($CDCl_3$) δ 7.13 (1 H, dd, J = 16, 11 Hz), 6.40 (1H, d, J = 11 Hz), 5.97 (1 H, dd, J = 16, 7 Hz), 3.75 (3 H, s), 3.34 (3 H, s), 2.12 (3 H, s), 1.94 (3 H, s), 1.31 (3 H, s), 1.27 (3 H, s)] was established on comparison of spectroscopic (NMR, IR, UV, MS) and TLC data with those of the authentic substance prepared from natural rifamycin S.[15,16]

The hemithioacetal **15** was further converted to the sulfide **17**[6] [NMR ($CDCl_3$) δ 7.12 (1 H, dd, J = 16, 11 Hz), 6.39 (1 H, d, J = 11 Hz), 5.96 (1 H, dd, J = 16, 7 Hz), 3.74 (3 H, s), 3.32 (3 H, s), 2.50 (2 H, t, J = 7 Hz), 2.11 (3 H, s), 2.01 (3 H, s), 1.94 (3 H, s), 1.23 (6 H, s), 0.99 (3 H, d, J = 7 Hz), 0.95 (3 H, d, J = 7 Hz), 0.87 (3 H, d, J = 7 Hz), 0.85 (3 H, d, J = 7 Hz)]. After the hemithioacetal group was hydrolyzed to the corresponding hemiacetal, the tetrahydropyranyl ring of **15** was opened reductively. Selective acetylation of the C-25 hydroxyl group of **16**[6] was achieved via prior selective silylation of the C-29 primary hydroxyl group with *tert*-butyldiphenylsilyl chloride treatment.[17]

The synthesis of the optically active sulfide **17** from the optically active aldehyde **9**[7] via the route reported is currently in progress in our laboratory. A total synthesis of racemic rifamycin S (**1**) from the aliphatic building block **17** and the aromatic building block **3**[18] will be described in the following communication.

Acknowledgment. Financial assistance from the National Institutes of Health (NS 12108) and National Science Foundation (CHE 78-06296) is gratefully acknowledged. W.R. expresses his gratitude to the Swiss National Science Foundation for a postdoctoral research fellowship, and H.I. expresses his gratitude to the Yamada Science Foundation for the support of travel expenses from Japan to the U.S.

Supplementary Material Available: NMR spectra of new compounds described in this paper (20 pages). Ordering information is given on any current masthead page.

(15) The authentic substance was prepared from a degradation product of rifamycins, described by M. Kinoshita, K. Tatsuta, and M. Nakata (*J. Antibiot.* **1978**, *31*, 630), in two steps; i.e., compound **4** in the paper quoted was treated with $MeSH/ZnCl_2/CH_2Cl_2/0$ °C and then with 2,2-dimethoxypropane/acetone/CSA/room temperature.

(16) We are indebted to Drs. Bickel and Scartazzini, CIBA-GEIGY, Basel, for a generous gift of rifamycin S and a sample of the aromatic segment **3**.

(17) The alcohol **16** was successfully converted to the aldehyde **2**[6] [NMR ($CDCl_3$) δ 9.82 (1 H, t, J = 2 Hz), 7.11 (1 H, dd, J = 15, 11 Hz), 6.38 (1 H, d, J = 11 Hz), 5.94 (1 H, dd, J = 15, 7 Hz), 3.75 (3 H, s), 3.29 (3 H, s), 2.02 (3 H, s), 1.94 (3 H, s), 1.23 (6 H, s)] in excellent yield in four steps (i.e., steps 1 through 3 are the same as those under (h) in Scheme II; step 4: $Me_2SO/(COCl)_2/CH_2Cl_2/-60$ °C, and then Et_3N[20]). In spite of extensive degradation studies by many groups, the aldehyde **2** had never been obtained from naturally occurring rifamycins. A practical, highly reproducible method to prepare the aldehyde **2** in 30–35% overall yield from rifamycin S in three steps [i.e., (1) 2,2-dimethoxypropane/acetone/CSA/room temperature; (2) NaOH/MeOH/room temperature; (3) MCPBA/THF/5% aqueous $NaHCO_3$/0 °C, followed by treatment with Et_2O/aqueous Na_2SO_3/5% aqueous $NaHCO_3$/room temperature] was developed in our laboratory. The authentic aldehyde **2** was found identical with the synthetic substance on comparison of spectroscopic and TLC data. The aldehyde **2**, thus prepared, was converted to the sulfide **17** in three steps (i.e., (1) $NaBH_4$/MeOH/0 °C; (2) MsCl/Et_3N/CH_2Cl_2/0 °C; (3) MeSNa/THF/room temperature) which was found identical with the totally synthetic substance on comparison of spectroscopic and TLC data.

