37. *A Modified Grignard Reaction in the Synthesis of Hydrocarbons.*

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Investigation of the products of reaction of butyl, octyl, nonyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl and benzyl halides with magnesium in ether shows that the three reactions

(1) formation of the Grignard reagent	$RI + Mg = R{\cdot}MgI$
(2) Wurtz reaction	$2RI + Mg = R_2 + MgI_2$
(3) disproportionation	$2RI + Mg = RH + R'H + MgI_2$

take place concurrently. The extent to which each reaction takes place depends on the halogen and on the alkyl radical. Repeated addition of iodine, followed by magnesium, leads to yields of 65% or more of the long-chain paraffins R_2. The same method of synthesis is even more successful in the case of benzyl halides. Experimental evidence on the mechanisms of the various reactions is discussed, and an improved method of purifying long-chain paraffins is described.

APART from their biological interest, long-chain compounds are of increasing importance in certain physicochemical investigations [for references, see Ubbelohde, *Trans. Faraday Soc.* (in the press)]. On account of difficulties in their purification, it is very desirable, in a study of the physical properties, to prepare long-chain compounds by a number of different synthetic methods. The present paper gives details of the synthesis of the paraffins RH and R_2 from the alcohol R·OH. This method can be readily applied in preparing the paraffins $C_{12}H_{26}$, $C_{14}H_{30}$, $C_{16}H_{34}$, $C_{18}H_{38}$, $C_{24}H_{50}$, $C_{28}H_{58}$, $C_{32}H_{66}$, $C_{36}H_{74}$, etc., and thus fills in the gaps left by the Kolbe–Petersen method (cf. Piper, Chibnall, Hopkins, Pollard, Smith, and Williams, *Biochem. J.*, 1931, **25**, 2072), which is only suitable for paraffins such as $C_{22}H_{46}$, $C_{26}H_{54}$, $C_{30}H_{62}$, and $C_{34}H_{70}$. The same method has been investigated for the benzyl halides, in order to show that it can be applied in the synthesis of any symmetrical hydrocarbon R_2. The experiments may be divided into an investigation on the Grignard reaction with a number of halides, and investigations on the synthetic method proposed.

The Grignard Reaction with Alkyl Halides.—The method of carrying out the reactions and isolating the products is described in the experimental part. The table summarises experiments designed to give a survey of the whole field, and detailed experiments on dodecyl chloride and iodide, hexadecyl iodide, and benzyl chloride and iodide.

Extent of Various Reactions Between n-*Alkyl Halides and Magnesium.*

Halide.	Grignard compound, %.	Dispropor-tionation, %.	Wurtz reaction, %.
C_4H_9I	—	—	9·2
$C_8H_{17}I$	—	—	25·0
$C_9H_{19}I$	—	—	25·0
$C_{11}H_{23}I$	—	—	26·0
$C_{12}H_{25}Cl$	91·5	3·7	4·7
$C_{12}H_{25}I$	64·8	5·6	29·2
$C_{12}H_{25}I$ *	15·8	20·7	62·5
$C_{12}H_{25}I$ ‡	—	39·0	32·6
$C_{14}H_{29}I$	64·0	6·4	29·6
$C_{16}H_{33}I$	64·4	8·8	27·8
$C_{16}H_{33}I$ *	22·5	13·7	63·8
$C_{18}H_{37}I$	66·5	7·7	27·8
$C_6H_5{\cdot}CH_2Cl$	87·5	—	9·4
$C_6H_5{\cdot}CH_2I$	62·0	—	38·0
$C_6H_5{\cdot}CH_2I$ †	—	—	68·4

* Five additions of iodine and magnesium. † One addition of iodine.

‡ Grignard compound boiled for 6½ hours with an equivalent amount of $C_{12}H_{25}I$.

Attention may be drawn to the following features of this table:

Relative extent of the Wurtz and the Grignard reaction, etc. The figures are calculated on the assumptions that all the hydrocarbon R_2 is formed by the Wurtz reaction, $2RI + Mg \longrightarrow MgI_2 + R_2$, and that the hydrocarbon RH is formed both from the Grignard compound on addition of dilute hydrochloric acid, $R{\cdot}MgI + HCl \longrightarrow RH + MgICl$, and in the disproportionation reaction, *e.g.*, $2C_{12}H_{25}I + Mg \longrightarrow MgI_2 + C_{12}H_{26} + C_{12}H_{24}$. The basis of these assumptions is discussed below.

