230 mg of a 71/29 mixture of 2-(pent-4-enylidene)-1,3-dithiane (72% yield) and residual allyl diethyl phosphate, respectively: bp 100 °C (0.15 torr, Kugelrohr). A sample of the ketene dithioacetal collected by VPC had the following analytical data: ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.20 (6 H, m), 2.88 (4 H, m), 4.90–5.18 (7, 2 H), 5.60–6.05 (1 H, m), 5.92 (1 H, t, J = 7 Hz).

Anal. Calcd for $C_9H_{14}S_2$: C, 58.01, H, 7.57; S, 34.41. Found: C, 58.12; H, 7.59; S, 34.26.

γ Allylation of 2-Ethylidene-1,3-dithiane with 2,3-Dibromoprop-1-ene (Table II, Entry 3). The cuprous ketene dithioacetal **4** was prepared on a 1.14-mmol scale (vide supra) and alkylated with 2,3-dibromoprop-1-ene to provide 201 mg (68% yield) of 2-(4-bromopent-4-enylidene)-1,3-dithiane: bp <180 °C (0.02 torr, Kugelrohr); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 2.16 (2 H, m), 2.47 (4 H, m), 2.86 (4 H, br t, J = 6 Hz), 5.38 (1 H, d, J = 2 Hz), 5.57 (1 H, br s), 5.87 (1 H, t, J = 7 Hz); mass spectrum (70 eV) m/e (relative intensity) 266 (3, M^+), 264 (3, M^+), 187 (3), 185 (7), 147 (10), 146 (9), 145 (100), 86 (22), 71 (56).

Anal. Calcd for $C_9H_{13}S_2Br$: C, 40.75; H, 4.94. Found: C, 40.63; H, 5.12.

Acknowledgment. The financial support of the National Institutes of Health—National Cancer Institute (Grant CA 16432) and Hoffmann-LaRoche (Nutley) is greatly appreciated. The Bruker HX-270 NMR is supported by National Institutes of Health Grant 1-P07-PR00798 from the Division of Research Sources.

