i.e., X = OMe in structure **10**, in about 70% overall yield from **10**.

Treatment of **9** (1 equiv) with **11** (1 equiv) in dimethylformamide in the presence of potassium carbonate at room temperature yielded a mixture of the four possible diastereomers **12a–d** with respect to the C-12, C-27, and C-29 positions in about equal amount. The yield based on the consumed aromatic segment **9** was 86%, while the yield based on the aliphatic segment **11** was 31%, due to the gradual decomposition of **11** to the corresponding vinyl sulfide under these conditions. By preparative thin-layer chromatography (Merck semianalytical silica gel plates/97.5:2.5 methylene chloride–methanol/5 developments), two diastereomers, **12a**[2] [NMR ($CDCl_3$) δ 3.89 (3 H, s), 3.83 (3 H, s), 3.74 (3 H, s), 3.42 (3 H, s), 2.37 (3 H, s), 2.03 (6 H, s), 1.95 (3 H, s), 1.93 (3 H, s), 1.65 (3 H, s), 1.22 (6 H, s)] and **12b**[2] [NMR ($CDCl_3$) δ 3.89 (3 H, s), 3.83 (3 H, s), 3.74 (3 H, s), 3.17 (3 H, s), 2.37 (3 H, s), 2.12 (3 H, s), 2.03 (3 H, s), 1.95 (3 H, s), 1.93 (3 H, s), 1.67 (3 H, s), 1.22 (6 H, s)], were isolated in the pure form, but the remaining two diastereomers, **12c** and **12d**, were an inseparable mixture. Fortunately, the two diastereomers **12a** and **12b**, isolated as pure forms, were shown to have the *natural* relative stereochemistry with respect to the C-12 and C-27 positions, while the two inseparable diastereomers **12c** and **12d** were shown to have the *unnatural* relative stereochemistry (vide infra). Therefore, in order to continue the synthesis, it was sufficient to separate the mixture of **12a** and **12b** from that of **12c** and **12d**.

The mixture of diastereomers **12a** and **12b** was successfully converted to the methyl ester **13** as summarized in Scheme II. The protecting groups of **9** were chosen in such a way that the necessary functionalization of the alkylated naphthalene **12** was possible. The hydrolysis of the *p*-methoxybenzyl group was achieved under acidic conditions mild enough that the C-12 ketal group was not affected. Before this acid hydrolysis the sulfide group of **12** was oxidized to the corresponding sulfoxide, which was more acid stable. Olefin formation from the sulfoxide was smoothly effected in *o*-dichlorobenzene containing diisopropylamine at 160 °C to give an approximately 1:1 mixture of the trans and cis olefins. Oxidation of this mixture with Fremy's salt yielded an about 1:1 mixture (NMR) of the trans and cis olefin methyl esters **13a** and **13b**, which could be separated by preparative thin-layer chromatography (Merck semianalytical silica gel plates/40:15:4 chloroform–hexane–acetone/5 developments). The overall yield from **12a–d** to **13a–d** was 65–70%, respectively. The trans olefin methyl ester **13a**[2] [NMR ($CDCl_3$) δ 6.14 (1 H, d, J = 12 Hz), 5.21 (1 H, dd, J = 12, 8 Hz), 3.93 (3 H, s), 3.74 (3 H, s), 3.05 (3 H, s), 2.30 (3 H, s), 2.25 (3 H, s), 1.97 (3 H, s), 1.92 (3 H, s), 1.71 (3 H, s), 1.20 (6 H, s)] was found identical with the authentic substance, prepared from natural rifamycin S,[3,19] on comparison of spectroscopic (NMR, IR, UV, MS) and TLC data. The structure of the cis olefin methyl ester **13b**[2] [NMR ($CDCl_3$) δ 6.05 (1 H, d, J = 6 Hz), 4.80 (1 H, dd, J = 9, 6 Hz), 3.94 (3 H, s), 3.75 (3 H, s), 3.20 (3 H, s), 2.29 (3 H, s), 2.26 (3 H, s), 2.05 (3 H, s), 1.93 (3 H, s), 1.69 (3 H, s), 1.22 (6 H, s)] was concluded from its spectroscopic data, in particular the spin–spin coupling constant (J = 6 Hz) of the C-28 and C-29 olefinic protons. By the same sequence of reactions, the mixture of two inseparable diastereomers **12c** and **12d** was also converted to an about 1:1 mixture of the trans and cis olefin methyl esters **13c** and **13d**, which could be separated by preparative thin-layer chromatography. The trans olefin methyl ester **13c**[2] [NMR ($CDCl_3$) δ 6.09 (1 H, d, J = 12 Hz), 5.25 (1 H, dd, J = 12, 8 Hz), 3.93 (3 H, s), 3.74 (3 H, s), 2.98 (3 H, s), 2.30 (3 H, s), 2.26 (3 H, s), 1.95 (3 H, s), 1.93 (3 H, s), 1.71 (3 H, s), 1.20 (6 H, s)] was found very similar to **13a**, although definitely different, on comparison of spectroscopic and TLC data. The same was found for the relationship between the cis olefin methyl esters **13b** and **13d**[2] [NMR ($CDCl_3$) δ 6.11 (1 H, d, J = 6 Hz), 4.82 (1 H, dd, J = 9, 6 Hz), 3.93 (3 H, s), 3.75 (3 H, s), 3.15 (3 H, s), 2.30 (3 H, s), 2.25 (3 H, s), 2.03 (3 H, s), 1.93 (3 H, s), 1.69 (3 H, s), 1.23 (6 H, s)]. Thus the relative stereochemistry at the C-12 and C-27 positions of the previously mentioned four diastereomers was established.

