of benzene. The cold mixture was poured over ice and extracted with ether. The extracts were thoroughly washed with water, sodium bicarbonate solution and again with water. The dried ether solution was distilled, a fraction boiling at 115–125° (2 mm.) and weighing 136 g. (55%) being collected. The analytical sample boiled at 103–104° (1 mm.), $n^{25}\mathrm{D}$ 1.5211.

Anal.[8] Calcd. for $C_{15}H_{22}O_2$: C, 78.02; H, 9.01. Found: C, 77.98; H, 8.79.

Ethyl β-(2-Isopropyl-5-methyl)-phenylbutyrate.—A solution of 32 g. of the unsaturated ester in 150 ml. of ethanol was reduced with 0.3 g. of platinum oxide. The calculated amount of hydrogen was taken up in three hours. Removal of solvent followed by distillation gave 30 g. of product (94%) boiling at 95–110° (1.3 mm.). The analytical sample boiled at 95–96° (1 mm.), $n^{25}\mathrm{D}$ 1.4922.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.36; H, 9.74. Found: C, 78.04; H, 9.66.

β-(2-Isopropyl-5-methyl)-phenylbutyric Acid.—Saponification of 29 g. of the ester with 125 ml. of 90% ethanol containing 15 g. of potassium hydroxide yielded a viscous oil, b.p. 140–150° (2 mm.), wt. 21.8 g. (84%), which could not be induced to crystallize. The analytical sample boiled at 141–142° (1.8 mm.), $n^{25}\mathrm{D}$ 1.5085.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.84; H, 8.93.

3,4-Dimethyl-7-isopropylindanone.—A mixture of 20 g. of the acid and 25 g. of thionyl chloride was heated on the steam-bath for 2 hours and allowed to stand overnight. Distillation gave 20.5 g. of acid chloride, b.p. 105–115° (2 mm.) which was poured cautiously into 50 ml. of dry benzene containing 15 g. of aluminum chloride. After 12 hours the mixture was decomposed with ice-hydrochloric acid and extracted with ether. Distillation of the washed and dried extracts gave 13.5 g. of indanone (73%), b.p. 95–115° (1.5 mm.). The analytical sample boiled at 96–98° (1 mm.), $n^{25}\mathrm{D}$ 1.5412.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.11; H, 8.97. Found: C, 83.19; H, 8.81.

1,7-Dimethyl-4-isopropylindan.—Reduction of 88 g. of the indanone with amalgamated zinc in the manner described earlier[9] yielded 52 g. of a fraction boiling in the range 60–90° (2 mm.) and 23 g. boiling at 95–125° (2 mm.), apparently largely unreduced ketone. On redistillation 41 g. (79% based on recovered material) of indan was collected at 78–83° (2 mm.). The analytical sample boiled at 76–78° (1.5 mm.), $n^{23}\mathrm{D}$ 1.5200.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.00; H, 10.72.

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[8] Analyses by Clark Microanalytical Laboratory, Urbana, Ill.

[9] W. Herz, THIS JOURNAL, **73**, 4295 (1951).

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The Purification and Stability of Hypophosphorous Acid

BY WILMER A. JENKINS AND RICHARD T. JONES

Hypophosphorous acid, H_3PO_2, has been the subject of extensive experimental investigation,[1] but to our knowledge, the acid previously used has always contained from one to five mole per cent. phosphorous acid. In the course of some kinetic and analytical investigations of this substance, it became necessary to prepare it in a very pure form. The following procedure was devised to meet the purpose, and represents, as far as we know, a method which has never before been tried with hypophosphorous acid. This method yields solid hypophosphorous acid containing less than 0.1 mole per cent. phosphorous acid and less than 0.1 mole per cent. phosphoric acid.

Purification of Hypophosphorous Acid.—Hypophosphorous acid from almost any source will serve as a starting material, as long as it is about 10 *f*. The commercial grade 50% acid (Merck and Co., Inc.), which usually contains from two to three mole per cent. phosphorous acid, meets this requirement and was used in all of our preparations. If more dilute acid from another source is used, it is advisable to concentrate it by vacuum desiccation before proceeding with this purification method.

