desoxybenzoin is in reality desoxybenzoin; the true methyl ether has been obtained by the action of diazomethane on the oxymethylene ketone. Certain of the reactions of the acetals and the methyl ether are described and a general outline of the behavior of oxymethylene ketones toward alkylating agents is presented.

WASHINGTON, D. C. RECEIVED JANUARY 26, 1938

[CONTRIBUTION FROM MELLON INSTITUTE OF INDUSTRIAL RESEARCH AND E. R. SQUIBB & SONS]

Halogeno-alkyl Glycosides. II. Dihalogeno-alkyl Derivatives

BY HAROLD W. COLES,[1] MARY L. DODDS[1] AND FRANK H. BERGEIM[2]

The preparation of various monohalogeno-alkyl glycosides has been described.[3] It was indicated in that paper that the ease of preparation was influenced by the stability of the acylhalogeno sugar, the type of halogenohydrin employed, and whether the bromo- or chlorohydrin was used. It seemed desirable to determine whether dihalogen compounds, such as glycerol dichlorohydrin or dibromohydrin, could be condensed with acylhalogeno sugars in the presence of silver carbonate.

A number of syntheses were carried out. It was found that the dihalogenohydrins condensed much less readily with acetobromoglucose or acetobromoxylose than did the monohalogenohydrins. The β-benzobromoglucose condensed with glycerol dichlorohydrin to form a white crystalline substance which, despite repeated recrystallizations, did not analyze correctly.

The condensations are described in the experimental part. The authors are indebted to Dr. George D. Beal, Assistant Director of Mellon Institute, for his advice during the progress of this work.

Experimental Part

Tetraacetyl-β-*d*-(dibromomethyl-methyl)-glucoside.—Six grams of β-acetobromoglucose, 7.2 g. of silver carbonate and 68.1 g. of glycerol α,γ-dibromohydrin were combined in a small Erlenmeyer flask. The evolution of carbon dioxide was slight. The flask was warmed very cautiously on the water-bath for several hours which increased the production of carbon dioxide. The flask was allowed to stand overnight at room temperature in complete darkness.

The silver salts were removed by filtration and washed with a very small amount of hot methanol. The condensation product was thrown out of solution by the addition of 50% methanol to the filtrate. The colorless needles formed slowly and crystallization was completed by immersion of the flask in ice water. The crystals were removed to a Büchner funnel where they were washed with cold 50% methanol. They were recrystallized from a minimum of hot methanol. The yield was very low. The crystals, which gave a strong Beilstein test for halogen, melted at 107.5°.[4]

Anal. Calcd. for $C_{17}H_{24}O_{10}Br_2$: Br, 29.16. Found: Br, 28.98.[5]

Tetraacetyl-β-*d*-(dichloromethyl-methyl)-glucoside.—The reaction between 13 g. of acetobromoglucose, 7.2 g. of silver carbonate and 20 g. of glycerol α,γ-dichlorohydrin was permitted to proceed overnight at room temperature in total darkness. The silver salts were removed and washed with a small amount of hot absolute alcohol. Considerable distilled water was added to the filtrate, which addition threw out a mobile oil. The supernatant liquid was decanted, and the oil washed several times with water.

The oil was taken up in a small amount of alcohol, and the solvent slowly removed by vacuum. Crystals started to form, and crystallization was completed by the addition of a small amount of water and chilling. The crystals were washed on a Büchner funnel with a cold alcohol-water mixture. The crystals were redissolved in a small amount of hot absolute alcohol, the solution filtered, and crystallization completed by strong chilling. The colorless crystals melted at 122–123°; yield 1 g.

Anal. Calcd. for $C_{17}H_{24}O_{10}Cl_2$: C, 44.44; H, 5.26. Found: C, 44.56; H, 5.29.

Triacetyl-β-*d*-(dibromomethyl-methyl)-xyloside.—This compound was obtained as the result of the reaction between 18.7 g. of glycerol α,γ-dibromohydrin, 5 g. of acetobromoxylose and 5 g. of silver carbonate. This mixture was allowed to stand at room temperature until all spontaneous bubbling ceased. The flask was warmed gently on the water-bath, which quickened the evolution of carbon dioxide, for one-half hour, and was then stored overnight.

The silver salts were removed and washed with a small amount of absolute alcohol. A large amount of distilled water was added to the alcohol filtrate, at which the condensation product and the excess dibromohydrin were thrown out. The supernatant liquid was removed by means of a separatory funnel. Enough alcohol was added to the dibromohydrin layer to take the dibromohydrin into solution, and the supernatant liquid decanted from the residual sirup. The sirup was washed several times with

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[2] Research Laboratories, E. R. Squibb & Sons, Brooklyn, N. Y.

[3] Coles, Dodds and Bergeim, THIS JOURNAL, **60**, 1020 (1938).

[4] Melting points are corrected for stem exposure.

[5] Micro-analyses by Saul Gottlieb, Columbia University.

an alcohol–water mixture and crystallized spontaneously. These crystals were recrystallized from an alcohol–water mixture. They gave the usual Beilstein test for halogen, did not reduce Benedict's solution, and melted at 156–157°.

Anal. Calcd. for $C_{14}H_{20}O_8Br_2$: C, 35.29; H, 4.23. Found: C, 35.53; H, 4.42.

