Preparation and Properties of *N*-Arylhydroxamic Acids

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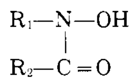
Preparation and properties of 15 N-arylhydroxamic acids derived from halogen- and nitro-substituted benzoic acids are described. These hydroxamic acids were prepared for use as possible analytical reagents for metal ions. Preliminary studies show that these acids form chloroform-extractable violet complex with vanadium(V) in concentrated hydrochloric acid solutions.

In previous communications (*4, 7, 11*), the preparation and properties of 64 *N*-arylhydroxamic acids were reported. Further work on 15 *N*-arylhydroxamic acids, represented by the following general formula, is described here.

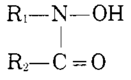


$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\;\; | \\ R_2\text{—C}=\text{O} \end{array}$$

R_1 = phenyl, *m*-tolyl, or *p*-tolyl
R_2 = halogen- or nitro-substituted phenyl

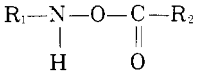
All these hydroxamic acids, except *N*-phenyl-*o*-iodobenzohydroxamic acid, are reported for the first time, and these were synthesized for possible analytical applications.

When an *N*-arylhydroxylamine reacts with acid chloride, both of its hydrogen atoms, attached to the nitrogen and oxygen atoms, are attacked, thereby producing mono-(I,II)- and di-(III)-substituted derivatives.



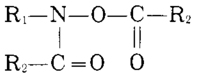
I

$$\begin{array}{l} R_1\text{—N—OH} \\ \quad\;\; | \\ R_2\text{—C}=\text{O} \end{array}$$



II

$$\begin{array}{l} R_1\text{—N—O—C—}R_2 \\ \quad\;\; | \qquad\;\; \| \\ \quad\;\; \text{H} \qquad\; \text{O} \end{array}$$



III

$$\begin{array}{l} R_1\text{—N—O—C—}R_2 \\ \quad\;\; | \qquad\;\; \| \\ R_2\text{—C}=\text{O} \;\; \text{O} \end{array}$$

The *N*-acylated derivatives (I) are moderately soluble in aqueous ammonium hydroxide or 5–10% aqueous sodium hydroxide. This property has been used for separating I from II and III (*1-3, 8, 9*), because *O*-acylated and diacylated derivatives are insoluble in base. However, this procedure of isolation of the *N*-acylated derivative from the mixed product by repeated extraction by base is time-consuming and tedious. Besides, the desired *N*-acylated derivative (I) is partially decomposed, presumably due to its base-catalyzed hydrolysis. The ammonium hydroxide extracts which are initially colorless gradually become deep blue or green. Recent kinetic studies in this laboratory (*10*), which show that the hydrolytic decomposition of *N*-arylhydroxamic acid is catalyzed both by hydronium and hydroxyl ions, provide evidence for this observation.

Table I.

S. no.	Benzohydroxamic acid	Mp, °C	Yield, %	Ir spectra[a] frequency, cm^{-1} ν_{O-H}	$\nu_{C=O}$	ν_{N-O}	Uv spectra λ_{max}, $m\mu$	$10^{-3}\epsilon$
1	*N*-phenyl-*o*-fluoro-	129	75	3170	1628	938	267	10.0
2	*M*-*m*-tolyl-*o*-fluoro-	98	60	3160	1620		265	11.5
3	*N*-*p*-tolyl-*o*-fluoro-	135	65	3150	1630	935	267	11.0
4	*N*-*m*-tolyl-*p*-fluoro-	111	72	3070	1605	928	269	10.4
5	*N*-*m*-tolyl-*p*-chloro-	140	68	3175	1590	920	274	9.8
6	*N*-*m*-tolyl-*o*-bromo-	120	65	3180	1610	920	260	11.1
7	*N*-*m*-tolyl-*m*-bromo-	83	60	3180	1590	920	272	9.9
8	*N*-*m*-tolyl-*p*-bromo-	157	60	3175	1615	930	272	9.9
9	*N*-phenyl-*o*-iodo	129[b]	60	3202	1625	923	230 260 233	12.5 9.5 13.3
10	*N*-*m*-tolyl-*o*-nitro-	168	65	3125	1639	926	255	15.6
11	*N*-*p*-tolyl-*o*-nitro-	167	65	3165	1613	933	255	18.7
12	*N*-*m*-tolyl-*m*-nitro-	118	58	3279	1600	917	265	16.0
13	*N*-*m*-tolyl-*p*-nitro-	158	65	3125	1626	935	255	14.1
14	*N*-*m*-tolyl-3,5-dinitro-	150	60	3125	1626	917	235[c]	22.1
15	*N*-*p*-tolyl-3,5-dinitro-	136	65	3125	1639	921	235[c]	24.0

[a] Spectra were recorded as nujol mulls except for compound nos. 1, 2, 3, 4, 6, 7, 8, and 9 which were studied as KBr pellets. [b] Reported mp, 128° C (*8*). [c] Inflexion.

