

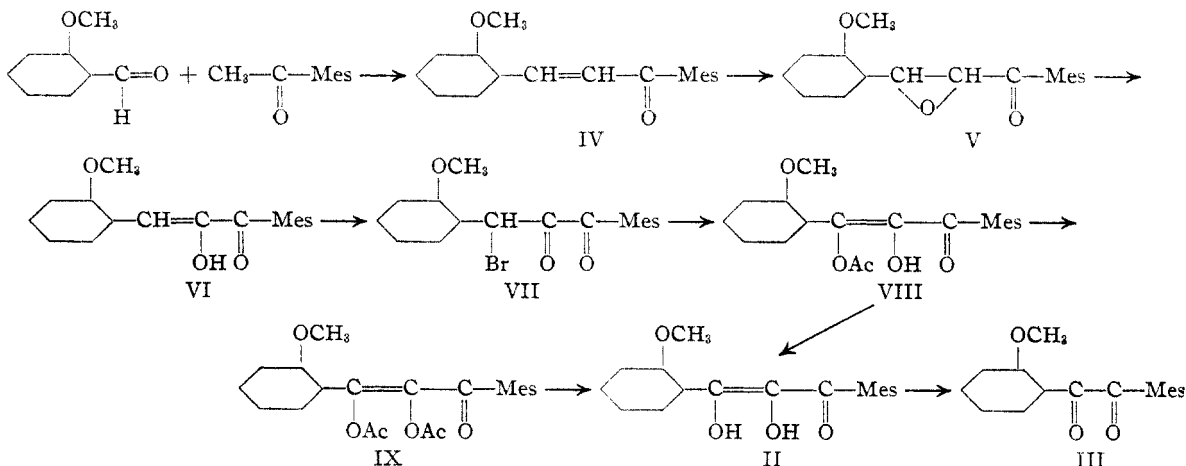
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HOWARD UNIVERSITY]

The Preparation and Properties of an Ene-diol. α -*o*-Methoxyphenyl- β -mesityl-acetylene Glycol

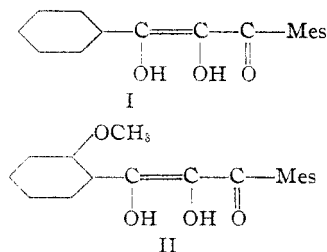
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The effect of 2,2'-dimethoxyl substitution on the stability of benzoin and its ene-diolic modifi-

cates the manner in which the ene-diol (II) is obtained



cation has already been pointed out.² This work was undertaken to determine the effect of introducing the methoxyl group in the ortho position of the phenyl group in α -phenyl- β -mesitylacetyleneglycol³ (I). It has been found that the methoxyl-substituted compound (II) is more stable than the unsubstituted compound (I).



The ene-diol (II) is a colorless needle-like crystalline solid, extremely soluble in alcohol, very appreciably soluble in water and only sparingly soluble in ether and petroleum ether. It gives a deep greenish-blue color with alcoholic ferric chloride, which color fades gradually to yellow. It bleaches iodine and 2,6-dichlorobenzeneoneindophenol. It is slowly oxidized by atmospheric oxygen. The end-product of these reactions is *o*-methoxyphenylmesityl diketone (III).

The following schematic representation indi-

Experimental

α -Methoxybenzalacetomesitylene (IV).—A solution of 15 g. of sodium hydroxide in 40 cc. of water was diluted with 100 cc. of alcohol. To this alkaline alcoholic solution was added 23 g. of acetylmesitylene with stirring and chilling. To this cold solution was added slowly and with stirring 28 g. of *o*-methoxybenzaldehyde. At the end of twenty minutes considerable solid material had separated. Stirring was continued for one hour. The product was filtered, washed, dried and recrystallized from alcohol. The yield was 36 g. of a pale yellow solid, melting at 95°.

Anal. Calcd. for $C_{19}H_{20}O_2$: OCH_3 , 11.07. Found: OCH_3 , 11.06.

α -*o*-Methoxyphenyl- β -mesitylethylene Oxide (V).—To a solution of 31 g. of α -methoxybenzalacetomesitylene in 200 cc. of alcohol was added 14 cc. of 30% hydrogen peroxide. This solution was made alkaline with 25 cc. of 20% sodium hydroxide. It was warmed gently with stirring. As the reaction proceeded considerable heat was evolved. The reaction mixture was maintained at room temperature by cooling. On standing in the cold a cream-colored solid separated. The solution was diluted with water and the product was filtered, washed and dried. Recrystallized from alcohol, the yield was 26 g. of colorless solid, melting at 73–74°.

Anal. Calcd. for $C_{19}H_{20}O_3$: OCH_3 , 10.47. Found: OCH_3 , 10.29.

The Enolic Modification of Mesityl-*o*-methoxybenzylglyoxal (VI).—To a solution of 23 g. of the ethylene oxide, dissolved in 125 cc. of alcohol, was added a solution of 15 g. of sodium hydroxide in 30 cc. of water. The mixture was boiled gently for ten minutes. The solution became deep yellow in color. It was cooled and poured into a cold dilute solution of hydrochloric acid. A pale yellow solid

(1) In partial fulfillment of the requirements for the Master's degree.

(2) R. P. Barnes and W. M. Lucas, *THIS JOURNAL*, **64**, 2258 (1942).

(3) R. P. Barnes and Leila S. Green, *ibid.*, **60**, 1549 (1938).

separated. The solid was filtered, washed, dried and recrystallized from alcohol. The yield was 16 g., melting at 137°.

