	*d*	3·5
Titre *a* (ml.)	0·1	2·2	7·2	11·8	11·7	13·8	11·4
Titre *b* (ml.) [h]	1·2	2·5	8·0	11·6	13·5	*d*	12·4
Recovery (%) of C_4 material	100·5	*d*	85·0	98·0	91·0 [i]	*d*	99·0

[a–i] See text.

Reaction between n-*Butyl Iodide and Magnesium in* iso*Propylbenzene.*—*n*-Butyl iodide (13·00 g., 0·071 mole) was added during 30 min. with stirring to magnesium turnings (3·0 g., 0·123 g.-atom) in *iso*propylbenzene (36·5 g., 0·306 mole) at 130°. Reaction proceeded readily after a 10-min. induction period. Heating at 130° was continued for a further 1½ hr. Butane (8·5%) and butene (0·5%) were collected in a trap at −70°. After being kept for *ca.* 30 min., 1-ml. portions of the clear supernatant liquid and the stirred suspension were hydrolysed and titrated against 0·097N-hydrochloric acid: 11·8 and 11·6 ml. respectively were required, equivalent to a 73% yield of total organomagnesium compounds [titres (*a*) and (*b*) in the Tables]. Iodine

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[1] Bryce-Smith, *J.*, 1956, 1603.

[2] *Idem*, *J.*, 1955, 1712.

in aliquot samples of the supernatant liquid was estimated as silver iodide in the usual way: 1 ml. gave 0·065 g. of silver iodide, equivalent to a yield of 17·5% of *n*-butylmagnesium iodide. By subtraction, the yield of di-*n*-butylmagnesium was 55·5%. The supernatant liquid gave a strong positive reaction in the test for organomagnesium compounds with Michler's ketone reagent.[3] After hydrolysis of the bulk of the product with dilute hydrochloric acid, the separated and dried organic material was fractionated, to give octane (0·63 g., 16%; estimated as previously described [1]) and 2 : 3-dimethyl-2 : 3-diphenylbutane (0·25 g., 3·0%), m. p. and mixed m. p. 118°. The total recovery of C_4 material was 98%.

Notes to Table 1: [a] One equivalent refers to the hypothetical reaction $2BuI + Mg \longrightarrow 2Bu\cdot + MgI_2$. Two equivalents would theoretically be required to form butylmagnesium compounds. In expt. 6, magnesium powder (80—100 mesh) was used, and in the other experiments, magnesium turnings (<40 mesh). [b] This experiment demonstrates the effects attributable to any pyrolysis of the organomagnesium compounds. [c] These longer reaction periods were necessary to ensure complete reaction. The rather low recovery in expt. 3 suggests that this reaction may not have been quite complete after 2 hr. [d] No determination was made. [e] A negative reaction with Michler's ketone reagent was observed: in the other experiments, the reactions were strongly positive for organomagnesium compounds. The yields are based on titre *a*. [f] If allowance is made for butane produced by the reaction $Bu^n + C_6H_5\cdot CHMe_2 \longrightarrow n\text{-}BuH + C_6H_5\cdot CMe_2\cdot$, the butane : butene ratios in expts, 1, 2, 3, and 5 approximate to unity. [g] 2 : 3-Dimethyl-2 : 3-diphenylbutane. The quoted yields refer to material of m. p. >114° and are based on *n*-butyl iodide. [h] These figures should be regarded as approximate owing to the experimental difficulty of obtaining satisfactory aliquot parts of the suspension. [i] Reaction with solid carbon dioxide gave *n*-valeric acid (29%), b. p. 180—185° (*p*-bromophenacyl ester m. p. and mixed m. p. 73°. Several sources quote m. p. 64° for this compound: others quote a m. p. close to 73°. On a previous occasion, we obtained crystals melting sharply at 63·5°: after 6 years, the sample was found to melt sharply at 73°. This seems to be a case of dimorphism. We have been unable to repeat the preparation of the lower-melting, and evidently less stable, form).

TABLE 2. *Reactions of* n-*butyl chloride and* n-*butyl iodide with magnesium* (3·5 *equiv.* : <40 *mesh*) *in* iso*propylbenzene.*

Wt. % of Bu^nCl	100	100	100	85
,, Bu^nI	0	0	0	15
Reaction temp.	138—152° [a]	132°	110° [b]	100° [c]
Heating period (min.)	40	40	90	60
Yield (%) of total C–Mg material	25	35·5	0	61
,, $n\text{-}C_4H_{10}$	26	*d*	0	8·5
,, $n\text{-}C_4H_8$	3	*d*	0	1·5
,, $n\text{-}C_8H_{18}$	28	23	0	12
,, $C_{18}H_{22}$ [e]	0·9 [f]	0·65	0	0·9

[a–f] See text.

