664. *Organometallic Compounds of Group II. Part II.*[1] *Alkylation of Aromatic Hydrocarbons by Use of Magnesium and Alkyl Halides.*

By D. BRYCE-SMITH and W. J. OWEN.

Magnesium reacts with n-butyl chloride in benzene to give s-butylbenzene. Hydrogen chloride is evolved. No butylmagnesium chloride is obtained. n-Butyl bromide reacts with an excess of magnesium in benzene to give both s-butylbenzene and butylmagnesium bromide without evolution of hydrogen bromide, whereas n-butyl iodide gives no s-butylbenzene but a 75% yield of butylmagnesium iodide. The alkylations proceed more readily in toluene, and with higher yields. t-Butyl chloride and benzyl chloride are relatively inert to magnesium in boiling benzene, but a modified procedure enables them to be used in alkylations.

These alkylations are considered to be of the Friedel–Crafts type, and to involve the production of a catalytically active form of magnesium halide. Magnesium chloride prepared from magnesium ammonium chloride hexahydrate functions as a weak alkylation catalyst.

SEVERAL scattered reports have referred to aromatic alkylations arising from attempts to prepare Grignard reagents in aromatic media. Thus, Schorigin, Issaguljanz, and Gussewa[2] reported low yields of *p*-butyltoluene and *p*-isopentyltoluene from reactions of n-butyl chloride and isopentyl chloride respectively with magnesium in toluene. This contrasts interestingly with the exclusive α-alkylation of toluene subsequently shown by Morton and Fallwell[3] to occur with the use of sodium in such reactions. Schorigin *et al.* claimed to have shown by a control experiment that anhydrous magnesium chloride is inactive as a Friedel–Crafts catalyst, and suggested either a direct reaction between first-formed alkylmagnesium chloride and toluene, or attack on the ring by free alkyl radicals. Kharasch, Goldberg, and Mayo[4] reported some related alkylation experiments using Grignard reagents which were carried out in the presence of traces of ether: a statement that the presence of water is necessary was subsequently withdrawn.[5] Kharasch and Reinmuth,[5] and Waters[6] considered that these alkylations involve free alkyl radicals. Handler[7] treated magnesium with pentyl bromide in diphenyl ether and obtained *p*-pentyldiphenyl ether. He suggested that this product arose from an alkylation catalysed by magnesium bromide. In Part I,[1] evidence was obtained for the production of a little *p*-butylisopropylbenzene from a reaction of n-butyl chloride with excess of magnesium in isopropylbenzene.

We have further investigated these alkylations in the light of observations that alkylmagnesium halides do not react directly with aromatic hydrocarbons, and that free n-butyl radicals do not readily attack the benzene nucleus.[1,8]

Repetition of the experiments of Schorigin *et al.*[2] with isopentyl chloride and n-butyl chloride in toluene confirmed their report of *para*-alkylation (*ca.* 10% yield), but it was found that *ortho*- and *meta*-alkylation also occur, and that hydrogen chloride is evolved. Modification of their experimental conditions gave considerable improvements. Thus, the reaction of magnesium with n-butyl chloride in an excess of toluene for 6¼ hours at *ca.* 105° gave monobutyltoluenes (74%: probably largely s-butyl) and dibutyltoluenes

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[1] Bryce-Smith and Cox, *J.*, 1958, 1050, is regarded as Part I.
[2] Schorigin, Issaguljanz, and Gussewa, *Ber.*, 1933, **66**, 1426.
[3] Morton and Fallwell, *J. Amer. Chem. Soc.*, 1938, **60**, 1429; 1941, **63**, 327.
[4] Kharasch, Goldberg, and Mayo, *J. Amer. Chem. Soc.*, 1938, **60**, 2004.
[5] Kharasch and Reinmuth, " Grignard Reactions of Nonmetallic Substances,' Constable, London, p. 64 and footnote.
[6] Waters, " The Chemistry of Free Radicals," Oxford Univ. Press, London, 1948, p. 211.
[7] Handler, *J. Org. Chem.*, 1959, **24**, 1339.
[8] Bryce-Smith, *J.*, 1956, 1603.

