procedure developed by Jones and Swift,[3] and also by a combination acidimetric-iodometric method in which total acid was determined by titration with standard NaOH to the phenolphthalein end-point, and phosphorous acid was determined by the method of Jones and Swift. It should be pointed out here that no reliable method for the analysis of mixtures of hypophosphorous and phosphorous acids, involving only volumetric procedures, was found in the literature. Confirmatory data, demonstrating the accuracy of the method of Jones and Swift, will appear in a subsequent publication.[3]

The results of the analyses can be briefly summarized as follows: The mole percentage of phosphorous acid in solid hypophosphorous acid which had not been subjected to the liquefaction-filtration process was about 2.6%. Two filtration-liquefaction cycles reduced the mole percentage of phosphorous acid to 0.15%. Three such cycles reduced it to 0.05%.

Qualitative tests for phosphate were run on aqueous solutions of some batches of solid hypophosphorous acid prepared by this method, using the ammonium molybdate procedure recommended by Swift,[4] modified by the substitution of perchloric acid for nitric acid. At no time was any yellow coloration or yellow precipitate noted. Comparison tests run on mixtures of hypophosphorous acid and NaH_2PO_4 showed this test to be sensitive to about 0.1 mole per cent. phosphate in the presence of hypophosphorous acid.

Stability of Hypophosphorous Acid and Sodium Hypophosphite Solutions.—In acid solution, the hypophosphite ion is slowly air-oxidized. In neutral and basic solutions, the mechanism of decomposition is more complex.[1] Since very few data are available on this point, we conducted some experiments to ascertain the extent of decomposition of H_3PO_2 under various conditions. The results were as follows: (1) Solid acid, stored in a desiccator at 5°, underwent no appreciable decomposition in three months. (2) The phosphorous acid content of 0.1 *f* solutions of solid acid, stored at 5°, increased about 0.1% in three months. (3) The rate of decomposition of 0.05 *f*. solutions of C.P. sodium hypophosphite, stored at room temperature, increased with *p*H,[5] the percentage decomposition in a year being 85% for a solution of *p*H 5 and 0.8% for a solution of *p*H 1.5.

Acknowledgments.—We are indebted to Professor E. H. Swift for his invaluable aid with the analytical problems. One of us (W. A. J.) wishes to thank the Research Corporation for a grant in aid in partial support of this research.

(3) R. T. Jones and E. H. Swift, to be submitted to *Anal. Chem.*

(4) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, N. Y., 1946, p. 550.

(5) *p*H varied by adding HCl.

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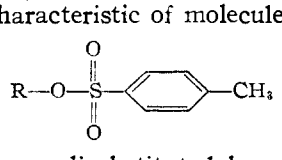
Infrared Absorption Spectra of *p*-Toluenesulfonic Acid and of Some of Its Esters

BY R. STUART TIPSON

In a study of certain *p*-toluenesulfonic esters of sugars and sugar derivatives, their infrared absorption spectra have been recorded. For interpretation of these spectra, it became desirable to identify the frequencies characteristic of molecules of the type



For (a) a para-disubstituted benzene ring, the Colthup chart[1] predicts a weak band in the 1590–1650 cm.$^{-1}$ region and a strong band in the 800–855 cm.$^{-1}$ region; for (b) $ROSO_2R'$, it predicts[1] strong bands in the 1330–1420 cm.$^{-1}$ and 1150–1200 cm.$^{-1}$ regions, respectively.

The infrared absorption spectra of *p*-toluenesulfonic acid (monohydrate) and of five of its esters have now been recorded;[2] the observed bands presumed due to the $-OSO_2$-*p*-C_7H_7 group are given in Table I.

TABLE I

INFRARED ABSORPTION OF *p*-TOLUENESULFONIC ACID AND ESTERS

Compound	Observed bands at (cm.$^{-1}$)	
p-Toluenesulfonic acid monohydrate[a]	1605, 815;	1240, 1065, 1030
Phenyl *p*-toluenesulfonate[a]	1600, 816;	1375, 1192, 1170
2,4-Dinitrophenyl *p*-toluenesulfonate[b]	1610, 822;	1355, 1190, 1175
β-Phenoxyethyl *p*-toluenesulfonate[b]	1600, 815;	1350, 1185, 1168
Tetra-O-*p*-toluenesulfonylerythritol[c]	1600, 815;	1365, 1190, 1180
1-O-*p*-Toluenesulfonylglyceritol[d]	1605, 827, 810;	1360, 1180, 1170

[a] Eastman Kodak Co. [b] R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944). [c] R. S. Tipson and L. H. Cretcher, *ibid.*, 8, 95 (1943). [d] R. S. Tipson, M. A. Clapp and L. H. Cretcher, THIS JOURNAL, 65, 1092 (1943).

