(m, 5 H), 8.61 (dd, 1 H, J = 8 Hz, J' = 2 Hz), 8.75 (m, 1 H), 9.05 (d, 1 H, J = 7 Hz); ^{13}C NMR (D_2O) δ 26.9, 48.3, 58.5, 127.0, 127.5, 129.3, 131.4, 140.2, 147.1, 147.6, 149.8, 150.9, 153.2; UV (water) λ_{max} 273 nm.

Anal. Calcd for $C_{13}H_{14}N_2SO_3$: C, 56.11; H, 5.04; N, 10.07. Found: C, 55.90; H, 5.13; N, 9.90.

Supplementary Material Available: IR spectra for compounds **4a** and **6** and mass spectra for compounds **6** and **7** (1 page). Ordering information is given on any current masthead page.

Synthesis of Substituted 1,4-Oxathianes. Mechanistic Details of Diethoxytriphenylphosphorane- and Triphenylphosphine/Tetrachloromethane-Promoted Cyclodehydrations and ^{13}C NMR Spectroscopy

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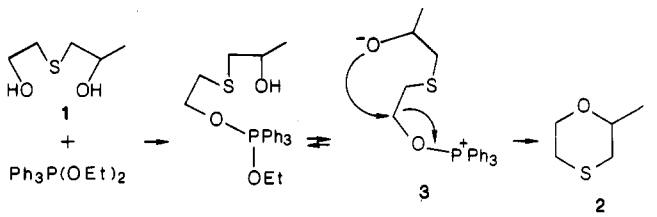
Diethoxytriphenylphosphorane (DTPP) initiates stereospecific cyclodehydrations of 2,2′-bis(hydroxyethyl) sulfides to the corresponding 1,4-oxathianes in a single step (70–85%) by GLC and ^{13}C NMR analyses. The mechanistic details of Ph_3P/CCl_4- and $Ph_3P(OEt)_2$-promoted cyclodehydrations are probed by specific deuterium labeling in combination with ^{1}H and ^{13}C NMR spectroscopy. Carbon-13 NMR shift correlations, which are valuable for stereochemical and conformational assignments of substituted 1,4-oxathianes, are also reported.

Substituted 1,4-oxathianes are important precursors in the synthesis of biologically significant 1,4-oxathiins, which are themselves useful as fungicides and pesticides.[1] In addition, stereochemical and conformational descriptions of substituted 1,4-oxathianes and their *S*-oxides have attracted considerable attention.[2] While several preparative methods are available for their construction, few exhibit the synthetic versatility suitable for strategic placement of various substituents within the basic heterocycle.[3]

Results of recent studies from our laboratories have demonstrated that diethoxytriphenylphosphorane (DTPP) is useful for converting diols to cyclic ethers,[4] α,ω-mercapto alcohols to cyclic sulfides,[5] and β-amino alcohols to aziridines.[6] Therefore, we envisioned that DTPP would efficiently convert substituted 2,2′-bis(hydroxyethyl) sulfides to 1,4-oxathianes. It seemed reasonable that this objective could also be accomplished with high regio- and stereospecificity since the mechanism of cyclodehydration of diols with DTPP does not involve steps that would compromise the stereochemical integrity of critical stereocenters.[4]

Scheme I



Cyclodehydration. The specific formulation described in Scheme I represents the synthetic format as well as the mechanistic rationale for DTPP-promoted cyclodehydration of 1,5-diols. Specifically, reaction of 2-hydroxypropyl 2-hydroxyethyl sulfide (1) [prepared by regiospecific mercaptide (i.e., $^-SCH_2CH_2OH$) ring opening of propylene oxide][7] with DTPP (40 °C, 48 h) affords 2-methyl-1,4-oxathiane (**2**; 80% by GLC and ^{13}C NMR).

From Scheme I, cyclodehydration of diol **1** with DTPP requires initial phosphoranylation of the primary hydroxyl group[8] followed by loss of ethanol to afford betaine **3**, the quintessential intermediate governing cyclization. In fact, the stereospecific syntheses of *trans*- and *cis*-2,3-dimethyl-1,4-oxathiane (*trans*-**4**, *cis*-**4**) from reaction of *threo*- and *erythro*-2-hydroxy-3-[(2-hydroxyethyl)thio]-butane (*threo*-**5**, *erythro*-**5**) with DTPP (see Table I) strongly support initial phosphoranylation of the primary hydroxyl and subsequent intramolecular displacement of triphenylphosphine oxide (TPPO) by secondary alkoxide ion from an intermediate synonymous to **3** (vide infra).

