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NEW COMPOUNDS

An Improved Preparation of 1-Naphthylpropiolic Acid

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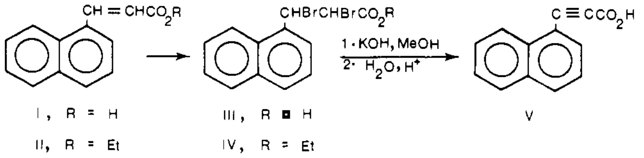
The preparation of 1-naphthylpropiolic acid can be facilitated by an improvement in the preparation of 1-naphthylpropanoic acid dibromide. A recrystallized sample of 1-naphthylpropenoic acid can be brominated quickly by the use of boiling carbon tetrachloride. Although, a priori two diastereomeric dibromides are possible, bromination under these conditions proceeded to supply only one isomer.

1-Naphthylpropiolic acid (V) has been prepared (*1*) by dehydrobromination of the dibromide IV obtained from the photoinduced bromination of ethyl 1-naphthylpropenoate (II). Esterification prior to bromination was necessary since direct bromination of the acid I in ice-cold carbon tetrachloride was found extremely slow. We now report that 1-naphthylpropenoic acid (I) may be brominated directly and in an excellent yield by using boiling carbon tetrachloride to yield only one isomer, mp 181–182 °C. Dehydrobromination of III was accomplished smoothly with 25% methanolic KOH solution instead of the 98% solution used in the older procedure. The overall yield of acid V from the starting acid I was 82%.



Experimental Section

Melting points were measured in an electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on Pye-Unicam SP 300 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on Bruker WP 80-SY spectrometer with Me_4Si as an internal standard.

***3-(1-Naphthyl)propanoic Acid Dibromide* (*III*).** To a suspension of 3-(1-naphthyl)propenoic acid (*2*) (89.5 g, 0.25 mol) and carbon tetrachloride (750 mL) in a two-necked round-bottomed flask fitted with a reflux condenser and a separatory funnel, heated to boiling with continuous stirring, was added bromine (40.0 g, 0.25 mol) in carbon tetrachloride (100 mL). The bromine color disappeared slowly at first, then rapidly so that all bromine was added in the course of 30 min. The solution was poured into a large dish, and all the carbon tetrachloride and unused bromine allowed to evaporate. The dibromide III separated as fine crystals which formed a solid cake in the bottom of the dish. Crystallization from CCl_4 afforded 144 g (89%) of white crystals of III, mp 181–182 °C; NMR ($CDCl_3$) δ 7.52 (m, 7 H, Ar*H*), 6.33 (d, 1 H, C*H*, J = 12 Hz), 5.34 (d, 1 H, C*H*, J = 12 Hz), and 11.72 (s, 1 H, COO*H*). Elemental analysis (C, H, Br) in agreement with theoretical values was obtained and submitted for review.

***3-(1-Naphthyl)propiolic Acid* (*V*).** A mixture of 2-(1-naphthyl)propanoic acid dibromide (118 g, 0.33 mol) in 25% potassium hydroxide/methanol (400 mL) was heated for 30 min over a steam bath. The mixture was poured into a large dish and the solvent allowed to evaporate. The dry residue was dissolved in water and acidified. The precipitated acid was collected and recrystallized from water to give white needles, 59.4 g (92%), mp 137–139 °C (lit. (*3*) 137 °C) ν_{max} $CHCl_3$ 2210, 1695 cm^{-1}; NMR ($CDCl_3$) δ 7.41 (m, 7 H, Ar*H*) and 11.37 (s, 1 H, COO*H*). Elemental analysis (C, H) in agreement with theoretical values was obtained and submitted for review.

Registry No. I, 13026-12-5; III, 97352-00-6; V, 4843-42-9.

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Synthesis and Properties of Some New Hydroxamic Acids

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Five new hydroxamic acids are synthesized for their plausible analytical applications. These acids are characterized by elemental analysis, melting points, UV, IR, NMR, and mass spectra. Their physicochemical properties have been determined.

Introduction

Hydroxamic acids are weak acids widely used for organic and inorganic analysis including pharmaceuticals, as food additives, and in nuclear fuel processing (*1–7*). In the present communication five new hydroxamic acids have been reported and

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Table I. Physical Properties of the Hydroxamic Acids

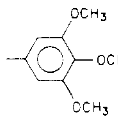
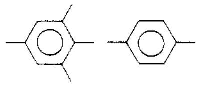
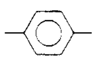
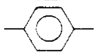
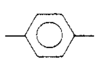
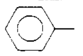
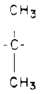
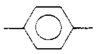
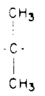
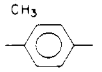
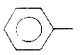
compd no.	hydroxamic acids	mol formula	mol wt	mp, °C	% yield
I	N-4-chlorophenyl 3,4,5-trimethoxycinnamo–	$C_{18}H_{18}O_5NCl$	363.80	169	75
II	N-4-chlorophenyl-4-butoxybenzo–	$C_{17}H_{18}O_6NCl$	319.80	164	70
III	N-phenyl-4-butoxybenzo–	$C_{17}H_{19}O_3N$	285.34	136	75
IV	N-4-chlorophenyl-4-chlorophenoxyisobutyro–	$C_{16}H_{15}O_3NCl_2$	340.21	144	50
V	N-phenyl-4-chlorophenoxyisobutyro–	$C_{16}H_{16}O_3NCl$	305.76	125	50

