

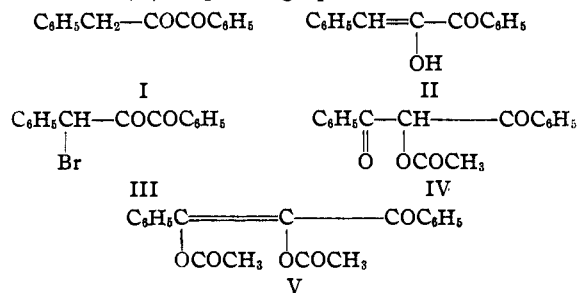
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

## The Preparation and Properties of 2,4,6-Trimethylbenzylmesitylgyoxal

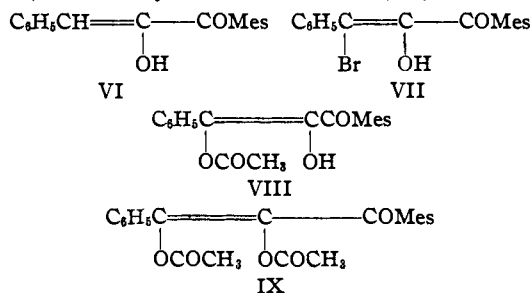
BY R. PERCY BARNES AND ALFRED E. BRANDON<sup>1</sup>

In 1934 Kohler and Barnes<sup>2</sup> began the study of a series of alpha diketones with benzyl phenyl diketone (I). In this study it was shown that both the ketonic (I) and enolic modification (II) existed in the solid state, and that each of these when dissolved, or melted and dissolved, reverted to an equilibrium mixture. We found that upon acetylation, only the O-derivative was obtained whereas upon methylation, a mixture of O- and C-products resulted.

It was discovered later<sup>3</sup> that phenyl bromobenzyl diketone (III) could be acetylated to either dibenzoyl carbinol acetate (IV) or to the diacetate (V), depending upon the medium.



In furthering this study we made the enolic modification of mesitylbenzylglyoxal<sup>4</sup> (VI), and found that it existed only in that form. Thus the effect of substituting the mesityl nucleus for the phenyl group in phenylbenzylglyoxal (I) is to increase enolization and stabilize the enol. Here methylation gives 100% O-compound, and acetylation 100% O-compound. Here the alpha bromo derivative (VII) is enolic, and gives rise to the expected enolic monoacetate (VIII), in contrast to the behavior of  $\alpha$ -bromophenylbenzylglyoxal (III), and also yields the diacetate (IX).<sup>5</sup>



When we substitute the mesityl nucleus for the phenyl group at the other end of the molecule,<sup>6</sup>

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

(2) E. P. Kohler and R. P. Barnes, *THIS JOURNAL*, **56**, 211 (1934).

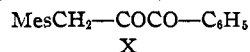
(3) R. P. Barnes and Victor J. Tulane, *ibid.*, **62**, 894 (1940).

(4) R. P. Barnes, *ibid.*, **57**, 937 (1935).

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

(6) R. Percy Barnes and Robert J. Brown, *ibid.*, **65**, 412 (1942).

in 2,4,6-trimethylbenzylphenylglyoxal (X), we find that the ketonic nature of the molecule is enhanced. The compound is 100% ketonic and does not brominate in the side chain. It does give 100% O-compound on acetylation, however.



In order to complete the study of the effect of the mesityl nucleus, we have now made and are reporting the properties of 2,4,6-trimethylbenzylmesitylgyoxal (XI).

2,4,6-Trimethylbenzalacetomesitylene (XII) was oxidized by means of alkaline hydrogen peroxide to isomeric forms of the ethylene oxide (XIII). The low-melting oxide was easily converted to the high-melting form by dissolving in ethanol and exposing to direct sunlight—the reverse could not be effected.

