Bis(4,4-dimethyl-2,6-dioxacyclohexyl)methane (8). A 75% yield of a white crystalline solid, mp 118°, was obtained by distilling off at 124°/1.5 mm the product obtained from the alcoholysis of 1,1,3,3-tetramethoxypropane with 2,2-dimethylpropanediol-1,3; PMR ($CDCl_3$): triplet (2 H) 5.4 τ, AB quartet (8 H) 6.5 τ, triplet (2 H) 8.0 τ, singlet (6 H) 8.8 τ, singlet (6 H) 9.3 τ, IR (neat): 1010 w, 1030 m, 1100 s, 1137 s.

Anal. Calcd. for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 63.7; H, 9.8.

3,3,9,9 - Tetramethyl - 2,4,8,10 - tetraoxaspiro[5.5]undecane (9). A 70% yield, mp 113–115°, was obtained by sublimation at 85°/760 mm of the solid product obtained by the reaction of pentaerythritol with 2,2-dimethoxypropane; PMR ($CDCl_3$): singlet (8 H) 6.3 τ, singlet (12 H) 8.6 τ; IR (Nujol): 1023 s, 1045 s, 1068 s, 1088 s, 1153 s, 1170 s.

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.9; H, 9.1.

GENERAL PROCEDURE

Reactants were heated together in molar ratio quantities using 0.2 mole for the smallest amount with five drops of concentrated hydrochloric acid as a catalyst and no solvent. The reaction temperature was controlled to remove only the alcoholysis product. If the reactants were not miscible on heating, a magnetic stirrer was used. The reaction was continued until 85–100% of the theoretical amount of alcoholysis product was distilled off. In reactions involving 2,2-dimethoxypropane, a three-fold excess was used to compensate for its loss in the reaction because it formed an azeotrope with methanol.

Spectra. The PMR spectra were obtained on a Varian HR-60-IL spectrometer (frequency sweep mode) at room temperature. The samples were run neat or as solids dissolved in $CDCl_3$ at 5 to 10% with TMS acting as internal lock. Chemical shifts are reported in τ (TMS = 10.0).

The infrared measurements were made on a Perkin-Elmer 521 reporting only the bands between 1000 and 1200 cm^{-1}.

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Preparation and Properties of *N*-Arylhydroxamic Acids

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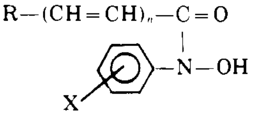
The preparation and properties of eight new *N*-arylhydroxamic acids, derived from *p*-methoxy- and 3,4-methylenedioxycinnamic acids, are described. These acids were synthesized for use as possible analytical reagents for metal ions.

N-phenylcinnamohydroxamic acid [PCHA] (*8*) is the most sensitive spectrophotometric reagent for the determination of vanadium(V) from the family of *N*-arylhydroxamic acids. Our interest in developing more sensitive spectrophotometric reagents from this family led to the synthesis of several new compounds (*2*) of the general formula I (where *n* = 0, 1, 2; X = Cl, CH_3 at different positions; R = alkyl, aryl, 2-furyl, etc.)



$$R-(CH=CH)_n-C(=O)-N(OH)-C_6H_4X$$

I

In general, with the increase in π-π conjugation, the sensitivities of the corresponding reagents for vanadium(V) reaction also increase. Thus, the molar absorptivities of the bands used in the determinations of vanadium(V) with *N*-phenylbenzohydroxamic acid (*n* = 0), PCHA (*n* = 1), and *N*-phenyl-3-styrylacrylohydroxamic acid (*n* = 2) are 4650, 6300, and 7500 (*2, 7, 8*), respectively.

In an attempt to observe the effect of *n*-π conjugation on the sensitivity of the vanadium(V) reaction, we examined several *N*-arylhydroxamic acids derived from *p*-methoxycinnamic acid and 3,4-methylenedioxycinnamic acid. The preparation and properties of eight such hydroxamic acids are presented here. The relevant data are summarized in Table I.

Preliminary investigations show that these new reagents equal *N*-phenyl-3-styrylacrylohydroxamic acid in the sensitivity of vanadium(V) color reactions (ϵ at λ_{max} being ~7500 with all reagents). Thus, the methoxy group at the para position or methylenedioxy at the 3,4 positions is equivalent to one —CH=CH— group. In future, it will be worthwhile to prepare new hydroxamic acids by further simultaneous extension of *n*-π and π-π conjugation.