Generally, the cyclodehydration of 2,2′-bis(hydroxyethyl) sulfides with DTPP gives substituted 1,4-oxathianes in yields ranging from 66 to 85% by GLC and ^{13}C NMR analyses (Table I). These results are especially significant when comparisons are made with other popular prepara-

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(2) (a) Frieze, D. M.; Evans, S. A., Jr. *J. Org. Chem.* **1975**, *40*, 2690. (b) Frieze, D. M.; Hughes, P. H.; Merrill, R. L.; Evans, S. A., Jr. *J. Org. Chem.* **1977**, *42*, 2206. (c) Rooney, R. P. Ph.D. Thesis, University of North Carolina, 1980. (d) Carretero, J. C.; Garcia Ruano, J. L.; Radriquez, J. H. *Tetrahedron Lett.* **1984**, *25*, 3029–3032. (e) Lee, D.; Keifer, J. C.; Rooney, R. P.; Garner, T. B.; Evans, S. A., Jr. *J. Org. Chem.* **1979**, *44*, 2580. (f) Evans, S. A., Jr.; Goldsmith, B.; Merrill, R. L., Jr.; Williams, R. E. *J. Org. Chem.* **1977**, *42*, 438. (g) Zefirov, N. S.; Balgoveshchensky, U. S.; Kazimirchik, I. V.; Surova, N. S. *Tetrahedron* **1971**, *27*, 3111. (h) Hronowski, J. J.; Szarek, W. A. *J. Med. Chem.* **1982**, *25*, 522–526. (i) Lopez Aparicio, F. J.; Zorrilla Benitez, F.; Santoyo Gonzalez, F. *Carbohydr. Res.* **1982**, *110*, 195–205. (j) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 3554–3572. (k) Mattay, J.; Dittmer, C. *J. Org. Chem.* **1986**, *51*, 1894–1897.

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(5) Robinson, P. L.; Kelly, J. W.; Evans, S. A., Jr. *Phosphorus Sulfur*, in press.

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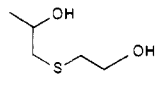
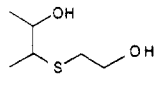
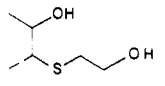
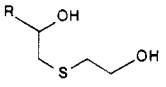
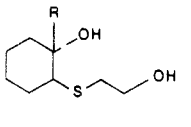
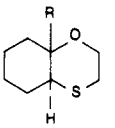
(7) (a) Owen, L. N.; Smith, P. N. *J. Chem. Soc.* **1951**, 2973. (b) Rooney, R. P.; Evans, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 180–183.

(8) Kelly, J. W.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7681–7685.

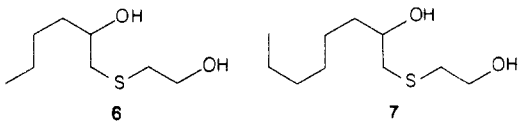
0022-3263/87/1952-0525$01.50/0

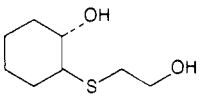
Table I. Cyclodehydration of 2,2′-Bis(hydroxyethyl) Sulfides with DTPP

diol	oxathiane	yield,[a,b] %
 1	 2	80 (44)[b]
 *erythro*-5	 *cis*-4	80
 *threo*-5	 *trans*-4	70
 19, R = C_6H_5	 14	66 (44)
18, R = $CH_2(CH_2)_6CH_3$	15	70 (54)
 17, R = CH_3	 16	80 (44)
8, R = H	9	85 (47)

[a] The yields are determined by both GLC and ^{13}C NMR analyses using retention times and chemical shifts from authentic samples. [b] Isolated yields derived from medium-pressure chromatographic separation of desired material from the reaction mixture.

tive routes to 1,4-oxathianes. For example, cyclodehydration of diol **1** with orthophosphoric acid gives oxathiane **2** in only 17%[9] while cyclodehydration of diols **6**–**8** with *p*-toluenesulfonic acid affords the appropriate

