Single-Step Syntheses of Epoxides and Other Cyclic Ethers by Reaction of a Diaryldialkoxysulfurane with Diols[1,2]

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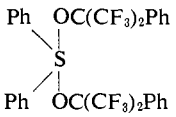
Abstract: Diaryldialkoxysulfurane **1** [$Ph_2S(OR_F)_2$, where $R_F = C_6H_5C(CF_3)_2$] reacts with 1,2-diols under mild conditions to form epoxides in excellent yields. The formation of cyclohexene oxide from *trans*-1,2-cyclohexane diol, but not from the *cis*-diol, is consistent with a mechanism involving collapse of an intermediate β-hydroxyalkoxysulfonium ion in an antiperiplanar intramolecular nucleophilic displacement of diphenyl sulfoxide. Stereospecific epoxide formation results from exclusive preference for a secondary over a tertiary hydroxyl ligation site in the reaction of **1** with steroidal *trans*-diol **21**. In other cases significant carbonium ion character is exhibited in the epoxide forming reaction; isobutylene glycol specifically ^{18}O-labeled at the tertiary position cleanly loses the labeled oxygen upon conversion to isobutylene oxide, and *meso*-2,3-diphenylbutane-2,3-diol gives small yields of 3,3-diphenyl-2-butanone (5.2%) and *cis*-2,3-epoxy-2,3-diphenylbutane (1–2%) in addition to the major product, *trans*-2,3-epoxy-2,3-diphenylbutane (90%). Quantitative conversion of the *meso*-diol to the *trans*-epoxide occurs at reduced temperatures. The conversion of *dl*-2,3-diphenylbutane-2,3-diol to *cis*-2,3-epoxy-2,3-diphenylbutane at a more rapid rate than the conversion of the *meso*-diol to the *trans*-epoxide argues against an intramolecular displacement transition state model involving a high degree of phenyl–phenyl eclipsing and suggests that the transition state is achieved at an earlier stage in this exothermic reaction. Ethylene glycol is converted to ethylene oxide at a rate comparable to the rate of conversion of methanol to CH_3OR_F, suggesting a transition state characteristic of a concerted displacement of an alkoxysulfonium ion. Treatment of 1,4-, 1,5-, and 1,6-alkylidene diols with **1** leads to progressively lower yields of cyclic ethers as open-chain ether formation becomes competitive with ring closure. Treatment of 1,3-propanediol with **1** fails to form oxetane, but when structural features preclude olefin formation and favor ring closure, as in the case of 2,2-dimethylpropane-1,3-diol, a good yield of 3,3-dimethyloxetane results. The possible contribution of the *gem*-dialkyl effect to rates of epoxide and larger ring formation is discussed.

The remarkable utility of sulfurane **1** [$Ph_2S(OR_F)_2$, $R_F = C_6H_5(CF_3)_2$] as a reagent in the dehydration



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of alcohols[3] and its unique reactions with amides[4] and with amines[4] have spurred extensive exploration of synthetic applications of sulfurane **1** in this laboratory. We report here the reaction of **1** with 1,2-diols to form epoxides in excellent yields under mild conditions. The scope of the reaction in forming larger cyclic ethers is defined by its extension to longer chain diols.

Experimental Section

Except where noted, diols were commercially available. Sulfurane **1** was prepared according to a published[5] procedure and according to a simplified standard procedure developed by us.[6] All reactions were carried out in reaction vessels allowing rigorous exclusion of water or in an inert atmosphere glove box under dry nitrogen.

Chloroform-*d*, chloroform, methyene chloride, and carbon tetrachloride were dried by passage through alumina. Reagent grade ether was dried by treatment with and storage over sodium wire.

General Procedures for the Reactions of 1 with Diols. Method A. To a solution of 1–2 equiv of **1** in dry chloroform-*d*, chloroform, ether, or carbon tetrachloride is introduced 1 equiv of diol. The reaction mixture is stirred for 10–20 min at room temperature, and R_FOH is removed by extraction with 20% aqueous KOH. Ether should be replaced with $CHCl_3$, CH_2Cl_2, or CCl_4 before extraction since KOR_F is quite soluble in ether. Evaporation of the solvent and chromatography of the mixture on a short silica gel column (eluting with 1:8 ether–pentane or pentane) to remove the polar sulfoxide gives, after solvent evaporation, pure cyclic and acyclic nonvolatile ethers.

Method B. Reagents are combined as in method A but, following base wash, the volatile products are flash distilled from diphenyl sulfoxide, and the distillate is concentrated to gain the liquid products which may be further purified by preparative glpc on one of the following columns: column A, 5 ft × 0.25 in. 20% SE-30 on Chromosorb W; column B, 10 ft × 0.25 in. 10% SE-30 on Chromosorb W; column C, 3 ft × 0.25 in. 80–100 mesh Porapak Q; column D, 9 ft × 0.25 in. 80–100 mesh Porapak Q; column E, 20 ft × 0.25 in. 20% Carbowax 20M on 60–80 mesh Chromosorb P.

Method C. One equivalent of diol and 2–3 equiv of **1** are combined in $CDCl_3$ or CCl_4 in an nmr tube. The ^1H and ^{19}F nmr spectra of the product mixtures are used to determine the yields by careful integration of fully resolved product peaks, using the total aromatic integral as an internal proton nmr standard. Quantitative glpc analysis of the reaction mixture using standard solutions of authentic compound were carried out using the glpc columns mentioned above to verify nmr yields and product identity or to determine product yields when nmr yields were not available due to overlapping product peaks.

Reactions of 1 and 19 with Glycols. (a) **3β-Chloro-5α,6β-cholestanediol (21)** was prepared according to the method of Shoppee, *et al.*:[7] mp 127.5–129° (lit.[7] mp 126°); mass spectrum (70 eV) *m/e* 438 ($M\cdot^+$). The diol (465 mg, 1.06 mmol) was treated with sulfurane **1** (1.2 g, 1.8 mmol) in ether according to method A to give 417 mg (93%) of crystalline 3β-chloro-5α,6α-epoxycholestane

(1) Part XIV in a series of papers on sulfuranes. For part XIII of this series, see J. C. Martin and M. M. Chau, *J. Amer. Chem. Soc.*, **96**, 3319 (1974).

(2) A preliminary account, covering some of the subject matter of this paper, was presented by R. J. Arhart, J. A. Franz, and J. C. Martin, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract, ORGN 175.

(3) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 5003 (1972).

(4) J. A. Franz and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 2017 (1973); J. A. Franz and J. C. Martin, manuscript in preparation, presented in part at the 23rd National Organic Chemistry Symposium, Tallahassee, Fla., 1973.

(5) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997 (1972).

(6) J. C. Martin, R. J. Arhart, J. A. Franz, E. F. Perozzi, and L. J. Kaplan, *Org. Syn.*, submitted for publication.

(7) C. W. Shoppee, R. J. Bridgwater, D. N. Jones, and G. H. R. Summers, *J. Chem. Soc.*, 2492 (1956).

(22), mp 97–97.5° (lit.[8] mp 97.5°) (after two recrystallizations from absolute alcohol and drying overnight at 70° and 10^{-2} Torr). The 220-MHz nmr, ir, mass, and ^{13}C nmr spectra matched those of the authentic material, prepared according to Heilbron, *et al.*[8]

(b) 2,3-Dimethylbutane-2,3-diol. To 0.16 mmol of **1** in $CDCl_3$ was added 17.2 mg (0.146 mmol) of diol in $CDCl_3$. The ^1H nmr spectrum shows quantitative conversion to the epoxide (singlet, δ 1.30). Isolation by method B and purification by preparative glpc at 50° on column A gave a liquid whose mass spectrum displayed a molecular ion (*m/e* 100) and fragments comparable to those of an authentic sample.[9] The ^1H nmr spectrum displayed a singlet at δ 1.30.

