Experimental

To a mixture of 9.0 g. (0.506 mole) of phenanthrene in 75 ml. of glacial acetic acid was added 45 ml. of 50% hydrogen peroxide (0.792 mole). On warming slowly, the white paste went into solution. At 60–70°, the exothermic reaction commenced and the deep red solution was kept at a slow reflux for two hours. On refrigeration, 8.0 g. of yellow-white needles crystallized. These were collected and dissolved in warm caustic. After filtering the undissolved quinone, diphenic acid was precipitated as a white powder by acidification of the filtrate with concd. hydrochloric acid. Additional diphenic acid was recovered from the mother liquor by adding it slowly with stirring into warm caustic to decompose the excess peroxide and any peracetic acid formed *in situ*. The solution was treated with charcoal and filtered, and the filtrate was acidified.

The total yield of phenanthrenequinone was 0.5 g. (4%), m.p. 204–206°; of diphenic acid was 8.3 g. (68%), m.p. 229–230°.

A mixed melting point of the latter with a known sample of diphenic acid gave no depression.

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Addition Compound of Boron Tribromide and Trimethylamine

BY ROBERT C. OSTHOFF, CHARLES A. BROWN AND FRANK H. CLARKE

In view of the fact that the trimethylamine addition compounds of boron trifluoride[1] and boron trichloride[2] have been isolated and characterized, it is surprising that the similar ammine of boron tribromide, $Br_3BN(CH_3)_3$, has not been reported previously.

Johnson[3] attempted preparation of $Br_3BN(CH_3)_3$ by the introduction of gaseous trimethylamine into a solution of boron tribromide in carbon tetrachloride, but he was unable to isolate any product which could be characterized. However, Johnson did report the addition compounds of boron tribromide with triethylamine, dimethylaniline and pyridine.

The authors were able to prepare the stable white solid compound of boron tribromide and trimethylamine by direct combination. This compound further illustrates the ability of the boron halides to form stable coördinate covalent bonds with simple tertiary amines.

The following method for the study of the reaction was used. In a typical run tensiometrically pure Eastman Kodak Co. "White Label" trimethylamine (2.106×10^{-3} mole) was introduced into a previously evacuated reaction bulb by means of a compensating gas buret. The pressure of the completely vaporized sample was determined at room temperature and the trimethylamine was "frozen out" with liquid nitrogen. Successive small weighed amounts of boron tribromide[4] (vapor pressure at 23° obsd. 61 mm.; calcd. 62 mm.) were added, the reaction bulb warmed to 25° and the pressure determined following each addition.

The pressures were plotted against mole ratio, $BBr_3/N(CH_3)_3$ giving a straight line (see Fig. 1) which intersected the mole ratio axis at a value of one, corresponding to the formation of $Br_3BN(CH_3)_3$. Continued addition of boron tribromide showed formation of no other compound, and gave only the expected increase in pressure.

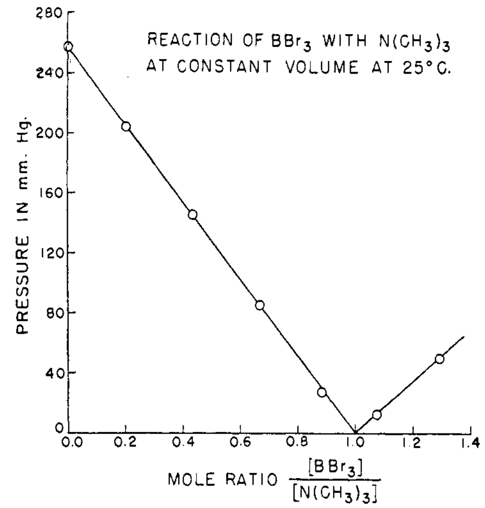

Fig. 1.

The white solid obtained from the reaction was found to be stable in air. It crystallized as long white needles from benzene, melting at 238–240° with some decomposition. The substance was soluble in benzene, chloroform and carbon tetrachloride and insoluble in water at 10°.

Anal. Calcd. for $Br_3BN(CH_3)_3$: C, 11.62; H, 2.90; N, 4.52; Br, 77.55. Found: C, 11.77; H, 2.98; N, 4.79; Br, 78.25.

Cryoscopic measurements in anhydrous benzene gave a molecular weight value of 321 (calcd. for $Br_3BN(CH_3)_3$ 310).

The infrared spectrum of the compound in chloroform solution was obtained with a Baird spectrophotometer. The principal absorption bands in the range of 2–16 mμ were: 3.19, 6.75, 6.87, 9.00, 10.46 and 12.22 mμ.

DEPARTMENT OF CHEMISTRY
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[1] H. Meerwein, E. Bottenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 83 (1939).