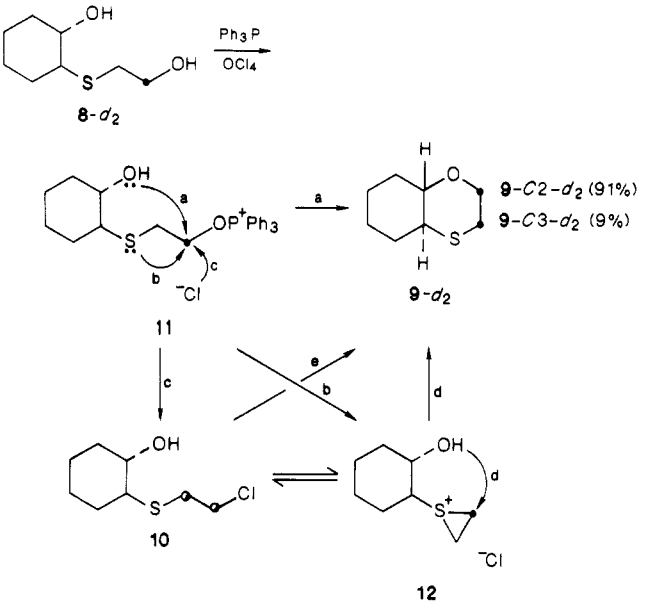

6 7


8

oxathianes in 22, 16, and 17% yields, respectively.[10] Finally Garcia Ruano and co-workers report a five-step stereospecific synthesis of *trans*-**4** from *threo*-**5** and *erythro*-**5**,[2d] respectively. By contrast, reactions of *threo*-**5** and *erythro*-**5** with DTPP afford separately *trans*-**4** and *cis*-**4**, each in >98% diastereomeric excess with chemical yields of 70 and 80%, respectively, by ^{13}C NMR and GLC analyses.

DTPP vs. PPh_3/CCl_4: Mechanistic Insights. In a previous report,[11] we had examined the reaction between *trans*-2-hydroxycyclohexyl 2-hydroxyethyl sulfide (**8**) and reagent PPh_3/CCl_4, which gave *trans*-2-hydroxycyclohexyl 2-chloroethyl sulfide (**10**) as the predominant product (73%) along with 6% of *trans*-1,4-oxathiadecalin (**9**). Diol **8** constituted the remainder (21%) of the reaction mixture. We determined by specific deuterium labeling (SCH_2CD_2OH, 8-d_2) and ^1H NMR analysis that the

Scheme II. Mechanistic Scheme for 9-*C2*-d_2 to 9-*C3*-d_2 Ratio in 9-d_2[a]



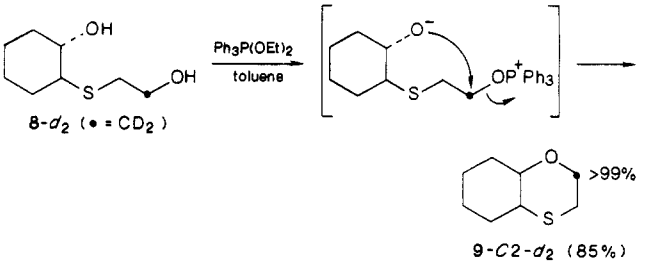
[a] Key: ●, CD_2; ⊖, $CD_2/2$.

presence of thiiranium ion intermediate **12** (Scheme II) was essential in rationalizing the equal deuterium distribution in the two methylene groups of the 2-chloroethyl sulfide fragment arising during the conversion of **8** → **10**.[11,12]

Using ^1H NMR techniques, we have now also determined the extent and position of deuterium in oxathiadecalin **9**-d_2, the minor product resulting from reaction of 8-d_2 with Ph_3P/CCl_4. Two regioisomers are obtained, **9**-*C2*-d_2 (91%) and **9**-*C3*-d_2 (9%), and these results imply that at least 18% of this regioisomeric mixture must experience thiiranium ion **12** (Scheme II).

DTPP-promoted cyclodehydration of diol **8** affords an excellent yield of oxathiadecalin **9**, and an attempt to assess the comparative importance and consequences of the cyclization chemistry involving possible thiiranium ion intermediates initiated by both the Ph_3P/CCl_4 and DTPP reagents seemed quite appropriate. Reaction of *trans*-2-hydroxycyclohexyl 2-hydroxyethyl-d_2 sulfide (8-d_2) with DTPP affords only **9**-*C2*-d_2! There is no ^1H or ^{13}C NMR evidence for deuterium incorporation at C3 in heterocycle **9** (see Figure 2). These results support a simple displacement of TPPO by the C1 alkoxide group and shed valuable light on the possible origin and significance of thiiranium ion **12**.

