FACTORS INFLUENCING THE COURSE AND MECHANISM OF GRIGNARD REACTIONS. XIX. THE PREPARATION OF SUBSTITUTED BIBENZYLS FROM GRIGNARD REAGENTS, ALKYL HALIDES, AND ALKYLBENZENES, IN THE PRESENCE AND ABSENCE OF COLBALTOUS CHLORIDE

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INTRODUCTION

It has been established in this Laboratory that the reaction of free methyl radicals with ether results in a gaseous mixture of a composition indicated in Example A, Table I. However, results have also been obtained which indicate that when free methyl radicals are generated from methylmagnesium bromide and some organic halides (in the presence of cobaltous chloride), they attack not only the solvent (ether), but the organic halide as well. This conclusion is based upon the following facts: (a) The larger amounts of methane formed in reactions B and C, Table I, than in reaction A; (b) the formation of high-boiling materials in reactions B and C, Table I, and none in reaction A.

To extend the knowledge of this side-reaction, and to attempt to put it to practical preparative use, cobaltous chloride-catalyzed reactions of Grignard reagents with alkyl halides were conducted in the presence of alkylbenzenes. These hydrocarbons were chosen because they do not react with Grignard reagents under ordinary conditions, and because a previous study (4) has shown that free methyl radicals react with them to give substituted bibenzyls. Isopropylbenzene was chosen as the most useful of these hydrocarbons because its reaction with free methyl radicals (generated by the decomposition of a diacetyl peroxide) gives almost pure 2,3-dimethyl-2,3-diphenylbutane.

Cobaltous chloride-catalyzed reactions of methylmagnesium bromide and methyl bromide in the presence of isopropylbenzene. In the first experiments, this reaction was carried out in the presence of about 500 ml. of ether. The results obtained are recorded in Table II. It is clear that at lower temperatures, the free methyl radicals attack predominantly the solvent ether, and the yield of 2,3-dimethyl-2,3-diphenylbutane is very small. However, when most of the ether was removed and the reaction temperature was increased to 100°, the yield of 2,3-dimethyl-2,3-diphenylbutane was increased to 23%, and, as was to be expected, the yield of methane was correspondingly larger than in the other experiments.

Cobaltous chloride-catalyzed reactions of n-propylmagnesium bromide with n-propyl bromide in isopropylbenzene. Somewhat better yields of 2,3-dimethyl-2,3-diphenylbutane were obtained when a solution of n-propylmagnesium bromide (ether removed) in isopropylbenzene, to which cobaltous chloride (6 mole %) had been added, was treated with a solution of n-propyl bromide in isopropylbenzene. At 35°, a yield of 25% of 2,3-dimethyl-2,3-diphenylbutane was obtained, and at 100°, 36%. The experimental details are recorded in Table III.

Thermal reactions of Grignard reagents with alkyl halides in isopropylbenzene solution at 100°. It was found (Table IV) that at 100°, Grignard reagents react

TABLE I

GAS COMPOSITION AND YIELD OF HIGHER-BOILING PRODUCTS IN REACTIONS OF METHYL-MAGNESIUM BROMIDE WITH ORGANIC HALIDES IN THE PRESENCE OF COBALTOUS CHLORIDE

REACTANTS	YIELD OF HIGHER-BOILING PRODUCTS (%)	COMPOSITION OF GASEOUS PRODUCTS(%)		
		CH_4	C_2H_6	C_2H_4
(A) $C_6H_5MgBr + CH_3Br(1)$	None	62	18	20
(B) $CH_3MgBr + (CH_2)_5CHCl(2)$	6.0	85	9	6
(C) $CH_3MgBr + C_6H_5CH_2CH_2CH_2Cl(3)$	37.2	90	5	5

TABLE II

COBALTOUS CHLORIDE-CATALYZED REACTIONS OF METHYLMAGNESIUM BROMIDE WITH METHYL BROMIDE IN THE PRESENCE OF ISOPROPYLBENZENE

REACTION WITH CH_3MgBr IN PRESENCE OF 6 MOLE % $CoCl_2$	GRIGNARD REAGENT (MOLE)	i-PrC_6H_5 (MOLES)	METHYL BROMIDE (MOLE)	GAS EVOLVED (MOLE)	YIELD DIMER[a] (%)	GAS ANALYSIS (%)		
						CH_4	C_2H_6	C_2H_4
Solvent Et_2O present, 0°	1.21	2.65	1.09	1.51	1	68	16	16
Solvent Et_2O present, 35°	0.91	2.50	0.78	1.21	6.1	70	14	16
Solvent Et_2O removed, 0°	.84	2.45	.54	0.93	5	70	14	16
Solvent Et_2O removed, 35°	1.28	2.45	1.01	1.55	13	70	15	15
Solvent Et_2O removed, 100°	0.44	4.58	0.35	0.36	23	82	10	8

[a] 2,3-Dimethyl-2,3-diphenylbutane.

