ing, dibenzoylphenylethane crystallized from the ether solution, and was recrystallized from ethanol. The yield in a number of runs averaged 60–65%. The rest of the material was accounted for as a high-melting secondary product (never more than 5% under these conditions) and an intractable resin.

In one experiment using a titrated solution of phenylmagnesium bromide, successive portions of dibenzoylethylene were added and the reaction mixture analyzed for products by withdrawing samples. It was found that the yield of dibenzoylphenylethane was good until a ratio of approximately half an equivalent of dibenzoylethylene had been added, and the yield then dropped practically to zero. On the other hand, from this point on unchanged dibenzoylethylene was found among the reaction products in increasing amounts.

The Formation of the Secondary Products.—When the Grignard reagent was added to a suspension of dibenzoylethylene in ether, the yield of dibenzoylphenylethane was negligible and that of the secondary product as high as 70–85%.

The secondary product contains magnesium and halogen and is difficult to free from these impurities. It is recrystallized with difficulty, best from chloroform directly or by Soxhlet extraction, and shows an unsharp melting point ranging from 145 to 200°. Fractional crystallizations have yielded one substance of m. p. 272–274° which is apparently an individual.

Anal. Calcd. for $C_{38}H_{28}O_3$: C, 85.71; H, 5.26; mol. wt. (b. p. method) 532. Found: C, 84.98, 85.27, 85.49, 84.95, 85.48; H, 5.50, 5.62, 5.39, 5.72; mol. wt. 500, 590, 450.

The reaction with methylmagnesium iodide led mainly to non-crystalline products, but traces of two crystalline compounds were isolated which were recrystallized from ethanol. One of these melted at 215–216°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.55; H, 7.7.

The other melted at 170°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found: C, 80.3; H, 7.5.

1,2-Di-[2,4,6-trimethylbenzoyl]-phenylethane, $(CH_3)_3C_6H_2COCH_2CH(C_6H_5)COC_6H_2(CH_3)_3$.—Prepared as above from di-[trimethylbenzoyl]-ethylene; yields 59–60%; crystallized from ethanol as short prisms of m. p. 137° (corr.).

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.37; H, 7.59. Found: C, 84.16; H, 7.69.

1,2-Di-[p-bromobenzoyl]-phenylethane, $BrC_6H_4COCH_2CH(C_6H_5)COC_6H_4Br$.—Prepared as above from di-[bromobenzoyl]-ethylene; yields 53%; crystallized from acetone; m. p. 160° (corr.).

Anal. Calcd. for $C_{22}H_{16}O_2Br_2$: Br, 33.86. Found: Br, 33.66.

Summary

Diaroylethylenes add phenylmagnesium bromide 1,4, giving diaroylphenylethanes.

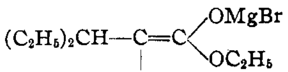
UNIVERSITY, VIRGINIA RECEIVED JANUARY 12, 1934

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Reaction of Dialkyl Sulfates with ROMgBr Compounds

BY ARTHUR C. COPE[1]

In a recent investigation[2] it was shown that the product obtained by alkylation of the bromomagnesium enolate of ethyl diphenylmethyl malonate (I) with diphenylmethyl bromide was the C-alkyl derivative (II), rather than an O-alkyl derivative, as was originally proposed.[3] While the structure of II was still under investigation, the reaction of the enolate (I) with dimethyl sulfate was examined, since the structure of the expected methyl derivative would be much easier to determine than that of the diphenylmethyl derivative.



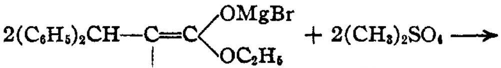
$(C_2H_5)_2CH{-}C(COOC_2H_5){=}C(OMgBr)(OC_2H_5)$

I

$[(C_6H_5)_2CH]_2C(COOC_2H_5)_2$

II

The enolate (I) reacted vigorously with dimethyl sulfate, but on decomposing the reaction mixture with water the product obtained was ethyl diphenylmethyl malonate, $(C_6H_5)_2CHCH(COOC_2H_5)_2$ (III), the same ester that is obtained by decomposing the enolate with water directly. This was perplexing, for it necessitated explaining how dimethyl sulfate could react with the enolate without introducing a methyl group. The course of the reaction became clear when the insoluble magnesium compound precipitated during the reaction was found to be $Mg(CH_3SO_4)_2$, and when it was observed that after reaction with dimethyl sulfate the solution still contained an amount of basic magnesium equivalent to the quantity originally present, as determined by titration. The reaction was therefore



