Studies on *N*-Arylhydroxamic Acids

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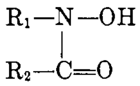
Preparation and properties of 10 new *N*-arylhydroxamic acids derived from naphthoic acid and methoxy-substituted benzoic acids are described. These hydroxamic acids, which are white crystalline compounds, were characterized by their infrared and ultraviolet spectra.

In the present communication, 10 new *N*-arylhydroxamic acids, represented by the general formula



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

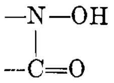
have been reported for the first time. Where R_1 = *N*-phenyl, *o*-tolyl, *m*-tolyl, or *p*-tolyl, and R_2 = naphthoic acid or methoxy-substituted benzoic acids.

The preparation was made by adapting the procedure of Priyadarshini and Tandon (*10*), which is satisfactory for the preparation of most hydroxamic acids. However, the *o*- and *m*-substituted hydroxamic acids were generally difficult to prepare. Hydroxamic acids derived from 2,4-dimethoxybenzoic acid are difficult to prepare by the recommended procedure because of their insufficient solubility in diethyl ether. Use of benzene instead of diethyl ether, however, proved satisfactory.

The physical properties of the *N*-arylhydroxamic acids are given in Table I. All the hydroxamic acids are white crystalline solids. These are sparingly soluble in water but are readily soluble in alcohol, benzene, chloroform, dioxane, and carbon tetrachloride.

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

The infrared and ultraviolet spectra of synthesized hydroxamic acids were determined. In the infrared absorption spectra only those bands which are associated with the hydroxamic acid functional group,



$$\begin{array}{l} {-}N{-}OH \\ \;\;\; | \\ {-}C{=}O \end{array}$$

have been assigned. The presence of the (O—H) stretching band is assigned in the region at about 3200 cm^{-1} and in conformity with the reported value (*1, 5, 6, 8, 9*). The lower shift of the (O—H) was due to the intramolecular hydrogen bonding of the type —OH . . . C=O. The (C=O) and (N—O)

Table I. Physical Properties of *N*-Arylhydroxamic Acids

Compound	Hydroxamic acids	Formula	Mol wt	Mp, °C	Yield, %	Ir spectra[a] frequency, cm^{-1} ν_{O-H}	$\nu_{C=O}$	ν_{N-O}	Uv spectra λ_{max}, mμ	10^{-3} ε
1	*N*-Phenyl-*m*-methoxybenzo-	$C_{14}H_{13}NO_3$	243.30	79	65	3260	1610	917	275	9.7
2	*N*-*o*-Tolyl-*m*-methoxybenzo-	$C_{15}H_{15}NO_3$	257.29	106	60	3160	1610	938	255	8.2
3	*N*-*m*-Tolyl-*m*-methoxybenzo-	$C_{15}H_{15}NO_3$	257.29	110	68	3170	1620	935	255	10.0
4	*N*-*p*-Tolyl-*m*-methoxybenzo-	$C_{15}H_{15}NO_3$	257.29	110	65	3240	1610	910	273	9.9
5	*N*-Phenyl-2,4-dimethoxybenzo-	$C_{15}H_{15}NO_4$	273.27	132	50	3125	1613	925	260[b] to 290	10.0
6	*N*-*m*-Tolyl-2,4-dimethoxybenzo-	$C_{16}H_{17}NO_4$	287.30	172	50	—	1605	925	290 253	8.0 10.0
7	*N*-*p*-Tolyl-2,4-dimethoxybenzo-	$C_{16}H_{17}NO_4$	287.30	180	55	3150	1600	930	260[b] to 290	10.0
8	*N*-Phenyl-2-naphtho-	$C_{17}H_{13}NO_2$	263.28	156	70	3250	1625	910	275 226	13.9 41.0
9	*N*-*m*-Tolyl-2-naphtho-	$C_{18}H_{15}NO_2$	277.33	115	70	3190	1630	941	275 226	13.4 42.1
10	*N*-*p*-Tolyl-2-naphtho-	$C_{18}H_{15}NO_2$	277.33	145	70	3175	1608	935	274 226	14.0 42.0

[a] Spectra were recorded as Nujol mulls except for compound numbers 1, 2, 3, 4, 7, and 9 which were studied as KBr pellets. [b] Inflection.
Note: Elemental analysis (C, H, N) in agreement with theoretical values, were obtained and submitted for review.