TABLE III

REACTIONS OF GRIGNARD REAGENTS WITH ALKYL HALIDES IN ISOPROPYLBENZENE SOLUTION IN THE PRESENCE OF COBALTOUS CHLORIDE (6 MOLE %); (ETHER REMOVED BY EVACUATION)

REACTIONS IN i-PrC_6H_5	G. R. (MOLE)	i-PrC_6H_5 (MOLES)	ALKYL HALIDE[a] (MOLE)	GAS EVOLVED (MOLE)	DIMER YIELD,[b] %	GAS (C_3H_8:C_3H_6 RATIO)
n-$PrMgBr + n$-$PrBr$, 35–40°	1.15	3.15	0.73	1.12	25	69:31
n-$PrMgBr + n$-$PrBr$, 100°	0.392	3.29	.368	0.714	32	65:35
n-$PrMgBr + n$-$PrBr$, 100°	.71	3.22	.58	1.04	31	86:14
n-$PrMgBr + n$-$PrBr$, 100°	.23	1.41	.205	0.41	36	66:34
$MeMgBr + n$-$PrBr$, 100°	.22	1.69	.194	.34	22	gas m. wt.[c] 28.6

[a] Used in about 10% excess. Consumption of alkyl halide was determined by Volhard analysis.

[b] Percentage of free radicals undergoing reaction with isopropylbenzene. The moles of free radicals are calculated by doubling the moles of n-propyl bromide consumed. The dimer is 2,3-dimethyl-2,3-diphenylbutane.

[c] Gas contains propane, propylene, methane, ethane, ethylene.

readily with alkyl halides and isopropylbenzene to yield substantially the same products as are formed (Table III) at lower temperatures in the presence of cobaltous chloride. The yields of 2,3-dimethyl-2,3-diphenylbutane are, in gen-

eral, slightly lower than in analogous cobaltous chloride-catalyzed reactions. However, with isopropylmagnesium bromide, isopropyl bromide, and isopropylbenzene, the highest yield of dimer (2,3-dimethyl-2,3-diphenylbutane) yet observed in these types of reactions was obtained.

Methylmagnesium bromide, an alkyl halide, and isopropylbenzene do not yield any dimer (2,3-dimethyl-2,3-diphenylbutadiene) at 100° in the absence of cobaltous chloride or other catalysts of this type. Even at 150°, the reaction between methylmagnesium bromide and n-propyl bromide and isopropylbenzene is very slow—100 ml. of gas was evolved in six hours.

Cobaltous chloride-catalyzed reactions of methylmagnesium bromide in various solvents. The cobaltous chloride-catalyzed reaction of methylmagnesium bromide with methyl bromide in the presence of diphenylmethane gave a small yield of symmetrical tetraphenylethane. The same reaction in p-methoxy-n-propylbenzene solution gave 13% of an equimolecular mixture of meso and racemic hexesterol dimethyl ethers.

DISCUSSION

In previous publications from this Laboratory, we have described the preparation of substituted bibenzyls by two methods which involve free radicals as intermediates. These are illustrated below by a series of steps which lead to the formation of 2,3-dimethyl-2,3-diphenylbutane from isopropylbenzene and 2-chloro-2-phenylpropane, respectively.