(18) A synthesis of the aromatic building block **3** has recently been completed in our laboratory; a paper has been submitted to *Tetrahedron Lett.*

(19) Uchida, K.; Uchimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215.

(20) Mancuso, A. J.; Juang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

(21) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 398.

(22) Corey, E. J.; Gilman, N. W.; Gariem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616.

(23) A Guggenheim fellow (1980–81).

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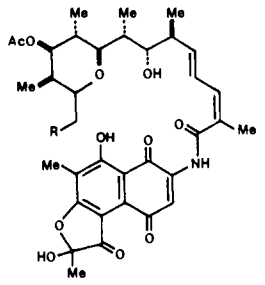
Received August 18, 1980

Total Synthesis of Rifamycins. 2. Total Synthesis of Racemic Rifamycin S

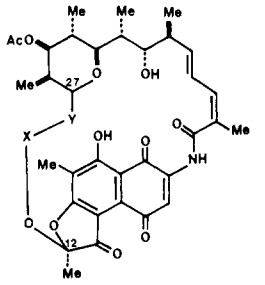
Sir:

Having the totally synthetic aliphatic building block for rifamycin in hand,[1] we have now turned our attention to methods to effect the ansa-ring construction. We first investigated the lactam-ring formation by using the amino acid **2**[2] [NMR ($CDCl_3$) δ 3.04 (3 H, s), 2.22 (3 H, s), 1.97 (6 H, s), 1.70 (3 H, s), 1.21 (6 H, s)], prepared from natural rifamycin S (**1**).[3] The desired lactam bond was cleanly formed by the methods summarized in Scheme I. Reduction of the naphthoquinone moiety was necessary to increase the nucleophilicity of the C-2[4] amino group.[5] Lindlar catalyst at low temperature was used for this purpose to avoid reduction of the olefinic bonds. Both methods tested were found effective for formation of the lactam bond, but the mixed anhydride procedure gave a slightly better overall yield.[6]

The alternative possibility for the ansa-ring construction, the *intramolecular* enol ether formation, seemed more attractive as there was the possibility that the relative stereochemistry at the C-12 and C-27 positions might be controlled in this approach. The feasibility of this plan was tested by using the acetal **3**[2] and the thioacetal **4**,[2] prepared from rifamycin S (**1**).[7] The expected ansa



3, R = $CH(OMe)_2$
4, R = $CH(SMe)_2$



5, X-Y = -CH=CH- (*trans*)
6, X-Y = $-CH(OH)CH_2-$

product **5** from these compounds is known to be a degradation product of formic acid treatment of rifamycin S.[8] Numerous attempts were uniformly fruitless, but the following observations are worth mentioning. On acid treatment (CSA/benzene/reflux), the acetal **3** yielded a new product which was isolated by flash silica gel chromatography in about 15% yield. The NMR spectrum of this product was very characteristic; one of the methyl group doublets appears at 0.35 ppm. Based on the NMR spectrum,[9] one of the most likely structures for the new product seemed to be the ansa hemiacetal **6**, but all efforts to convert it to **5** were unsuccessful. Under these circumstances, the approach involving the *intermolecular* enol ether formation was studied.[10]

(1) Nagaoka, H.; Rutsch, W.; Schmid, G.; Iio, H.; Johnson, M. R.; Kishi, Y. *J. Am. Chem. Soc.* **1980**, *102*, preceding paper in this issue.

(2) Satisfactory spectroscopic data (NMR, MS, IR, UV) were obtained for this substance.