Experimental

The source of each compound studied is indicated in Table I.

The infrared absorption spectra were recorded[2] on a Baird spectrophotometer; the wave length accuracy of this instrument is better than ±0.05 micron. All spectra were obtained for suspensions of the solid samples in Nujol. The relevant bands observed are given in Table I.

The bands exhibited by *p*-toluenesulfonic acid monohydrate are compatible with the frequencies predicted by the Colthup chart[1] for molecules of the type RSO_3H.

(1) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

(2) The author is indebted to Dr. Foil A. Miller and R. B. Hannan, Jr., of the Department of Research in Chemical Physics, Mellon Institute, for recording the infrared spectra.

DEPARTMENT OF RESEARCH IN ORGANIC CHEMISTRY
MELLON INSTITUTE
PITTSBURGH 13, PENNSYLVANIA RECEIVED OCTOBER 29, 1951

The Synthesis of δ-(*p*-Chlorophenyl)-hydantoic Acid-Cl^{36}

BY HOWARD H. WOEBER[1]

Many derivatives, formed by the reaction of phenyl isocyanate with amino acids, are described in the literature. These hydantoic acids are usually crystalline compounds soluble in organic solvents, and when labeled with a radioactive isotope, should be useful in amino acid determinations. δ-*p*-Chlorophenyl isocyanate-Cl^{36} was selected for study and the glycine derivative prepared. Although the steps in the synthesis are not new, considerable modification was necessary for the use of radioactive chlorine.[2]

***p*-Chloroacetanilide-Cl^{36}.**—Chlorine (35 mg., 5 microcuries) was evolved by the addition of cold, fuming sulfuric acid (3 ml., 15% SO_3) to $NaCl^{36}$ dissolved in superoxol (1 ml.) cooled in ice (chlorine yield, 95–100%). The chlorine was passed into 30 ml. of a saturated solution of acet-

(1) 1325 N. W. 6th Ave., Gainesville, Florida.

(2) For material supplementary to this article order Document 3408 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film), or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

anilide and the chloroacetanilide-Cl^{36} recrystallized from water; yield 23.8 mg. (28.6%).

δ-(*p*-Chlorophenyl)-hydantoic Acid-Cl^{36}.—Chloroacetanilide-Cl^{36} was hydrolyzed by heating under reflux with 0.5 ml. of concd. HCl and *p*-chlorophenyl isocyanate Cl^{36} was formed by the reaction of *p*-chloroaniline-Cl^{36} hydrochloride with phosgene in dioxane. Excess phosgene was removed by evacuation at 0° and the isocyanate reacted with glycine (30 mg.) in alkaline solution. Acidification precipitated δ-(*p*-chlorophenyl)-hydantoic acid-Cl^{36}; yield 17.6 mg. (15.6%). Non-radioactive hydantoic acid, prepared by this method, melted at 189–191° with decomposition.

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Synthesis of α-Aminocyclopropylacetic Acid

BY PETER H. LOWY

In a study of the biological effect of analogs of the naturally occurring amino acids, D,L-α-aminocyclopropylacetic acid was synthesized. It was prepared by a Strecker synthesis from cyclopropanecarboxaldehyde. The intermediate hydroxynitrile was aminated in methanolic ammonia.[1] Because of the instability of cyclopropane compounds toward acids the hydrolysis was carried out with barium hydroxide.[2] Like many other D,L-amino acids cyclopropylaminoacetic acid tastes slightly sweet. The structure was confirmed by oxidation with ninhydrin to cyclopropanecarboxaldehyde.

The amino acid did not affect the growth of wild type *Neurospora crassa* 25a on minimal medium[3] in concentrations of 10 and 40 γ per 3 ml.[4]

Experimental

Cyclopropylcyanide was prepared from γ-chlorobutyronitrile[5] by the method of Schlatter.[6]

Cyclopropane carboxaldehyde was prepared by reduction of cyclopropyl cyanide with one-quarter mole of lithium aluminum hydride according to Smith and Rogier.[7]

α-Aminocyclopropylacetic Acid.—A solution of 12.7 g. of ammonium chloride in 32 ml. of water was kept at 0–5° and stirred mechanically while 14 g. of cyclopropane carboxaldehyde, followed by a solution of 14.3 g. of potassium cyanide in 22 ml. of water, was added dropwise. The mixture was stirred for 2 hours at room temperature and allowed to stand overnight. It was extracted with six 30-ml. portions of ether. After removal of the ether by distillation, the residue of the combined ether extracts was dissolved in 80 ml. of methanol. The solution was saturated with dry ammonia at 0–5°, and allowed to stand for 4 days. Excess ammonia was driven off with an air stream and the solvent removed *in vacuo*. The residual crude cyclopropylaminoacetonitrile weighed 9.9 g.