[2] E. Wiberg, *Z. anorg. Chem.*, **202**, 355 (1931).

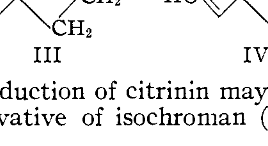
[3] A. R. Johnson, *J. Phys. Chem.*, **16**, 1 (1912).

[4] L. F. Audrieth, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Company, Inc., New York, N. Y., 1950. p. 27.

The Preparation of 6-Hydroxyisochroman[1]

BY L. SCHIELER[2] AND R. D. SPRENGER

Recent investigations[3,4,5] have shown that the antibiotic citrinin has the structure (I). Dihydrocitrinin (II) which has been obtained by the catalytic reduction of citrinin may thus be considered a derivative of isochroman (III). The desirability of



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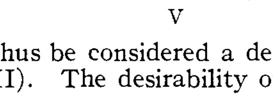

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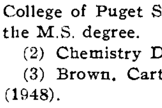
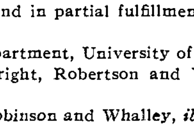
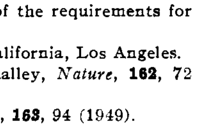


III



IV



V

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[1] This work was supported by a grant from the Research Corporation and is a portion of a thesis presented by Leroy Schieler at the College of Puget Sound in partial fulfillment of the requirements for the M.S. degree.

[2] Chemistry Department, University of California, Los Angeles.

[3] Brown, Cartwright, Robertson and Whalley, *Nature*, **162**, 72 (1948).

[4] Cartwright, Robinson and Whalley, *ibid.*, **163**, 94 (1949).

[5] Brown, Robertson, Whalley and Cartwright, *J. Chem. Soc.*, 867 (1949).

studying certain model compounds related to citrinin prompted the preparation of 6-hydroxyisochroman (IV) since this compound upon oxidation might be expected to give the unique *p*-methylene quinoid structure (V) characteristic of citrinin.

Although the preparation of isochroman has been previously described[6,7] no substituted compounds of known orientation have been reported. After several unsuccessful attempts to prepare the desired 6-hydroxyisochroman by modifications of the methods reported in the literature, a satisfactory procedure was developed using a different approach. *m*-Hydroxy-β-phenylethyl alcohol, prepared from the corresponding methoxy compound[8] was converted by the Gattermann reaction into 4-hydroxy-3-(β-hydroxyethyl)-benzaldehyde. Upon reduction of the latter to the carbinol, water spontaneously split out to form 6-hydroxyisochroman.

This method has been extended to the preparation of other substituted 6-hydroxyisochromans and the properties of these compounds and their relationship to citrinin are presently under investigation.

Experimental

All melting points are uncorrected.

***m*-Hydroxy-β-phenylethyl Alcohol.**—In a three-liter round-bottomed flask fitted with a reflux condenser was placed 65.2 g. (0.43 mole) of *m*-methoxy-β-phenylethyl alcohol,[8] 940 ml. of glacial acetic acid and 100 ml. of 48% hydrobromic acid. After vigorously refluxing for six hours, the excess acid was distilled off at atmospheric pressure, the residue diluted with 200 ml. of water and the solution neutralized by the cautious addition of solid sodium carbonate. Three hundred ml. of a saturated sodium carbonate solution was then added and the mixture boiled for 30 minutes. The cooled alkaline solution was extracted with ether and the ether in turn extracted with 2 *N* sodium hydroxide. From the alkaline solution the phenol was recovered by strong acidification with concd. hydrochloric acid followed by ether extraction. After drying and removal of the ether the product was vacuum distilled giving 30.2 g. (54%) of a yellow, highly viscous oil boiling at 168–173° (4 mm.).

Anal. Calcd. for $C_8H_{10}O_2$: C, 72.00; H, 6.60. Found: C, 72.01; H, 6.65.

A 3,5-dinitrobenzoate was obtained in the usual manner as light yellow needles, m.p. 146.5–147°.

Anal. Calcd. for $C_{15}H_{12}O_7N_2$: N, 8.43. Found: N, 8.51.

2-(β-Hydroxyethyl)-4-hydroxybenzaldehyde.—In a 250-ml. wide-mouthed bottle fitted with a stirrer, reflux condenser and gas inlet tube was placed 6.0 g. (0.044 mole) of *m*-hydroxy-β-phenylethyl alcohol, 7.8 g. (0.066 mole) of anhydrous zinc cyanide, a pinch of sodium chloride and 50 ml. of anhydrous ether. The reaction mixture was cooled in an ice-bath and 8.8 g. (0.066 mole) of anhydrous aluminum chloride dissolved in 50 ml. of cold anhydrous ether added. Anhydrous hydrogen chloride was passed through the reaction mixture with ice-bath cooling until the ether was saturated with hydrogen chloride (about 2 hr.). The reaction mixture was then allowed to come to room temperature and hydrogen chloride added for another five hours. At the end of this time a viscous, pink oil had settled out. The ether was decanted, the imide hydrochloride washed with a small volume of anhydrous ether and then hydrolyzed by boiling in water. After extracting with ether, drying and distilling 3.3 g. (45.8%) of the aldehyde was obtained as a faintly pink oil boiling at 153–162° (6 mm.).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.00; H, 6.03. Found: C, 64.87; H, 6.25.

