The monoalkyl malonic esters underwent a varying ratio of C to C as compared to C to O cleavage, depending upon the nature of the substituent. Six dialkylmalonic esters cleaved smoothly and completely to give methanol and dialkylcarbinylcarbinols. In contrast with this is the fact that α,γ-diacetyl-β-methyl(or phenyl)glutaric esters showed little if any C to C cleavage.

It appears that the C to O linkage in a primary carbinol group is in many cases more readily cleaved than in a secondary alcohol. The presence of a carbon to carbon double bond facilitates the cleavage of C to O linkages.

A considerable amount of information in regard to the hydrogenation and hydrogenolysis of a variety of organic compounds has been presented in tabular form and cannot be more briefly summarized here.

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# THE REDUCING ACTION OF THE GRIGNARD REAGENT. III. HYDROCARBONS FORMED DURING REDUCTION

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Of the various types of reduction that may take place during the reaction of an aldehyde or ketone with a Grignard reagent,[1] the type most frequently encountered occurs only when a hydrogen bearing carbon atom is adjacent to the carbon atom that *is combined with magnesium*. This may be represented by the equation

$$R_2C{=}O + R_2CH{-}C(MgX)R_2 \longrightarrow R_2C(OMgX)H + R_2C{=}CR_2$$
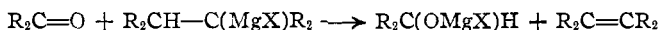
where R may be either hydrogen or a radical.

Thus far no careful investigation has been made of the hydrocarbon formed during the reduction. Hess and Wustrow[2] reported that primary addition products of ethylmagnesium bromide, isobutylmagnesium bromide, and isobutylmagnesium chloride with cinnamic aldehyde had been isolated in a pure state and that on heating they lost in weight an amount equivalent to one mole of unsaturated hydrocarbon. Meisenheimer[3] was unable to confirm these results and also pointed out that while Hess and Wustrow claim the quantitative loss of isobutylene from the addition product of isobutylmagnesium bromide and cinnamic aldehyde, they actually isolated from the addition product of isobutylmagnesium chloride and cinnamic aldehyde only 8.5% of the theoretical amount of isobutylene as the dibromide. It should be mentioned that in Hess and Wustrow's

[1] For a summary of the different types of reduction and references to previous work on this subject, see the first article of this series, THIS JOURNAL, 53, 635 (1931).

[2] Hess and Wustrow, *Ann.*, 437, 256 (1924).

[3] Meisenheimer, *ibid.*, 442, 180 (1925).

experiments with crotonic aldehyde in which the addition product was not isolated, the amount of unsaturated hydrocarbon isolated as dibromide was equivalent to about 25% of that expected from the amount of crotyl alcohol isolated. Meisenheimer states that while only a few investigations were made, in the reaction of benzaldehyde with ethylmagnesium and isobutyl-magnesium bromides they were never able to isolate an amount of unsaturated hydrocarbon equivalent to the amount of benzyl alcohol formed and frequently they obtained no unsaturated hydrocarbon at all. He assumed that the discrepancy might be due to the removal of the hydrocarbon by some unknown condensation reaction. Blicke and Powers[4] isolated approximately 25% of the total amount of alkyl radical as propylene dibromide in a reaction that gave about 50% reduction of benzophenone to benzohydrol.

A knowledge of the relative amounts of unsaturated hydrocarbon and reduction product is part of the information necessary for a thorough understanding of the reducing action of aliphatic Grignard reagents. Whether or not the unsaturated hydrocarbon is accompanied by saturated hydrocarbons having the same number of carbon atoms should also be determined since one proposed mechanism[4] for the reduction indicates that such should be the case. Moreover, in certain reactions such as that of diisobutylmagnesium with benzophenone,[1] it is difficult to isolate the reduction product quantitatively and the isolation of the unsaturated hydrocarbon should be a satisfactory method for determining the amount of reduction providing that unsaturated hydrocarbon and reduction product are formed in equivalent amounts.

With these points in mind we have attempted to determine whether one mole of isobutylene can be isolated per mole of benzohydrol in the reaction of isobutylmagnesium bromide with benzophenone. The reaction was run in n-butyl ether solution in order to facilitate the isolation of the hydrocarbon. Since the most satisfactory method for determining the amount of benzohydrol was by filtering and decomposing its bromomagnesium salt,[4] it was necessary to work with fairly large quantities to obtain the required accuracy. This necessitated the condensation of the hydrocarbon and weighing it as a liquid.[5]

It was found as shown in Table I that when one takes into account the solubility of the bromomagnesium salt and of isobutylene in butyl ether, and also the mechanical losses, the amount of hydrocarbon isolated is equivalent to the amount of benzohydrol within less than 0.2%. Without such corrections the amount of reduction as calculated by the hydrocarbon

[4] Blicke and Powers, THIS JOURNAL, 51, 3378 (1929).