Table II. Analytical Data on N-Arylhydroxamic Acids

compd no.	vanadium extraction		molar absorptivity, L mol^{-1} cm^{-1}	pK_a[b]
	color[a]	λ_{max}		
I	BV	570	6.9×10^3	12.00
II	V	540	5.0×10^3	12.56
III	V	535	4.5×10^3	12.92
IV	RV	510	4.3×10^3	13.30
V	RV	505	4.2×10^3	13.78

[a] BV = bluish violet; V = violet; RV = reddish violet. [b] With dioxan–water (70%); the pK_a values are accurate to ±0.03.

Table III. Proton NMR Data of Hydroxamic Acids

compd no.	group	δ[a]	multiplicity	J
I	O-H	10.8	1	0
		3.9	2	1.8
	-CH=CH-	6.7	2	4.6
		7.4	2	10.0
II	O-H	10.7	1	0
	CH_3-	1.0	3	6.0
	-CH_2CH_2-	1.8	6	16.0
	-CH_2O-	3.9	3	12.5
		6.8	2	9.0
		7.2	2	14.0
III	O-H	10.9	1	0
	CH_3-	0.5	3	5.5
	-CH_2CH_2-	1.1	6	14.0
	-CH_2O-	3.4	3	12.0
		6.3	2	8.0
		7.0	6	36.0
IV	O-H	10.5	1	0
		1.6	1	0
		7.4	4	13.0
V	O-H	10.5	1	0
		1.6	1	0
		6.8	2	9.0
		7.4	4	17.0

[a] Chemical shift.

Table IV. Mass Spectral Data of Hydroxamic Acids[a]

m/z	rel abundance	m/z	rel abundance	m/z	rel abundance
Compd I		Compd III		142	25
367	1	285	3	141	27
365	3	270	20	134	18
347	16	269	40	127	35
238	28	212	5	111	60
221*	100	196	2	76	32
193	30	177*	100		
183	7	120	12	Compd V	
180	14	92	30	307	21
142	20	77	20	305	60
76	30	76	24	289	32
		57	35	196	11
Compd II				169*	100
321	0.5	Compd IV		136	23
319	1.5	343	7.5	127	14
304	18	341	48	111	28
303	60	339	75	105	24
246	7	323	12	104	21
218	14	196	10	92	37
177*	100	169*	100	77	26
149	15			76	17
142	12				
76	12				
57	20				

[a] An asterisk denotes base peak.

their synthesis has been carried out on the basis of the modified procedure of Agrawal and Tandon (*8*). The synthesized acids are characterized by their melting points, elemental analysis, IR, UV, NMR, and mass spectra. Preliminary studies show that the acids form a chloroform-extractable violet complex with vanadium(V) in concentrated hydrochloric acid solution. The physical properties of these acids are given in Table I.

All the acids are white crystalline compounds except N-4-chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid which is light yellow in color. They are readily soluble in chloroform, dioxan, carbon tetrachloride, alcohol, and benzene and insoluble in water. The purity of these acids is estimated from TLC and potentiometric titration to be approximately 99%.

The ultraviolet spectra of the acids in 95% ethanol show two distinct bands, one around 208–240 nm and the other between 254 and 326 nm. Compound I shows bathochromic shift in its absorption band as compared to the reported (*8*). The infrared spectra of the acids as KBr pellets show the frequencies of the hydroxyl, carbonyl, and N–O absorptions which are similar to those reported earlier (*8*). The proton NMR data have been summarized in Table III and the mass spectral data in Table IV.

The ionization constants of the synthesized hydroxamic acids are determined in aqueous dioxan media at 35 °C and are given in Table II.

Experimental Section

Materials and Apparatus. The pH measurements were made on a Systronic Digital pH meter. The ultraviolet and infrared spectra were recorded on C.Z. Jena, VSU 2-P and Perkin Elmer Model 221 spectrophotometers, respectively. The NMR spectra were recorded on a Varian T-60 spectrophotometer operating at 60 MHz for protons, in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra were recorded on AEI (UK) mass spectrophotometer Model No. MS 3074 at 70 eV.

Acid Chlorides. The acid chlorides were prepared by the action of thionyl chloride on the corresponding carboxylic acids and then vacuum distilled.

Hydroxylamines. *N*-phenyl- and *N*-4-chlorophenylhydroxylamines were freshly prepared by the reduction of nitrobenzene and 4-chloronitrobenzene, respectively, with zinc dust and ammonium chloride in aqueous alcoholic solutions (*8*).

Hydroxamic Acids. The procedure for the preparations are essentially the same as that reported earlier (*8*). The acids are synthesized by reacting the arylhydroxylamine with acid chloride at low temperature in diethyl ether containing aqueous suspensions of sodium bicarbonate.

