The treatment of 1a–c, 3a–c, 5, and 6 with an excess of potassium amide in liquid ammonia failed to give more than a trace amount of cyclic product arising from a benzyne intermediate. Usually polymeric material or starting material was isolated; however, trace amounts of products were obtained from the cyclization of chloroamide 1a (mp 124–129°, $C_{15}H_{13}NO$) and chloroester 1c mp 146–147°, $C_{32}H_{27}O_3$).

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Acetals and Ketals

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Thirteen open-chain simple cyclic and spirocyclic acetals and ketals were studied. The synthesis of all the cyclic compounds was accomplished by an alcoholysis reaction. The infrared and proton magnetic resonance spectra were measured and correlated.

A number of cyclic acetals and ketals were synthesized and their proton magnetic resonance (PMR) and infrared spectra were compared with some purchased open-chain acetals and ketals. The cyclic compounds included one spirocyclic case.

All the compounds synthesized were prepared by an alcoholysis reaction. This proved to be a simple and expedient method for obtaining the cyclic compounds and it made no difference whether an ethoxy or methoxy acetal or ketal were alcoholyzed.

The synthesis of spirocyclic orthocarbonates by the alcoholysis of methyl or ethyl orthocarbonate was not possible because all attempts to prepare methyl and ethyl orthocarbonates (*4, 6*) by the reaction of chloropicrin and alkoxides and with several variants proved futile and resulted in a violent explosion when an attempt was made to distill the product. The Ponzio (*5*) synthesis using carbon tetrabromide was not attempted since only "a very small quantity" was reported to form.

Attempts to substitute boron trifluoride etherate, aluminum chloride, or benzenesulfonic acid for hydrochloric acid as a catalyst resulted in poorer yields. The compounds studied were 1-13 (Figure 1).

The primary use of the infrared determinations was to establish the absence of any carbonyl or hydroxyl absorption in the acetal or ketal studied. The correlations reported earlier (*2*) for the C—O—C—O—C bands in acetals and ketals were in the range of 1000-1200 cm^{-1} and are reported for compounds 1-13. The presence of a minimum of two bands between 1150 and 1080 characteristic of the C—O—C antisymmetric stretch in cyclic compounds free of substantial ring strain and open chain compounds suggested by Tchamler (*7*) appeared in all of the compounds. The predicted band between 1050 and 1110 cm^{-1} occurred in all compounds. The compounds in which the C—O—C—O—C group was in a ring (1-7) showed at least a single band in this region which may or may not be a duplicate of the band between 1080 and 1150 cm^{-1}. In all of the open-chain compounds (11-13) except 10, three bands were present in a rather precise location (±2 cm^{-1}): 1058, 1078,

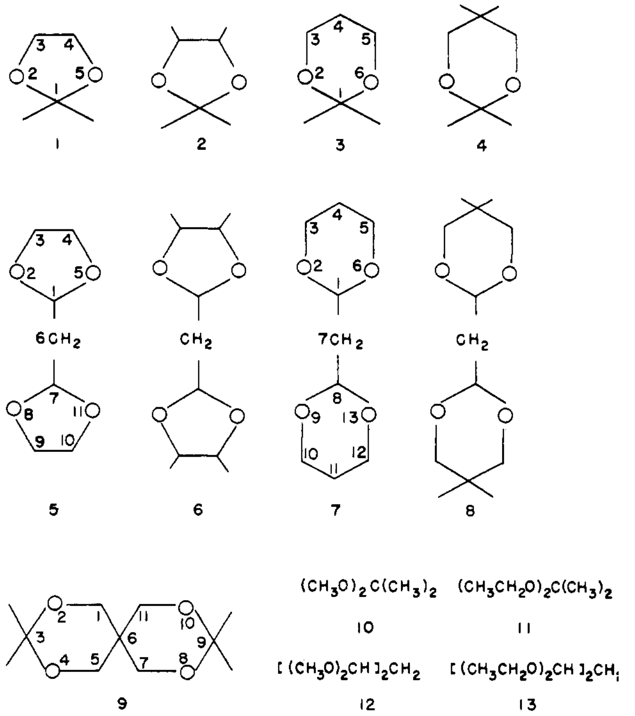

Figure 1. Acetal and ketal structures

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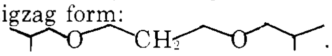
and 1098 cm^{-1}. In compound 10, strong bands were observed at 1056 and 1082 only.

