processes have been described before by Mazzocchi and Lustig[8] in the photolysis of phenylcyclopropane. Once again, the most substituted bond (C_1–C_2) is the one that cleaves preferentially.

Experimental Section

Apparatus. Photolyses were carried out in a cylindrical quartz cell 2 cm in diameter × 1 cm deep with Suprasil windows. The light source was a Hanovia 8-W mercury resonance lamp which was made of Suprasil glass. The lamp was operated from a constant voltage transformer.

Materials. 1,2-Diethylcyclopropane was synthesized by the addition of methylene to 3-hexene. The other alkylcyclopropanes were obtained from Chemical Samples Co. (Columbus, Ohio). The solvents used were spectroscopic grade pentane and isooctane from Baker (Photrex). All reactants were photolyzed separately in both solvents in order to be able to analyze for gaseous as well as isomeric products. No solvent effect was observed.

Analysis. Solutions were analyzed by gas chromatography on a Hewlett-Packard 5750 instrument fitted with a 10 ft oxydipropionitrile (20%) column and operated at ambient room temperature. The column was calibrated with authentic samples of the various products.

Procedure. Solutions (10^{-2} M) of the reactants were photolyzed at room temperature to conversions of 15% or less. Since the products were olefins which absorbed much more intensely than the starting materials, the rates of photolyses were strongly time dependent. The values given in Table I are initial rates of formation which were obtained by extrapolation of the experimental data to time zero.

Registry No. IVa, 71032-66-1; IVb, 71032-67-2; V, 4127-45-1; VI, 4127-47-3; C_2H_4, 74-85-1; C_3H_6, 115-07-1; 1-butene, 106-98-9; 2-methylpropene, 115-11-7; (*Z*)-3-hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; (*E*)-3-heptene, 14686-14-7; 2,4-dimethyl-2-pentene, 625-65-0; 2,4-dimethyl-1-pentene, 2213-32-3; methylene, 2465-56-7.

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Ketene Dithioacetals. 2.[1] The Control of α vs. γ Allylation Using Cuprous Salts

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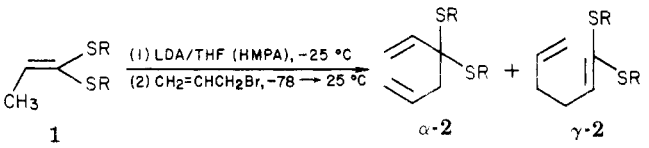
Ketene dithioacetals have recently received attention as viable synthetic intermediates.[3] It has been demonstrated[4] that their lithium anions undergo α alkylation to provide the dithianes of α,β-unsaturated ketones. We have sought to control the γ alkylation of these anions, thereby allowing them to serve as β-propionate anion equivalents.[5] Efforts to control α vs. γ alkylation in heteroatom-stabilized allylic anions[6] and resonance-stabilized enolates[7] have focused upon alteration of steric environment and variation of counterions and solvent.

Table I



1 α-2 γ-2

		with HMPA (3 equiv)			without HMPA		
entry	R	α	γ	yield[a]	α	γ	yield[a]
1a	$(CH_2)_3$	94	6	88	88	12	71[b]
1b	CH_3	73	27	66	74	26	82
1c	CH_2CH_3	70	30	80			
1d	$CH(CH_3)_2$	45	55	94	43	57	89

[a] Yields are of distilled material, unless otherwise noted. All new compounds provided satisfactory elemental analytical and spectral data. [b] VPC yield using an internal standard.

The effect of the variation of the alkyl group R on the α/γ ratio, in regard to both cyclic vs. acyclic structure and steric bulk, is outlined in Table I.

It is apparent that regioselectivity for α allylation is greater in the cyclic dithiane **1a** than in the acyclic analogues. Although the diisopropyl ketene dithioacetal has $\alpha/\gamma < 1$ (entry **1d**), it represents a limiting case in terms of steric bulk, since the *tert*-butyl analogues are not easily prepared. Moreover, the use of 3 equiv of hexamethylphosphoramide (HMPA) had no effect on the regioselectivity.[4b] Although Cope rearrangement of the 1,5-hexadienes α-**2** could be effected at 240 °C providing the ketene dithioacetals as the thermodynamic products, extensive decomposition occurred. It was confirmed by the collection–reinjection technique that rearrangement did not occur during VPC analysis.

