(20) Moulin, N., Hussonnois, M., Brillard, L., Guillaumont, R., *J. Inorg. Nucl. Chem.*, **37**, 2521 (1975).
(21) Nakamura, K., Kawamura, K., *Bull. Chem. Soc. Jpn.*, **44**, 330 (1971).
(22) Peppard, D. F., Mason, G. W., Hucher, I., *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).
(23) Rard, J. A., Spedding, F. H., *J. Phys. Chem.*, **79**, 257 (1975).
(24) Reuben, J., Fiat, D., *J. Chem. Phys.*, **51**, 4909 (1969).
(25) Rumanova, I. M., Volodina, G. F., Belov, N. V., *Sov. Phys.-Crystallogr.*, **9**, 545 (1965).
(26) Sayre, E. V., Miller, D. G., Freed, S., *J. Chem. Phys.*, **26**, 109 (1957).
(27) Spedding, F. H., Baker, J. L., Walters, J. P., *J. Chem. Eng. Data*, **20**, 189 (1975).
(28) Spedding, F. H., Csejka, D. A., DeKock, C. W., *J. Phys. Chem.*, **70**, 2423 (1966).
(29) Spedding, F. H., Cullen, P. F., Habenschuss, A., *J. Phys. Chem.*, **78**, 1106 (1974).
(30) Spedding, F. H., Derer, J. L., Mohs, M. A., Rard, J. A., *J. Chem. Eng. Data*, **21**, 474 (1976).
(31) Spedding, F. H., Mohs, M. A., Derer, J. L., Habenschuss, A., *J. Chem. Eng. Data*, submitted, 1976.
(32) Spedding, F. H., Naumann, A. W., Eberts, R. E., *J. Am. Chem. Soc.*, **81**, 23 (1959).
(33) Spedding, F. H., Pikal, M. J., Ayers, B. O., *J. Phys. Chem.*, **70**, 2440 (1966).
(34) Spedding, F. H., Rard, J. A., Saeger, V. W., *J. Chem. Eng. Data*, **19**, 373 (1974).
(35) Spedding, F. H., Saeger, V. W., Gray, K. A., Boneau, P. K., Brown, M. A., DeKock, C. W., Baker, J. L., Shiers, L. E., Weber, H. O., Habenschuss, A., *J. Chem. Eng. Data*, **20**, 72 (1975).
(36) Spedding, F. H., Shiers, I. E., Brown, M. A., Baker, J. L., Gutierrez, L., McDowell, L. S., Habenschuss, A., *J. Phys. Chem.*, **79**, 1087 (1975).
(37) Spedding, F. H., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **20**, 88 (1975).
(38) Spedding, F. H., Walters, J. P., Baker, J. L., *J. Chem. Eng. Data*, **20**, 438 (1975).
(39) Spedding, F. H., Weber, H. O., Saeger, V. W., Petheram, H. H., Rard, J. A., Habenschuss, A., *J. Chem. Eng. Data*, **21**, 341 (1976).
(40) Spedding, F. H., Witte, D., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **19**, 369 (1974).
(41) Urgo, J. V., unpublished Ph.D. Thesis, Iowa State University, Ames, Iowa, 1967.
(42) Volodina, G. F., Rumanova, I. M., Belov, N. V., *Sov. Phys.-Crystallogr.*, **6**, 741 (1962).
(43) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., *Natl. Bur. Stand. (U.S.) Tech. Note*, **No. 270-(1-6)** (1968–1971).

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Supplementary Material Available: Tables IV, V, and VI, listings of the ϕ_L, $\bar{L}_2$, and L_1 data for the rare earth chlorides, perchlorates, and nitrates at even concentrations, are available (23 pages). Ordering information is given on any current masthead page.