An examination of Scheme II reveals that formation of 9-d_2 from reaction of 8-d_2 and Ph_3P/CCl_4 is possible via several routes, and attempts to distinguish between them require a brief comment. First, we have determined that



formation of **9**-*C2*-d_2 or **9**-*C3*-d_2 exclusively via route e is unlikely because equilibration of the deuterium label be-

(9) Black, D. K. *J. Chem. Soc. C* **1966**, 1708.
(10) Dranou, V. I.; Nigmanillina, P. F.; Krivonogou, V. P.; Aminer, I. Kh.; Gakin, E. G.; Nirinn, Yu, E. *Bull. Acad. Sci USSR* **1977**, *26*, 1010.
(11) Barry, C. N.; Baumrucker, S. J.; Andrews, R. C.; Evans, S. A., Jr. *J. Org. Chem.* **1982**, *47*, 3980–3983.
(12) Billington, D. C.; Golding, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 208.

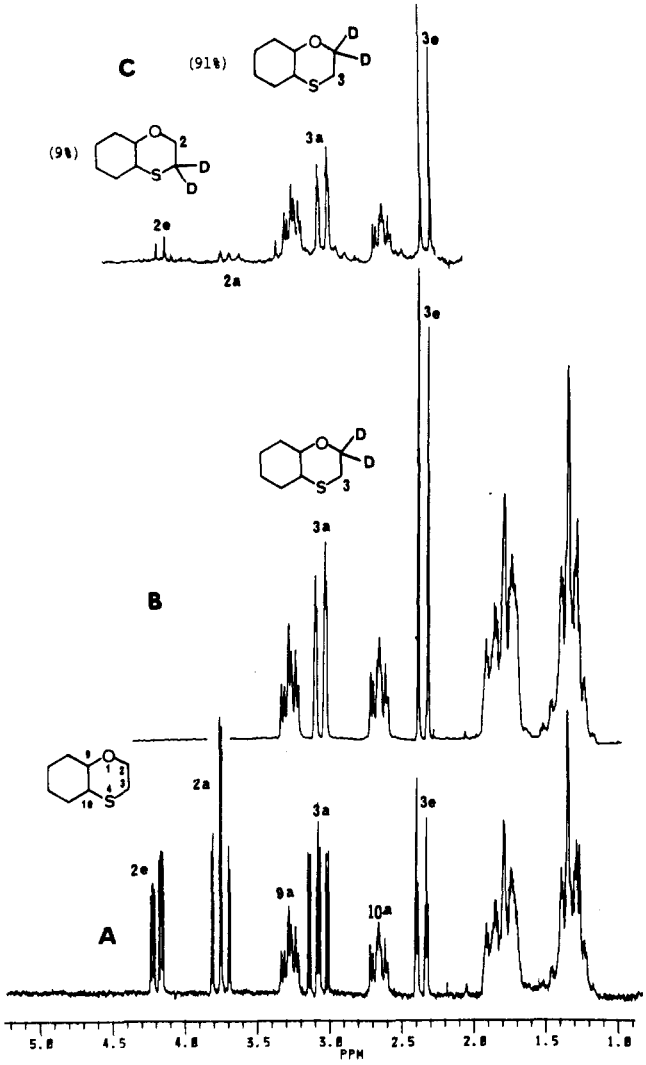


Figure 1. ^{1}H NMR spectra: (A) **9** without deuterium; B, **9**-*C2*-d_2 from cyclodehydration of **8**-d_2 with DTPP; C, **9**-*C2*-d_2 (91%) and **9**-*C3*-d_2 (9%) from cyclodehydration of **8**-d_2 with Ph_3P/CCl_4.

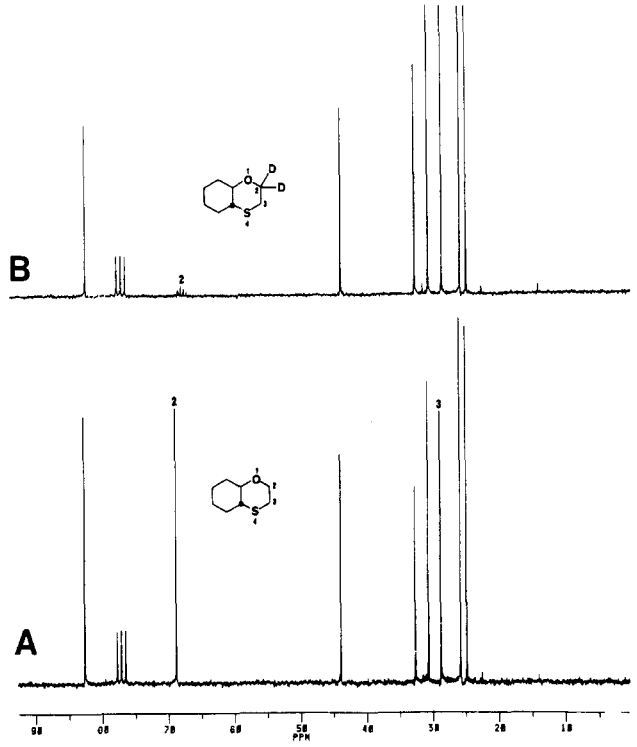


Figure 2. ^{13}C NMR spectra: (A) **9** in $CDCl_3$ solvent (25 °C) from cyclodehydration of **8** with DTPP; B, **9**-*C2*-d_2 in $CDCl_3$ solvent (25 °C) from cyclodehydration of **8**-d_2 with DTPP.