(13%). Of the halide that reacted, 93·5% appeared as hydrogen chloride and 6·0% as magnesium chloride. Most of the magnesium remained unchanged, and no butylmagnesium chloride was detected. An analogous reaction with benzene in place of toluene was much slower, probably owing to the lower temperature of refluxing, but a 32% yield of s-butylbenzene was obtained.

Some halides, notably t-butyl chloride, were inert to magnesium in boiling benzene or toluene, and gave little or no alkylation of the solvent or other reactions. Prior treatment of the metal with a little of the more reactive n-butyl chloride, followed by removal of the volatile products, gave a catalyst active for alkylations with these " inert " halides. The presence of residual magnesium metal was not necessary for catalytic activity.

In the absence of catalysts, chlorobenzene reacts with ordinary magnesium at a conveniently rapid rate only above 150°, and gives phenylmagnesium chloride without any detectable phenylation of aromatic solvents.[9]

The evolution of hydrogen chloride, the formation of s-butylbenzene from n-butyl chloride, the failure to observe phenylation, and the evident stability of the alkylating agent to hydrogen chloride strongly suggested that the alkylations were of Friedel–Crafts type and, despite the contrary report,[2] catalysed by a form of magnesium chloride.

Support for this view was provided when magnesium chloride, prepared by heating magnesium ammonium chloride hexahydrate in dry hydrogen chloride, was found to act as a weak catalyst for the alkylation of benzene or toluene by t-butyl chloride or benzyl chloride. n-Butyl chloride reacted very much more slowly under analogous conditions, but slight alkylation of benzene and toluene was detected after several weeks at the reflux temperature, and a little hydrogen chloride was evolved. On a weight for weight basis, magnesium chloride prepared from magnesium and n-butyl chloride was at least several hundred times more active catalytically than that prepared from magnesium ammonium chloride hexahydrate. This can probably be largely ascribed to differences in surface area, although differences in crystal structure cannot yet be ruled out.

Suggestions have been made that the alkylation of aromatic compounds by alkyl halides and magnesium is a homolytic process.[5,6] Since reactions of alkylmagnesium compounds with alkyl halides produce free alkyl radicals,[1] these were probably formed to some extent under the present conditions. However, the generation of free n-butyl radicals in benzene from the photolysis of di-n-butylmercury gave little or no butylbenzene. This result, coupled with a similar one from previous work,[8] indicates that free radicals are not significantly involved in the present alkylations.

The use of n-butyl bromide or iodide favours the production of alkylmagnesium compounds. Thus, n-butyl bromide and an excess of magnesium in refluxing benzene gave a little s-butylbenzene, but the principal product was n-butylmagnesium bromide: no hydrogen bromide was evolved. On the other hand, reduction in the proportion of magnesium to one tenth gave mainly s-butylbenzene, with the evolution of much hydrogen bromide. The production of s-butylbenzene in the presence of an excess of butylmagnesium bromide, and without evolution of free hydrogen bromide, is an interesting example of the occurrence of a Friedel–Crafts reaction under essentially basic conditions. Alkyl chlorides can behave similarly.[10] It appears that the present catalysts can function in the absence of free hydrogen halide.

With n-butyl iodide, no alkylation was detected, and n-butylmagnesium iodide was produced in 75% yield. That magnesium iodide can indeed catalyse alkylation was shown by an experiment in which magnesium was heated with n-butyl iodide until no free metal or organometallic compound remained. After removal of volatile matter, the solid residue showed slight catalytic activity in the alkylation of toluene by t-butyl chloride.

The general course of reactions which involve an alkyl halide, RX, and magnesium in an aromatic medium, ArH, can be summarised as follows (the ratio R/X in the

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[9] Bryce-Smith and Cox, unpublished work; Cox, Ph.D. Thesis, Reading, 1959.

