

methylpyridinium bromide (**1b**) (3 mmol) and arylidene-2-acetobiphenyl (3 mmol) in glacial acetic acid (6.0 mL) was added ammonium acetate (3.0 g), and the mixture was allowed to reflux for 6-8 h. Ice cold water (10.0 mL) was then added to the solution for complete precipitation. The precipitated solid was filtered, washed with methanol, dried, and recrystallized from suitable solvents to yield pyridines (**3k-t**) (Table I).

Route B. An equimolar amount of (4-phenylphenacyl)-pyridinium bromide (**1c**) (3 mmol) and substituted arylidene-2-acetonaphthone was refluxed in the presence of ammonium acetate (3.0 g) in glacial acetic acid (10.0 mL) for 3 h. Similar workup of the reaction mixture led to the formation of a solid mass, recrystallization of which from appropriate solvents gave the title pyridines in fair to good yields (Table I).

Acknowledgment

The authors thank the Director, Harcourt Butler Technological

Institute, Kanpur, for providing facilities. S.C.C is grateful to the C.S.I.R., New Delhi, for the award of SRF. D.K.N. thanks U.G.C., New Delhi, for financial assistance.

Literature Cited

- (1) R. S. Tewari, D. K. Nagpal, and S. C. Chaturvedi, *Indian J. Chem.*, in press.
- (2) L. C. King, *J. Am. Chem. Soc.*, **66**, 894 (1944).
- (3) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, 1954, p 274.
- (4) G. L. Cook and F. M. Church, *J. Phys. Chem.*, **61**, 458 (1957).
- (5) L. C. King, M. McWhirter, and R. Rowland, *J. Am. Chem. Soc.*, **70**, 239 (1948).
- (6) F. Krohnke, *Ber. Dtsch. Chem. Ges. B*, **66**, 604 (1933).
- (7) T. Immediata and A. R. Day, *J. Org. Chem.*, **5**, 517 (1940).
- (8) A. I. Vogel, "A Text Book of Practical Organic Chemistry", Longman, New York, 1948, p 962.
- (9) H. Gilman and A. H. Blatt, "Organic Synthesis", Collect. Vol. 1, Wiley, New York, 1958, p 127.

Received for review August 3, 1979. Accepted April 21, 1980.

Preparation and Properties of Some Halohydroxamic Acids

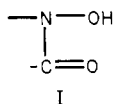
Yadvendra K. Agrawal* and Ranjan D. Roshania

Analytical Laboratories, Pharmacy Department, Faculty of Technology and Engineering, M.S. University of Baroda, Kalabhavan, Baroda—390 001, India

The preparation and properties of some new *N*-(*p*-chlorophenyl)hydroxamic acids have been described. They are characterized by their melting point, elemental analysis, and IR and UV spectra.

Introduction

The hydroxamic acids, with functional group (I), are excellent



complexing reagents and are generally used in organic and inorganic analysis.

In the present investigation the halo-substituted hydroxamic

Table I^a

hydroxamic acids, <i>N</i> - <i>p</i> -chlorophenyl	formula	mp, °C	yield %	IR spectra, cm ⁻¹			UV spectra λ _{max} , nm
				ν _{O—H}	ν _{C=O}	ν _{N—O}	
<i>p</i> -ethoxybenzohydroxamic acid	C ₁₁ H ₁₄ O ₃ NCl	162	65	3150	1620	810	278
<i>o</i> -bromobenzohydroxamic acid	C ₁₃ H ₉ O ₂ NClBr	130	62	3130	1620	825	288 332
<i>p</i> -bromobenzohydroxamic acid	C ₁₃ H ₉ O ₂ NClBr	161	66	3180	1640	830	240 275
<i>p</i> -iodobenzohydroxamic acid	C ₁₃ H ₉ O ₂ NClI	190	60	3150	1635	820	238 338
<i>n</i> -stearohydroxamic acid	C ₂₄ H ₄₀ O ₂ NCl	90	68	3175	1620	830	285
<i>n</i> -chloroacetohydroxamic acid	C ₈ H ₇ O ₂ NCl ₂	117	72	3160	1635	825	284
<i>2</i> -naphthohydroxamic acid	C ₁₇ H ₁₂ O ₂ NCl	202	67	3350	1632	810	286
<i>cinnamohydroxamic acid</i>	C ₁₅ H ₁₂ O ₂ NCl	181	69	3150	1640	828	292

^a Elemental analysis (C, H, N), in agreement with theoretical values, were obtained and submitted for review.