Table II. ^{13}C NMR Shifts (δ) of 1,4-Oxathianes[a]

1,4-oxathiane	C2	C3	C5	C6	C2 Me	C3 Me
2	74.11	32.73	26.21	69.13	22.10	
14	80.41	33.22	26.32	69.80		
15	78.15	36.40	26.51	69.21		
trans-**4**	80.42	39.78	28.92	68.85	19.59	17.28
cis-**4**	77.51	36.48	22.65	68.59	19.32	14.10

[a] See the Experimental Section for details on acquisition of ^{13}C NMR data. [b] See Table I for the appropriate structures of numbered compounds.

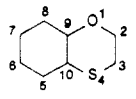
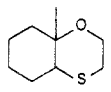
tween the two methylene groups in the 2-chloroethyl fragment of sulfide **10** occurs faster than formation of oxathiadecalin **10** from **9**. For example, an authentic sample of **10** gives <4% oxathiadecalin **9** when heated for 48 h at 70 °C, which is 2.5 times longer than the reaction time established for **8** and Ph_3P/CCl_4. Route a alone would, of course, be inconsistent with the experimental findings (i.e., formation of **9**-*C3*-d_2). Sequential routes b and d are also unlikely since reaction of diol **8**-d_2 with $Ph_3P(OEt)_2$, giving presumably an oxyphosphonium ion similar to intermediate **11**, affords >99% **9**-*C2*-d_2 (vide supra). In order to adequately rationalize formation of the 9% **9**-*C3*-d_2, at least 18% of **9**-d_2 must arise through path c, giving initially **10**, which equilibrates the deuterium label through thiiranium ion **12** (i.e., sulfur-assisted displacement of chloride ion). C1 Hydroxyl trapping of thiiranium ion (path d) and/or hydroxy displacement of chloride ion (path e) would lead to equal amounts of **9**-*C2*-d_2 and **9**-*C3*-d_2. We believe that the remaining 82% of **9**-*C2*-d_2 results from path a.

One final conclusion emerges from these findings. The efficiency of the DTPP-promoted cyclodehydration of **8** to **9** is sparked by favorable *alkoxide* displacement of triphenylphosphine oxide (TPPO) as opposed to the Ph_3P/CCl_4-initiated cyclodehydration of **8**, which requires neutral *hydroxy group* displacement of TPPO to afford **9**. Presumably, the low yield of **9** in the Ph_3P/CCl_4 reactions results from the fact that Cl^- is certainly not basic enough to remove a proton from the hydroxy group; consequently, the more nucleophilic chloride ion displaces TPPO from **11** to give **10**.

Carbon-13 NMR. No systematic compilation of ^{13}C NMR data has appeared for substituted 1,4-oxathianes, and it seems appropriate to make a few comments based on the NMR data we have obtained.[13] Table II lists the ^{13}C resonances for C2, C3, C5, C6, and, where appropriate, the methyl groups of some 1,4-oxathianes. From the ^{13}C NMR shifts for parent 1,4-oxathiane (**13**) as reference, some potentially useful trends in ^{13}C NMR substituent-induced shifts become evident. First, 1,4-oxathiane exhibits ^{13}C NMR resonances at δ 68.5 for C2,C6 and 27.5 ppm for C3,C5. Relative to 1,4-oxathiane, 2-methyl-1,4-oxathiane (**2**) exhibits downfield shifts of 4.6 (C2) and 5.7 ppm (C3), due to α- and β-methyl effects, respectively.[14] Replacing the C2 methyl substituent with a phenyl group (cf. **14**) causes further downfield shifts of 6.3 (C2) and 0.5 ppm (C3) relative to those in **2**. The shift difference at C2 between **2** and **14** are attributable to two additional β effects arising from the two ortho carbons of the phenyl

(13) See, however: Rooney, R. P.; Evans, S. A., Jr. *J. Org. Chem.* **1980**, *45*, 180–183.
(14) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972; Chapter 5, pp 128–205.

