Preparation and Properties of *N*-Arylhydroxamic Acids

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Ultraviolet and infrared spectra of 16 new hydroxamic acids derived from *N*-*p*-chlorophenylhydroxylamine are described.

The preparation and properties of 94 *N*-arylhydroxamic acids were reported recently (*1, 2, 5, 10, 11*). In an attempt to study the substituent effects on their absorption spectra, 16 new hydroxamic acids derived from *N*-*p*-chlorophenylhydroxylamine were prepared by following basically the modified procedure of Priyadarshini and Tandon (*10*). Generally, three or more crystallizations from benzene and petroleum ether gave highly pure products suitable for analytical work. Their ultraviolet spectra in spectroscopic grade 95% ethanol and infrared spectra were studied for their characterizations. These data are presented in Table I. Chloroform solutions of all the hydroxamic acids reported here give violet extracts with vanadium(V) and concentrated hydrochloric acid and offer potentialities of use for developing spectrophotometric methods of determining vanadium(V).

The absorption band of hydroxamic acids is due to benzenoid absorption, and the large red shift of the first primary band of benzene from 203 nm up to 284 nm, owing to substitutions, is in accord with currently accepted rules of spectroscopy (*3, 4, 9*). The low frequencies of carbonyl and O—H bands in the infrared spectra are due to conjugation and intramolecular hydrogen bonding (*6, 7*).

The nuclear magnetic resonance spectra of compounds 1, 5, 12, and 17 taken on a Varian 60 MC/sec as dimethyl sulfoxide solution, show the signals at 647, 647, 659, and 630 cps, respectively, which disappear on deuterium exchange and correspond to one proton due to the O—H group.

Infrared spectra of compounds 2, 3, 4, and 9 were recorded on Perkin-Elmer Model 21 infrared spectrophotometer as KBr

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

Compound no.	Hydroxamic acids	Formula	M.p., °C	Yield, %	λ_{max}, nm	ϵ, 10^{-3}	ν (O—H), cm^{-1}	ν (C=O), cm^{-1}
1	*N*-*p*-Chlorophenyl-benzo-	$C_{13}H_{10}NO_2Cl$	158[b]	60	274	11.5	3185 s 3106 s	1613 s
2	*N*-*p*-Chlorophenyl-*o*-methylbenzo-	$C_{14}H_{12}NO_2Cl$	154	70	266	13.7	3106 s	1613 vs
3	*N*-*p*-Chlorophenyl-*m*-methylbenzo-	$C_{14}H_{12}NO_2Cl$	103	90	276	12.3	3115 vs	1603 vs
4	*N*-*p*-Chlorophenyl-*p*-methylbenzo-	$C_{14}H_{12}NO_2Cl$	159	85	276	12.9	3185 vsb	1613 vs
5	*N*-*p*-Chlorophenyl-*o*-chlorobenzo-	$C_{13}H_9NO_2Cl_2$	159	83	266	10.7	3115 s	1621 vs 1605 vs
6	*N*-*p*-Chlorophenyl-*m*-chlorobenzo-	$C_{13}H_9NO_2Cl_2$	108	70	276	10.9	3106 s	1625 vs 1606 vs
7	*N*-*p*-Chlorophenyl-*p*-chlorobenzo-	$C_{13}H_9NO_2Cl_2$	142	86	276	11.0	3225 vs 3106 s	1629 vs
8	*N*-*p*-Chlorophenyl-*m*-bromobenzo-	$C_{13}H_9NO_2ClBr$	126	90	276	10.3	3112 s	1620 vs
9	*N*-*p*-Chlorophenyl-*p*-fluorobenzo-	$C_{13}H_9NO_2ClF$	137	75	276	9.6	3195 vsb 3077 vsb	1618 vs
10	*N*-*p*-Chlorophenyl-*m*-nitrobenzo-	$C_{13}H_9N_2O_4Cl$	124	80	266	15.2	3118 vs 3100 s	1620 vs
11	*N*-*p*-Chlorophenyl-*p*-nitrobenzo-	$C_{13}H_9N_2O_4Cl$	123	50	256	14.3	3170 s 3118 s	1625 vs 1603 vs
12	*N*-*p*-Chlorophenyl-*o*-methoxybenzo-	$C_{14}H_{12}NO_3Cl$	116	75	270	10.7	3185 s	1613 vs
13	*N*-*p*-Chlorophenyl-*m*-methoxybenzo-	$C_{14}H_{12}NO_3Cl$	104	85	278	10.4	3106 s	1625 vs
14	*N*-*p*-Chlorophenyl-*p*-methoxybenzo-	$C_{14}H_{12}NO_3Cl$	163	90	284	15.6	3180 vsb	1620 vs
15	*N*-*p*-Chlorophenyl-phenylaceto-	$C_{14}H_{12}NO_2Cl$	124	73	260	13.6	3170 vs	1630 vs
16	*N*-*p*-Chlorophenyl-phenoxyaceto-	$C_{14}H_{12}NO_3Cl$	183	60	260	14.0	3170 sb 3130 sb	1650 vs
17	*N*-*p*-Chlorophenyl-*n*-butyro-	$C_{10}H_{12}NO_2Cl$	94	70	260	12.3	3195 s	1631 vs