Registry No. 1a, 51102-62-6; **1b**, 6251-15-6; **1c**, 13879-93-1; **1d**, 32821-32-2; α-**2** (R = $(CH_2)_3$), 71118-36-0; α-**2** (R = CH_3), 71118-37-1; α-**2** (R = CH_2CH_3), 71118-38-2; α-**2** (R = $CH(CH_3)_2$), 71118-39-3; γ-**2** (R = $(CH_2)_3$), 71118-40-6; γ-**2** (R = CH_3), 71118-41-7; γ-**2** (R = CH_2), 71118-42-8; γ-**2** (R = $CH(CH_3)_2$), 71118-43-9; **3**, 71118-44-0; **4**, 71119-09-0; **5** (R = CH_2=$CBrCH_2$), 71118-45-1; **5** (R = HC≡CCH_2), 71118-46-2; **5** (R = (*Z*)-HDC=$CHCH_2$), 71118-47-3; **5** (R = (*E*)-CH_3CH=$CHCH_2$), 71118-48-4; **5** (R = (*Z*)-CH_3CH=$CHCH_2$), 71118-49-5; **5** (R = CH_2=$CHCHCH_3$), 71118-50-8; **5** (R = $(CH_3)_2C$=$CHCH_2$), 71118-51-9; **5** (R = CH_2=$CHC(CH_3)_2$), 71118-52-0; **5** (R = CH_2=$C(CH_3)CHCH_3$), 71118-53-1; **5** (R = CH_2=$C(CH_3)CH(CH_2)_3CH_3$, 71118-54-2; **5** (R = CH_3), 51102-63-7; 2-(2-bromo-2-propenyl)-2-vinyl-1,3-dithiolane, 71118-55-3; 2-allenyl-2-vinyl-1,3-dithiolane, 71118-56-4; 2-(3-deuterio-2-propenyl)-2-vinyl-1,3-dithiolane, 71129-29-8; 2-(2-butenyl)-2-vinyl-1,3-dithiolane, 71118-57-5; (*E*)-2-(2-butenyl)-2-vinyl-1,3-dithiolane, 71118-58-6; 2-(3-methyl-2-butenyl)-2-vinyl-1,3-dithiolane, 71118-59-7; 2-(1,1-dimethyl-2-propenyl)-2-vinyl-1,3-dithiolane, 71118-60-0; (*E*)-2-(4-methylhept-4-enylidene)-1,3-dithiolane, 71118-61-1; (*Z*)-2-(4-methylhept-4-enylidene)-1,3-dithiolane, 71118-62-2; (*E*)-2-(4-methylnon-4-enylidene)-1,3-dithiolane, 71118-63-3; (*Z*)-2-(4-methylnon-4-enylidene)-1,3-dithiolane, 71118-64-4; 2-methyl-2-vinyl-1,3-dithiolane, 64087-39-4; CH_2=$CHCH_2Br$, 106-95-6; CH_2=$CHCH_2OPO(OC_2H_5)_2$, 3066-75-9; CH_2=$CBrCH_2Br$, 513-31-5; HC≡CCH_2Br, 106-96-7; (*Z*)-HDC=$CHCH_2Br$, 60699-35-6; (*E*)-CH_3CH=$CHCH_2Br$, 29576-14-5; (*Z*)-CH_3CH=$CHCH_2Br$, 39616-19-8; (*E*)-CH_3CH=$CHCH_2OPO(OC_2H_5)_2$, 71118-65-5; CH_2=$CHCHBrCH_3$, 22037-73-6; CH_2=$CHCHOPO(OC_2H_5)_2CH_3$, 71118-66-6; $(CH_3)_2C$=$CHCH_2Br$, 870-63-3; $(CH_3)_2C$=$CHCH_2Cl$, 503-60-6; $(CH_3)_2C$=$CHCH_2OPO(OC_2H_5)_2$, 64135-15-5; CH_2=$CHC(CH_3)_2OPO(OC_2H_5)_2$, 71118-67-7; CH_2=$C(CH_3)CHOPO(OC_2H_5)_2CH_3$, 71138-56-2; CH_2=$C(CH_3)CHOPO(OC_2H_5)_2(CH_2)_3CH_3$, 71118-68-8; CH_3I, 74-88-4; CH_3OTs, 80-48-8; MeOD, 1455-13-6.

Use of Sulfite Esters To Establish Stereochemistry of Chiral Pinacols

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3,4-Dimethyl-3,4-hexanediol is a symmetrical pinacol with two chiral carbon atoms and therefore exists in a DL and a meso configuration. From the mixture of isomers obtained by the reduction of ethyl methyl ketone with magnesium, small amounts of one isomer of mp 52 °C can be separated on cooling;[1] the filtrate consists of a mixture of both isomers. Recently, this solid isomer was shown to have the DL configuration from the ^{1}H NMR spectra of its formaldehyde cyclic acetal.[2] Independently of this work, we have also established the stereochemistry of the solid diol by preparing its sulfite ester from the pinacol and thionyl chloride. This method is particularly attractive because the tetrahedral sulfur causes the meso pinacol to give two sulfite esters and the DL isomer only one, and the structures of the cyclic sulfite esters, separated by VPC, can then be confirmed from their NMR spectra.

Table I. Properties of Sulfite Esters of 3,4-Dimethyl-3,4-hexanediols

peak no.	a	b	chemical shifts, δ c	d	e
1	*Z*-meso	13.5	1.30	2.0–2.4	1.07 (J = 7.3 Hz)
2	DL	15.3	1.28	1.5–2.4	1.04 (J = 7.3 Hz)
			1.50		1.07 (J = 7.3 Hz)
3	*E*-meso	16.8	1.50	1.5–2.0	1.04 (J = 7.3 Hz)

[a] Stereochemistry assigned to sulfite ester. [b] Retention time, min, with a helium flow of 50 mL/min at 150 °C on a Versamide-900 column. [c] Singlet methyl resonances. [d] Methylene resonances with a multiplet AB pattern. [e] Triplet methyl resonances.