Treatment of the red THF solution of lithium anion **1a** at −78 °C with cuprous iodide–trimethyl phosphite complex[8] provided a yellow solution containing a precipitated white solid. Warming of the reaction mixture to temperatures in excess of −25 °C caused the reaction mixture to turn black and become ineffective at alkylation. However, addition of an alkylating agent at −78 °C followed by warming to room temperature provided homogeneous yellow to yellow-green solutions. Often, solution was effected at −78 °C upon addition of the electrophile. By this procedure, exclusive γ allylation could be achieved as outlined in Table II. The γ-allylation products do not arise from copper-catalyzed isomerization of the α-allylation products. This was confirmed by reacting **4** with allyl bromide in the presence of α-**2** (R = $CH_2CH_2CH_2$). The product distribution indicated quantitative recovery of α-**2** and 70% yield of γ-**2** (R = $CH_2CH_2CH_2$).

Both allylic chlorides and bromides are suitable substrates. Since allylic alcohols are often conveniently

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(2) National Institutes of Health Career Development Awardee, 1973–1978.
(3) See ref 1, footnote 2, and N. H. Andersen, P. F. Duffy, A. D. Denniston, and D. B. Grotjahn, *Tetrahedron Lett.*, 4315 (1978); V. L. Mizyuk annd A. V. Semenovsky, *ibid.*, 3603 (1978); B. Cazes and S. Julia, *ibid.*, 4065 (1978).
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(5) Ketene dithioacetals have been converted to esters with $HgCl_2$ in aqueous alcohol: U. Schubert, *Synthesis*, 364 (1978).
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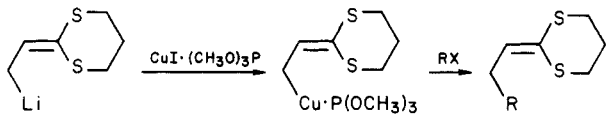
Table II



3 4 5

entry	RX	5[a] mode of attack (E/Z) S_N2'	S_N2	% yield distilled
1	CH_2=$CHCH_2Br$			68
2	CH_2=$CHCH_2Y$[b]			72
3	CH_2=$CBrCH_2Br$			68
4	HC≡CCH_2Br	90 (allene)	10 (acetylene)	85
5	(Z)-HDC=$CHCH_2Br$	82	18	c
6	CH_3CH=$CHCH_2Br$, E/Z = 83/17	79	21 (81/19)	91
7	(E)-CH_3CH=$CHCH_2Y$	95	5	91
8	CH_2=$CHCHBrCH_3$	54 (63/37)	46	91
9	CH_2=$CHCHYCH_3$	48 (60/40)	52	96
10	$(CH_3)_2C$=$CHCH_2Br$	67	33	84
11	$(CH_3)_2C$=$CHCH_2Cl$	80	20	81
12	$(CH_3)_2C$=$CHCH_2Y$	85	15	60
13	CH_2=$CH(CH_3)_2Y$	55	45	d
14	CH_2=$C(CH_3)CHYCH_3$	43 (60/40)	57	84
15	CH_2=$C(CH_3)CHY(CH_2)_3CH_3$	47 (72/28)	53	80
16	CH_3I			53[e,f]
17	CH_3OTs			44[e,g]
18	MeOD (−78 °C)			80[h]

[a] S_N2 refers to direct γ substitution (5) at the C-X bond of RX. S_N2' refers to its transposed γ isomer. [b] Y = OPO-$(OC_2H_5)_2$. [c] Halide contaminated with ether; yield not determined; cf. entry 1. [d] Phosphate decomposes on distillation. Crude material used in reaction. [e] VPC yield vs. internal standard. [f] γ/α = 5.7. [g] γ/α = 1.5. [h] 100% α.

prepared by the addition of vinylic organometallics to aldehydes and ketones, we have employed the derived phosphate esters[9] and have found that they react smoothly with 4. The use of the phosphate ester precludes the necessity of converting alcohols to allylic halides, a transformation often accompanied by isomerization.

Allylic acetates, although they react with cuprates,[10] do not serve as suitable electrophiles. Thus, (E)-1-acetoxy-2-butene, 3-acetoxy-1-butene, and 1-acetoxy-3-methyl-2-butene all failed to react to any significant extent.

In all instances where isomers could be formed in respect to the electrophile, the ratio of S_N2'/S_N2 product was greater than 0.67. Moreover, the isomeric pairs of electrophiles (Table II, entries 6 and 8, 7 and 9, and 12 and 13) clearly indicate that a symmetrical π complex is not an intermediate in the reaction. The unbiased example (isotope effects precluded) of (Z)-deuterioallyl bromide (entry 5) indicates a strong preference for S_N2' attack.[11]

Methylation of anion 4 (entries 16 and 17) was only moderately selective, preferring γ over α substitution. However, protonation or deuteration (entry 18) provided only the deconjugated product.

