CCL.—*Syntheses by Means of Magnesium Amyl Halides. Part II. The Reduction of Benzophenone.*

By WALTER CULE DAVIES, ROBERT SINCLAIR DIXON, and WILLIAM JACOB JONES.

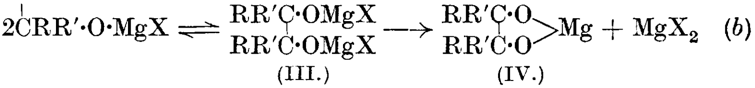
THE reducing action of Grignard reagents on benzophenone and the isolation of benzhydrol and of ethylenic hydrocarbons have been described by several investigators (Sabatier and Mailhe, *Compt. rend.*, 1904, **139**, 343; 1905, **141**, 298; Konovalov, Miller, and Timtschenko, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 447; Lagrave, *Ann. Chim.*, 1927, **8**, 372; Blicke and Powers, *J. Amer. Chem. Soc.*, 1929, **51**, 3378). Pinacols have been isolated from the products of interaction between diaryl ketones and Grignard reagents; thus, benzpinacol was prepared both by Schmidlin (*Ber.*, 1906, **39**, 4202), through the action of benzophenone on the magnesium derivative of triphenylchloromethane in the presence of excess of magnesium, and by Gilman and Fothergill (*J. Amer. Chem. Soc.*, 1929, **51**, 3149) in the apparent absence of magnesium. The pinacol was also obtained by Gomberg and Bachmann (*J. Amer. Chem. Soc.*, 1927, **49**, 237, 2666) on heating together benzophenone, magnesium, and phenyl halide and hydrolysing the product. Barnett, Cook, and Nixon (J., 1927, 505), from the product of the interaction between magnesium phenyl bromide and the esters of *o*-benzylbenzoic acid, obtained *s*-*oo'*-dibenzylbenzpinacol, which, they suggest, is formed by the reduction of the intermediate *o*-benzylbenzophenone. These authors, however, according to a private communication to Boyd and Hatt (J., 1927, 909), could not obtain the pinacol when they used a filtered Grignard solution. Lagrave (*loc. cit.*), by the action of magnesium propyl bromide obtained 1—2% of benzpinacol, and 2—3% with the *n*- and *iso*-butyl compounds.

In the present work we have established that reduction occurs when employing *n*-amyl, *dl*-β-methylbutyl, and *iso*amyl (γ-methylbutyl) Grignard reagents, and have isolated benzhydrol and benzpinacol from the products of reaction.

The following explanation, which appears to be in conformity with the views of Gomberg (*loc. cit.*; *Rec. trav. chim.*, 1929, **48**, 847), of Blicke and Powers (*loc. cit.*), and of Gilman and Brown (*J. Amer. Chem. Soc.*, 1930, **52**, 1128), accounts for the mechanism of the reducing action of alkyl magnesium halides on ketones :

$$\mathrm{R{\cdot}CO{\cdot}R' + C_nH_{2n+1}MgX \longrightarrow \underset{(I.)}{\overset{|}{C}_nH_{2n+1}} + \underset{(II.)}{\overset{|}{C}RR'{\cdot}O{\cdot}MgX}} \quad . \quad (a)$$

The deep, red colour, which develops on the addition of benzophenone to amyl Grignard reagents, may be ascribed to the formation of the halogenomagnesium ketyl radical (II), the magnesious halide analogue of the highly-coloured sodium ketyls described by Schlenk, Weickel, and Thal (*Ber.*, 1911, **44**, 1182; 1913, **46**, 2840).



$$\mathrm{2\overset{|}{C}RR'{\cdot}O{\cdot}MgX \rightleftharpoons \underset{(III.)}{\begin{array}{l}RR'C{\cdot}OMgX\\ \;\;\;\;\;|\\ RR'C{\cdot}OMgX\end{array}} \longrightarrow \underset{(IV.)}{\begin{array}{l}RR'C{\cdot}O\\ \;\;\;\;\;|\\ RR'C{\cdot}O\end{array}}{>}Mg + MgX_2} \quad (b)$$

$$\mathrm{2\overset{|}{C}_nH_{2n+1} \longrightarrow C_{2n}H_{4n+2}} \quad . \quad . \quad . \quad . \quad . \quad (c)$$

$$\mathrm{\overset{|}{C}_nH_{2n+1} + \overset{|}{C}RR'{\cdot}O{\cdot}MgX \longrightarrow C_nH_{2n} + CHRR'{\cdot}OMgX} . \quad (d)$$