The extent to which the iodides from *n*-octyl iodide to *n*-octadecyl iodide undergo the Wurtz reaction only changes from 25 to 28%, and the marked change from butyl to octyl iodide may be connected with the greater facilities for the supply of activation energy in the longer alkyl radicals (cf. Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 362). Special experiments on hexadecyl iodide showed that the proportion of the product formed by the Wurtz reaction is not greatly affected by changes in the mode of addition of halide to the system, and that the volume of ether used cannot be much varied without leading to inconvenience of manipulation. Benzyl iodide shows a somewhat greater proportion formed by the Wurtz reaction, for reasons discussed below.

It follows from this table that the chloride should be used whenever the Grignard compound is intended for further syntheses, since this involves the minimum loss of halide in the Wurtz reaction (cf. also Johnson and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1944; Zoellner, *Chem. Abstracts*, 1935, **29**, 5413).

Mechanism of the Wurtz reaction and of the formation of unsaturated compounds. In addition to the Grignard and the Wurtz reaction, the halides react to the extent of 4—8% to give unsaturated hydrocarbons of the same chain length as the alkyl radical. Information on the mechanism of both this reaction and the Wurtz reaction is obtained from experiments on the effect of prolonged boiling of excess of dodecyl iodide or benzyl iodide with the corresponding Grignard compound. In the case of dodecyl iodide, it will be seen from the table that in 6½ hours the extent of the Wurtz reaction is hardly affected, whereas the amount of disproportionation is increased sevenfold. Since the total time of interaction of dodecyl iodide with the Grignard compound is as much as twenty-five times as long in this experiment as in the primary interaction with magnesium, it is clear that the Wurtz reaction does *not* proceed by the mechanism $RI + R{\cdot}MgI \longrightarrow MgI_2 + R_2$, whereas disproportionation depends to an important extent on the reaction $C_{12}H_{25}I + C_{12}H_{25}{\cdot}MgI \longrightarrow MgI_2 + C_{12}H_{24} + C_{12}H_{26}$, which may involve the temporary formation of free radicals in solution (cf. Späth, *Monatsh.*, 1913, **34**, 1978; Gilman and Fothergill, *J. Amer. Chem. Soc.*, 1928, **50**, 3334).

The benzyl halides show a marked contrast with the alkyl halides in this respect. When benzylmagnesium chloride was boiled with an equivalent amount of benzyl iodide for 10 minutes, the reaction (*A*) $C_6H_5{\cdot}CH_2I + C_6H_5{\cdot}CH_2{\cdot}MgCl \longrightarrow MgClI + (C_6H_5{\cdot}CH_2)_2$ took place to the extent of 87·5% of the theoretical.

Use of the Results in the Wurtz Synthesis of Hydrocarbons.—The unsatisfactory yield of hydrocarbon R_2 obtained when sodium is used with the higher alkyl halides is probably connected with the disproportionation reaction. In the action of alkyl halides on magnesium, the data show this to be relatively unimportant compared with the Wurtz reaction. A synthesis which does not waste the large amounts of Grignard compound formed at the same time (cf. Levene, West, and v. der Scheer, *J. Biol. Chem.*, 1915, **20**, 521) is possible as follows : The alkyl iodide is first allowed to react with magnesium under standard conditions, leading to about 25% of product formed by Wurtz reaction. An amount of iodine is now added equivalent to the Grignard compound formed, the reaction being assumed to be $I_2 + R{\cdot}MgI \longrightarrow RI + MgI_2$. The requisite amount is calculated from a blank reaction, or by cautiously adding iodine till the colour persists. A fresh amount of magnesium is added to react with the alkyl iodide recovered, and the sequence of operations is repeated till a sufficient yield of R_2 has accumulated to make isolation profitable. Although the yield of product formed by the Wurtz reaction decreases in geometric proportion in the successive interactions with magnesium, it cannot be brought to 100% by indefinite addition of iodine and magnesium, owing to the concurrent loss of alkyl halide by the disproportionation reaction. Yields of 65% can be obtained by a series of five additions of iodine and magnesium. This compares very favourably with any other method of making long-chain paraffins, both in the yield and in the purity of the products.

Although magnesium only acts slowly on iodine in ether, the simultaneous addition of iodine and an alkyl iodide to magnesium was not found to be as satisfactory as the alternate addition of iodine and magnesium to the Grignard compound.