[5] Gasometric determination of the amount of hydrocarbon formed would allow the use of smaller quantities of reagents but all attempts to use such a procedure gave low results.

method is about 3% higher than that calculated by the benzohydrol method.

One mechanism proposed to account for both the normal addition and reduction postulates the intermediate formation of free radicals which may then undergo various reactions of addition and disproportionation.[4] Such a mechanism would predict also the formation of pinacol and of saturated hydrocarbon in addition to the reduction product, unsaturated hydrocarbon and normal addition product.

In previous work[6] we have never been able to detect the formation of benzopinacol during the reaction of an alkylmagnesium bromide with benzophenone, nor has any been obtained in the present work.[7] It was therefore of interest to determine whether any saturated hydrocarbon, in this case isobutane, was present in the isobutylene. The liquefied hydrocarbon was volatilized in portions and the isobutylene removed by washing with concentrated sulfuric acid. The combined residual gases were analyzed for us by Dr. F. Blacet and found by a micro-combustion method[8] to contain what was apparently isobutane, to the extent, however, of only 0.1% of the original hydrocarbon mixture. Since no attempt was made rigidly to dry our system, it seems entirely possible that sufficient moisture may have been present on the walls of the glass apparatus and in the rubber stoppers and connections to account for this minute amount.[9]

It has recently been shown that in the decomposition of hydrocarbons in the gaseous phase, the postulation of the primary formation of free radicals accounts not only for the products formed but also for the relative amounts of these products.[10] In the present instance, however, it appears to us that the reactions are best explained by using the older idea[11] that a primary addition product[12] is formed which then rearranges and that reduction takes place during the rearrangement.

The procedure used in this work is now being employed to determine the

[6] Noller and Hilmer, THIS JOURNAL, 54, 2503 (1932); cf. also Ref. 1.

[7] The possibility that the reactions of the free radicals leading to the formation of normal addition product and of reduction product are much more rapid than that leading to pinacol formation does not seem likely since Gomberg and Bachmann, THIS JOURNAL, 49, 236 (1927), have found that when a mixture of magnesium and magnesium iodide is allowed to compete with phenylmagnesium iodide for benzophenone, about 50% of benzopinacol and 40% of triphenylcarbinol are formed.

[8] Blacet and Leighton, Ind. Eng. Chem., Anal Ed., 3, 266 (1931).

[9] Assuming two moles of Grignard reagent to react with one of water, the amount of water necessary to account for the amount of isobutane formed in a 0.05 mole run in which 75% reduction took place would be 0.3 mg.

[10] Rice, THIS JOURNAL, 53, 1959 (1931).

[11] V. Braun and Kirschbaum, Ber., 52, 1725 (1919); Meisenheimer and Casper, ibid., 54, 1655 (1921), and Ref. 3.

[12] Direct evidence for the formation of such an addition product is given in the experimental part.

amount of unsaturated hydrocarbon and hence the amount of reduction in those cases where the halogenomagnesium salt of the reduction product is soluble in the reaction mixture.

Experimental

Apparatus.—The preparation of the Grignard reagent and all subsequent reactions were carried out in an atmosphere of nitrogen which was purified by the absorption train recommended by Fieser.[13] The apparatus for carrying out the reaction consisted of a reservoir for the Grignard reagent connected to a 50-cc. buret which was in turn connected through a three-way stopcock and rubber stopper to one of the small necks of a 500-cc. reaction flask. To the second opening of the three-way stopcock was sealed a tube for introducing the solution of benzophenone. This tube also served to admit nitrogen when sweeping out the apparatus. A mercury-sealed stirrer passed through the central neck of the flask and the remaining small neck carried a thermometer and a bent tube which connected the flask to the condensing system. This consisted of a train of three U-tubes made from 10-mm. glass tubing and measuring 4.5 by 16 cm. An enlargement was blown in the lower end of the tubes so that they might hold at least 5 cc. of liquid without interfering with the passage of gas. The first tube was indented to increase the condensing surface and was kept at room temperature by means of a water-bath in order to condense any high boiling substances that might distil. The second and third tubes were filled with copper turnings for condensing surface and small stopcocks were sealed to both ends of the tube. During the reaction they were immersed in solid carbon dioxide–acetone mixture contained in 570-cc. wide-mouthed Dewar flasks. The last tube was protected from the air by connecting it to a tube immersed a few millimeters in mineral oil.

