Experimental Section

All melting points were determined on a Thomas Hoover "Uni-Melt" capillary melting apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 727B grating spectrophotometer. Nuclear magnetic resonance spectra were recorded at 60 MHz on a Varian EM 360 A spectrometer, with tetramethylsilane used as an internal standard. Low resolution mass spectra were obtained on a Finnigan 4023 GC/MS/DS instrument operated in the electron impact mode (70 eV). Optical rotations were measured at ambient temperature on a Rudolph Model 62 polarimeter, using a 1-dm tube. Analytical TLC was performed on Brinkmann silica gel 60-F254 precoated (0.25 mm) glass plates and preparative layer chromatography on Brinkmann 20 × 20 cm glass plates coated with the same adsorbent (2 mm). Column chromatography was performed on columns packed with J. T. Baker ("Baker Analyzed") silica gel powder of 60–200-mesh particle size. Microanalyses were performed by either Galbraith Laboratories Inc. or Midwest Microlabs Inc.

4′-Bromo-rot-2′-enonic Acid (7). The method of Unai and Yamamoto was employed.[2] The white crystalline product was filtered, washed with a small amount of methanol, and dried in vacuo to give 6.1 g (51%) of **7**, mp 151–152 °C (lit.[2] mp 152–154 °C), based on 10.0 g (25.4 mmol) of rotenone and 6.4 g (25.5 mmol) of boron tribromide: NMR ($CDCl_3$) δ 7.73 (d, 1, J = 9 Hz), 6.78 (s, 1), 6.51 (d, 1, J = 9 Hz), 6.44 (s, 1), 5.60 (br t, 1, J = 7 Hz), 4.90 (m, 1), 4.60 (dd, 1, J = 12, 3.5 Hz), 4.14 (d, 1, J = 12 Hz, 3.89 (s, 2), 3.86 (d, 1, J = 3.5 Hz), 3.80 (s, 3), 3.74 (s, 3), 3.37 (d, 2, J = 7 Hz), 1.91 (s, 3).

4′-Phenylthio-rot-2′-enonic Acid (6). Thiophenol (0.3 g, 2.7 mmol) was added in one portion to a stirred suspension of 99% NaH (65 mg, 2.7 mmol) in 5 mL of anhydrous THF. The resulting mixture was stirred at room temperature under nitrogen until H_2 evolution ceased (1 h). A solution of **7** (1.2 g, 2.5 mmol) in 4 mL of THF was then added and the mixture stirred at room temperature for 12 h after which it was heated to reflux and refluxed for 30 min. After dilution with water (20 mL), the organic layer was separated and the aqueous layer further extracted with ether. The combined organic extracts were then washed with saturated brine, dried ($MgSO_4$), and evaporated. The residue (1.2 g) was purified by chromatography on silica gel (60 g) utilizing CH_2Cl_2–acetone mixtures (to 9:1) as eluent. Compound **6** was obtained as a yellow foam: 0.9 g (71%); $[\alpha]^{25}_D$ −7.3° (c 2.2, $CHCl_3$); NMR ($CDCl_3$) δ 7.80 (d, 1, J = 9 Hz), 6.95–7.40 (m, 6), 6.85 (s, 1), 6.58 (d, 1, J = 9 Hz), 6.50 (s, 1), 5.30 (br t, 1, J = 7 Hz), 4.68 (dd, 1, J = 12, 3.5 Hz), 4.78 (m, 1), 4.13 (d, 1, J = 12 Hz), 3.88 (d, 1, J = 3.5 Hz), 3.81 (s, 3), 3.75 (s, 3), 3.20–3.53 (m, 4), 1.93 (br s, 3); mass spectrum m/z (relative intensity) 504 (2), 394 (2), 203 (16), 192 (100). Anal. Calcd for $C_{29}H_{28}O_6S$: C, 69.04; H, 5.59. Found: C, 68.80; H, 5.32.