Notes to Table 2: [a] Reflux temperature. [b] Very little reaction occurred at this temperature. [c] Initiated at 135°. [d] Not determined. [e] 2 : 3-Dimethyl-2 : 3-diphenylbutane. [f] The high-boiling material which remained after removal of $C_{18}H_{22}$ by recrystallisation was oxidised by a slight excess of chromium trioxide in glacial acetic acid at 130° for 24 hr. Terephthalic acid (0·5%, based on $n\text{-}C_4H_9Cl$) was obtained, and estimation *via* the dithallous salt [4] showed that it contained not more than 1% of *iso*phthalic acid. This result is under further investigation.

Preparation of n-*Butyltriphenylsilane.*—The *n*-butylmagnesium reagent was prepared from *n*-butyl iodide (13·0 g., 0·071 mole) as in expt. 4, Table 1. Chlorotriphenylsilane (12·5 g., 0·043 mole) was added and the mixture was heated under reflux with stirring for 95 min. After cooling, excess of organomagnesium compounds was destroyed by the addition of dilute hydrochloric acid. The separated and dried organic layer was fractionated to remove *iso*propylbenzene. The addition of absolute ethanol to the residue gave colourless crystals of *n*-butyltriphenylsilane (11·5 g., 85·5%), m. p. 86°. Recrystallisation from absolute methanol raised the m. p. to 88° (Found: C, 83·5; H, 7·5. Calc. for $C_{22}H_{24}Si$: C, 83·45; H, 7·65%). Gilman,

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[3] Gilman and Schulz, *J. Amer. Chem. Soc.*, 1925, **47**, 2002.

[4] Bryce-Smith, *Chem. and Ind.*, 1953, 244.

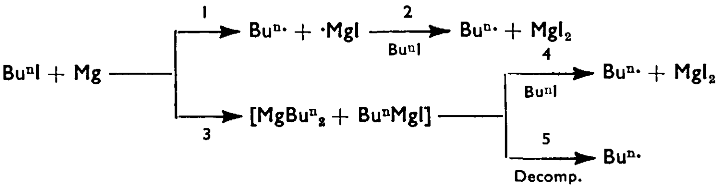
Benkeser, and Dunn [5] prepared this compound in 85% yield by the reaction of *n*-butyl-lithium with chlorotriphenylsilane, and reported m. p. 87·5—88°.

Several attempts were made to prepare tetra-*n*-butylsilane by a method analogous to the above, using silicon tetrachloride. Moderate yields of a product with b. p. close to the reported value were obtained; but analyses were always unsatisfactory (*e.g.*, Found: C, 77·75; H, 12·3. Calc. for $C_{16}H_{36}Si$: C, 74·9; H, 14·15%). Other material, presumably containing partially butylated compounds, was also obtained. After hydrolysis, this gave silicone-like oils.

DISCUSSION

Recently,[1] the production of 2 : 3-dimethyl-2 : 3-diphenylbutane was used to detect, and approximately to estimate, the free alkyl radicals which are formed during the reactions between alkyl halides and alkali metals in *iso*propylbenzene. It was shown in the case of lithium that the radicals arise from reactions of the type $RBr + RLi \longrightarrow 2R\cdot + LiBr$, and not from the initial reaction between the halide and the metal or from thermal decomposition of RLi. Kharasch and Urry [6] found that free radicals are formed during the reactions between certain alkyl halides and alkylmagnesium halides in the presence of catalytic quantities of cobalt halides. A chain mechanism was proposed, involving cobalt subhalides. A slower free-radical reaction which occurred in the absence of added catalyst was similarly suggested to involve magnesium subhalide produced by a reaction $RMgHal \longrightarrow R\cdot + MgHal$. More recently, Kharasch and Reinmuth [7] have made the alternative suggestion that a direct homolytic reaction can occur, *viz.*, $RMgHal + RHal \longrightarrow 2R\cdot + MgHal_2$.* This reaction is analogous to that found [1] to occur with alkyllithium compounds. The present work has shown that *n*-butyl iodide produces free *n*-butyl radicals to approximately the same extent with magnesium as with lithium: the yields of 2 : 3-dimethyl-2 : 3-diphenylbutane under comparable conditions were 18·5 and 17% respectively.

