

**$\alpha$ -Acetoxymercuri- $\beta$ -methoxy- $\beta$ -phenyl- $p$ -chloropropiophenone.**—A solution of 10 g. of benzal- $p$ -chloro-acetophenone and 13 g. of mercuric acetate in 300 cc. of absolute methyl alcohol, prepared by heating the mixture for a short time on the steam-bath, was allowed to stand several days, concentrated to 50 cc. and again allowed to stand, when about 50% of the mercury compound was slowly precipitated. Recrystallized from methyl alcohol, it melted at 124°.

*Analysis.* Calc. for  $C_{18}H_{17}O_4ClHg$ : Hg, 37.6. Found: 37.6.

Sodium chloride solution was added to the filtrate from the acetate and the chloride precipitated. Recrystallized from methyl alcohol, it melted at 160°.

*Analysis.* Calc. for  $C_{16}H_{14}O_2Cl_2Hg$ : Hg, 39.3. Found: 39.0.

### Summary

1. The reaction of several  $\alpha,\beta$ -unsaturated ketones with alcoholic mercuric acetate has been studied. The products obtained were saturated ketones formed by the addition of the groups  $-HgX$  and  $-OR$  to the double linkage.

2. The reaction of unsaturated ketones with mercuric acetate has been compared with that of mercuric halides.

3. Reactions and derivatives of the mercury compounds have been described.

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### NOTES

**Absorption of Halogens by Mercurous Salts: Preliminary Note.**—The present work grew out of an attempt to make a more effective mercurial preparation for external application by treating calomel with iodine. In spite of the large amount of work which has been done on various complex mercuric compounds,<sup>1</sup> the mixed mercuric salts,  $X-Hg-Y$ , have not been prepared by the action of halogens on mercurous compounds. During the present study, mercurous chloride, sulfate, and nitrate have been treated with alcoholic solutions of iodine and bromine in excess. Mercurous chloride yields mercuric iodochloride,  $HgICl$ , and mercuric bromochloride,  $HgBrCl$ . The sulfate yields di-iodomercuric sulfate,  $(IHg)_2SO_4$ , and a perbromide,  $(BrHg)_2SO_4.Br_2$ . The latter compound reacts with dry chlorine to give dichloromercuric sulfate,  $(ClHg)_2SO_4$ . The nitrate gives a per-iodide,  $(IHgNO_3)_2.I_2$ , and a perbromide,  $(BrHgNO_3)_2.Br_2$ . The former compound, when treated with chlorine, differs from the corresponding sulfate by giving a perchloride,  $(ClHgNO_3)_2.Cl_2$ .

It is too early to discuss definitely the constitution of this series of compounds of mercury. They exhibit a number of interesting peculiarities

<sup>1</sup> Ditte, *Compt. rend.*, **87**, 794 (1879); **92**, 353 (1881). Varet, *ibid.*, **123**, 497 (1896). Harth, *Z. anorg. Chem.*, **14**, 323 (1897). Dobrosserdoff, *J. Russ. Phys. Chem. Soc.*, **33**, 303, 387 (1901). Sherrill, *Z. physik. Chem.*, **43**, 705 (1903). Borelli, *Gazz. chim. ital.*, **38**, I, 361 (1908); **38**, II, 421 (1908).

which are being actively studied by physicochemical means. The study of their therapeutic effects may lead to interesting developments. As they contain easily reactive halogen atoms, they might be useful in making other compounds of mercury, or in organic synthesis.

The experimental details of the preparation and properties of the substances, as well as the analytical data, will be published in a later paper on their constitution.

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Received September 18, 1922

**The Catalytic Bromination of Aliphatic Acid Chlorides.**—The use of iron, ferric chloride, aluminum chloride, etc., in brominating and chlorinating aromatic compounds has found widespread application. In the aliphatic series, however, the use of iron as a catalyst in introducing bromine within the molecule has been limited chiefly to saturated and unsaturated hydrocarbons.

Meyer<sup>1</sup> and Kronstein<sup>2</sup> have presented a series of papers dealing with the bromination of hydrocarbons using iron as a catalyst. Willstätter and Bruce<sup>3</sup> used iron powder in preparing 1,2-dibromocyclobutane, and recently Mereshkowsky<sup>4</sup> has studied the ratio of reaction products obtained in the bromination of hydrocarbons and their bromine derivatives by using iron wire, ferric bromide, aluminum, and aluminum trichloride as catalysts. In brominating acetic acid and its homologs the use of sulfur as catalyst is well known.

During the course of researches on derivatives of camphoronic acid,  $(\text{CH}_3)_2\text{C}(\text{COOH})-\text{C}(\text{CH}_3)(\text{COOH})-\text{CH}_2\text{COOH}$  (a description of which will appear later), it was found necessary to brominate anhydrocamphoronyl chloride,  $\text{C}_6\text{H}_{11}(\text{CO})_2\text{OCOCl}$ . The bromination hitherto has been carried out by Brecht<sup>5</sup> either by heating one or both isomers with bromine in a sealed tube at elevated temperatures, or in an open vessel on the water-bath, the reaction product being a mixture of two isomeric bromo-anhydrocamphoronyl chlorides in which it is known that the bromine is attached to the primary carbon atom of the molecule. The latter scheme required about 12 hours for complete reaction to take place.

The above procedure was modified by treating anhydrocamphoronic acid,  $\text{C}_6\text{H}_{11}(\text{CO})_2\text{OCOOH}$ , formed in quantitative yields by heating pure, optically-active camphoronic acid under a vacuum at  $180^\circ$  in an oil-bath with 1.1 molecular equivalents of phosphorus pentachloride in a flask

<sup>1</sup> Meyer, *Ber.*, **24**, 4247 (1891); **25**, 3304 (1892).

<sup>2</sup> Kronstein, *Ber.*, **24**, 4245 (1891); **26**, 2436 (1893); **54**, 1 (1921).

<sup>3</sup> Willstätter and Bruce, *Ber.*, **40**, 3983 (1907).

<sup>4</sup> Mereshkowsky, *Ann.*, **431**, 113 (1923).

<sup>5</sup> Brecht, *Ann.*, **299**, 142 (1899).