[10] Blues and Bryce-Smith, unpublished work.

organomagnesium product is normally >1, and the actual stoicheiometry more complicated.[1,9]):

$$RX + Mg \longrightarrow \text{"}RMgX\text{"} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\text{"}RMgX\text{"} + RX \longrightarrow 2R\cdot\ (\text{etc.}) + MgX_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$RX + ArH \xrightarrow{MgX_2} ArR + HX \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\text{"}RMgX\text{"} + HX \longrightarrow RH + MgX_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The decreasing tendency for alkylation in the series BuCl > BuBr > BuI may probably be ascribed to (*a*) correspondingly decreasing reactivity of these halides, particularly the iodides, in reactions of type (3) (cf. ref. 10*a*), (*b*) decreasing catalytic activity in the order $MgCl_2 > MgBr_2 > MgI_2$ (cf. ref. 10*b*), and (*c*) increase in facility of reactions of type (1) in the order BuCl < BuBr < BuI, although many analogies, *e.g.*, with n-butyl-lithium suggest that (*c*) must be counter-balanced to some extent by a similarly increasing tendency towards reactions of type (2). The question whether alkylmagnesium halide or alkylbenzene predominates in a particular case should be largely determined by the relative rates of reactions (1), (2), and (3). The formation of alkylmagnesium halides is favoured by increase in temperature and the use of increased proportions of magnesium; and also by the presence of substances such as ethers which can catalyse reaction (1), and which by co-ordination reduce the electrophilic character of the magnesium halide. Kharasch, Goldberg, and Mayo's results[4] (which we have confirmed for the case of benzylation of benzene) suggest, however, that in certain cases the presence of a *trace* of ether promotes *alkylation* through catalysis of reaction (1) under conditions where, without a catalyst, no reaction at all would occur. Even with alkyl chlorides, and no added catalyst, reaction (1) can be made to predominate at temperatures somewhat higher (*e.g.*, 130°) than those now employed.[1,9] Adjustment of these various factors should provide a means of control for combinations of alkyl halide and aromatic hydrocarbon not yet specifically examined.

EXPERIMENTAL

Alkyl chlorides and bromides were purified by treatment with concentrated sulphuric acid, washing with sodium carbonate solution and water, drying ($CaCl_2$), and fractional distillation. Benzene (sulphur-free) was purified by repeated partial freezing, followed by fractional distillation. Toluene (sulphur-free) was heated under reflux for 3 hr. with sodium and then fractionally distilled. Magnesium was used in the form of "Grignard" turnings or powder (B.D.H., *ca.* 150 mesh): aluminium could not be detected qualitatively. A subsequent experiment with n-butyl chloride and toluene using the purest available magnesium (Magnesium Electron Ltd.: Al, 0·007; Zn, 0·011%) showed no significant variation from the results below. Reactions were conducted under nitrogen, and anhydrous conditions were maintained.

Reaction of n-Butyl Chloride with Magnesium in Toluene.—n-Butyl chloride (20·0 g., 0·216 mole), magnesium (6·0 g., 0·247 g.-atom; turnings), and toluene (60 g., 0·65 mole) were heated with stirring at 100°. After 7 min., evolution of hydrogen chloride commenced. Heating under gentle reflux was continued for a total of 6¼ hr., the temperature of the mixture progressively rising to 112°. Unchanged n-butyl chloride (2·1 g.) was recovered from a cold trap, but only traces of butane and butene were detected. Hydrogen chloride (93·5%) was estimated by titration with standard alkali. The main product was treated with dilute sulphuric acid, and the separated aqueous layer analysed (Volhard) for chloride. Chloride equivalent to 0·553 g. of magnesium chloride was found, *i.e.*, 6% based on the n-butyl chloride consumed. This implied that only 0·142 g. (*ca.* 2%) of the magnesium entered into reaction, since in the presence of free hydrogen chloride all the reacted magnesium must have been present as magnesium chloride. Magnesium metal is unreactive towards dry hydrogen chloride, even at temperatures considerably above 100°.