The trans olefin methyl ester **13a** was then converted to rifamycin S (**1**) in 55% overall yield by using the previously described method. The totally synthetic substance was found identical with natural rifamycin S[3] on comparison of spectroscopic (NMR, IR, UV, MS) and TLC data.

Further studies on the improvement of the stereochemistry control around the C-12, -27, and -29 positions are currently in progress in our laboratory.

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Supplementary Material Available: NMR spectra of new compounds described in this paper (21 pages). Ordering information is given on any current masthead page.

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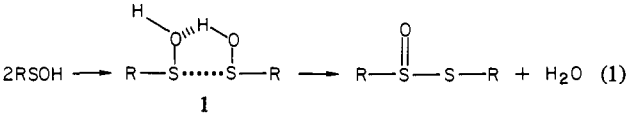
Chemistry of Sulfenic Acids. 2.[1] Formation of Hydrogen Peroxide from Sulfenic Acids

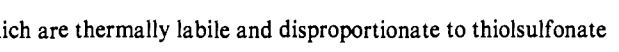
Sir:

Sulfenic acids (RSOH) have been implicated as key intermediates in a wide variety of reactions including biological transformations.[2,3] The possibility that sulfenic acids may regulate the catalytic activity of certain enzyme systems provides added incentive for understanding their chemistry.[4] The difficulty in elucidating the fundamental chemistry of these species results not only from their high reactivity but also from the scarcity of methods for preparing them under conditions where they can be conveniently studied.[2a] In this communication we present evidence for the involvement of sulfenic acids in the oxidation of thiols and the discovery of a new primary reaction of sulfenic acids, formation of hydrogen peroxide and disulfide.

The reaction considered to be most characteristic of sulfenic acids is dehydration to thiosulfinates (RS(O)SR), possibly via an intermediate such as **1** (eq 1).[2,5,6] Thiosulfinate intermediates,



(1)



(2)

which are thermally labile and disproportionate to thiolsulfonate

(1) Part 1: F. A. Davis, S. Q. A. Rizvi, R. Ardecky, D. J. Gosciniak, A. J. Friedman, and S. G. Yocklovich, *J. Org. Chem.*, **45**, 1650 (1980).