Table III. ^{13}C NMR Shifts (δ) of 1,4-Oxathiadecalins[a]

1,4-oxathiadecalin	C2	C3	C5	C6	C7	C8	C9	C10	CMe
 9	68.88	28.86	30.75	25.86	24.97	32.74	82.68	44.00	
 16	61.09	29.15	30.08	26.41	23.32	39.20	74.21	49.62	14.67

[a] See the Experimental Section for details on acquisition of ^{13}C NMR data.

ring. Finally, 2-octyl-1,4-oxathiane (**15**) shows a similar trend in shifts where C2 and C3 are shifted downfield 4.0 and 3.7 ppm, respectively, compared to those in **13**.

For the 2,3-disubstituted oxathianes, diastereomeric *cis*-**4** and *trans*-**4** are particularly interesting. For both isomers, the ^{13}C resonances at C2 and C3 are 10–15 ppm downfield of **13**, due of course, to the α- and β-methyl effects on each carbon. Some interesting spectral features become discernible by comparing the shifts of the two diastereomers. For example, all of the ring carbons in *cis*-**4** are consistently upfield by ca. 3 ppm relative to those in *trans*-**4**. This trend can be adequately explained from shielding interactions resulting from γ-steric shift effects and subsequent ring distortions, both of which are known to induce shielding of the participating atoms.[15] In *cis*-**4**, one of the two methyl groups must be oriented axially and should experience γ-gauche interactions with the methylene groups at C5 and C6.

The trans diastereomer, *trans*-**4**, exists in the preferred chair conformation where the C2 and C3 methyl groups occupy the diequatorial conformation. Here, γ-gauche interactions between the methyls and the ring methylenes are impossible, and the methyl carbons are expected to resonate downfield of those in *cis*-**4**. Interestingly, all of the carbon resonances for *cis*-**4** occur upfield of *trans*-**4**, and the shift differences are smallest at C2 and the attached methyl substituents (0.25 and 0.29 ppm, respectively). These results imply that the preferred conformation of *cis*-**4** has the C3 methyl group oriented axially while the C2 methyl occupies the equatorial conformation.

Not unexpectedly, 1,4-oxathiadecalin **9** displays large downfield shifts at C2 (14.2 ppm) and C3 (17 ppm) relative to oxathiane **13** caused by the combination of one α and two β effects.

The ^{13}C NMR spectrum of *trans*-9-methyl-1,4-oxathiadecalin (**16**) is also noteworthy (Table III). An additional α effect at C9 (from the CH_3 group) would be expected to induce a downfield shift of approximately 5 ppm relative to that observed in **9**; however, an upfield shift of 8.48 ppm is found. Clearly, the C9 methyl group must occupy the axial position when the ring juncture is trans, as dictated by the method of synthesis. Consequently, there are three γ-gauche interactions involving the axial methyl group attached to C9 which leads to a large compression effect $CH_3 \rightarrow$ C9 and subsequent large upfield shift at C9. This shielding effect can also be observed at C2, C5, and C7, which are shifted upfield by 8.69, 0.74, and 1.65 ppm, respectively, compared to the respective carbon NMR shifts in **9**. The C9 methyl resonance at δ 14.7 in **16** is also upfield of the methyls in *cis*- and *trans*-**4**, with the exception of the axial C3 CH_3 group in *cis*-**4**. Finally, C10 should not experience steric compression from the C9 methyl group, but it does "feel" the β effect and is shifted downfield by 4.6 ppm relative to the shift in **9**.

In conclusion, we have reported a high-yield, stereospecific synthesis of C2- and C3-substituted 1,4-oxathianes utilizing DTPP and the appropriate 2,2′-bis(hydroxyethyl) sulfides. The mechanisms for formation of oxathiane **9** using DTPP and Ph_3P/CCl_4 have been compared by using specific deuterium labeling. We have also examined the ^{13}C NMR spectra of several substituted 1,4-oxathianes to establish a rational and convenient basis for their identification and stereochemical assignments. We have shown that while α and β substituent effects are important, compression effects are also significant, particularly when the perturbing substituent occupies the axial conformation in the 1,4-oxathiane ring.