Summary

Glycerol α,γ-dibromohydrin was condensed with acetobromoglucose and acetobromoxylose to give tetraacetyl-*β*-*d*-(dibromomethyl-methyl)-glucoside and triacetyl-*β*-*d*-(dibromomethyl-methyl)-xyloside, respectively.

Glycerol α,γ-dichlorohydrin was condensed with acetobromoglucose to give tetraacetyl-*β*-*d*-(dichloromethyl-methyl)-glucoside.

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BROOKLYN, N. Y. RECEIVED MARCH 19, 1938

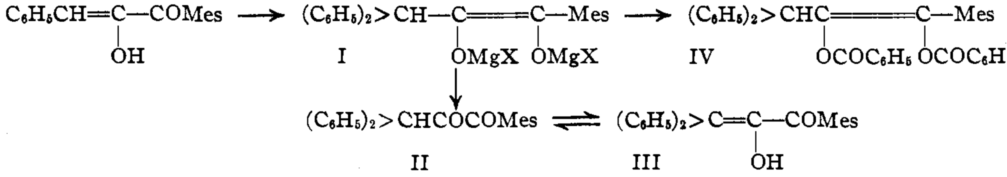
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

Steric Hindrance in Alpha Diketones. II. Mesitylbenzylglyoxal

BY R. P. BARNES

In an earlier paper[1] we stated that other carbonyl group reactions of mesitylbenzylglyoxal were still under investigation. Recently, however, Kohler and Thompson[2] have reported several of the products which we have obtained by different methods. It is, therefore, the purpose of this paper to set forth the results of our investigation.

Because of steric hindrance to 1,2-addition to the carbonyl, phenylmagnesium bromide reacts by 1,4-addition with the enolic modification of mesitylbenzylglyoxal, producing a compound which is very obviously a magnesium dienolate (I), since it yields a dibenzoate (IV). Upon acidification, the magnesium derivative gives rise to a yellow oil, which presumably is the diketone (II), for it is easily isomerized to the enol (III).

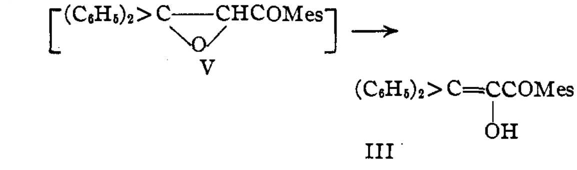


$$C_6H_5CH{=}\underset{OH}{C}{-}COMes \longrightarrow \underset{I}{(C_6H_5)_2{>}CH{-}\underset{OMgX}{C}{=}\underset{OMgX}{C}{-}Mes} \longrightarrow \underset{IV}{(C_6H_5)_2{>}CHC{=}\underset{OCOC_6H_5}{C}{-}\underset{OCOC_6H_5}{C}{-}Mes}$$

$$\downarrow$$

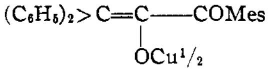
$$\underset{II}{(C_6H_5)_2{>}CHCOCOMes} \rightleftharpoons \underset{III}{(C_6H_5)_2{>}C{=}\underset{OH}{C}{-}COMes}$$

The structure of the enol (III) was established by converting *β*-phenylbenzalacetomesitylene, by way of its oxide, (V), into the enol (III).



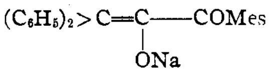
$$(C_6H_5)_2{>}C{=}CHCOMes \longrightarrow \underset{V}{\left[(C_6H_5)_2{>}C\overset{O}{—}CHCOMes\right]} \longrightarrow \underset{III}{(C_6H_5)_2{>}C{=}\underset{OH}{C}COMes}$$

This enol is 100% enolic as shown by indirect titrations with bromine; reacts with methylmagnesium iodide to give one mole of methane; forms metallic derivatives (VI) and (VII); and is cleaved by alkaline hydrogen peroxide to benzophenone and trimethylbenzoic acid.



$$(C_6H_5)_2{>}C{=}\underset{OCu^{1}/_{2}}{C}{—}COMes$$

VI



$$(C_6H_5)_2{>}C{=}\underset{ONa}{C}{—}COMes$$

VII

On bromination the enol is converted quantitatively into the α-monobromo ketone (VIII). An acetone solution of the pale yellow enol is partially cleaved by potassium permanganate to benzophenone and trimethylbenzoic acid and partially oxidized to the more highly colored tetraketone (IX). The same tetraketone is obtained by the interaction of iodine and the sodium salt (VII). The C–C linkage between the two symmetrical halves of the tetraketone does not seem to be particularly strong, which fact is evidenced by its ease of bromination, yielding a monobromo ketone which is identical with the bromination product, (VIII), of the enol. This is further substantiated by the fact that it is oxidized to trimethylbenzoic acid and benzophenone by alkaline hydrogen peroxide.

Here, as in the case of mesitylbenzylglyoxal,[1] the mesityl group seems to promote enolization and exert a stabilizing influence upon the enol. This influence seems to manifest itself directly in con-

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[1] R. P. Barnes, THIS JOURNAL, 57, 937 (1935).

[2] E. P. Kohler and R. B. Thompson, *ibid.*, 59, 887 (1937).