I. (a) $(CH_3COO)_2 \rightarrow CH_3 \cdot + CO_2 + CH_3COO \cdot$
   (b) $CH_3 \cdot + C_6H_5(CH_3)_2CH \rightarrow CH_4 + C_6H_5(CH_3)_2C \cdot$
   (c) $2C_6H_5(CH_3)_2C \cdot \rightarrow C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5$

II. (a) $CH_3MgCl + CoCl_2 \rightarrow CH_3CoCl + MgCl_2$
   (b) $CH_3CoCl \rightarrow CH_3 \cdot + CoCl \cdot$
   (c) $C_6H_5(CH_3)_2CCl + CoCl \cdot \rightarrow C_6H_5(CH_3)_2C \cdot + CoCl_2$
   (d) $2C_6H_5(CH_3)_2C \cdot \rightarrow C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5$

A comparison of the intermediate products of the reactions postulated in I and II, suggested that if free radicals are actually generated in reaction II (b), then it should be possible to prepare substituted bibenzyls by the interaction of methylmagnesium bromide, methyl bromide, isopropylbenzene, and a small amount of cobaltous chloride or bromide. And such, indeed, was found to be the case. The formation of substituted bibenzyls from a mixture of such reagents may be represented by the following reactions:

III. (a) $CH_3MgBr + CoCl_2 \rightarrow CH_3CoCl + MgBrCl$
   (b) $CH_3CoCl \rightarrow CH_3 \cdot + CoCl \cdot$
   (c) $CH_3Br + CoCl \cdot \rightarrow CH_3 \cdot + CoBrCl$
   (d) $C_6H_5(CH_3)_2CH + CH_3 \cdot \rightarrow CH_4 + C_6H_5(CH_3)_2C \cdot$
   (e) $2C_6H_5(CH_3)_2C \cdot \rightarrow C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5$
   (f) $C_2H_5OC_2H_5 + CH_3 \cdot \rightarrow$ gaseous products $(CH_4 + C_2H_6 + C_2H_4)$[1]

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[1] It has been shown that the formation of methane, ethane, and ethylene in the CoCl$_2$-catalyzed reactions of methylmagnesium bromide with organic halides does not proceed by

However, the processes of formation of bibenzyls from acetyl peroxide and isopropylbenzene, as indicated in scheme I, and from the Grignard reagent and isopropylbenzene, as in scheme III, are not strictly comparable, although in both cases free methyl radicals are involved. Thus, in scheme I, the free methyl radicals react only with isopropylbenzene, while in the reaction proceeding according to scheme III, the free methyl radicals react not only with isopropylbenzene, but with the ethyl ether[2] as well III (f). It is, therefore, not surprising that, while the yield of the substituted bibenzyls from reaction scheme I is quantitative, on the basis of the reaction mechanism outlined, the yield of substituted bibenzyls is only 13% of the amount calculated on the basis of the reactions postulated in scheme III. An attempt to increase the yield of bibenzyls in scheme III by complete removal of the ether failed. No substituted bibenzyls were

<div align="center">TABLE IV</div>

<div align="center">THERMAL REACTIONS OF GRIGNARD REAGENTS WITH ALKYL
HALIDES IN ISOPROPYLBENZENE SOLUTION AT 100°</div>

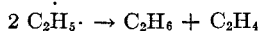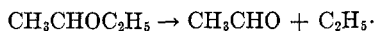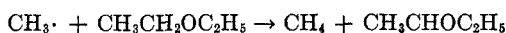| REAGENTS (ETHER REMOVED)	GRIGNARD REAGENT (MOLE)	i-PrC$_6$H$_5$ (MOLES)	ALKYL HALIDE[a] (MOLE)	GAS EVOLVED (MOLE)	DIMER YIELD[b] (%)	GAS $\left(\frac{C_nH_{2n+2}:}{C_nH_{2n}}\text{RATIO}\right)$
CH$_3$MgBr + CH$_3$Br...............	0.44	4.38	[c]	No reaction in absence of CoCl$_2$		
CH$_3$MgBr + n-C$_3$H$_7$Br............	.22	1.69	0.19	No reaction in absence of CoCl$_2$		
C$_2$H$_5$MgBr + C$_2$H$_5$Br...............	.276	2.68	.255	0.48	23	60:40
n-C$_3$H$_7$MgBr + n-C$_3$H$_7$Br...........	.14	1.43	.13	.26	25	65:35
i-C$_3$H$_7$MgBr + i-C$_3$H$_7$Br...........	.163	2.12	.116	.170	45	78:22

[a] Used in about 10% excess. Consumption of alkyl halide was determined by Volhard analysis.

[b] Percentage of free radicals undergoing reaction with isopropylbenzene. The moles of free radicals are calculated by doubling the moles of n-propyl bromide consumed. The dimer is 2,3-dimethyl-2,3-diphenylbutane.