(−)-Rot-2′-enonic Acid (8). To a solution of **7** (1.9 g, 4.0 mmol) in 20 mL of HMPA was added 1.0 g (16 mmol) of sodium cyanoborohydride. The resulting solution was heated to 70 °C under nitrogen, maintained at that temperature for 2.5 h and then cooled to room temperature, and diluted with water (200 mL). The crude product which separated was extracted with ether–hexane (3:1). The combined extracts were then washed with saturated brine, dried ($MgSO_4$), and evaporated to dryness. Purification of the residue (1.4 g) by chromatography over 70 g of silica gel with CH_2Cl_2–acetone (9:1) afforded 1.1 g (70%) of pure **8**. An analytical sample was obtained by recrystallization from methanol: mp 207–208 °C (lit.[3] 206–208 °C); $[\alpha]^{27}_D$ +27.9° (c 2.0, $CHCl_3$); NMR ($CDCl_3$) δ 7.84 (d, 1, J = 9 Hz), 6.88 (s, 1), 6.75 (br s, 1), 6.60 (d, 1, J = 9 Hz), 6.54 (s, 1), 5.28 (br t, 1, J = 7 Hz), 4.99 (t, 1, J = 3.5 Hz), 4.70 (dd, 1, J = 12, 3.5 Hz), 4.20 (d, 1, J = 12 Hz), 3.88 (d, 1, J = 3.5 Hz), 3.83 (s, 3), 3.78 (s, 3), 3.40 (d, 2, J = 7 Hz), 1.80 (s, 3), 1.70 (s, 3). Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.80; H, 6.09.

(−)-Dihydrodeguelin (9). A solution of **8** (1.3 g, 3.2 mmol) and 0.2 g of tosic acid in benzene (60 mL) was refluxed with stirring under nitrogen for 1 h. The solution was then cooled to room temperature, diluted with more benzene (25 mL), washed successively with water, 5% $NaHCO_3$, and brine, and dried ($MgSO_4$). Concentration left 1.3 g of crude **9**. Recrystallization from methanol afforded analytically pure material: mp 155–156 °C (lit.[4] mp 155–156 °C); $[\alpha]^{27}_D$ −98.1° (c 4.1, benzene); NMR ($CDCl_3$) δ 7.80 (d, 1, J = 9 Hz), 6.90 (s, 1), 6.50 (d, 2, J = 9 Hz), 6.50 (s, 1), 4.95 (t, 1, J = 3.5 Hz), 4.70 (dd, 1, J = 12, 3.5 Hz), 4.20 (d, 1, J = 12 Hz), 3.87 (d, 1, J = 3.5 Hz), 3.84 (s, 3), 3.80 (s, 3), 2.69 (t, 2, J = 7 Hz), 1.77 (t, 2, J = 7 Hz), 1.34 (s, 3), 1.28 (s, 3). Anal. Calcd for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 69.75; H, 6.48.

(−)-Deguelin (1). To a stirred, nitrogen-blanketed solution of **8** (1.98 g, 5 mmol) in CH_2Cl_2 (60 mL), cooled to −30 °C in a dry ice–acetone bath, 1.05 g (5.5 mmol) of phenylselenyl chloride was added in one portion. The resulting solution was allowed to warm to room temperature during 2 h and stirred an additional 1 h. Evaporation of the solvent at reduced pressure left 2.9 g of a diastereomeric mixture (1:1) of phenylselenoethers **11**, contaminated with a small amount of PhSeCl: NMR ($CDCl_3$) δ 7.82 (d, 1, J = 9 Hz), 7.20–7.72 (m, 5), 6.87 (s, 1), 6.40–6.67 (m, 2), 4.94 (m, 1), 4.68 (dd, 1, J = 12, 3.5 Hz), 4.18 (d, 1, J = 12 Hz), 3.88 (d, 1, J = 3.5 Hz), 3.85 (s, 3), 3.80 (s, 3), 3.30–3.60 and 2.80–3.20 (m, total 3 H), 1.53, 1.47, 1.43, and 1.33 (s, total 6 H).

