

TABLE I
 BENZOATES OF THE NITROPHENYLPHENOLS

Nitrophenylphenol used	Yield, %	Solvent	M. p., °C.	Analyses, %			
				Calcd. C	Calcd. H	Found C	Found H
2-Nitro-4-phenyl- ³	82	Ethanol	111 ⁶				
4-(4-Nitrophenyl)- ⁴	Quant.	Propanol	209-210	71.4	4.1	71.2	4.8
2,6-Dinitro-4-phenyl- ⁵	91.5	Propanol	157-158	62.6	3.3	62.4	4.1
2-Nitro-4-(4-nitro-phenyl)- ⁴	Quant.	Propanol	151-152	62.6	3.3	62.5	4.0
2,6-Dinitro-4-(4-nitrophenyl)- ⁶	60	Propanol	168	55.8	2.7	55.4	3.3

Acknowledgment is gladly made to the Dow Chemical Company, Midland, Michigan, for the supply of 4-phenylphenol used in this work.

The Nitrophenylphenyl Benzoates.—These benzoates were prepared by treating the necessary phenols with benzoyl chloride in the presence of pyridine. The individual compounds are described in Table I.

Nitration of 4-Phenylphenyl Benzoate.—Ten grams of 4-phenylphenyl benzoate¹ dissolved in 80 ml. of glacial acetic acid was treated with a mixture of 5 ml. of fuming nitric acid and 2.5 ml. of concentrated nitric acid, which was added slowly at room temperature. The mixture was stirred and heated gently for a short time on an electric heater. After cooling, filtering and one recrystallization from glacial acetic acid, 4.8 g. of product was obtained. Several more recrystallizations from glacial acetic acid gave lustrous colorless plates which melted at 208-210°. A mixture of equal amounts of this product and 4-(4-nitrophenyl)-phenyl benzoate melted without depression at 209-211°.

(3) Raiford and Colbert, *THIS JOURNAL*, **47**, 1457 (1925).

(4) Bell and Kenyon, *J. Chem. Soc.*, **129**, 3048 (1926).

(5) Banús and Guiteras, *Anales soc. españ. fis. quim.*, **21**, 126 (1922).

(6) Colbert, Meigs and Stuerke, *THIS JOURNAL*, **56**, 2129 (1934).

DEPT. OF CHEMISTRY
 STATE COLLEGE OF WASHINGTON
 PULLMAN, WASHINGTON

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Some Reactions of Morpholine¹

BY ALVIN R. INGRAM² AND W. F. LUDER

In the course of an investigation of the conductivity of morpholine solutions, the following reactions were observed.

Morpholine, a weak base, reacts with the acidic stannic chloride^{3,4} to give the expected addition compound $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_9\text{NO}$. It is similar to the compounds of morpholine prepared by Haendler and Smith.⁵ Dilute solutions of morpholine and stannic chloride in carbon tetrachloride were mixed in a ratio of two moles of morpholine to one

(1) Abstracted from a portion of a thesis presented by Alvin R. Ingram to the faculty of Northeastern University in partial fulfillment of the requirements for the M.S. degree, June, 1942.

(2) Present address: General Chemical Defense Corporation, Claymont, Delaware.

(3) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(4) W. F. Luder, *Chem. Rev.*, **27**, 547 (1940).

(5) H. M. Haendler and G. McP. Smith, *THIS JOURNAL*, **63**, 1164 (1941).

of stannic chloride. A white precipitate formed immediately. This product was washed in carbon tetrachloride, absolute alcohol and petroleum ether. It was insoluble in the common organic solvents, water and dilute acids, but it dissolved with decomposition in hot concentrated acids. It melted with decomposition between 215° and 235°. *Anal.* Calcd. for $\text{SnCl}_4 \cdot 2\text{C}_4\text{H}_9\text{NO}$: Sn, 27.3; Cl, 32.7. Found: Sn, 27.3; Cl, 32.0.

Morpholine also reacts with carbon tetrachloride and chloroform to give morpholinium chloride. Similar reactions have been observed previously with piperidine to form piperidinium chloride.⁶ Because these reactions of morpholine with carbon tetrachloride and chloroform were of no concern to the investigation under way, no attempt was made to isolate other products in addition to morpholinium chloride. However, from the work of Powell and Dehn,⁶ the principal ones may be N-trichloromethyl and N-dichloromethyl morpholine.

A 4.5% by weight solution of morpholine in carbon tetrachloride, made up for another purpose, contained a large quantity of needle-like crystals when noticed about four months later. The crystals melted at 177° and when dissolved in water gave a white precipitate with silver nitrate. Mixed melting points, using morpholinium chloride prepared by the reaction of dry hydrogen chloride with morpholine, confirmed the conclusion that the crystals were morpholinium chloride. When approximately equal volumes of morpholine and carbon tetrachloride were warmed to temperatures from 50 to 100°, the morpholinium chloride was formed in a few hours, and the remaining liquid became yellow or brown depending on time and temperature. Distillation of the colored liquid gave a colorless distillate which deposited more morpholinium chloride immediately upon cooling. The residue was viscous and dark brown. When mixed in a ratio of two moles of morpholine to one mole of carbon tetrachloride (both being dried over calcium chloride or calcium sulfate)

(6) S. G. Powell and W. M. Dehn, *ibid.*, **39**, 1717 (1917).

crystals formed within one day at room temperature leaving a colorless solution. The reaction took place even with calcium oxide present.