$2(C_6H_5)_2CH{-}C(COOC_2H_5){=}C(OMgBr)(OC_2H_5) + 2(CH_3)_2SO_4 \longrightarrow$

III

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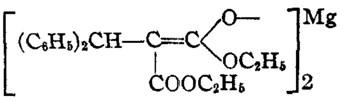
[1] National Research Fellow in Chemistry.

[2] Cope, THIS JOURNAL, **56**, 721 (1934).

[3] Kohler, *Am. Chem. J.*, **34**, 132 (1905).



$$\left[(C_6H_5)_2CH{-}\underset{COOC_2H_5}{C}{=}C{\begin{smallmatrix}O{-}\\ OC_2H_5\end{smallmatrix}}\right]_2 Mg + 2CH_3Br + Mg(CH_3SO_4)_2 \quad (1)$$

IV

The magnesium enolate (IV) would obviously yield the original ester (III) on decomposing with water.

It would be predicted that it should be possible to obtain the desired methyl derivative by reaction of another mole of dimethyl sulfate with the magnesium enolate (IV). This enolate is very unreactive, however, and even with an excess of dimethyl sulfate the reaction does not proceed beyond this stage when ether is used as a solvent. At higher temperatures in benzene or toluene alkylation does occur in accordance with equation (2)

$$\text{IV} + 2(CH_3)_2SO_4 \longrightarrow 2(C_6H_5)_2CH{-}C(CH_3)(COOC_2H_5)_2 + Mg(CH_3SO_4)_2 \quad (2)$$

V

Equations (1) and (2) were proved definitely by carrying out the reaction quantitatively as described in the experimental part. Methyl bromide was obtained in 99.4% yield; enolate (IV), 94.2%; $Mg(CH_3SO_4)_2$ from (1), 99%; from (2), 99%. The yield of the ester (V) was only 72%, due to the ordinary losses incurred in purification.

In order to determine whether or not the mode of reaction observed with the enolate (I) was general for ROMgBr compounds, the reaction of dimethyl sulfate with representative ROMgBr compounds was investigated quantitatively. In each case, with the bromomagnesium derivative of phenol and of a primary, a secondary and a tertiary alcohol, the reaction proceeded just as it did with the enolate, or according to the general equation

$$2ROMgBr + 2(CH_3)_2SO_4 \longrightarrow (RO)_2Mg + 2CH_3Br + Mg(CH_3SO_4)_2 \quad (3)$$

Diethyl sulfate reacts in the same way

$$2ROMgBr + 2(C_2H_5)_2SO_4 \longrightarrow (RO)_2Mg + 2C_2H_5Br + Mg(C_2H_5SO_4)_2 \quad (4)$$

Consequently the primary reaction of ROMgX compounds with dialkyl sulfates produces magnesium alkoxides and alkyl halides rather than ethers. Gilman and Hoyle[4] have reported that the reaction of the bromomagnesium derivative of benzohydrol with one mole of diethyl sulfate gave a 35% yield of benzohydryl ethyl ether. The reaction was assumed to proceed as follows

$$(C_6H_5)_2CHOMgBr + (C_2H_5)_2SO_4 \longrightarrow (C_6H_5)_2CHOC_2H_5 + C_2H_5(MgBr)SO_4$$

It is shown in the experimental part that the benzohydryl ethyl ether which they obtained was not formed in this manner, but must have been produced in the process employed for isolating the reaction products, *i. e.*, through the distillation of a mixture of benzohydrol and diethyl sulfate.