Anal. Calcd. for $C_{19}H_{20}O_3$: OCH_3 , 10.47. Found: OCH_3 , 10.60.

An alcoholic solution of this substance gives a cherry-red color with ferric chloride. Kurt Meyer titrations⁴ indicate that it is 98% enolic.

α -Bromo-*o*-methoxybenzylmesitylglyoxal (VII).—To a solution of 8 g. of the enol in 75 cc. of carbon tetrachloride was added 8 g. of precipitated calcium carbonate. A solution of 4.4 g. of bromine in 30 cc. of carbon tetrachloride was added dropwise with stirring to the solution containing the calcium carbonate in suspension. Hydrogen bromide was evolved. The enol in solution decolorized the bromine solution instantaneously with the addition of each drop. The resulting orange-colored solution was filtered from the suspended material, and evaporated in a stream of dry air. Final traces of carbon tetrachloride and moisture were removed *in vacuo*. Eleven grams of a deep yellow oil resulted. This oil was crystallized from methanol in golden-yellow needles, melting at 84°.

Anal. Calcd. for $C_{19}H_{19}O_3Br$: OCH_3 , 8.2. Found: OCH_3 , 8.3.

The bromo compound is non-enolic.

The Acetate of α -Oxy-*o*-methoxybenzylmesityl- α -diketone (VIII).—To a solution of 5.5 g. of the bromo compound in 50 cc. of acetic acid was added 11 g. of freshly fused potassium acetate. The solution was refluxed gently for four hours. It turned cherry-red. The solution was cooled thoroughly and poured into a large volume of cold water and stirred vigorously. A yellow oil separated and solidified. It was filtered, washed and dissolved in alcohol. On chilling a cream colored solid separated, melting from 84–86°. On recrystallization from alcohol, it melted at 94°. The yield was 3 g.

Anal. Calcd. for $C_{21}H_{22}O_5$: OCH_3 , 8.75. Found: OCH_3 , 8.84.

This compound in alcoholic solution gives a cherry-red color with alcoholic ferric chloride. It is enolic⁴ to the extent of 80%.

The Diacetate of α -*o*-Methoxyphenyl- β -mesitoylacetylene Glycol (IX).—One gram of the monoacetate was dissolved in 10 cc. of acetyl chloride and refluxed for one hour. The excess acetyl chloride was pumped off and the oily residue taken up in alcohol, from which solution a colorless solid, melting at 103–104°, was obtained. The yield was 0.8 g.

Seven grams of the bromo compound was dissolved in 66 g. of acetic anhydride, to which solution 10 g. of freshly fused potassium acetate was added. The mixture was refluxed gently for one and one-half hours. It became light yellow and potassium bromide separated. The thoroughly chilled mixture was poured into a large volume of cold

water and stirred. An orange-red oil separated. It was washed several times with cold water and finally taken up in alcohol, from which solution a colorless solid melting and mix-melting with the above substance at 103–104°, was obtained.

Anal. Calcd. for $C_{23}H_{24}O_6$: OCH_3 , 7.83. Found: OCH_3 , 7.84.

This substance gives no color with alcoholic ferric chloride.

α -*o*-Methoxyphenyl- β -mesitoylacetylene Glycol (II).—Four grams of the monoacetate was dissolved with stirring in 50 cc. of cold concd. sulfuric acid. The solution was orange colored. It was allowed to stand for thirty minutes at 0°. It was then poured onto finely cracked ice in a g. s. flask. The air in the flask was displaced by nitrogen, the flask was stoppered and shaken vigorously. A fine needle-like colorless solid separated. It was allowed to stand overnight at 0°. It was filtered, washed with a little iced water, then with ether. It was recrystallized from dilute alcohol, yielding 3 g., melting at 105°.

Four grams of the diacetate was treated similarly. The result was about 2 g. of colorless needles, melting and mix-melting with the above substance at 105°.

Anal. Calcd. for $C_{19}H_{20}O_4$: OCH_3 , 9.9. Found: OCH_3 , 9.8.

This substance is extremely soluble in alcohol and quite soluble in water. It is rather insoluble in ether and insoluble in petroleum ether. It produces a bluish-green color with alcoholic ferric chloride, which color fades gradually to yellow. It decolorizes iodine solution and bleaches 2,6-dichlorobenzeneoneindophenol instantaneously.

The Diketone (III).—Alcoholic test solutions of the ene-diol with ferric chloride, iodine and indophenol blue all resulted in yellow solutions from which a yellow solid, melting at 132°, was obtained. Atmospheric oxidation goes on slowly producing a more highly colored solid, which upon crystallization results in the same light yellow solid, melting at 132°.

Anal. Calcd. for $C_{18}H_{18}O_3$: OCH_3 , 10.89. Found: OCH_3 , 10.90.

The diketone is cleaved by alkaline hydrogen peroxide, yielding mesitoic and *o*-methoxybenzoic acids, identified by comparison with known samples.

Summary

A new ene-diol, α -*o*-methoxyphenyl- β -mesitoylacetylene glycol, has been synthesized and its properties listed.

The *o*-methoxyl in the phenyl group has rendered the ene-diol more stable than the unsubstituted α -phenyl- β -mesitoylacetylene glycol.

The only product which is obtainable from oxidation reactions is the diketone.

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(4) S. R. Cooper and R. P. Barnes, *Ind. Eng. Chem., Anal. Ed.*, **10**, 379 (1938).