

Table I. Percentage of Trans Isomer<sup>a</sup>

substrate	LiAlH <sub>4</sub>	NaBH <sub>4</sub>	B <sub>2</sub> H <sub>6</sub> (THF)	L-Selectride	Al(O- <i>i</i> -Pr) <sub>3</sub>	Raney Ni
1	85 <sup>b</sup>			<1 <sup>c</sup>	72 <sup>b</sup>	
2-methylcyclohexanone	79 <sup>d,e</sup>	73, <sup>f</sup> 60 <sup>g</sup>	74 <sup>h</sup>	0.7 <sup>i</sup>	85 <sup>j</sup>	
2	5 <sup>b</sup>	7.5, <sup>b</sup> 19 <sup>k</sup>	18 <sup>b</sup>	70, <sup>b,l</sup> 76, <sup>b</sup> 27 <sup>k</sup>		
3-methylcyclohexanone	15 <sup>h</sup>	23, <sup>g</sup> 14 <sup>m</sup>	23 <sup>h</sup>	94.5, <sup>i</sup> 88 <sup>k</sup>	22 <sup>n</sup>	
3	5.5 <sup>b</sup>	10.3 <sup>b</sup>	10.7 <sup>b</sup>	76 <sup>b</sup>	21.5 <sup>b</sup>	22.5 <sup>b</sup>
3- <i>tert</i> -butylcyclohexanone	15, <sup>o</sup> 18 <sup>h</sup>	24 <sup>g</sup>	30 <sup>h</sup>	72 <sup>p</sup>		

<sup>a</sup> Percent of trans alcohol in the mixture of cis + trans isomers taken as 100. <sup>b</sup> This work. <sup>c</sup> Reference 3. <sup>d</sup> Reference 11. <sup>e</sup> Reference 12. <sup>f</sup> Reference 13. <sup>g</sup> Reference 14. <sup>h</sup> Reference 15. <sup>i</sup> Reference 8. <sup>j</sup> Reference 16. <sup>k</sup> Reference 6. <sup>l</sup> Under the same conditions as described in ref 6. <sup>m</sup> Reference 17. <sup>n</sup> Reference 18. <sup>o</sup> Reference 19. <sup>p</sup> Since the data on the reduction with L-Selectride have not been reported, we include the value obtained with another bulky reagent, lithium perhydro-9b-boraphenylhydride.<sup>19</sup>

signal is very similar in chemical shift (and shape) to the septet of the C-4 proton of 8.

### Experimental Section

The preparation and characterization of the ketones 1 and 3 and of the alcohols 4-9 have been previously described.<sup>3,4</sup>

2-Methyltetrahydropyran-4-one (2) was prepared by oxidation of alcohol 8 with Jones' reagent. The following general procedure was utilized: The alcohol 8 (10 g, 0.1 mol) dissolved in acetone (250 mL) was treated with a slight excess of Jones' reagent and left 1 h at room temperature. The excess of reagent was destroyed with 2-propanol, and the solution was neutralized with solid K<sub>2</sub>CO<sub>3</sub>. Evaporation and distillation gave 2 (6.6 g): bp 88-90 °C (43 mmHg); *n*<sub>D</sub><sup>20</sup> 1.4452 [lit.<sup>20</sup> bp 70 °C (20 mmHg); *n*<sub>D</sub><sup>20</sup> 1.4469]. Characterization was accomplished as the 2,4-dinitrophenylhydrazone, mp 140-141 °C (lit.<sup>20</sup> mp 140 °C).