(2) For discussions of chemistry of sulfenic acids see: (a) F. A. Davis, A. J. Friedman, and U. K. Nadir, *J. Am. Chem. Soc.*, **100**, 2844 (1978); (b) D. R. Hogg in *Compr. Org. Chem.*, **4**, 261 (1979).

(3) (a) Methanesulfenic acid: R. E. Penn, E. Block, and L. K. Revelle, *J. Am. Chem. Soc.*, **100**, 3622 (1978); (b) sulfenic acid trapping: D. N. Jones, P. D. Cottam, and J. Davies, *Tetrahedron Lett.*, 4977 (1979); A. G. M. Barrett, D. H. R. Barton, and S. Nagubandi, *J. Chem. Soc. Perkin Trans. 1*, 237 (1980).

(4) W. S. Allison, *Acc. Chem. Res.*, **9**, 293 (1976), and references cited therein.

(5) (a) E. Block and J. O'Connor, *J. Am. Chem. Soc.*, **96**, 3929 (1974); (b) J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, **8**, 205 (1973); (c) D. R. Hogg and J. Stewart, *J. Chem. Soc., Perkin Trans. 2*, 43 (1974); (d) for a review on thiosulfinate chemistry see: N. Isenberg and M. Grdinic, *Int. J. Sulfur Chem.*, **8**, 307 (1973).

(6) F. A Davis, S. G. Yocklovich, and G. S. Baker, *Tetrahedron* Lett., 97 (1978).

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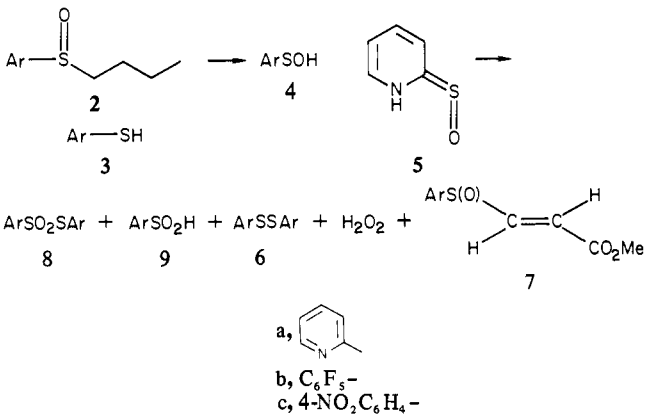
Table I. Reactions of Sulfenic Acids

entry	sulfenic acid	methods and conditions	products (% yield)[a]
1	4a	FVP of 2a at 550 °C	6a (70–79%), H_2O_2 (25–30)[b]
2		FVP of 2a at 550 °C + 20% HC≡CCO_2Me–PhMe	6a (75–80), no 7a
3		thermolysis of 2a in HC≡CO_2Me–PhMe for 3 days	3a (54), 7a (43)
4		oxidation of 3a with 1 equiv of 10 at 25 °C	6a (67–75), H_2O_2 (65–75)[b] (41–42)[c]
5		oxidation of 3a with 0.5 equiv of 10	6a (75–80), H_2O (70)
6	4b[d]	FVP of 2b at 350 °C	6b (60–65), H_2O_2 (63)[b] (58)[c]
7		FVP of 2b at 350 °C + 20% HC≡CCO_2Me–PhMe	6b (75)
8		oxidation of 3b with 1 equiv of 10 for 144 h	3b (53), 6b (48), 10 (54)[b]
9	4c[e]	FVP of 2c at 400 °C	2c (7), 6c (40), 8 (14), 9 (23)
10		FVP of 2c at 400 °C + 20% HC≡CCO_2Me–PhMe	6c (45), 7c (12), 9 (10)
11		oxidation of 3c with 1 equiv of 10 for 4.5 h	6c (90), 11 (75), PhCHO (30)

[a] Products were isolated by preparative TLC (silica gel G) unless otherwise noted. [b] Iodometric titration, see ref 15. [c] NMR integration by using the internal standard method, see ref 2a and 18. [d] Gas chromatographic analyses were performed on a Perkin-Elmer 900 gas chromatograph with a 6 ft × 1/8 in. 3% OV-17 on Anakorm Q 90/100-mesh column. The analyses were determined by comparison of peak areas with standard solutions of the reaction products. [e] Chromatography on Florisil; see also ref 2a.