About 600 ml. of concentrated hypophosphorous acid is placed in a one-liter filtering flask, the side-arm of which is connected to a water aspirator. Through a two-hole stopper in the top of the flask run a thermometer and a coarse gas dispersion tube, which opens below the liquid surface and is connected to a source of dry nitrogen. The flask rests on a hot-plate. After all of the air has been thoroughly flushed out of the system with nitrogen, the aspirator and hot-plate are turned on, and the nitrogen flow is cut down to a small stream of bubbles. The hot-plate is regulated so that the temperature remains around 40° during the evaporation. The evaporation is continued until the volume of the solution is about 300 ml., at which point the evaporation will appear to cease. The hot-plate is now turned off and the solution allowed to cool. The nitrogen supply and the aspirator are then turned off and the liquid in the flask poured into a wide-mouthed erlenmeyer flask which is stoppered well and placed in a Dry Ice–acetone-bath. After a few hours in the bath, the contents of the flask will freeze; in some cases, it may be necessary to scratch the walls of the flask to induce solidification. The flask is then removed from the bath and allowed to stand in a cold room or refrigerator (∼5°) for about 12 hours, after which time the flask contents should be from 30 to 40% liquid.

The following operations must be carried out in a cold room.[2] The mixture is now filtered by suction through a *rapid*, retentive paper such as Whatman No. 44. The filtrate is discarded, the solid pressed dry on the paper, transferred to a crystallizing dish, and allowed to stand in the cold until about 20 to 30% of it liquefies. It is then refiltered, allowed to stand to 30% liquefaction, and filtered a third time. After the last filtration, the solid is stored over $Mg(ClO_4)_2$ in an evacuated desiccator in a cold room.

This entire procedure is very empirical; nevertheless, it yields a very pure product. For best results, careful attention should be paid to the following points: (a) the temperature should not rise above 45° during the evaporation process. (b) If the evaporation is not continued until a minimal amount of water is left in the acid, the mixture may liquefy completely in a few hours after it is removed from the Dry Ice–acetone-bath. This can usually be avoided if the liquid is evaporated to about half its original volume, at which point the evaporation will appear to cease. (c) All operations involving solid hypophosphorous acid must be carried out at temperatures well below its melting point (26.5°). A cold room at 5° is entirely satisfactory in this regard.[2] (d) At least two or three filtrations, with partial liquefaction in between, are essential. The yield in this preparation is necessarily low, about 10%.

If large crystals of this product are desired, they can be prepared by recrystallizing the white solid from *n*-butanol. (The high solubility of hypophosphorous acid in the lower alcohols renders them impractical for recrystallization purposes.) Just enough *n*-butanol is added to the solid to dissolve it at room temperature, and the solution is then cooled in a salt–ice-bath (−20°) to deposit crystals. One of us (W. A. J.) carried out ten such cycles; analysis of the final product for phosphorous acid showed no increase in purity over that obtained from two filtrations as described above. No attempt was made to remove all of the *n*-butanol from the crystals, and it is not known whether or not the crystals contained *n*-butanol of crystallization.

Analysis of the Purified Product.—Aqueous solutions of the white solid from the above procedure were analyzed for hypophosphorous and phosphorous acids by an iodometric

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[1] Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, chapter 6.

[2] A referee has suggested to us that in lieu of a cold room, the apparatus described by Schwab and Wichers, *J. Research Natl. Bur. Standards*, **32**, 253 (1944), could be used. We feel that this point is well taken, but we cannot guarantee success if this method is used, since we have not tried it.

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.

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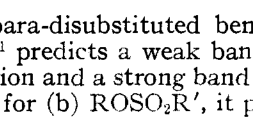
Infrared Absorption Spectra of *p*-Toluenesulfonic Acid and of Some of Its Esters

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*-Toluenesulfonylglycerītol[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.

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[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.

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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-

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[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.