The Preparation of Certain Nitrogen-Substituted Sulfon-*m*-toluidides and Sulfon-*p*-toluidides

BY GEORGE H. YOUNG

This paper is a continuation of an investigation of N-alkyl-*p*-toluene sulfonanilides.[1] Yields of 80–98% of *m*-sulfontoluidides and 60–91% of *p*-isomers were obtained. Recrystallized from methanol (the ethyl *m*-toluidide from 5:1 ethanol–ether), these compounds deposit as blunt needles or thick prisms. They are insoluble in water, difficultly soluble in ether and soluble in most other common solvents, with the meta derivatives usually having the greater solubility.

TABLE I

THE SULFON-*m*-TOLUIDIDES

p-Toluene sulfon-*m*-toluidide	Formula	M. p., °C.	Sulfur analyses, % Calcd.	Found
N-Methyl	$C_{15}H_{17}O_2NS$	63	11.64	11.61
Ethyl	$C_{16}H_{19}O_2NS$	60.5–61	11.07	11.08
n-Propyl	$C_{17}H_{21}O_2NS$	51	10.56	10.71
Isoamyl	$C_{19}H_{25}O_2NS$	76.5	9.55	9.61

TABLE II

THE SULFON-*p*-TOLUIDIDES

p-Toluene sulfon-*p*-toluidide	Formula	M. p., °C.	Sulfur analyses, % Calcd.	Found
N-Isopropyl	$C_{17}H_{21}O_2NS$	107	10.56	10.76
Isobutyl	$C_{18}H_{23}O_2NS$	73	10.09	10.04
n-Amyl	$C_{19}H_{25}O_2NS$	59.5–60	9.55	9.70
Isoamyl	$C_{19}H_{25}O_2NS$	89.5–90	9.55	9.43

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[1] Young, THIS JOURNAL, **56**, 2167, 2783 (1934).

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Preparation of 5-Keto-gluconic Acid by Bromine Oxidation

BY ELMER W. COOK AND RANDOLPH T. MAJOR

In the oxidation of glucose with bromine generated electrolytically according to the Isbell[1] method it was noticed that a reducing substance remained even after electrolysis had been continued longer than was necessary theoretically to convert the glucose to gluconic acid.

Sheppard and others[2] have observed likewise the presence of a reducing substance during the oxidation of glucose or gluconic acid with bromine.

This reducing substance has been isolated and proved to be the 5-keto-gluconic acid first described by Boutroux.[3]

Experimental

The oxidation of glucose was carried out as described by Isbell. The electrolyte consisted of 7 g. of glucose, 5 g. of calcium carbonate, and 5 g. of calcium bromide in 140 cc. of water. Electrodes of platinum were used. The electrolysis was continued for four ampere hours at a current density of 2.5 amperes per sq. dm.

At the end of the electrolysis the calcium carbonate was filtered and the resulting solution concentrated to 30 cc. Alcohol was added to a slight permanent turbidity and the solution allowed to stand for two to three weeks. The precipitate which had formed slowly during this time was filtered and dissolved in boiling water. After standing for forty-eight hours a calcium salt had settled out in the form of a fine crystalline crust consisting of small rhombohedra; yield 0.8 g. The properties[4] of this salt agreed in every respect with those of the well-known calcium 5-keto-gluconate. It reduced Fehling's solution, dissolved in about 50 parts of boiling water, and lost practically no weight when dried *in vacuo* at 85–90° (distinction from calcium saccharate). A 2% solution obtained by dissolving the calcium salt in the calculated amount of hydrochloric acid gave $\alpha^{20}{}_D$ $-14°$, based on the free acid.

Anal. Calcd. for $Ca(C_6H_9O_7)_2 \cdot 3H_2O$: Ca, 8.34; C, 29.98; H, 5.04. Found: Ca, 8.46; C, 30.18; H, 5.18.

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[1] Isbell and Frush, *Bur. Standards J. Research* **6**, 1145 (1931).

[2] Everett, Edwards and Sheppard, *J. Biol. Chem.*, **104**, 11 (1934); Sheppard and Everett, *ibid.*, Proc. Am. Soc. Biol. Chemists, XXVIII, Annual Meeting, p. LXXX, 1934.

[3] Boutroux, *Compt. rend.*, **102**, 924 (1886); **127**, 1224 (1898).

[4] Ruff, *Ber.*, **32**, 2270 (1899); Kiliani, *ibid.*, **55**, 2820 (1922); Barch, THIS JOURNAL, **55**, 3653 (1933).

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The Indium Salts of Some Organic Acids

BY JOHN B. EKELEY AND WAYNE W. JOHNSON

Indium hydroxide forms basic salts when treated with propionic, *n*-butyric, trichloroacetic, benzoic or with ortho, meta or para-toluic acids.

The propionate and the *n*-butyrate were prepared by dissolving weighed quantities of the hydroxide in a slight excess of the pure acids and the excess acid evaporated off on the water-bath until the salts were precipitated. The precipitates were boiled with alcohol, filtered, washed with ether and dried over sulfuric acid. These salts are white powders insoluble in water, alcohol, and ether; yield quantitative.

The trichloroacetate was prepared in the same manner as the two preceding salts, except that, since the salt is soluble in water, alcohol and ether, the excess of acid was removed by drying the product to constant weight at 110°; yield quantitative.

