α-Acetoxymercuri-β-methoxy-β-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 α,β-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.

CAMBRIDGE 38, MASSACHUSETTS

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,[1] 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

---

[1] 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.

THE CHEMICAL LABORATORIES OF THE COLLEGE
BARODA, INDIA
KUVERJI GOSAI NAIK,
MAHADEO DATTATRAYA AVASARE

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[1] and Kronstein[2] have presented a series of papers dealing with the bromination of hydrocarbons using iron as a catalyst. Willstätter and Bruce[3] used iron powder in preparing 1,2-dibromocyclobutane, and recently Mereshkowsky[4] 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, $(CH_3)_2C(COOH)-C(CH_3)(COOH)-CH_2COOH$ (a description of which will appear later), it was found necessary to brominate anhydrocamphoronyl chloride, $C_6H_{11}(CO)_2OCOCl$. The bromination hitherto has been carried out by Bredt[5] either by heating one or both isomers with bromine in a sealed tube at elevated temperatures, or in an open vessel on the waterbath, 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, $C_6H_{11}(CO)_2OCOOH$, formed in quantitative yields by heating pure, optically-active camphoronic acid under a vacuum at 180° in an oil-bath with 1.1 molecular equivalents of phosphorus pentachloride in a flask

[1] Meyer, *Ber.*, **24**, 4247 (1891); **25**, 3304 (1892).

[2] Kronstein, *Ber.*, **24**, 4245 (1891); **26**, 2436 (1893); **54**, 1 (1921).

[3] Willstätter and Bruce, *Ber.*, **40**, 3983 (1907).

[4] Mereshkowsky, *Ann.*, **431**, 113 (1923).

[5] Bredt, *Ann.*, **299**, 142 (1899).

bearing a ground-glass tube and condenser together with a separatory funnel sealed to its side. The mixture was warmed and when the reaction had ceased, without distilling the phosphorus oxychloride, a small amount of iron powder (0.2–0.5 g.) was added. Then, while the mixture was heated on the water-bath, 1.1 molecular equivalents of bromine was slowly added through the separatory funnel. A violent bromination of the camphoronyl chlorides followed. After all the bromine had been added the mixture was heated for 45 minutes to insure complete reaction. At the end of this time, when no fumes of bromine could be detected, the flask was removed and allowed to stand at room temperature for 24 hours to permit the crystallization of the α-bromo-anhydrocamphoronyl chloride. The contents of the flask were filtered and the crude product, obtained in yields of 75%, was repeatedly washed with small amounts of absolute ether to remove both its readily soluble isomer and ferric bromide. The solid was dissolved in hot benzene, boiled with Norite two or three times and finally allowed to cool. Transparent crystals of the pure product melting at 168° were obtained. The original filtrate contained some α-bromo acid chloride together with ferric bromide and the β-, or isomeric, bromo acid chloride. The latter compound has never been obtained in a pure state.

This method of catalytic halogenation appears to have considerable value in the catalytic preparation of α-halogen acids. It is the intention of the writer to continue investigation of the reaction, extending it not only to other acid chlorides, but also to other classes of aliphatic compounds to which it has not been applied.

CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

WALTHER F. GOEBEL

Received July 23, 1923

The Purity of Alpha-Gamma-Dichlorohydrin Prepared by the Action of Hydrogen Chloride on Glycerol.—In the preparation of α,γ-dichlorohydrin from glycerol by the action of hydrogen chloride there is the possibility of forming considerable amounts of α,β-dichlorohydrin (the dichloride of allyl alcohol). The complete separation of such a mixture by distillation would be very difficult. In order to obtain information in regard to the purity of the dichlorohydrin prepared in this way, we investigated the action of *p*-nitrobenzoyl chloride on the final product of the reaction which was collected over a 3° range and over a 7° range. The preparation and distillation was carried out as described in "Organic Syntheses," Vol. II, p. 29. Five g. of the material was mixed with 20 g. of pyridine and 8 g. of *p*-nitrobenzoyl chloride; the mixture was heated for 3 hours on the steam-bath, then allowed to stand overnight and finally treated with dil. hydrochloric acid and extracted with ether. After the removal of nitrobenzoic acid by means of aqueous sodium carbonate, the ether was dried and evaporated. From the 3° portion 10.2 g. of ester was obtained, m. p. 55–58° (94% yield), and 10.0 g. from the 7° portion, m. p. 53–57.5° (92% yield). The pure ester after several recrystallizations melted at 58–59°.

Calc. for $C_9H_9O_4NCl_2$: Cl, 25.5. Found: 25.4.

The isomeric ester of α,β-dichlorohydrin was made in a similar fashion from the allyl alcohol dichloride. It melted after several recrystallizations at 35.5–37°.

Calc. for $C_9H_9NCl_2$: Cl, 25.5. Found: 25.7.

A mixture of 90% of the α,γ-ester and 10% of the α,β-ester melted at 26–48°. The crude product from the 3° and 7° portions must, therefore, have contained much less than 10% of the isomeric ester. Since the yields of this crude ester were 94 and 92%, the original portions must have contained at least 91% and 89% of α,γ-dichlorohydrin (assuming the melting points corresponded to 97% purity). Considering the losses in the manipulation, etc., it is probable that the purity is several per cent. higher than this; the relatively high melting point of the crude ester points to the almost complete absence of the α,β-dichlorohydrin from both portions.

CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS
J. B. CONANT AND O. R. QUAYLE
Received August 13, 1923

NEW BOOKS

The Phase Rule and the Study of Heterogeneous Equilibria: an Introductory Study. By A. C. D. RIVETT, D.Sc., Associate Professor of Chemistry in the University of Melbourne. Oxford University Press, American Branch, New York, 1923. 204 pp. 118 figs. 20 × 13 cm. Price $3.50.

This little book by Professor Rivett is a welcome addition to our very limited textbook literature of the phase rule. Outside of Roozeboom's "Die heterogenen Gleichgewichte," which is too encyclopedic for any but a specialist, and Bancroft's "Phase Rule," which has had its greatest use in bringing to the attention of chemists the value of the phase rule at a time when it was but little known, there have been only two readable books on the phase rule, as far as the reviewer knows, which could be put in the hands of a graduate student or an investigator needing an acquaintance with the phase rule for the purposes of his research—namely, Findlay's, "Phase Rule" and Clibbens' "Principles of the Phase Theory." This third book fulfils the requirement of being another readable book—perhaps more so than Clibbens—and at the same time presents, in clear and understandable language much material that is not found in either of the others. The author states that it is not "either a treatise or a book of reference," but is intended as "an introduction to the subject." In the opinion of