Experimental Section

Tetrahydrofuran (THF) was distilled from benzophenone ketyl. Diisopropylamine and hexamethylphosphoramide (HMPA) were distilled from CaH_2 and stored over 4-Å molecular sieves under N_2. Gas chromatograms were obtained by using a Varian Aerograph Model 90-P instrument with a 6 ft × 0.25 in., 5% SE-30 on Anakrom 60–70-mesh SD column or a Varian Series 1400 instrument with a 6 ft × 0.125 in., 1.5 or 3% OV-101 or 10% Carbowax on Chrom GHP 100–120-mesh column. NMR spectra were obtained on Perkin-Elmer R32, Bruker HX-270, or Varian EM 360 instruments, using $(CH_3)_4Si$ as an internal standard. Elemental analyses were performed by Atlantic Microlabs and Olin Corp.

Allylation of 1,1-Bis(ethylthio)-1-propylene in the Presence of HMPA (Table I, Entry 1c). To a solution of 1.1 mmol of lithium diisopropylamide[1] in 4 mL of THF at −25 °C under a nitrogen atmosphere was added 0.52 mL (3.0 mmol) of HMPA via syringe followed by 160 mg (1.0 mmol) of 1,1-bis(ethylthio)-1-propylene (1c) in 1 mL of THF. After 20 min the orange solution was cooled to −78 °C and 0.1 mL (1.2 mmol) of freshly distilled allyl bromide was added, forming a yellow suspension. The reaction mixture was allowed to slowly warm to 25 °C over a period of 4–5 h and then stirred for an additional 12 h at 25 °C. The reaction mixture was diluted with benzene, washed successively with water and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated to give 233 mg of yellow liquid. Distillation (70 °C, 0.20 torr, Kugelrohr) afforded 162 mg (80%) of a mixture of α-2 and γ-2 in a ratio of 70/30, respectively, as determined by VPC analysis. The VPC-collected materials had the following spectral properties. α-2: ^1H NMR ($CDCl_3$, 60 MHz) δ 1.21 (6 H, t, J = 7 Hz), 2.52 (6 H, m), 4.90–5.34 (4 H, m), 5.59–6.00 (2 H, m); mass spectrum (70 eV) m/e (relative intensity) 202 (6, M^+), 173 (44), 161 (58), 148 (metastable, $173^2/202$), 142 (33), 141 (52), 111 (28), 101 (29), 81 (55), 79 (100), 75 (41), 71 (62), 63.5 (metastable, $101^2/161$). γ-2: NMR ($CDCl_3$, 90 MHz) δ 1.21 (6 H, t, J = 7 Hz), 2.05–2.89 (8 H, m), 4.87–5.12 (2 H, m), 5.59–5.96 (1 H, m), 6.13 (1 H, t, J = 7 Hz); mass spectrum (70 eV) m/e (relative intensity) 202 (3, M^+), 173 (63), 161 (100), 148 (metastable, $173^2/202$, 101 (46), 75 (46), 71 (68), 63.5 (metastable, $101^2/161$).

γ Allylation of 2-Ethylidene-1,3-dithiane with Allyl Diethyl Phosphate (Table II, Entry 2). To a solution of 1.35 mmol of LDA in 2.5 mL of THF at −25 °C maintained under an N_2 atmosphere was added 177 mg (1.21 mmol) of 2-ethylidene-1,3-dithiane in 1 mL of THF. The resultant red solution was stirred 0.5 h and then cooled to −78 °C. A solution of 500 mg (1.6 mmol) of cuprous iodide–trimethyl phosphite complex[8] in 1 mL of THF was added, forming a yellow-white suspension. After 0.5 h, 270 mg (1.35 mmol) of allyl diethyl phosphate[9] was added as the reaction mixture was warmed to 25 °C over a period of 4–5 h followed by stirring at 25 °C for 12 h. The reaction mixture was diluted with ether and washed thoroughly with 10% aqueous NaCN, water, and brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, concentrated, and distilled to provide

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(10) R. Rona, L. Toekes, J. Tremble, and P. Crabbé, *Chem. Commun.*, 43 (1969); R. J. Anderson, C. A. Henrick, and J. B. Siddall, *J. Am. Chem. Soc.*, **92**, 735 (1970); R. J. Anderson, C. A. Henrick, J. B. Siddall, and R. Zurfluh, *ibid.*, **94**, 5379 (1972); H. L. Goering and V. D. Singleton, *ibid.*, **98**, 7854 (1976).
(11) Analyzed by ^2H NMR (41.4 MHz) and corrected for the deuterium distribution in the halide.

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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