[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ACTION OF BASES ON ALPHA,BETA-DIBROMO KETONES AND RELATED SUBSTANCES

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RECEIVED JULY 16, 1930 PUBLISHED SEPTEMBER 5, 1930

The reaction between α,β-dibromo ketones and bases has often been used for the preparation of other substances but has seldom been studied with care. It has the interesting peculiarity of yielding products so diverse that some of them can be hydrolyzed to β-diketones while others serve as the basis of a very general method for preparing the corresponding α-derivatives.

The process leading to β-diketones was discovered by Sorge[1] and studied by Wieland,[2] who showed that the action of methyl alcoholic potassium hydroxide on one of these dibromides occurs in a number of steps which ultimately end in an acetal of a β-diketone.

$$p\text{-}NO_2C_6H_4CHBrCHBrCOC_6H_5 \longrightarrow p\text{-}NO_2C_6H_4C(OCH_3)_2CH_2COC_6H_5$$

The method of converting these dibromides into α-diketones was discovered by Dufraisse and Moureu.[3] After careful study these authors decided that the action of the base—in this case piperidine—must be represented by the following scheme

$$RCHBrCHBrCOR \longrightarrow RCH{=}CBrCOR \longrightarrow RCH_2C(NC_5H_{10})BrCOR \longrightarrow RCH{=}C(NC_5H_{10})COR$$

This scheme assumes a mode of addition of piperidine which is different from that which has been observed in every case in which a base or any other hydrogen compound has been added to an α,β-unsaturated ketone or ester. Dufraisse and Moureu attribute this "inverse" addition to the influence of the bromine in the α-position—a conclusion that has important theoretical consequences and which should, if possible, be confirmed. An examination of this mechanism was the principal object of our investigation.

The mode of attack was based on observations that were made while preparing a series of β-diketones by the method of Sorge. In the course of these preparations it became evident that in many cases the yields are far from ideal because products are formed which cannot be hydrolyzed to β-diketones. Moreover, the solutions that are left, after removing the β-diketone completely as copper derivative, have a yellow color that is strongly suggestive of that of solutions of α-diketones. Since the reaction with piperidine has already been carefully studied by Dufraisse and Moureu, we decided to work with sodium alcoholates, and a casual observa-

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[1] Sorge, *Ber.*, **35**, 1065 (1902).

[2] Wieland, *ibid.*, **37**, 1148 (1904).

[3] Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 457 (1927).

tion led us to select the dibromide of benzal-*p*-bromo-acetophenone for investigation.

When this dibromide was boiled with excess of methyl alcoholic sodium methylate, it formed a yellow solution from which after much manipulation we finally obtained two solids which separated from ether in large colorless crystals. These proved to be stereoisomeric acetals of a type very different from the one obtained by Wieland, namely,

$$C_6H_5CHOCH_3CHOHC(OCH_3)_2C_6H_4Br$$

These acetals constituted only about 40% of the products of the reaction, the remainder being composed of oils which on hydrolysis gave *p*-bromodibenzoylmethane. When sodium ethylate was substituted for the methylate all products were solid and it was possible to establish that the reaction leads almost exclusively to substances that are represented by the formulas

$$C_6H_5C(OC_2H_5){=}CHCOC_6H_4Br \text{ and } C_6H_5CHOC_2H_5CHOHC(OC_2H_5)_2C_6H_4Br$$

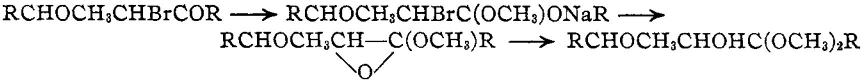
From these results it is clear that the reaction between α,β-dibromo ketones and alcoholates is not as simple as has been assumed. Following the course charted by Wieland, the dibromides first lose a molecule of hydrogen bromide to form an unsaturated α-bromo compound which in the alkaline solution combines with alcohol and forms a saturated bromo ether

$$RCHBrCHBrCOR \longrightarrow RCH{=}CBrCOR \longrightarrow RCHOCH_3CHBrCOR$$

Thus far all the dibromo ketones behave alike, and both the unsaturated and the saturated bromo compounds can be isolated when the solubility relations are favorable. Beyond this point the results depend upon the other groups present in the dibromides. In all the cases that we have examined some of the saturated bromo ether follows the course outlined by Wieland

$$RCHOCH_3CHBrCOR \longrightarrow RCOCH_3{=}CHCOR \longrightarrow RC(OCH_3)_2CH_2COR$$