While the formation of an alkyl halide through the reaction of a dialkyl sulfate with a ROMgX compound has not been reported previously, Gilman and Heck[5] observed that *n*-butyl halides are formed in the reaction of *n*-butyl-*p*-toluene sulfonate (which should react in the same manner as the dialkyl sulfates) with both RMgX and ROMgX compounds. In the case of RMgX compounds the reaction was represented by the following equations

$$RSO_2O\text{-Alkyl} + R'MgX \longrightarrow R'\text{Alkyl} + RSO_2OMgX \quad (5)$$

$$RSO_2OMgX + RSO_2O\text{-Alkyl} \longrightarrow \text{Alkyl X} + (RSO_2O)_2Mg \quad (6)$$

For ROMgX compounds the first equation would become

$$RSO_2O\text{-Alkyl} + R'OMgX \longrightarrow R'O\text{ Alkyl} + RSO_2OMgX \quad (5a)$$

Thus through the reaction of *n*-butyl-*p*-toluene sulfonate with C_2H_5OMgI and C_6H_5OMgI, *n*-butyl iodide was formed, and its formation was explained[6] by equation (6). However, although the reaction of *n*-butyl-*p*-toluene sulfonate and C_6H_5OMgI gave a 54% yield of butyl iodide, it is stated (Ref. 5, p. 2228, footnote *f*) that a special search failed to reveal any *n*-butyl phenyl ether; instead phenol was recovered almost quantitatively. It should be noted that if the alkyl halide is really formed in accordance with equation (6), at least an equal amount of the ether R'O-Alkyl must be formed, for (6) can only follow (5a). The fact that phenol rather than butyl phenyl ether was produced therefore proves that the alkyl halide could not have been formed according to equation (6), and suggests that the reaction is really similar to (3), *i. e.*

$$2R'OMgX + 2RSO_2O\text{-Alkyl} \longrightarrow (R'O)_2Mg + 2\text{ Alkyl X} + (RSO_2O)_2Mg$$

While equation (3) represents the complete reaction between ROMgBr and dimethyl sulfate, it does not designate the mechanism of the process.

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[4] Gilman and Hoyle, THIS JOURNAL, **44**, 2621, 2969 (1922).

[5] Gilman and Heck, *ibid.*, **50**, 2223 (1928).

[6] Ref. 5, p. 2226.

It is probable that the over-all reaction (3) results from the displacement of the equilibrium

$$2\text{ROMgBr} \rightleftharpoons (\text{RO})_2\text{Mg} + \text{MgBr}_2 \qquad (7)$$

by the removal of magnesium bromide through reaction with the dimethyl sulfate

$$\text{MgBr}_2 + 2(\text{CH}_3)_2\text{SO}_4 \longrightarrow 2\text{CH}_3\text{Br} + \text{Mg}(\text{CH}_3\text{SO}_4)_2 \qquad (8)$$

It was possible to demonstrate that an equilibrium corresponding to (7) actually exists in solutions of the bromomagnesium enolate (I) by applying the method developed by Schlenk and Schlenk[7] for precipitating—MgX compounds from Grignard reagents. Work now in progress indicates that reactions similar to those given above are involved in the reaction of Grignard reagents with dimethyl sulfate.

If the reaction of dialkyl sulfates or alkyl sulfonates with ROMgX compounds is to be utilized for the preparation of ethers, two moles of the alkylating agent must be used to one of ROMgX, since one mole is consumed in producing alkyl halide (equation 3). Since (3) is rapid and apparently quantitative, alkylation of the magnesium alkoxides formed in (3) would be necessary to produce ethers

$$(\text{RO})_2\text{Mg} + 2(\text{CH}_3)_2\text{SO}_4 \longrightarrow 2\text{ROCH}_3 + \text{Mg}(\text{CH}_3\text{SO}_4)_2$$

This second phase of the reaction was not investigated, because it is not a practical method for synthesizing ethers, and because a previous research has shown that the reaction proceeds as indicated.[8]

Experimental Part

The results of the quantitative investigation of the reaction between dimethyl and diethyl sulfate and ROMgBr compounds in equimolecular proportions are recorded in Table I. The yields of the various products recorded represent the percentage of the quantity theoretically possible (according to equations 3 and 4) which was actually obtained. These data prove that the reaction proceeds according to equation (3) (or 4) in each case. The yield of alkyl bromide was quantitative within the limits of experimental error except in the experiments with $(\text{C}_6\text{H}_5)_2$-CHOMgBr. The low yields of alkyl bromide in this case are due to the fact that reaction (3) (and 4) did not go to completion because of the insolubility of the bromomagnesium derivative rather than to any competing ether formation. This is proved by the high yields of benzohydrol (96 and 98%) obtained on decomposing the magnesium compounds with water. The percentage yield of $(\text{R}'\text{O})_2\text{Mg}$ in the cases where R′ is $(\text{C}_6\text{H}_5)_2\text{CH}$ thus represents $(\text{R}'\text{O})_2\text{Mg}$ plus unreacted R′OMgBr.

