vigorously until solution was complete, then cooled first in ice water and finally in a freezing mixture. It deposited 30 g. of a mixture of solids which was readily separated by recrystallization from methyl alcohol. The principal product was sparingly soluble in methyl alcohol but was readily recrystallized from a mixture of acetone and methyl alcohol from which it separated in colorless plates melting at 126°.

Anal. Calcd. for $C_{17}H_{17}O_3Br$: C, 58.5; H, 4.9. Found: C, 58.4; H, 5.0.

The bromomethoxy compound was obtained even more readily by shaking a suspension of α-bromo-benzalacetylanisole in anhydrous methyl alcohol containing a small quantity of sodium methylate. In the hope of getting a stereoisomeric bromomethoxy compound we also added mercuric acetate to benzalacetylanisole and brominated the product, but these operations gave the same bromo compound. This substance was, doubtless, also obtained by Weygand by boiling a suspension of the dibromide with methyl alcoholic potassium hydroxide. Weygand naturally assumed that the product would be an α-bromo-benzalacetylanisole and attributed his analytical results to the difficulties met with in the analysis of methoxyl compounds.

The remainder of the solid product was a mixture which was separated by recrystallization from ether and petroleum ether into the α-bromo and β-methoxy derivatives of benzalacetylanisole. These substances have been accurately described by Weygand.

A solution of the bromomethoxy compound in methyl alcohol was shaken with an excess of sodium methylate for thirty-six hours. The product was isolated in the usual manner but failed to give any solid compounds. It was therefore hydrolyzed with aqueous acetic acid. It yielded the diketone (about 70%) and an oil from which it has not as yet been possible to obtain any solid compounds.

Summary

1. α,β-Dibromo ketones may react with alcoholates in two different ways which ultimately lead to very different types of acetals

$$RC(OR)_2CH_2COR' \longleftarrow RCHBrCHBrCOR' \longrightarrow RCH(OR)CHOHC(OR)_2R'$$

2. Most dibromo ketones yield both acetals, but when the hydrogen in the β-position is unusually active, the acetal of a β-diketone may be the only product.

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THE "MACHINE" FOR ANALYSIS WITH GRIGNARD REAGENTS

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Since the appearance of the original paper on an "apparatus for determining both the quantity of gas evolved and the amount of reagent consumed in reactions with methyl magnesium iodide,"[1] the apparatus has been redesigned and considerably improved. In view of a steadily increasing number of inquiries, dealing largely with the special stopcock, it seems desirable to publish the new design and to show how this beautiful but troublesome stopcock has been eliminated.

[1] Kohler, Stone and Fuson, THIS JOURNAL, **49**, **3181** (1927).

By introducing the reagent into the top of the buret we have been able to use an ordinary two-way stopcock which comes in contact with the reagent at but one point, hence can often be used for a month or more without being regreased. In redesigning the apparatus we also eliminated the ground-glass joint at the top of the reservoir A and improved the shoulder, i, in order to secure a better control of the temperature of the gas inclosed in the shoulder.

