

Studies on Hydroxamic Acids. Preparation and Properties of N-Aryl Hydroxamic Acids Derived from Aromatic Carboxylic Acids

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The preparation and properties of a large number of N-aryl hydroxamic acids were reported recently¹⁻⁴. In the present communication preparation and spectral properties of 19 N-aryl hydroxamic acids are described, derived from N-phenylhydroxylamine and N-(*o*, *m*, or *p*) tolylhydroxylamine.

For preparing hydroxamic acids derived from N-*o*-tolylhydroxylamine, the method of Tandon and Priyadarshini² was used with some modifications. Under the conditions employed the formation of diacyl derivative was prevented and the product was readily purified by two to three crystallizations.

Ultraviolet and infrared spectra of the newly prepared hydroxamic acids have been determined for their characterisation. It is observed that these data are not yet reported for the two previously known acids, namely N-*o*-tolylbenzo- and N-*m*-tolylbenzohydroxamic acids^{5,6} (Table-1).

EXPERIMENTAL

Ultraviolet and visible absorption spectra of the hydroxamic acids were scanned on a Beckmann Model DK-2 ratio recording spectrophotometer using two 10 mm. matched silica cells. The absorption measurements, made at constant wavelengths for the calculation of molar absorptivity, ϵ , were performed on an Unicam Sp-500 Spectrophotometer. Molar absorptivity determined at the wavelength of maximum absorption is expressed in units of liters per mole cm. Spectroscopic grade of 95% ethanol was used for preparing standard solutions of hydroxamic acids.

All the acid chlorides used in this study were prepared by the action of excess of thionyl chloride on the corresponding acids. After refluxing the solution for about two hours over the steam bath excess of thionyl chloride was distilled off and the pure acid chlorides obtained by distillation under reduced pressure.

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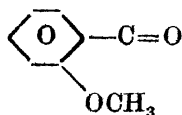
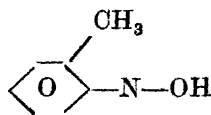
N-Phenyl hydroxylamine⁷ and N-*p*-tolylhydroxylamine⁸ were freshly prepared. The preparation of N-ortho- and N-meta- tolylhydroxylamines are briefly described here because the experimental conditions for preparing them could be established after a lot of experimentation.

N-m-Tolylhydroxylamine : To a mixture of 30 g. (0.22 mole) of *m*-nitro toluene, 20 ml. of water, 30 ml. of ethyl alcohol and 2 g. (0.04 mole) of ammonium chloride, 30 g. (0.46 mole) of zinc dust were added in about 30 mins. The temperature of the reaction mixture was not allowed to rise above 70° and the stirring was continued for another 20 mins after which white hydrous zinc oxide was filtered off. This was washed with 15 to 20 ml. of hot water and finally with 25 ml. of ethyl alcohol. The filtrate was then poured on 500 ml. of ice cold water and crushed ice. Yellowish white flakes of N-*m*-tolylhydroxylamine were filtered off and recrystallized from a mixture of benzene and petroleum ether. White shining flakes, m.p. 69°, yield 75%.

N-o-Tolylhydroxylamine : It was reported⁹ that this compound, m.p. 44° is obtained in 10% yield after three days of reduction with sodium hydrosulphide and calcium chloride. However, we could not obtain it in solid state. Similar difficulty was experienced by other workers⁵. As such acylation was done *in situ* after reduction of *o*-nitrotoluene with zinc dust and ammonium chloride and assuming 60% yield of *o*-tolylhydroxylamine and testing its presence at different intervals with Tollen's reagent during the reaction.

A typical preparation of N-arylhdroxamic acid from N-*o*-tolylhydroxylamine is described below :

N-o-Tolyl-o-methoxybenzohydroxamic acid :



Into a 500 ml. three necked flask fitted with a mechanical stirrer, dropping funnel and thermometer was taken, about 13 g. (0.1 mole) of *o*-tolylhydroxylamine in 150 ml. of diethyl ether, obtained from the reduction of 25 g. of *o*-nitrotoluene by the given method. To this a fine suspension of 12.6 g. (0.15 mole) of sodium bicarbonate in 15 to 25 ml. of water was added. The mixture was cooled externally to 0° or below and mechanically stirred. To this was added dropwise 17.1 g. (0.1 mole) of *o*-methoxybenzoyl chloride in 100 ml. of diethyl ether in course of an hour. During the course of the reaction the presence of free

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TABLE I
Properties of *N*-Aryl Hydroxamic Acids