Scheme I



and disulfide (eq 2),[2a,5d,7] have often been evoked in reactions believed to involve sulfenic acids. Alkanesulfenic acids[5a] and more recently arenesulfenic acids, prepared by flash vacuum pyrolysis (FVP) of *tert*-butyl sulfoxides,[6] have unequivocably been demonstrated to undergo this reaction (eq 1) when present in high concentration. FVP is an important technique for preparing sulfenic acids in high concentration under conditions where they are stable.[6,8]

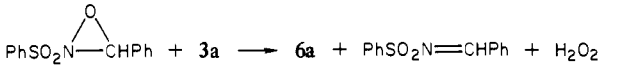
FVP of *n*-butyl 2-pyridyl sulfoxide (**2a**)[9,10] at 550 °C gives 2-pyridinesulfenic acid (**4a**) or, more likely, the tautomeric pyridinethione *S*-oxide (**5**)[11] as a yellow solid on a cold finger cooled to −196 °C (Table I, entry 1). On thawing the color changes from yellow to white and a 70–79% isolated yield of 2,2'-dipyridine disulfide (**6a**) is the only organic product detected by TLC, NMR, and GLC (Scheme I). However, iodometric titration[15] of the reaction mixture gave 25–30% active oxygen based on **2a** (entry 1).[16] This active oxygen species is most likely hydrogen peroxide (H_2O_2) formed by coupling of two sulfenic acid units (eq 3).

$$2RSOH \rightarrow R\text{-}S\text{-}S\text{-}R + H_2O_2 \quad (3)$$

Pentafluorobenzenesulfenic acid (**4b**), prepared by FVP of **2b**,[9] gives similar results, affording disulfide **6b** (60–70%) and H_2O_2 (58–68%) (entry 5).[15,16] However, 4-nitrobenzenesulfenic acid (**4c**), also prepared by FVP of **2c**,[9] gave no peroxide, affording, instead, disulfide **6c**, thiosulfonate **8c**, and sulfinic acid **9c** (entry 9). The product distribution from this sulfenic acid is similar to that reported for the generation of **4c** via thermolysis of *N*-benzylidene-4-nitrobenzenesulfinimine (4-$NO_2C_6H_4S(O)N$=CHPh).[2a] These results were previously interpreted in terms of formation of the thiosulfinate (eq 1) followed by disproportionation (eq 2) and coupling of two sulfenic acid units to give thiol and sulfinic acid.[2a]

Trapping of sulfenic acids, **4a–c**, by cocondensation with a 20% solution of methyl propiolate in toluene on the cold finger[6] was successful only for **4c**, affording sulfoxide **7c** in 12% yield (entry 10).[9b] 2-Pyridinesulfenic acid (**4a**) was, however, trapped in excellent yield to give **7a** when generated in very low concentration by thermolysis of **2a** in methyl propiolate–toluene (entry 3).[9b] We interpret these results to mean that reaction of **4a,b** with themselves (vide infra) is much faster than trapping with methyl propiolate. On the other hand, the 4-nitro group in **4c** must stabilize this sulfenic acid toward dehydration (eq 1) so that it can be trapped.[6]

Addition of 1 equiv of the aprotic oxidizing reagent, 2-(benzenesulfonyl)-3-phenyloxaziridine (**10**),[1,17] to a 0.03–0.09 M $CDCl_3$ solution of 2-mercatopyridine (**3a**) at ambient temperature in an NMR tube produces an immediate reaction affording disulfide **6a** (67–75%), sulfonimine **11** (90–93%), and hydrogen peroxide



(40–75%) (entry 2). Yields are determined by isolation of **6a** and integration of the appropriate ^1H NMR signals by using the

(7) P. Koch, E. Ciuffarin, and A. Fava, *J. Am. Chem. Soc.*, **92**, 5971 (1970); J. L. Kice and G. B. Large, *Tetrahedron Lett.*, 3537 (1965).