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bands are assigned at about 1620 cm^{-1} and 920 cm^{-1}, respectively.

In the ultraviolet region there is a characteristic intense band at about 250 mμ which is assigned as benzene band II (*2*). This band is discriminated by its position an magnitude of intensity. Substitution of R_2 by a naphthalene ring results in greater bathochromic shift and the bands observed at 225 and 270 mμ are the naphthalene bands I and II, respectively. The assignment of these bands are supported by comparing the spectra of *N*-arylhydroxamic acids with structurally related compounds (*7, 11*). In the hydroxamic acids derived from naphthoic acid, the ratio of bands II, and I, λ_{II}/λ_{I}, is generally found at about 1.22 (*3, 4*).

EXPERIMENTAL

Materials and Apparatus. Infrared spectra were recorded in the 2- to 15-μ region on a Perkin-Elmer Model 221 or Model 137 spectrophotometer equipped with sodium chloride optics and calibrated by standard methods. Solids were dried over P_2O_5 finely powdered in an agate mortar, and examined as KBr pellets or mulls in Nujol.

The ultraviolet absorption spectral measurements were recorded on a Hilger and Watts Model H 9998/62271 ratio recording spectrophotometer, with 10-mm matched stoppered quartz cells in the 200- to 350-mμ region.

Spectroscopic grade 95% ethyl alcohol, which was sufficiently transparent up to 200 mμ, was specially purified from ethanol.

Acid Chlorides. The acid chlorides were prepared by the action of thionyl chloride on the corresponding carboxylic acids and were vacuum distilled. The pure 2,4-dimethoxy benzoyl chloride is difficult to prepare, because it gives a dark violet color on addition of thionyl chloride to 2,4-dimethoxy benzoic acid. The pure white solid acid chloride was obtained after two to three distillations under vacuum. All the other acid chlorides except 2-naphthoyl chloride, which is a solid, were obtained as colorless liquids.

Preparations. All arylhydroxylamines were freshly prepared and crystallized two times from a mixture of benzene and petroleum ether.

A typical preparation of *N*-phenyl-2-naphthohydroxamic acid is given below.

10.9 Grams (0.1 mole) of *N*-phenylhydroxylamine was dissolved in 150 ml of cold diethyl ether, and the solution was stirred mechanically with external cooling to lower the temperature to 0° or below. Powdered sodium bicarbonate [12.6 grams (0.15 mole)] suspended in 15 ml of water were added to this solution. To this, 18.95 grams (0.95 mole) of the 2-naphthoyl chloride dissolved in 100 ml of diethyl ether were added dropwise during the course of 1 hr. The reaction mixture was always kept basic. Usually a yellowish white liquid was obtained, which was precipitated with petroleum ether at low temperature. The ether layer was removed under vacuum at room temperature. Any solid material thus obtained was combined with the bulk of the product which was thoroughly triturated in a porcelain mortar with an excess of saturated sodium bicarbonate solution to remove the acid impurities. The solution was filtered, and the solid was washed with water and dried. The product was crystallized from a mixture of benzene and petroleum ether. The yield of once crystallized product, mp 156°, was 70%.

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Synthesis and Transition Temperatures of *N*-(*p*-Alkoxybenzylidene)-*p*′-acyloxyanilines

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The discovery of the dynamic light scattering effect in certain nematic liquid crystals when subjected to an electrical field (*5*) has stimulated widespread interest in these compounds because of their potential application in flat panel displays (*4*). In searching for nematic liquid crystal systems (*6*) having favorable mesomorphic temperature ranges, we prepared an extensive series of *N*-(*p*-alkoxybenzylidene)-*p*′-acyloxyanilines (I). The synthesis and transition temperatures for these compounds are reported here.

Our synthetic approach involved the acylation of the corresponding *N*-(*p*-alkoxybenzylidene)-*p*′-hydroxyaniline (II)l Many of the reported acylation reactions (*7*) proved impractica.

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