Colorimetric Tests. The well-known color reaction which takes place in 6 M HCl between vanadium(V) and hydroxamic acid was adopted (*1-3*). The standard vanadium was extracted with a known volume of hydroxamic acid solution (in chloroform). The violet-colored layer was separated and diluted to 25 mL with chloroform, and the absorbance was measured against a reagent blank. The concentration of the hydroxamic acid was computed from a standard calibration curve.

Potentiometric Tests. A known weight of the hydroxamic acid is dissolved in 50 mL of dimethylformamide and titrated with 0.1 M sodium methoxide by using platinum and calomel electrode (saturated KCl in methanol) in the presence of nitrogen.

Ionization Constants. These were determined at 35 ± 0.1 °C in 70% dioxan water medium (Table II). The calculation method for pK_a is described elsewhere (*1*).

The ionization of hydroxamic acid (HA) in aqueous solution gives hydrogen ion and hydroxamate ion and the equilibrium constant may be

$$K_a(aq) = ([H^+][A^-])/[HA]\,Y_{H^+}Y_{A^-}/Y_{HA} \tag{i}$$

or

$$K_a = -\log\,[H^+] + \log\,[HA]/[A^-] - 2\log\,Y_\pm \tag{ii}$$

assuming the activity coefficient of un-ionized acid is unity and the empirical correction for "medium effect" as suggested by Van Uitert and Haas (*1*, *9*) as

$$-\log\,[H^+] = B + \log\,U_H{}^0 + \log\,Y_\pm \tag{iii}$$

The final form of the equation for calculating the ionization constants in dioxan-water mixture is

$$pK_a = B + \log\,U_{H^0} + \log\,[HA]/[A^-] - \log\,Y_\pm \tag{iv}$$

where B is the pH meter reading and $\log U_{H^0}$ is determined experimentally (*1*, *10*).

In the thermostated (35 ± 0.1 °C) titration vessel carrying a glass electrode, a calomel electrode, and a microburet (5 × 0.01 mL), 0.25 M of hydroxamic acid and 47.5 mL of solvent (70% v/v dioxan:water) were taken. It was titrated after being deaerated by passage of nitrogen (presaturated with solvent), and after 15 min the highest steady B value was noted after each increment.

Registry No. I, 91097-78-8; II, 95333-99-6; III, 95334-00-2; IV, 97877-85-5; V, 97877-86-6; *p*-$BuOC_6H_4C(O)Cl$, 33863-86-4; *p*-$ClC_6H_4OCH_2CH(CH_3)C(O)Cl$, 97877-84-4; *p*-$ClC_6H_4NHOH$, 823-86-9; PhNHOH, 100-65-2; 3,4,5-trimethoxycinnamoyl chloride, 10263-19-1.

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Structural Information on Uranyl Sulfate Complexes with Some Bidentate Ligands

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Coordination compounds formed by uranyl sulfate with 1,10-phenanthroline, 2,2′-bipyridyl, 2,2′-bipyridyl *N,N′*-dioxide, 2,2′-bipyridylamine, 4,4′-bipyridyl, 4,4′-bipyridyl *N,N′*-dioxide, methylpyrazine, quinoxaline, 2,3-dimethylquinoxaline, hexamethylenetetramine, 1,3-di-4-pyridylpropane, 2-methylbenzothiazole, and nicotinic acid have been prepared. The compounds isolated in the solid state have been characterized by analytical data and IR spectroscopy down to 200 cm^{-1} to elucidate the U(VI)-ligand and U(VI)-sulfate bonding modes. Tentative coordination number and stereochemical environments around U(VI) are assigned in each case.

Introduction

Coordination compounds formed by transition- and nontransition-metal(II) salts with potentially bidentate ligands with nitrogen and/or oxygen/sulfur as the donor sites have been the subject of extensive investigations. Few studies have, however, appeared on the complexes of uranyl salts with such ligands. The present communication describes the coordination compounds formed by the interaction of uranyl sulfate with 1,10-phenanthroline (phen), 2,2′-bipyridyl (2,2′-bpy), 2,2′-bipyridyl *N,N′*-dioxide (2,2′-bpyO_2), 2,2′-bipyridylamine (2,2′-bpyA), 4,4′-bipyridyl (4,4′-bpy), 4,4′-bipyridyl *N,N′*-dioxide (4,4′-bpyO_2), methylpyrazine (MP), quinoxaline (Q), 2,3-dimethylquinoxaline (DMQ), hexamethylenetetramine (HMTA), 1,3-di-4-pyridylpropane (DPP), 2-methylbenzothiazole (MBT), and nicotinic acid (NA) (Figure 1). IR spectroscopy has been used to elucidate the U(VI)-ligand and U(VI)-sulfate bonding modes and the tentative stereochemistry around U(VI) in each case.

Experimental Section

Materials. Uranyl sulfate was obtained from B.D.H. and used as such. Phen, 2,2′-bpy, 4,4′-bpy, 2,2′-bpyA, Q, MBT, and NA

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