(c) *trans*-1,2-Cyclohexanediol. A solution of 127 mg (0.19 mmol) of **1** in $CDCl_3$ was combined with a solution of 22.5 mg (0.17 mmol) of *trans*-1,2-cyclohexanediol in $CDCl_3$. The aliphatic region of the ^1H nmr spectrum was identical with that of authentic 1,2-epoxycyclohexane. Analysis by glpc on column A verified the product identity and established the yield at 97%. Isolation by method B using glpc column A gave material which displayed nmr, ir, and mass spectra identical with those of authentic material.

(d) *cis*-1,2-Cyclohexanediol. To 123.7 mg (1.07 mmol) of *cis*-1,2-cyclohexanediol in $CDCl_3$ was added 1.32 g (1.97 mmol) of sulfurane **1** in $CDCl_3$. The nmr spectrum displayed a complex aromatic region and an aliphatic spectrum similar to cyclohexanone. No olefinic or aldehydic peaks were present. Quantitative glpc on column A established the yield of cyclohexanone at 28%. The nmr, ir, and mass spectra of the liquid were identical with those of authentic cyclohexanone. Cyclohexene oxide, cyclohexene, cyclopentanecarboxaldehyde, and cyclohexane-1,2-dione were all shown to be absent (glpc, nmr). Glpc on column A at 200° showed diphenyl sulfide and diphenyl sulfoxide along with trace products. Analytical lc on a 4 ft × $^3/_8$ in. Corasil column (Waters Associates) showed one additional major product. This compound, 2-(2-phenylthiophenyl)cyclohexanone (**9**), was isolated by preparative scale lc on a 4 ft × $^3/_8$ in. Porasil TT lc column yielding, from 363.3 mg (3.13 mmol) of the *cis*-diol, 183 mg (0.65 mmol, 21%) of **9**, an oil which was not obtained in crystalline form: 100-MHz ^1H nmr ($CDCl_3$) δ 7.6–7.0 (m, 9 H, $C_6H_5SC_6H_4$), 4.28 (d of d, 1 H, –COCHAr, J = 11.4 and 5.3 Hz), 2.55–1.50 ppm (m, 8 H, methylene H); ir ($CHCl_3$) 1720 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* 282 ($M\cdot^+ - PhS$). *Anal.* Calcd for $C_{18}H_{18}OS$: C, 76.54; H, 6.43; S, 11.36. Found: C, 75.76; H, 6.36; S, 10.98.

(e) *dl*-2,3-Diphenylbutane-2,3-diol (11). Samples of **1** (165.4 mg, 0.246 mmol) and diol (52.1 mg, 0.213 mmol) were combined in *ca.* 0.5 ml of $CDCl_3$. The ^1H nmr spectrum displayed a singlet at δ 1.78, indicating 100% conversion (by nmr integration) of the diol to *cis*-2,3-epoxy-2,3-diphenylbutane (**13**). Using method A, 1.66 g (6.81 mmol) of the diol was added to 5.44 g (8.1 mmol) of **1** to give 1.48 g (6.6 mmol, 97%) of **13**, mp 43–50°. One recrystallization from pentane at −25° gave mp 52.5–54.5° (lit.[10] mp 52–53°): nmr (CCl_4) δ 7.0–6.6 (m, 10 H, $C_6H_5CCH_3$), 1.78 ppm (s, 6 H, CH_3); mass spectrum (70 eV) *m/e* 224 ($M\cdot^+$).

To a solution of 183.9 mg (0.76 mmol) of **11** and 110.5 mg (1.03 mmol) of 2,6-lutidine in *ca.* 1.0 ml of $CDCl_3$ was added 515 mg (0.81 mmol) of alkoxysulfonium triflate **19**[11] in *ca.* 1 ml of $CDCl_3$. The mixture nmr spectrum displayed a complex aromatic region and an aliphatic region with fully resolved methyl peaks of 2,6-lutidine, 3,3-diphenyl-2-butanone (52%), **13** (17%), unreacted diol (19%), and **16** (12%). Approximately 16% of the sulfonium triflate was hydrolyzed by adventitious water. Neither **13** nor **16** reacted with the diarylalkoxysulfonium triflate reagent in the presence of 2,6-lutidine in $CDCl_3$. Shaking the mixture with D_2O to complete hydrolysis of the diarylalkoxysulfonium triflate reagent gave a product mixture in which the epoxides underwent no reaction. In addition, the composition of the original reaction mixture itself showed no change after a week following the combination of reagents.

(f) *meso*-2,3-Diphenylbutane-2,3-diol (14). To 1.25 g (5.18 mmol) of the *meso*-diol[12] in *ca.* 10 ml of CH_2Cl_2 was added 5.12 g (7.6 mmol) of sulfurane **1** in *ca.* 15 ml of CH_2Cl_2 at room temperature. The mixture nmr spectrum evidenced *trans*-2,3-epoxy-2,3-diphenylbutane (**16**, 92%), 3,3-diphenyl-2-butanone (*ca.* 6%), and epoxide **13** (1–2%). Isolation by method A gave 1.047 g (90%) of crystalline **16** and an oil (*ca.* 150 mg) which contained small amounts of **13** and **16** and 3,3-diphenyl-2-butanone. Recrystallization of the crystalline epoxide gave mp 110–112.5° (lit.[10] mp 107°): nmr ($CDCl_3$) δ 7.5–7.3 (m, 10 H, C_6H_5), 1.28 ppm (s, 6 H, $-CH_3$); mass spectrum (70 eV) *m/e* 224 ($M\cdot^+$). Purification of the oil by preparative high-pressure liquid chromatography (lc) on a 4 ft × $^3/_8$ in. Porasil TT column (1:5 CH_2Cl_2–cyclohexane) gave 61 mg (5.2%) of 3,3-diphenyl-2-butanone, identical by nmr, ir, and retention time on a 4-ft Corasil analytical lc column to an authentic sample,[13] and *ca.* 12 mg (1%) of **13**, identified by nmr and lc retention time on the Corasil analytical lc column, which resolved a mixture of authentic **13**, **16**, and 3,3-diphenyl-2-butanone.

When **14** (60 mg, 0.25 mmol) was treated with excess **1** at *ca.* 50° in $CDCl_3$, formation of **16** occurred in 100% yield by integration of the ^1H nmr singlet at δ 1.28.

(g) Ethylene Glycol. According to method C, 46.2 mg (0.743 mmol) of ethylene glycol and excess **1** were combined in $CDCl_3$ at $<-50°$ and sealed in an nmr tube. The ^1H nmr spectrum displayed, in addition to the familiar peaks of Ph_2SO and R_FOH, the sharp singlet of ethylene oxide at δ 2.62, 60% by nmr integration. The product identity was verified by glpc analysis of the reaction mixture and of a solution of authentic ethylene oxide in chloroform on column C at 95°.

(h) Isobutylene glycol was prepared by a procedure similar to that of Long and Pritchard.[14] Enriched (34.88% ^{18}O) water (300 μl) was treated with 5 μl of 70% H_3PO_4 and 14 successive 50-μl portions of isobutylene oxide while being stirred over a period of 1 hr. The glycol was exchanged several times with portions of unlabeled water to remove deuterium. Preparative glpc of the crude mixture on column C at 175° gave the pure glycol. The $^{18}O/^{16}O$ isotope ratio was determined from the mass spectrum according to the published procedure,[13] establishing 32% ^{18}O at the tertiary hydroxyl site and *ca.* 1% ^{18}O at the primary hydroxyl site.