The free-radical reactions which could be involved when *n*-butyl iodide reacts with magnesium are indicated in the following scheme:



The possibility that reaction (5) occurs under the present conditions is excluded by the result of expt. 7, Table 1. The yields of *n*-butylmagnesium compounds and of 2 : 3-dimethyl-2 : 3-diphenylbutane were almost unchanged by increasing the period of heating at 130° from 2 to 12 hours.

In considering reactions (1), (2), (3), and (4) as possible competing fates for *n*-butyl iodide, one is dealing with a competition between heterogeneous and homogeneous reactions, the rate of (4) depending also on the heterogeneous reaction (3). It seems a valid assumption that the relative rates of (1) and (3) should be independent of the surface area of the magnesium and the weight ratio of *n*-butyl iodide and magnesium. The 85·5% yield of *n*-butylmagnesium compounds obtained in expt. 6, Table 1, indicates that (3) must be much faster than (1): and some of the 14·5% deficiency of *n*-butylmagnesium compounds can certainly be attributed to the occurrence of reaction (4). Further, increasing the

* But contrast ref. 7, p. 1059.

[5] Gilman, Benkeser, and Dunn, *J. Amer. Chem. Soc.*, 1950, **72**, 1689.

[6] Kharasch and Urry, *J. Org. Chem.*, 1948, **13**, 101.

[7] Kharasch and Reinmuth, " Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, 1954; Constable, London, p. 131.

proportion of magnesium (*i.e.*, increasing the available surface area) from 1 to 3·5 equivalents increased the yield of *n*-butylmagnesium compounds from 0 to 73%, or, when magnesium powder was used, to 85·5%; reactions (1), (2), and (3) thereby become more important than reaction (4). At the same time, the yield of 2 : 3-dimethyl-2 : 3-diphenylbutane fell from 18·5 to *ca.* 3%. The radical yield * must therefore be mainly determined by the extent of reaction (4), rather than reactions (1) and (2). The deficiency from quantitative in the yields of *n*-butylmagnesium compounds may be attributed mainly to the homolytic reaction (4) (and related heterolytic coupling and elimination reactions [1]) rather than to reactions (1) and (2), and the yields of 2 : 3-dimethyl-2 : 3-diphenylbutane are approximately proportional to this deficiency. The precision of the results does not, however, justify the complete exclusion of reactions (1) and (2) as minor radical contributors. It seems probable that di-*n*-butylmagnesium and *n*-butylmagnesium iodide are both involved in reaction (4), but the question whether they are equally involved must remain open.

Preparation of Organomagnesium Compounds in iso*Propylbenzene.*—*iso*Propylbenzene was used as a solvent in this work because of its ability to function as a radical detector; but it has also been found to be an unexpectedly good solvent for the preparation of *n*-butylmagnesium compounds under certain conditions. The numerous attempts to prepare Grignard reagents in non-donor media have been summarised by Kharasch and Reinmuth.[8] Usually, the addition of small quantities of an ether or tertiary amine has been found necessary in order to obtain acceptable yields in conveniently short reaction periods. Tschelinzeff [9] reported the preparation of several Grignard reagents at approximately 140° in the absence of added solvent and catalyst: Schlenk [10] also obtained these in benzene, the reactions requiring two months for completion. In *iso*propylbenzene, we find that the main product with *n*-butyl iodide is di-*n*-butylmagnesium, with a much smaller proportion of *n*-butylmagnesium iodide. By use of a 75% excess of magnesium powder (rather than turnings), a combined yield of 85·5% was obtained (Table 1, expt. 6) identical with that reported by Gilman *et al.*[11] for a conventional preparation of *n*-butylmagnesium iodide in ether. Use of a more finely divided magnesium powder would probably give an even higher yield.

The use of *n*-butyl chloride was also investigated, and the results are summarised in Table 2. The radical yields were much lower than from the iodide. Yields of organomagnesium compounds were also lower, although a 61% yield was obtained from a mixture of *n*-butyl chloride and a little *n*-butyl iodide. This yield also could almost certainly be improved upon by the use of a more finely divided magnesium.

The possible synthetic usefulness of these new reagents has been suggested by the preparation of *n*-valeric acid (29% yield) from carbon dioxide, and of *n*-butyltriphenylsilane (85·5% yield) from chlorotriphenylsilane. A reaction with silicon tetrachloride, expected to give tetra-*n*-butylsilane, gave a product which we were unable to obtain pure.

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* This does not include any radicals which might be captured by the magnesium, but refers to radicals which are sufficiently " free " to react with the solvent.

[8] *Op. cit.*, pp. 50 *et seq.*

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

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

[11] Gilman, Zoellner, and Dickey, *J. Amer. Chem. Soc.*, 1929, **51**, 1576, 1583.