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Table II. Boiling Points or Melting Points (°C) of Compounds I-IV

substituents compd	I	II	III	IV
CH_3	145 (1 mm)	157 (1 mm)	mp 90-91	145 (1 mm)
C_3H_7	140-143 (1 mm)	mp 71.5-73.5	mp 143-144.5	140 (1 mm)
C_4H_9	180-181 (1 mm)	172-173 (1 mm)	mp 96-98	180 (1 mm)
i-C_4H_9	163-165 (1 mm)	165-168 (1 mm)	mp 92.5-93.5	165 (1 mm)
C_5H_{11}	159-160 (1 mm)	173-178 (1 mm)	175-180 (1 mm)	160 (1 mm)
$PhCH_2$	mp 109.5-110.5	180-190 (1 mm)	mp 141-142	mp 109.5-110.5
$PhCH_2CH_2$	185-187 (1 mm)	220-222 (2 mm)	mp 103.5-104.5	187 (1 mm)

oxycycloalkene. The cyclopentanone compounds are arranged in increasing percent enol in Table I. Replicate determinations were ±0.3% in five of six cases and ±0.8% for the exception.

The infrared method was substantially superior to the NMR method when applied to this problem.

The percent enol for the cyclopentanones range from 1 to 13%, and for the cyclohexanones they range from 4 to 37%. The largest difference is in the first entry——the unsubstituted 2-cyanocycloalkanones, i.e., 1% vs. 37%. In the cyclopentanone series the lower enol values tend to be related to symmetry of identical simple substituents.

Comparison of enolization of the five-membered compounds with their six-membered analogues generally supports the Brown prediction. There are three exceptions according to this data, but the differences are not striking.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Section Model 237B instrument. NMR spectra were obtained on a Perkin-Elmer R24 instrument. Elemental analyses were by G. I. Robertson Laboratory, Florham Park, NJ, and were submitted to the editor. All spectra were consistent with the assigned structures, and representative curves will be published in the Sadtler Series at a later date. 1-Methyl-3-*p*-tolyltriazene was purchased from Willow Brook Laboratories, Inc., P.O. Box 526, Waukesha, WI 53186.

Synthetic Sequence. The additional cyclopentanones required for this study were synthesized via the previously described (*3*) sequence; i.e., alkylation of the appropriate alkylphenylacetonitrile with 1-bromo-3-chloropropane to the 5-chloro-2-alkyl-2-phenylpentanenitrile (I) → 2-alkyl-2-phenylhexanedinitrile (II) → 2-alkyl-2-phenyl-5-cyanocyclopentanonimine (⇌ enamine tautomer) (III) → 2-alkyl-2-phenyl-5-cyanocyclopentanone (IV). Although several of the precursor compounds in this sequence were previously reported (*6*), we found some differences in properties and have listed all additional compounds prepared in our work. The boiling points or melting points are listed in Table II.

1-Cyano-2-methoxycyclopentenes. Equimolar quantities of the 2-cyanocyclopentanones and 1-methyl-3-*p*-tolyltriazene were dissolved separately in ether. Slow addition of the ketone usually evolved nitrogen. When gas evolution was not spontaneous, the mixture was refluxed for 10-30 min. The mixture stood overnight, and then 10% HCl was added. Further washes with dilute NaOH and then water were followed by drying ($MgSO_4$). After being filtered, the solution was concentrated. Liquids were purified by distillation and solids by recrystallization from 50% ethanol. Pure products were obtained in 50-80% yields. The parent compound had bp 101-104 °C (25 mm). The 3,3-disubstituted compounds were as follows: CH_3, CH_3 (bp 123-128 °C (1 mm)); Ph, n-C_5H_{11} (bp 160-166 °C (5 mm)); Ph, Ph (mp 118-119 °C). These compounds were utilized as the calibration standards as previously described (*2*) for the four types of cyclopentanones: H, H; alkyl, alkyl; phenyl, alkyl; and diphenyl.

Determination of Enols. The previously described procedure was utilized (*2*).

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Preparation and Properties of *N*-Arylhydroxamic Acids[†]

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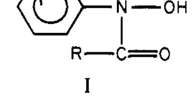
Thirteen new *N*-substituted hydroxamic acids were prepared by the acylation of *N*-arylhydroxylamine with appropriate acid chloride at low temperature in ethereal solutions containing a suspension of sodium bicarbonate. The yields range from 40% to 90%. These compounds were characterized in terms of elemental analyses, melting points, and ultraviolet and infrared spectra.

