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: $2\ \mathrm{I} \rightleftharpoons \mathrm{IV} + MgBr_2$. 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.

ide solution to a slight excess of silver nitrate, the excess being removed from the precipitate by washing with water. The barium hydroxide was Analytical Reagent material, and the other bases were U. S. P. quality.

The reactions were carried out in a 1-liter round-bottomed short-necked flask, closed by a rubber stopper carrying a condenser, a mercury-sealed motor stirrer and an inlet tube or separatory funnel extending to near the bottom of the flask, through which the butyl bromide was introduced into the reaction mixture after it had been brought to the desired temperature by means of a water-bath. The upper end of the condenser was closed by a rubber stopper carrying a delivery tube arranged for collecting gaseous olefins over water in a 3-liter flask.

In carrying out a reaction, the metallic hydroxide was dissolved or suspended in 500 cc. of water in the reaction flask, which was then stoppered and placed in a water-bath. When the desired temperature was reached, the butyl bromide was introduced into the reaction mixture through the separatory funnel and the stirrer was started. With secondary butyl bromide, reaction was considered complete when there was no further evolution of gas, though the stirring and heating were continued for considerably longer periods of time. With the tertiary butyl bromide, where there was but slight evolution of gas, the reaction time could be estimated only roughly. Upon completion of reaction, air was passed through the reaction mixtures to carry over any olefin remaining in the reaction flask or condenser.

The gases which were collected over water were analyzed for butene by absorption in fuming sulfuric acid in an Orsat gas analysis apparatus.

The reaction mixtures were made barely acid to phenolphthalein with nitric acid, and about 150 cc. was distilled into tared flasks through a Pyrex fractionating column, 90 × 2 cm., containing 75 cm. of cut glass rings. The distillates from the reactions with tertiary butyl bromide were analyzed for the alcohol by means of an Abbe refractometer. Those from the reactions with secondary butyl bromide always contained small amounts of unchanged bromide, so no alcohol determinations were made on those distillates.

The silver bromide from reactions using silver oxide was filtered off and weighed. Aliquot portions from the other reaction mixtures were analyzed gravimetrically for bromine. From these results the weights of butyl bromide reacting were calculated.

Summary of Reactions with *s*-Butyl Bromide

Unless otherwise stated, 500 cc. of water was used in each of these reactions. The number of moles of butyl bromide reacting was calculated from the weight of metallic bromide found on analysis. The yield of olefin was determined by means of an Orsat gas analysis apparatus. Most of the reactions were carried out at 60°, a few at 30 and 50°. Variations in temperature, within this range, had no effect on the yield of olefin, but a temperature increase of 10° was found to approximately double the speed of reaction as measured by the time during which the olefin was delivered into the receiver.

Silver Hydroxide.—A total of seven reactions was carried out. In each case 0.09 mole of the reagent was used, while the amount of the butyl bromide which reacted varied from 0.060 to 0.063 mole. Yields of olefin of from 28.3 to 31.4% were obtained. Reaction temperatures were 30, 50 and 60°, and the time of olefin formation varied from 0.75 to six hours.

Potassium Hydroxide.—Two runs were made using 0.18 mole of potassium hydroxide, with 0.06 and 0.07 mole of the bromide reacting. The yields of olefin were 21.6 and 24%, respectively. The reactions were carried out at 50 and 60°, and the times of reaction were fifteen and seven and a half hours.

Four runs were made using 0.50 mole of potassium hydroxide and from 0.06 to 0.07 mole of the bromide. The yield of olefin varied from 38.6 to 39.8%. The reaction temperatures were 50 and 60°, and the reaction time varied from seven and a half to fifteen hours.

Two runs were made using 1.1 moles of potassium hydroxide (dissolved in 200 cc. of water instead of the customary 500 cc.), with 0.05 mole of the bromide. The yields of olefin were 46.9 and 47.7%. A reaction temperature of 60° was used, and the time of reaction was eleven hours.

Sodium Hydroxide.—Two runs were made using 0.50 mole of sodium hydroxide with 0.07 and 0.08 mole of the bromide. Yields of olefin were 34.7 and 34.9%.

In another two runs, 0.75 mole of the reagent was used with 0.08 mole of the bromide. Yields of olefin were 36.8 and 37.5%. The reaction temperature for all of these reactions was 60°, and the time of reaction was seven hours.

Calcium Hydroxide.—Two runs were made with 0.07 mole of the hydroxide and 0.07 and 0.08 mole of the bromide; 13.4 and 13.8% yields of olefin were obtained. The reaction temperature was 60° and the time of reaction was seven and a half hours.

Barium Hydroxide.—Two runs with 0.27 mole of the hydroxide and 0.06 mole of the bromide gave yields of olefin of 25.7 and 25.9%. The reactions took place at 60°, and required seven hours.

Summary of Reactions with *t*-Butyl Bromide

Five hundred cc. of water was used in each experiment.

Silver Hydroxide.—Three runs were made at 30°, using 0.25 mole of the reagent with 0.12 mole of the bromide, and 0.08 mole of the reagent with 0.05 mole of the bromide. No olefin could be detected and the alcohol was obtained in 99% yields.