The labeled glycol (27.7 mg, 0.308 mmol) in $CDCl_3$ was treated with 350.5 mg (0.522 mmol) of sulfurane **1** in $CDCl_3$. The nmr spectrum revealed the disappearance of the glycol and the appearance of the singlets of isobutylene oxide at δ 2.54 and 1.25, 65% by nmr integration. Preparative glpc using column E at 103° afforded several milligrams of isobutylene oxide which was collected on *ca.* 4 mg of charcoal for mass spectroscopic analysis. The mass spectrum displayed peaks at *m/e* 72 ($M\cdot^+$) and 74 in the ratio 1.000:0.015, indicating *ca.* 1% enrichment over natural abundance. The reaction mixture was washed three times with 15% NaOH and the solvent was evaporated, leaving a clear oil which crystallized from pentane to give diphenyl sulfoxide. The sulfoxide's ^{18}O content was established as 19% from the ratio of the peaks at *m/e* 202 ($M\cdot^+$) and 204. These results are consistent with exclusive removal of the oxygen at the tertiary site during the formation of isobutylene oxide, after correction for the level of ^{18}O incorporated at the primary site of the glycol and after correction for the dilution of the ^{18}O label in the diphenyl sulfoxide by the hydrolysis of excess **1** with unlabeled water.

(i) 1,3-Propanediol. To 34.9 mg (0.46 mmol) of 1,3-propanediol in $CDCl_3$ was added 903 mg (1.35 mmol) of sulfurane in *ca.* 2 ml of $CDCl_3$. The ^1H nmr spectrum displayed the fully resolved aliphatic and olefinic peaks of $R_FOCH_2CH{=}CH_2$ and $R_FO(CH_2)_3OR_F$ and revealed no detectable oxetane. The ^{19}F nmr spectrum displayed two singlets at 72.4 and 72.6 ppm upfield from $CFCl_3$ [$-CF_3$ of $R_FC(CH_2)_3OR_F$ and $R_FOCH_2CH{=}CH_2$] in the ratio 2.5:1.0 by integration. The total ^{19}F integral was used as a standard to establish the yields at 39% [$R_FO(CH_2)_3OR_F$] and 31% ($R_FOCH_2CH{=}CH_2$). Analysis of the reaction by glpc on column A at 100° gave a peak with identical retention time and mixed retention time as that of an authentic sample of $R_FOCH_2CH{=}CH_2$ prepared from allyl alcohol (see below).

Treatment of 308 mg (4.05 mmol) of 1,3-propanediol with 6.72 g (10 mmol) of sulfurane **1** in CH_2Cl_2 and work-up by method A gave, after evaporation of the volatile ether, $R_FOCH_2CH{=}CH_2$, 0.65 g (30%) of $R_FO(CH_2)_3OR_F$ as an oil, which was crystallized from pentane (−78°): mp 55.5–57°; nmr ($CDCl_3$) δ 7.7–7.2 [m, 10 H, $C_6H_5C(CF_3)_2$–], 3.8 (t, 4 H, R_FOCH_2–, J = 6 Hz), 2.08 ppm (quintet,

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(9) P. Brown and C. Djerassi, *Tetrahedron*, **24**, 2949 (1968).

(10) P. Ramart-Lucas and M. E. Salmon-Legagneur, *Bull. Soc. Chim. Fr.*, **45**, 718 (1929).

(11) L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973).

(12) Prepared according to ref 10. The *meso*-glycol contained no *dl*-glycol impurity (by nmr).

(13) Prepared according to K. Sisido and H. Nozaki, *J. Amer. Chem. Soc.*, **70**, 776 (1948).

(14) F. A. Long and J. G. Pritchard, *J. Amer. Chem. Soc.*, **78**, 2663 (1956).

Table I. Competitive Reactions of Glycol Mixtures with Sulfurane 1

Quantity of 1, mmol	Mixture components, mmol	Solvent	Products	k_{rel}
1.54	Tetramethylethylene glycol (5.02)	$CDCl_3$	Tetramethylethylene oxide	10.9
	tert-Butyl alcohol (3.18)		Isobutylene	1
0.56	*tert*-Butyl alcohol (0.64)	$CDCl_3$	Isobutylene	2.82
	11 (0.66)		**13**	2
0.31	Isobutylene glycol (0.32)	$CDCl_3$	Isobutylene oxide	1.7
	11 (0.26)		**13**	1.0
0.83	**11** (0.912)	Ether, −78°	**13**	3.76
	14 (0.933)		**16**	1
1.51	**11** (1.35)	$CDCl_3$	**13**	1.6
	14 (1.68)		**16**	1
3.69	**11** (5.16)	$CDCl_3$	**13**	24.6
	Methanol (12.87)		CH_3OR_F	1.0
1.41	Methanol (0.85)	$CDCl_3$	CH_3OR_F	1.2
	Ethylene glycol (1.63)		Ethylene oxide	1.0

2 H, $R_FOCH_2CH_2$, J = 6 Hz); ^{19}F nmr ($CDCl_3$) 72.4 ppm upfield from $CFCl_3$ [s, 12 F, $-CF_3$ of $R_FO(CH_2)_3OR_F$]; mass spectrum (70 eV) m/e 528 ($M\cdot^+$). *Anal.* Calcd for $C_{21}H_{16}F_{12}O_2$: C, 47.72; H, 3.05. Found: C, 47.97; H, 3.14.

(j) 2,2-Dimethylpropane-1,3-diol. To 47.3 mg (0.46 mmol) of diol in $CDCl_3$ was added 374.2 mg (0.56 mmol) of sulfurane **1** in $CDCl_3$. The proton nmr spectrum displayed singlets at δ 4.31 and 1.27 [OCH_2 and $(CH_3)_2C$–], of 3,3-dimethyloxetane, 86%, using the integral of the total aromatics as an internal standard. Using method B, 1.05 g (10.1 mmol) of diol was treated with 11 g (16.4 mmol) of **1** in CH_2Cl_2 and stirred for 30 min. The distillate gave, after purification by preparative glpc at 55° on column A, sufficient material for characterization: nmr ($CDCl_3$) δ 4.31 (s, 4 H, OCH_2), 1.27 ppm [s, 6 H, $(CH_3)_2C$]; mass spectrum (70 eV) m/e 56 ($M\cdot^+ - CH_2O$).

(k) 1,4-Butanediol. To 59.9 mg (0.667 mmol) of diol was added 962.6 mg (1.43 mmol) of sulfurane **1** in CH_2Cl_2 and the reaction mixture was diluted to 2.00 ml. The ^{19}F nmr spectrum displayed a singlet at 70.0 ppm upfield from $CFCl_3$ [$-CF_3$ of $R_FO(CH_2)_4OR_F$] and 75 ppm ($-CF_3$ of R_FOH). The ratio of these indicated 12% yield of $R_FO(CH_2)_4OR_F$. Analysis of the reaction mixture by glpc on column A at 35° using a standard solution of tetrahydrofuran (THF) established the yield of THF as 72%.

A preparative reaction was carried out to confirm the identity of $R_FO(CH_2)_4OR_F$. To 6.1705 g (9.2 mmol) of **1** in 10 ml of CH_2Cl_2 was added 521 mg (5.8 mmol) of 1,4-butanediol in CH_2Cl_2. Work-up using method A gave 333 mg (10.3%) of semisolid $R_FO(CH_2)_4OR_F$, which, after two crystallizations from pentane (−78°), had mp 92–92.5°: nmr ($CDCl_3$) δ 7.5 (br s, 10 H, $C_6H_5C(CF_3)_2$–], 3.85–3.45 (m, 4 H, R_FOCH_2), 2.05–1.75 ppm (m, 4 H, $R_FOCH_2CH_2$–); ^{19}F nmr 70.0 ppm upfield from $CFCl_3$ [s, 12 F, $PhC(CF_3)C$]; mass spectrum (70 eV) m/e 542 ($M\cdot^+$). *Anal.* Calcd for $C_{22}H_{18}F_{12}O_2$: C, 48.70; H, 3.35. Found: C, 48.66; H, 3.30.