The PMR spectra were relatively straightforward but some generalizations are worth noting. The methyl groups attached to a dioxygenated carbon absorb at 8.6-8.8 τ (1-4, 9-11). The methyl groups attached to a nonoxygenated carbon absorb at 8.9 τ (2, 6, 11, 13). The spectrum of compound 2 (Figure 2), since it consists of a mixture of epimers, is a complex multiplet of lines (*1*) with an intensity equivalent to 12 protons. Two sets of doublets make up the multiplet, one slanting downfield and one upfield. The downfield pointing doublet assigned to the vicinal methyl protons at 8.9 τ agrees with compound 6 and the chemical shift for the gem methyl groups at 8.7 τ agrees with those of compounds 1, 3, 4, 9, 10, and 11. The four equivalent methylene hydrogens of compound 1, free of geometric isomers, appear as a singlet at 6.1 τ while the methine hydrogens in 2 present in both cis and trans forms appear as a complex multiplet at 5.9 τ. Methyl groups bonded to a nonoxygenated carbon appear at still higher field, 9.1 τ for compound 4 and 9.3 τ for the equatorial methyl in compound 8. The axial methyl being closer to the oxygen atom appears downfield at 8.8 τ. This difference is evident in the conformation in which both rings are in the chair form which may be viewed so that only one edge of both rings is visible in the planar zigzag form: 

. In this conformation, unrestricted rotation is possible around both bonds attached to the methylene shown. If either or both of the chairs are flipped, this is no longer true. Evidence for the presence of the indicated conformation is the appearance of an AB quarter for the ring methylenes each bearing an axial and equatorial hydrogen. The methoxyl appears at 6.9 and 6.8 τ for 10 and 12, respectively. The methylene attached to oxygen in the acyclic case appeared at 6.6 (11) and 6.5 τ (13) while their cyclic analogs varied between 6.0 and 6.6 τ. The methylene group separating the rings of compounds 5 to 8 varied slightly (8.0-8.2 τ) and gave no indication of the size of the rings they separated. However, the adjacent methine hydrogens do indicate ring size (*3*). The methine shift for the dioxolanes, 5 and 6, occurs at 5.1 and 5.0 τ, and for the two dioxanes, 7 and 8, the corresponding signals occur at 5.3 and 5.4 τ, respectively.

EXPERIMENTAL

The four liquids, 10-13, were commercially obtained and their neat PMR and infrared spectra, respectively, are:

10: singlet (6 H) 6.9 τ, singlet (6 H) 8.8 τ; 1056 s, 1082 s, 1145 m, 1183 s.

11: quartet (4 H) 6.6 τ, singlet (6 H) 8.8 τ, triplet (6 H) 8.9 τ; 1058 s, 1077 s, 1099 m, 1112 m, 1119 m (sh), 1170 s.

12: triplet (2 H) 5.6 τ, singlet (12 H) 6.8 τ, triplet (2 H) 8.2 τ; 1000 w, 1058 s, 1078 s, 1098 s, 1118 s, 1122 s (sh), 1183 m, 1195 m.

13: Triplet (2 H) 5.5 τ, multiplet (8 H) 6.5 τ, triplet (2 H) 8.2 τ, triplet (12 H) 8.9 τ; 1058 s, 1062 s, 1112 s, 1114 s.

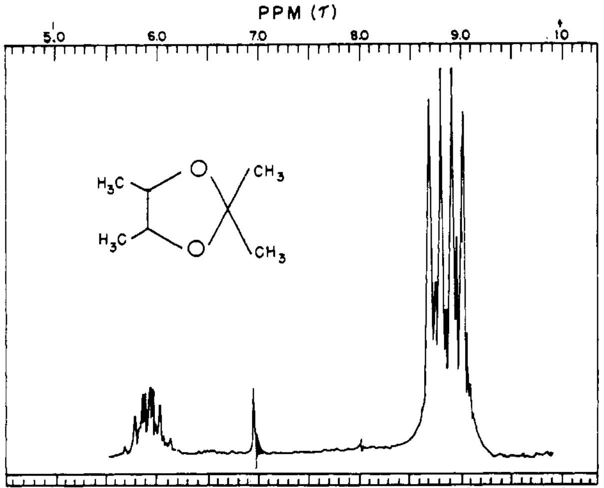


Figure 2. PMR of structure 2

1,1-Dimethyl-2,5-dioxacyclopentane (1). The product obtained from the alcoholysis of 2,2-dimethoxypropane with ethylene glycol was distilled at 92°/760 mm as a colorless liquid in 85% yield; PMR (neat): singlet (4 H) 6.1 τ, singlet (6 H) 8.7 τ; infrared (IR) (vapor): 1069 s, 1079 s, 1151 s, 1162 s.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.5; H, 9.9.