Occasionally acetals of this type form the sole products of the reaction but this happens only when the dibromide has an unusually active hydrogen atom in the β-position as, for example, the *p*-nitro compound examined by Wieland and the ketonic esters studied by Rice.[4] In all other cases some of the saturated bromo ether reacts in a different manner



$$RCHOCH_3CHBrCOR \longrightarrow RCHOCH_3CHBrC(OCH_3)ONaR \longrightarrow RCHOCH_3\underbrace{CH{-}C}_{O}(OCH_3)R \longrightarrow RCHOCH_3CHOHC(OCH_3)_2R$$

The discovery that ethylene oxides may play a role in the reaction between bases and dibromo ketones supplies a basis for a new interpretation of the very interesting results of Dufraisse and Moureu. Our work on this phase of the problem has not been completed but in our opinion the course of the reaction between dibromo ketones and piperidine is quite different

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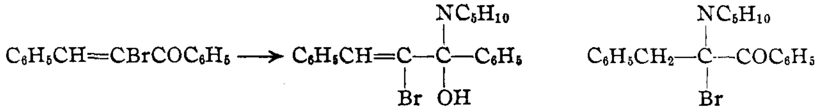
[4] Rice, This Journal, 50, 1481 (1928).

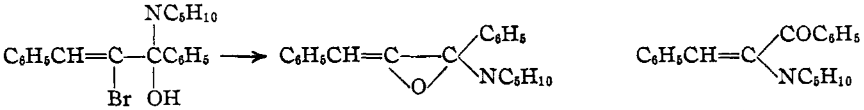
from that which was assumed by the French investigators. After the usual elimination of a molecule of hydrogen bromide the next step is 1,2-addition of piperidine to the carbonyl group. The result is the amine equivalent of a hemi-acetal; hence the great instability of the substance and the ease with which it loses hydrogen bromide—properties which appear to be quite inconsistent with the formula of Dufraisse and Moureu



$$C_6H_5CH{=}CBrCOC_6H_5 \longrightarrow C_6H_5CH{=}\underset{Br}{C}{-}\overset{NC_5H_{10}}{\underset{OH}{C}}{-}C_6H_5 \qquad C_6H_5CH_2{-}\overset{NC_5H_{10}}{\underset{Br}{C}}{-}COC_6H_5$$

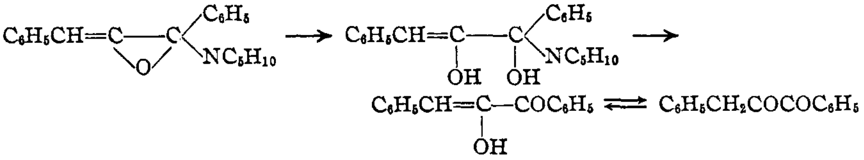
D. and M.

When this unsaturated bromohydrin is allowed to react with sodium methylate or a second molecule of piperidine, it undergoes the usual loss of hydrogen bromide and passes into an ethylene oxide



D. and M.

Like other ethylene oxides the product is capable of combining with bases, acetic acid and like substances. When it is hydrolyzed it inevitably passes into an α-diketone



In our opinion, then, Watson's brilliant red piperidine derivative is the first representative of an exceedingly interesting type of unsaturated ethylene oxide.[5] The twinning of the oxide ring with an ethylenic linkage results in a system that is almost as actively unsaturated as that of the ketenes. Like ketenes, therefore, it is highly colored, readily undergoes autoxidation and enters into a variety of reactions that involve the entire system.

Experimental Part

I. *p*-Bromo Series

Three substances were employed in the *p*-bromo series: the dibromide I, the α-bromo unsaturated ketone II, and the α-bromo-β-methoxy ketone III.

$C_6H_5CHBrCHBrCOC_6H_4Br$ (I) $\quad C_6H_5CH{=}CBrCOC_6H_4Br$ (II) $\quad C_6H_5CHOCH_3CHBrCOC_6H_4Br$ (III)

These substances were compared with respect to their behavior toward

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[5] Watson, *J. Chem. Soc.*, **85**, 1322 (1904).

methyl alcoholic sodium methylate at the ordinary temperature and also at the boiling point; with two moles of the methylate and with thrice this quantity. The distribution of the material between the two types of reaction differed but little if any, but at the higher temperature there was considerable cleavage of the products which lead to the β-diketone, and the difficulty of isolating solid substances was correspondingly increased.