Experimental Section

Melting points were measured in open capillary tubes with a Mel-Temp apparatus and are uncorrected. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at ambient temperature (15–28 °C) on a Bruker-IBM Model AC-200 NMR spectrometer. ^1H and ^{13}C NMR shifts are reported in deuteriochloroform solvent relative to tetramethylsilane (Me_4Si). Gas–liquid chromatographic (GLC) analyses were obtained on a Hewlett-Packard Model 5754B research gas chromatograph, using a stainless-steel column (0.125-in. i.d. × 10-ft height, packed with 20% Carbowax 20M on Chromosorb W-HP-AW-DMCS, 100–200 mesh). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Diethoxytriphenylphosphorane is easily prepared by the oxidation addition of diethyl peroxide to triphenylphosphine and has been reported elsewhere.[4-6] All 2,2′-bis(hydroxyethyl) sulfides were prepared by mercaptide ring opening of the corresponding epoxides.[7,16] All epoxides are commercially available except 1-methyl-1,2-cyclohexene oxide, which was provided by our colleague Paul J. Kropp (University of North Carolina). *erythro*- and *threo*-**5** were obtained from J. R. Garcia Ruano (University of Madrid). *trans*-2-Hydroxycyclohexyl 2-hydroxyethyl-d_2 sulfide (**8**-d_2) was prepared by reduction ($LiAlD_4$) of *trans*-2-hydroxycyclohexyl carboethoxymethyl sulfide.[11] Reaction of **8**-d_2 with Ph_3P/CCl_4 has been reported.[11]

Reaction of Diols with DTPP. The reaction of 2-hydroxypropyl 2-hydroxyethyl sulfide (**1**) with DTPP is representative of the general procedure. In a sealable 10-mm NMR tube were added **1** (272 mg, 2.0 mmol), DTPP (3.0 mL, ca. 0.8 M, 2.4 mmol), and 0.5 mL of benzene-d_6 (used as an NMR lock solvent) under an argon atmosphere. The NMR tube was cooled to −78 °C (acetone–dry ice bath), evacuated, and sealed by flame. The tube was allowed to warm to ambient temperature and then heated at 40 °C for 48 h. ^{31}P NMR analysis indicated the complete disappearance of DTPP (δ −55.1) and formation of Ph_3PO (δ 25.2). GLC and ^{13}C NMR analyses indicated an 80% conversion to oxathiane **2**; isolation of the product was accomplished by flash chromatography using 5% ethyl acetate and 95% hexanes as eluent to afford 102 mg (44%) of homogeneous **2**.

2-Hydroxypropyl 2-hydroxyethyl sulfide (1): ^1H NMR ($CDCl_3$) δ 1.20 (d, 3 H) 2.42 (d, 1 H), 2.52 (d, 2 H), 2.70 (m, 2 H),

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3.21 (s, 1 H), 3.74 (t, 2 H), 3.85 (m, 1 H); lit.[9] ^{1}H NMR (CD_3OD) δ 1.17 (d), 2.60 (m), 3.66 (s), 4.74 (s); ^{13}C NMR ($CDCl_3$) δ 21.95, 35.22, 41.07, 61.03, 66.43.

2-Phenyl-1,4-oxathiane (14): ^{13}C NMR ($CDCl_3$) δ 26.32, 33.22, 69.80, 80.39; ^{13}C NMR ($CDCl_3$) δ 26.38, 33.23, 69.78, 80.39.[17]

2-Octyl-1,4-oxathiane (15): mp 4-5 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 7 Hz, CH_3), 1.27 [br s, 10 H, $(CH_2)_5$], 2.30 (m, 2 H), 2.61 (m, 1 H), 2.87 (m, 1 H), 3.45-3.59 (br d, 1 H, OC*H* octyl), 1.30-1.50 [m, 4 H, $(CH_2)_2$], 3.73 (td, 1 H, J = 2.8, 12.0 Hz, C*H*O octyl), 4.22 (dt, 1 H, J = 2.8, 12.0 Hz, CHO octyl); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.61, 25.22, 26.55, 29.20, 29.46, 29.53, 31.37, 31.81, 36.40, 69.22, 78.15. Anal. Calcd for $C_{12}H_{24}OS$: C, 66.76; H, 11.11; S, 14.81. Found: C, 66.76; H, 11.16; S, 15.72.

***trans*-9-Methyl-1,4-oxathiadecalin (16)**: mp 7-8 °C; ^{1}H NMR ($CDCl_3$) δ 1.43, (s, 3 H, CH_3), 1.45-1.82 [m, 8 H, $(CH_2)_4$], 2.37 (dt, 1 H, J = 2.1, 13.3 Hz, C*H*S), 2.91-3.11 (m, 2 H, CH_2S), 3.82 (dq, 1 H, J = 1.9, 12.3 Hz, C*H*O), 4.04 (td, 1 H, J = 2.3, 12.3 Hz). Anal. Calcd for $C_9H_{16}OS$: C, 62.79, H, 9.30; S, 18.60. Found: C, 62.61; H, 9.30; S, 19.17.