vs—very strong, s—strong, b—broad.
[a] Elemental analyses (C, H, N, Cl) in agreement with theoretical values have been obtained and were submitted for review. [b] Reported, mp 155°C (*8*).

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pillets; 1, 5, 12, 17 on Perkin-Elmer 137 B infracord and other compounds were recorded on Backmann IR-4 spectrophotometer as mulls in Nujol, equipped with a rock salt prism as the monochromator and calibrated by standard methods. The ultraviolet spectra were recorded on a Hilger and Watts Ultrascan spectrophotometer using 10-mm matched quartz cells.

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Reactions of Primary Amines with 2-Acyl-1,3-indandiones

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Ethyl- and isopropylamine react with various 2-acyl-1,3-indandiones to form the corresponding 2[1-(alkylimino)alkyl]-1,3-indandiones or 3-alkylimino-2-acyl-1-indanones. Tertiary butylamine forms the tertiary butyl ammonium salts of 2-acyl-3-hydroxyindones. Spectral data (infrared, ultraviolet, nuclear magnetic resonance) are given for the compounds.

As a continuation of our work on the condensation of amines with 2-diphenylacetyl-1,3-indandione (*1*, *5*), we investigated the reactions of primary amines with 2-acyl-1,3-indandiones having straight and branched-chain acyl groups.

Ethyl- and isopropylamine react with 2-acyl-1,3-indandiones to give the imines **1** when 2-propionyl-1,3-indandione is used and imines **2** when 2-isobutyryl- and 2-pyvalyl-1,3-indandione are used (Figure 1). The structures of these compounds are based on elemental analyses and spectral data. The uv absorption peaks of imines **1** are slightly shifted bathochromically in comparison with those of imines **2**, and the extinction coefficients at each peak are similar, with the exception of the extinction coefficients at 325–30 mμ, which increase from 5000 for compounds **2** to 31,000 for compounds **1**.

The similarities of the uv spectra of imines **2** with that of 2-(diphenylacetyl)-3-isopropylamino-1-indanone, prepared by Bechara (*1*) from 2-(diphenylacetyl)-1,3-indandione, 1-hydrazone, and excess isopropylamine, support the assigned position of the imino group in compounds **2**. This structure proof of imines **2** is obviously an indirect proof for the structure of imines **1**, since the latter can have only the alternative structure.

The positions of the imino groups in these compounds are further substantiated by the fact that four equivalent aromatic protons at δ7.7 ppm are present in the nmr spectra of imines **1**, and three equivalent aromatic protons at 7.6, along with one nonequivalent or deshielded proton at 7.8, are present in imines **2** (*4*).

Tertiary butylamine reacts with 2-propionyl-, 2-isobutyryl-, and 2-pyvalyl-1,3-indandione to give the tertiary butyl ammonium salts of the corresponding 2-acyl-3-hydroxyindones (**3a–c**) (Figure 1). The structures of these compounds are based on elemental analyses and are consistent with the ir and nmr spectra.

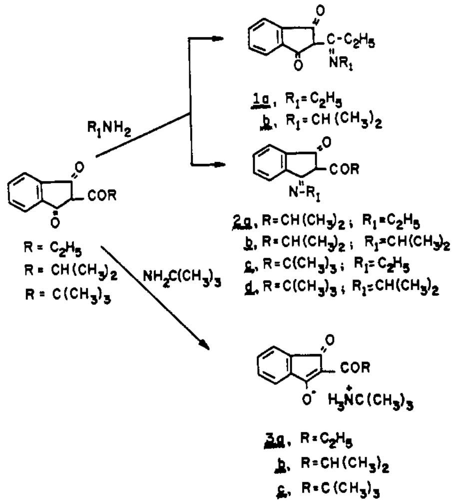

Figure 1. Reactions of primary amines with 2-acyl-1,3-indandiones

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