Synthesis of *N*-Arylhydroxamic Acids

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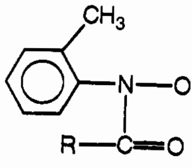
Preparation and properties of ten new *N*-arylhydroxamic acids derived from *O*-tolylhydroxylamine are described. These acids are white crystalline solids and characterized by elemental analysis and infrared spectra.

In the previous communication the preparation and properties of 25 hydroxamic acids derived from *p*- and *m*-tolylhydroxylamine have been described (*1*, *2*). Further work on ten *N*-arylhydroxamic acids derived from substituted benzoic acid with the general formula (I) are reported for the first time



I

where R is substituted benzoic acid derivatives.

The procedure based on the Schotten and Baumann reaction was used for the preparation of these *N*-arylhydroxamic acids. Thus freshly prepared *N*-*o*-tolylhydroxylamine and vacuum distilled acid chloride in equimolar proportions are reacted at low temperature in diethyl ether containing an aqueous suspension of sodium bicarbonate. The *N*-arylhydroxamic acids so obtained are purified by crystallization from a mixture of benzene and petroleum ether.

Discussion

The physical properties of *N*-arylhydroxamic acids are given in Table I. All the hydroxamic acids are white crystalline solids except the iodo and nitro derivatives which are light pink and yellow, respectively. They are sparingly soluble in water but readily soluble in benzene, ethyl alcohol, dioxane, diethyl ether, and chloroform.

The infrared spectra of the synthesized hydroxamic acids were determined primarily for their characterization. In the infrared spectra only those bonds which are associated with the hydroxamic acid functional group, -N(OH)-C═O have been assigned. The presence of the (O–H) stretching band is assigned in the region of 3200 cm^{-1} and conforms with the reported value (*1–6*). The lower shift of (O–H) was due to the intramolecular hydrogen bonding of the type -OH···C═O. The (C═O) and (N—O) bands are assigned at about 1620 and 920 cm^{-1}, respectively.

Experimental Section

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

Acid Chlorides. These were prepared by the action of thionyl chloride on the corresponding benzoic acids. The boiling points and yields of the acid chlorides, thus produced, were in agreement with the values given in literature (*7*).

Procedure. A typical procedure for *N*-*o*-tolyl-*p*-fluorobenzohydroxamic acid is described here.

Into a 500-ml, three-necked flask, equipped with stirrer, dropping funnel, and thermometer, 100 ml of diethyl ether, 12.3 g (0.1 mol) of freshly crystallized *O*-tolylhydroxylamine, and a

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

						IR spectra (cm^{-1})		
Compd no.	Benzohydroxamic acid	Mol formula	Mp, °C	% yield	Color	ν_{O-H}	$\nu_{C=O}$	ν_{N-O}
I	*N-o*-Tolyl-*o*-fluoro-	$C_{14}H_{12}NO_2F$	130	70	White	3165	1625	935
II	*N-o*-Tolyl-*p*-fluoro-	$C_{14}H_{12}NO_2F$	140	70	White	3160	1620	930
III	*N-o*-Tolyl-*o*-bromo-	$C_{14}H_{12}NO_2Br$	110	60	White	3175	1620	930
IV	*N-o*-Tolyl-*m*-bromo-	$C_{14}H_{12}NO_2Br$	90	65	White	3175	1625	925
V	*N-o*-Tolyl-*p*-bromo-	$C_{14}H_{12}NO_2Br$	155	65	White	3180	1620	923
VI	*N-o*-Tolyl-*p*-iodo-	$C_{14}H_{12}NO_2I$	140	60	Light pink	3200	1625	930
VII	*N-o*-Tolyl-*o*-nitro-	$C_{14}H_{12}N_2O_4$	150	70	Light yellow	3170	1615	930
VIII	*N-o*-Tolyl-*m*-nitro-	$C_{14}H_{12}N_2O_4$	101	70	Light yellow	3165	1600	920
IX	*N-o*-Tolyl-*p*-nitro-	$C_{14}H_{12}N_2O_4$	170	65	Light yellow	3175	1620	925
X	*N-o*-Tolyl-3,5-dinitro-	$C_{14}H_{11}N_3O_6$	140	65	Light yellow	3125	1630	920