(8) For a recent monograph on the FVP technique see: R. F. C. Brown, "Pyrolytic Methods in Organic Chemistry," Academic Press: New York, 1980.

(9) (a) Sulfoxides **2a–c** were prepared by oxidation of the corresponding sulfides with *m*-chloroperbenzoic acid. (b) All new compounds gave satisfactory elemental analyses and had IR and NMR spectra consistent with their structures.

(10) FVP was carried out on 100–150-mg samples of **2a-c** at pressures of 10–20 μm Hg. The pyrolysate was collected on a cold finger cooled to −196 °C. The temperature of the pyrolysis was monitored at the center of the 1.5-cm i.d. pyrolysis chamber by using a Barber–Coleman thermocouple which is estimated to be ± 10 °C. Contact times are approximately 10^{-3} s. This FVP apparatus will be described in a forthcoming publication.

(11) The yellow color observed for **4a** is suggestive of the tautomeric form 2-pyridinthione *S*-oxide (**5**). This compound **5** was believed to be generated as an unstable intermediate in the cleavage of S^1-monooxide of 2-pyridine mesityl disulfides.[12] The chemistry of thioamide *S*-oxides, including sulfenic acid thioamide *S*-oxide tautomerism, is discussed in a review by Walter.[13] The X-ray structure of an aryloxyiminomethanesulfenic acid has been reported.[14]

(12) W. Walter and P. M. Hell, *Liebigs Ann. Chem.*, **727**, 50 (1969).

(13) W. Walter in "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, 1967, Chapter 14.

(14) K. Kato, *Acta Crystallorg., Sect. B*, **28**, 55 (1972).

(15) Iodometric titration of hydrogen peroxide was carried out by using the following procedure: In a 250 mL three-necked flask equipped with a magnetic stirring bar, nitrogen inlet, and inlet for a buret was placed 0.5 mL of glacial acetic acid, 9.5 mL of deionized distilled water, and 1.0 g of KI. The reaction mixture was added and the solution rapidly stirred under nitrogen. The liberated I_2 was titrated with standard 0.1 N $Na_2S_2O_3$. Under these conditions **2**, **6**, and **11** did not liberate iodine.

(16) Hydrogen peroxide is catatically decomposed by trace metals, dust, etc., and is reported to be less stable under basic conditions. For a review of hydrogen peroxide chemistry, see: A. F. Chadwick and G. L. K. Hoh, *Kirk-Othmer Encycl. Chem. Technol., 2nd Ed.*, **11**, 391 (1966).

(17) F. A. Davis, R. Jenkins, Jr., and S. G. Yocklovich, *Tetrahedron Lett.*, 5171 (1978).

internal standard method.[2a] Hydrogen peroxide appears in the ^1H NMR as a broad singlet (7 Hz at half-height) at δ 2.3. This absorption exchanges with D_2O, increases in intensity on addition of 30% H_2O_2 (H_2O absorption is observed at δ 5.1), and gives 40-45% peroxide on iodometric titration.[15,18]

The fact that the same product distribution is obtained for both the FVP of **2a** and oxidation of **3a** argues convincingly for a common intermediate, 2-pyridinesulfenic acid (**4a**). Furthermore, when the oxidation of **3a** is carried out between -50 and -20 °C, the solution remains yellow in color with no H_2O_2 formation until it is warmed to room temperature. A similar yellow color is observed in the FVP synthesis of **4a** (**5**). Attempts to trap **4a** (**5**) at -20 °C with methyl propiolate, diazomethane, or methyl iodide have been unsuccessful. However, addition of methanolic $FeCl_3$ at this temperature generates a green solution which becomes colorless when warmed.[21] Iron complexes of thioamide *S*-oxides, i.e., **5**, have been reported to be this color.[12]

Similarly, oxidation of pentafluorobenzenethiol (**3b**) with **10** is very slow, with less than half of **3b** and **10** being consumed after 144 h. The disulfide **6b** is the principal product (entry 8). 4-Nitrobenzenethiol (**3c**) is completely oxidized by **10** to give a quantitative yield of disulfide **6c** after 4.5 h without consuming all of the oxidizing reagent (entry 11).

