thors showed definite hydrogen bonding characteristics in oxychloride and chloroform solutions by a determination of heats of mixing.

Finally, we wish to emphasize that the type of solvation that exists in the $SeOCl_2$–$H_2O$ system must, in view of the facts, be necessarily different from that observed in $CH_3COOH$–$H_2O$[3] mixtures. Both may be considered as undergoing solvate formation but only one system has an accompanying alteration in its electronic configuration. The authors feel that some such explanation could plausibly account for the phenomena observed by the magneto-optic method.

## Summary

The magneto-optic rotations of aqueous solutions of $SeOCl_2$ were determined. The mole per cent., density, Verdet constant and molecular Verdet constant were determined and tabulated for each solution.

The curve of mole per cent. against molecular Verdet constant was plotted. A definite discontinuity was noted at 33.3 mole per cent. corresponding to the solvate $SeOCl_2 \cdot 2H_2O$ with accompanying alteration in the internal bond configuration. The probable structure is shown.

BROOKLYN, N. Y. RECEIVED JULY 30, 1942

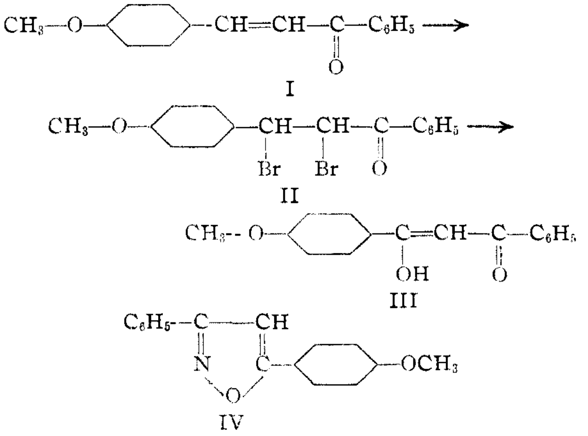
---

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HOWARD UNIVERSITY]

# The Properties of *p*-Methoxydibenzoylmethane

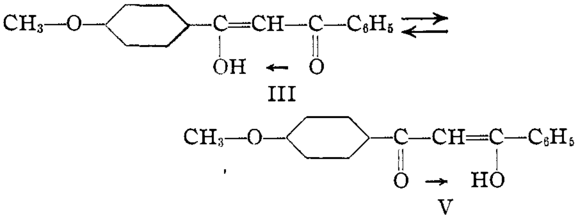
BY R. PERCY BARNES AND ALFRED BRANDON[1]

In 1900, Pond and Shoffstall[2] investigated the action of sodium alcoholate upon anisylidene acetophenone dibromide (II), which was obtained by brominating anisylidene acetophenone (I), obtained by condensing anisaldehyde with acetophenone. These investigators obtained several intermediates between anisylidene acetophenone dibromide and the final product which they characterized as α-oxyanisylidene acetophenone (III), and state that α-oxyanisylideneacetophenone (III) yields the isoxazole (IV) upon treatment with hydroxylamine, whereas anisylideneacetophenone dibromide (II) yields an isomeric isoxazole.



In the light of the behavior of dibromochalcones and the enolic modifications of 1,3-diketones, one would expect (II) and (III) to give rise to one and the same isoxazole (IV).

Because of the well-established mechanism for the formation of enolic modifications of 1,3-diketones,[3] and because of the *p*-methoxyl effect,[4,5,6,7] we set out to make the isomer of α-oxyanisylidene acetophenone (V), with the prediction that the chemical reactions of these extreme forms of the resonance hybrid would be those of (V)



Thus we condensed *p*-methoxyacetophenone with benzaldehyde to produce benzal-*p*-methoxyacetophenone (VI). This substance was brominated to give dibromobenzal-*p*-methoxyacetophenone (VII). The dibromide was treated with freshly fused potassium acetate in glacial acetic acid solution, yielding the α-bromobenzal-*p*-methoxyacetophenone (VIII) which is a viscous yellow oil. This α-bromo unsaturated ketone was converted to the methyl ether (IX), which was in

---

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

(2) Pond and Shoffstall, THIS JOURNAL, **22**, 658 (1900).