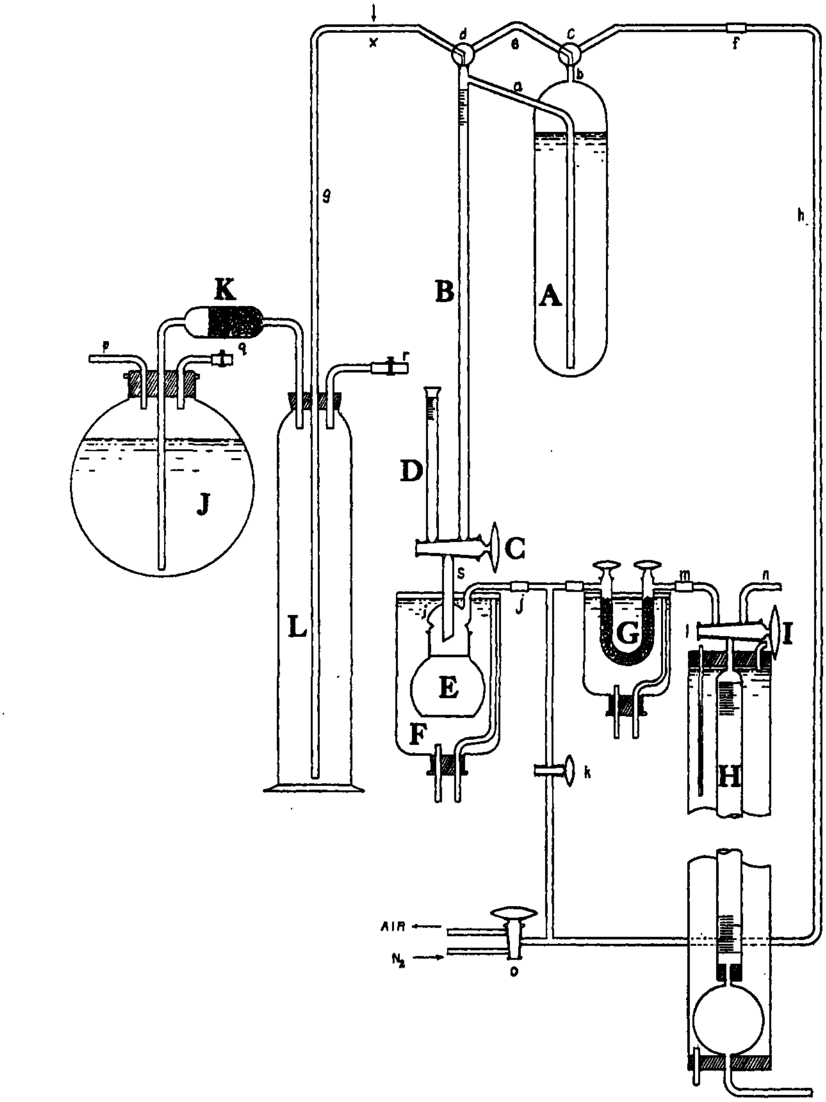

Fig. 1.

These alterations do not necessitate any serious changes in the operation of the machine. In order to clean the reservoir it is now necessary to dismount the entire machine but since a single charge serves for about a hundred analyses we do not regard this as a serious matter. After filling the reservoir we cut the tube g at x and clean the small section between x and d with a pipe cleaner. This leaves a light, compact apparatus which is relatively free from strain, and which we hold with a single clamp on the reservoir.

The reagent is now pressed from the reservoir to the reagent buret through a. After the desired amount has been introduced into the buret the stopcocks c and d are turned to open the reservoir to the air for an instant; this relieves the excess pressure in A. Then c and d are turned in such a manner that the nitrogen presses the reagent remaining in a, back into the reservoir, after which A is again momentarily opened to the air. All stopcocks can be removed, cleaned and regreased in a properly directed current of nitrogen without affecting the titer of the solution. It is well also to sweep the system o–k–j–i with nitrogen while spraying the shoulder i with alcohol and ether after an analysis has been completed.

For the preparation of the methyl magnesium iodide necessary to fill the 500-cc. reservoir we use the following procedure. In a one-liter three-necked, round-bottomed flask, equipped with motor stirrer, dropping funnel and condenser, are placed 12 g. of magnesium and 100 g. of isoamyl ether (distilled *in vacuo*, over sodium). In the course of one hour, with the temperature maintained below 20°, 60 g. of methyl iodide in 50 g. of isoamyl ether is added. Stirring is continued for two hours. The reagent is then diluted by the addition of 270 g. of isoamyl ether. The condenser is removed and the flask, immersed in an oil-bath, is heated at 120° for two hours; meanwhile a current of purified nitrogen is passed over the reaction mixture to carry away any readily volatile products. After being allowed to stand overnight, the reagent is transferred to the apparatus.

We have found it advantageous to substitute dehydrite for the phosphorus pentoxide in G, and to enlarge the overflow bulb in the gas buret H to 50 cc.

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