(3) We are indebted to Drs. Bickel and Scartazzini, CIBA-GEIGY, Basel, for a generous gift of rifamycin S and a sample of the naphthoquinone **7**.

(4) The numbering corresponds to that of rifamycin S—see structure **1** in the preceding paper.

(5) This type of chemistry was discussed in relation to the mitomycin synthesis. See: Kishi, Y. *J. Nat. Prod.* **1979**, *42*, 549.

(6) Recently, Corey and Clark reported results almost identical with method C: Corey, E. J.; Clark, D. A. *Tetrahedron Lett.* **1980**, 2045.

(7) The acetal **3** was synthesized from rifamycin S by HCl–MeOH treatment. The thioacetal **4** was synthesized from rifamycin S by BF_3Et_2O–MeSH treatment.

(8) Kump, W.; Bickel, H. *Helv. Chim. Acta* **1973**, *56*, 2323.

(9) It is known that rifamycins and their derivatives with the ansa bridge give a methyl group doublet at unusually high magnetic field. See: Prelog, V. *Pure Appl. Chem.* **1963**, *7*, 551. Oppolzer, W.; Prelog, V. *Helv. Chim. Acta* **1973**, *56*, 2287.

(10) A possible alternative structure for this product, i.e., the hemiketal involving the C-11 ketonic and the C-29 hydroxyl groups in **6**, could not be excluded. After having recognized dramatic difference in chemical behavior between compounds like **9** and **7**, we attempted the intramolecular enol ether formation on compounds with the same naphthalene moiety as **9** without fruitful results.

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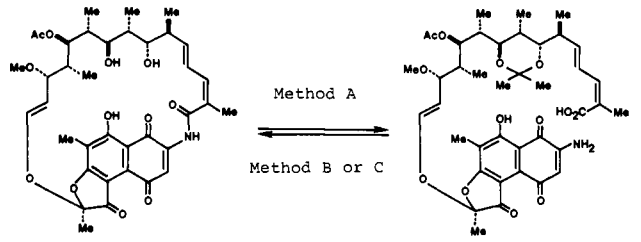
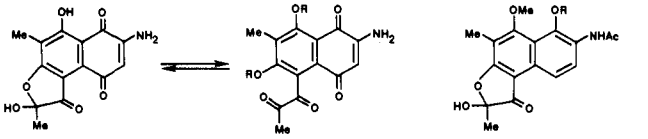
Scheme I[a]



1, rifamycin S 2

[a] Method A: (1) 2,2-dimethoxypropane/acetone/CSA/room temperature; (2) NaOH/MeOH/room temperature; (3) sodium ascorbate/aqueous DME/room temperature, followed by treatment with aqueous NaOH/DME/room temperature, and then $K_3Fe(CN)_6$ workup. Method B: (1) H_2/Lindlar catalyst/THF/−20 °C; (2) $(EtO)_2P(O)CN/Et_3N$/DMF/room temperature,[20] followed by $K_3FE(CN)_6$ workup; (3) HCl/aqueous THF/room temperature. Method C: (1) $ClCO_2Et/Et_3N/CH_2Cl_2$/room temperature; (2) H_2/Lindlar catalyst/THF/−20 °C; (3) THF/50 °C, followed by $K_3Fe(CN)_6$ workup; (4) HCl/aqueous THF/room temperature.

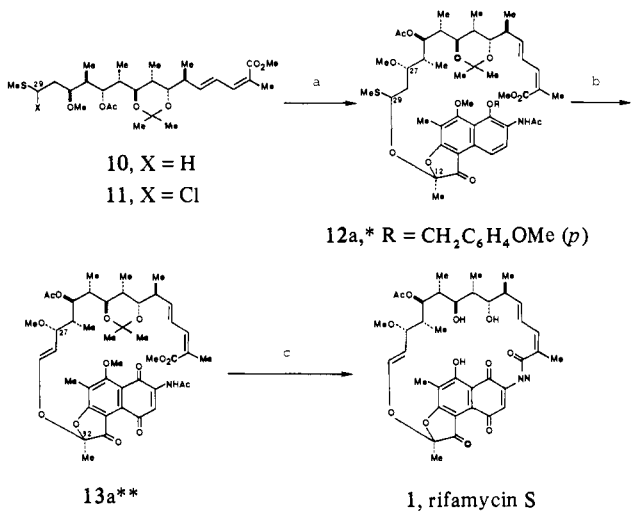
Although the aromatic quinone **7** exists primarily as its closed tautomeric form, cf. **7A** ⇄ **7B**, particularly under acidic conditions,



