

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 $C_{14}H_{20}O_5Br_2$: 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.

PITTSBURGH, PENNA.
BROOKLYN, N. Y.

RECEIVED MARCH 19, 1938

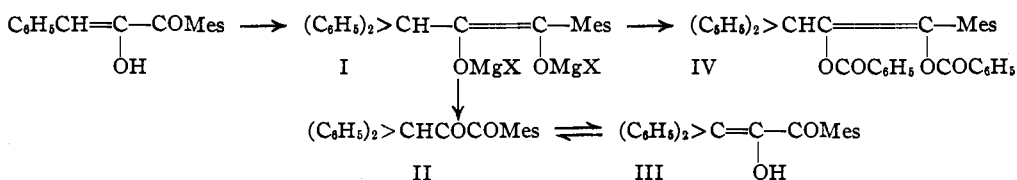
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HOWARD UNIVERSITY]

Steric Hindrance in Alpha Diketones. II. Mesitylbenzylglyoxal

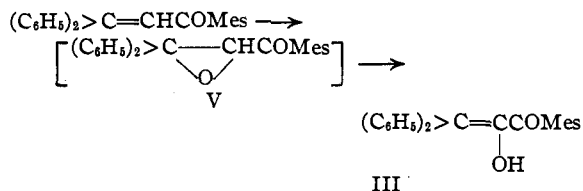
BY R. P. BARNES

In an earlier paper¹ we stated that other carbonyl group reactions of mesitylbenzylglyoxal were still under investigation. Recently, however, Kohler and Thompson² 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).

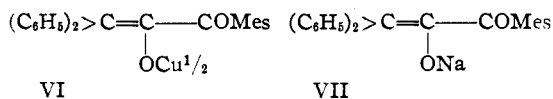


The structure of the enol (III) was established by converting β -phenylbenzalacetomesitylene, by way of its oxide, (V), into the enol (III).



This enol is 100% enolic as shown by indirect titrations with bromine; reacts with methylmag-

nesium 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.



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-

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

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

Oxidation. The Tetraketone, IX.—A solution of 2 g. of the enol in non-reducing acetone was oxidized with potassium permanganate. The manganese dioxide was filtered off and washed with acetone. The solution was decolorized with sulfur dioxide and refiltered. The acetone was distilled off and the deep yellow oily residue taken up in ether and washed with sodium carbonate. The aqueous layer yielded 0.3 g. of trimethylbenzoic acid, identified by comparison with an authentic sample. The ethereal layer was concentrated and steam distilled, yielding 0.4 g. of benzophenone. The yellow residue upon crystallization from ether, deposited 1.2 g. of deep yellow crystalline solid, which melted at 192°.

An absolute ethereal suspension of 1.5 g. of the sodium derivative of the enol was treated with 1 g. of iodine dissolved in absolute ether. Sodium iodide separated out. The solution was decolorized with sodium thiosulfate, washed with water, dried and evaporated. The residue was taken up in methyl alcohol which deposited 0.2 g. of deep yellow plates, melting at 192°. The mixed melting point with the oxidation product was the same.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 84.4; H, 6.2. Found: C, 84.7; H, 6.5.

A methyl alcoholic solution of 0.5 g. of the tetraketone was heated with excess alkaline hydrogen peroxide. Very slowly the color faded. The ethereal extract of the alkaline solution yielded benzophenone; the alkaline solution upon acidification gave trimethylbenzoic acid.

A solution of 1 g. of the tetraketone in chloroform was treated with an excess of bromine with gentle warming. A deep yellow bromo compound, identical in melting point and mixed melting point with that produced from the enol, was obtained.

Alkylation Product, X.—To a solution of 10 g. of the enol in 30 cc. of methyl alcohol was added 16.4 g. of methyl iodide. To this solution was added dropwise 10% sodium methylate equivalent to 3.5 g. of sodium. The solution turned red with each drop of methylate. It was refluxed for six hours. Finally it was poured into water and extracted with ether and washed with water. The solution was evaporated and residue taken up in methyl alcohol. It crystallized, yielding a practically colorless solid, melting at 53°, which gave no color with alcoholic ferric chloride.

Anal. Calcd. for $C_{24}H_{21}O-OCH_3$: $-OCH_3$, 8.71. Found: $-OCH_3$, 8.96.

Oxybenzhydrylmesitylgyoxal, XIII.—A solution of 7 g. of the α -bromoketone in 75 cc. of glacial acetic acid was re-

fluxed for thirty minutes with 15 g. of freshly fused potassium acetate. A colorless solid, which proved to be potassium bromide, separated out. The reaction mixture was allowed to cool and was poured into a large volume of water. A deep yellow oil separated out which solidified. It was recrystallized from ether as golden-yellow plates which melted at 125°. The mixed melting point with the parent bromo compound was 110°. The yield was 6 g.

Anal. Calcd. for $C_{24}H_{22}O_3$: C, 80.4; H, 6.1. Found: C, 80.0; H, 6.2.

Excess acetyl chloride was added to 2 g. of the α -oxy- α -diketone and the solution refluxed for an hour. The excess acetyl chloride was pumped off and the deep yellow oily residue crystallized, giving a quantitative yield of a sweet-smelling, golden-yellow solid, melting at 132°.

Anal. Calcd. for $C_{26}H_{24}O_4$: C, 78.0; H, 6.0. Found: C, 78.14; H, 6.07.

This acetate upon warming with alcohol and sulfuric acid gives an odor of ethyl acetate, and a yellow oil which crystallizes from both alcohol and ether in golden-yellow plates that melt at 125°; mixed melting point with the oxy compound unchanged.

Treatment of a glacial acetic acid solution of the oxy compound with concd. hydrobromic acid gives again the α -bromo compound, identified by its melting point and mixed melting point.

Reaction of the Enol of Mesitylbenzylglyoxal with Methylmagnesium Iodide.—A methylmagnesium iodide solution made from 2.1 g. (3 moles) of magnesium was treated with an ethereal solution of 7.5 g. (1 mole) of the enol of mesitylbenzylglyoxal. With the addition of each drop of the enol a cherry-red color developed and gas was produced. After complete addition the reaction mixture was refluxed for one-half hour, and finally decomposed with ice and hydrochloric acid. A total recovery of 6 g. of pure unchanged starting material was made.

Summary

1. Further evidences of the steric hindrance effects of the mesityl nucleus to 1,2-addition to the carbonyl are herein presented, together with its attendant effect in promoting enolization and stabilizing the enol.

2. The preparation of an α -oxy- α -diketone is given.

WASHINGTON, D. C.

RECEIVED MARCH 11, 1938