Five runs were made at 40°. In three of these 0.15 mole of the hydroxide was used with 0.09 mole of the bromide. In the remaining two runs, 0.08 mole of the hydroxide and 0.05 mole of the bromide were used. Yields of olefin amounted to 0.07 and 0.2%, and the yields of alcohol varied from 94.3 to 99.6%.

Two runs at 60°, using 0.20 mole of the hydroxide with 0.11 mole of bromide, and 0.08 mole of hydroxide with 0.05 mole of the bromide, gave yields of olefin of 2 and 1%, and alcohol to the extent of 96.2 and 99%, respectively.

Potassium Hydroxide.—Two runs at 50° (0.3 mole of hydroxide and 0.08 mole of the bromide) formed 1.3% olefin and 96.1 and 96.7% alcohol. Four other runs, using 0.2 and 2.0 moles of the reagent with 0.10 mole of the bromide gave positive qualitative tests for olefin and alcohol in yields of 94 to 98.9%.

Barium Hydroxide.—Three runs were made at 50°, using 0.35 mole of the base with 0.12 mole of the bromide, and 0.15 mole of the hydroxide with 0.07 mole of the bromide. The yields of olefin were 2.2 and 0.8%. The yields of alcohol varied from 91.8 to 97.2%.

In analyzing the distillates from the reaction mixtures for tertiary butyl alcohol, use was made of the indices of refraction of aqueous solutions of that substance given in the "International Critical Tables," Vol. 7, page 68, supplemented by the following new determinations.

TABLE I

REFRACTIVE INDICES OF AQUEOUS TERTIARY BUTYL ALCOHOL SOLUTIONS

t-Butyl alcohol, %	0.857	1.26	1.95	1.96	2.49
n_D^{25} reduced to vacuum	1.3336	1.3342	1.3348	1.3349	1.3356
t-Butyl alcohol, %	3.64	3.83	5.33	5.67	6.57
n_D^{25} reduced to vacuum	1.3366	1.3367	1.3384	1.3385	1.3397
t-Butyl alcohol, %		7.35	7.63	7.65	9.43
n_D^{25} reduced to vacuum		1.3404	1.3407	1.3408	1.3426

The Abbe refractometer was accurate to 0.0002, which in the experiments reported in this paper corresponds to about 0.1 g. of tertiary butyl alcohol. This represents a possible error in analysis of approximately 1.3% in the amount of alcohol reported in the experimental part.

The reactions with tertiary butyl bromide took place much more rapidly than did those with the secondary bromide, and formed the alcohol as the chief product. The maximum yield of butene amounted to but slightly more than 2%, and in the reactions using silver hydroxide at 30°, there was no evidence of olefin formation.

Considerable quantities of butene were formed in all of the reactions with secondary butyl bromide, the yields varying from 13 to 47%. Except in those reactions using silver hydroxide, the amount of olefin produced varied roughly as the concentration of dissolved base. In general, then, the course of the reaction is affected by the concentration of the hydroxide ion, but is little affected by the nature of the metallic ion, although sodium hydroxide gave somewhat lower yields of butene than did potassium hydroxide solutions of the same concentration. Silver hydroxide, however, formed olefin to the extent of 30%, thus approximating the yields from moderately concentrated solutions of potassium hydroxide.

Summary

1. The action of several inorganic hydroxides on secondary and tertiary butyl bromides was investigated, using aqueous solutions in varying concentrations.
2. Olefin was obtained from secondary butyl bromide in yields of from 13 to 47%, the amount varying roughly with the amount of dissolved hydroxide. Silver hydroxide was an exception to this generalization, since it formed relatively large quantities of the olefin.
3. Tertiary butyl bromide gave yields of olefin which varied from 0 (using silver hydroxide at 30°) to 2.2%.

COLUMBIA, MISSOURI

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Decomposition of Alpha Keto Acids

BY CHARLES D. HURD AND HARRY R. RATERINK

A study was made of the pyrolysis of benzoylformic (phenylglyoxylic) and phenylpyruvic acids to gain further insight into the behavior of α-keto acids. Claisen[1] and later Bouveault[2] found the former to yield benzoic acid and benzaldehyde at 200–250°. Air was not excluded and no study was made of the gaseous reaction products. In the present work (270°) the yields of carbon monoxide and carbon dioxide were about 19 and 49%, respectively; the yields of aldehyde were about 25–15%, and of acid 35–45%. An experiment at 500° resulted in a 62% yield of benzaldehyde.

Phenylpyruvic acid, $C_6H_5CH_2COCOOH$, melts with decomposition. In the present work carbon monoxide, carbon dioxide and phenylacetic acid were established as pyrolytic products. The yield of phenylacetic acid was about 35%. No phenylacetaldehyde was isolable. Phenylpyruvic acid differs from phenylglyoxylic in having a methylene group alpha to the carbonyl. Evidently this —CH_2CO— group sponsored dehydra-

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[1] Claisen, *Ber.*, **10**, 431, 1667 (1877).

[2] Bouveault, *Bull. soc. chim.*, [3] **15**, 1015 (1896).