The chemistry of hydroxamic acid has been of considerable interest to this research group since 1960 (*1*). Over this period the preparation and the properties of more than 200 hydroxamic acids were reported (*2*-*13*). The present investigation deals with the preparation and the properties of 13 *N*-arylhydroxamic acids, I



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[†] Part of the Ph.D. Thesis of V.C.K., Ravishankar University, Raipur, India, 1981.

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Table I. Physical Properties of *N*-Arylhydroxamic Acids[c]

compd no.	hydroxamic acid	formula	mol wt	mp, °C	yield,[a] %	aqueous solubility at 25 °C, mg L^{-1}	UV spectra		IR spectra, cm^{-1}		
							λ_{max}, nm	$10^{-3}\epsilon$, L mol^{-1} cm^{-1}	ν_{O-H}	$\nu_{C=O}$	ν_{N-O}
1	*N*-phenyl-*m*-fluorobenzo-	$C_{13}H_{10}NO_2F$	231.23	84	67	575	205 272	19.0 9.6	3180 s	1615 s	930 w
2	*N*-*o*-tolyl-*m*-fluorobenzo-	$C_{14}H_{12}NO_2F$	245.26	81	63	720	205 258	23.7 6.6	3140 m	1625 s	935 vw
3	*N*-*m*-tolyl-*m*-fluorobenzo-	$C_{14}H_{12}NO_2F$	245.26	55	74	–	205 273	28.5 9.0	3080 w	1610 m	910 w
4	*N*-*o*-tolyl-2,4-dichlorobenzo-	$C_{14}H_{11}NO_2Cl_2$	296.15	149	89	20	208 235	– inf	3090 s	1630 vs 1610 sh	920 s
5	*N*-*m*-tolyl-2,4-dichlorobenzo-	$C_{14}H_{11}NO_2Cl_2$	296.15	150	76	10	207 259	36.2 9.9	3110 s	1625 sh 1610 s	925 w
6	*N*-(*o*-chlorophenyl)-2,4-dichlorobenzo-	$C_{13}H_8NO_2Cl_3$	316.57	172	46	–	206 265	39.7 14.2	3110 m	1625 m 1605 s	–
7	*N*-phenyl-3,5-dimethoxybenzo-	$C_{15}H_{15}NO_4$	273.29	103	73	215	207 270	27.6 9.9	3110 m	1635 s 1602 m	920 m
8	*N*-*o*-tolyl-3,5-dimethoxybenzo-	$C_{16}H_{17}NO_4$	287.32	117	69	65	209 255	30.9 8.1	3245 s	1620 s 1602 m	945 m
9	*N*-*m*-tolyl-3,5-dimethoxybenzo-	$C_{16}H_{17}NO_4$	287.32	106	72	70	208 272	25.9 9.8	3210 m	1615 m 1592 s	910 w
10	*N*-(*p*-chlorophenyl)-2-naphtho-	$C_{17}H_{12}NO_2Cl$	297.74	170	47	1	224 276	34.3 17.1	3200 s	1625 sh 1615 s	905 m
11	*N*-*o*-tolylhydrocinnamo-	$C_{16}H_{17}NO_2$	255.32	56	49	410	208 238	18.4 4.4	3170 s	1625 s 1605 s	905 w
12	*N*-*m*-tolylhydrocinnamo-	$C_{16}H_{17}NO_2$	255.32	62	59	100	210 255	23.6 9.6	3180 s	1640 sh 1625 s	900 m
13	*N*-phenyloleo-[b]	$C_{24}H_{39}NO_2$	373.58	51	60	–	207 253	– –	3170 s	1625 sh 1618 s	900 w

[a] Average of at least three trials, and calculated for once-crystallized product. [b] Compound **13** could be obtained as a sticky white solid only. This product was prone to air oxidation and turned yellow during filtration. On storage it turned into a brown oil. UV and IR spectra were determined with fresh product. [c] Note: Elemental analyses (C, H, N, and Cl) in agreement with theoretical values were obtained and submitted for review. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; –, studies not made; inf, infletion; sh, shoulder or inflection.

where X is H, *o*-CH_3, *m*-CH_3, *o*-Cl, or *p*-Cl, and R is alkyl, substituted alkyl, aryl, or substituted aryl. All of these hydroxamic acids are reported for the first time. Interest in the preparation of these *N*-arylhydroxamic acids was derived from the study of their analytical applications and the modification of analytical properties by the substituent groups.