Compd. No.	Hydroxamic Acid	M.P. °C	Yield	U.V. λ_{max} (m μ)	10 ⁻³ $\nu(O-H)$ cm ⁻¹	ϵ -IR Spectra $\nu(C=O)$ cm ⁻¹		Analyses					
						Calculated	Found	C	H	N	C	H	N
1.	<i>N</i> -Phenyl- <i>o</i> -methoxybenzo-	115 ⁵	65	254	10.3	3175	1603	69.12	5.40	5.76	69.47	5.75	5.54
2.	<i>N</i> - <i>o</i> -Tolyl-benzo-	106*	80	GA	—	3145	1639	73.99	5.77	6.16	74.38	6.15	6.16
3.	<i>N</i> - <i>o</i> -Tolyl- <i>p</i> -methylbenzo-	141	80	GA	—	3100	1650	74.67	6.27	5.80	74.70	6.38	5.90
4.	<i>N</i> - <i>o</i> -Tolyl- <i>m</i> -methylbenzo-	92.5	45	GA	—	3115	1625	74.67	6.27	5.80	75.06	6.66	5.71
5.	<i>N</i> - <i>o</i> -Tolyl- <i>o</i> -methylbenzo-	90	56	GA	—	3125	1610	74.67	6.27	5.80	75.10	6.47	5.72
6.	<i>N</i> - <i>o</i> -Tolyl- <i>p</i> -chlorobenzo-	120	70	GA	—	3125	1613	65.25	4.62	5.35	65.15	4.87	5.40
7.	<i>N</i> - <i>o</i> -Tolyl- <i>o</i> -iodobenzo-	95	45	GA	—	3090	1625	47.61	3.42	3.97	47.87	3.40	4.00
8.	<i>N</i> - <i>o</i> -Tolyl- <i>o</i> -chlorobenzo-	111	50	GA	—	3100	1600	64.25	4.62	5.35	65.28	5.10	5.04
9.	<i>N</i> - <i>o</i> -Tolyl- <i>o</i> -methoxybenzo-	100	65	GA	—	3040	1653	70.03	5.88	5.44	70.02	6.03	5.73
10.	<i>N</i> - <i>p</i> -Tolyl- <i>o</i> -methoxybenzo-	127.5	85	256	10.3	3175	1608	70.03	5.88	5.44	69.85	5.75	5.54
11.	<i>N</i> - <i>p</i> -Tolyl- <i>m</i> -nitrobenzo-	106	50	255	15.7	3077	1613	61.76	4.44	10.23	61.40	4.52	10.03
12.	<i>N</i> - <i>m</i> -Tolylbenzo-	67.0†	50	262	8.5	3155	1618	73.99	5.77	6.16	73.87	6.10	6.08
13.	<i>N</i> - <i>m</i> -Tolyl- <i>p</i> -methylbenzo-	101	60	255	13.4	3077	1639	74.67	6.27	5.80	74.87	6.31	5.82
14.	<i>N</i> - <i>m</i> -Tolyl- <i>m</i> -methylbenzo-	57	40	262	8.5	3100	1640	74.67	6.27	5.80	74.59	6.33	6.00
15.	<i>N</i> - <i>m</i> -Tolyl- <i>o</i> -methylbenzo-	97	80	255	9.5	3100	1610	74.67	6.27	5.80	74.59	6.33	6.00
16.	<i>N</i> - <i>m</i> -Tolyl- <i>o</i> -iodobenzo-	143	60	230	15.7	3100	1630	47.61	3.42	3.97	47.87	3.70	4.35
17.	<i>N</i> - <i>m</i> -Tolyl- <i>o</i> -chlorobenzo-	97	65	254	11.0	3100	1610	64.25	4.62	5.35	64.27	4.59	5.30
18.	<i>N</i> - <i>m</i> -Tolyl- <i>p</i> -methoxybenzo-	112.5	82	268	15.4	3100	1625	70.03	5.88	5.44	69.98	6.02	5.43
19.	<i>N</i> - <i>m</i> -Tolyl- <i>o</i> -methoxybenzo-	111	65	256	10.5	3100	1625	70.03	5.88	5.44	70.18	5.98	5.74

* Reference (5) melting point 105°

† Reference (6) melting point 70°

GA = General Absorption.

hydroxylamine was tested in the reaction mixture by putting one drop of the solution on a piece of filter paper soaked in Tollen's reagent. A black area around the drop on the filter paper due to reduction of silver nitrate indicates free hydroxylamine. If the black area was not obtained it was assumed that all the hydroxylamine had reacted and the addition of acid chloride was stopped. The solution was stirred for about 20 minutes more and the temperature was kept low. Some of the product was precipitated as a white solid while the ethereal layer was light yellow. The ethereal layer was separated from the aqueous layer and ether was removed under vacuum. The yellowish white solid thus obtained was combined with the bulk of the product which was triturated with a saturated solution of sodium bicarbonate in a mortar to remove acidic impurities. The solid was filtered off and washed with cold water. The yield of the crude air dried product, m.p. 96°, was 80%. Three crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave very light white needles, m.p. 100°.

Most of the reactions proceeded as usual with 50 to 80% yield. Oily products were obtained when *o*-tolyl hydroxylamine was reacted with aliphatic acid chlorides. All the hydroxamic acids gave characteristic colour test of vanadium(V) in strong hydrochloric acid medium.

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