The benzoate was prepared by precipitating

ANALYSES

Salt	In, %			C, %			H, %			Cl, %		
	Calcd.	Found		Calcd.	Found		Calcd.	Found		Calcd.	Found	
$(C_2H_5COO)_2InOH$	41.31	41.40	41.48	25.91	25.72	25.80	3.99	3.93	4.02			
n-$(C_3H_7COO)_2InOH$	37.54	37.67	37.62	31.38	31.32	31.20	4.94	4.76	4.84			
$(CCl_3COO)_2InOH$	25.12	24.96	25.03	10.51	10.61	10.56	0.22	0.25	0.29	46.60	46.63	46.38
$(C_6H_5COO)_2InOH$	30.71	30.71	30.48	44.94	44.82	44.75	2.94	2.91	3.01			
o-$(C_8H_8COO)_2InOH$	28.56	28.62	28.42	47.77	47.62	47.71	3.76	3.72	3.67			
m-$(C_8H_8COO)_2InOH$	28.56	28.63	28.52	47.77	47.70	47.83	3.76	3.65	3.60			
p-$(C_8H_8COO)_2InOH$	28.56	28.41	28.39	47.77	47.70	47.86	3.76	3.71	3.80			

the salt from an acid indium sulfate solution by means of a solution of sodium benzoate and washing the precipitate with alcohol and ether; yield quantitative.

The ortho, meta and para toluates were each prepared by adding indium hydroxide to a slight excess over the theoretical quantity of the melted acid and the mixture kept in the melted state until all the hydroxide was dissolved. After being cooled, the excess acid was removed by boiling the melt in water, filtering off the salt and washing it with alcohol and ether; yield quantitative.

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d-Ribose from the Croton Bean

BY JOSEPH R. SPIES WITH NATHAN L. DRAKE

Cherbuliez and Bernhard[1] have recently isolated from the croton bean, *Croton tiglium* (L), a new glycoside, which they identified as 2-hydroxy-6-amino-purine-*d*-riboside, and which they proposed to call a "crotonoside." They did not, however, succeed in crystallizing the sugar residue obtained by hydrolysis.

The accumulation of a quantity of this material has afforded us an opportunity to examine it. We have succeeded in crystallizing the sugar residue and have conclusively established its identity as *d*-ribose, thus confirming the findings of these workers.

Experimental

Isolation of the Crotonoside.—The glycoside was extracted from the ground unshelled beans with methanol and isolated as described by Cherbuliez and Bernhard.[1] From 125 kg. of beans was obtained 345.0 g. of crude product which contained about 25% of pure crotonoside (0.07%). When recrystallized to constant melting point and dried in the Abderhalden at 110°, it decomposed at 245–247°. (All melting points were taken with standardized Anschütz thermometers.)

Anal. Calcd. for $C_{10}H_{13}O_5N_5$: C, 42.37; H, 4.59; N, 24.73. Found: C, 42.01; H, 4.47; N, 24.56.[2]

Crystallization of *d*-Ribose.—The crotonoside was hydrolyzed and the ribose isolated as described by Cherbuliez and Bernhard.[1] The sirup obtained was dried in a vacuum over phosphorus pentoxide, and when nucleated with an authentic specimen of *d*-ribose it slowly crystallized.[3] Recrystallization three times from absolute ethanol and once from dry isopropanol gave a product that melted constantly at 83–87° with previous softening at 80°. The melt, however, was cloudy; $[\alpha]^{20-25}\mathrm{D}$ $-17.5°$ (c = 5.00 g./100 ml.); (Levene and Jacobs, 85°, $[\alpha]^{20}\mathrm{D}$ $-19.2°$)[4] (Phelps, Isbell and Pigman, 87°, $[\alpha]^{1}\mathrm{D}$ $-23.7°$.)[5]

Tetraacetate.—The tetraacetate (tetraacetylribose) was prepared as described by Levene and Tipson,[6] who give 110° as the melting point and $[\alpha]^{24}\mathrm{D}$ $-52.0°$ and $[\alpha]^{25}\mathrm{D}$ $-54.3°$ in chloroform. The present writers' product was recrystallized to constant melting point from ethanol; m. p. 108–109°; in chloroform $[\alpha]^{24}\mathrm{D}$ $-54.1°$ (c, 6.52 g./100 ml.).

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.06; H, 5.66. Found: C, 49.33; H, 5.88.

Phenylosazone.—The phenylosazone was recrystallized to constant melting point from 40% ethanol; m. p. 165–165.5° (Levene and LaForge, 166°).[7]

***p*-Bromophenylhydrazone.**—The *p*-bromophenylhydrazone was prepared as described by Cherbuliez and Bernhard.[1] It was recrystallized to constant melting point from an absolute ethanol–ether solution; m. p. 164° (Ekenstein and Blanksma,[8] 164°) (Levene and Jacobs,[9] 170°).

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(1) Cherbuliez and Bernhard, *Helv. Chim. Acta*, **15**, 464 (1932).

(2) The authors are indebted to Mr. H. M. Duvall of the University of Maryland for the micro Kjeldahl determination.

(3) The writers are indebted to Mr. F. P. Phelps, of the Bureau of Standards of the U. S. Dept. of Commerce, for this material.

(4) Levene and Jacobs, *Ber.*, **42**, 2469, 2474 (1909).

(5) Phelps, Isbell and Pigman, THIS JOURNAL, **56**, 747 (1934).

(6) Levene and Tipson, *J. Biol. Chem.*, **92**, 109 (1931).

(7) Levene and LaForge, *ibid.*, **20**, 429 (1915).

(8) Ekenstein and Blanksma, *Chem. Weekblad*, **10**, 664 (1913).

(9) Levene and Jacobs, *Ber.*, **42**, 2703 (1909).

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The Decomposition of Acetylphthalimide

BY CHARLES D. HURD, MALCOLM F. DULL AND
J. W. WILLIAMS

It was reported earlier[1] that acetylphthalimide decomposed at 240–325° into phthalimide, acetic

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(1) Hurd and Dull, THIS JOURNAL, **54**, 2437 (1932).