

The inactive antimony present in the aqueous phase was estimated by precipitating the sulfide with hydrogen sulfide in 1 *f* hydrochloric acid solutions and comparing, visually, the volume of the sulfide centrifuged to the bottom of a 5-ml. centrifuge cone with that obtained by precipitation of known quantities of antimony sulfide.

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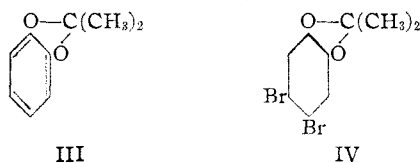
## Bromination of Catechol

By MORITZ KOHN

Cousin<sup>1</sup> reported that the bromination of catechol in acetic acid with two moles of bromine yielded a dibromocatechol, m. p. 92°. This compound was shown to be 4,5-dibromocatechol (I) since 4,5-dibromoveratrol was produced by the methylation of I. A German patent<sup>2</sup> claims the



product of the bromination of catechol with 2 moles of bromine is dibromocatechol, m. p. 120°; however, this patent gives no information on how the product should be prepared, nor any information on the position of the bromine. Another German patent<sup>3</sup> claims the bromination of catechol with 3 moles of bromine gives 3,4,5-tribromocatechol (II) since II can be methylated to 3,4,5-tribromoveratrol. Sloof<sup>4</sup> reported the preparation of a derivative of catechol which he believed to be 4,5-dibromocatechol, m. p. 121°, identical to that described in the German patent. In his preparation, acetone was condensed with catechol to the cyclic isopropylidene ether of catechol (III) which was then brominated to 4,5-dibromo-isopropylidene catechol (IV). On saponification IV gives 4,5-dibromocatechol (I).



Frejka and Sefranek<sup>5</sup> did not believe the 4,5-dibromocatechol prepared by Cousin<sup>1</sup>, m. p. 92°, to be identical to the dibromocatechol, m. p. 120°, claimed by the patent.<sup>2</sup> Furthermore, they believed the dibromocatechol, m. p. 120°, to be the 3,6-dibromo derivative (V). They also claim that the bromination of V yields 3,4,6-dibromocatechol VI. Further investigations in these laboratories have shown the observations of Frejka and Sefranek<sup>5</sup> are incorrect. When dibromocatechol is

(1) Cousin, *Ann.*, [7] **13**, 487 (1898).  
(2) Chem. Fabrik von Heyden, German Patent 207,544; *Chem. Zentr.*, **80**, I, 1283 (1909).  
(3) Chem. Fabrik von Heyden, German Patent 215,337; *Chem. Zentr.*, **80**, II, 1710 (1909); Frejka and Sefranek, *Collection Czechoslov. Chem. Commun.*, **8**, 130 (1936).  
(4) Sloof, *Rec. trav. chim.*, **64**, 995 (1935).  
(5) Frejka and Sefranek, *Collection Czechoslov. Chem. Commun.*, **11**, 165 (1939).



prepared by the method of Cousin,<sup>1</sup> the product may melt close to 92°, but after thorough drying, melts at 121°. The same dibromo derivative may be prepared from the isopropylidene ether of catechol by the method of Sloof.<sup>4</sup> Both of these dibromocatechols yield the same 4,5-dibromoveratrol on methylation as well as the same diacetate on acetylation. On bromination of these dibromocatechols, 3,4,5-tribromocatechol is produced. The 3,4,6-tribromocatechol (VI) is reported by Kohn and Steiner<sup>6</sup> and the properties of the two isomeric tribromocatechols and their derivatives are entirely different. From this

	3,4,5-	3,4,6-
Tribromocatechol, m. p., °C.	139-141	105
Methyl ether, m. p., °C.	86	69
Diacetate, m. p., °C.	119-121	141

evidence it is obvious that the dibromocatechol reported by Cousin,<sup>1</sup> Sloof<sup>4</sup> and the German patent<sup>2</sup> is identical and is 4,5-dibromocatechol.

### Experimental

**Preparation of Anhydrous 4,5-Dibromocatechol. A.**—To 11 g. of catechol dissolved in 50 cc. of cold glacial acetic acid is added a solution of 11 cc. of bromine in 50 cc. of glacial acetic acid. Hydrogen bromide and acetic acid are removed by distillation under reduced pressure on a water-bath. The residue is quenched with a 350-g. mixture of ice and water. The white precipitate is dried in a vacuum desiccator over sulfuric acid. Ten grams of this crude product is recrystallized from 50 cc. of benzene. The crystals are collected on a suction filter and dried at 80°; yield 6 g., m.p. 119-121°.

**B.**—The same substance, m.p. 119-121°, is obtained by the method of Sloof.<sup>4</sup> Both the products from A and B yield the same 4,5-dibromoveratrol, m.p. 92-93°, by methylation and the same 4,5-dibromocatechol diacetate, m.p. 108-109°, by acetylation.

**Bromination of 4,5-Dibromocatechol.**—A solution of 1.3 cc. of bromine in 30 cc. of chloroform is slowly added to 6.5 g. of 4,5-dibromocatechol in 75 cc. of chloroform. After 12 hours, the chloroform is evaporated on the water-bath. The residue is dried at 90°. The yield is 8 g. Four grams of the crude substance is recrystallized from benzene yielding 3.3 g. of 3,4,5-tribromocatechol, m.p. 139-141°. The methyl ether melts of 85-87°, and the diacetate at 119-120°.

(6) Kohn and Steiner, *J. Org. Chem.*, **12**, 31 (1947).

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## Derivatives of Cyclobutanecarboxylic Acid<sup>1</sup>

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Cyclobutanecarboxylic acid is a valuable intermediate in the preparation of a number of other cyclobutane derivatives. A thorough literature search has revealed that few solid derivatives of this acid have been prepared and characterized. A number of such derivatives have been prepared

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