The same general procedure was followed in each experiment. The reactions were carried out in a 200-cc. three-necked flask fitted with a mercury-sealed stirrer, reflux condenser, dropping funnel and a tube for admitting nitrogen. Exactly 0.05 mole of the Grignard reagent, which was $\text{C}_6\text{H}_5\text{MgBr}$ in the case of the enolate I and $\text{C}_2\text{H}_5\text{MgBr}$ in all other cases, was introduced into the flask from a buret.[9] In the case of the enolate (I) 12.4 g. (0.05 mole) of ethyl benzalmalonate in 30 cc. of pure dry benzene was then introduced dropwise and the solution stirred and refluxed for thirty minutes. In the other cases 0.05 mole of the appropriate ROH compound was introduced in 30 cc. of benzene and the solution refluxed for ten minutes. The solutions were then cooled and the reflux condenser turned off and connected to a train of five Erlenmeyer flasks. In the cases in which the alkyl halide formed was methyl bromide, these flasks contained a total of 100 cc. of approximately 10% sodium hydroxide in 90% alcohol (prepared by dissolving 5.8 g. of sodium in 100 cc. of 90% alcohol). In the cases in which ethyl bromide was formed, the flasks contained an excess of 15% silver nitrate in 80% alcohol. The dialkyl sulfate (0.05 mole in 20 cc. of dry ether) was then introduced dropwise with stirring. In all cases in which the ROMgBr was soluble a precipitate formed at once. After the sulfate was added the solutions were heated to 85° during fifteen to twenty minutes and kept at 85–95° for the length of time designated in Table I. The entire operation was performed in a slow current of dry, oxygen-free nitrogen, and during the heating the alkyl halide, the ether, and part of the benzene distilled through the condenser into the absorption train. After the designated period of refluxing the train was disconnected and the flask cooled. After removing the stirrer and reflux condenser the contents of the flask were forced with nitrogen pressure through a tube extending to the bottom of the flask into a dry nitrogen filled sintered glass funnel of porosity 3. The solution was filtered under a nitrogen pressure of 15 cm. of mercury into a dry, nitrogen-filled 100-cc. volumetric flask, and the transfer of material to the funnel completed and the precipitate washed by adding four portions of dry ether to the flask. In the case of the enolate (I) the magnesium enolate (IV) formed was soluble in the ether–benzene mixture and was determined by titration of 10-cc. aliquots of the filtrate (made up to 100 cc.) for basic magnesium, using the method employed by Gilman[10] for titrating Grignard reagents. The insoluble salt in the funnel was dried to constant weight in vacuum at 100° and proved by analysis to be $\text{Mg}(\text{CH}_3\text{SO}_4)_2$ ($\text{Mg}(\text{C}_2\text{H}_5\text{SO}_4)_2$ in the experiment with diethyl sulfate). In the other cases the $(\text{R}'\text{O})_2\text{Mg}$ was practically insoluble in the ether–benzene mixture, and consequently

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(7) Schlenk and Schlenk, *Ber.*, **62**, 920 (1929).

(8) Cerchez, *Bull. soc. chim.*, **43**, 762 (1928).

(9) The Grignard reagents were prepared, stored and introduced into the buret under nitrogen. They were standardized by acid titration according to the method used by Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576 (1929). The $\text{C}_6\text{H}_5\text{MgBr}$ was approximately 1 molar, the $\text{C}_2\text{H}_5\text{MgBr}$ approximately 2 molar.

(10) Gilman, Zoellner and Dickey, THIS JOURNAL, **51**, 1576 (1929).