The semicarbazone, prepared in the usual manner, was obtained as light tan crystals, m.p. 244–245° dec.

Anal. Calcd. for $C_{10}H_{14}O_3N_3$: N, 18.75. Found: N, 19.21.

6-Hydroxyisochroman.—In a 200-ml. three-necked flask fitted with a mercury-seal stirrer, reflux condenser and dropping funnel was placed 0.65 g. (0.018 mole) of lithium aluminum hydride in 25 ml. of dry ether. A solution of 3.0 g. (0.018 mole) of 2-(β-hydroxyethyl)-4-hydroxybenzaldehyde in 40 ml. of anhydrous ether was added dropwise at such a rate that a gentle reflux was maintained. After standing for one hour with stirring the mixture was hydrolyzed with dilute hydrochloric acid and the ether layer separated and dried. On removal of the ether 1.8 g. (66%) of a colorless oil was obtained boiling at 153–162° (7 mm.).

Anal. Calcd. for $C_9H_{10}O_2$: C, 69.56; H, 7.25. Found: C, 69.21; H, 7.13.

A 3,5-dinitrobenzoate was readily obtained as yellow needles melting at 152.5–154°.

Anal. Calcd. for $C_{16}H_{12}O_7N_2$: N, 8.14. Found: N, 8.16.

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(6) von Braun and Zobel, *Ber.*, **56**, 2149 (1923).

(7) Buschmann and Michel, German Patents 614,461 (May 23, 1935); 617,646 (Aug. 8, 1935); *C. A.*, **30**, 492 (1936).

(8) Natelson and Gottfried, THIS JOURNAL, **61**, 1001 (1939).

2-Methyl-2-monoalkylaminopropyl and Dialkylaminoethyl Aryloxyacetates[1]

BY J. STANTON PIERCE, WILLIAM K. EASLEY AND H. H. HANNABAS, JR.

Most of the plant growth-regulating substances reported are acids and their salts, esters or amides.[2,3] In the study of over one thousand compounds as plant growth-regulating substances, Thompson, Swanson and Norman[4] included two alkylaminoalkyl aryloxyacetates, β-diethylaminoethyl 2,4-dichlorophenoxyacetate and β-diethylaminoethyl 2,4,5-trichlorophenoxyacetate, although no physical constants or analyses are given.

Since so many of the simple salts and esters of aryloxyacetates have been found to be active hormones for plant growth, it seemed well to prepare for study a few alkylaminoalkyl aryloxyacetate hydrochlorides, which are esters and at the same time are salts, usually soluble in water.

In the work reported below, esters were formed with phenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid and β-naphthoxyacetic acid and dimethylaminoethanol, diethylaminoethanol and various 2-methyl-2-monoalkylaminopropanols. The latter compounds, secondary amino alcohols, were chosen for this study, since in this Laboratory hydrochlorides of many 2-methyl-2-monoalkylaminopropyl esters of alkoxybenzoic acids,[5] arylacetic and alkarylacetic acids[6] and alkoxyhydrocinnamic acids[7] have been found to crystallize more readily than corresponding esters of 2-monoalkylaminoethanols and 2-monoalkylaminobutanols. The hydrochlorides of some of the esters in this study were obtained as crystalline solids and some as oils. The crystalline products

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(1) Acknowledgment is made to Dr. E. Emmet Reid, Research Adviser to the Chemistry Department of the University of Richmond, for his advice in this work.

(2) F. A. Gilbert, *Chem. Revs.*, **39**, 199 (1946).

(3) M. S. Newman, W. Fones and M. Renoll, THIS JOURNAL, **69**, 718 (1947).

(4) H. E. Thompson, C. P. Swanson and A. G. Norman, *The Botanical Gazette*, **107**, 476 (1946).

(5) J. S. Pierce, J. M. Salsbury, W. W. Haden and L. H. Willis, THIS JOURNAL, **64**, 2884 (1942).

(6) J. S. Pierce, W. W. Haden and R. D. Gano, *ibid.*, **67**, 408 (1945).

(7) J. S. Pierce, R. D. Gano and J. M. Lukeman, *ibid.*, **70**, 255 (1948).