Preparation and Properties of *N*-Arylhydroxamic Acids

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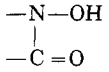
Preparation and properties of several new *N*-arylhydroxamic acids, containing side chain double bonds in conjugation with the carbonyl group, are described. These acids were synthesized for use as possible analytical reagents for metal ions.

THE PREPARATION and properties of 49 *N*-arylhydroxamic acids have been described (*5, 8*). These acids were synthesized for developing superior reagents for the detection and determination of vanadium (V) (*3, 4*). The introduction of side chain double bonds in conjugation with the carbonyl group of the hydroxamic acid functional grouping



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

formed reagents which had better sensitivity for the vanadium (V) color reaction. For example, the molar absorptivity of the vanadium (V) reaction was improved to 6300 ± 50 with *N*-phenylcinnamohydroxamic acid, compared to 4650 ± 50 with *N*-phenylbenzohydroxamic acid, both measured at the corresponding wavelengths of maximum absorption and expressed in terms of vanadium (*3, 4*). Further work in this direction produced several hydroxamic acids with increasing length of conjugated systems and different substituent groups. Preparation and properties of 15 such *N*-arylhydroxamic acids are presented here. Two of these acids were reported earlier (*9*), but their ultraviolet and infrared spectra are reported for the first time.

All the hydroxamic acids were prepared by following basically the modified procedure of Priyadarshini and Tandon (*5*). Freshly prepared *N*-arylhydroxylamine and acid chloride in equimolar proportions reacted at low temperature in ether medium containing aqueous suspensions of sodium bicarbonate. The mono derivative was the main product, with negligible amounts of diderivative, and could be easily purified by two or three crystallizations from mixtures of benzene and petroleum ether.

The data on hydroxamic acids are given in Table I.

Table I. Properties of Hydroxamic Acids

Compound No.	Hydroxamic Acid	Formula	M.P., °C.	Yield, %[a]	U. V. Spectra λ_{max}, mμ	U. V. Spectra 10^{-3}	ν(C=O) Cm.$^{-1}$ in Nujol	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1	*N*-Phenyl-3-styrylacrylo-	$C_{17}H_{15}NO_2$	175	50	323	40.7	1630	76.96	5.70	5.28	77.26	5.83	5.29
2	*N*-Phenylsorbo-	$C_{12}H_{13}NO_2$	138	60	266	24.6	1650	70.92	6.45	6.89	71.17	6.60	6.69
3	*N*-*m*-Tolylsorbo-	$C_{13}H_{15}NO_2$	96	65	265	23.8	1640	71.87	6.96	6.45	71.95	6.94	6.22
4	*N*-*p*-Tolylsorbo-	$C_{13}H_{15}NO_2$	160	70	265	24.5	1645	71.87	6.96	6.45	71.86	6.93	6.60
5	*N*-*p*-Chlorophenylsorbo-	$C_{12}H_{12}NO_2Cl$	173	50	270	25.2	1650	60.64	5.09	5.89[b]	60.85	5.18	5.63
6	*N*-Phenyl-2-furanacrylo-	$C_{13}H_{11}NO_3$	120	60	315	27.3	1643	68.11	4.84	6.11	68.03	4.99	6.26
7	*N*-*m*-Tolyl-2-furanacrylo-	$C_{14}H_{13}NO_3$	109	70	315	26.1	1645	69.11	5.39	5.76	69.31	5.46	5.78
8	*N*-*p*-Tolyl-2-furanacrylo-	$C_{14}H_{13}NO_3$	160	67	315	26.9	1650	69.11	5.39	5.76	69.00	5.32	6.00
9	*N*-*p*-Chlorophenyl-2-furanacrylo-	$C_{13}H_{10}NO_3Cl$	182	51	315	27.0	1650	59.20	4.09	5.32[c]	58.97	4.08	5.20
10	*N*-*o*-Tolylcinnamo-	$C_{16}H_{15}NO_2$	141	60	282 217	23.5 16.2	1655	75.87	5.97	5.53	75.92	6.29	5.80
11	*N*-*m*-Tolylcinnamo-	$C_{16}H_{15}NO_2$	101	56	292	21.4	1625	75.87	5.97	5.53	75.89	6.22	5.53
12	*N*-*p*-Chlorophenylcinnamo-	$C_{15}H_{12}NO_2Cl$	187	55	295	24.00	1640	65.82	4.32	5.12[d]	65.94	4.63	5.12
13	*N*-Phenylcrotono-	$C_{10}H_{11}NO_2$	112	60	278 216	8.7 19.6	1670	67.78	6.26	7.91	67.92	6.63	8.17
14	*N*-*p*-Tolylcrotono-	$C_{11}H_{13}NO_2$	114	60	280 216	8.3 19.6	1660	69.09	6.85	7.32	69.33	7.09	7.22
15	*N*-*p*-Chlorophenylcrotono-	$C_{10}H_{10}NO_2Cl$	118	59	280 216	8.2 19.6	1650	56.75	4.76	6.62[e]	56.65	4.99	6.86