The pyramidal configuration of the sulfoxide group is well known; optically active ethyl *p*-toluenesulfinate was prepared in 1925,[3] and the E_a for inversion of typical sulfoxides has been shown to be 35 to 40 kcal mol^{-1}.[4] A number of cyclic sulfite esters of simple 1,2- and 1,3-glycols have been prepared and some have had their stereochemistry established by NMR.[5] The stereochemistry of the pinacol 1,1,1,4,4,4-hexafluoro-2,3-bis(4-methylphenyl)-2,3-butanediol was solved by VPC analysis.[6]

We here report our results with 3,4-dimethyl-3,4-hexanediol to provide an example of this elegant and general method of establishing the stereochemistry of chiral, symmetrical pinacols. The DL isomer, which forms only one cyclic sulfite ester, shows two methyl resonances and two ethyl resonances since only one of each of the alkyl groups is cis to the sulfoxide bond of the sulfite ester. The *E*-meso isomer (two ethyl groups trans to the sulfoxide oxygen) has one methyl resonance and one ethyl resonance. Likewise, the *Z*-meso isomer has one methyl resonance and one ethyl resonance with different chemical shifts from the *E* isomer.

The sulfite esters of the pinacol isomer of mp 52 °C and also of the liquid mixture of pinacol isomers were prepared from the respective pinacols by reaction with thionyl chloride in excess dry pyridine. Separation by VPC was accomplished preferably on a Versamide-900 column or alternately on a silicone DC-710 column. The peaks overlap, but the fractions collected were 80 to 90% pure which was adequate for obtaining their NMR spectra. The results in Table I are for the fractions obtained from a Versamide 900 column; identical results were obtained with the silicone DC-710 column.

The *E* and *Z* configurations for the meso structures were established by adding increasing amounts of $Eu(fod)_3$ shift

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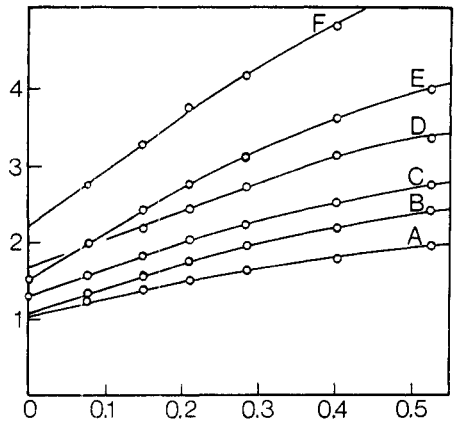

Figure 1. Observed chemical shifts with DL-sulfite ester (0.5 M solution in $DCCl_3$) in the presence of $Eu(fod)_3$: A, CH_3CH_2 trans to =S→O; B, CH_3CH_2 cis to =S→O; C, Me trans to =S→O; D, CH_3CH_2 trans to =S→O; E, Me cis to =S→O; F, CH_3CH_2 cis to =S→O.

reagent to a 0.5 M solution of the DL isomer in deuteriochloroform. The results are shown in Figure 1.

Of the two singlet methyl signals, the one at δ 1.50 showed a much greater chemical shift and is therefore cis to the sulfoxide group.[7] This methyl signal is the same as the methyl signal of peak number 3 which therefore must be the *E* isomer. The relative chemical shifts of the methylene and the triplet methyl signals confirm these assignments.

Experimental Section

The infrared spectra were determined with a Perkin-Elmer Model 337. The NMR spectra of the samples separated by VPC were obtained by Mr. Mark Mattingly, using a Varian XL-100; other NMR spectra were measured on a Varian EM-360. Chemical shift values are expressed as δ values downfield from tetramethylsilane internal standard. VPC separations were carried out on an F&M Model 300, using 6.3-mm diameter copper tubing 2-m long packed with the 10% F&M Versamid-900 on 60/80 mesh Diatoport-S for one column and with 20% DC silicon fluid 710 on 80/100 mesh DMCS Chromosorb-P for the other column. Elemental analyses were performed under the direction of Dr. Franz J. Kasler.