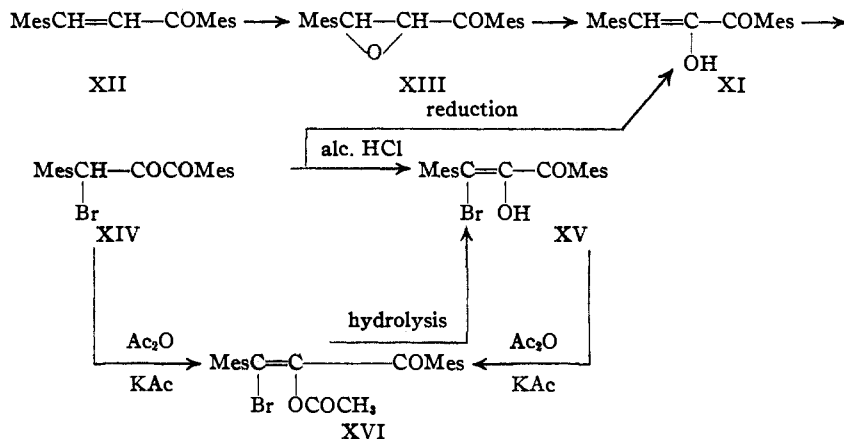
The isomeric ethylene oxides were isomerized with alkali to the corresponding enolic glyoxals (XI). We were unable to interconvert these enols, which were not completely enolic in alcoholic solution, as indicated by the modified Kurt Meyer titration.<sup>7</sup> Thus the symmetrical substitution in the phenyl groups renders these enols similar to phenylbenzylglyoxal, although the ketonic form could not be obtained. These isomeric oxides and enols are in all probability geometric isomers.

The isomeric enolic glyoxals (XI) were easily brominated in methanol to the same yellow monobromo derivative (XIV), which upon reduction with potassium iodide in acetone yields solely the high-melting enol. This bromo derivative does not produce any color with alcoholic ferric chloride. When refluxed with methanolic hydrochloric acid, a colorless enolic modification (XV) is obtained. Both of these bromo compounds when refluxed with acetic anhydride and freshly fused potassium acetate, yield the acetate (XVI) of the enolic form. In these respects these brominated isomeric glyoxals (XIV), (XV) differ from phenyl bromophenyl diketone (III). When the acetate is hydrolyzed in methanolic hydrochloric acid, the colorless enolic bromo compound (XV) is obtained.

## Experimental

**The Isomeric  $\alpha$ -Mesityl- $\beta$ -mesityl Ethylene Oxide: (XIII).—The low-melting form.** To a solution of 20 g. of 2,4,6-trimethylbenzalacetomesitylene in 250 cc. of methanol, maintained at 30°, was added 20 cc. of 30% hydrogen peroxide. The solution was made alkaline with a solution of 6 g. of sodium hydroxide in 50 cc. of water. The solution was stirred vigorously for one hour. The reaction mixture was then chilled, and a colorless solid separated

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



It was filtered, washed thoroughly with water and dried in air. The yield was practically quantitative. Recrystallization from methanol gave a colorless solid melting at  $95^\circ$ .

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2$ : C, 81.8; H, 7.8. Found: C, 82.1; H, 7.6.

*The high-melting form.*—A solution of 0.2 g. of the low-melting oxide in 5 cc. of ethanol in a stoppered flask was exposed to direct sunlight for two hours. The solution turned yellow and on chilling a colorless solid, melting at  $110^\circ$ , was obtained.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2$ : C, 81.8; H, 7.8. Found: C, 82.1; H, 7.6.

A solution of 20 g. of 2,4,6-trimethylbenzalacetomesitylene in 250 cc. of ethanol was treated as above. On chilling, the colorless solid which separated in a quantitative yield, when recrystallized from methanol, melted sharply at  $110^\circ$  and mix-melted with the above  $110^\circ$  melting material at  $110^\circ$ .

**The Isomeric Enolic Modifications of 2,4,6-Trimethylbenzylmethylglyoxal (XI).**—Twenty grams of the low-melting oxide was dissolved in 200 cc. of methanol. To this solution was added a solution of 15 g. of sodium hydroxide in 30 cc. of water. The mixture was stirred and boiled cautiously for twenty minutes. The solution turned yellow. It was chilled and acidified with dilute hydrochloric acid. A light tan-colored solid separated. The solid was filtered off, washed thoroughly with water, and dried. Recrystallization from methanol gave 14.1 g. of a light tan solid, melting at  $128^\circ$ .

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2$ : C, 81.8; H, 7.8. Found: C, 81.9; H, 7.8.

This substance produces a red color with alcoholic ferric chloride, and is enolic<sup>7</sup> to the extent of about 40%. From the mother liquors from the recrystallization was obtained a voluminous colorless paste upon dilution with water. This paste upon drying weighed only about 2 g. When recrystallized from methanol, it melted sharply at  $143^\circ$ .

