Solubility of Strychnine Acid Sulfate in Sulfuric Acid

BY BENJ. M. G. ZWICKER[1] AND REX J. ROBINSON

Information concerning the solubility of strychnine acid sulfate in sulfuric acid was of interest to the authors in the separation of strychnine from some of its reduction products in a 60% (by weight) sulfuric acid medium. Since this information was not available in the literature, it became necessary to determine it experimentally.

Merck U. S. P. XI Strychnine Sulfate was dissolved in 64% sulfuric acid to the extent of 10.5 g. of base per 100 g. of solvent. Portions of this solution were weighed into glass-stoppered bottles. Appropriate quantities of water were added to these aliquots, carefully mixed, warmed and then allowed to attain equilibria at 20°. After several hours, the bottles were reweighed and the crystalline strychnine acid sulfate was separated by decanting through a weighed Jena sintered-glass micro-crucible of porosity II. The strychnine acid sulfate was converted to strychnine by macerating it with 6 *N* ammonium hydroxide. The insoluble base was then transferred to the filter, washed with a little dilute ammonium hydroxide, dried *in vacuo* at 60° and then weighed.

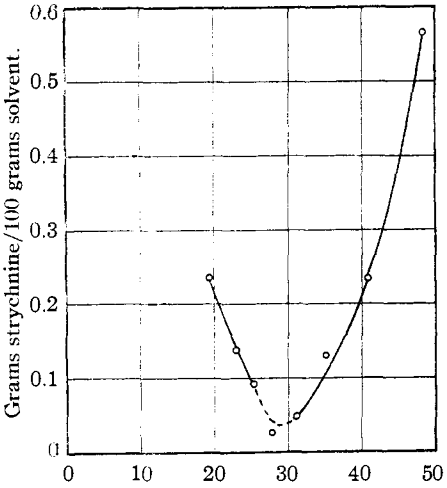

Fig. 1.—Solubility of strychnine acid sulfate in sulfuric acid.

The solubilities, determined by difference, are shown in Fig. 1 as grams of strychnine per 100 g. of sulfuric acid solution. These data indicate a minimum solubility of strychnine at an acid concentration of about 28.5%. At 20° the solubility was 0.029 g. per 100 g. of 28.5% acid. Also it was found that by lowering the temperature to 6° the solubility was decreased to 0.020 g. per 100 g. of 28.5% acid.

TABLE I

SOLUBILITY OF STRYCHNINE ACID SULFATE IN SULFURIC ACID AT 20°

% H_2SO_4	Strychnine, g.	Strychnine per 100 g. solvent, g.
59.7	0.4016	10.29[a]
48.3	.0280	0.569
40.9	.0142	.237
35.3	.0092	.133
31.1	.0040	.051
27.8	.0026	.029
25.4	.0093	.095
23.0	.0150	.139
19.4	.0298	.237

[a] Not a completely saturated solution.

CHEMICAL AND OCEANOGRAPHIC LABORATORIES
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON
RECEIVED AUGUST 18, 1941

---

[1] Present address: The Hydrocarbon Chemical and Rubber Co., The B. F. Goodrich Co., Akron, Ohio.

NEW COMPOUNDS

Oxime of Furfuralacetone

This compound was prepared in very poor yield (5%) by the method of Harries and DeOsa[1] for the oxime of benzalacetone. It was recrystallized several times from dilute ethanol and formed small tan-colored leaflets; melting point, 88–90°.

Anal. Calcd. for $C_8H_9O_2N$: N, 9.27. Found: N, 9.30. The analysis was performed by Dr. T. S. Ma.

---

(1) Harries and DeOsa, *Ber.*, **36**, 2998 (1903).

260 ADDISON ROAD
RIVERSIDE, ILL.
RICHARD D. KLEENE
RECEIVED SEPTEMBER 8, 1941

Derivatives of 1-Phenylcycloparaffin-1-carboxylic Acids

For purposes of identification the following derivatives of 1-phenylcyclobutane-, 1-phenylcyclopentane- and 1-phenylcyclohexane-1-carboxylic acids have been prepared. The acids were prepared by conventional methods,[1] and their physical constants agreed with those given in the literature.

The acids were refluxed with a slight excess of thionyl chloride for ten to twenty minutes and then, after cooling, a benzene solution of the appropriate amine was added and the entire mixture refluxed for a few minutes. The warm solution was suction-filtered to remove the precipitated amine hydrochloride, and the filtrate was washed succes-

---

(1) Case, THIS JOURNAL, **56**, 715 (1934).

sively with small amounts of water, sodium hydroxide solution, dilute hydrochloric acid, and again with water. The benzene was then evaporated on a steam-bath and the residue recrystallized from water–alcohol mixtures. The method was found to work satisfactorily with quantities of acid as small as 50 mg. In some cases it was found necessary to use a small amount of decolorizing charcoal to render the product colorless.

The analyses were performed by Dr. T. S. Ma.

