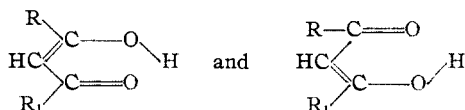


[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HOWARD UNIVERSITY]

**The Properties of *o*-Methoxybenzoylmesitylmethane**

BY R. P. BARNES AND CHAPPELLE C. COCHRANE

In an earlier paper<sup>1</sup> we reported two series of reactions which gave a single enol, although, according to the mechanism, one would expect two isomeric enols. Sidgwick<sup>2</sup> states that coördination of hydrogen occurs in ordinary chelation in keto-enols



He states further that the strain in the 6-ring with two double links is very small and that the same position of the atoms fits either structure. Thus the fact that two isomeric enols of this type have never been isolated is accounted for.

Steric hindrance is also a very important factor, contributing to the non-existence of two isomeric enols. In this communication we are reporting two parallel series of reactions which give rise to a single enol. The effect of the mesityl nucleus in offering hindrance to 1,2-addition reactions to adjacent carbonyls is well known, and one would predict a single enol on this basis alone in this case. This enol is obviously chelated, being a beta-diketone,<sup>3</sup> and this is evidenced by the fact that it is neither acetylated by the ordinary reactions of acetylation, nor does it yield to O-methylation.

The following series of reactions indicates the manner in which the enol is obtained.

**Experimental**

The  $\alpha,\beta$ -unsaturated ketone (I) and the dibromides (III) and (IV) were prepared according to standard methods as given in "Organic Syntheses,"<sup>4a,b</sup>

The methyl ethers (V) and (VI) were obtained by refluxing 1 g. of each of the respective dibromides for one and one-half hours in methyl alcoholic sodium methylate made by dissolving 0.2 g. of metallic sodium in 20 cc. of the alcohol. Sodium bromide separated. The cooled mixture was poured into a large volume of cold water. The oils which separated in each case were crystallized

(1) R. P. Barnes, Charles I. Pierce and Chappelle C. Cochran, *THIS JOURNAL*, **62**, 1084 (1940).

(2) Sidgwick, *Annual Reports of the Chemical Society*, **XXXI**, 41 (1934).

(3) Hilbert, Wulf, Hendricks and Liddel, *THIS JOURNAL*, **58**, 548 (1936).

(4)(a) "Org. Syn.," Col. Vol. I, p. 71; (b) p. 200.

from methyl alcohol as colorless solids, producing no color with alcoholic ferric chloride.

One gram of each of the methyl ethers (V) and (VI) was dissolved in 50 cc. of methyl alcohol and refluxed for one hour with 10 cc. of concd. hydrochloric acid. On cooling, colorless solids separated, which upon filtering and recrystallizing from methanol melted and mix-melted at 105°. This enol gives a deep red color with alcoholic ferric chloride and is 100% enolic.<sup>5</sup> Repeated treatments with diazomethane always resulted in a recovery of unchanged enol. In like manner treatment with acetic anhydride and sulfuric acid or with acetyl chloride did not effect acetylation of the enol.

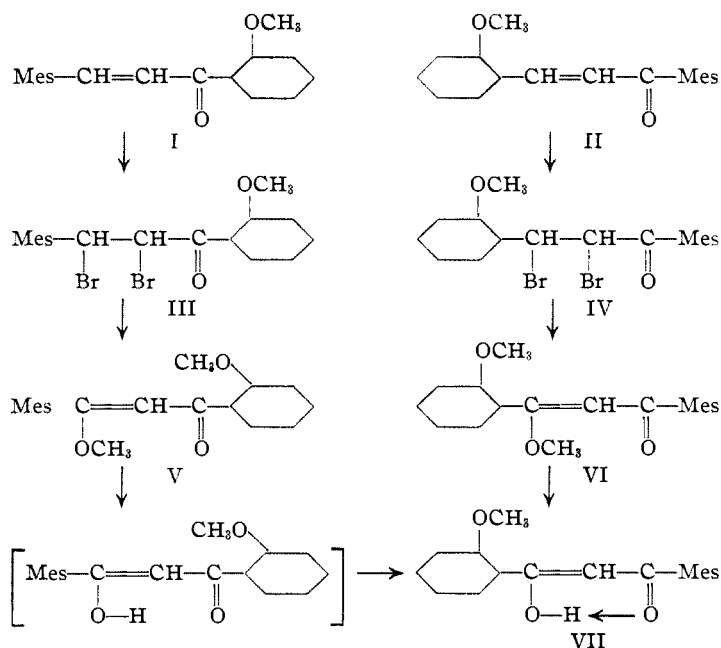


TABLE I

Compound	Melting point, °C.	Formula	OCH <sub>3</sub> Analyses, %		Found
			Calcd.	Found	
I	118	C <sub>19</sub> H <sub>20</sub> O <sub>2</sub>	11.07	11.00	
III	135	C <sub>19</sub> H <sub>20</sub> O <sub>2</sub> Br <sub>2</sub>	7.04	7.01	
IV	86	C <sub>19</sub> H <sub>20</sub> O <sub>2</sub> Br <sub>2</sub>	7.04	7.00	
V	87	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	20.00	20.20	
VI	85	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	20.00	19.93	
VII	105	C <sub>19</sub> H <sub>20</sub> O <sub>3</sub>	10.47	10.50	

**Summary**

Herein are reported two parallel series of reactions which give rise to a single enol, for which there is given some chemical evidence of hydrogen bonding.

WASHINGTON, D. C.

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