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{24}\text{O}_2$ : C, 81.8; H, 7.8. Found: C, 81.9; H, 7.9.

This substance produces a red color with alcoholic ferric chloride, and is enolic<sup>7</sup> to the extent of about 70%.

Twenty grams of the high-melting oxide was isomerized as indicated above. On working up as above a practically quantitative yield of colorless solid melting and mix-melting with the above described colorless material at  $143^\circ$  was obtained.

These isomeric enols could not be interconverted as was true in case of the oxides.

**The Isomeric Bromo Derivatives of the Enols (XIV and XV).**—Five grams of each of the enols was suspended in 40 cc. of methanol in separate containers. To each was added slowly, with shaking, 2.5 g. of bromine dissolved in 10 cc. of methanol. The bromine was instantaneously decolorized

and a yellow solid began to separate. The solutions were shaken for five minutes, chilled and filtered. Each yielded about 5 g. of yellow solid which upon recrystallization from methanol, melted and mix-melted at  $137$ – $138^\circ$ .

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{Br}$ : C, 65.2; H, 5.9. Found: C, 65.3; H, 6.1.

This substance produces no color with alcoholic ferric chloride.

Two grams of the bromo compound was suspended in 75 cc. of methanol and 20 cc. of concd. hydrochloric acid was added. The suspension was refluxed for twelve hours. On chilling a colorless solid was obtained. Recrystallized from methanol, it melted at  $143^\circ$ . This substance mix-melts with the yellow monobromide at  $115$ – $120^\circ$ . It is enolic as indicated by the dark brown-green color produced with alcoholic ferric chloride. It is enolic<sup>7</sup> to the extent of about 5%.

*Anal.* Calcd. for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{Br}$ : C, 65.2; H, 5.9. Found: C, 65.3; H, 5.7.

One gram of each of the bromo compounds was dissolved in 20 cc. of acetone in separate containers. To each was added an excess of aqueous potassium iodide, and the solution made acid with a few drops of acetic acid. Each solution turned red. The liberated iodine was removed by stirring in a small amount of sodium sulfite. The solutions were poured into water, extracted with ether, washed with water, dried over anhydrous sodium sulfate and concentrated. Each produced the colorless high-melting enol, melting, and mix-melting with the original enol at  $143^\circ$ .

**The Acetate of the Enolic Modification of the Bromo-compound (XVI).**—In separate containers, 4 g. of each of the monobromo compounds was dissolved in 80 cc. of acetic anhydride, to which 8 g. of freshly fused potassium acetate was added. The solutions were refluxed for one hour, then chilled and poured into large volumes of water. On cooling, a brown solid separated. It was filtered, washed, dried, and recrystallized from methanol as a yellow solid which melted at  $133$ – $134^\circ$ . It mix-melts with the yellow bromo compound at  $110$ – $115^\circ$ .

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{26}\text{O}_4\text{Br}$ : C, 64.3; H, 5.8. Found: C, 64.5; H, 5.9.

This compound gives a Beilstein test for halogen, and is non-enolic. It gives an odor of ethyl acetate when warmed with concd. sulfuric acid and ethanol.

Two grams of the acetate was dissolved in 50 cc. of hot methanol. To this hot solution were added 20 cc. of concd. hydrochloric acid and 25 cc. of methanol. The solution was refluxed for four hours and then chilled. A colorless solid separated which, upon washing with water and drying, weighed 1.2 g. It was recrystallized from methanol, melting at  $142$ – $143^\circ$  and mix-melting with the enolic bromo compound unchanged. It produces the same dark brown-green color with alcoholic ferric chloride.

## Summary

We have reported herein the preparation and properties of the enolic geometric isomers of

2,4,6-trimethylbenzylmesityl glyoxal obtained by way of the geometric isomeric  $\alpha$ -mesityl- $\beta$ -mesityl ethylene oxides.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

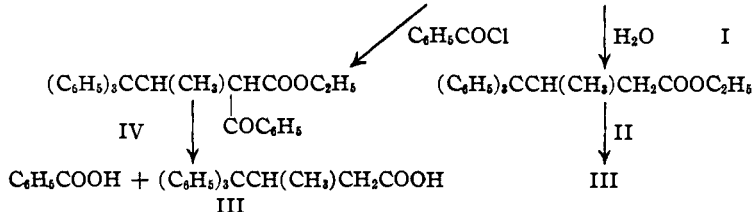
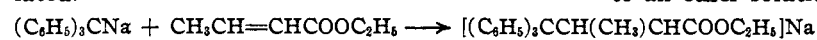
## The Reaction of Triphenylmethylsodium with Esters of $\alpha,\beta$ -Unsaturated Acids