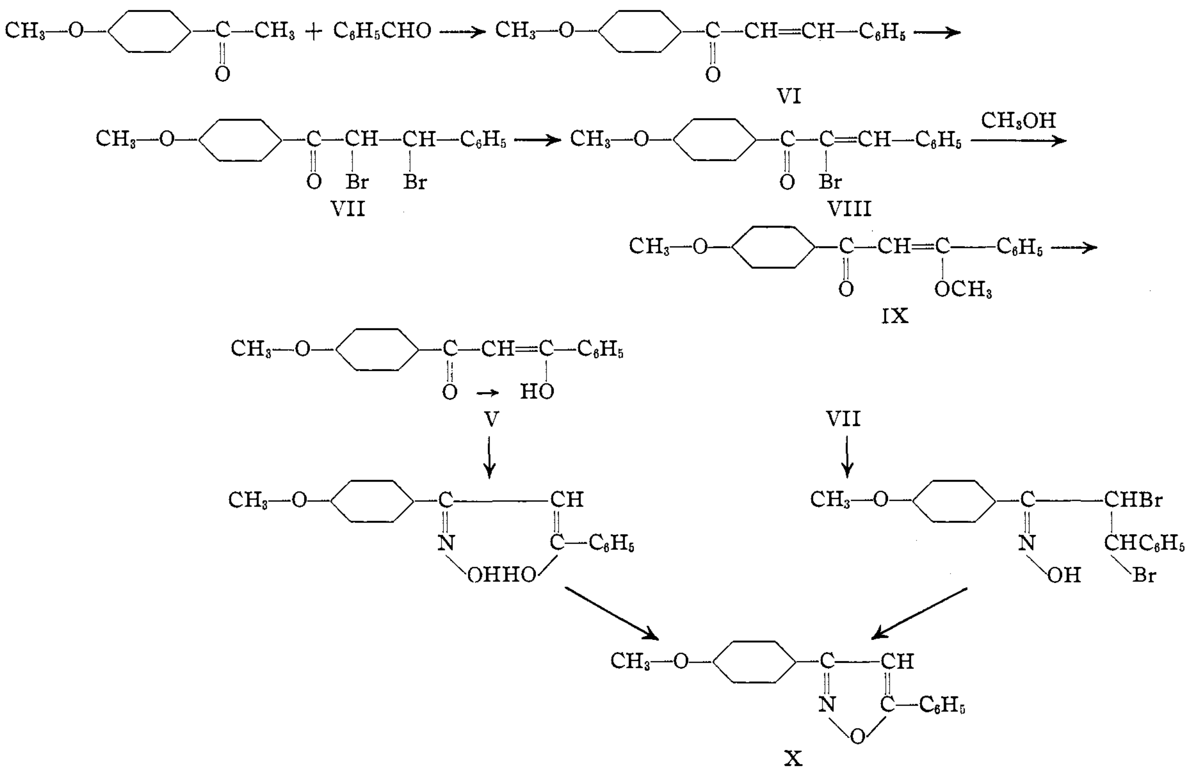
(3) E. P. Kohler and R. Johnston, *Am. Chem. J.*, **33**, 35 (1905).

(4) R. P. Barnes and V. J. Tulane, THIS JOURNAL, **63**, 867 (1941).

(5) R. P. Barnes and Wendell M. Lucas, *ibid.*, **64**, 2258 (1942).

(6) R. P. Barnes and Wendell M. Lucas, *ibid.*, **64**, 2260 (1942).