When the reactions are carried out at the ordinary temperature the result is a pale yellow solution. In order to get any solid from this solution it is necessary to remove the methyl alcohol completely, without allowing the solution to come in contact with acid, secure a solution in equal parts of dry ether and petroleum ether, and allow this to evaporate slowly through a tube that protects it against the acid fumes of the laboratory. It then, in time, usually begins to deposit one or two substances in colorless crystals which gradually grow to unusual dimensions and which can be readily separated mechanically. The first crystals are extremely difficult to secure, but once these are available crystallization can be induced immediately by inoculation.

The structure of these colorless products was established in the following manner. The analyses showed that the composition of both substances is represented by the formula $C_{18}H_{21}O_4Br$, that each has three methoxyl groups and one active hydrogen atom, and that neither has any other group capable of reacting with methyl magnesium iodide. These quantitative results indicate acetals with hydroxyl and a third methoxyl group strung on the chain of benzal-*p*-bromo-acetophenone. Gentle hydrolysis confirmed this conclusion because each substance gave a product which had but one methoxyl group, and along with it an active hydrogen and a group, presumably carbonyl, capable of reacting with one equivalent of methyl magnesium iodide.

In order to get substances more suitable for degradation, each of these hydrolysis products was treated with phenyl magnesium bromide. The result was two new substances and when these were cautiously oxidized with chromic acid, each yielded methyl benzoate and *p*-bromo-benzophenone. These transformations bear but one interpretation

$$\underset{\text{IV}}{C_6H_5CHOCH_3CHOHC(OCH_3)_2C_6H_4Br} \longrightarrow \underset{\text{V}}{C_6H_5CHOCH_3CHOHCOC_6H_4Br} \longrightarrow$$

$$\underset{\text{VI}}{C_6H_5CHOCH_3CHOHC(OH)(C_6H_5)C_6H_4Br} \longrightarrow C_6H_5CO_2CH_3 + CO_2 + C_6H_5COC_6H_4Br$$

The separation of the stereoisomeric trimethoxy compounds (IV) from the ethereal solution was, naturally, incomplete but it was possible to get a fairly accurate estimate of the quantities formed by hydrolyzing the entire product. The resulting β-diketone could be removed completely as its copper derivative, leaving only the isomeric hydrolysis products V which are stable and crystallize much more readily than the corresponding acetals.

Preparation of Materials.—The dibromide I has been described by Weygand,[6] who found a melting point of 184°. Our material was repeatedly recrystallized from chloroform and melted at 187°. The α-bromo compound II has also been prepared by Weygand, who distilled it in a high vacuum and noted a boiling point of 136–143°. We found that it distils without decomposition at 230° under 3 mm.

Anal. Calcd. for $C_{15}H_{10}OBr_2$: C, 49.2; H, 2.7. Found: C, 49.2; H, 3.0.

α-Bromo-β-methoxy-benzyl-*p*-bromo-acetophenone, III.—The bromo methoxy compound was made by the procedure of Middleton.[7] A suspension of equivalent quantities of benzal-*p*-bromo-acetophenone and mercuric acetate in dry methyl alcohol was warmed until the clear colorless solution gave no test for mercuric acetate with alkali. The solution was then evaporated to a small volume. It deposited a solid which after recrystallization from acetone melted at 140°.

Anal. Calcd. for $C_{18}H_{17}O_4BrHg$: Br, 13.8. Found: Br, 13.9.

The mercury compound was suspended in dry methyl alcohol, the suspension was cooled to 0° and treated with an equivalent quantity of bromine. The mixture was set aside until all the color had disappeared, then evaporated in a current of air. It left a colorless oil. This was dissolved in ether, the solution freed from mercury salts by shaking with saturated potassium bromide solution, dried and evaporated. The product was an oil which would not crystallize and could not be distilled. A sample which had been kept in a vacuum desiccator for several weeks was analyzed.

Anal. Calcd. for $C_{16}H_{14}O_2Br_2$: C, 48.3; H, 3.5; OCH_3, 8.0. Found: C, 48.5; H, 3.5; OCH_3, 8.2.