BY WARREN D. MCPHEE AND EDDIE G. LINDSTROM

The use of triphenylmethylsodium has become an important method in synthetic chemistry.<sup>1</sup> The reagent has the ability of forming rather rapidly the sodium salts of the enol forms of most esters which have enolizable hydrogen atoms. It is a more powerful agent than sodium or potassium ethoxide, being capable of forming sodium enolates of esters that are unaffected by these reagents, such as ethyl isobutyrate and ethyl isovalerate.<sup>2</sup>

In the present investigation it was originally hoped that triphenylmethylsodium would be of value in enolizing esters of acetylenic acids prior to condensation with ethyl oxalate. Since sodium and potassium ethoxide are known to add to the triple bond of such esters, giving rise to complex products,<sup>3</sup> they are useless as condensation agents.

Preliminary experiments were carried out with triphenylmethylsodium and ethyl crotonate. It has been found that triphenylmethylsodium adds to the conjugated system of ethyl crotonate and effects little if any enolization of this ester. Ethyl crotonate instantaneously decolorizes the red solution of the reagent with the evolution of heat. Decomposition of the reaction mixture yields ethyl 3-methyl-4,4,4-triphenylbutyrate (II). This ester could not be obtained in crystalline form, but could be hydrolyzed to the corresponding acid (III) in 89% over-all yield. No triphenylmethane, the by-product of enolization, could be isolated.



This new ester (II) undoubtedly arises from the addition of triphenylmethylsodium to the conju-

gated double bond system of ethyl crotonate forming the organosodium complex (I). Hydrolysis of (I) liberates the ester (II).

In view of the fact that triphenylmethylsodium generally reacts with active hydrogen atoms, its addition to the conjugated system of ethyl crotonate is significant. This is the first case in which enolization, where possible, was not found to occur.<sup>4</sup>

The addition of triphenylmethylsodium to conjugated double bonds has been demonstrated by Ziegler and Jakob<sup>5</sup> in the case of butadiene. Three isomeric triphenylpentenes were obtained and one was shown to be the result of 1,4-addition by its oxidation to triphenylpropionic acid. Recently, Michael and Saffer<sup>6</sup> found that the reagent adds to ethyl and methyl cinnamate to form in low yield the esters of 3,4,4,4-tetraphenylbutyric acid. In all these examples, however, there is no enolizable hydrogen atom in any of the compounds used.

It is of interest that Michael and Saffer<sup>6</sup> did not observe any addition in the case of methyl crotonate. They treated an ether solution of methyl crotonate with triphenylmethylsodium and isolated triphenylmethane in 91% yield. This result is in marked contrast to our experience, namely, the isolation of the 1,4-addition product of ethyl crotonate in 89% yield. In order to determine whether or not the mode of addition could account for the difference, we added the reagent to an ether solution of ethyl crotonate and were able to isolate the acid (III) in 76% yield.

It had been expected that the sodium enolate of ethyl crotonate, if formed by reaction with triphenylmethylsodium, would react with benzoyl chloride to produce ethyl  $\gamma$ -benzoylcrotonate. However, it was found that

the product is ethyl 1-benzoyl-3-methyl-4,4,4-tri-

(1) Cf. Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Vol. I, Chapter 9.

(2) Hudson and Hauser, *THIS JOURNAL*, **63**, 3156 (1941); Hauser and Renfrow, *ibid.*, **59**, 1823 (1937).

(3) Feist, *Ann.*, **345**, 100 (1908); Wislicenus and Schöllkopf, *J. prakt. Chem.*, **95**, 269 (1917).

(4) Baumgarten and Hauser, in a private communication, report an experiment involving the addition of *n*-propyl crotonate to triphenylmethylsodium followed by treatment with solid carbon dioxide. None of the carbonated product could be isolated. This failure to carbonate is indirect evidence that the ester anion is not present.

(5) Ziegler and Jakob, *Ann.*, **511**, 45 (1934).

(6) Michael and Saffer, *J. Org. Chem.*, **8**, 60 (1943).