The above product mixture was dissolved in THF (60 mL), cooled to 0 °C and treated with 1.0 mL (~9 mmol) of 30% hydrogen peroxide solution. The resulting solution was stirred for 1 h at 0–5 °C and then at room temperature for 18 h, diluted with ether (60 mL), and washed successively with two 20-mL portions of 5% $NaHCO_3$ and saturated brine. After drying ($MgSO_4$), evaporation of the solvent left 2.1 g of oily residue which was chromatographed over 100 g of silica gel with CH_2Cl_2–acetone mixtures (to 95:5). Pure (−)-deguelin was obtained as a bright yellow oil: 1.6 g (81%); $[\alpha]^{27}_D$ −97.2° (c 0.2, benzene); NMR ($CDCl_3$) δ 7.83 (d, 1, J = 9 Hz), 6.87 (s, 1), 6.74 (d, 1, J = 10 Hz), 6.54 (s, 1), 6.54 (d, 1, J = 9 Hz), 5.61 (d, 1, J = 10 Hz), 4.97 (m, 1), 4.71 (dd, 1, J = 12, 3.5 Hz), 4.21 (d, 1, J = 12 Hz), 3.88 (d, 1, J = 3.5 Hz), 3.86 (s, 3), 3.82 (s, 3), 1.47 (s, 3), 1.40 (s, 3). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.04; H, 5.62. Found: C, 69.70; H, 5.32.

Acknowledgments. The author thanks his colleagues Dr. Robert J. Cregge and Dr. Norton P. Peet for helpful discussions and Mr. Robert J. Barbuch for the mass spectral and optical data.

Registry No. **1**, 522-17-8; **6**, 70145-43-6; **7**, 70191-70-7; **8**, 70191-71-8; **9**, 70145-44-7; **11** isomer 1, 70145-45-8; **11** isomer 2, 70191-72-9; thiophenol, 108-98-5; phenylselenyl chloride, 5707-04-0.

(9) D. G. Carlson, D. Weisleder, and W. H. Tallent, *Tetrahedron*, **29**, 2731 (1973).

Structural Studies of Organosulfur Compounds. 4. Stereochemistry and Conformational Properties of α- and β-2-Methoxy-*trans*-hexahydrobenzoxathiane 4,4-Dioxides

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In previous report,[1] we described the stereochemistry and conformational properties of α- and β-2-methoxy-*trans*-hexahydrobenzoxathiane (**1α, 1β**) and our results indicated that the 2-methoxy group prefers the equatorial or α conformation by as much as 2.07 kJ/mol (0.49 kcal/mol) in cyclohexane solvent. We attributed this preference to repulsive steric and Coulombic interactions between the methoxy oxygen and the ring sulfur and the synaxial hydrogen at C9. The Coulombic interaction

(1) S. A. Evans, Jr., B. Goldsmith, R. L. Merrill, Jr., and R. E. Williams, *J. Org. Chem.*, **42**, 438 (1977).

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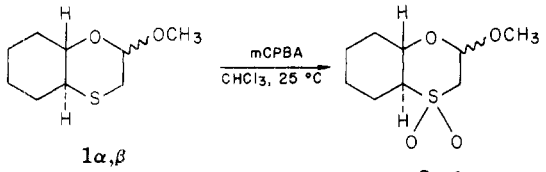
between sulfur and oxygen has been previously referred to as the "hockey sticks effect".[2] We have now completed our studies on the diastereoisomeric 2-methoxy-*trans*-hexahydrobenzoxathiane 4,4-dioxides (**2α**, **2β**) and in this report, we describe NMR and solvent-dependent conformational properties of sulfones **2α** and **2β**.

Results and Discussion

Diastereoisomers **2α** and **2β** were synthesized by direct oxidation of an ca. 1:1 mixture of **1α** and **1β**[1,3] with 2 equiv of *m*-chloroperoxybenzoic acid (mCPBA) in chloroform solution. The mixture of **2α** and **2β** was separated by column chromatography (see Experimental Section) and the stereochemistry of each was determined by ^1H and ^{13}C NMR spectroscopy.