(l) *cis*-2-Butene-1,4-diol. To 28.8 mg (0.33 mmol) of *cis*-2-butene-1,4-diol was added 227.6 mg (0.34 mmol) of **1** in $CDCl_3$. The ^1H nmr spectrum displayed two singlets at δ 5.86 (2 H) and 4.65 (4 H) of 2,5-dihydrofuran, 84%, by nmr integration. Treatment of 510 mg (5.75 mmol) of diol with 6.97 g (10.35 mmol) of **1** in 15 ml of CH_2Cl_2 gave, after work-up following method B and purification by preparative glpc on column B at 50°, pure 2,5-dihydrofuran, which displayed an nmr spectrum identical with a spectrum of authentic material[15a] and a mass spectrum with a molecular ion and fragmentation pattern similar to that of a published spectrum.[15b]

(m) 1,5-Pentanediol. According to method A, 0.1776 g (1.7 mmol) of 1,5-pentanediol was treated with 3.11 g (4.63 mmol) of **1** in $CHCl_3$ to give 553 mg (58%) of $R_FO(CH_2)_5OR_F$ as a clear oil which, after two crystallizations from pentane at −25 and −50°, gave mp 38–39.5°: nmr ($CDCl_3$) δ 7.7–7.0 [m, 10 H, $C_6H_5C(CF_3)_2O$], 3.7–3.3 (m, 4 H, OCH_2), 2.0–1.5 ppm (m, 6 H, $OCH_2CH_2CH_2CH_2$); ^{19}F nmr ($CDCl_3$) 72.3 ppm upfield from $CFCl_3$ (s, 12 F); mass spectrum ($CFCl_3$, 70 eV) m/e 556 ($M\cdot^+$). *Anal.* Calcd for $C_{23}H_{20}F_{12}O_2$: C, 49.63; H, 3.62. Found: C, 49.87; H, 3.67.

To determine the yield of tetrahydropyran, the reaction was repeated using 34.3 mg (0.33 mmol) of diol and 512.2 mg (0.76 mmol) of sulfurane **1** in CH_2Cl_2. The solution was diluted to 2.00 ml. A standard solution of authentic tetrahydropyran in CH_2Cl_2 was used in the glpc analysis using column A at 77° to establish the yield of tetrahydropyran as 39%.

(n) Diethylene Glycol. A solution of 0.35 mmol of **1** in $CDCl_3$ was added to an nmr tube containing 13.3 mg (0.12 mmol) of diethylene glycol in $CDCl_3$. The rapid exothermic reaction gave dioxane (40%) and $R_FOCH_2CH_2OCH_2CH_2OR_F$ (60%). The nmr spectrum displayed, in addition to the aromatic peaks, two singlets at δ 3.75 [$(R_FOCH_2CH_2)_2O$] and δ 3.62 (dioxane) in the ratio 3:2. The ^{19}F spectrum displayed a singlet at 70.2 ppm upfield from $CFCl_3$ [$-CF_3$ of $(R_FOCH_2CH_2)_2O$]. Analysis of the reaction mixture by glpc using column A gave a peak with a retention time and mixed retention time identical with those of an authentic sample of dioxane. Using method A, the reaction was repeated with 3.435 g (5.12 mmol) of **1** in $CDCl_3$ and 0.2749 g (2.59 mmol) of diol in $CDCl_3$ to give 0.865 g (60%) of crystalline $(R_FOCH_2CH_2)_2O$, mp 56–63°. Two recrystallizations from pentane at −25° gave mp 68–70°: nmr ($CDCl_3$) δ 7.8–7.1 [m, 10, $C_6H_5C(CF_3)_2O$–], 3.75 ppm [s, 8, $(R_FOCH_2CH_2)_2O$]; ^{19}F nmr ($CDCl_3$) 70.2 ppm upfield from $CFCl_3$ (s, 12 F); mass spectrum m/e 556 ($M\cdot^+$). *Anal.* Calcd for $C_{22}H_{18}F_{12}O_3$: C, 47.11; H, 3.36. Found: C, 47.40; H, 3.29.

(o) 1,6-Hexanediol, 192.6 mg (1.63 mmol), was treated (method A) with 3.3094 g (4.93 mmol) of **1** in ether to give 0.907 g (97.5%) of $R_FO(CH_2)_5OR_F$, mp 69–75°. Recrystallization from pentane gave mp 77.5–79°: nmr ($CDCl_3$) δ 7.9–7.2 [m, 10 H, $C_6H_5C(CF_3)_2O(CH_2)_6OC(CF_3)_2C_6H_5$], 3.7–3.5 (m, 4 H, R_FOCH_2), 2.2–2.1 ppm [m, 8 H, $R_FOCH_2(CH_2)_4CH_2OR_F$]; ^{19}F nmr 70.4 ppm upfield from $CFCl_3$ [s, 12 F, $PhC(CF_3)_2O$]; mass spectrum (70 eV) m/e 343 [$R_FO(CH_2)_6O^+$], 227 [$PhC(CF_3)_2^+$]. No $M\cdot^+$ was observed. *Anal.* Calcd for $C_{24}H_{22}F_{12}O_2$: C 50.51; H, 3.89. Found: C, 50.46; H, 3.84.

Competitive Reactions of Glycol and Glycol–Alcohol Mixtures with 1. A standard procedure was used for competitive reactions of two or more reagents with **1**. To a rapidly stirring solution of a mixture of glycol or alcohol substrates in $CDCl_3$ (at *ca.* −50°) or ether (−78°) was added dropwise a solution of sulfurane **1** in $CDCl_3$ or ether. After the reaction mixture had warmed to room temperature, its nmr spectrum provided the ratios of products and starting materials. The quantities of reagents, solvent, and products are summarized in Table I. The relative rate constants (k_{rel}) are calculated from the integrated rate equation $k_{rel} = \log [(A - X)/A]/\log [(B - Y)/B]$, where A and B are initial concentrations of starting materials and X and Y are the concentrations of their respective products.

When ether was used as a solvent, it was evaporated from the nonvolatile products and replaced with $CDCl_3$ for nmr analysis.

In the competitive reaction of **11** and **14** with **1**, addition of excess **1** to the glycol mixture at *ca.* −50° gave quantitative conversion to the mixture of **13** and **16** with no detectable incursion of the pinacol rearrangement product (3,3-diphenyl-2-butanone).

(15) (a) "Nuclear Magnetic Resonance Spectra," Sadtler Research Laboratories, Philadelphia, Pa., 1968, spectrum no 5024; (b) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Vol. I, Interscience, New York, N. Y., 1959, p 60.

Results

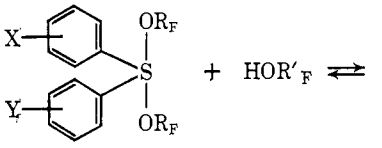
Table I lists relative rate constants for the reactants of several mixtures of substrates with sulfurane **1**. Table II lists the composite relative rate constants for the entire series. Even though the addition of sulfurane was done at −50 or −78° with rapid stirring, the reactions of some substrates with **1** are so rapid that we cannot be sure that some local depletion of reagents did not occur. The k_{rel} scale may be, for this reason, slightly compressed. Table III lists the yields of products in reactions of **1** with individual glycols.

