

# Synthesis of *N*-Arylhydroxamic Acids

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The preparation and properties of seven new *N*-arylhydroxamic acids have been described. They are characterized by their melting point, elemental analysis, and IR and UV spectra.

## Introduction

The hydroxamic acids are versatile complexing reagents and are used widely for the colorimetric determination of trace metals (1, 2, 13, 14). They exhibit antitubercular agents and antifungal activity (10, 16). In connection with the previous communication (3, 4), seven new hydroxamic acids have been synthesized for the purpose of obtaining better analytical properties.

## Experimental Section

Infrared spectra were recorded in the 2–15- $\mu$  region on a Perkin-Elmer Model 137 or 221 spectrophotometer equipped with sodium chloride optics and calibrated by standard methods. The hydroxamic acids were dried under vacuum over  $P_2O_5$  and examined as KBr pellets.

The UV absorption spectra of hydroxamic acids in 95% ethyl alcohol were recorded on a VSU2-P spectrophotometer in the 200–350-nm region.

**Acid Chlorides.** These were prepared by the action of thionyl chloride on the corresponding benzoic acids, refluxing the mixture for about 2–2.5 h. The solution was allowed to cool and excess thionyl chloride was distilled off. Finally the solutions were distilled under vacuum. The boiling points and yields of the acid chlorides thus produced were in agreement with literature (17).

**Hydroxylamines.** The phenylhydroxylamine (13) and *N*-*p*-tolyl-, *N*-*m*-tolyl-, and *N*-*p*-chlorophenylhydroxylamines are prepared as described elsewhere (3, 4).

**Preparation of *N*-Phenyl-*p*-ethoxybenzohydroxamic Acid.** A typical procedure for *N*-phenyl-*p*-ethoxybenzohydroxamic acid is described here.

Into a 500-mL three-necked flask, equipped with a dropping funnel, stirrer, and thermometer, about 75 mL of diethyl ether, 10.9 g (0.1 mol) of freshly crystallized phenylhydroxylamine, and a fine suspension of 15.9 g (0.15 mol) of sodium carbonate in 25 mL of water were added. After the mixture was cooled to 0 °C or lower, 15.7 g (0.09 mol) of *p*-ethoxybenzoyl chloride dissolved in 50 mL of diethyl ether was added dropwise over a period of about an hour. The temperature was maintained

at 0 °C for an additional 30 min. Some of the product separated 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 solid, triturated for about 15 min on a porcelain mortar with a saturated solution of sodium bicarbonate, filtered, and washed with cold water. The yield of air-dried product, mp 143 °C, was 70%. Two crystallizations from a mixture of benzene and petroleum ether (60–80 °C) gave a white product, mp 146 °C.

## Discussion

The physical properties of *N*-arylhydroxamic acids are given in Table I. The ethoxy and chloro derivatives are a white crystalline solid while the iodo derivatives are light pink. They are sparingly soluble in water but soluble in benzene, ethyl alcohol, diethyl ether, and chloroform except *N*-*p*-chlorophenyl-*m*-chlorobenzohydroxamic acid which is sparingly soluble in benzene.

The infrared spectra of the synthesized hydroxamic acids were determined primarily for their characterization. In the infrared spectra only those bands which are associated with the hydroxamic acid functional group (I) have been assigned.



In the hydroxamic acids examined here the band due to (O–H) stretching vibrations has been assigned in the region around 3230  $\text{cm}^{-1}$  (Table I). It is known that the absorption band due to (O–H) stretching vibration, when free, appears around 3600  $\text{cm}^{-1}$ ; hydrogen bonding shifts these bands to lower frequencies (5, 6, 8, 9). Most of the changes in (O–H) stretching vibration are mainly due to the ability of acidic hydrogen of the hydroxyl group to form hydrogen bonds with the electron-rich atom. In the hydroxamic acids the lower shift of the (O–H) was due to the intramolecular hydrogen bonding of the type  $\text{—OH}\cdots\text{C=O}$ . The (C=O) and (N–O) bands are assigned at about 1620 and 920  $\text{cm}^{-1}$ , respectively.

In the ultraviolet region there is a characteristic band at about 250 nm which is assigned as benzene band II (7). This band is discriminated by its position and magnitude of intensity. In hydroxamic acids this band is assigned around 270 nm. The assignment of the band is supported by comparing the spectra of *N*-arylhydroxamic acid with structurally related compounds (11, 15).

