quinone, it would appear that because of the symmetry of this molecule, interaction between the two keto-group vibrations occurs to produce two separate regions of absorption in a way similar to that well known for normal and cyclic anhydrides. In the chrysenequinone, however, even though the carbonyl bonds are adjacent, only one band attributable to the C=O vibration was observed. (c) The relative position of the bands associated with the carbonyl vibration in the two pyrenequinones (6.10 μ) and acetylpyrene (6.02 μ) are almost identical to that of *p*-benzoquinone (6.01 μ) and acetophenone (5.92 μ),[10] the carbonyl attached directly to the ring in each case being shifted almost 0.1 μ to longer wave lengths than that for the carbonyl in a side chain. The presence of a C—C linkage between the conjugated nucleus and the carbonyl group appears to diminish the shifting effect of conjugation. (d) The location of the absorption due to the pyrenequinones is about 0.1 μ to longer wave lengths than that previously recorded for keto-type C=O groups, conjugated or not conjugated, in oxidation products of hydrocarbons.[1-6] This may have a relation to the size of these highly conjugated molecules, for theoretical studies of bond fixation in compounds containing the carbonyl group led Coulson[11] to state that "...the larger the molecule in general the less fixed are the bonds; in other words the more like a metallic conductor does the system become...."

These results from the examination of the location of the infrared band associated with the carbonyl group in highly conjugated polycyclic compounds are evidence of the interest of this sort of study. Much work is necessary, however, before general conclusions on the mechanism of the band shifting can be drawn. This investigation forms a part of a research project supported by a research grant from the division of Research Grants and Fellowships of the National Institutes of Health, United States Public Health Service.

(10) *Ibid.*, pp. 165–166.

(11) C. A. Coulson, *Trans. Faraday Soc.*, **42**, 106 (1946).

INFRARED SPECTROSCOPY LABORATORY
FISK UNIVERSITY
NASHVILLE 8, TENNESSEE

RECEIVED DECEMBER 6, 1950

Enrichment of Antimony Activity through the Szilard–Chalmers Separation[1]

BY MILTON KAHN[2]

The two stable isotopes of antimony, Sb^{121} and Sb^{123}, capture thermal neutrons to form 2.8-day Sb^{122} and 60-day Sb^{124}, respectively.[3] Williams[4] reported that triphenylstibine is a suitable compound for the enrichment of the antimony activity through the Szilard–Chalmers separation. This reaction had previously been independently investigated by the author and in view of the fact that Williams did not give experimental details or enrichment factors it was thought worth while to report the results obtained by the author.

A solution of triphenylstibine in benzene was irradiated with thermal neutrons. Several portions of this solution were then extracted with various aqueous solutions. In each case a large fraction of the total antimony activity appeared in the aqueous phase associated with a small amount of inactive antimony. The results are summarized in Table I.

TABLE I

Aqueous soln.	Enrichment factor[a]	Sb/activity in aq. phase, %
H_2O	200	47
2.5 *f* HCl	200	54
6 *f* HCl	600	65
3 *f* NH_4OH	300	85
1 *f* NaOH	300	88

[a] Specific activity of antimony in aqueous phase divided by specific activity of antimony in benzene phase before extraction.

The appearance of as much as 1 mg. of antimony in the various aqueous solutions suggested that the triphenylstibine was initially contaminated with antimony in a water-soluble state. Accordingly, an experiment was carried out wherein a benzene solution of triphenylstibine was washed with 2.5 *f* hydrochloric acid prior to irradiation. In this case 58% of the antimony activity was enriched by a factor of 6000.

Composite decay curves of the antimony activity in the benzene phase and the aqueous phase of the foregoing experiment were obtained over a period of 36 days, zero time being approximately 3 days after the irradiation. An analysis of these curves, assuming that the long-lived component of each composite decay curve was 60-day Sb^{124}, revealed that they were made up of two components, the shorter lived component in each curve having a 2.8-day half-life. It was found that the same fraction of the total antimony activity appeared in the aqueous phase regardless of whether the calculations were based on the Sb^{122} activity or on the Sb^{124} activity. This suggests that this particular Szilard–Chalmers reaction is the same for both isotopes of antimony.

Experimental

Triphenylstibine obtained from Eastman Kodak Co. was used without further purification. A 0.75 *f* solution of triphenylstibine in thiophene-free benzene was irradiated with neutrons produced in the Washington University cyclotron. Paraffin blocks were placed around the solution in order to slow down the neutrons. Five ml. of the irradiated solution was transferred to a separatory funnel, diluted to 25 ml. with thiophene-free benzene, and extracted with 40 ml. of a given aqueous solution. A 5-ml. portion of the benzene phase, a 5-ml. portion of the aqueous phase, and a 5-ml. portion of the original active benzene solution were transferred to separate six-inch Pyrex test-tubes. Each tube was then counted in a reproducible geometry with a thick-walled Geiger-Mueller counter, the gamma radiation associated with the decay of Sb^{122} and Sb^{124} being detected. The activity determined in each case was of the order of 1000 counts per minute. In all experiments the sum of the activity in each phase equalled the total activity initially present in the benzene solution before extraction within a probable error of 4%. The stability of the Geiger–Mueller counter was checked from day to day with a gamma-ray standard which consisted of a sealed tube containing a solution of cobalt chloride with approximately 1000 counts per minute of 5.3-year Co^{60} activity.

---

(1) Presented before the Thirty-First Annual Meeting of the New Mexico Academy of Science, Physical Science Section, at Albuquerque, October, 1949.

(2) Department of Chemistry, University of New Mexico, Albuquerque, New Mexico.

(3) Livingood and Seaborg, *Phys. Rev.*, **52**, 135 (1937).

(4) Williams, *J. Phys. Colloid Chem.*, **52**, 603 (1948).

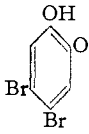
The inactive antimony present in the aqueous phase was estimated by precipitating the sulfide with hydrogen sulfide in 1 *f* hydrochloric acid solutions and comparing, visually, the volume of the sulfide centrifuged to the bottom of a 5-ml. centrifuge cone with that obtained by precipitation of known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

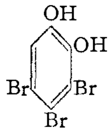
DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
SAINT LOUIS, MISSOURI
RECEIVED AUGUST 7, 1950

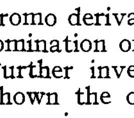
Bromination of Catechol

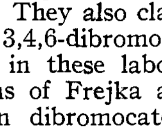
BY MORITZ KOHN

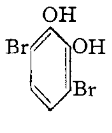
Cousin[1] reported that the bromination of catechol in acetic acid with two moles of bromine yielded a dibromocatechol, m. p. 92°. This compound was shown to be 4,5-dibromocatechol (I) since 4,5-dibromoveratrol was produced by the methylation of I. A German patent[2] claims the product of the bromination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

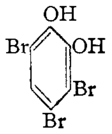

I


II


III


IV


V


VI

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 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 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.

	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

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.