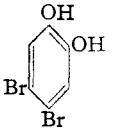
The inactive antimony present in the aqueous phase was estimated by precipitating the sulfide with hydrogen sulfide in 1 *f* hydrochloric acid solutions and comparing, visually, the volume of the sulfide centrifuged to the bottom of a 5-ml. centrifuge cone with that obtained by precipitation of known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

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
SAINT LOUIS, MISSOURI RECEIVED AUGUST 7, 1950

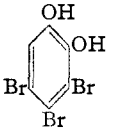
Bromination of Catechol

BY MORITZ KOHN

Cousin[1] 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[2] claims the

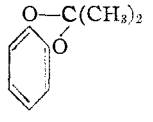


I

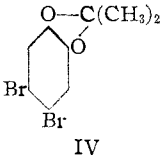


II

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[3] 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[4] 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-dibromoisopropylidenecatechol (IV). On saponification IV gives 4,5-dibromocatechol (I).

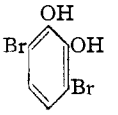


III

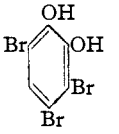


IV

Frejka and Sefranek[5] did not believe the 4,5-dibromocatechol prepared by Cousin[1], m. p. 92°, to be identical to the dibromocatechol, m. p. 120°, claimed by the patent.[2] 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[5] are incorrect. When dibromocatechol is



V



VI

prepared by the method of Cousin,[1] 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.[4] 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) was reported by Kohn and Steiner[6] 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,[1] Sloof[4] and the German patent[2] 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.[4] 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°.

(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.*, **54**, 995 (1935).

(5) Frejka and Sefranek, *Collection Czechoslov. Chem. Commun.*, **11**, 165 (1939).

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

CHEMICAL LABORATORY OF THE ACADEMY OF COMMERCE AND THE
CHEMICAL LABORATORY OF THE TECHNICAL UNIVERSITY IN VIENNA
VIENNA, AUSTRIA RECEIVED MAY 23, 1950

Derivatives of Cyclobutanecarboxylic Acid[1]

BY D. L. KANTRO AND H. E. GUNNING

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

(1) This work was supported by Contract No. AT(11-1)-43 with the U.S. Atomic Energy Commission.

TABLE I

Derivative	M. p., °C. (cor.)	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Other Calcd.	Other Found
p-Toluide	123	$C_{12}H_{15}ON$	76.15	75.46	7.99	7.87	7.40	7.62		
Hydrazide	156.0–156.5	$C_{11}H_{14}ON_2$	69.44	70.20	7.42	7.32	14.73	14.03		
p-Bromophenacyl ester	81.5–82.0	$C_{18}H_{13}O_3Br$	52.54	52.77	4.41	4.59			(Br) 26.89	27.07
p-Phenyl phenacyl ester	91.5	$C_{19}H_{18}O_3$	77.53	77.45	6.16	6.31				
Benzylisothiouronium salt	160–161	$C_{18}H_{18}O_2N_2S$	58.62	58.65	6.81	6.72	10.52	10.34	(S) 12.04	12.04

in this Laboratory by standard methods[2] and are listed in Table I. The anilide, m.p. 111°, has been reported previously.[3]

(2) Shriner and Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N.Y., 1944, pp. 154–159.

(3) Freund and Gudeman, *Ber.*, **21**, 2692 (1888).

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS RECEIVED AUGUST 4, 1950

Non-reduction of the Acetal Group by Lithium Aluminum Hydride

BY C. S. MARVEL AND H. W. HILL, JR.[1]

We have recently had occasion to prepare the glycol acetal (II) and it occurred to us that the reduction of the corresponding malonic ester derivative (I) would produce this substance if the acetal group were not affected by the action of lithium aluminum hydride.

$$(C_2H_5O)_2CHCH_2CH_2CH(CO_2C_2H_5)_2 \longrightarrow$$
I

$$(C_2H_5O)_2CHCH_2CH_2CH(CH_2OH)_2$$
II

Preliminary tests of the action of lithium aluminum hydride on acetal, $CH_3CH(OC_2H_5)_2$, indicated no reaction. Hence the ester was prepared by the condensation of the diethylacetal of β-chloropropionaldehyde with sodium malonic ester[2] and the reduction of the acetal ester accomplished with lithium aluminum hydride. The glycol acetal (II) was isolated from the alkaline medium in 33% yield.

