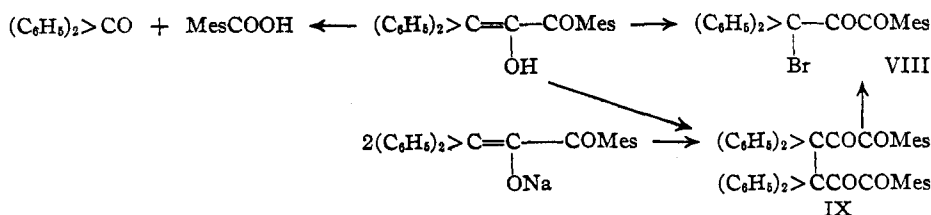
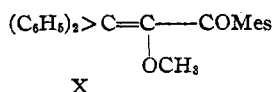


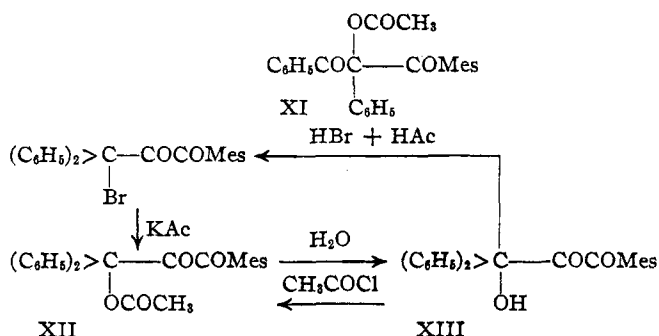
(2) E. P. Kohler and R. B. Thompson, *ibid.*, **59**, 887 (1937).



nection with the acidity of the enol,<sup>3</sup> for methylation with methyl iodide gives 100% O-compound (X) which further substantiates an argument recently presented.<sup>3</sup>



When the  $\alpha$ -bromodiketone (VIII) is treated with freshly fused potassium acetate in glacial acetic acid solution a direct substitution of halogen results. This is what one would predict, rather than the rearrangement product (XI) which would involve the migration of a phenyl group.<sup>4</sup> Thus there is formed the acetate of the  $\alpha$ -hydroxy  $\alpha$ -diketone (XII) which is hydrolyzed very easily to the parent  $\alpha$ -hydroxy- $\alpha$ -diketone (XIII). These are all golden-yellow solids.



Methylmagnesium iodide reacts vigorously with mesitylbenzylglyoxal. When the reaction product is worked up, however, a practically quantitative yield of the starting material is obtained.

### Experimental

**Reaction with Phenylmagnesium Bromide. I-III.**—A solution of 20 g. of the enol of mesitylbenzylglyoxal in 160 cc. of ether was added to phenylmagnesium bromide made from 4 g. of magnesium. The solution turned reddish-brown. After standing overnight much crystalline solid had separated. The reaction mixture was decomposed with ice and hydrochloric acid. The ethereal solution was washed with dilute sodium hydroxide and finally with water, and dried over calcium chloride. On concentrating, it did not crystallize. Diphenyl was re-

moved by steam distillation and the residue vacuum distilled at 150–155° (2 mm.) as a golden-yellow oil. The yield was 20 g. The distillate was dissolved in 60 cc. of methyl alcohol and boiled for three minutes with 11.5 g. of sodium hydroxide in 20 cc. of water. The solution turned red. It was chilled and acidified with dilute hydrochloric acid, giving 12 g. of pale yellow crystals. On crystallizing from methyl alcohol, shining pale yellow plates were formed melting at 120°. This product gives a deep red color with alcoholic ferric chloride.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{20}\text{O}_3$ : C, 84.2; H, 6.4 Found: C, 83.7; H, 6.7.

**The Dibenzoate, IV.**—An absolute ethereal suspension of 5 g. of the magnesium derivative was allowed to stand for several days with an excess of benzoyl chloride. On working up there resulted a colorless oil which crystallized from alcohol, melting at 158°.

*Anal.* Calcd. for  $\text{C}_{38}\text{H}_{30}\text{O}_4$ : C, 82.6; H, 5.8. Found: C, 82.3; H, 6.1.

**Oxidation of  $\beta$ -Phenylbenzalacetomesitylene.**—This  $\alpha$ ,  $\beta$ -unsaturated ketone is very insoluble in methyl alcohol. By ordinary treatment with alkaline hydrogen peroxide no oxide could be isolated. When, however, 5 g. of this material was boiled with excess alkaline hydrogen peroxide, a red solution resulted, which upon acidification yielded 3.0 g. of pale yellow crystals whose m. p. and mixed melting point with the product of the Grignard reaction is 120°.

**Metallic Derivatives, VI and VII.**—An ether-petroleum ether solution of the enol was shaken with saturated cupric acetate solution. A glistening brown crystalline solid separated out, which melted with decomposition at 123°. The enol was regenerated upon acidification.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{20}\text{O}_4\text{Cu}$ : Cu, 8.5. Found: Cu, 8.2.

When an absolute ether solution of 2 g. of the enol was refluxed with 0.2 g. of metallic sodium, there separated, on cooling, 2 g. of orange-red needles. This material upon treatment with acid yields the enol.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{Na}$ : Na, 6.3. Found: Na, 6.3.

**Bromination Product, VIII.**—To a chilled absolute ether solution of 5 g. of the enol was added 2.2 g. of bromine in 20 cc. absolute ether. The bromine was taken up almost instantly, with evolution of hydrogen bromide. On evaporation, a quantitative yield of golden-yellow crystalline solid resulted. It was recrystallized from ether, melting at 155°. It is reduced easily to the parent enol with potassium iodide and acid.

*Anal.* Calcd. for  $\text{C}_{24}\text{H}_{21}\text{O}_2\text{Br}$ : C, 68.4; H, 5.0. Found: C, 68.0; H, 5.2.

(3) R. P. Barnes and Noble F. Payton, *THIS JOURNAL*, **58**, 1300 (1936).

(4) A. H. Blatt, *J. Wash. Acad. Sci.*, **28**, 1 (1938).

**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  $C_{18}H_{12}O_4$ : 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  $C_{24}H_{20}O—OCH_3$ :  $—OCH_3$ , 8.71. Found:  $—OCH_3$ , 8.96.

**Oxybenzhydrylmesitylglyoxal, XIII.**—A solution of 7 g. of the  $\alpha$ -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  $\alpha$ -oxy- $\alpha$ -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  $\alpha$ -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  $\alpha$ -oxy- $\alpha$ -diketone is given.

WASHINGTON, D. C.

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