***trans*-2-Methyl-2-hydroxycyclohexyl 2-hydroxyethyl sulfide (17)**: mp 34.5-36.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.25-1.58 (m, 4 H), 1.66-1.87 (m, 3 H, CH_2, SCH_2CHH_e), 2.0-2.08 (m, 1 H, SCH_2CHH_a), 2.61-2.87 (m, 3 H, $CHSCH_2CH_3$), 3.34 (br s, 1 H, O*H*), 3.60 (br s, 1 H, O*H*), 3.74-3.85 (m, 2 H, CH_2OH); ^{13}C NMR ($CDCl_3$) δ 21.58, 22.95, 25.88, 32.43, 35.17, 39.87, 56.94, 61.20, 72.64. Anal. Calcd for $C_9H_{18}O_2S$: C, 56.84, H, 9.47; S, 16.84. Found: C, 56.52; H, 9.54, S, 16.78.

2-Hydroxydecyl 2-hydroxyethyl sulfide (18): mp 26-27 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 6.0 Hz, CH_3), 1.25 [m, 11 H, $(CH_2)_5CH$], 1.40-1.55 (br d, 3 H, $CHCH_2$), 2.70-2.82 (m, 3 H) 3.58-3.65 (br d, 1 H, C*H*OH), 3.72 (t, 2 H, J = 5.8 Hz, CH_2OH); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.51, 25.60, 29.13, 29.41, 29.50, 31.72, 35.51, 36.23, 39.84, 61.12, 70.32. Anal. Calcd for $C_{12}H_{24}O_2S$: C, 61.54; H, 11.11; S, 13.68. Found: C, 61.45; H, 11.32; S, 13.57.

2-Phenyl-2-hydroxyethyl 2-hydroxyethyl sulfide (19): mp 43-45 °C; ^{1}H NMR ($CDCl_3$) δ 2.5-2.9 (m, 4 H, CH_2SCH_2), 3.57-3.70 (br d, 2 H), 3.80-3.92 (br d, 2 H), 3.97 (dd, 1 H, J = 5.7, 8.1 Hz, C_6H_5CHOH), 7.36 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 35.56, 41.56, 61.26, 73.07, 125.85, 127.79, 128.83, 142.81. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.61; H, 7.07; S, 16.16. Found: C, 60.13; H, 7.15; S, 16.17.

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Syntheses and Chemistry of Some Dibenz[*c*,*e*]azepines

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5-Methyl-, 5,7-dimethyl-, and 5,7-diphenyl-substituted and unsubstituted 5*H*-dibenz[*c*,*e*]azepines were prepared by two general routes from [1,1'-biphenyl]-2,2'-dicarboxaldehyde. The unsubstituted dibenzazepine was converted into 1a,9b-dihydrophenanthro[9,10-*b*]azirine both by lithium diisopropylamide (LDA) and by UV irradiation. The disubstituted azepine derivatives failed, however, to undergo valence isomerization under such conditions. *N*-Benzylphenanthrene 9,10-imine was obtained directly from 2'-(bromomethyl)[1,1'-biphenyl]-2-carboxaldehyde and excess benzylamine. Aerial oxidation of 5,7-diphenyldibenz[*c*,*e*]azepine in the presence of 50% aqueous NaOH led, under phase-transfer conditions, to 5,7-diphenyldibenz[*c*,*e*]azepin-5-ol. Special structural features of this carbinol found by X-ray analysis are discussed.

In a previous paper[1] we postulated that polycyclic arene imines are active metabolites of mutagenic and carcinogenic hydrocarbons. The aziridines were assumed to be formed in vivo by interaction of cellular nitrogen nucleophiles with arene oxides followed by enzymatic ring closure of the resulting amino alcohols. Support for this hypothesis has recently been found by biological tests which demonstrated unusually high mutagenic potencies of all polycyclic arene imines[2,3] as well as direct correlation between their activities and those of the corresponding epoxides.[2] Since the synthetic routes developed, so far, for aromatic imines[1,4-14] failed to be applicable to a considerable number of representative derivatives of carcinogenic polycycles,[15] we found it imperative to further investigate their preparation by new methods. It seemed that an attractive approach to these polycyclic aziridines could be the valence isomerization of diaryl[*c*,*e*]azepines. The syntheses of the latter compounds have, however, been

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