***N*-(*p*-Chlorophenyl)hydroxylamine.** It is prepared by the reduction of *p*-chloronitrobenzene with zinc dust in aqueous alcoholic media (2).

Preparation of *N*-(*p*-Chlorophenyl)-*p*-ethoxybenzohydroxamic Acid. A typical procedure for the preparation of *N*-(*p*-chlorophenyl)-*p*-ethoxybenzohydroxamic acid is as follows.

Into a 500-mL filtration flask, fitted with a dropping funnel by a B-24 joint, were added 75 mL of diethyl ether, 14.35 g (0.1 mol) of freshly prepared and purified *N*-(*p*-chlorophenyl)-hydroxylamine, a fine suspension of 10.2 g (0.1 mol) of sodium carbonate, and 50–60 mL of distilled water, and the mixture was stirred with a magnetic stirrer. After the mixture was externally cooled below 0 °C, 16.6 g (0.1 mol) of *p*-ethoxybenzoyl chloride dissolved in 75 mL of diethyl ether was added dropwise to the cooled reactants over a period of 1–1.5 h. The stirring was continued for another 30 min and the temperature kept low to prevent possible side reactions. Almost the entire amount of the hydroxamic acid was precipitated as white solid. The light yellow ethereal layer gave on separation and distillation under vacuum a yellow solid which was combined with the precipitated white solid, triturated for about 15 min on a porcelain mortar with a saturated solution of sodium bicarbonate, filtered, and washed with cold water. The solid was crystallized from a mixture of benzene and petroleum ether (60–80 °C), yielding a white product, mp 162 °C.

The physical properties of halohydroxamic acids are given in Table I. All the acids are white crystalline compounds except *p*-iodo- and cinnamo-substituted hydroxamic acids which are light pink and light yellow. They are insoluble in water, sparingly soluble in carbon tetrachloride and cold benzene, but readily soluble in hot benzene, diethyl ether, dioxane, chloroform, and ethanol.

Acknowledgment

R.D.R. is grateful to U.G.C., New Delhi, for the award of a Junior Research Fellowship.

Literature Cited

- (1) Agrawal, Y. K., Tandon, S. G., *J. Indian Chem. Soc.*, **49**, 911 (1972).
- (2) Agrawal, Y. K., D.Sc. Thesis, A.P.S. University Rewa, India, 1979.
- (3) Vogel, A. I., "A Text-Book of Practical Organic Chemistry", 3rd ed., Longmans, London, 1968.
- (4) Wagner, R. B., Zook, H. D., "Synthetic Organic Chemistry", Wiley, New York, 1953, p 546.

Received for review September 4, 1979. Accepted May 28, 1980. The authors are thankful for the financial support by C.S.I.R., New Delhi.

Correction

Solubilities of 1,10-Phenanthroline and Substituted Derivatives in Water and in Aqueous Methanol. John Burgess and Robert I. Haines, *J. Chem. Eng. Data* **1978**, *23*, 196.

The value quoted for the enthalpy of solution of 1,10-phenanthroline monohydrate in water is incorrect. The correct value is +26 kJ mol⁻¹. This value, derived from the variation of solubility with temperature over the range 298.2 to 323.2 K, may be compared with an estimate of +21 ± 2 kJ mol⁻¹ which we have recently obtained directly by calorimetry (at 298.2 K). It is proving difficult to obtain a precise and accurate value by calorimetry as the 1,10-phenanthroline monohydrate is sparingly soluble in water and dissolves only slowly. We are grateful to Dr. K. C. James of the Welsh School of Pharmacy for pointing this error out to us.