NOTE: Acceptable elemental analyses for carbon, hydrogen, nitrogen, and halogens were obtained and submitted for review.

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In view of the above difficulties, in the present study the procedure of Priyadarshini and Tandon (*7*) is adapted. Thus *N*-arylhydroxylamine and acid chloride (equimolar) react at low temperature in diethyl ether medium containing aqueous suspensions of sodium bicarbonate. If the recommended experimental conditions are closely adhered to, the major product is I, while II and III are produced in negligible amounts. It is thus possible to isolate the desired mono *N*-acylated derivative in good yield and analytically pure form by two crystallizations from benzene and petroleum ether.

The method adapted here was satisfactory for the preparation of most of the hydroxamic acids. However, the *meta*-substituted hydroxamic acids were generally difficult to prepare; in several preparations oily products were obtained. All attempts to prepare *N*-*meta*-tolyl-substituted hydroxamic acids derived from *n*-butyric, *n*-valeric, caprylic, 2-ethylhexoic, and 2-furoic acids failed.

The physical properties of *N*-arylhydroxamic acids are given in Table I. Percentage yields are reported for once-crystallized products. All the hydroxamic acids, except the nitro-substituted acids which are yellow, are white. These are stable to heat, light, and air. These are sparingly soluble in water but are readily soluble in ethyl alcohol, benzene, chloroform, diethyl ether, dioxane, and carbon tetrachloride. The spectral data on the hydroxamic acids were obtained basically for their characterization.

Chloroform solutions of all the hydroxamic acids gave characteristic violet extracts with vanadium(V) from strong hydrochloric acid (2–10*M*) solutions.

EXPERIMENTAL

Absorption Spectra. The uv absorption spectra of the *N*-arylhydroxamic acids in 95% ethyl alcohol, were recorded on Hilger and Watts Model H9998/62271 ratio recording spectrophotometer in 200–350-nm region.

Infrared spectra were recorded in the 2–15-μ region on Perkin-Elmer Model 137 or 221 spectrophotometer equipped with sodium chloride optics and calibrated by standard methods. *N*-arylhydroxamic acids were dried in vacuum over P_2O_5 and examined as Nujol mulls or KBr pellets.

***N*-phenyl- and *N*-*p*-tolylhydroxylamine.** These were freshly prepared by the reduction of nitrobenzene and *p*-nitrotoluene, respectively, with zinc dust and ammonium chloride from aqueous solutions and recrystallized from benzene and petroleum ether (*5, 12*). *N*-phenylhydroxylamine, mp 81° C [reported 81–2° C (*5*)], is obtained in 60 to 65% yield as white needles. *N*-*p*-tolylhydroxylamine, mp 93° C [reported 93° C (*12*)], is obtained in 60% yield as white plates.

***N*-*m*-tolylhydroxylamine.** This is a known compound but its preparation is briefly described here because optimum conditions for getting maximum yield were established after repetitive work. Thus, a mixture of 25 grams of *m*-nitrotoluene, 20 ml of ethyl alcohol, 10 ml of water, and 2 grams of ammonium chloride was stirred mechanically and treated with 30 grams of zinc dust in small lots of 1–1.5 grams during the course of 25–30 min. The reaction temperature was maintained between 60 and 65° C throughout, and stirring was continued for another 15 min. While hot, the zinc oxide was filtered and washed with 3 × 10 ml of hot ethyl alcohol. On the addition of about 250 grams of ice to the filtrate, a light yellow product was obtained which on crystallization from benzene and petroleum ether gave white plates in 80% yield; mp 68° C [reported 68.5° C (*6*)].

Acid Chlorides. These were prepared by the action of thionyl chloride on the corresponding carboxylic acids. The boiling points and yields of the acid chlorides, thus produced, were in agreement with the values given in the literature (*13*).

A typical preparation of an *N*-arylhydroxamic acid is described here.

N-PHENYL-O-FLUOROBENZOHYDROXAMIC ACID

Procedure. Into a 500-ml, three-necked flask, equipped with a stirrer, dropping funnel, and thermometer, 150 ml of diethyl ether, 10.9 grams (0.1 mole) of freshly crystallized *N*-phenylhydroxylamine, and a fine suspension of 12.6 grams (0.15 mole) of sodium bicarbonate in 25 ml of water were added. After the mixture was cooled to 0° C, 23.12 grams (0.1 mole) of *o*-fluorobenzoyl chloride dissolved in 100 ml of diethyl ether was added dropwise over a period of 1 hr. Then an additional time of 30 min was allowed and the temperature was maintained at 0° C or lower. Some of the product was precipitated as a white solid while the ether layer was separated and the ether removed under vacuum. The light yellow residue was combined with the precipitated white product, triturated for about 15 min in a porcelain mortar with a saturated solution of sodium bicarbonate to remove the acid impurities, filtered, and washed with cold water. The yield of air-dried product, mp 125° C, was 80%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave white needles, mp 129° C.

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