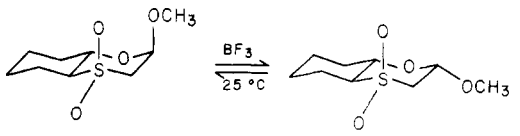


1α,β **2α,β**

The crystalline substance with melting range 130.0–130.5 °C exhibited a quartet pattern for the lowfield C2 hydrogen (δ 4.70) which is characteristic of unequal coupling to C2-H from the vicinal C3 hydrogens ($^3J_{aa}$ = 8.20 Hz and $^3J_{ae}$ = 2.48 Hz). From these data it is clear that the C2 methoxy group occupies the equatorial or α conformation. It is noteworthy that $^3J_{2a,3a}$ and $^3J_{2a,3e}$ in both **1α** (for **1α**, $^3J_{2a,3a}$ = 8.63 Hz and $^3J_{2a,3e}$ = 2.37 Hz) and **2α** are only slightly different. This result was somewhat unexpected since we had anticipated that a change in the coupling constants might indicate ring flattening resulting from the 1,3-synaxial steric interaction between the sulfonyl oxygen atom and the C2,C9 hydrogens.[4] The higher melting isomer, **2β** (mp 155–157 °C), exhibited what appeared as a "triplet" pattern for the C2 hydrogen (δ 5.01) suggestive of nearly equal vicinal coupling contributions ($^3J_{ee}$ = $^3J_{ea}$ = 2.64 Hz in deuteriochloroform solvent) from the C3 methylene hydrogens; thus, the C2 methoxy group in **2β** has the axial conformation. The C3 methylene hydrogens are equivalent (δ 3.28) and appear as a doublet while the vicinal couplings suggest a substituent orientation similar to that reported for **1α** ($^3J_{ee}$ = 1.93 Hz and $^3J_{ea}$ = 2.45 Hz).

In addition to being useful in corroborating the stereochemical assignments of the isomeric sulfones, a number of interesting features evolved when comparisons of ^{13}C NMR shifts were made between compounds **1α** and **2α** and **1β** and **2β**. For example, introduction of an axial sulfonyl oxygen atom (e.g., **1β** → **2β**) results in an upfield shift for C9 (Δδ = 3.56) presumably arising from the γ gauche interaction while C2 is shifted to low field (Δδ = 2.09) apparently resulting from the 1,3-synaxial array of electronegative atoms.[5] Comparisons involving **1α** → **2α** show that while C2 is shielded by ca. 3 ppm, C9 is shielded by a remarkable 8.84 ppm. To our knowledge this is one of the largest γ effects between sulfonyl oxygen and carbon in ananomeric six-membered rings. Exactly why the C2 carbon when bonded to two oxygens is shifted upfield to such an extent is not precisely known, but it is striking, particularly in light of the C2,C9 shifts in **3** and **4**. Oxidation of sulfur (S → SO_2) results in the expected downfield shift of the adjacent carbons (C3, C10) by 20–25 ppm while the carbocyclic ring carbons (except for C5) and the methoxy carbons are practically invariant.

Table I. Solvent-Dependent Conformational Free Energies of the 2-Methoxy Group in 2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxide[a]



2β **2α**

solvent (ε)	K_{eq}	$-\Delta G^\circ_{25,0}$,[b] kJ/mol
C_6H_{12} (2.02)	11.25 ± 0.21	6.10 ± 0.31 (2.05 ± 0.17)
C_6H_6 (2.28)	3.82 ± 0.24	3.38 ± 0.14 (1.63 ± 0.25)
CCl_4 (2.24)	6.48 ± 0.16	4.71 ± 0.15 (1.63 ± 0.13)

[a] See Experimental Section for details of acid-catalyzed equilibration and methods of analytical analyses. [b] The entries in parentheses are $-\Delta G^\circ_{30,0}$ values for axial ⇄ equatorial equilibria for α- and β-2-methoxy-*trans*-hexahydrobenzoxathianes in the solvents specified. These values have been reported previously and are included here for purposes of comparison.[1]

Diastereoisomers **2α** and **2β** were equilibrated from both sides as pure samples at 25 °C with boron trifluoride etherate (BF_3·OEt_2) as catalyst in three solvents. Free energies calculated from the equilibrium constants gave the data in Table I. The free energy data determined in the appropriate solvents for the equilibrium between **1α** and **1β** have been included for comparison. It is clear that the addition of an axial sulfonyl oxygen when compared to the case for sulfur lone pair electrons causes the preference for the equatorial conformation by methoxy to increase by nearly 4 kJ/mol (1 kcal/mol). The destabilization of the axial conformation for the C2 methoxy group is probably both Coulombic and steric in origin. Drieding molecular models suggest that the synaxial sulfonyl oxygen atom–electrostatic interactions between the polarized bonds (or atoms) are maximized in this conformation. The solvent dependence of the ΔG°'s do, in fact, imply that dipole–dipole interactions are of considerable importance. The solvent benzene, which possesses a higher "effective" dielectric constant than that shown, appears to stabilize **2β** relative to **2α** to a greater extent than cyclohexane or carbon tetrachloride but is not as influential in shifting the equilibrium **1β** ⇌ **1α** toward **1β**. The polar characteristics of benzene are thought to arise from the orientations of the polarized aromatic solvent and the solute dipole(s).[6] Here, the effect of benzene on the equilibria for these two systems reflects the ability of this solvent to minimize more effectively the larger electrostatic interactions in **2β** as compared to those in **1β**.