The Isomeric Methyl Acetals, IV.—These acetals were first obtained by treating 200 g. of the dibromide in the manner described earlier in this section. One of them crystallized from ether in very large colorless prisms which melt at 90°; the other, which is formed in much smaller quantities, separated from petroleum ether in tables melting at 77°. These substances were subsequently obtained more easily and in relatively larger quantities from the α-bromo compound II. The procedure was as follows.

A suspension of 50 g. of the bromo compound in 50 g. of dry methyl alcohol and a solution of 4.5 g. of sodium in 80 cc. of the same alcohol were cooled to 0° and mixed. The mixture was left to itself for three hours during which the temperature was allowed to rise to that of the room. The orange-colored solution was then evaporated under diminished pressure and the residue poured into ether and ice water. The ethereal layer was thoroughly washed with ice water, which reduced the color to a very pale yellow, then dried with calcium chloride, concentrated, mixed with an equal volume of low-boiling petroleum ether and inoculated with both acetals. It deposited in the course of a week 15.5 g. of the higher and 2.2 g. of the lower-melting acetal. The bromomethoxy compound III on similar treatment gave almost exactly the same results: 14.9 g. of the higher-melting and 2.0 g. of the lower-melting acetal from 50 g. of the bromo ketone.

Anal. Calcd. for $C_{18}H_{21}O_4Br$: C, 56.7; H, 5.5; OCH_3, 24.4. Found: (90°) C, 56.8; H, 5.6; OCH_3, 24.5. Found: (77°) C, 56.6; H, 5.5; OCH_3, 25.0.

The acetals are moderately soluble in petroleum ether, readily soluble in ether and other common organic solvents. Neither is stable in the air; the crystals of the higher-melting form gradually become opaque as they become covered with a film of the hydrolysis product and the lower-melting modification soon liquefies and then, as hydrolysis becomes nearly complete, resolidifies.

Hydrolysis.—When the acetals are hydrolyzed with dilute acetic acid, each gives

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[6] Weygand, *Ann.*, **459**, 118 (1927).

[7] Middleton, THIS JOURNAL, **45**, 2763 (1923).

but one compound, while treatment with methyl alcoholic hydrochloric acid generally gives a mixture of both hydrolysis products. A solution of 5 g. of the higher-melting isomer in 25 g. of glacial acetic acid was diluted with an equal volume of water, and then digested on a steam-bath for thirty minutes. The clear colorless solution, on dilution, precipitated a colorless oil. This was collected in ether. The washed and dried ethereal solution on evaporation deposited a colorless solid which separated from ether–petroleum ether in stout needles or plates melting at 89°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 57.3; H, 4.5; OCH_3, 9.2. Found: C, 57.2; H, 4.7; OCH_3, 9.4.

The lower-melting isomer, when treated in the same manner, gave a product which crystallized in tables or stout prisms and melted at 96°.

Anal. Calcd. for $C_{16}H_{15}O_3Br$: C, 57.3; H, 4.5; OCH_3, 9.2. Found: C, 57.1; H, 4.8; OCH_3, 8.7.

In the machine[8] these isomeric hydrolysis products behaved alike; each consumed two moles of reagent and liberated one mole of gas.

The Grignard Products, α-Phenyl-α-methoxy-β-hydroxy-γ-phenyl-γ-(4-bromophenyl)-γ-hydroxy-propane, VI.—An ethereal solution of 1.5 g. of the hydrolysis product (89°) was added to a solution of phenyl magnesium bromide prepared from 1 g. of magnesium. The mixture was boiled for fifteen minutes and then decomposed with iced acid. After the usual manipulations the operation yielded 1.5 g. of a solid product which crystallized from ether–petroleum ether in fine needles and melted at 119–120°.

Anal. Calcd. for $C_{22}H_{21}O_3Br$: C, 64.0; H, 5.1; OCH_3, 7.5. Found: C, 64.0; H, 5.3; OCH_3, 7.5.