7A 7B, R = H; 8, R = CH_2OMe 9, R = $CH_2C_6H_4OMe$-*p*

all attempts on acid or metal ion catalyzed enol ether formation were unsuccessful. It seemed hopeless to alkylate the tertiary alcoholic group of the closed form in the presence of a base. Indeed, **7**[1,3] reacted smoothly with chloromethyl methyl ether in methylene chloride containing diisopropylethylamine, to yield exclusivly the open-form product **8**[2] [NMR ($CDCl_3$) δ 3.61 (3 H, s), 3.44 (3 H, s), 2.55 (3 H, s), 2.33 (3 H, s)].[11,12] Nonetheless,[13] the possibility of alkylating the tertiary alcoholic group of the closed form was further investigated with the hope that a structural modification at the C-4 position of **7** might produce the desired product. Among numerous derivatives of **7** tested,[14] the naphthalene **9**[2] [NMR ($CDCl_3$) δ 3.86 (3 H, s), 3.83 (3 H, s), 2.36 (3 H, s), 1.94 (3 H, s), 1.70 (3 H, s); UV (EtOH) λ_{max} (log ε) 228 (4.53), 270 (4.48), 323 (3.89), 382 (3.69) nm] was found to satisfy all the requirements for this synthesis. First, alkylation of **9** with various alkyl halides and alkyl mesylates was smoothly effected in dimethylformamide in the presence of potassium carbonate to yield *exclusively the closed-form product* in excellent yield. Second, the necessary functionalization of the naphthalene ring after the alkylation could be realized as described later. Third, a practical synthetic route to **9** from **7** was developed.[15]

Scheme II[a]



10, X = H
11, X = Cl

12a,* R = $CH_2C_6H_4OMe$ (*p*)

13a** 1, rifamycin S

[a] Reagents: (1) 11 (1 equiv) + 9 (1 equiv)/DMF/K_2CO_3/room temperature. (b) (1) MCPBA/CH_2Cl_2/−78 °C; (2) 2,2-dimethoxypropane/acetone/CSA/room temperature; (3) diisopropylamine/*o*-$C_6H_4Cl_2$/160 °C/30 min; (4) Fremy's salt/acetone/phosphate buffer (pH 7)/room temperature. (c) (1) MgI_2Et_2O/C_6H_6/room temperature;[21] (2) sodium ascorbate/aqueous DME/room temperature, followed by treatment with aqueous NaOH/DME/room temperature, then $K_3Fe(CN)_6$ workup; (3) NaOH/MeOH/room temperature/5 min. Steps 4 through 7 (or 4 through 6) are the same as steps 1 through 4 of method C (or steps 1 through 3 of method B). [b] *12b is the diastereomer of 12a at the C-29 position. 12c and 12d are diastereomers at the C-29 position, having the unnatural relative stereochemistry with respect to the C-12 and C-27 positions. **13b is the cis isomer of 13a at the C-28 and C-29 double bond. 13c and 13d are the trans and cis isomers at the C-28 and C-29 double bond, having the unnatural relative stereochemistry with respect to the C-12 and C-27 positions.