1,1,3,4-Tetramethyl-2,5-dioxacyclopentane (2). An 80% yield of clear liquid was obtained by the distillation at 118-119°/760 mm of the product obtained by the alcoholysis of 2,2-dimethoxypropane with 2,3-butanediol; PMR (neat): multiplet (2 H) 5.9 τ, multiplet (6 H) 8.7 τ, multiplet (6 H) 8.9 τ; IR (neat): 1008 s, 1033 s, 1086 s, 1104 s, 1143 m, 1188 s.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.2; H, 11.0.

1,1-Dimethyl-2,6-dioxacyclohexane (3). A yield of 70% of clear liquid was obtained from the distillation at 125-127°/760 mm of the product obtained by the alcoholysis of 2,2-dimethoxypropane with 1,3-propanediol; PMR (neat): triplet (4 H) 6.2 τ, quintet (2 H) 8.5 τ, singlet (6 H) 8.7 τ; IR (neat): 1062 s, 1100 s, 1145 s, 1155 s, 1199 s.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.42. Found: C, 62.2; H, 10.5.

1,1,4,4-Tetramethyl-2,6-dioxacyclohexane (4). A yield of 85% of clear liquid was obtained by distillation at 112°/760 mm of the product obtained by the alcoholysis of 2,2-dimethoxypropane with 2,2-dimethylpropanediol-1,3; PMR (neat): singlet (4 H) 6.6 τ, singlet (6 H) 8.7 τ, singlet (6 H) 9.1 τ; IR (vapor) 1021 s, 1042 s, 1053 w, 1090 s, 1150 s, 1175 s.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.8; H, 11.2.

Bis(2,5-dioxacyclopentyl)methane (5). An 81% yield of clear liquid was obtained by distillation at 91°/2.0 mm of the product of the alcoholysis of 1,1,3,3-tetramethoxypropane with ethylene glycol; PMR (neat): triplet (2 H) 5.1 τ, multiplet (8 H) 6.1 τ, triplet (2 H) 8.1 τ; IR (neat): 1028 s, 1083 s, 1126 s, 1138 s.

Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.6; H, 7.6.

Bis(3,4-dimethyl-2,5-dioxacyclopentyl)methane (6). A clear liquid in 80% yield was obtained by the distillation at 85°/0.6 mm of the alcoholysis product of 1,1,3,3-tetraethoxypropane by 2,3-butanediol; PMR (neat): multiplet (2 H) 5.0 τ, multiplet (4 H) 6.0 τ, quartet (2 H) 8.2 τ, doublet (12 H) 8.9 τ; IR (neat): 1034 s, 1057 m, 1087 s, 1120 s, 1170 s.

Anal. Calcd. for $C_{11}H_{20}O$: C, 61.09; H, 9.32. Found: C, 60.8; H, 9.2.

Bis(2,6-dioxyacyclohexyl)methane (7). A white crystalline solid, mp 115°, was obtained by the distillation of a clear liquid at 115°/1.6 mm in 78% yield from the product of the alcoholysis of 1,1,3,3-tetraethoxypropane with 1,3-propanediol; PMR ($CDCl_3$): triplet (2 H) 5.3 τ, multiplet (8 H) 6.0τ, triplet (2 H) 8.1 τ, multiplet (4 H) 8.7 υ; IR (Nujol): 1030 s, 1052 s, 1097 s, 1138 s.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.4; H, 8.7.

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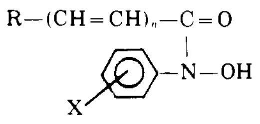
The preparation and properties of eight new N-arylhydroxamic acids, derived from p-methoxy- and 3,4-methylenedioxycinnamic acids, are described. These acids were synthesized for use as possible analytical reagents for metal ions.

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.)



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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