ORGANIC SECTION

Studies on Hydroxamic Acids

Preparation and Properties of *N*-1-naphthylhydroxamic Acids

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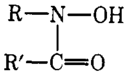
Twelve *N*-arylhydroxamic acids reported here were prepared by the condensation of *N*-1-naphthylhydroxylamine and acid chloride in diethyl ether medium. An aqueous suspension of sodium bicarbonate was added to neutralize the liberated hydrochloric acid. The formation of diacylated derivative was practically prevented by carrying out the reaction at low temperature, preferably below 0°C. These acids were synthesized with the object of using them as possible organoanalytical reagents for metal ions. Spectral characteristics in ultraviolet and infrared regions, analyses, melting points, and storage qualities important for characterization are described. All of these acids formed chloroform-extractable reddish-violet/violet complexes with vanadium(V) from concentrated hydrochloric acid media.

The preparation and properties of more than 150 *N*-arylhydroxamic acids have been reported recently (*1, 3, 7, 8, 12, 18*). These acids were prepared for possible analytical applications and for studying effect of various substituents on the complexing properties of the hydroxamic acid functional grouping, represented by the general formula, I.



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

I

Recent studies have shown that *N*-arylhydroxamic acids, I, find extensive applications as reagents in spot test, gravimetric and colorimetric analyses, and in separations involving solvent extraction (*1, 2, 4, 6, 9–16, 18, 19*). Introduction of certain groups and conjugated systems increase the molar absorptivity of the corresponding vanadium (V) complex considerably (*4, 13, 19*). Too, bulkier reagents are more sensitive for gravimetric estimations due to the weighing effect. One of the most familiar and spectacular examples of weighting effect is the precipitate produced by cupferron (ammonium salt of nitrosophenylhydroxylamine) and neocupferron (ammonium salt of nitrosonaphthylhydroxylamine) with large numbers of metal ions in an acidic medium. The latter compound containing the bulky naphthyl group gives less soluble and bulkier precipitates with metal ions and is more sensitive (*17*). Therefore it is expected that the introduction of a naphthyl group may enhance the gravimetric sensitivity of the reagent. *N*-1-naphthylbenzohydroxamic acid has been reported in literature as a reagent for metal ions (*9*). Therefore, 12 hydroxamic acids derived from *N*-1-naphthylhydroxylamine are synthesized and reported here for the first time.

In the present investigation all the hydroxamic acids were prepared by following basically the modified procedure of Tandon and Priyadarshini (*7, 13*), which is based on Schotten-Baumann reaction (*5*). Equimolar proportions of *N*-1-naphthylhydroxylamine and appropriate acid chlorides were reacted at low temperature in diethyl ether medium containing aqueous suspension of sodium bicarbonate to neutralize the liberated hydrochloric acid.

N-1-naphthylhydroxylamine is highly susceptible to air oxidation. Often the hydroxamic acids derived from it are contaminated with difficultly removable light red complex impurities. It is desirable to start the preparation with freshly prepared pure *N*-1-naphthylhydroxylamine following the recommended experimental conditions rigidly.

The ultraviolet and infrared spectra of the synthesized hydroxamic acids have been determined for their characterization and are given in Table I.

EXPERIMENTAL

Materials and Apparatus. Ultraviolet spectra of hydroxamic acids in spectroscopic grade 95% ethanol were measured on a Beckman Model DK-2 ratio recording spectrophotometer using two 10-mm matched silica cells. The absorption measurements made at constant wavelengths for calculation of molar absorptivity, ϵ, were performed on Unicam SP-500 Spectrophotometer. Molar absorptivity, determined at the wavelength of maximum absorption, is expressed in units of liter/mole cm.

For spectroscopic work all hydroxamic acids were recrystallized from mixtures of benzene and petroleum ether at least three times and were vacuum dried.

Preparation. All the carboxylic acids were converted into acid chlorides by the action of excess of thionyl chloride (*20*).

Twenty grams of 1-nitronaphthalene were dissolved in 500 ml of absolute alcohol in a flask, and the flask was cooled in ice. The cooled solution was saturated successively by ammonia and hydrogen sulfide until the golden yellow crystals of NH_4HS were obtained in the flask which was kept in a freezing mixture for 24 hr. Then a large volume of ice water was added to it. Yellow crystals of *N*-1-naphthylhydroxylamine were filtered and recrystallized from benzene and petroleum ether and used within 1 to 2 hr. The melting point was 78°C. Precautions were taken to minimize the air oxidation of *N*-1-

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Table I. Properties of *N*-Naphthylhydroxamic Acids[a]