[a] Average of at least three trials, and calculated for once crystallized product. [b] Calcd. Cl, 14.92. Found. Cl, 15.19. [c] Calcd. Cl, 13.44. Found. Cl, 13.78. [d] Calcd. Cl, 12.95. Found. Cl, 12.80. [e] Calcd. Cl, 16.75. Found. Cl, 16.81.

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EXPERIMENTAL

Materials and Apparatus. Ultraviolet and visible spectra of hydroxamic acids were scanned on a Perkin-Elmer 350 recording spectrophotometer using two 10-mm. matched silica cells. For calculation of the molar absorptivity, ϵ, the absorption measurements were made at constant wavelength on an Unicam SP 500 spectrophotometer. Molar absorptivity is expressed in units of liters per mole centimeter.

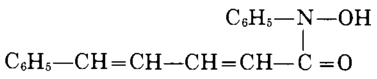
All the hydroxamic acids were recrystallized from mixtures of benzene and petroleum ether at least twice and were vacuum-dried. Standard solutions were prepared in spectroscopic grade 95% ethyl alcohol.

Preparation. 3-Styrylacrylic (cinnamylidene acetic) (*6*) and 2-furanacrylic (*1*) acids were prepared according to reported methods. Other carboxylic acids were available commercially. These acids were converted into the corresponding acid chlorides by the action of thionyl chloride on their benzene solutions. Unreacted thionyl chloride and benzene were distilled off and the acid chloride was obtained by distillation under reduced pressure. The yields were generally 85 to 90%. 3-Styrylacrylyl chloride distilled at 145° C./2.5 mm., while the other acid chlorides distilled at reported temperatures (*10*).

N-Arylhydroxylamines (*2, 7*) were freshly prepared by the reduction of the corresponding nitrobenzenes with zinc dust and ammonium chloride from aqueous or aqueous ethanolic solutions and crystallized from mixtures of benzene and petroleum ether. *N*-*o*-Tolylhydroxylamine could not be isolated in the solid state and was therefore used in further preparations *in situ*.

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

In a three-necked round-bottomed flask, fitted with a mechanical stirrer, *N*-phenylhydroxylamine (5.95 grams, 0.05 mole), sodium bicarbonate (8.4 grams, 0.1 mole), diethyl ether (100 to 125 ml.), and water (8 to 10 ml.) were externally cooled to 0° C. or lower. To this, 3-styrylacrylyl chloride (9.62 grams, 0.05 mole) dissolved in diethyl ether (100 to 125 ml.) was added dropwise from a separating funnel during about an hour. A yellowish crystalline mass separated as the reaction proceeded. On the completion of the reaction the ethereal layer was decanted off and the dissolved hydroxamic acid was precipitated by the addition of petroleum ether. This was mixed with the solid material left in the aqueous layer and was triturated with a saturated solution of sodium bicarbonate in a porcelain mortar for about 15 minutes to remove the acidic impurities. It was then filtered under suction, washed with cold water, and dried under folds of filter paper. On crystallization from a mixture of benzene and petroleum ether yellow plates were obtained. Two crystallizations gave a pure product. Yield of once crystallized product, *N*-phenyl-3-styrylacrylohydroxamic acid,



$$\begin{array}{r} C_6H_5{-}N{-}OH \\ | \\ C_6H_5{-}CH{=}CH{-}CH{=}CH{-}C{=}O \end{array}$$

was 7.1 grams, 50% of the theoretical.

ACKNOWLEDGMENT

The authors are indebted to the authorities of Government Science College, Jabalpur, for facilities. They thank T.R. Govindachari, CIBA Research Center, Bombay, and V.S. Pansare, National Chemical Laboratory, Poona, for the microanalyses of the compounds.

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RECEIVED for review June 19, 1967. Resubmitted October 29, 1968. Accepted January 22, 1969. Grateful acknowledgment is made to the Chemical Society, London, van't Hoff Fund, Amsterdam, and Jabalpur University, Jabalpur, for partial financial support.