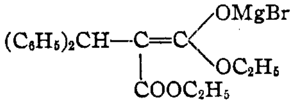
the insoluble salt was a mixture of $(R'O)_2Mg$ and $Mg(CH_3SO_4)_2$ (or $Mg(C_2H_5SO_4)_2$). This mixture was analyzed for $(R'O)_2Mg$, and the presence of $Mg(CH_3SO_4)_2$ (or $Mg(C_2H_5SO_4)_2$) inferred by difference and by analogy with the case of the enolate (I), where the separation was possible. The method employed in determining $(R'O)_2Mg$ varied with the nature of R'. Thus when R' was C_6H_5, $(C_6H_5)_2CH$ and $(C_6H_5)_3C$ the salt was decomposed with 200 cc. of 5% acetic acid and the ether removed by warming the solution. In the last two cases the yield of benzohydrol and of triphenylcarbinol gave the amount of $(R'O)_2Mg$; the yield of phenol was determined by converting it to tribromophenol with bromine followed by sodium bisulfite. In the experiments with n-C_4H_9OMgBr a slight excess of 1 *N* hydrochloric acid was added to the salt mixture and the solution back titrated with standard sodium hydroxide after heating to boiling. The percentage of the original basic magnesium gave the yield of $(R'O)_2Mg$ directly. The presence of $Mg(CH_3SO_4)_2$ (or $Mg(C_2H_5SO_4)_2$) did not interfere under these conditions. The amount of methyl bromide formed was determined after rinsing the contents of the absorption flasks into a 500-cc. Erlenmeyer flask, boiling off the alcohol and ether, cooling, acidifying with nitric acid and making up to 500 cc. in a volumetric flask by titration of a 25-cc. aliquot with 0.05 *N* silver nitrate by the Volhard method. In the cases where ethyl bromide was produced the absorption flasks were allowed to stand overnight to ensure complete reaction of the ethyl bromide with the alcoholic silver nitrate, then the combined solutions were boiled to remove alcohol and ether, acidified with nitric acid and the silver bromide determined gravimetrically.

Ethyl methyl diphenylmethylmalonate (V) (from reaction 2): to the 90 cc. of ether–benzene solution containing the magnesium enolate (IV) remaining after titration of a 10-cc. aliquot for basic magnesium (experiment 1, Table I) was added 8.5 g. (50% excess) of dimethyl sulfate in 50 cc. of benzene. The ether was removed by distillation and the benzene solution refluxed for twenty-four hours. The reaction mixture was then cooled, filtered through a sintered glass funnel and the insoluble salt washed with ether. The salt proved to be $Mg(CH_3SO_4)_2$; yield 5.50 g. (99%). *Anal.* Calcd. for $Mg(CH_3SO_4)_2$: Mg, 9.94; S, 26.01. Found: Mg, 9.73; S, 25.30. The filtrate was washed with dilute hydrochloric acid, the solvent evaporated and the residue distilled in vacuum. The yield was 11.0 g. (72%), b. p. 180–182° (2 mm.). Crystallization from petroleum ether gave the pure ester crystallizing in rods, m. p. 41–42°. *Anal.* Calcd. for $C_{21}H_{24}O_4$: C, 74.07; H, 7.11. Found: C, 74.20; H, 7.17. The ester was proved to be the C-methyl derivative (V) rather than O-methyl by a Zeisel determination, which showed 1.97 OR groups.

Reaction of $(C_6H_5)_2CHOMgBr$ and $(C_2H_5)_2SO_4$. While the data recorded in Table I show conclusively that no benzohydryl ethyl ether is formed through this reaction, it seemed wise to repeat Gilman and Hoyle's experiment[4] exactly, since their $(C_6H_5)_2CHOMgBr$ was prepared differently and ether alone was used as a solvent. Phenylmagnesium bromide was thus prepared from 2.34 g. of magnesium and 15.7 g. (0.1 mole) of bromobenzene in 60 cc. of ether. The solution was cooled in ice and 10.6 g. of benzaldehyde (0.1 mole) in 20 cc. of ether added dropwise during fifteen minutes. The suspension was then heated to