[c] Gas bubbled through solution.

formed in the complete absence of ether, possibly because of the insolubility of the Grignard reagent and the cobaltous chloride in the isopropylbenzene. Even

a mechanism of the type postulated by Evans and his co-workers [Evans and Lee, *J. Am. Chem. Soc.*, **56**, 654 (1934); Evans and Field, *J. Am. Chem. Soc.*, **58**, 720, 2284 (1936); Evans and Braithwaite, *J. Am. Chem. Soc.*, **61**, 898 (1939)] for the electrolysis of methylmagnesium iodide in ethers:

$$CH_3 \cdot + CH_3CH_2OC_2H_5 \rightarrow CH_4 + CH_3\overset{\cdot}{C}HOC_2H_5$$

$$CH_3\overset{\cdot}{C}HOC_2H_5 \rightarrow CH_3CHO + C_2H_5 \cdot$$

$$2\ C_2\overset{\cdot}{H}_5 \cdot \rightarrow C_2H_6 + C_2H_4$$

In studying the CoCl$_2$-catalyzed reaction of n-hexylmagnesium bromide with methyl bromide, a careful but unsuccessful search was made for octanol-2, the reaction product to be expected from the reaction of acetaldehyde with n-hexylmagnesium bromide.

[2] Another point of difference is that the peroxide reaction scheme I is homogeneous, while the Grignard reaction as in scheme III is, in part at least, heterogeneous.

at 100°, with a minimum of ether present, the yield of the 2,3-dimethyl-2,3-diphenylbutane was only 23%.

In order to decrease the loss of free radicals by attack on the ether molecules [reaction III (f)], the behavior of free propyl radicals on isopropylbenzene in ether solution was studied. We had previously established the following facts: (a) Free propyl radicals, generated by the decomposition of dibutyryl peroxide, react with isopropylbenzene to give propane (90%), propylene (10%), and a high yield (78%) of 2,3-dimethyl-2,3-diphenylbutane. (b) Free propyl radicals generated from propylmagnesium chloride, an alkyl halide, and cobaltous chloride, do not attack the ethyl ether-Grignard complex, but disproportionate to yield equal quantities of propane and propylene. In some respects, our predictions were confirmed. Thus, comparison of the results described in Tables II and III show that despite their lesser reactivity, and their tendency to disproportionate, the propyl radicals are somewhat more effective in their attack on isopropylbenzene (25%) than are free methyl radicals (13%) in the presence of ethyl ether.[3]

However, further consideration of the data disclosed that the improvement in the yield attained by using free propyl radicals cannot be due exclusively to the fact that the free propyl radicals do not attack ether molecules. Thus, we may infer, on the basis of the experimental evidence, that it is easier for a free propyl radical to remove the tertiary hydrogen atom of the isopropylbenzene molecule, than a hydrogen atom of the ether molecule.

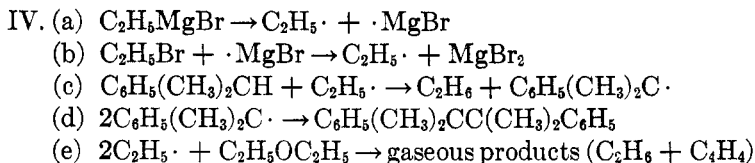$$C_6H_5(CH_3)_2CH + R\cdot \rightarrow C_6H_5(CH_3)C\cdot + RH$$
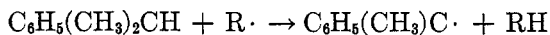
It should follow, therefore, that free methyl radicals, in the presence of large amounts of isopropylbenzene and some ether, should also attack extensively, if not preferentially, isopropylbenzene. Yet, at 35°, only about 13% of the free methyl radicals attacked the isopropylbenzene. Furthermore, it is to be noted that a higher percentage (ca. 64%) of the free propyl radicals, generated from propylmagnesium bromide, propyl bromide, and cobaltous chloride at 100°, undergo disproportionation (reaction 4, Table III) than free propyl radicals generated by the thermal decomposition of butyryl peroxide in isopropylbenzene at 125° (ca. 22%).