The slow rate of oxidation of thiols **3b,c** by **10** results in formation of sulfenic acids **4b,c** in the presence of a large excess of thiol. The exclusive formation of disulfide in the oxidation of these thiols (entries 8 and 11) is consistent with a mechanism whereby **3b,c** attacks the corresponding sulfenic acids to give water and disulfide (eq 4). As predicted by this mechanism **6a** and water

$$\text{R-SOH} + \text{R-SH} \rightarrow \text{R-S-S-R} + \text{H}_2\text{O} \qquad (4)$$

were formed quantitatively on oxidation of **3a** with 0.5 equiv of **10** (entry 5).

Biologically the most important reaction of thiols is their oxidation to disulfides and higher sulfur oxides.[4,7,19,20] Our experiments provide the first definitive evidence for the involvement of sulfenic acids in both of these important transformations (eq 4). Significantly, the oxidation of protein sulfhydryl groups to protein sulfenic acids has been considered necessary for the activity of certain enzyme systems as well as for the deactivation of other enzymes.[4,20,22] The formation of protein disulfides observed in the oxidation of protein thiols could well involve a reaction similar to that depicted in eq 4.[4,20,23]

Although the metal-catalyzed autoxidation of thiols to disulfides and hydrogen peroxide is well documented,[19,20,24] the coupling of two seemingly neutral units to disulfide and hydrogen peroxide (eq 3) is apparently unprecedented.[25] The possibility that hydrogen peroxide and disulfide could be formed in a manner other than that depicted in eq 3, such as from the thioamide *S*-oxide or from a thiosulfinate intermediate, is unlikely. 2-Pyridinethione *S*-oxide (**5**) reacts as the sulfenic acid **4a** (vida supra), and sulfenic acid **4b** cannot for a related structure. Although the reaction of water with an intermediate thiolsulfinate to afford H_2O_2 and disulfide cannot be eliminated absolutely, this possibility is unlikely. Thiolsulfinates have not been observed to undergo such reactions,[5d,28] and pyridine arylthiosulfinates (PySS(O)Ar) are reported to disproportionate according to eq 2.[30]

The reaction most characteristic of simple sulfenic acids when present in relatively high concentration is thiolsulfinate formation (eq 1).[31] The reason why sulfenic acids **4a-b** afford H_2O_2 and disulfide (eq 3) is unclear, but may be related to the strong electron-attracting pyridyl and pentafluorophenyl groups attached to the SOH group. We are currently exploring the scope of this unusual transformation.

Acknowledgment. We Thank Professor John Kice, Texas Tech University, for valuable discussions. We acknowledge financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE 7819890).

(18) The discrepancies in the yields of H_2O_2 determined by iodometric titration and determined by integration of NMR signals probably result from water and H_2O_2 absorbing at the same signal, thereby giving a high value. Water could be formed as illustrated in eq 4. A separate absorption for water does not appear until the concentration reaches approximately 10^{-4} M in the NMR.

(19) (a) For a general review on the oxidation of thiols, see G. Capossi and G. Modena, *Chem. Thiol. Group*, **2**, 367 (1974); (b) P. C. Jocelyn, "Biochemistry of the SH Group", Academic Press, New York, Chapter 4, 1972; (c) N. Kharasch and A. S. Arora, *Phosphorus Sulfur*, **2**, 1 (1976).