[a] Elemental analyses (C, H, N) in agreement with theoretical values were obtained and submitted for review.

fine suspension of 12.6 g (0.15 mol) of sodium bicarbonate in 25 ml of water were added. After the mixture was cooled to 0 °C, 23.12 g (0.1 mol) of *O*-fluorobenzoyl chloride dissolved in 50 ml of diethyl ether was added dropwise over a period of 1 h. Then an additional time of 30 min was allowed and the temperature was maintained at 0 °C or lower. Some of the product was precipitated as 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 to remove the acid impurities, filtered, and washed with cold water. The yield of air dried product, mp 135 °C, was 70%. Two crystallizations from a mixture of benzene and petroleum ether without the use of charcoal gave white needles, mp 140 °C.

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Literature Cited

(1) Agrawal, Y. K., Tandon, S. G., *J. Chem. Eng. Data,* **16,** 371 (1971).
(2) Agrawal, Y. K., Tandon, S. G., *J. Chem. Eng. Data,* **16,** 495 (1971).
(3) Agrawal, Y. K., Tandon, S. G., *J. Indian Chem. Soc.,* **49,** 911 (1972).
(4) Baumgarten, H. E., Staklis, A., Miller, E. M., *J. Org. Chem.,* **30,** 1203 (1965).
(5) Exner, O., Kakak, B., *Collect. Czech. Chem. Commun.,* **28,** 1656 (1953).
(6) Hadzi, D., Prevorsk, D., *Spectrochim. Acta,* **10,** 38 (1957).
(7) Wagner, R. B., Zook, H. D., "Synthesis Organic Chemistry", Wiley, New York, N.Y., 1953, p 546.

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Solubility of Hydrogen Sulfide and Carbon Dioxide in an Aqueous Diisopropanolamine Solution

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The solubility of H_2S and CO_2 individually in a 2.5 kmol m^{-3} DIPA solution has been determined at 40 and 100 °C for partial pressures of H_2S ranging from 2.0 to 3207 kPa and for partial pressures of CO_2 ranging from 2.7 to 5888 kPa.

Aqueous alkanolamine solutions are widely used for the removal of the acid gases (H_2S and CO_2) from natural gas and synthesis gas streams. The most commonly used amine is monoethanolamine (MEA). Its primary advantage is its low molecular weight. Since the acid gases and amines react on an equivalent rather than a weight basis MEA requires lower circulation rates than other higher molecular weight amines. As well MEA is a stronger base than other alkanolamines. However, MEA reacts irreversibly with carbonyl sulfide (COS) and for this reason diethanolamine (DEA) solutions are commonly employed for natural gases containing COS and for refinery gases (*3*).

Diisopropanolamine (DIPA) has been widely used in Europe for the removal of the acid gases from synthesis gas and refinery gases and liquids. It is used in the Adip process, the Sulfinol process, and the SCOT process, all licensed by Shell. The Adip process was originally described by Bally (*1*) and recent developments and operating data have been provided by Klein (*2*). DIPA solutions are reported to be less corrosive than MEA or DEA solutions, have a greater selectivity for H_2S over CO_2 than either MEA or DEA, and as well are able to remove COS with excessive degradation of the solution. Another advantage claimed for DIPA solutions is that they require less heat in the regeneration of the solution.

In the Sulfinol process, aqueous DIPA is in combination with the physical solvent sulfolane (a typical Sulfinol solution contains 40% DIPA, 40% sulfolane, 20% water). The SCOT process, a tail-gas treating process employs a DIPA solution in order to effect a selective removal of H_2S from a stream containing H_2S and CO_2. DIPA is regarded as the best compromise among the alkanolamines (*8*).

Few solubility data for the acid gases in DIPA solutions have been published. Bally (*1*) presented a small-scale plot showing