Mechanism of the Action between Iodine and Grignard Compounds.—The fact that no other reaction of importance has been missed in the interaction between alkyl compounds and magnesium may be verified as follows : Suppose that, in a single addition of alkyl halide to magnesium, the three competing reactions

$$\begin{aligned}
&RI + Mg \longrightarrow R{\cdot}MgI\\
&RI + \tfrac{1}{2}Mg \longrightarrow \tfrac{1}{2}R_2 + \tfrac{1}{2}MgI_2\\
&RI + \tfrac{1}{2}Mg \longrightarrow \tfrac{1}{2}[RH + R'H] + \tfrac{1}{2}MgI_2
\end{aligned}$$

take place to the extent x, y, and $1 - (x + y)$ respectively. If the addition of iodine to the product leads to the re-formation of alkyl iodide wholly by the reaction $I_2 + R{\cdot}MgI \longrightarrow RI + MgI_2$, the fraction x of the original alkyl iodide will be re-formed. In the next addition of magnesium, the hydrocarbons now present being assumed not to affect the relative extent of the three reactions, the fraction of Grignard compound formed will be x^2, and the total yield produced by the Wurtz reaction, $y + xy$. After five additions of iodine and magnesium, the total yield of R_2 according to these assumptions will be $y(1 + x + x^2 + x^3 + x^4)$ or, in the case of dodecyl iodide, $0{\cdot}29(1 + 0{\cdot}65 + 0{\cdot}42 + 0{\cdot}27 + 0{\cdot}18) = 73{\cdot}0\%$, which compares with a found yield of 62·5%. For hexadecyl iodide the corresponding figures are : theoretical yield, 69·5%; found, 63·8%. Further evidence on the action of iodine on the Grignard compounds is obtained as follows :

Action of iodine on the compounds R·MgCl. In these experiments the alkylmagnesium chloride was formed in the usual way; the theoretical amount of iodine for complete decomposition of the Grignard compound was slowly added, and finally the products were separated by addition of dilute hydrochloric acid and fractionation and analysed.

From a comparison of the yield in blank experiments with the yields of various products, the following reactions take place on the addition of iodine to dodecylmagnesium chloride :

(1) $C_{12}H_{25}{\cdot}MgCl + I_2 \longrightarrow MgICl + C_{12}H_{25}I$ 71·0%
(2) $C_{12}H_{25}{\cdot}MgCl + I_2 \longrightarrow MgI_2 + C_{12}H_{25}Cl$ 16·4%
(3) $C_{12}H_{25}{\cdot}MgCl + \tfrac{1}{2}I_2 \longrightarrow \tfrac{1}{2}C_{24}H_{50} + MgICl$ 5·1%
(4) $C_{12}H_{25}{\cdot}MgCl + \tfrac{1}{2}I_2 \longrightarrow \tfrac{1}{2}(C_{12}H_{26} + C_{12}H_{24}) + MgICl$ 4·3%

The points of interest in this result are :

(a) Dodecylmagnesium chloride reacts at least partly in this form, and not wholly as $Mg(C_{12}H_{25})_2 + 2I_2 \longrightarrow MgI_2 + 2C_{12}H_{25}I$, which might be possible according to the results of Schlenk and Schlenk (*Ber.*, 1929, **62**, 920 ; 1931, **64**, 734) if the equilibrium $2C_{12}H_{25}{\cdot}MgCl \rightleftarrows Mg(C_{12}H_{25})_2 + MgCl_2$ is sufficiently displaced to the right.

(b) Chlorides may be used equally well in the synthesis of R_2.

(c) Reaction (3), which may possibly proceed as

$$Mg(C_{12}H_{25})_2 + I_2 \longrightarrow MgI_2 + C_{24}H_{50}$$

only takes place to the extent of 5·1%.

This contrasts with the behaviour of benzyl chloride, in which the reactions are

$$\begin{aligned}
&(1)\ C_6H_5{\cdot}CH_2{\cdot}MgCl + I_2 \longrightarrow MgICl + C_6H_5{\cdot}CH_2I \quad 8{\cdot}7\% \\
&(2)\ C_6H_5{\cdot}CH_2{\cdot}MgCl + I_2 \longrightarrow MgI_2 + C_6H_5{\cdot}CH_2Cl \quad 10{\cdot}2\% \\
&(3)\ C_6H_5{\cdot}CH_2{\cdot}MgCl + \tfrac{1}{2}I_2 \longrightarrow \tfrac{1}{2}(C_6H_5{\cdot}CH_2)_2 + MgICl \quad 80{\cdot}0\%.
\end{aligned}$$

Reaction (3) in this case most probably proceeds as shown in (*A*) (p. 203). (For the addition of other halogens to Grignard compounds, see Datta and Mitter, *J. Amer. Chem. Soc.*, 1919, **41**, 282.)