Sulfite Ester of (DL)-3,4-Dimethyl-3,4-hexanediol. To 3 g (0.021 mol) of the solid pinacol,[1] mp 50 °C, dissolved in 28 mL of pyridine and 23 mL of dry ether, was added dropwise at 15 °C with mechanical stirring 8.5 mL (0.12 mol) of thionyl chloride. After the addition, the reaction mixture was stirred for 1 h at room temperature and then poured onto ice. The ether extract was washed with water, dried ($MgSO_4$), and distilled to give 1.7 g (43% yield) of the sulfite ester: bp 67–68 °C (0.6 mm); IR (film) 3000, 2950, 2890, 1460, 1380, 1210 (S=O),[5a] 1135, 995, 885, 810, 780, 715, and 620 cm^{-1}; ^1H NMR ($DCCl_3$) δ 2.3–1.6 (m, 4, $-CH_2-$), 1.50 (s, 3, CH_3 cis to sulfoxide), 1.28 (s, 3, CH_3 trans to sulfoxide), 1.07 (t, 3, J = 7.3 Hz, CH_2CH_3 cis to sulfoxide), and 1.04 (t, 3, J = 7.3 Hz, CH_2CH_3 trans to sulfoxide).

Anal. Calcd for $C_8H_{16}O_3S$: C, 49.97; H, 8.39; S, 16.67. Found: C, 50.13; H, 8.53; S, 16.90.

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Registry No. DL-3,4-Dimethyl-3,4-hexanediol sulfite ester, 71076-42-1; (*E*)-*meso*-3,4-dimethyl-3,4-hexanediol sulfite ester, 71116-99-9; (*Z*)-*meso*-3,4-dimethyl-3,4-hexanediol sulfite ester, 71117-00-5; pinacol, 76-09-5.

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Synthesis and Reactions of Perfluoroneopentyllithium

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The low-temperature-gradient (LTG), direct fluorination of neopentane can synthesize *F*-neopentane (I) in yields approaching 70%.[1] Furthermore, our own research has shown that it is possible to optimize not only *F*-neopentane but also 1-hydryl-*F*-neopentane (II) and 1,3-dihydryl-*F*-neopentane (III). This development has made multigram quantities of all of these unique fluorocarbon molecules available for further research into their derivative chemistry.[2]

The metalation of compounds II or III is possible by known procedures[3,4] (eq 1); however, to our knowledge no

$$(F_3C)_3CCF_2H + RLi \rightarrow (F_3C)_3CCF_2Li + RH \quad (1)$$

$$R = CH_3, n\text{-Bu}, t\text{-Bu}$$

attempt has been made to metalate so sterically crowded a system as the *F*-neopentane derivatives. Furthermore, the synthesis of the lithium derivatives provides a route for the introduction of the unique *F*-neopentyl group into existing molecules where it can be utilized as a probe group or a label or for the introduction of specific properties such as high oxygen solubility.[5,6]

Results and Discussion

F-Neopentyllithium is somewhat more thermally stable than other *F*-alkyllithium derivatives. This stability is undoubtedly due to both its inability to "β eliminate" lithium fluoride to form an olefin and the inductive effect of the *F*-*tert*-butyl group. *F*-Neopentyllithium will, however, undergo "α elimination" of lithium fluoride to form *F*-*tert*-butylfluorocarbene near 0 °C.[7] *F*-Neopentyllithium may be prepared in ethyl ether (CH_3Li) or alkane (*n*-butyl- and *tert*-butyllithium) solvents. The initial metalation in both ether and alkane is good, as measured by methane evolution or product yields, respectively, but *F*-neopentyllithium attacks the ether solvent and must be used rapidly. Routinely, in ether 20–50% of the fluorocarbon residue is recovered as 1-hydryl-*F*-neopentane. An, as yet, unidentified hydrofluorocarbon ether is recovered in addition to starting material if the ether–*F*-alkyllithium solution stands at −78 °C overnight. Virtually all the *F*-neopentyllithium is consumed on standing overnight at −78 °C. The alkane-*F*-alkyllithium solutions are much more stable. Alkanes are the solvents of choice for investigating the reactions of the carbene species generated by the α elimination of lithium fluoride.

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