Table I<sup>a</sup>

Name of compd, benzohydroxamic acids	Mol formula	Mp, °C	% yield	IR spectra, $\text{cm}^{-1}$			UV spectra $\lambda_{\text{max}}$ , nm
				$\nu_{\text{O—H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{N—O}}$	
<i>N</i> -Phenyl- <i>p</i> -ethoxy-	$\text{C}_{15}\text{H}_{15}\text{O}_3\text{N}$	146	60	3226	1623	926	272
<i>N</i> - <i>m</i> -Tolyl- <i>p</i> -ethoxy-	$\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$	98	70	3226	1626	926	275
<i>N</i> - <i>p</i> -Tolyl- <i>p</i> -ethoxy-	$\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}$	167	60	3220	1626	930	258
<i>N</i> -Phenyl- <i>p</i> -iodo-	$\text{C}_{13}\text{H}_{10}\text{O}_2\text{NI}$	150 dec	62	3226	1626	905	272
<i>N</i> - <i>m</i> -Tolyl- <i>p</i> -iodo-	$\text{C}_{14}\text{H}_{12}\text{O}_2\text{NI}$	141	63	3225	1615	920	272
<i>N</i> - <i>p</i> -Tolyl- <i>p</i> -iodo-	$\text{C}_{14}\text{H}_{12}\text{O}_2\text{NI}$	180 dec	64	3220	1620	920	268
<i>N</i> - <i>p</i> -Chloro- <i>m</i> -chloro-	$\text{C}_{13}\text{H}_9\text{O}_2\text{Cl}_2$	218	72	3175	1626	926	272

<sup>a</sup> Elemental analyses (C, H, N), in agreement with theoretical values, were obtained and submitted for review.

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**Literature Cited**

- (1) Agrawal, Y. K., *Sep. Sci.*, **8**, 709 (1973).
- (2) Agrawal, Y. K., *Mikrochim. Acta*, **2**, 595 (1976).
- (3) Agrawal, Y. K., Tandon, S. G., *J. Chem. Eng. Data*, **7**, 553 (1962).
- (4) Agrawal, Y. K., *J. Chem. Eng. Data*, **22**, 70 (1977).
- (5) Agrawal, Y. K., Tandon, S. G., *J. Indian Chem. Soc.*, **49**, 911 (1972).
- (6) Bellamy, L. J., "Infrared Spectra of Complex Molecules", Methuen, London, 1954.

- (7) Bladen, P., "Ultraviolet and Visible Spectroscopy in Physical Methods in Organic Chemistry", J. P. C. Swartz, Ed., Oliver and Boyd, London 1961, p 146.
- (8) Cross, A. D., "An Introduction to Practical Infrared Spectroscopy", 2nd ed, Butterworths, London, p 67.
- (9) Hadzi, D., Prevorsek, D., *Spectrochim. Acta*, **10**, 38 (1957).
- (10) Hase, J., Kobashi, K., Kawaguchi, N., Sakamoto, K., *Chem. Pharm. Bull.*, **19**, 363 (1971).
- (11) Kamlet, M. J. E., "Organic Electronic Spectral Data", Vol. I, Interscience, London, 1960, pp14, 138, 298, 506.
- (12) Majumdar, A. K., "N-Benzoylphenylhydroxylamine and Its Analogues", Pergamon, London, 1971.
- (13) Priyadarshini, U., Tandon, S. G., *J. Chem. Eng. Data*, **12**, 143 (1967).
- (14) Stary, J., "The Solvent Extraction of Metal Chelates", Pergamon, Oxford, 1964, pp 123, 127.
- (15) Ungnade, H. E., Ed., "Organic Electronic Spectral Data", Vol. I, Interscience, London, 1960, pp 4, 97, 139, 352.
- (16) Urbanski, T., *Nature (London)*, **186**, 267 (1950).
- (17) Wagner, R. B., Zook, H. D., "Synthetic Organic Chemistry", Wiley, New York, N.Y., 1953, p 546.

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## Electron-Impact-Induced Fragmentation of *N*-(Triarylmethyl)- and *N*-(Triarylsilyl)triarylphosphinimines

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Mass spectra of *N*-(triarylmethyl)- and *N*-(triarylsilyl)triarylphosphinimines are presented. The cleavage products of *N*-(triarylmethyl)triarylphosphinimines are analogous to those of *N*-phenyltriphenylphosphinimine and derivatives previously reported. The relative intensities are considerably different.