The glycol is sparingly soluble in petroleum ether, readily soluble in ordinary ether and in methyl alcohol. It is very readily oxidized by chromic acid. A solution of 0.45 g. of the substance in 20 g. of glacial acetic acid was warmed to 70°. Into this solution was dropped an aqueous solution of chromic acid as long as the color disappeared immediately. The solution was then poured into cold water, which precipitated a crystalline solid. This was identified as pure *p*-bromobenzophenone by comparison with a sample on hand. The filtrate from the ketone was saturated with salt and extracted with ether. The ethereal solution, freed from acids by extraction with bicarbonate, was evaporated. It left an oil which was identified as methyl benzoate by the odor and by hydrolysis to benzoic acid.

The isomeric hydrolysis product (96°) was also treated with phenyl magnesium bromide but failed to give a crystalline product. The colorless oil that was left after evaporating the ethereal solution was therefore oxidized with chromic acid. Like its isomer it yielded *p*-bromobenzophenone, methyl benzoate and no other products. The hydrolysis products and the acetals from which they are formed must, therefore, be stereoisomers.

The Ethyl Acetal, $C_6H_5CHOC_2H_5CHOHC(OC_2H_5)_2C_6H_4Br$.—When the dibromide of benzal-*p*-bromo-acetophenone was shaken with excess of cold sodium ethylate it yielded, after the usual manipulation, a pale yellow solution that ultimately solidified almost completely. The solid was composed mainly of β-ethoxy-benzal-*p*-bromo-acetophenone and an acetal. The unsaturated ethoxyl compound was readily isolated because it is far less soluble than the acetal but the isolation of pure acetal required patient fractional crystallization. It separates from petroleum ether in large colorless plates and melts at 99°.

Anal. Calcd.: C, 59.6; H, 6.4; OC_2H_5, 31.9. Found: C, 59.8; H, 6.6; OC_2H_5, 30.6.

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[8] Kohler and Richtmyer, THIS JOURNAL, **52**, 3736 (1930).

Hydrolysis, $C_6H_5CHOCH_2CH_5OHCOC_6H_4Br$.—The acetal, like the corresponding methoxyl compounds, is unstable in the air of the laboratory; it first liquefies, then resolidifies. The solid is the pure hydroxy ketone. This is easily obtained in quantity by hydrolyzing the acetal with dilute acetic acid in the usual manner. It is readily soluble in all organic solvents, crystallizes in needles and melts at 72°.

Anal. Calcd. for $C_{17}H_{17}O_3Br$: C, 58.4; H, 4.9; OC_2H_5, 12.9. Found: C, 58.4; H, 5.2; OC_2H_5, 14.2.

β-Ethoxy-benzal-*p*-bromo-acetophenone, $C_6H_5C(OC_2H_5){=}CHCOC_6H_4Br$.—The ethoxyl compound crystallizes well from all solvents, separating in plates from methyl alcohol and in very large tables from ether and from petroleum ether. It melts at 112° and on hydrolysis yields *p*-bromodibenzoylmethane.

Anal. Calcd. for $C_{17}H_{15}O_2Br$: C, 61.6; H, 4.5. Found: C, 61.7; H, 4.6.

II. Other Dibromides

A. *p*-Nitro Compounds

The behavior of a few other dibromides was examined for the purpose of ascertaining how the distribution of the material is affected by the presence of substituents in the phenyl groups. Wieland[2] treated the dibromide of *p*-nitro-benzalacetophenone (VII) with methyl alcoholic potassium hydroxide and obtained only the dimethyl acetal of *p*-nitrodibenzoylmethane. We employed sodium methylate and extended the experiments to include the two stereoisomeric unsaturated α-bromo compounds VIII, and the bromo methoxyl compound IX. All of these substances yielded at least 95% of the acetal obtained by Wieland.

$NO_2C_6H_4CHBrCHBrCOC_6H_5$
VII

$NO_2C_6H_4CH{=}CBrCOC_6H_5$
VIII

$NO_2C_6H_4CHOCH_3CHBrCOC_6H_5$
IX

α-Bromo-*p*-nitrobenzalacetophenone, VIII.—Weygand[9] boiled the dibromide VII with methyl alcoholic potassium acetate for eight hours and distilled the product in a high vacuum. He obtained an α-bromo compound that melted at 106°. This was evidently a mixture of the two stereoisomers. We suspended the dibromide in a mixture of equal volumes of acetone and methyl alcohol, added excess of potassium acetate and allowed the reaction to proceed in the cold. All the dibromide disappeared within an hour. The solution was evaporated in a current of air. It left an oil that soon solidified. By systematic fractional crystallization from acetone–methyl alcohol mixtures the solid was separated into pale yellow needles melting at 130° and darker yellow plates that melted at 62°.