(7) R. P. Barnes, S. R. Cooper, Victor J. Tulane and Harold Delaney, "The Acetylation of Some Desoxybenzoins," accepted for publication by *J. Org. Chem.*, Jan., 1943.



turn hydrolyzed to (V). This enol obtained by this series of reactions is identical with the α-oxyanisylideneacetophenone obtained by Pond and Shoffstall, melting and mix-melting, when pure, at 130°. It yields the isoxazole (X). Dibromobenzal-*p*-methoxyacetopheone (VII) yields exactly the same isoxazole (X), which is identical with that obtained by Pond and Shoffstall.

It is thus obvious that the structure (IV) assigned to the isoxazole obtained by Pond and Shoffstall is not correct and must be represented by (X). This is in consequence of the fact that the *p*-methoxyl effect causes the resonating hybrid system to react chemically in the enolic modification as (V). The isomeric isoxazole described by Pond and Shoffstall from anisylidene acetophenone dibromide would arise from the unstable enolic modification (III).

## Experimental

**Benzal-*p*-methoxyacetophenone Dibromide** (VII).—A solution of 86 g. of the unsaturated ketone in 600 cc. of carbon disulfide was stirred and treated by dropwise addition of 60 g. of bromine in 60 g. of carbon tetrachloride. The solvent was removed in a stream of air. The resulting spongy mass was filtered and washed with cold methanol. The yield of colorless air-dried product was 70.4 g. Recrystallized from methanol, it melts at 162°.

*Anal.* Calcd. for $C_{16}H_{14}O_2Br_2$: C, 48.2; H, 3.5; —$OCH_3$, 7.79. Found: C, 48.5; H, 3.6; —$OCH_3$, 7.69.

**α-Bromo-benzal-*p*-methoxyacetophenone** (VIII).—A solution of 40 g. of the dibromide in 450 cc. of glacial acetic acid was refluxed for two hours with 80 g. of freshly fused potassium acetate. The solution became yellowish brown. It was chilled and poured into a large volume of cold water. A yellow oil separated. It was dissolved in ether; washed with water; and freed of the last traces of acetic acid by shaking with sodium bicarbonate solution; washed with water; dried over anhydrous sodium sulfate and evaporated *in vacuo* over solid potassium hydroxide. A viscous yellow oil resulted, weighing 27.3 g.

*Anal.* Calcd. for $C_{16}H_{13}O_2Br$: C, 60.6; H, 4.1; —$OCH_3$, 9.78. Found: C, 60.6; H, 4.3; —$OCH_3$, 9.72.

**The Methyl Ether of 1-Phenyl-3-*p*-methoxyphenylpropene-one-1-3-ol-1** (IX).—A solution of 13 g. of α-bromo-benzal-*p*-methoxyacetophenone in 50 cc. of alcohol was refluxed for one hour with sodium methylate made by dissolving 1.3 g. of metallic sodium in 15 cc. of methanol. After refluxing, the solution was cooled and poured into a large volume of water. A red oil separated. It was taken up in ether; washed with water; dried over anhydrous sodium sulfate and finally evaporated *in vacuo* over solid potassium hydroxide. During evaporation yellow crystals separated, which, upon further evaporation, oiled out, indicating that the compound is low-melting. It could not be crystallized from the ordinary solvents.

*Anal.* Calcd. for $C_{17}H_{16}O_3$: C, 76.1; H, 6.0; —$OCH_3$, 23.20. Found: C, 75.9; H, 5.9; —$OCH_3$, 23.13.

**1-Phenyl-3-*p*-methoxyphenylpropene-one-3-ol-1** (V).—A solution of 5 g. of the methyl ether was dissolved in about 50 cc. of methanol and refluxed for one hour with 20 cc. of concd. hydrochloric acid. On cooling, an almost colorless solid crystallized. The melting point of this substance is

128–129° and it mix-melts at the same temperature with the substance prepared according to the method of Pond and Shoffstall.

**3-*p*-Methoxyphenyl-5-phenylisoxazole (X).**—A solution of 2.5 g. of the enol in 25 cc. of hot methanol was treated with 2 g. of hydroxylamine hydrochloride in 5 cc. of water. The solution was refluxed for three hours, and finally allowed to cool. On chilling, a colorless solid separated. It was filtered and recrystallized from methanol, melting and mix-melting at 119° with the substance obtained according to Pond and Shoffstall. The yield was 1.25 g.