Fractional distillation of the dried organic products over sodium gave monobutyltoluenes (21·2 g., 74%), b. p. 189—195° (bulk at 193—194°) (Found: C, 89·1; H, 10·9. Calc. for $C_{11}H_{16}$:

[10a] Friedel and Crafts, *Compt. rend.*, 1877, **84**, 1392.
[10b] Russell, *J. Amer. Chem. Soc.*, 1959, **81**, 4834, and references therein.

C, 89·1; H, 10·9%), and dibutyltoluenes (2·5 g., 13%), b. p. 245—265° (Found: C, 88·5; H, 11·7. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).

The yield of butyltoluenes was only 13% from an experiment in which the procedure of Schorigin *et al.*[2] was followed. Repetition of their preparation of *p*-pentyltoluene from isopentyl chloride, toluene, and magnesium gave a 12% yield of pentyltoluenes, oxidation of which with chromium trioxide in glacial acetic acid gave a mixture of tere-, iso- and *o*-phthalic acids together with other unidentified products. Tere- and iso-phthalic acids were separated *via* the thallous salts:[11] the ratio was *ca.* 12 : 1. No attempt was made to find improved conditions for this reaction.

Reaction of n-Butyl Chloride with Magnesium in Benzene.—n-Butyl chloride (20·0 g., 0·216 mole), magnesium (6·0 g., 0·247 g.-atom; powder), and benzene (80 g., 1·03 moles) were heated with stirring under reflux. Evolution of hydrogen chloride commenced after 80 min., and was still slowly continuing after 17 hr. when heating was discontinued. n-Butyl chloride (40·5%) was recovered, but probably incompletely, so yields have been based on starting materials in this case. Hydrogen chloride (38%) was evolved. Working up as previously gave magnesium chloride (7%) and s-butylbenzene (8·6 g., 32%) (Found: C, 89·7; H, 10·4. Calc. for $C_{10}H_{14}$: C, 89·5; H, 10·5%). Some di-s-butylbenzene appeared to be produced, but was not obtained pure. The infrared spectrum of this s-butylbenzene was closely similar to that of authentic material prepared as described by Birch *et al.*[12] A few very minor differences were probably due to the presence of other isomers. The *p*-sulphonamide, prepared by Huntress and Autenrieth's method,[13] had m. p. and mixed m. p. 76·5—77·5° (Found: S, 15·2. Calc. for $C_{10}H_{15}O_2NS$: S, 15·05%). In a further experiment, it was found that the induction period was reduced to *ca.* 5 min. in the presence of a trace of iodine; but the course of the subsequent reactions was virtually unaffected.

Reaction of n-Butyl Bromide with Magnesium in Benzene.—A mixture of n-butyl bromide (29·63 g., 0·216 mole), magnesium (6·0 g., 0·247 g.-atom; powder), and benzene (80 g., 1·03 moles) was heated with stirring under reflux for 17 hr. No hydrogen bromide was evolved, but butane (15%) and butene (3%) were found. A positive test for organomagnesium compounds was obtained by using Michler's ketone reagent.[14] Acid titration of hydrolysed aliquot parts of the clear supernatant liquid indicated a 3% yield of dibutylmagnesium. Halogen was not found. Acid titration of aliquot parts of the stirred suspension indicated a 50% yield of organomagnesium compounds, but the accuracy of this figure is doubtful owing to the difficulty of obtaining true aliquot portions free from magnesium metal. Hydrolysis of the whole reaction mixture with dilute sulphuric acid gave butane equivalent to a 38% yield of butylmagnesium compounds: this figure is believed to be reliable. Evidently, most of the butylmagnesium products remained in suspension. Fractional distillation of the separated and dried ($MgSO_4$) organic products gave s-butylbenzene, b. p. 170—172° (1·24 g., 4%), characterised by its infrared spectrum; *ca.* 1 g. of n-octane was also found from examination of refractive-index curves.[8]

In a further experiment, reduction in the proportion of magnesium to one tenth led to a moderately brisk evolution of hydrogen bromide and the formation of s-butylbenzene in high yield. Naturally, no organomagnesium compounds were obtained. Some at least of the butane evolved during the previous reaction must have arisen from the action of hydrogen bromide on butylmagnesium compounds.