Purification of Long-chain Paraffins.—A method of purifying paraffins has been described by Piper *et al.* (*loc. cit.*), according to which the paraffin is heated with concentrated sulphuric acid at 130° till no more charring is observed during 2 hours. Blank experiments on the rate of removal of added cetene ($C_{16}H_{32}$), and alkyl halides, showed that a very much more rapid purification could be effected by heating the paraffins with 20% oleum at 100° till the test for halide was negative, followed by a short treatment with concentrated sulphuric acid at 130° to remove any sulphonic acids formed. Owing to the appreciable oxidation of certain liquid paraffins at 130° it is advisable to hinder the circulation of air over the surface of the paraffin during the purification.

After treatment with sulphuric acids the paraffins are washed, dried, and distilled in a vacuum. Mixed melting points are of little use in estimating the purity of paraffins, but *X*-ray and calorimetric measurements [Ubbelohde, *Trans. Faraday Soc.* (in the press)] showed that paraffins prepared and purified by the methods described here were of the highest purity yet obtained.

EXPERIMENTAL.

As the work was largely concerned with homologous or closely similar compounds, it is sufficient to give details of a limited number of experiments.

Dodecyl Chloride (Schuchardt, b. p. 132—134°/18 mm.).—To 1·2 g. of magnesium in 40 c.c. of ether, 10·2 g. of the chloride and one crystal of iodine were added ; the mixture was kept for at least 30 minutes in the cold, and the reaction then completed by 3 hours' boiling under reflux with protection from atmospheric moisture. After addition of dilute hydrochloric acid, washing with water, sodium thiosulphate solution and again with water, drying at 100°/25 mm., and fractionation, the total yield was 8·35 g. On distillation at 18 mm., 7·90 g. distilled, leaving a residue of much higher b. p., the amount of which (0·4 g.) was too small for analysis for halogen content. The distillate contained 0·4% of chlorine (Stepanov's method) and 1·9% of dodecene, determined by adding bromine in carbon tetrachloride and estimating the excess iodometrically after 1 hour.

Addition of iodine to dodecylmagnesium chloride. To the Grignard compound formed as above (9·2 g. of the chloride, 37 c.c. of ether, and 1·1 g. of magnesium), 12 g. of iodine were slowly added, the mixture being kept cool. The colour faded instantly for the first 10 g., then more slowly. The solution was boiled for 5 minutes to complete the reaction, and dilute hydrochloric acid added before the products were isolated as above. The total product was 11·92 g., of which 10·97 g. distilled below 180°/18 mm., leaving a high-boiling residue (0·91 g.).

The distillate was analysed for total halogen by Stepanov's method, and the relative amounts of chloride and iodide were determined by using a known excess of silver nitrate in precipitating the halides, and determining the excess. The distillate contained 2·67% of chlorine, 33·0% of iodine, and 0·29% of unsaturated hydrocarbon, the rest being saturated hydrocarbon. The residue contained 11·5% of iodine, which could be separated as a volatile iodide on redistillation.

Dodecyl Iodide.—This was prepared from dodecyl alcohol (Schuchardt) by heating at 140° for 3 hours with 10% more than the theoretical quantities of red phosphorus and iodine; the product was cooled, dissolved in ether, washed with 10% sodium hydroxide solution and with water, dried, and distilled in a vacuum (b. p. 159—160°/15 mm.). To 80 c.c. of ether and 1·8 g. of magnesium, 20·7 g. of the iodide were added in 15 minutes. After addition of dilute hydrochloric acid, the total product isolated was 12·1 g., with 3·7 g. of high-boiling residue after distillation. The unchanged iodide was determined by Stepanov's method, the residue containing 2·1%, and the distillate 1·3% of iodine. The unsaturated hydrocarbon in the distillate corresponded with 4% of dodecene. A small amount of unsaturated substances in the residue was investigated in more detail in the case of hexadecyl iodide (below).

Repeated addition of iodine. After preparation of the Grignard compound as above (15·3 g. of the iodide, 60 c.c. of ether, and 1·3 g. of magnesium), alternate additions were made of the following amounts of iodine, 9·7, 7·0, 5·0, 4·0, and 3·0 g., and the following amounts of magnesium, 0·9, 0·7, 0·6, 0·5, and 0·4 g. The iodine was added slowly with cooling, and the mixture was boiled for 5 minutes before the next addition of magnesium and for 15 minutes before the next addition of iodine. A double layer of liquid was formed owing to the salting-out effect of magnesium iodide. The total product was 8·9 g., of which 5·8 g. did not distil below 180°/18 mm. The residue contained 1·2% of iodine, and 1·5% of unsaturated substances, calculated on the basis of $C_{24}H_{48}$. The distillate contained 17·2% of dodecene.