18.5 g. of barium hydroxide octahydrate was dissolved in its crystal water (steam-bath). It was stirred mechanically at *ca.* 95° while the nitrile (thinned with 5 ml. of methanol) was added dropwise over 40 minutes. After heating and stirring for another 40 minutes, 100 ml. of hot water was added. The hot solution was saturated with carbon dioxide and filtered by suction with the aid of Super-Cel. The precipitate was extracted twice with 50 ml. of hot water while bubbling with carbon dioxide. The combined clear filtrates were concentrated *in vacuo* to 10–20 ml. 2.21 g. (9.3% based on the aldehyde) of the crude amino acid was obtained in several crops (directly from the aqueous concentrate and by precipitation with methanol or ethanol).

Anal. Calcd. for $C_5H_9O_2N$: C, 52.15; H, 7.88; N, 12.17. Found: C, 51.99; H, 7.66; N, 12.33.[8]

Degradation with Ninhydrin.—To 115 mg. of the amino acid dissolved in 5 ml. of hot water a solution of 700 mg. of ninhydrin in 20 ml. of 0.2 molar citrate buffer (*p*H 5) was added.[9] The mixture turned dark purple and was heated in a steam-bath for 20 minutes, while with a slow stream of nitrogen the volatile aldehyde was driven into a trap containing a solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The 2,4-dinitrophenylhydrazone alone as well as mixed with that prepared from authentic cyclopropanecarboxaldehyde melted at 186°.

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(2) J. Ford, THIS JOURNAL, **67**, 876 (1945); *Org. Synth.*, **27**, 1 (1947).
(3) G. W. Beadle and E. L. Tatum, *Am. J. Bot.*, **32**, 678 (1945).
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(9) S. Moore and W. H. Stein, *J. Biol. Chem.*, **176**, 367 (1948).

KERCKHOFF LABORATORIES OF BIOLOGY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIFORNIA RECEIVED NOVEMBER 5, 1951

Ion Aggregation in Gallium(III) Chloride Solutions Containing Added Alkali

BY THERALD MOELLER AND GLENDALL L. KING

In an earlier communication,[1] it was reported that solutions of gallium(III) chloride, bromide, or nitrate may be treated with up to approximately 3 moles of hydroxyl ion per mole of gallium ion initially present without effecting precipitation of the hydrous oxide. Such solutions remain perfectly clear but flocculate sharply and completely upon addition of more alkali. Although appreciable delays in hydrous oxide or hydroxide precipitation are not particularly uncommon, lack of precipitation in the presence of essentially stoichiometric quantities of hydroxyl ion is unusual. Either excessive ion aggregation in solution due to added hydroxyl ion or peptization of the hydrous oxide by excess gallium ion may be regarded as a possible explanation.

Electrometric titration data[1] indicate that in the range prior to flocculation added hydroxyl ion is consumed without appreciable increase in *p*H, but they do not permit decision between an ion aggregation process and a peptization process. If, however, the diffusion current in a gallium(III) salt solution is proportional to gallium ion concentration and remains reasonably constant, polarographic data might permit such a decision. It seems reasonable that any ion aggregation resulting from binding of gallium ions by hydroxyl ions would manifest itself in a corresponding reduction in the magnitude of the diffusion current, whereas if the nature of the gallium species remained the same (as in peptization), no alterations in diffusion current would result when hydroxyl ion is added.

Zeltzer[2] reported that gallium(III) is reduced irreversibly at the dropping mercury electrode at a potential of −1.08 v. (*vs.* normal calomel electrode) from dilute solutions of its salts in 0.001 *N* hydrochloric acid. For solution of the present problem, irreversibility is of no consequence if level diffusion regions can be obtained. Experiment showed this to be possible in chloride solutions containing 0.05 *M* potassium chloride as supporting electrolyte. Corrected diffusion current values obtained by subtracting residual current values were found to be

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