The addition reaction would be represented by the equation

$$\mathrm{\overset{|}{C}_nH_{2n+1} + \overset{|}{C}RR'{\cdot}O{\cdot}MgX \longrightarrow CRR'(C_nH_{2n+1}){\cdot}OMgX} . \quad (e)$$

By the mutual oxidation of the free alkyl radical (I) and reduction of the radical (II), represented by equation (*d*), there would result in the case of magnesium amyl bromide and benzophenone, after hydrolysis, benzhydrol and amylene. Hydrolysis both of the halogenomagnesium pinacolate (III) and of the magnesium pinacolate (IV) would account for the formation of benzpinacol.

Reactions (*a*), (*b*), (*c*), (*d*), and (*e*) are all to be considered as proceeding simultaneously, when, as in the present experiments, the ketone is added gradually to the Grignard reagent, and the actual proportions of ethylenic and dialkyl hydrocarbons and of pinacol, hydrol, and carbinol in the final product will be determined by the relative speeds of these reactions, which, in turn, will be determined by the particular ketone and Grignard reagent used. For instance, where magnesium methyl and ethyl halides are employed, benzophenone yields mainly the methyl- and ethyl-diphenylcarbinols, and in those cases benzpinacol and benzhydrol are subsidiary products. Moreover, when methyl ethyl ketone and acetophenone react with magnesium *n*-amyl bromide, there result fair yields of the products of addition, *viz.*, methylethyl-*n*-amylcarbinol and phenylmethyl-*n*-amylcarbinol, respectively (Davies, Dixon, and Jones, this vol., p. 468), and then the reducing action of the amyl Grignard reagents is not prominent.

It may be noted that the mechanism here offered to account for the reduction of benzophenone by magnesium amyl bromides demands, in consequence of equations (*c*) and (*a*), that decane in excess of that produced by the synthetic action of magnesium [equation (*f*)] should be present in the final product of the reaction :

$$2C_nH_{2n+1}Br + Mg \longrightarrow C_{2n}H_{4n+2} + MgBr_2 \quad . \quad . \quad . \quad (f)$$

In the present experiments equivalent weights of magnesium, amyl bromide, and benzophenone were employed, and, therefore, owing to the synthetic action [equation (*f*)], the Grignard reagent was rather deficient of being equivalent to the benzophenone used. However, more benzophenone was recovered from the products of the reaction than was accounted for by this deficiency of Grignard reagent, and this may be ascribed to (1) lenity of interaction between the ketone and the reagent, and (2) oxidation of the bromomagnesium ketyl radical by air. That both these causes are operative is shown, first, by an experiment in which the system, after the complete addition of benzophenone, was immediately treated with ice and dilute sulphuric acid, and, secondly, by the results of the experiments of Gomberg and Bachmann, in which they actually convert the iodomagnesium ketyl radical entirely back to ketone by the action of oxygen.

It should be pointed out that in our experiments the Grignard solutions were decanted off from unused magnesium before the benzophenone was added, but were not filtered.

Incidentally, enolisation during Grignard reactions, where possible, can be explained in a natural way by the present theory, thus :

$$R{\cdot}CO{\cdot}CH_3 + C_nH_{2n+1}MgX \longrightarrow CR(OMgX){:}CH_2 + C_nH_{2n+2} \quad (g)$$

since Gomberg (*Rec. trav. chim.*, 1929, **48**, 851) has pointed out that the binary system ($MgX_2 + Mg$), or magnesious halide, MgX, possesses many of the properties of metallic sodium.

EXPERIMENTAL.

Reactions.—A solution of 50 g. of the amyl bromide (*n*-amyl, *dl*-β-methylbutyl, or *iso*amyl) in 100 c.c. of absolute ether was added gradually to 8·1 g. of magnesium, a trace of iodine, and 100 c.c. of ether, contained in an apparatus which permitted of continuous stirring of the liquid. The resulting Grignard solution was syphoned without contact with the air into a reaction bottle where it was cooled to 10°, and a solution of 60 g. of benzophenone in 100 c.c. of ether was added to it drop by drop. The interaction was not vigorous. A deep red colour developed and usually persisted until the end of the addition, a crystalline mass having then separated.