In our estimation, these divergent, apparently irreconcilable, results are best explained on the basis that the free radicals remain attached to the Grignard reagent-ether complex, and these react less readily with the hydrocarbon solvents than do the free radicals themselves. In other words, while it is permissible to compare the reactivity of hydrogen atoms in hydrocarbons toward free radicals, an additional mechanism must be taken into account if the activities of these hydrogen atoms are compared with the activity of hydrogen atoms in ethers in a medium containing a Grignard reagent. Furthermore, the temporary formation of free radical-Grignard reagent-ether complexes, may account for the extensive

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[3] A careful study of the results described in Table III discloses that at 100°, free propyl radicals are able to remove a hydrogen atom from ethyl ether. For example, in some experiments much less 2,3-dimethyl-2,3-diphenylbutane is obtained than would be expected from the yield of propane.

disproportionation of free propyl radicals in ether containing a Grignard reagent, as compared with the limited disproportionation of these free radicals in the presence of hydrocarbons which react readily with free radicals. It must also be borne in mind that the free radicals generated in the Grignard reaction in the presence of isopropylbenzene are generated in part at least at a liquid-solid interface, and that many of them could there disporportionate before they have an opportunity to escape into the solution and attack the hydrocarbon molecules.[4]

We have also noted that at 100°, in the presence of only small amounts of ether, and in the absence of cobaltous chloride, ethyl-, n-propyl-, and isopropylmagnesium bromides react with their respective halides and isopropylbenzene to yield the same products (gaseous, as well as 2,3-dimethyl-2,3-diphenylbutane) that are formed in the cobaltous chloride-catalyzed reactions at lower temperatures. Thus, for instance, the same ratio of propane to propylene (65% propane) is formed in the two cases. Upon this basis, these high-temperature reactions may also be looked upon as free-radical chain reactions (5).

IV. (a) $C_2H_5MgBr \rightarrow C_2H_5 \cdot + \cdot MgBr$

    (b) $C_2H_5Br + \cdot MgBr \rightarrow C_2H_5 \cdot + MgBr_2$

    (c) $C_6H_5(CH_3)_2CH + C_2H_5 \cdot \rightarrow C_2H_6 + C_6H_5(CH_3)_2C \cdot$

    (d) $2C_6H_5(CH_3)_2C \cdot \rightarrow C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5$

    (e) $2C_2H_5 \cdot + C_2H_5OC_2H_5 \rightarrow$ gaseous products $(C_2H_6 + C_4H_4)$

Of the free radicals generated in this manner, the free isopropyl radical proved more effective in attacking isopropylbenzene (45%) than either the free propyl (25%) or the free ethyl (23%) radicals.

Whereas the steric factor involved can scarcely vary greatly among the three free radicals in reaction with the hydrocarbon, and whereas the reaction of free isopropyl radicals with isopropylbenzene is almost certainly not the one most favored from an energetic standpoint, it is reasonable to attribute this apparent superiority in reactivity of the free isopropyl radical not to reaction IV (C) above, but rather to the greater stability of the free isopropyl radical with respect to the competing disproportionation reaction in the presence of ether-Grignard reagent complex. Because of the lower reactivity of the isopropyl radical, it is to be expected that, in the absence of ether-Grignard reagent complex, higher yields of 2,3,dimethyl-2,3-diphenylbutane (and less disproportionation) should result from an attack of free ethyl or propyl radicals than from that of isopropyl radicals on isopropylbenzene, in spite of the greater stability at all times of the free isopropyl radical toward disproportionation.

The formation of free aliphatic radicals by the thermal decomposition of Grignard reagents in the presence of an alkyl halide is not applicable to the generation of free methyl radicals from either methylmagnesium chloride or methylmagnesium bromide.[5] Thus, in the absence of cobaltous chloride, no reaction takes place when methyl bromide is bubbled through an isopropylbenzene-

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[4] This problem will be investigated later.

[5] The formation of free methyl radicals from methylmagnesium iodide is discussed by Kharasch, Morrison, and Urry (6).

methylmagnesium bromide mixture held at 100°. The possibility that this unreactivity is due to insufficient solubility of methyl bromide in isopropylbenzene was disproved in two ways. First, it was found that reaction between methylmagnesium bromide, methyl bromide, and isopropylbenzene could be induced under these conditions, by periodic additions of small amounts of cobaltous chloride. Second, it was found that methylmagnesium bromide in isopropylbenzene does not react with n-propyl bromide at 100°. Even at 150°, the mixture reacted very slowly. The unreactivity, therefore, is attributable primarily to the stability of the methylmagnesium bromide under the experimental conditions imposed.