(20) Oxidation of protein thiols: (a) W. S. Lin, G. M. Gaucher, D. A. Armstrong, and M. Lal, *Can J. Chem.*, **54**, 242, (1976); (b) K. S. You, L. V. Benitez, W. A. McConachie, and W. S. Allison, *Biochim. Biophys. Acta*, **384**, 317 (1975); (c) M. Costa, L. Pecci, B. Pensa, and C. Cannella, *Biochem. Biophys. Res. Commun.*, **78**, 596 (1977).

(21) Methanolic $FeCl_3$ gave no color with **6a**, **10**, or **11**. A brown color was observed on addition of **3a** and H_2O_2 to methanolic $FeCl_3$ in $CHCl_3$.

(22) W. S. Allison and L. V. Benitez, *Proc. Natl. Acad. Sci.* U.S.A., **69**, 3004 (1972).

(23) W. S. Lin, D. A. Armstrong, and C. M. Gaucher, *Can. J. Biochem.*, **53**, 298 (1975).

(24) P. P. Trotto, L. M. Pinkus, and A. Meister, *J. Biochem.*, **249**, 1915 (1974).

(25) Certain sulfenyl halides (RSX; X = Br, I) decompose on standing to give X_2 and disulfide,[26] and thionitrosobenzene (PhN=S) disproportoinates to azobenzene (PhN=NPh) and sulfur.[27]

(26) See P. S. Magee, *Sulfur Org. Inorg. Chem.* **1**, 261 (1971); J. P. Danehy, *ibid.* **1**, 327 (1971).

(27) F. A. Davis and E. W. Skibo, *J. Org. Chem.*, **41**, 1333 (1976).

(28) Phenyl benzenethiosulfinate and 2,4,6-triisopropylbenzenethiosulfinate when treated under the reaction conditions with water proved to be unreactive. Attempts to synthesize independently the thiosulfinates corresponding to **4a,b** by oxidation of disulfides **6a,b** were unsuccessful. 4-Nitrophenyl 4-nitrobenzenethiosulfinate which is undoubtedly involved in the reactions of sulfenic acid **4c**, generated by FVP of **2c** (Table I, entry 9,10), could not be detected. Significantly aryl arenethiosulfinates with strong electron-attracting groups have never been prepared or even detected.[5d,29]

(29) S. Oae and S. Kawamura, *Bull. Chem. Soc. Jpn.*, **35**, 1156 (1962).

(30) W. Walter and P. M. Hell, *Liebigs Ann. Chem.*, **727**, 35 (1969).

(31) Hydrogen peroxide could not be detected in the reactions of benzenesulfenic acid generated by FVP of *tert*-butyl phenyl sulfoxide. See also ref 6.

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Reactions of Metal Complexes with Carbohydrates. 1. Synthesis and Characterization of Novel Blue Paramagnetic Nickel(II) Complexes Containing *N*-Glycosides

Sir:

We report the synthesis and characterization of new blue paramagnetic Ni(II) complexes containing *N*-glycosides which were derived from the reaction of tris(ethylenediamine)nickel(II) dichloride dihydrate with D-(+)-glucose (D-gl), D-(+)-mannose (D-man), or D-(-)-fructose (D-fru).

We isolated three Ni(II) complexes containing *N*-glycosides by the following procedure.

To a stirred solution of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (2.90 g, 8.38 mmol) in 50 mL of methanol was added 4.53 g (25.14 mmol) of a monosaccharide (D-gl, D-man, or D-fru). The solution was warmed to about 70 °C with stirring and became blue after about 1 h. The reaction solution was evaporated to 30 mL and loaded on a LH-20 gel permeation column and eluted with methanol. The colored materials separated into a major blue band and minor purple, yellow, and green ones. The blue band fractions were collected and concentrated to dryness under reduced pressure. Each blue compound thus obtained was recrystallized from a minimum amount of hot methanol. The crystals were collected and washed with ethanol followed by ether and dried in vacuo.[1] Elemental analyses[2] indicated that the D-gl and D-man complexes,

(1) The yields were 4.16, 1.13, and 4.53 g for the D-gl, D-man, and D-fru compounds, respectively.

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