Reaction of n-Butyl Iodide with Magnesium in Benzene.—A mixture of n-butyl iodide (19·9 g., 0·11 mole), magnesium (3·0 g., 0·123 g.-atom), and benzene (40 g., 0·51 mole) was heated with stirring under reflux. A vigorous reaction commenced after 5 min. and the product became very pasty. Heating under reflux was continued for 21 hr., although the reaction was probably largely complete after 1 hr. No hydrogen iodide was evolved, and only a trace (0·3 g.) of butane and butene (*ca.* 2 : 1).

Titration of hydrolysed aliquot parts of the clear supernatant liquor indicated a 10% yield in solution of organomagnesium compounds corresponding to $BuMgI,0{\cdot}285Bu_2Mg$.* Hydrolysis

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* For reasons to be discussed in a future paper it seems improbable that such solutions contain simple *mixtures* of RMgI and R_2Mg.

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

[12] Birch, Dean, Fidler, and Lowry, *J. Amer. Chem. Soc.*, 1949, **71**, 1362.

[13] Huntress and Autenrieth, *J. Amer. Chem. Soc.*, 1941, **63**, 3446

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

of the whole product gave butane equivalent to a 75% yield of butylmagnesium compounds. Fractional distillation of the dried organic layer gave octane (5%) but no trace of butylbenzene: not even the characteristic odour was detected. Iodide equivalent to 98·5% of the initial n-butyl iodide was found in the aqueous layer.

t-Butylation of Benzene.—Solutions of t-butyl chloride in benzene and toluene were heated under reflux with magnesium for long periods without any detectable reaction with the metal, or the formation of alkylated products. Iodine was ineffective as an initiator. The following modified procedure was therefore adopted.

n-Butyl chloride (1 g.), magnesium (1 g.; powder), and toluene (10 ml.) were heated for 40 min. under reflux, during which time hydrogen chloride was freely evolved. The product was then taken to dryness *in vacuo*. t-Butyl chloride (20 g., 0·215 mole) and benzene (80 g., 1·03 moles) were then added, and the mixture was stirred under reflux for 5 hr. Hydrogen chloride (20%) was evolved, and magnesium chloride (0·238 g., 2·3%) was found after hydrolysis. Fractional distillation gave t-butylbenzene (4 g., 14%), b. p. 167—170°, n_D^{20} 1·4912, and *p*-di-t-butylbenzene (0·3 g., 1%), m. p. and mixed m. p. 77·5°. The identity of t-butylbenzene was confirmed by its infrared spectrum. Subsequent experiments have indicated that the above method is capable of yielding more active catalysts. The catalyst in this case may have been partially poisoned by traces of moisture, to which it is very sensitive.

Benzylation of Benzene.—In a preliminary experiment, benzyl chloride was heated with magnesium in an excess of benzene under reflux. A very slow evolution of hydrogen chloride was detected after 10½ hr., and after 28 hr., when heating was discontinued, only 10% of the theoretical amount of hydrogen chloride had been evolved. In view of the low reactivity of benzyl chloride towards magnesium under these conditions, the " two-stage " procedure was employed, as with t-butyl chloride.