TABLE I

REACTION OF R_2SO_4 AND $R'OMgBr$ IN EQUIMOLECULAR PROPORTIONS

R'OMgBr	R_2SO_4	Reaction time, hrs.[a]	% RBr	% $(R'O)_2Mg$	% $Mg(RSO_4)_2$
 $(C_6H_5)_2CH{-}C(COOC_2H_5){=}C(OMgBr)(OC_2H_5)$	$(CH_3)_2SO_4$	0.5	99.4[b]	94.2	99.0[c]
	$(C_2H_5)_2SO_4$	.5	97.0	97.0	99.0[d]
C_6H_5OMgBr	$(CH_3)_2SO_4$	.25	96.4	95.0	
n-C_4H_9OMgBr	$(CH_3)_2SO_4$	.5	95.8	98.2	
n-C_4H_9OMgBr	$(C_2H_5)_2SO_4$	.6	92.6	96.0	
$(C_6H_5)_2CHOMgBr$	$(CH_3)_2SO_4$	1.5	82.0	96.2	
$(C_6H_5)_2CHOMgBr$	$(C_2H_5)_2SO_4$	0.75	53.8	98.0	
$(C_6H_5)_3COMgBr$[e]	$(CH_3)_2SO_4$	.75	91.3	94.5	

[a] In all cases except with $(C_6H_5)_2CHOMgBr$ (which was insoluble in the ether–benzene mixture) the reaction appeared to be quite rapid at room temperature. Consequently, except in the experiments with $(C_6H_5)_2CHOMgBr$, the designated period of heating was probably not essential for the completion of reaction (3) (or 4), but it was necessary to ensure complete distillation of the alkyl bromides from the reaction mixture.

[b] In a duplicate experiment the absorption train containing alcoholic sodium hydroxide was replaced by two test-tubes each of which contained 20 cc. of dry ether and 1.5 g. of magnesium. After the completion of the reaction the solution of CH_3MgBr was decanted into a 100-cc. volumetric flask. Titration of an aliquot showed that the yield of CH_3MgBr was 83%; reaction of another portion with mercuric bromide gave CH_3HgBr, m. p. 159–160°.

[c] Purified only by washing with ether and drying to constant weight in vacuum at 100°. Magnesium was determined in the ordinary manner by conversion to $Mg_2P_2O_7$, while in the sulfur determination the sample was evaporated several times with hydrochloric acid to convert the CH_3OSO_2OH completely to sulfuric acid before precipitation with barium chloride [Rabcewicz-Lubkowsky, *J. prakt. Chem.*, [2] **86**, 319 (1912)].

Anal. Calcd. for $Mg(CH_3SO_4)_2$: Mg, 9.94; S, 26.01. Found: Mg, 10.32; S, 25.05.

[d] Analyzed as in (*c*). Calcd. for $Mg(C_2H_5SO_4)_2$: Mg, 8.86; S, 23.35. Found: Mg, 9.26; S, 22.30.

[e] In 25 cc. of ether and 75 cc. of benzene; the solution was not cooled before the addition of dimethyl sulfate in order to keep the $(C_6H_5)_3COMgBr$ in solution.

refluxing and 15.4 g. (0.1 mole) of diethyl sulfate added. After two hours of refluxing the suspension was cooled and filtered. The insoluble magnesium compound was washed with three portions of ether and then decomposed with 200 cc. of 5% acetic acid. After warming to remove ether the solution was cooled; 14.7 g. (80%) of benzohydrol separated. Distillation of the ethereal filtrate gave 13 g. (85%) of recovered diethyl sulfate. Obviously there had been no reaction between the $(C_6H_5)_2CHOMgBr$ and diethyl sulfate, presumably because of the insolubility of the bromomagnesium compound. In Gilman's procedure the reaction mixture was decomposed with dilute hydrochloric acid and extracted with ether; the ether extract was distilled and a 35% yield of benzohydryl ethyl ether obtained, b. p. 190–195° (150 mm.). The present experiment shows that the ether extract of the reaction mixture contained only benzohydrol and unreacted diethyl sulfate, which must have reacted during distillation to give benzohydryl ethyl ether.