Grignard Reagent.—The Grignard reagent was prepared in the usual manner from 24.4 g. of clean magnesium turnings, 137 g. of isobutyl bromide and 250 cc. of dry n-butyl ether. The reaction started almost immediately without the use of iodine and the temperature was kept below 30° during the reaction by means of a water-bath. The total time required for the addition of the bromide was about three hours. At the end of the reaction, the stirrer was removed and replaced by a line to a vacuum pump and the mixture heated at 20 mm. until butyl ether distilled. The product, freed from low boiling substances, was forced by nitrogen pressure through a 44 G3 Jena glass filter, on which a 3-mm. layer of ignited kieselguhr had been placed, into a graduated flask. The solution was analyzed by acid titration[14] and then diluted so that the concentration of active Grignard reagent was approximately 0.002 equivalent per cubic centimeter.

[13] Fieser, THIS JOURNAL, **46**, 2639 (1924).

[14] Gilman and co-workers, *ibid.*, **45**, 150 (1923); **51**, 1576 (1929).

It was then transferred to the storage reservoir and the concentration checked again by analysis.

Reduction of Benzophenone.—The U-tubes of the apparatus previously described were weighed to the nearest centigram, immersed in the Dewar flasks containing a mixture of solid carbon dioxide and acetone and connected to the system. This was completely swept with purified nitrogen and then 27.5 cc. (0.055 equivalent) of the isobutylmagnesium bromide solution run into the reaction flask. This was cooled to $-5°$ and a solution of 9.1 g. (0.05 mole) of benzophenone in 10 cc. of warm butyl ether was added drop by drop with constant stirring. On the addition of each drop of benzophenone solution, an orange precipitate formed which immediately dissolved imparting a pink color to the solution. Normally after about half of the benzophenone had been added the precipitate no longer went into solution. If, however, the addition of the benzophenone was very slow and the stirring rapid, it was possible to force all of the precipitate into solution and to obtain a clear pink solution after addition of the benzophenone was complete.[15] The reaction mixture was allowed to warm to room temperature and then gradually heated to $100°$ with constant stirring. In cases where no attempt was made to get all of the initial precipitate into solution at $-5°$, the undissolved precipitate readily went into solution at $90-100°$. After stirring for thirty minutes at this temperature a slow stream of nitrogen was passed through the system to sweep all of the hydrocarbon into the condensers. The solution was then allowed to cool with continued stirring and a fine white precipitate formed.

The stopcocks of the condensers were closed and the condensers rapidly washed in alcohol and ether, wiped dry and weighed. From the increase in weight of the tubes, the percentage reduction was calculated.

The mixture in the reaction flask was filtered onto a Büchner funnel and washed three times with 10-cc. portions of dry benzene, care being taken not to suck air through the filter cake before the final washing. The precipitate was decomposed with a saturated solution of ammonium chloride and the liberated benzohydrol extracted three times with 50-cc. portions of ethyl ether. The combined extracts were placed in a tared beaker

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[15] The occurrence of this precipitate is visible evidence of the formation of a primary addition product although attempts to isolate it have not been successful. By the use of a gasometric apparatus indication was obtained that the hydrocarbon is liberated as the precipitate dissolves. The fact that hydrocarbon is evolved and yet a clear solution obtained indicates that the bromomagnesium salt of benzohydrol has not yet formed since this material is quite insoluble (0.006 g. per cc. at 25°). That a supersaturated solution was not present was shown by the fact that the addition of a small amount of the bromomagnesium salt of benzohydrol did not cause precipitation. The above results would be those expected if the second intermediate compound $R_2C=O \cdots HMgX$ postulated by Hess and Rheinbold, *Ber.*, **54**, 2043 (1921), existed and were soluble in butyl ether.

and the ether evaporated on a warm hot-plate. While still warm the beaker was placed in a vacuum desiccator over phosphorus pentoxide for two hours, weighed again, and the percentage reduction calculated.