A solution of 5 g. of benzal-*p*-methoxyacetophenone dibromide in 100 cc. of boiling ethanol was treated with 1.75 g. of hydroxylamine hydrochloride in 2.5 cc. of water. While still hot, this solution was treated with 4.25 g. of potassium hydroxide in 5 cc. of water. The colorless solution gradually became yellow, and a colorless solid (KBr) separated. The mixture was allowed to stand for ten minutes and filtered. Upon cooling, colorless needles separated. This material was filtered, and recrystallized from ethanol, producing a colorless solid, melting and mix-melting with the above described materials at 119°.

## Summary

1. We have prepared the enolic modification of *p*-methoxydibenzoylmethane by a series of reactions different from that by which it has been prepared previously, and have shown that the products of the two series of reactions are identical.

2. We have shown that this enolic modification reacts as 1-phenyl-3-*p*-methoxyphenylpropene-one-3-ol-1 (V) in that this enolic modification as well as benzal-*p*-methoxyacetophenone dibromide gives rise to the isoxazole (X).

WASHINGTON, D. C. RECEIVED JANUARY 23, 1943

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

# The Preparation and Reactions of 2-Benzimidazolecarboxylic Acid and 2-Benzimidazoleacetic Acid

BY RALPH A. B. COPELAND[1] AND ALLAN R. DAY

Of the acids in the 2-substituted benzimidazole series, only 2-benzimidazolecarboxylic acid and β-2-benzimidazole-propionic acid have been reported previously. The former was prepared by Bistrzycki and Przeworski,[2] but no derivatives other than the barium salt have been reported. The benzimidazole-propionic acid together with the amide and the methyl and ethyl esters have been prepared by Meyer and Luders,[3] and more recently by Chatterjee.[4]

The fact that these acids are bifunctional compounds, resembling the amino acids in that they contain acidic and basic groups, suggested that a study of their reactions might be of interest. Furthermore, similarities between these acids and heterocyclic acids of known physiological activity may also be worthy of attention.

2-Benzimidazolecarboxylic acid (I) was prepared by the permanganate oxidation of 2-hydroxymethylbenzimidazole.[2] Attempts to prepare the acid chloride by the action of phosphorus chlorides or thionyl chloride on the acid were unsuccessful. Refluxing the acid with a large excess of thionyl chloride gave a yellow compound which contained no chlorine. Analyses and equivalent weight determinations indicated this product to be dibenzimidazo-(1,2-a,1′,2′-d)-tetrahydropyrazine-6,13-dione (II). This compound may be regarded as a cyclic diamide or as a substituted diketopiperazine.

The reactions of II fully substantiate the proposed structure. Prolonged refluxing with dilute hydrochloric acid has little effect on the molecule. Concentrated hydrochloric acid gradually dissolves the compound on heating with the formation of 2-benzimidazolecarboxylic acid. Dilute sodium hydroxide solution hydrolyzes the compound readily to the soluble sodium salt of 2-benzimidazolecarboxylic acid. Aqueous ammonia and primary and secondary amines react to form the amide or substituted amides. The use of dilute aqueous solutions of the amine results in lower yields of the amides, due to the competitive reaction of hydrolysis and subsequent salt formation.

Esters of 2-benzimidazolecarboxylic acid were likewise prepared from the cyclic diamide (II). The esters may be prepared by refluxing the diamide with a dry alcoholic solution of hydrogen chloride or by treating the diamide with an alcoholic solution of the corresponding sodium alk-

---

[1] Present address, Agfa Film Corporation, Binghamton, N. Y.

[2] Bistrzycki and Przeworski, *Ber.*, **45**, 3483 (1912).

[3] Meyer and Luders, *Ann.*, **415**, 29 (1918).

[4] Chatterjee, *J. Chem. Soc.*, 2965 (1929).