TABLE I

Acid	Derivative	M. p., °C. (uncor.)	Empirical formula	N analyses, % calcd.	Found
1-Phenylcyclobutane-1-carboxylic	Amide	75–76	$C_{11}H_{13}ON$	8.00	7.83
	Anilide	96–96.2	$C_{17}H_{17}ON$	5.57	5.36
	p-Toluide	129–131	$C_{18}H_{19}ON$	5.28	4.98
	o-Bromoanilide	82–83	$C_{17}H_{16}ONBr$	4.23	4.24
1-Phenylcyclopentane-1-carboxylic	Anilide	98–99	$C_{18}H_{19}ON$	5.28	5.54
	p-Toluide	145–146	$C_{19}H_{21}ON$	5.02	4.95
	o-Bromoanilide	75–76	$C_{18}H_{18}ONBr$	4.07	4.13
1-Phenylcyclohexane-1-carboxylic	Anilide	85–86	$C_{19}H_{21}ON$	5.03	5.01
	p-Toluide	165–166	$C_{20}H_{23}ON$	4.78	4.89
	o-Bromoanilide	167–169	$C_{19}H_{20}ONBr$	3.91	3.93

CHEMISTRY DEPARTMENT
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS RICHARD D. KLEENE

RECEIVED SEPTEMBER 25, 1941

α-Naphthylisopropylpotassium

This compound was prepared according to the method of Ziegler[1] for the preparation of the corresponding phenyl compound.

Methyl Ether of α-Naphthyldimethylcarbinol.—Twenty grams of the carbinol was refluxed with 8 g. of sodamide in 75 ml. of dioxane and then with 40 g. of methyl iodide. After removal of the solvent, and two vacuum distillations, 8 g. of a colorless, fragrant oil was obtained boiling at 100–101° at 3 mm. pressure. The substance displayed a light purple fluorescence: d^{20}_4 1.0422, n^{20}_D 1.5867, M_D (calcd.) 63.76, M_D (obs.) 64.49.

Anal. Calcd. for $C_{14}H_{16}O$: OCH_3, 15.5; C, 84.00; H, 8.00. Found: OCH_3, 15.24; C, 84.14; H, 7.98.

α-Naphthylisopropylpotassium.—Three grams of the methyl ether was sealed off in a flask under nitrogen with 100 ml. of absolute diethyl ether and excess sodium–potassium alloy. The cleavage started almost immediately and the solution turned a deep cherry-red color, showing the presence of an organometallic compound. The alkyl was identified by treatment with carbon dioxide, followed by isolation of the resulting carboxylic acid.

α-Naphthylisobutyric Acid.—The flask containing the alkyl solution was broken open, and gaseous carbon dioxide introduced. The acid was isolated as small white needles, which after recrystallization from alcohol melted at 121–122°. The yield was 32% based on the amount of methyl ether originally taken.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.50; H, 6.55; neut. equiv., 214. Found: C, 78.88; H, 6.63; neut. equiv., 215.

CHEMISTRY DEPARTMENT
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS RICHARD D. KLEENE

RECEIVED SEPTEMBER 25, 1941

Tetrahydrofuran Compounds. II. Preparation of 1-Tetrahydrofuryl-3-chlorobutane

This compound was prepared with the view of determining the effect of the tetrahydrofuryl group as a substituent in alkyl halides.

1-Tetrahydrofurylbutanol-3.—Thirty-four grams (0.25 mole) of Eastman Kodak Co. furfuralacetone was placed in a rotating-type steel bomb along with 3 g. of nickel oxide catalyst and 30 ml. of ethanol. The initial hydrogen pressure was 100 atmospheres. The contents were then heated at 125° for four hours. After the reaction was complete, the catalyst was separated and the desired product was obtained as a colorless liquid, n^{20}_D 1.4512. The yield was 63%.

1-Tetrahydrofuryl-3-chlorobutane.—Forty grams of the alcohol with 28 g. of pyridine was placed in a 3-necked, 500-ml. flask with stirrer, dropping funnel and condenser. Forty grams of thionyl chloride was added dropwise during thirty minutes. The temperature was not allowed to rise above 50°. On standing overnight, a precipitate of pyridine hydrochloride settled out. The liquid was decanted, and the precipitate washed thoroughly with dry diethyl ether. The washings were combined with the main product, thoroughly washed with water, and then dried over anhydrous sodium sulfate. The ether was distilled off, and the residue distilled in vacuum. There was obtained 19.5 g. of a colorless liquid with a pungent odor, boiling at 58–60° at 3 mm. pressure: n^{20}_D 1.4505, d^{20}_{20} 0.9976, M_D(calcd.) 43.46, M_D(obs.) 43.82. The product was insoluble in water.

Anal. Calcd. for $C_8H_{15}OCl$: Cl, 21.82. Found: Cl, 22.04.

2211 BURLING STREET
CHICAGO, ILLINOIS RICHARD D. KLEENE

RECEIVED SEPTEMBER 25, 1941

2-Methyl-tetradecanol-1

Thirty-three grams (0.12 mole) of ethyl methyl-*n*-dodecylacetate (b. p. 166° (6 mm.), n^{20}_D 1.4369, from methyl-*n*-dodecylacetic acid of setting point 36.50°) was dissolved in 330 ml. of petroleum ether (b. p. 70–80°), 40 g. of sodium added and the mixture refluxed; 200 ml. of butyl alcohol[1] was added in portions of 10–15 ml. and the mixture refluxed for eight hours; 410 ml. of 96% ethyl alcohol was then added and the mixture refluxed for another hour. After cooling, 300 ml. of water was added cautiously and the resulting alkaline bottom layer, which contained unreduced acid as sodium salt, removed. The top layer was washed with 600 ml. of hot water and the petroleum ether and butyl alcohol removed (the latter by

---

[1] Ziegler, *et al.*, *Ann.*, **473**, 1 (1929).

[1] Bleyberg and Ulrich, *Ber.*, **64**, 2506 (1931).