Action of dodecyl iodide on dodecylmagnesium iodide. The Grignard compound was prepared as above (15·6 g. of the iodide, 60 c.c. of ether, and 1·3 g. of magnesium), 15·7 g. of dodecyl iodide added, and the whole boiled for 6½ hours (reflux condenser; calcium chloride guard-tube). On isolation the total product was 21·7 g. Distillation left 3·8 g. containing 9·8% of iodine and 2·9 g. of hydrocarbon. The distillate contained 9·25 g. of hydrocarbon, 20·8% of iodine, and 9·9% of unsaturated hydrocarbon (calculated on the basis of $C_{12}H_{24}$). The residue contained 0·1 double bond per mole of $C_{24}H_{50}$, calculated on the bromine absorption.

Hexadecyl Iodide.—The experiments with this iodide were parallel to those with the other iodides, the only special feature being an attempt to determine the nature of the unsaturated substance in the residue. Only one experiment need be described.

Repeated addition of iodine. The Grignard compound was formed as above from 20·3 g. of the iodide, 80 c.c. of ether, and 2·1 g. of magnesium. Five additions of iodine, 7·5, 5·8, 4·3, 3·2, and 2·4 g., alternating with 1·4, 1·1, 0·8, 0·6, and 0·4 g. of magnesium, were made as above. The total product was 13·0 g., with 8·3 g. of high-boiling residue (18 mm.). The unsaturation in the distillate, calculated on the basis of $C_{16}H_{32}$, was 19%. The unsaturation in the residue was 0·054 double bond per mole of $C_{32}H_{66}$. This residue, recrystallised from benzene, gave 70% of dotriacontane, $C_{32}H_{66}$, m. p. 71—72°, with no absorption of bromine; the mother-liquor on evaporation gave a pasty yellow mass, which contained 0·2 double bond per mole of $C_{32}H_{66}$. The amount present is practically the same as in a single addition of hexadecyl iodide to magnesium, so the process leading to its formation is not an important part of the reaction between alkyl iodides and magnesium.

Benzyl Halides.—These were treated in a precisely similar manner to the alkyl halides, the only difference being that no determination of the disproportionation reaction, if any, could be made. The high-boiling residue was shown to be mainly dibenzyl by the mixed melting point method, but the possibility of the presence of small amounts of other hydrocarbons was not excluded.

Identification of Paraffins, Blank Experiments, etc.—The lower paraffins were identified by their b. p.'s and their resistance to the action of concentrated sulphuric acid at 130°, and the higher paraffins by their m. p.'s and resistance to sulphuric acid. Mixed melting points are of little use as a test of the freedom of the products from homologues, but *X*-ray and calorimetric investigations of octadecane obtained from *n*-nonyl alcohol showed that any impurity did not exceed 1%, which compares very favourably with the purity of paraffins made by the electrolysis of the potassium salts of fatty acids.

In the estimation of the relative extent of the Wurtz and the Grignard reaction taking place when an alkyl iodide is added to magnesium, the separation of the product into a high- and a low-boiling fraction becomes somewhat unsatisfactory as the chain length increases, owing to the fact that in the vapour-pressure equation $\ln p = -\lambda/\boldsymbol{R}T + B$ the increase in the latent heat λ with chain length is partly compensated by the increase in the constant term B (cf. Ubbelohde's data, *Trans. Faraday Soc., loc. cit.*). A check on the efficiency of separation was made by redistilling a mixture of hexadecane and dotriacontane, and showed that the probable error in the yields given for these substances is not more than 4%. A further check was obtained from the reproducibility of the yields when the experiments were repeated. Distillation of a mixture of cetene and dotriacontane showed that the former behaved in a similar manner to hexadecane, as might have been expected. The absorption of bromine observed for the crude dotriacontane cannot be wholly due to traces of cetene, in view of this result, but was not further investigated on account of the small amounts available.

The method of analysis of the halides was checked on dodecyl chloride (Found: Cl, 17·7. Calc., 17·3%) and on octadecyl iodide (Found: I, 35·0. Calc., 33·7%). The method of estimation of unsaturated substances was checked on a known mixture of cetene, iodide, and paraffin containing 4·0% of cetene (Found, 4·2%).

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