In view of the recent interest in mass spectrometric behavior of *N*-phenyltriphenylphosphinimines (*N*-phenyliminotriphenylphosphoranes) (1) (I-IV, Table I), it was thought worthwhile to

examine the mass spectra of the structurally related *N*-(triarylmethyl)triarylphosphinimines (V-VIII, Table I) and of *N*-(triarylsilyl)triarylphosphinimines (XIII-XVIII, Table III) (3). The most interesting fragment ions, *m/e* greater than 100, are summarized in Tables I-III.

**Discussion**

An interesting anomaly is observed in the spectra of compounds XI and XII (Table II). No molecular ions are observed. The peaks at *m/e* 461, which correspond to the molecular ions of compounds IX and X, suggest that isomers XI and XII lose

Table I. Main Fragment Ions of *N*-Aryltriphenylphosphinimines (I-IV) and *N*-(Triarylmethyl)triphenylphosphinimines (V-VIII) [*m/e* and Their Relative Intensities (%)]

Compound	X	[M] <sup>+</sup>	[M - Ph] <sup>+</sup>	[PPh <sub>3</sub> ] <sup>+</sup>	[PPh <sub>2</sub> ] <sup>+</sup>	[PPh <sub>2</sub> - 2H] <sup>+</sup>	[Ph <sub>2</sub> - 2H] <sup>+</sup>	[PPh] <sup>+</sup>
XC <sub>6</sub> H <sub>4</sub> N=P(Ph) <sub>3</sub>								
I	H	353 (100)	276 (9)	262 (15)	185 (14)	183 (52)	152 (12)	108 (13)
II	<i>p</i> -OCH <sub>3</sub>	383 (100)	306 (2)	262 (8)	185 (7)	183 (18)	152 (3)	108 (13)
III	<i>p</i> -F	371 (100)	294 (8.3)	262 (94)	185 (27)	183 (94)	152 (14)	108 (29)
IV	<i>m</i> -F	371 (100)	294 (6.2)	262 (62)	185 (18)	183 (75)	152 (8)	108 (12)
XC <sub>6</sub> H <sub>4</sub> C(Ph) <sub>2</sub> N=P(Ph) <sub>3</sub>								
V	H	519 (2)	442 (32)	262 (100)	185 (32)	183 (6)	152 (11)	108 (32)
VI	<i>p</i> -OCH <sub>3</sub>	549 (1)	472 (22)	262 (100)		183 (50)	152 (10)	108 (25)
VII	<i>p</i> -F	537 (1)	460 (48)	262 (100)		183 (53)	152 (13)	108 (53)
VIII	<i>m</i> -F	537 (3)	460 (40)	262 (100)	185 (13)	183 (80)	152 (3)	108 (50)

Table II. Main Fragment Ions of *N*-Aryl- and *N*-(Triarylmethyl)tris(*p*-methoxyphenyl)phosphinimines [*m/e* as Their Relative Intensities (%)]

Compound	X	[M] <sup>+</sup>	[M - C(Ph) <sub>2</sub> ] <sup>+</sup>	[M - C <sub>6</sub> H <sub>4</sub> F] <sup>+</sup>	HN=P(C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> ) <sub>3</sub>	P(C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> ) <sub>3</sub>	P(C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> ) <sub>2</sub>	P(C <sub>6</sub> H <sub>4</sub> -OCH <sub>3</sub> )	C <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub>
XC <sub>6</sub> H <sub>4</sub> N=P(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -OCH <sub>3</sub> ) <sub>3</sub>									
IX	<i>m</i> -F	461 (100)		366 (61)		352 (85)	245 (61)	138 (61)	107 (2)
X	<i>p</i> -F	461 (80)		366 (100)		352 (60)	245 (100)	138 (40)	107 (10)
XC <sub>6</sub> H <sub>4</sub> C(Ph) <sub>2</sub> N=P(C <sub>6</sub> H <sub>4</sub> - <i>p</i> -OCH <sub>3</sub> ) <sub>3</sub>									
XI	<i>m</i> -F		461 (8)		367 (40)	352 (12)	245 (40)	138 (100)	107 (60)
XII	<i>p</i> -F		461 (16)		367 (100)	352 (42)	245 (72)	138 (8)	107 (2)