Table II. Relative Rates of Reaction of **1** with Glycols and Alcohols at −50°

	k_{rel}
Tetramethylethylene glycol	910
tert-Butyl alcohol	83
Isobutylene glycol	50
dl-2,3-Diphenylbutane-2,3-diol (**11**)	30
meso-2,3-Diphenylbutane-2,3-diol (**14**)	18
Methanol	1.2
Ethylene glycol	1.0

acts to provide olefins (from tertiary or secondary alcohols) or ethers (R_FOR, from primary alcohols) in a remarkably facile reaction.

The relative rates of the degenerate exchange of R_FOH with various *S*-phenyl-substituted analogs of **1** follow a Hammett correlation with a ρ of approximately −3, suggesting that the transition state for the acid-catalyzed[3] ligand exchange process involves substantial positive charge development on sulfur (as in **4**) relative to the ground state.



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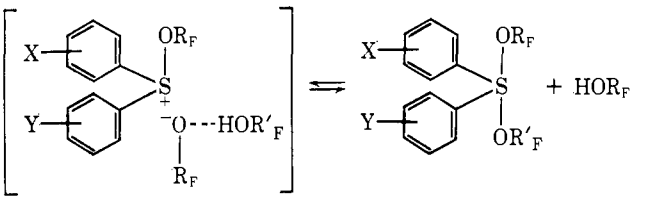

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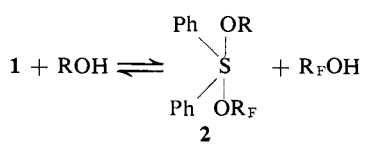
Table III. Reactions of Diols with **1** at Room Temperature

Diol	Solvent	Products	% yield
Ethylene glycol	$CDCl_3$	Ethylene oxide	60[a]
21	Et_2O	**22**	93[b]
11	Et_2O, $CDCl_3$	**13**	100[a], 97[b]
14	CH_2Cl_2, $CDCl_3$	**16**	90[b], 100[a,c]
		3,3-Diphenyl-2-butanone	5.2,[b] 0[a,c]
		13	*ca.* 1,[b] 0[a,c]
2,3-Dimethylbutane-2,3-diol	$CDCl_3$	Tetramethylethylene oxide	100[a]
trans-1,2-Cyclohexanediol	$CDCl_3$	Cyclohexene oxide	97[d]
cis-1,2-Cyclohexanediol	$CDCl_3$	Cyclohexanone	28[d]
	CH_2Cl_2	Diphenyl sulfide	10[b]
		2-(2-Phenylthiophenyl)-cyclohexanone	21[b]
Isobutylene glycol	$CDCl_3$	Isobutylene oxide	65[a]
1,3-Propanediol	$CDCl_3$	**29**	39,[a] 30[b]
		30	31[a]
2,2-Dimethyl-1,3-propanediol	$CDCl_3$, CH_2Cl_2	3,3-Dimethyloxetane	86[a]
1,4-Butanediol	$CDCl_3$, CH_2Cl_2	Tetrahydrofuran	72[d]
		$R_FO(CH_2)_4OR_F$	12,[a] 10.5[b]
cis-2-Butene-1,4-diol	$CDCl_3$	2,5-Dihydrofuran	84[a]
1,5-Pentanediol	$CDCl_3$, $CHCl_3$	Tetrahydropyran	39[d]
		$R_FO(CH_2)_5OR_F$	58[a,b]
Diethylene glycol	$CDCl_3$	Dioxane	40[a,d]
		$(R_FOCH_2CH_2)_2O$	60[a,b]
1,6-Hexanediol	Et_2O	$R_FO(CH_2)_5OR_F$	97.5[b]

[a] Yield determined by nmr integration using an internal standard. [b] Yield determined by weight of isolated product. [c] Reagents combined at *ca.* −50°. [d] Yield by quantitative glpc using authentic standards.

Discussion

Rapid exchange of alcohols with the alkoxy ligands of **1** has been observed[3,5,11] by nmr when alcohols which are relatively inert toward dehydration (perfluoro-*tert*-butyl alcohol, neopentyl alcohol, or R_FOH, which undergoes a degenerate exchange) are added to a solution of **1**. For many other alcohols intermediate **2** re-



2

Competitive reactions of mixtures of these same substituted sulfuranes (**3**) with *tert*-butyl alcohol are correlated with a ρ of −1.68, suggesting a somewhat smaller positive charge development on sulfur in this reaction than in the degenerate exchange of R_FOH with **3**. This result, when considered with the modest intramolecular kinetic isotope effect (k_H/k_D = 1.54) observed in the dehydration of 2-methyl-2-propanol-*1,1,1,3,3,3-d*$_6$ by **1** has been interpreted[5,11] in terms of a transition state for dehydration which has appreciable E1 character, resembling the *tert*-butyl cation.

In contrast, the rates of reaction of primary alcohols with **1** to give unsymmetrical ethers (ROR_F) respond

to substituents on the alcohol in a pattern suggesting SN2 character in a displacement of diphenyl sulfoxide by R_FO^-.

The reactions of **1** with the structurally diverse diols of Table III are rationalized in terms of a similar pattern, involving the development of carbonium ion character in the reactions of tertiary glycols and concerted nucleophilic displacements for the diols reacting at primary carbon centers.

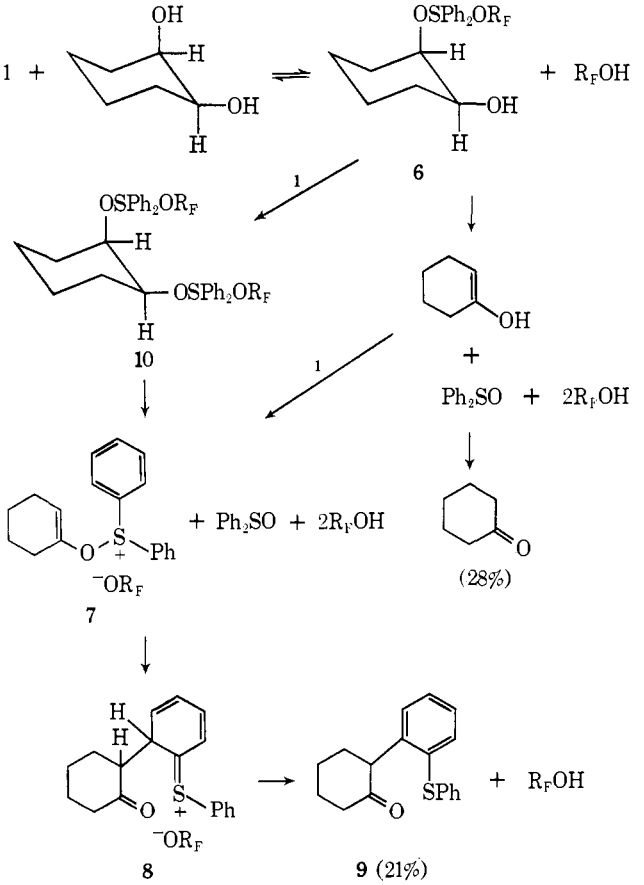
The introduction of a diol to a solution of **1** leads to complete destruction of **1** within seconds at room temperature to produce ethers (Table III). This provides a unique procedure for the direct conversion of 1,2-diols to epoxides in high yields under mild conditions.[16] As can be seen from the data of Table III, 1,2-diols capable of achieving a conformation with antiperiplanar disposition of hydroxyl groups give stereospecific reactions leading to excellent yields of epoxides to the total exclusion of olefin or acyclic ether products.