Anal. Calcd. for $C_{15}H_{10}O_3NBr$: C, 54.2; H, 3.0. Found: (136°) C, 54.6; H, 3.1. (62°) C, 54.2; H, 3.1.

The Bromo Methoxy Compound IX.—The preparation of this substance is exceedingly difficult because the reaction between the unsaturated ketone and mercuric acetate is both slow and incomplete even in boiling methyl alcohol. The mercury compound was not purified but treated directly with bromine. The product crystallized from acetone and methyl alcohol in colorless plates melting at 131°.

Anal. Calcd. for $C_{16}H_{14}O_4NBr$: C, 52.7; H, 3.8. Found: C, 52.8; H, 4.0.

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[9] Weygand, Ref. 6, p. 116.

All three of these compounds were treated with sodium methylate in the usual manner, but instead of attempting to isolate the acetals, the entire product was hydrolyzed with acetic acid. The residue left after removing the β-diketone as copper derivative in no case equaled 5% of the bromo compound that was used.

B. *m*-Nitro Compounds

In the *m*-nitro series we examined only the dibromide and the bromo methoxy compound. The former has been described by others; the latter was prepared as usual, by way of the mercury compound.

A suspension of 20 g. of the unsaturated ketone and an equivalent quantity of mercuric acetate in 500 cc. of dry methyl alcohol was boiled for twelve hours. The clear very pale yellow solution was concentrated step by step. It gradually deposited 20 g. of the mercury compound, which crystallized from acetone in hard nodules of colorless needles, sparingly soluble in ether and in methyl alcohol, readily soluble in acetone.

The mercury compound was suspended in methyl alcohol and treated with bromine. The reaction was very sluggish but the mercury compound gradually disappeared at the boiling point. The product, a colorless solid, was recrystallized from methyl alcohol.

Anal. Calcd. for $C_{16}H_{14}O_4NBr$: C, 52.7; H, 3.8. Found: C, 53.0; H, 4.0.

α-Bromo-β-methoxy-*n*-nitrobenzylacetophenone, $NO_2C_6H_4CHOCH_3CHBrCOC_6H_5$, is sparingly soluble in cold methyl alcohol, moderately soluble in hot methyl alcohol, readily soluble in acetone. It crystallizes from methyl alcohol in colorless needles melting at 132°. The yield was 80%.

α-Hydroxy-β-methoxy-*n*-benzylacetophenone, $NO_2C_6H_4CHOCH_3CHOHCOC_6H_5$.—The dibromide and the bromomethoxy compound were treated with sodium methylate in the usual manner, and in each case the mixture of products was immediately hydrolyzed with aqueous acetic acid. The ethereal solutions left after removing the β-diketone as copper derivative deposited the hydroxy ketone as a colorless solid. The substance was purified by recrystallization from ether–petroleum ether, from which it separated in colorless prisms melting at 110°. The yield from the dibromide was 30% and from the bromomethoxy compound 33%. As would be expected, the nitro group in the meta position has little influence.

Anal. Calcd. for $C_{16}H_{15}O_5N$: C, 63.8; H, 5.0. Found: C, 64.1; H, 5.2.

C. Anisyl Compounds

The behavior of the dibromide of benzalacetylanisole toward sodium methylate has been examined by Weygand[10] but we included it in our experiments because we expected it to be at least as favorable for the formation of the new type of acetal as the corresponding *p*-bromo compound. We have been unable to establish this because we did not succeed in getting either the acetal or its hydrolysis product in a crystalline form. In another respect, however, the behavior of the dibromide was gratifying; it provided the first case in which the dibromide could be transformed directly into the α-bromo-β-methoxy derivative.

α-Bromo-β-methoxy-benzylacetylanisole, $C_6H_5CHOCH_3CHBrCOC_6H_4OCH_3$.—A solution of 6 g. of sodium in 120 g. of anhydrous methyl alcohol was added to a suspension of 43.5 g. of the dibromide in 75 cc. of the same solvent. The mixture was shaken

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[10] Weygand, Ref. 6, p. 107.

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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RECEIVED AUGUST 12, 1930 PUBLISHED SEPTEMBER 5, 1930

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.

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