An interesting case where this thermal, free-radical reaction occurs with surprising ease is the reaction of ethylmagnesium bromide with cyclohexyl bromide. At the boiling point of that reaction mixture (about 40°), there is a steady evolution of gas (ethane, 54%; ethylene, 46%). A mixture of cyclohexane and cyclohexene (35% unsaturated) may be isolated from the reaction mixture.

Urion (7) had previously investigated the above reaction. He found that, when a solution of ethylmagnesium bromide and cyclohexyl bromide in ether is allowed to stand at room temperature, an exchange reaction takes place; he recovered 12% of cyclohexane. This exchange reaction has been confirmed in this Laboratory (8).

Urion further claimed that distillation of the ether from the reaction mixture removed ethyl bromide and caused a shift in the exchange equilibrium which gave him 40% of cyclohexane. This claim, however, is erroneous, since Urion failed to detect the presence of cyclohexene in his reaction. He also failed to note the evolution of ethane and ethylene.

EXPERIMENTAL PART

Reagents. Methyl-, ethyl-, n-propyl-and isopropyl-magnesium bromides were prepared according to the general method described by Kharasch, Morrison, and Urry. They were filtered through a coarse sintered-glass disc, and were titrated for Grignard reagent concentration and halogen content immediately before use.

Dow methyl bromide was used as such; ethyl bromide, n-propyl bromide, and isopropyl bromides were carefully distilled before use.

Anhydrous cobaltous chloride was prepared by heating the hydrated salt at 150° in a stream of dry hydrogen chloride.

Eastman's isopropylbenzene was distilled through a 100-plate Podbielniak column (b.p. 65.5° at 42 mm.; n_D^{20}, 1.4915).

p-Methoxy-n-propylbenzene was prepared by reduction of Eastman's anethole in ethyl alcohol over Raney nickel at 50 pounds pressure. It was purified by distillation through the 100-plate column (b.p. 76.5° at 6 mm.; n_D^{20}, 1.5040).

Eastman's diphenylmethane was sublimed *in vacuo* (m.p. 263–264°).

Eastman's cyclohexyl bromide was distilled through a 12-plate fractionating column (b.p. 79° at 48 mm.).

Typical procedure 1. Cobaltous chloride-catalyzed reaction of methylmagnesium bromide with methyl bromide in ether-isopropylbenzene solution. A solution of methylmagnesium bromide (500 ml. of a 1.83 N ether solution; 0.91 mole) was placed in a dried nitrogen-swept Grignard reaction apparatus composed of a 1-liter, three-necked flask fitted through ground glass joints with a condenser, a Tru-Bore stirrer lubricated with heavy grease, and a dropping-funnel. Isopropylbenzene (300 g.; 2.50 moles) was added, and stirring was started.

The mixture was warmed to 35° and held there during the reaction. One-fourth of the cobaltous chloride to be used in the reaction (7.1 g.) was added at first, similar portions were added as the reaction progressed. Methyl bromide was bubbled into the reaction mixture at the rate of about 200 ml. per minute. Gas evolution began at once, and the gas mixture flowed through the condenser and a trap held at −80° into a water-filled gas reservoir. During the reaction, a total of 27.2 liters (S.C.) of gas was collected. This gas was analyzed by the method of Kharasch, Lewis, and Reynolds (1). It contained methane (70%), ethane (14%), and ethylene (16%).

When gas evolution ceased, the reaction mixture was treated with dilute acetic acid. The ether-isopropylbenzene layer was separated and washed with water, 10% sodium carbonate solution, and again with water and was dried over calcium chloride. The aqueous washings were diluted to a known volume, and an aliquot was analyzed for halide ion concentration by the Volhard method. From the calculated quantity of halide ion in the washings was subtracted the halide ion from the Grignard reagent and the cobaltous chloride used. The difference (0.78 mole) was the quantity of halide ion derived from the methyl bromide, and, therefore, a measure of the methyl bromide participating in the reaction.

Upon distillation of the ether solution, isopropylbenzene (290 g.; n_D^{20} 1.4915) was recovered. After the isopropylbenzene had distilled, a residue remained. Upon crystallization from 95% ethanol, eleven grams of 2,3-dimethyl-2,3-diphenylbutane, which melted at 118–119°, was obtained.