Experimental Section

Materials and Apparatus. Spectrophotometric measurements were made with a Carl Zeiss, Jena SPECORD, recording spectrophotometer and with an Electronic Corp. of India, Model GS-865, spectrophotometer. Absorption spectra of the hydroxamic acids were recorded with the former, and the latter was used for fixed-wavelength measurements and the calculation of molar absorptivities. The molar absorptivity, ϵ, of any one hydroxamic acid at its wavelength of maximum absorption, λ_{max}, was determined by measuring the absorbance of at least three solutions of different concentrations. Molar absorptivity is expressed in units of L mol^{-1} cm^{-1}. Matched silica cells of 1-cm path length were used. A Mettler microbalance, Model No. AGCH-8606, was used for weighing the hydroxamic acids. A graduated apparatus of standard calibration was used for measurements. All melting points were measured with a calibrated thermometer by the capillary method and are uncorrected. The infrared spectra of all hydroxamic acids were recorded as Nujol mulls on a Perkin-Elmer Model 377 infrared spectrophotometer.

Hydroxamic acids were repurified by crystallization from benzene and petroleum ether and dried over phosphorus pentoxide under vacuum. Spectroscopic-grade ethyl alcohol was prepared by twice distilling 95% ethyl alcohol over potassium hydroxide and silver nitrate (*14*).

Acid Chlorides. All acid chlorides were prepared by the action of thionyl chloride on the corresponding carboxylic acids (*15*) and purified by distillation under reduced pressure. The boiling points of these acids chlorides were in agreement with the reported values (*15*, *16*).

N-Arylhydroxylamine. *N*-Phenylhydroxylamine (*17*), *N*-*m*-tolylhydroxylamine (*7*), and *N*-(*p*-chlorophenyl)hydroxylamine (*18*, *19*) were prepared by reported methods and their melting points tallied with those reported. *N*-*o*-Tolylhydroxylamine (*20*) and *N*-(*o*-chlorophenyl)hydroxylamine (*21*, *22*) could not be isolated in the solid state and were used in situ (*20*, *22*).

N-Arylhydroxamic Acids. These were prepared by the procedure reported earlier (*3*). Acylation of *N*-phenylhydroxylamine with *N*,*N*-dimethylcarbamoyl chloride to give *N*-phenyl-*N*,*N*-dimethylcarbamohydroxamic acid failed.

Properties. All of the *N*-arylhydroxamic acids described here are white crystalline solids. Except for compounds **8** and **12**, which gradually acquire brown coloration, all of these have excellent storage quality. Their solutions in water and other organic solvents are stable for several weeks when stored in amber bottles at room temperature; only on long storage do their solutions acquire brown color. The solutions of hydroxamic acids in alkaline media are unstable and rapidly (a few minutes to a few hours) acquire light green or blue color.

All of the hydroxamic acids are sparingly soluble in water and are readily soluble in organic solvents such as benzene, chloroform, carbon tetrachloride, ethyl alcohol, ethyl acetate, etc. *N*-(*p*-Chlorophenyl)-2-naphthohydroxamic acid shows poorer solubility in almost all solvents in comparison with other hydroxamic acids reported here. Likewise, 2,4-dichlorobenzohydroxamic acids also show poor solubility. Quantitative data on solubilities are given in Table I.

All of the hydroxamic acids gave characteristic purple coloration in aqueous media with ferric chloride and purple chloroform extracts with vanadium(V) from concentrated hydrochloric acid solutions.

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Corrections

J. W. Mullin and M. Šipek. Solubility and Density Isotherms for Potassium Aluminum Sulfate–Water–Alcohol Systems. *J. Chem. Eng. Data* **1981**, *26*, 164–5.

The spelling of the second authors name should be M. Šipek.

Masaaki Yoshida,* Hiroshi Hirota, Masahiro Minabe, and Kazuo Suzuki. Electrophilic Substitution of 4*H*-Cyclopenta[*def*]-phenanthrene Derivatives. *J. Chem. Eng. Data* **1981**, *26*, 220–3.

Page 221. In the third line of the last paragraph the quantity in parentheses after $AlCl_3$ should read (0.54 g, 4 mmol).

Page 222. In Table IV, the Me proton signal for **28** should be 2.79, 2.79.