Preparation of 5-Hydroxy-4-hydroxymethylpentanal Diethyl Acetal.—When 83.3 g. (0.286 mole) of 3,3-diethoxy-1-propylmalonic acid diethyl ester was added dropwise over a period of 2.5 hours to a solution of 14.6 g. (0.385 mole) of lithium aluminum hydride in 300 ml. of absolute ether and the excess hydride decomposed by the cautious addition of water, a product which boiled at 140–144° at 1.2 mm.; $n^{20}D$ 1.4540; d^{20}_4 1.0178 was obtained upon distillation of the ethereal solution. The yield was 19.5 g. (33.2%).

Anal. Calcd. for $C_{10}H_{22}O_4$: C, 58.22; H, 10.75; *MR*, 54.72. Found: C, 58.33; H, 10.99; *MR*, 54.89.

(1) Allied Chemical and Dye Corporation Fellow, 1949–1950. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

(2) D. T. Warner and O. A. Moe, THIS JOURNAL, **70**, 3470 (1948).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED JULY 31, 1950

Polyalkylene Sulfides. VII. The Polymer from Tetramethylenedithiol and Biallyl

BY C. S. MARVEL AND ALEX KOTCH

Marvel and Chambers[1] added tetramethylenedithiol to biallyl under the influence of ultraviolet light to obtain a low-molecular weight polymer. This addition reaction carried out in emulsion according to the method recently described[2] gives a polymer with an inherent viscosity of 0.52 which melts at 64–67°. The polymer can be cold drawn to give a fiber. Surprisingly enough we have also been able to form this polymer with an inherent viscosity of 0.63 and m.p. 65–68° from tetramethylene bromide and the disodium salt of hexamethylenedithiol in a benzene–alcohol mixture.

This condensation polymerization reaction was carried out by dissolving 0.46 g. of sodium in 15 ml. of absolute alcohol (distilled from magnesium ethoxide[3]) and then adding 1.5 g. of hexamethylenedithiol. The sodium salt of the dithiol precipitated and then redissolved when the mixture was heated. To this boiling solution were added 25 ml. of dry thiophene-free benzene and then 2.15 g. of tetramethylene bromide. Immediately a vigorous reaction set in, and vigorous refluxing of the solvent mixture occurred. When the spontaneous reaction subsided, the mixture was diluted with an additional 25 ml. of benzene and then heated under refluxing conditions overnight. The cold, filtered solution was poured into methanol, and the polymer was collected on a filter. The yield was 1.08 g. of polymer, m.p. 63–65° with an inherent viscosity of 0.36. The benzene insoluble material was treated with water and an additional 0.26 g. of polymer, m.p. 65–68°, with an inherent viscosity of 0.63 was obtained.

(1) C. S. Marvel and R. R. Chambers, THIS JOURNAL, **70**, 993 (1948).

(2) C. S. Marvel and P. H. Aldrich, *ibid.*, **72**, 1978 (1950).

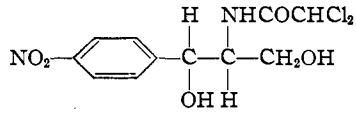
(3) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1941, p. 359.

NOYES CHEMICAL LABORATORY
URBANA, ILLINOIS RECEIVED JULY 31, 1950

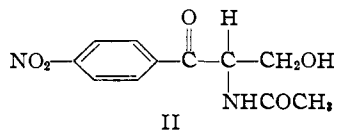
Chloromycetin.[1] Synthesis of α-Dichloroacetamido-β-hydroxy-*p*-nitropropiophenone

BY LOREN M. LONG AND H. D. TROUTMAN

In an earlier paper[2] the authors describe a method for the preparation of D-(*levo*)-*threo*-2-dichloroacetamido - 1 - *p* - nitrophenyl - 1,3 - propanediol (Chloromycetin, I) in which a necessary intermediate is *p*-nitroacetophenone. One of the latter steps in the synthesis involves the preparation of α-acetamido-β-hydroxy-*p*-nitropropiophenone (II). A comparison of the structure of II with that of I suggests that the substitution of a dichloroacetyl



I D-(*levo*)-*threo*



II

(1) Parke, Davis & Co. registered trademark for chloramphenicol.

(2) L. M. Long and H. D. Troutman, THIS JOURNAL, **71**, 2473 (1949).