Typical Procedure II. Cobaltous chloride-catalyzed reaction of n-propylmagnesium bromide with n-propyl bromide in isopropylbenzene. Quantitative details are recorded in Table III, reaction 2. This procedure differed from the one described above in three ways. First, the ether solvent was removed; second, the cobaltous chloride (4 g.) was added at the first of the reaction; and, third, a reaction temperature of 100° was maintained.

To remove the ether solvent, the Grignard reaction apparatus was evacuated through the condenser with the aid of a water aspirator pump while vigorous stirring was maintained. As the ether was removed, isopropylbenzene was slowly added through the dropping-funnel. The Grignard reagent separated as a white precipitate during this operation. After all the isopropylbenzene had been added and most of the ether had been removed, the mixture was held at 90° under water-pump vacuum for 1 hour.

Cobaltous chloride (4.0 grams) was added, and the mixture of n-propylmagnesium bromide and isopropylbenzene was then held at a temperature of 100° while a solution of n-propyl bromide in isopropylbenzene was dropped in over a period of 3 hours; gas evolution began at once. During the reaction, 16.0 liters (S.C.) of gas (m. wt. 44.5) was collected. Each successive 3-liter sample of gas collected was analyzed for unsaturation. Within the experimental error, all samples contained propane (65%) and propylene (35%).

After the gas evolution stopped, (ca. 4 hours) the reaction mixture was treated as in Procedure I. Distillation of the dried reaction mixture yielded first 10 ml. of ethyl ether that had remained in the reaction mixture. Isopropylbenzene (320 g.) was recovered, leaving a residue of 2,3-dimethyl-2,3-diphenylbutane (26.5 g.). The substance melted at 118–119°, after two crystallizations from 95% ethanol.

Typical Procedure III. Thermal reaction of isopropylmagnesium bromide with isopropyl bromide in isopropylbenzene. Quantitative data are given in Table IV, reaction 5. This experiment was conducted in the manner described in Procedure II except that no cobaltous chloride was used. Heating the reaction mixture for 12 hours at 100° was necessary to complete the reaction.

The reaction of ethylmagnesium bromide with cyclohexyl bromide. This reaction was conducted in a 1-liter, 3-necked flask fitted through ground glass joints with a dropping-funnel, a Tru-Bore stirrer, and a distilling head fitted with a down-draft condenser. Ethylmagnesium bromide (0.715 mole in 500 ml. of ether solution) and cyclohexyl bromide (116 g.; 0.70 mole) were placed in the reaction flask. The ether was slowly distilled by holding the reaction mixture at 46°. A slow gas evolution began with the distillation of the ether.

This gas was taken off through the distilling head, a condenser, a receiver, and a −80° trap into a gas reservoir. Gas evolution became more rapid as the ether was removed, and as the reaction temperature increased. After about two-thirds of the ether had distilled, 9 liters of gas, at standard conditions, had been collected and the reaction temperature reached 56°.

Suddenly, the reaction became very rapid, the remaining ether began to distill rapidly, and the rate of gas evolution increased. Even though the oil-bath surrounding the reaction vessel remained at 56°, the temperature at the still head reached 80° as the last liquid distilled. A total of 15 liters, at standard conditions, of gas collected (m. wt. 28.9; 46% unsaturated). It appeared to be an approximately equal mixture of ethane and ethylene.

All the distilled liquid was poured back into the reaction flask and the mixture was decomposed with dilute acetic acid. The ether solution was separated, washed with water, 10% sodium carbonate solution, and again with water, and dried over calcium chloride. A Volhard analysis of all aqueous washings indicated that the reaction was 93% complete.

Distillation of the ether solution yielded 41 grams of a mixture of cyclohexene and cyclohexane (b.p. 78–80°) which was found to be 35% unsaturated. Ten grams of cyclohexyl bromide was recovered.

SUMMARY

1. At low temperatures, (0–20°), Grignard reagents in the presence of cobaltous chloride, an alkyl halide, and alkylbenzenes give rise to substituted bibenzyls.

2. Bibenzyls were also obtained by adding alkyl halides to a mixture of a Grignard reagent (other than methyl) and an alkylbenzene at 100°.

3. Since the same substituted bibenzyls are also produced by the decomposition of acetyl peroxide in alkylbenzene solutions, the reaction mechanisms proposing free alkyl radicals as intermediates in both reactions are supported.

4. A discussion of the factors influencing these reactions, and of the reaction mechanism is included.

CHICAGO, ILL.

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