Experimental Section

Melting points were obtained in a Mel-Temp melting point apparatus with an open capillary tube and are uncorrected.

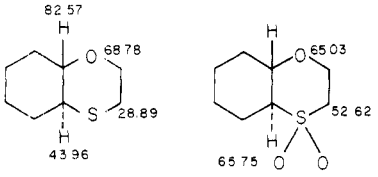
(2) N. S. Zefirov, V. S. Balgoveshchensky, I. V. Kazimirchik, and N. S. Surova, *Tetrahedron*, **27**, 3111 (1971).

(3) D. M. Frieze, P. F. Hughes, R. L. Merrill, Jr., and S. A. Evans, Jr., *J. Org. Chem.*, **42**, 2206 (1977).

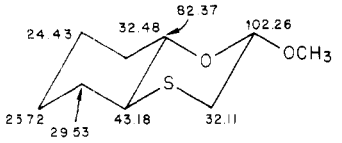
(4) Some indication of ring distoration was expected based on previous angle deformation studies involving *trans*-hexahydrobenzoxathiane (**3**) and *trans*-hexahydrobenzoxathiane *S,S*-dioxide (**4**).[3] Here, we noted that the O1–C2–C3–S torsional angle in **4** is reduced by 5–6° over the O1–C2–C3–S angle in **3** as estimated by a coupling constant analysis. The similarity in couplings in **1α** and **2α** may be due to the fact that energy minimization through ring flattening in **2α** requires a diminution in the torsional angle between the axial C3 hydrogen and the C2 equatorial methoxyl group. This could result in an increase in the eclipsing interaction which may be severe enough to effectively neutralize any ring distortion due to flattening.

(5) S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magn. Reson.*, **10**, 227 (1973).

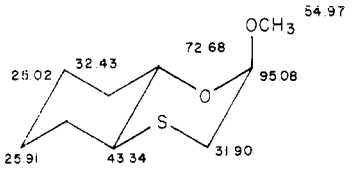
(6) For an excellent discussion, see M. H. Abraham, *J. Chem. Soc. B*, 299 (1971).



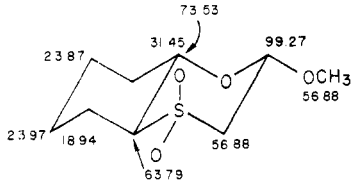
3 4



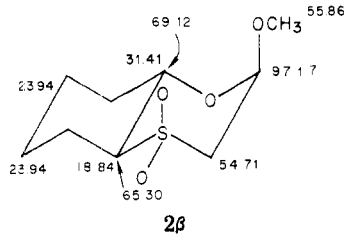
1α



1β



2α



2β

Microanalyses were performed by Galbraith Laboratories, Inc., and Integral Microanalytical Laboratories, Inc.

^{1}H NMR spectra were recorded on a JEOL Model C-60HL and a Varian Model XL-100-12 NMR spectrometer. The proton chemical shifts of samples as 5–8% (w/w) deuteriochloroform ($CDCl_3$) solutions are presented in parts per million (δ) downfield from internal tetramethylsilane (Me_4Si), and these values are considered accurate to ±0.01 ppm unless otherwise indicated. The coupling constants are given in hertz and are accurate to ±0.1 Hz unless otherwise specified. ^{1}H NMR coupling patterns are designated as s = singlet, d = doublet, m = multiplet, t = triplet, and dd = doublet of doublets. ^{13}C NMR FT spectra were recorded on a Varian Model XL-100-12 NMR spectrometer controlled by a 620/f computer. All FT spectra were obtained at ambient temperature (ca. 30 °C) and Fourier transforms were based upon 8K data points with off-resonance and noise decoupling.