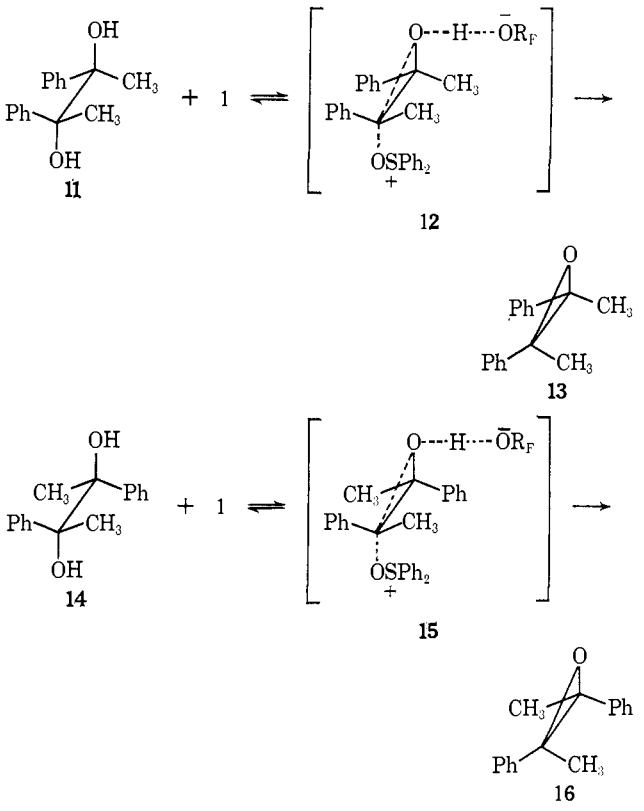
The failure of *cis*-cyclohexane-1,2-diol to form cyclohexene oxide, under conditions which provided a nearly quantitative conversion of the *trans*-diol to epoxide, shows that the accessibility of a conformation with an antiperiplanar disposition of hydroxyl groups is highly desirable. Ligand exchange to give **6** could be followed by trans elimination to give the enol of cyclohexanone which could either tautomerize to the ketone or react with **1** to generate vinyloxysulfonium species **7**. An electrocyclic rearrangement of **7** to **8** would lead to the observed product **9**. Cyclohexanone does not react with **1** to give this product. An alternative route through bis(sulfurane) **10** avoids the intermediacy of the enol and is, therefore, the favored route (Scheme I).

The order of reactivities seen in Table II for the diastereoisomeric 2,3-diphenylbutane-2,3-diols (**11** reacts 1.6 times more rapidly than **14**) is not that predicted[17] from a straightforward consideration of eclipsing strain in transition states **12** and **15** developing between substituents becoming cis related in **13** and **16**. Assuming some resemblance of transition states to products one would predict the opposite order of rates (**14** > **11**).[18]

If the preferred orientation for rotation about the alkoxysulfonium C–O bond in transition states **12** or **15** is that with the SPh_2 group roughly antiperiplanar to the bulky α-phenyl substituent, it is reasonable to expect that the repulsive interactions between the SPh_2 group and the β-phenyl substituent would be smaller in

Scheme I





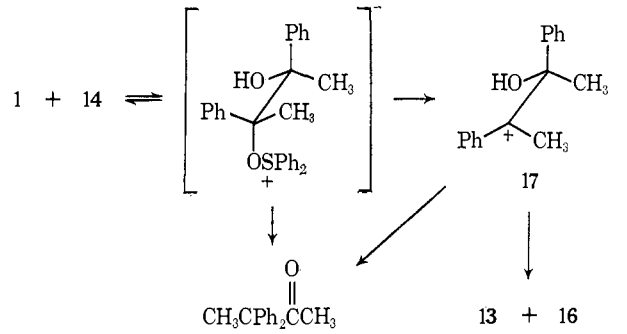
(16) Direct conversion of 1,2-diols to epoxides in the presence of acidic reagents has occasionally been observed, although the pinacol rearrangement is observed in the great majority of cases: (a) S. Winstein and R. B. Henderson, *Heterocycl. Compounds*, **1**, 19 (1950). In one case a steroid diol was converted directly to the epoxide by treatment with thionyl chloride; (b) J. M. Coxon, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, **21**, 2489 (1965). None of these methods is of general synthetic utility. For an extensive review of epoxide syntheses, see A. Rosowsky in "The Chemistry of Heterocyclic Compounds," Vol. 29, part I, A. Weissberger, Ed., Interscience, New York N. Y., 1964, Chapter 1.

(17) For a discussion of the "cis" effect, see D. Y. Curtin, *Rec. Chem. Progr.*, **15**, 111 (1954).

(18) A referee has suggested that the small rate differential noted for **11** and **14** might reflect ground state energy differences resulting from a greater importance of intramolecular hydrogen bonding in the less reactive **14**. High dilution (0.004 *M* in CCl_4) infrared spectra show a much larger H-bonded peak for **11** than for **14**, however (36 cm^{-1} lower in frequency than the free OH peak at 3620 cm^{-1}). Isomer **14** shows a small H-bonded peak 47 cm^{-1} lower in frequency than the free O–H peak (3620 cm^{-1}). The low intensity of the H-bonded peak of **14** makes its assignment somewhat ambiguous but clearly points to a small population of H-bonded conformations and argues against the importance of this ground state effect.

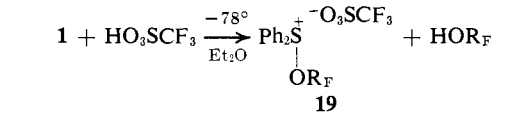
12 than in **15**. The proposed transition state[19] is reactant-like with little development of the product-like eclipsing strain between vicinal substituents.

The rapid reaction of **11** with **1** to yield epoxide **13** occurs cleanly and stereospecifically without detectable amounts of other products. This is also true for the more slowly reacting diastereoisomeric diol **14** at reduced temperature, but at room temperature reaction products characteristic of carbonium ions are formed in modest yield. In addition to **16** (90%) the reaction of **14** with **1** at room temperature gives 2,2-diphenyl-3-butanone (**18**, 5.2%) and the isomeric epoxide **13** (1-



2%). While the ketone may arise *via* phenyl migration either in concert with or following the departure of phenyl sulfoxide, the ring closure with retention which leads to *cis*-epoxide must involve the intermediacy of discrete carbonium ion **17**. Such carbonium ion pathways are clearly not far removed in energy from the favored stereospecific concerted epoxide ring closures.

The alkoxysulfonium triflate reagent **19**, prepared by

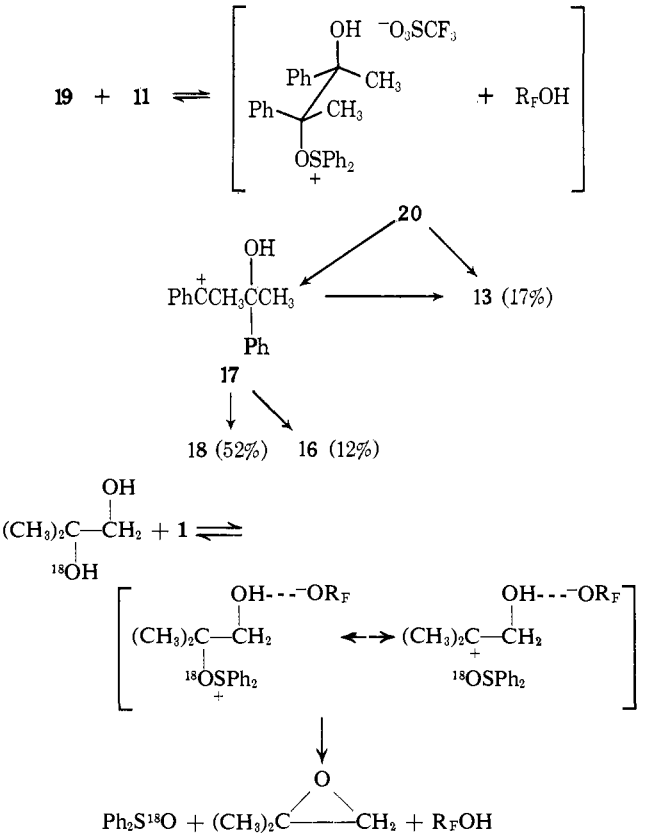


the treatment of **1** with trifluoromethanesulfonic acid,[11] is a reagent whose potential synthetic utility is under study in this laboratory. When **11** was treated with **19**, in the presence of 2,6-lutidine, ketone **18** was the major product, along with appreciable amounts of both isomeric epoxides. The *cis*-epoxide is formed in greater yield than the presumably more stable *trans*-epoxide, indicating that, in spite of great enhancement of the carbonium ion route, there remains a preference for the antiperiplanar disposition of hydroxyl and departing diphenyl sulfoxide.