Evidence for the existence of the equilibrium: $2\ \text{I} \rightleftharpoons \text{IV} + MgBr_2$. The enolate I was prepared in the usual manner from exactly 0.02 mole of C_6H_5MgBr in 35 cc. of ether and 4.96 g. (0.02 mole) of ethyl benzalmalonate in 25 cc. of benzene. After refluxing to ensure complete addition, the solution was cooled in ice and a solution of 3 g. of dioxane in 15 cc. of ether added during fifteen minutes. A precipitate formed immediately. The suspension was then washed into a dry, nitrogen-filled centrifuge bottle with 40 cc. of a solution of 3 g. of dioxane in 50 cc. of ether, and the insoluble material separated by centrifuging for thirty minutes. The clear solution was decanted into a 100-cc. volumetric flask and the solid broken up and washed by centrifuging again with 10 cc. of the solution of dioxane in ether. This solution was added to the volumetric flask, and after making up to volume 20-cc. aliquots were analyzed for basic magnesium[10] and halogen. The solution contained 62.5% of the original basic magnesium and only 3.3% halogen (also referred to the original basic magnesium, *i. e.*, 3.3% of 0.02 mole). If the equilibrium does not shift during the precipitation, this would indicate that the original solution contained 59% $(RO)_2Mg$ and (by difference) 41% ROMgBr.

This method probably cannot be used to prove the existence of an equilibrium in ether or benzene solutions of ROMgBr compounds in general, for in the other cases studied in this research the $(RO)_2Mg$ compounds were insoluble in ether and benzene, and consequently the addition of dioxane would be expected to result in complete precipitation of the magnesium compounds. That such an equilibrium exists, however, is indicated by work of Grignard and Fluchaire[11] and Meerwein and Schmidt,[12] who prepared ROMgX compounds through the reaction

$$(RO)_2\,Mg + MgX_2 \longrightarrow 2ROMgX$$

Summary

Representative compounds of the type ROMgBr, *i. e.*, the bromomagnesium derivative of an ester enol, of phenol, and of a primary, a secondary and a tertiary alcohol have been found to react with dialkyl sulfates according to the equation

$$2R'OMgBr + 2R_2SO_4 \longrightarrow (R'O)_2Mg + 2RBr + Mg(RSO_4)_2$$

Evidence is presented that in solutions of ROMgBr the following equilibrium exists

$$2R'OMgBr \rightleftharpoons (R'O)_2Mg + MgBr_2$$

It is probable that in the reaction of ROMgBr with dialkyl sulfates the actual reactants are R_2SO_4 and $MgBr_2$, the above equilibrium being shifted completely to the right due to the removal of $MgBr_2$

$$2R_2SO_4 + MgBr_2 \longrightarrow 2RBr + Mg(RSO_4)_2$$

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[11] Grignard and Fluchaire, *Ann. chim.*, **9**, 7 (1928).

[12] Meerwein and Schmidt, *Ann.*, **444**, 236 (1925).

CAMBRIDGE, MASS. RECEIVED JANUARY 19, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Action of Inorganic Bases on Secondary and Tertiary Butyl Bromides[1]

BY H. E. FRENCH, W. H. MCSHAN AND W. W. JOHLER

When aqueous solutions of inorganic bases act upon alkyl halides, alcohols are obtained as the chief products, with varying quantities of olefins often being formed as the result of side reactions. The purpose of this investigation was to determine the extent to which this side reaction takes place when certain alkyl bromides are acted upon by metallic hydroxides under varying conditions of concentration. The alkyl halides used were the secondary and tertiary butyl bromides, and the inorganic bases were the hydroxides of silver, sodium, potassium, calcium and barium. These were used only in aqueous solution or suspension.

Reagents, Apparatus and Procedure

The alcohols used were the best grade obtainable from the Eastman Kodak Company, and were redistilled before use. These were treated with gaseous hydrogen bromide in the preparation of the bromides. The boiling points of the secondary and the tertiary butyl bromides at 740 mm. were 90.3–90.5 and 72.7–72.9°, respectively. The silver hydroxide was prepared by adding potassium hydrox-

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[1] This paper is an abstract of the theses submitted by Mr. McShan and Mr. Johler in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.