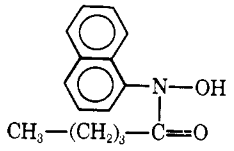
Hydroxamic acid	Molecular formula	Mol wt	Mp, °C	% Yield[b]	Uv spectra		Ir spectra	
				λ_{max}	mμ	$\epsilon \times 10^{-3}$	ν(O—H), cm^{-1}	ν(C═O), cm^{-1}
N-1-naphthyl-*n*-valero-	$C_{15}H_{17}O_2N$	243.310	102	65	277	8.3	3125	1634
N-1-naphthylcapro-	$C_{16}H_{19}O_2N$	257.337	114	70	278	10.8	3100	1650
N-1-naphthylcapri-	$C_{20}H_{27}O_2N$	313.445	89	65	278	10.7	3125	1639
N-1-naphthyllauro-	$C_{22}H_{31}O_2N$	341.499	97	75	278	10.1	3125	1639
N-1-naphthylmyristo-	$C_{24}H_{35}O_2N$	369.553	100	75	277	10.7	3100	1600
N-1-naphthylphenylaceto-	$C_{18}H_{15}O_2N$	277.308	115	75	277	9.5	3125	1625
N-1-naphthyl-*p*-methylbenzo-	$C_{18}H_{15}O_2N$	277.303	153	60	284	10.15	3125	1623
N-1-naphthyl-*o*-methylbenzo-	$C_{18}H_{15}O_2N$	277.308	153	68	284	9.2	3100	1630
N-1-naphthyl-*p*-chlorobenzo-	$C_{17}H_{12}O_2NCl$	297.752	148	55	278	12.3	3125	1626
N-1-naphthyl-*p*-nitrobenzo-	$C_{17}H_{12}O_4N_2$	308.282	175[c]	70	270	13.3	3077	1626
N-1-naphthyl-*p*-methoxybenzo-	$C_{18}H_{15}O_3N$	293.308	125	75	275	12.4	3090	1640
N-1-naphthyl-*o*-methoxybenzo-	$C_{18}H_{15}O_3N$	293.308	163.5	75	277	10.3	3100	1630

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.
[b] Average of at least three preparations. [c] Melts with decomposition.

naphthylhydroxylamine which otherwise becomes red owing to its decomposition.

A typical preparation of *N*-1-naphthylhydroxamic acid is described below.

***N*-1-naphthyl-*n*-valerohydroxamic Acid**



Into a 500-ml three-necked flask, equipped with a stirrer, dropping funnel, and thermometer, 150 ml of diethyl ether, 15.9 grams (0.1 mole) of freshly crystallized *N*-1-naphthylhydroxylamine, and a fine suspension of 12.6 grams (0.15 mole) of sodium bicarbonate in 15 to 25 ml of water were added. After the mixture was externally cooled to 0°C or lower, 12.05 grams (0.1 mole) of freshly distilled *n*-valeryl chloride dissolved in 100 ml of diethyl ether was added dropwise over a period of one-half hour. The reaction mixture was stirred for a further 15 min to complete the reaction, and the temperature was kept low to prevent the side reactions. A yellowish-white precipitate was obtained while the ether layer was reddish yellow. The ether layer was separated and ether was distilled under vacuum. The product obtained was about 0.5 gram of reddish-brown solid and was discarded.

The yellowish-white solid from aqueous layer was triturated with a saturated solution of sodium bicarbonate in a mortar for about 15 min to remove acidic impurities. It was filtered off and washed with water. It was purified by crystallization from a mixture of benzene and petroleum ether (boiling range 60–80°C) without the use of charcoal. White needles were obtained. Yield of once-crystallized product, 16 grams (about 65% of theoretical), melting point 100°C. The melting point improved to 102°C on further crystallizations.

Discussion. Most of the reactions proceeded as usual with 50–80% yield. The ortho-substituted benzoyl chlorides reacted with difficulty. They readily formed reddish-black products during reaction. For this reason the hydroxamic acids derived from *o*-nitro-, *o*-chloro-, *o*-iodobenzoic acids could not be prepared. Except for *N*-1-naphthyl-*p*-nitrobenzohydroxamic acid which is yellow, all the hydroxamic acids are white. Improperly prepared, hydroxamic acids are light grayish despite repeated purification by crystallization. Once prepared, they are generally stable except those derived from lower fatty acids which gradually become brown on storage. They are soluble in benzene, alcohol, chloroform, and *o*-dichlorobenzene, and the solutions are stable for about a week if stored in air-tight brown bottles. This property is of great use from the standpoint of analytical applications. All the hydroxamic acids give the characteristic color tests with iron(III) (*4, 6*) and vanadium(V) (*4, 13, 19*). All of these acids formed chloroform-extractable reddish-violet/violet complexes with vanadium(V) from concentrated hydrochloric acid media.

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