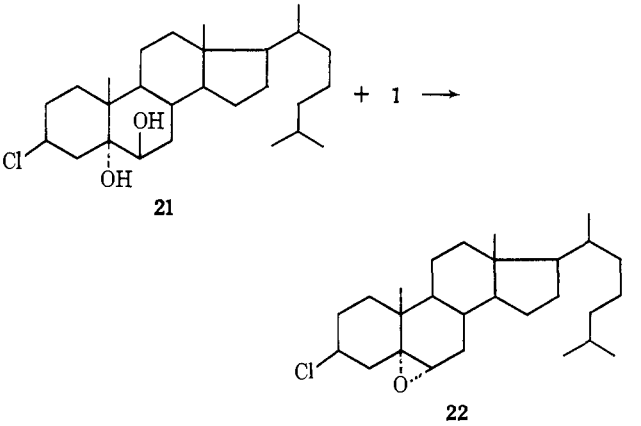
The substitution (in **20**) of triflate ion for the more basic R_FO^- of transition state **12** slows the concerted ring closure and allows more of the competitive carbonium ion process to occur, *via* **17**.

Another reaction providing evidence for carbonium ion character in these reactions is that of **1** with isobutylene glycol labeled with oxygen-18 specifically at the tertiary site. The resulting isobutylene oxide retains none of the label. All of it is found in the diphenyl sulfoxide. The preference for loss of the tertiary hydroxyl oxygen is consistent with a pathway in which C–O bond scission occurs at the site offering greater stabilization of developing positive charge.

(19) The loss of hydroxyl proton to base in transition states **12** and **15**, rather than in a preceding step, is suggested by analogy to the mechanism for the conversion of ethylene chlorohydrin to ethylene oxide established by C. G. Swain, A. D. Kelley, and R. F. W. Bader, *J. Amer. Chem. Soc.*, **81**, 2353 (1959).



The choice between hydroxyl oxygens in unsymmetrical glycols in the ligand exchange reaction enroute to epoxides cannot always be made by considering only relative stabilities of the two possible carbonium ions, however. The secondary hydroxyl is lost rather than the tertiary in the reaction of 3β-chlorocholestane-5α,6β-diol (**21**) leading to epoxide **22**, a result consistent with

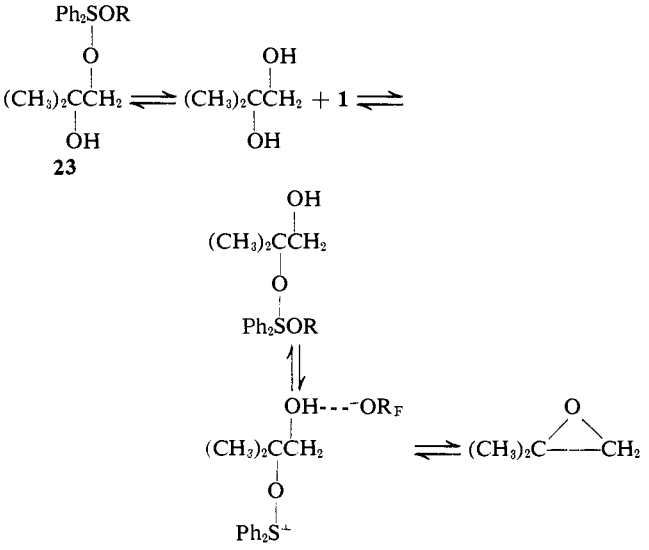


a choice of ligation sites based on steric considerations.[20]

A closer examination of the relative rates listed in Table II discloses evidence that both steric effects and electronic stabilization of centers of transition state positive charge are important determinants of rate in these reactions. The latter effect clearly predominates in determining the 910-fold faster reaction of pinacol compared with ethylene glycol. On the other hand,

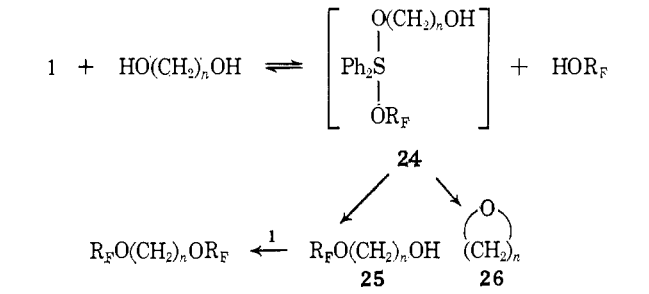
(20) (a) This parallels observations of the exclusive formation of a monoacetate ester[7] at the 6β position of **21** and of monomethane sulfonate formation at the 6β position of a 5α,6β-steroid diol: R. P. Graber, M. B. Meyers, and V. A. Landeryou, *J. Org. Chem.*, **27**, 2534 (1962). (b) Tosylate ester formation shows a preference for secondary over tertiary hydroxyl sites: J. Jacobus, *ibid.*, **38**, 402 (1973), and references cited therein.

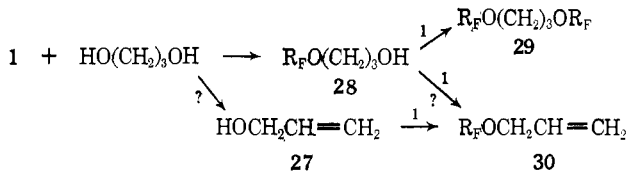
steric effects introduced upon ligation to sulfur must be important in slowing the 2,3-diphenylbutane-2,3-diols relative to pinacol. A statistical factor of 2 favors pinacol, with two tertiary centers, over isobutylene glycol, with only one. The additional factor of 9 deceleration seen for isobutylene glycol could reflect the tying up of isobutylene glycol in the sterically favored but unreactive complex **23**, an intermediate shown by



the oxygen-18 tracer experiments not to lie on the reaction pathway leading to epoxide. A better understanding of the factors influencing the choice of ligation sites of unsymmetrical glycols in the transition states leading to epoxides must await the results of further studies.