The mixture was kept for 24 hours, then poured on ice, and treated with 150 c.c. of 15% sulphuric acid and 30 c.c. of benzene to dissolve the precipitated substances. The ether–benzene layer was dried over potassium carbonate, and the solvents were removed at room temperature in a vacuum. A thick oil remained from which, after several days, a mass of crystals (A) separated. These crystals were separated from their mother-liquor (B), dried on porous plate, and shown to be a mixture of benzophenone and benzpinacol in the following way. They were washed by being allowed to stand in contact with 300 c.c. of light petroleum (b. p. 60—80°), with occasional stirring, for 24 hours. The crystals remaining undissolved after this treatment consisted of almost pure benzpinacol (Found: C, 85·0; H, 6·0. $C_{26}H_{22}O_2$ requires C, 85·2; H, 6·1%), identified by conversion into β-benzpinacolin, m. p. 180° (Gomberg and Bachmann, *loc. cit.*, give m. p. 179—180°). The wash-liquor on being concentrated by evaporation to 100 c.c. deposited a mixture (C) of crystals of benzpinacol and benzophenone. This crop of crystals was separated from the wash-liquor, which was then allowed to evaporate off completely, whereupon it yielded practically pure benzophenone (separation D).

The mother-liquor (B) contained the decane, benzophenone, benzhydrol, and probably some diphenylamylcarbinol, but practically no benzpinacol. It was apparently the decane that kept the benzophenone in solution in this liquor, and when the hydrocarbon was removed, benzophenone crystallised out. The composition of the mother-liquor (B) was established as follows. It was either preserved in the open air under protection from dust for 3 months, during which practically the whole of the benzophenone separated in the form of large crystals, or it was immediately cooled to − 10°, whereupon the benzophenone separated as small crystals, which were removed by filtration below 0°. The residual liquor from either treatment was distilled under low pressure, whereby there was obtained a large fraction (E) consisting mainly of benzhydrol, a first fraction (F) consisting of the decane being obtained in those cases in which the mother-liquor had been immediately cooled. The decane was purified by washing with concentrated sulphuric acid. In all cases in distillation at this stage, a residue of material, boiling higher than benzhydrol, was obtained.

The quantities (in g.) of the various products obtained per 8·1 g. of magnesium and its equivalent of amyl bromide and benzophenone are given in the following table, together with the m. p.'s or b. p.'s.

	Magnesium amyl bromide used.		
	n-Amyl.	*dl*-β-Methylbutyl.	*iso*Amyl.
Crystalline separation (A)	6·7 (85—160°)	8·2 (72—130°)	6·0 (80—155°)
Benzpinacol from (A)	2·3 (182—186°)	5·2 (182—184°)	3·0 (178—181°)
Mixture (C)	1·0 (42—160°)	0·4 (75—170°)	0·4 (76—165°)
Benzophenone (D) from (A)	3·1 (48°)	2·2 (48°)	2·5 (48°)
Benzophenone from (B) by freezing	13·0 (48°)	—	14·0 (48°)
Benzophenone from (B) on keeping	—	5·0 (48°)	—
Decane from (F)	5·6	—	4·9
Fraction (E) (mainly benzhydrol)	19·0 (146—150°/ 3 mm.)	15·0 (146—148°/ 3 mm.)	20·0 (148—151°/ 3 mm.)

That fraction (E) consisted mainly of benzhydrol was proved by freezing and separating the solid, whereby there were obtained crystals (Found : C, 84·8, 84·5; H, 6·2, 6·4. Calc. for $C_{13}H_{12}O$: C, 84·7; H, 6·6%), m. p. 66°, mixed m. p. with an authentic specimen of benzhydrol 66°, giving a bright red coloration with concentrated sulphuric acid.

The amount of decane given in the above table is not the total amount formed. In order to obtain an estimate of the total, a separate experiment was carried out in the case of magnesium *n*-amyl bromide and benzophenone in which the original ethereal solution was decanted off from the precipitated magnesium salts, deprived of its ether by evaporation, and the residue then treated with concentrated sulphuric acid; 7·7 g. of *n*-decane, b. p. 169°/760 mm., were thus obtained. This amount of the hydrocarbon is in excess of that obtained when amyl Grignard reagents interact either with certain other aldehydes and ketones (Davies, Dixon, and Jones, *loc. cit.*) or with antimony trichloride (Dyke, Davies, and Jones, this vol., p. 467).

In an experiment with magnesium *iso*amyl bromide in which the reaction product was not allowed to stand, but was immediately treated with ice and dilute sulphuric acid, the total amount of benzophenone recovered was 27·6 g., an amount greater than those given in the table.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF.

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