n-Butyl chloride (2 g.), magnesium (2 g.; powder), and toluene (5 ml.) were heated under reflux for 1 hr., during which time hydrogen chloride was freely evolved. The product was taken to dryness *in vacuo* and then brought to atmospheric pressure with dry nitrogen. A mixture of benzyl chloride (20 g., 0·158 mole) and benzene (80 g., 1·03 moles) was then quickly added, and stirring under reflux (*ca.* 88°) was maintained for 27½ hr. Hydrogen chloride (0·142 mole; 90%) was evolved during the latter period. Distillation of the organic products gave diphenylmethane (11·0 g., 42%), m. p. 24° and mixed m. p. 24·5°, and dibenzylbenzenes (4 g., 20%). Repeated crystallisation of the latter from ethanol gave crystals, m. p. 85·5°, probably *p*-dibenzylbenzene (m. p. 86°).

Use of Anhydrous Magnesium Chloride as an Alkylation Catalyst.—(a) *t-Butylation of benzene.* A mixture of benzene (80 g., 1·03 moles), t-butyl chloride (20 g., 0·216 mole), and powdered magnesium chloride (20 g.; anhydrous; preparation below) was stirred at 50—60° for 3 days. Hydrogen chloride (0·048 mole, 22%) was evolved. Distillation of the filtered product gave t-butylbenzene (3·5 g.), b. p. 166—169°, and a residue (0·95 g.) of higher b. p. which solidified on cooling. Recrystallisation of this from ethanol gave *p*-di-t-butylbenzene, m. p. and mixed m. p. 77·5°. The t-butylbenzene fraction was slightly unsaturated to bromine in carbon tetrachloride, and was purified by being heated under reflux with alkaline potassium permanganate for 15 min. Separation and distillation of the remaining hydrocarbon gave t-butylbenzene (1·5 g.), b. p. 166—168°, the identity of which was confirmed by its infrared spectrum.

(b) *Benzylation of benzene.* A mixture of benzene (80 g., 1·03 moles), benzyl chloride (20 g., 0·158 mole), and powdered anhydrous magnesium chloride (20 g.) was heated under reflux for 90 hr. Hydrogen chloride (0·148 mole, 87%) was evolved. Diphenylmethane (8·5 g., 32%), m. p. and mixed m. p. 25°, and dibenzylbenzenes (3·14 g., 15%) were obtained, together with much higher-boiling material, apparently polymeric.

Photolysis of Di-n-butylmercury in Benzene.—The photolysis cell and ultraviolet source have been described.[15] A solution of di-n-butylmercury (11·6 g.) in benzene (97 g.) was irradiated under reflux in a nitrogen atmosphere for 5 hr. Mercury (5·44 g., 73·5%) was liberated. Unchanged di-n-butylmercury was converted into butane (0·58 g., 27%) and n-butylmercuric chloride by the action of concentrated hydrochloric acid. Fractional distillation of the organic products gave octane (0·65 g.), but no fraction corresponding to butylbenzenes was obtained (cf. ref. 8 for a comparable experiment in which free n-butyl radicals were generated from the reaction of n-butyl-lithium with n-butyl bromide).

Preparation of Anhydrous Magnesium Chloride.—In preliminary experiments, attempts to

[15] Blair, Bryce-Smith, and Pengilly, *J.*, 1959, 3174.

dehydrate magnesium chloride hexahydrate by heating it in a stream of dry hydrogen chloride or in refluxing thionyl chloride gave oxygen-containing products. The following procedure proved satisfactory. " AnalaR " magnesium ammonium chloride hexahydrate ($NH_4Cl,MgCl_2,6H_2O$) was heated in a Pyrex boat in a current of dry hydrogen chloride. The temperature, initially *ca.* 300°, was increased very slowly at first, then more rapidly above 500° during a total period of 3 hr. up to the fusion point (715°), when the product was immediately cooled. Chloride analyses indicated a purity $>99{\cdot}7\%$. The material formed a clear, colourless melt: it was noticed that oxygen-containing products gave turbid melts. Pyrex glass was slowly attacked by the fused salt.

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