EXPERIMENTAL

Materials and Apparatus. Infrared spectra were recorded as mulls in Nujol with a Perkin-Elmer Infracord, Model 137. For comparison, the spectra of compounds 1, 5, and 6 were recorded with a Perkin-Elmer Model 472 spectro-

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Table I. Properties of Hydroxamic Acids[a]

Compound	Cinnamohydroxamic acid	Formula	Mol wt	Mp, ° C	Yield, %[b]	Uv spectra: λ_{max}, mμ	Uv spectra: $10^{-3}\epsilon$	ν(C=O), cm^{-1} (in Nujol)
1	*N*-Phenyl-*p*-methoxy-	$C_{16}H_{15}NO_3$	269.30	156	70	230 322	18.5 33.3	1635
2	*N*-*m*-Tolyl-*p*-methoxy-	$C_{17}H_{17}NO_3$	283.33	132	56	230 322	15.5 29.5	1625
3	*N*-*p*-Tolyl-*p*-methoxy-	$C_{17}H_{17}NO_3$	283.33	170	70	230 322	15.7 30.7	1640
4	*N*-*p*-Chlorophenyl-*p*-methoxy	$C_{16}H_{14}NO_3Cl$	303.75	184	60	230 322	13.0 31.7	1650
5	*N*-Phenyl-3,4-methylenedioxy-	$C_{16}H_{13}NO_4$	283.29	155	65	237 336	13.9 25.4	1635
6	*N*-*m*-Tolyl-3,4-methylenedioxy-	$C_{17}H_{15}NO_4$	297.32	141	56	237 336	12.5 24.2	1635
7	*N*-*m*-Tolyl-3,4-methylenedioxy-	$C_{17}H_{15}NO_4$	297.32	172	60	237 336	12.9 21.9	1650
8	*N*-*p*-Chlorophenyl-3,4-methylenedioxy-	$C_{16}H_{12}NO_4Cl$	317.74	178	45	238 338	11.3 22.3	1640

[a] Elemental analyses for C, H, and N submitted for review and in agreement with theoretical values. [b] Average of at least three trials and calculated for once-crystallized product.

photometer equipped with sodium chloride optics and calibrated by standard methods.

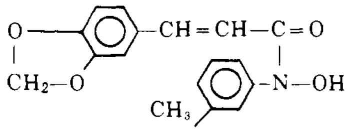
Ultraviolet spectra were studied in spectroscopic grade 95% ethanol. All other materials and apparatus were the same as described earlier (*3*).

Preparation. *p*-Methoxycinnamic acid (*4, 5*) and 3,4-methylenedioxycinnamic acid (*4, 5*) were prepared according to reported methods. The acid chlorides were prepared by the action of thionyl chloride on benzene solutions of these acids. As these acid chlorides are solids at room temperature, these were purified by crystallization from anhydrous benzene.

N-Arylhydroxylamines were freshly prepared, as described earlier (*1, 6*).

The hydroxamic acids could be readily prepared by following basically the modified procedure of Priyadarshini and Tandon (*9*). A typical preparation is described below.

A mixture of freshly crystallized *N*-*m*-tolylhydroxylamine (2.46 grams, 0.2 mole), sodium bicarbonate (5 grams, 0.2 mole), diethyl ether (100 to 125 ml), and water (8 to 10 ml) was externally cooled in a beaker to 0° C or lower. The reaction mixture was mechanically stirred and a solution of 3,4-methylenedioxycinnamoyl chloride (4.21 grams, 0.2 mole) in diethyl ether (100 ml) was added dropwise during about an hour. The hydroxamic acid separated as a yellow granular mass and the dissolved portion left in the ether medium was recovered by precipitation with petroleum ether. It was triturated with a saturated solution of sodium bicarbonate in a mortar to remove acidic impurities, filtered under suction, and washed with cold water. On crystallization from mixtures of benzene and petroleum ether, pale light yellow needles of *N*-*m*-tolyl-3,4-methylenedioxycinnamohydroxamic acid, were obtained. The yield of once-crystallized product was 3.33 grams, 56% of the theoretical.



Color Reaction. All the eight hydroxamic acids react with vanadium(V) in 2 to 10*M* hydrochloric acid solutions and yield stable bluish violet extracts with chloroform. The absorption spectra of these colored extracts were determined in the visible region, using chloroform as blank. The molar absorptivity of each extract was determined at its wavelength of maximum absorption in terms of its vanadium(V) content.

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