Gas–liquid chromatography (GLC) analyses were performed on Hewlett-Packard Model 5754 research gas chromatographs. The diastereoisomers of 2-methoxy-*trans*-hexahydro-1,4-benzoxathiane, 1α and 1β, were prepared by methods previously described.[1]

α- and β-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxides (2α, 2β). A solution of mCPBA (12.08 g, 70.0 mmol) in 65 mL of anhydrous chloroform was added dropwise over a period of 1 h to a solution of the isomeric 2-methoxybenzoxathianes 1α and 1β (6.8 g, 36 mmol) in anhydrous chloroform (20 mL) at 0–5 °C (ice bath). The solution was stirred for 17–18 h at ambient temperature and additional chloroform (90 mL) was added to dissolve *m*-chlorobenzoic acid. The solution was washed with a saturated solution of sodium bicarbonate (4 × 75 mL) and 100 mL of water and finally dried over magnesium sulfate. Removal of the solvent (rotary evaporator) gave 7.12 g (90%) of a colorless solid composed of 2α and 2β as determined by GLC.

Separation of the Diastereoisomeric Sulfones. Chromatographic separation of 2α and 2β was accomplished on a silica gel column (2.5 × 15 cm, 70–325 mesh, EM reagents, eluting with a 90:10 (v/v) chloroform–petroleum ether (bp 30–60 °C range) solution and collecting 20- to 40-mL fractions. The sulfones 2α and 2β were obtained analytically pure by this method. Alternatively, chromatographic separation could also be effected by using an alumina column and methylene chloride–ethyl acetate (75:25 (v/v)) solution as eluent. Under these conditions, 2β elutes first.

β-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxide (2β): mp 155–157 °C; ^{1}H NMR ($CDCl_3$) δ 1.03–2.48 (m, 8 H, CH_2), 2.85 (m, 1 H, SO_2CH), 3.28 (d, J = 2.64 Hz, 2 H, SO_2CH_2), 3.40 (s, 3 H, OCH_3), 4.07 (m, 1 H, OCH), 5.01 (t, J = 2.64 Hz, 1 H, $OCHOCH_3$). Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32. Found: C, 49.13; H, 7.35.

α-2-Methoxy-*trans*-hexahydro-1,4-benzoxathiane 4,4-Dioxide (2α): mp 130.0–130.5 °C; ^{1}H NMR ($CDCL_3$) δ 1.03–2.43 (m, 8 H, CH_2), 2.73 (m, 1 H, SO_2CH), 2.99 (dd, 1 H, J_{aa} = 8.20, J_{gem} = 13.28 Hz, SO_2CH_a), 3.48 (s, 3 H, OCH_3), 3.49 (m, 1 H, OCH), 3.28 (dd, 1 H, J_{ae} = 2.48, J_{gem} = 13.28 Hz, SO_2CH_e), 4.70 (dd, 1 H, J_{ee} = 2.48, J_{aa} = 8.20 Hz, $OCHOCH_3$). Anal. Found: C, 49.13; H, 7.40.

Equilibrations. Equilibrium concentrations of 2α and 2β were obtained by equilibrating pure samples of 2α and 2β from both sides at 300 K with boron trifluoride etherate as catalyst. Typically, 2α and 2β were separately dissolved in 2 mL of solvent along with 5 μL of BF_3·OEt_2 and sealed in ampules. After 1–2 h the reaction was complete and the reaction mixture was treated with 5% sodium hydroxide (10 mL), washed with water (15 mL), dried (anhydrous magnesium sulfate), and concentrated to dryness (rotary evaporator) to give crystalline material. GLC analyses were performed on samples of the solid material dissolved in chloroform on a 6 ft × 0.125 in. (i.d.) stainless steel column with 10% XE-60 nitrile on Chromosorb W-HP-AW-DMCS (100–120 mesh) at 200–210 °C. Response ratios were measured from the areas obtained from weighed samples.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the University Research Council (UNC) and the North Carolina Committee of Science and Technology for support of this research. We thank the National Science Foundation for a fellowship RPR and also Dr. David Harris for recording both noise-decoupled and off-resonance-decoupled ^{13}C NMR spectra.

Registry No. 1α, 60895-17-2; 1β, 60861-03-2; 2α, 70332-86-4; 2β, 70355-05-4.

Structure Elucidation of Polynitrated 2-Aminoperimidines

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One of the classic and most important approaches to determine trace quantities of sulfuric acid is to precipitate the quaternary salt of an organic amine, followed by its conversion to a product with a measurable, visible chromophore. Prior to 1970 this general procedure was limited

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(2) On leave with G.R.N. from Sambalpur University, Sambalpur (Orissa), India, 1975–1976.

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