Although giving lower yields of cyclization products, 1,3-, 1,4-, and 1,5-diols react with **1** to give cyclic ethers (oxetanes, tetrahydrofurans, and tetrahydropyrans), along with open-chain ethers or (in the case of 1,3-diols) elimination products. As n becomes larger, the collapse of **24** to **26** becomes less favored relative to formation of **25**. Under standard conditions yields of cyclic ethers decreased in the order of product ring size $3 > 5 > 6 > 4 \approx 7$. These yields of cyclic ethers fall in a familiar pattern reflecting the influences of ring strain and entropy of ring formation in intramolecular displacement reactions.[21] The highly unfavored intramolecular nucleophilic participation of the hydroxyl group of **24** ($n = 3$) upon treatment of 1,3-propanediol with **1** is reflected in the failure to produce oxetane. Instead, ethers **29** and **30** were formed in 39 and 31% yields. Allyl ether **30** could have arisen from reaction





of **1** with either **27** or **28**. Enhanced acidity of the 2-methylene protons due to the inductive effect of the bis(hydroxymethyl) groups in 1,3-propanediol or of the fluoroalkoxymethyl group of **28** would favor olefin formation. When structural features preclude olefin formation in 1,3-diols, or when substitution β to the hydroxyl group makes unsymmetrical ether formation slow (reminiscent of the relative inertness of neopentyl alcohol toward reaction with **1**[5]), oxetane formation becomes dominant. Furthermore, it is well known that *gem*-dialkyl substituents contribute greatly to the entropy of activation for ring closures leading to oxetanes.[21a] These factors contribute to the result that 2,2-dimethylpropane-1,3-diol is converted by **1** in 87% yield to 3,3-dimethyloxetane. This "*gem*-dialkyl effect" has been invoked to explain why the relative rates of base-catalyzed ring closure of substituted ethylene chlorohydrins are greatly enhanced over that of unsubstituted ethylene chlorohydrin.[22] This phenomenon may in part be responsible for the relative rate data of Table II; in particular it could contribute to the increase in rate of reaction of pinacol relative to isobutylene glycol. Since for substituted diols acceleration attributed to carbonium ion stabilization may parallel the rate enhancement of epoxide formation by the *gem*-dialkyl effect, both may play a role in the observed order of rates in Table II.

Conclusion

The yields in Table III illustrate the high overall synthetic utility of **1** in the formation of cyclic ethers. The yields of epoxides compare favorably with alternate two-step conversions. Our procedure for the preparation of 3,3-dimethyloxetane is clearly superior to a reported preparation of 3,3-dimethyloxetane in 12–57% yield which required introduction of 2,2-dimethyl-3-bromo-1-propanol to an alkaline medium and distillation from 95–180°.[23] The DMSO-catalyzed dehydration of 1,4-, 1,5-, and 1,6-diols to cyclic ethers used by Traynelis, *et al.*,[24] fails for 1,3-diols. A more common procedure used to prepare oxetanes is the base-catalyzed ring closure of γ-chloropropanols.[25]

The excellent yield of tetrahydrofuran (THF, 72%) from the treatment of 1,4-butanediol with **1** compares well with alternate synthetic pathways leading from 1,4-diols to THF derivatives.[24,26] The room temperature conversion of 1,4-butanediol to THF by **1** is distinctly more attractive than the lengthy reflux periods in DMSO[24,26] or the high temperatures (165–180°) of alumina-catalyzed dehydrations.[24]

(21) (a) A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 103–112; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1956, pp 104–165.

(22) H. Nilsson and L. Smith, *Z. Phys. Chem., Abt. A*, **166**, 136, (1933). Also see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 189, and ref 20.

(23) S. Searles, Jr., R. G. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959).

(24) V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

(25) For example, see C. R. Noller, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1965, pp 835–837, for a preparation of oxetane in 42–44% yield.

(26) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

In the case of *cis*-2-butene-1,4-diol, which is structurally disposed toward ring closure, treatment with **1** gave 84% of 2,5-dihydrofuran. The DMSO dehydration method gave only polymeric material.[26] Dehydration over alumina gives good yields of 2,5-dihydrofuran[27] but requires refluxing at elevated temperatures for extensive periods.

Treatment of 1,5-pentanediol and diethylene glycol with **1** gave 39 and 40% yields of tetrahydropyran and dioxane. Dehydration of 1,5-pentanediol by heating in DMSO at 190° for 24 hr gave a 47% yield of tetrahydropyran.[24] The method of Franke,[28] as applied by Traynelis, *et al.*,[24] involving heating the diol in 50% H_2SO_4, gave 76% tetrahydropyran. Thus, synthetically useful yields of six-membered ring cyclic ethers are available *via* the treatment of the respective diol with **1** under mild conditions.

Oxepane formation does not occur by treatment of 1,6-hexanediol with **1**. Instead, acyclic ether formation occurs quantitatively.

Acknowledgment. This work was supported in part by the National Science Foundation (GP 30491X and grants for the purchase of a 220-MHz nmr spectrometer and a Fourier transform spectrometer for carbon-13) and in part by the National Institutes of Health (CA 13963 and grants, CA 11388 and GM 16864, for the purchase of instrumentation for mass spectrometry).

(27) M. Strohmeyer, U. S. Patent 3,165,536 (1965), *Chem. Abstr.*, **62**, 11783*e*, 14633*f* (1965).
(28) A. Franke and A. Kroupa, *Monatsh. Chem.*, **69**, 167 (1936).

Photodehydrocyclizations in Stilbene-Like Compounds. IX.[1] 1,2-Phenyl Shifts in the Cyclization of 1-Phenylpentahelicenes

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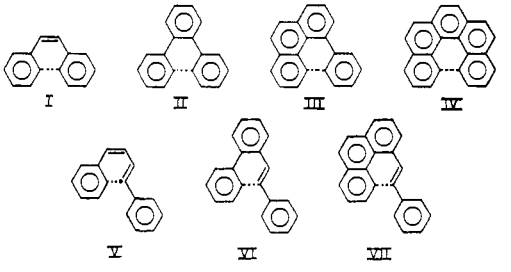
Abstract: Photodehydrocyclization of 8′-phenyldi-β-naphthylethylene (XI) gives rise to two monocyclization products, *viz.*, 10-phenylnaphtho[1,2-*a*]anthracene (XII) and 1-phenylpentahelicene (10-phenyldibenzo[*c*,*g*]phenanthrene) (VIII), and to 42% benzocoronene (IX). It appeared that IX is formed *via* VIII. It is shown that the first step of this reaction is the photocyclization to XXXIII. On oxidation it forms a radical XXXVII which can undergo a 1,2-phenyl radical shift. After a second oxidation step 7-phenylbenzo[*ghi*]perylene (XL) is formed which undergoes a rapid photodehydrocyclization into the benzocoronene. The more general applicability of the reaction was shown by the photocyclization of some derivatives of XI into substituted benzocoronenes.

Photodehydrocyclizations belong to the best known photoreactions and have appeared to be of great value in the synthesis of many polynuclear aromatics (*e.g.*, helicenes). Since the discovery of the photoconversion of stilbene (I) into phenanthrene (dotted line in I) this type of reaction has extensively been investigated on many stilbene-like compounds, and good insight has been gained into the reactivity of these compounds in photocyclizations.[2]

Meanwhile a quite similar reaction has been found in compounds in which part of the olefinic moiety in stilbene has been incorporated into an aromatic system, *viz.*, in ortho diaryl aromatics like *o*-terphenyl[3] (II), appropriate aryl substituted aromatics like 4-phenylphenanthrene[4] (III) or fully condensed aromatics like pentahelicene[5] (IV).

Furthermore, compounds in which one of the terminating aryl residues in I, II, or III has been replaced by an arylvinyl group (*e.g.*, styryl) as in 1,4-diphenylbutadiene[6] (V), *o*-styrylbiphenyl[7] (VI), and 4-styrylphenanthrene[8] (VII) give also analogous cyclizations on irradiation.



With several ortho-substituted stilbene-like compounds it has been demonstrated that the presence of alkyl groups or halogen atoms at ring positions involved in the cyclization step does not prevent ring closure.[9,10] Only in one case has migration of an ortho

(1) Part VIII: see W. H. Laarhoven and M. H. de Jong, *Recl. Trav. Chim. Pays-Bas*, **92**, 651 (1973).
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