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.

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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 Mueller[2] to include solubility data, and by Langley and Albrecht[3] 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 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 3°	Water 30°	Ethanol (95%) 3°	Ethanol (95%) 30°	*n*-Butanol 3°	*n*-Butanol 30°
Acetylcholine	...	...	...	...	0.09	0.40
Ammonium	14.2	...	2.57	6.22	.29	.39
Choline	...	...	2.81	...	.17	.26
Creatinine	2.65	4.54	1.08	1.52	.09	.43
as-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	0.46	..	.06
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
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BUFFALO, N. Y. RECEIVED JUNE 27, 1942

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

BY ALBERT L. LEHNINGER

During the course of some work on the derivatives of acetopyruvic acid,[1] the reaction between semicarbazide and acetopyruvic acid became of interest as a means of identification of the latter compound. Von Auwers and Cauer[2] 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) 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).

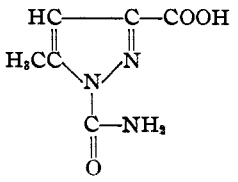
(1) Lehninger and Witzemann, THIS JOURNAL, **64**, 874 (1942).

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

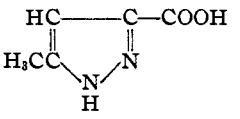
(3) Knorr and MacDonald, *Ann.*, **279**, 217 (1894).

By altering the conditions employed by von Auwers and Cauer, it was found that the expected carbamyl compound could be obtained easily and in large yields. Furthermore, the reason for their failure to obtain the compound became apparent on studying its properties.

This substance was found to hydrolyze readily to 5-methylpyrazole-3-carboxylic acid in water or in water–alcohol solutions on standing for several days at room temperature or on heating for short periods, with or without added acid. The long reaction periods employed by von Auwers and Cauer probably provided for the conversion of the primary product I into II.



I



II

The product of hydrolysis of the carbamyl compound was isolated and identified as 5-methylpyrazole-3-carboxylic acid.[3]

Experimental

1-Carbamyl-5-methylpyrazole-3-carboxylic Acid.—To a solution of 1.30 g. of acetopyruvic acid (prepared as previously described[1]) in 10 ml. of water was added 1.11 g. of semicarbazide hydrochloride dissolved in 10 ml. of water. The mixture was stirred and gently warmed. A white voluminous mass of microscopic needles immediately precipitated. The mixture was stirred for two minutes, filtered, washed copiously with cold water and dried over phosphorus pentoxide. The compound was thus obtained pure without recrystallization; yield, 80–85%; m. p. (dec. started at 155°, clear melt at 232–234° (cor.).

Anal. Calcd. for $C_6H_7O_3N_3$: C, 42.60; H, 4.17; N, 24.85. Found: C, 42.74; H, 4.13; N, 24.67. Amide N: Calcd. 8.28. Found (hydrolysis with H_2SO_4, followed by alkaline distillation of ammonia and titration), 8.12.

Hydrolysis to 5-Methylpyrazole-3-carboxylic Acid.—A suspension of 1.0 g. of the compound obtained above in 20 ml. of water was brought to the boiling point for one minute (evolution of carbon dioxide was apparent) and cooled. Crystals of 5-methylpyrazole-3-carboxylic acid separated. These were recrystallized from water; m. p. 236–236.5° (cor.); melting point of authentic sample (prepared according to Knorr and MacDonald[3]) 236–237°; a mixed melting point test showed no depression.

Anal. Calcd. for $C_5H_6O_2N_2$: C, 47.61; H, 4.80. Found: C, 47.42; H, 4.60. There was no detectable amide nitrogen.

DEPT. OF PHYSIOLOGICAL CHEMISTRY
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The Polymerization of Styrene Catalyzed by *p*-Bromobenzenediazonium Hydroxide

BY CHARLES C. PRICE AND DOROTHY ANN DURHAM

The presence of fragments from the catalyst in polystyrene and polymethyl methacrylate prepared in the presence of substituted peroxides[1] has been interpreted as evidence strongly supporting the suggestion that such catalysts first dissociate into free radicals[2] which then initiate the polymerization process.[3]

Since the reaction of alkaline diazotized *p*-bromoaniline with benzene and its derivatives to form *p*-bromobiphenyl and the corresponding derivatives[4] has been ascribed to the decomposition of the diazonium hydroxide to a *p*-bromophenyl free radical,[2] the action of the diazonium hydroxide as a catalyst for the polymerization of styrene has been tested.

p-Bromobenzenediazonium hydroxide has indeed been found to catalyze the polymerization of styrene. The directions followed for carrying out the polymerization were those described for the preparation of *p*-bromobiphenyl[4] with the single exception that styrene replaced benzene. Alkali was added slowly to a vigorously-stirred suspension of 30 cc. of styrene in an aqueous solution of 11 g. of diazotized *p*-bromoaniline at 0°. After the addition of alkali was complete, the reaction mixture was allowed to warm up to room temperature. The aqueous layer was decanted and alcohol was added to the viscous organic layer. The polystyrene which precipitated was purified further by several reprecipitations from ether solution by pouring into ice-cold alcohol. The viscosity of a sample of this polymer in tetralin was measured at 20°; $\eta_{sp.}/C_{gm.} = 1.16$. Using the revised[5] value for the constant of the Staudinger equation relating this expression to molecular weight, the polymer contained an average of about twenty-two styrene units.

Anal. Calcd. for $BrC_6H_4(C_8H_8)_{30}C_6H_4Br$: C, 88.07; H, 7.27; Br, 4.65. Calcd. for BrC_6H_4-

(1) Price, Kell and Krebs, THIS JOURNAL, **64**, 1103 (1942).

(2) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(3) Norrish and Brookman, *Proc. Roy. Soc.* (London), **A171**, 147 (1939); Norrish, *Trans. Faraday Soc.*, **35**, 1087 (1939); Kamenskaya and Medvedev, *Acta Physicochem., U. S. S. R.*, **13**, 565 (1940); Price and Kell, THIS JOURNAL, **63**, 2798 (1941).

(4) Gomberg and Bachmann, *ibid.*, **46**, 2339 (1924). See also Gilman and Blatt, "Organic Syntheses," Collected Volume I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 113.

(5) Kemp and Peters, Division of Paint, Varnish and Plastics, 103rd meeting of the American Chemical Society, Memphis, Tenn., April, 1942.