The behavior of morpholine with chloroform is similar. Morpholinium chloride was identified as the product by its melting point, by its reaction with aqueous silver nitrate, and by taking a mixed melting point with morpholinium chloride prepared from hydrogen chloride and from carbon tetrachloride.

HAYDEN MEMORIAL LABORATORIES
NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

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Solubility of the Flavianates of Certain Organic Bases in Water, Ethanol, and *n*-Butanol at 3 and 30°

BY WILSON D. LANGLEY AND THOMAS R. NOONAN

The use of 2,4-dinitronaphthol-7-sulfonic acid (flavianic acid) for the purification and characterization of organic bases, first recommended by Kossel and Edlbacher, and Kossel and Gross,¹ has been extended by Sievers and Mueller² to include solubility data, and by Langley and Albrecht³ to include crystallographic data. It has been our desire further to extend knowledge of the solubilities of the flavianates in certain solvents, so that flavianic acid may be more satisfactorily used for fractional precipitation of organic bases. Accordingly, we have determined the solubilities reported in the accompanying table. The solvents were selected as being suited for fractionation of extracts of tissues, and it was hoped that quantitative separations of bases could be accomplished readily once the components of mixtures were identified under the microscope. This work has been interrupted, and the prospects of it being resumed are remote.

The solvents used were purified by distillation just prior to use, and purity was established by constancy of boiling point, and by measurement of density (pycnometer). The flavianates used had been analyzed and reported upon previously.³ Equilibrium was attained by frequent shaking of solvent in contact with solid for various lengths of time ranging from several days to several months. The saturated solutions were filtered, and were

(1) A. Kossel and S. Edlbacher, *Z. physiol. Chem.*, **110**, 241 (1920); A. Kossel and R. E. Gross, *ibid.*, **135**, 167 (1924).

(2) H. Sievers and E. Mueller, *Z. Biol.*, **89**, 37 (1929); **92**, 513 (1932).

(3) W. D. Langley and A. J. Albrecht, *J. Biol. Chem.*, **108**, 729 (1935).

pipetted immediately by use of pipets which were calibrated at the temperatures used. Fifty-ml. portions (occasionally 20 ml.) of solutions were pipetted into weighed beakers, and the covered solutions were evaporated on a steam-bath. Final drying of the residue was done in an oven at 100°, constant weight being attained in each case.

SOLUBILITY OF FLAVIANATES IN G. PER LITER

Base	Water		Ethanol (95%)		<i>n</i> -Butanol	
	3°	30°	3°	30°	3°	30°
Acetylcholine	0.09	0.40
Ammonium	14.2	...	2.57	6.22	.29	.39
Choline	2.8117	.26
Creatinine	2.65	4.54	1.08	1.52	.09	.43
<i>α</i> S-Dimethylguanidine	1.85	...	1.30	3.2	.21	.30
Ethanolamine	2.45	6.8	.14	.28
Guanidine	1.30	3.34	1.64	3.57	.19	.19
Hydroxylamine	16 ^a	70 ^a	...	26 ^a	2.4 ^a	5.2 ^a
Hypoxanthine	1.3	3.6	0.95	3.36	0.34	0.4
Methylamine	7.6	...	1.95	4.10	.09	.17
Methylguanidine	2.53	5.7	2.6	4.7	.33	.35
Methylurea	36 ^a	.66	1.4 ^a
Piperidine	4.0	...	3.3 ^a	1.3	.13	0.35
Potassium	3.7 ^a	11.2 ^a	0.12	0.16	.04 ^a	.05
Putrescine	0.25	...	0.31	0.4606
Tetramethyl-						
ammonium	4.9 ^a	12.8 ^a	0.61	1.52	.04	.05
Trimethylamine	47 ^a	...	4.4 ^a	7.27	.12	.41
Tyramine	4.40	10.3 ^a	.34	.8
Urea	15.7 ^a	40 ^a	12.4	17	.56	.81

^a Single determinations.

The figures represent averages of values which were obtained after differences of several weeks in contact time, and which, except for the very small values, seldom disagreed by as much as 5%. Uncertain figures are depressed below the line. When the solubilities were great, duplicate determinations were not always made; these single values are marked.

DEPARTMENT OF BIOLOGICAL CHEMISTRY
UNIVERSITY OF BUFFALO MEDICAL SCHOOL

BUFFALO, N. Y.

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1-Carbamyl-5-methylpyrazole-3-carboxylic Acid

BY ALBERT L. LEHNINGER

During the course of some work on the derivatives of acetypyruvic acid,¹ the reaction between semicarbazide and acetypyruvic acid became of interest as a means of identification of the latter compound. Von Auwers and Cauer² had reported that they were unable to obtain the expected product, 1-carbamyl-5-methylpyrazole-3-carboxylic acid (I), since the carbamyl group was apparently lost on ring closure, leading instead to 5-methylpyrazole-3-carboxylic acid (II).³

(1) Lehninger and Witzemann, *This Journal*, **64**, 874 (1942).

(2) von Auwers and Cauer, *J. prakt. Chem.*, **126**, 146 (1930).

(3) Knorr and MacDonald, *Ann.*, **279**, 217 (1894).