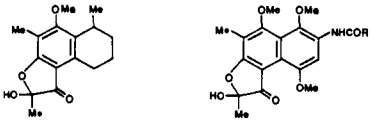
For the preparation of the properly functionalized aliphatic building block, α-halo sulfides appeared to be one of the best choices. The *N*-chlorosuccinimide chlorination of **10**[1] (NCS/benzene/room temperature)[16] yielded a diastereomeric mixture[17] of the reactive α-chloro sulfides **11**, the structure of which was established by two experiments: first, the NMR spectrum of **11** in deuterated benzene showed a triplet (J = 7 Hz) at 5.01 ppm and a double of doublets (J = 9 and 5 Hz) at 5.14 ppm;[17] second, the treatment of **11** with methanol in the presence of potassium carbonate yielded the corresponding methoxy compounds,[2,17,18]

(11) The NMR spectrum is most useful in determining the structure of open- or closed-form products; the chemical shift for the C-13 methyl group of the closed-form product is around 1.7 ppm, while that for the open-form product is around 2.5 ppm.

(12) Similar observations were made by Prelog and Oppolzer; see the papers quoted under ref 9.

(13) Kump and Bickel assigned the closed-form structure to the acetate obtained from **7** on treatment with acetic acid and DCC, i.e., the compound **11** in the paper quoted under ref 8, but this structure should be revised as the acetate of the open form on the basis of NMR (δ 2.47) and IR (ν 1785 cm^{-1}) data. Thus, there was no example known for acylation or alkylation on the tertiary alcoholic group of the closed form under *basic* or *neutral* conditions.

(14) Of interest is the fact that compound i yielded exclusively the closed-form product on alkylation, while ii exclusively the open-form product.



i ii

(15) The naphthalene **9** was synthesized in 55% overall yield from **7** in 6 steps, i.e., (1) $AcCl/ZnCl_2/CHCl_3$/reflux,[8] (2) MeI/Ag_2O/MeOH-$CHCl_3$/60 °C, (3) $TsNHNH_2/MgSO_4$/MeCN/60 °C, (4) H_2/Pd-C/Et-OAc-CH_2Cl_2/room temperature, (5) *p*-$MeOC_6H_4CH_2Br/K_2CO_3$/DMF/room temperature, and (6) 5% aqueous Na_2CO_3/MeOH/room temperature. The napthoquinone **7**, used for this synthesis, was obtained by degradation of natural rifamycin S.[1,3,8]

(16) For a review on NCS chlorination of sulfides, see: Paquette, L. A. *Org. React.* **1977**, *25*, 1.

(17) The ratio of the two diastereomers was about 4:3 (NMR).

(18) These products were identical with the authentic substance prepared from the aldehyde **2**, mentioned in the preceding paper, in two steps, i.e., (1) 2,2-dimethoxypropane/CSA/room temperature and (2) $MeSH/BF_3Et_2O/CH_2Cl_2$/−20 °C.

(19) The authentic substance was synthesized in about 40% overall yield from rifamycin S in four steps, i.e., (1) 2,2-dimethoxpropane/acetone/CSA/room temperature, (2) NaOH/MeOH/room temperature, (3) H_2/Lindlar catalyst/THF/−20 °C, followed by treatment with $AcCl/Et_3N$/−78 °C → room temperature and $K_3Fe(CN)_6$ workup, and (4) MeI/Ag_2O/MeOH-$CHCl_3$/60 °C.

(20) Yamada, S.; Kasai, Y.; Shioiri, T. *Tetrahedron Lett.* **1973**, 1598.

(21) Arkley, V.; Attenburrow, J.; Gregory, G. I.; Walker, T. *J. Chem. Soc.* **1962**, 1260.

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.

Acknowledgment. Finacial assistance from the National Institutes of Health (NS 12108) and National Science Foundation (CHE 78-06296) is gratefully acknowledged. H.I. expresses his gratitude to the Yamada Science Foundation for the support of travel expenses from Japan to the U.S.

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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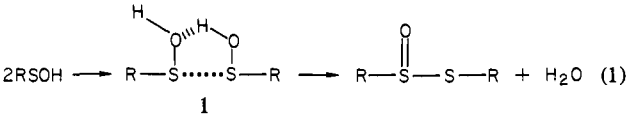
Received August 18, 1980

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,



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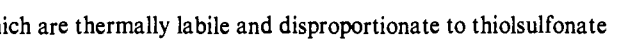

(2)

which are thermally labile and disproportionate to thiolsulfonate

(22) A Guggenheim fellow (1980–81).

(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).

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

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