Corrections for Errors.—The two methods used above for determining the amount of reduction are obviously in error due to the solubility of the solid and gas and to mechanical losses. In order to determine approximately the extent of these losses a weighed amount of isobutylene was passed through the reaction flask containing 37 cc. of butyl ether and into the condensing system. The flask was then heated with stirring and the gas finally swept out as in a regular run. On weighing the absorption tubes an average loss of 0.02 g. was observed. By adding this to the observed recovery of isobutylene, a corrected value for the percentage reduction was calculated. In a similar manner by adding 9.2 g. (0.05 mole) of benzo-hydrol in 10 cc. of butyl ether to 27.5 cc. (0.055 equiv.) of Grignard reagent, filtering the precipitate and isolating the benzohydrol as in a regular reduction, an average loss of 0.26 g. was observed. From this data corrected values for the percentage reduction by this procedure were obtained. The data for several typical runs are given in Table I. It will be observed that the average values for the two methods check each other within 0.2%. Moreover, the various values for the benzohydrol method show a maximum deviation within themselves of 3.5% while those for the hydrocarbon method of only 1%, indicating that the latter is the more accurate method of the two.

Analysis of the Hydrocarbon Gases.—The liquid hydrocarbon was transferred for analysis to a 100-cc. gas buret filled with mercury. This was readily accomplished by fitting the stopcock of the gas buret with a short piece of rubber tubing and filling the entire buret and tube with mercury. The glass tubing extending beyond the stopcock on the U-tube condenser was likewise filled with mercury and the U-tube inverted so that the liquid hydrocarbon was in the arm adjacent to this stopcock. The U-tube was connected to the buret by means of the rubber tubing, the stopcock on the buret opened and the leveling tube lowered. When the liquid in the U-tube came into equilibrium with its vapor and bubbling had ceased, the stopcock on the U-tube was quickly opened and closed. In this way a small amount of liquid hydrocarbon entered the buret and vaporized. The volume of the gas was noted and it was then transferred to a gas absorption pipet, where it was thoroughly washed with concentrated sulfuric acid. The residual gas was then transferred to a storage buret and its volume measured. A total of 102.1 cc. of gas gave 1.2 cc. (Sample A) or 1.2% unabsorbed by concentrated sulfuric acid. A second sample of gas collected more carefully showed a total of 1.25 cc. (Sample B) out of 349.8 cc. or 0.357% unabsorbed by concentrated sulfuric acid. We are indebted to Dr. F. Blacet for the microanalysis of both samples of this residual gas.

The results are listed in Table II and indicate that the combustible portion of the residual gas is isobutane and that it is present to the extent of about 0.1% of the original hydrocarbon mixture.

TABLE I

AMOUNT OF REDUCTION AS CALCULATED FROM THE AMOUNTS OF BENZOHYDROL AND ISOBUTYLENE RECOVERED

| Benzohydrol isolated | | Isobutylene isolated | | % Benzohydrol | % Isobutylene |
Wt.	%	Wt.	%	(corrected)	(corrected)
6.45	70.1	2.05	73.2	72.9	73.9
6.47	70.3	2.07	73.9	73.2	74.6
6.69	72.7 ·	2.07	73.9	75.5	74.6
6.62	72.0	2.06	73.6	74.8	74.3
6.58	71.5	2.07	73.9	74.4	74.6
6.64	72.2	2.07	73.9	75.0	74.6
	Av. 71.5		73.7	74.3	74.4

TABLE II

ANALYSIS OF GAS NOT ABSORBED BY CONCENTRATED SULFURIC ACID

Sample	Vol. used cu. mm.	Contraction, cu. mm.	Vol. of CO_2, cu. mm.
A	94.61	27.84	32.11
B	42.31	50.52	52.31

| | Vol. calcd. as C_4H_8 | | Vol. calcd. as C_4H_{10} | | % C_4H_{10} in residue | | % C_4H_{10} in original hydrocarbon |
	By contr.	By CO_2	By contr.	By CO_2	By contr.	By CO_2	
A	9.28	8.03	7.95	8.03	8.4	8.5	0.10
B	16.84	13.10	14.43	13.08	34.1	31.0	.11

Summary

1. In the reduction of benzophenone by isobutylmagnesium bromide, one mole of isobutylene has been isolated per mole of benzohydrol. Use is made of this fact in developing a new method for determining the amount of reduction caused by aliphatic Grignard reagents.

2. The isobutylene contains less than 0.1% of isobutane. This together with the fact that no benzopinacol is isolated indicates that it is unlikely that the reaction is preceded by the formation of free radicals.

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