**Analytical Procedure.** All GC analyses were performed on a Perkin-Elmer F-11 (FID) chromatograph under the following conditions. For the reduction products of 1, a 2.5-m glass column with 15% Carbowax 20M on 80-100-mesh silanized Chromosorb W (125 °C) was used; the ratio of the retention times of 5 and 4 was 1.00:1.75. For the reduction products of 2, the standard procedure was used to convert the crude products into the trimethylsilyl ethers. A 2.5-m glass column with 3% OV-17 on 80-100-mesh silanized Chromosorb W (75 °C) was used for the chromatography; the ratio of the retention times of the trimethylsilyl ethers of 6 and 8 was 1.00:1.24. The accuracy of the analysis was ensured by subjecting mixtures of different compositions of pure 6 and 8 to the same procedure; the response factor was 1.04 ± 0.02. The data reported in Table I should be accurate within ±2%. For the reduction products of 3 the same column used for 1 was employed (140 °C); the ratio of the retention times of 7 and 9 was 1.00:1.08.

**Reduction Conditions.** **LiAlH<sub>4</sub>.** The ketone (1 mmol) and LiAlH<sub>4</sub> (2.6 mmol) in Et<sub>2</sub>O (20 mL) were refluxed for 3 h and hydrolyzed with H<sub>2</sub>O (0.1 mL), 3 N NaOH (0.1 mL), and H<sub>2</sub>O (0.3 mL). In the reduction of 1 and 3 GC analysis was performed directly on the ether solution; for 2, the ether was evaporated on a steam bath before trimethylsilylation.

**NaBH<sub>4</sub>.** The ketone (1 mmol) and NaBH<sub>4</sub> (2.6 mmol) in 2-propanol (10 mL) were reacted for 2 h at 0 °C, the mixture was hydrolyzed with H<sub>2</sub>O (10 mL), acidified with 10% H<sub>2</sub>SO<sub>4</sub>, and extracted with Et<sub>2</sub>O (3 × 10 mL), and the extract was analyzed as above.

**L-Selectride.**<sup>7</sup> The ketone (1 mmol) in 10 mL of anhydrous THF at -78 °C was treated with 1 M L-Selectride in THF (2.0 mL) and the mixture was left for 3 h at -78 °C. The solution was brought to room temperature, hydrolyzed with 3 M NaOH (0.3 mL), treated with 36% H<sub>2</sub>O<sub>2</sub> (0.3 mL), stirred for 1 h, dried with K<sub>2</sub>CO<sub>3</sub>, and analyzed by GC as in the other reductions. The ratio of alcohols 6 and 8 was 76:24. The ketone 2 was also reduced under the conditions described by Wigfield and Feiner.<sup>8</sup> The ratio of alcohols 6 and 8 was 70:30.

**B<sub>2</sub>H<sub>6</sub>.** To the ketone (1 mmol) in 10 mL of anhydrous THF was added 1 M BH<sub>3</sub> in THF (1 mL) and the solution kept 6 h at 0 °C before being hydrolyzed with 3 N NaOH (0.5 mL), oxidized with 36% H<sub>2</sub>O<sub>2</sub> (0.5 mL, 1 h of stirring), and dried with K<sub>2</sub>CO<sub>3</sub>. The solution was analyzed as described above.

**Al(O-*i*-Pr)<sub>3</sub> Reduction.** The ketone (1 mmol) and aluminum isopropoxide (0.5 g) in 20 mL of 2-propanol were refluxed for 3 h and the 2-propanol was evaporated under reduced pressure. The residue was hydrolyzed with crushed ice and acidified with concentrated HCl (1.5 mL), and the mixture was extracted with Et<sub>2</sub>O (3 × 10 mL), washed with aqueous NaHCO<sub>3</sub>, dried (MgSO<sub>4</sub>), and analyzed as described above.

**Equilibration of 7 and 9.** The method of Eliel and Senda<sup>9</sup> was used. A solution of 3 (0.5 mmol) and 9 (0.5 mmol) in benzene (10 mL) was refluxed in the presence of purified Raney nickel, the equilibration being monitored by GC, until a constant 7:9 ratio was reached.

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**Registry No.** 1, 30448-27-2; 2, 1193-20-0; 3, 23659-44-1; 4, 55230-29-0; 5, 55230-31-4; 6, 55230-32-5; 7, 55522-90-2; 8, 33747-08-9; 9, 33747-10-3.

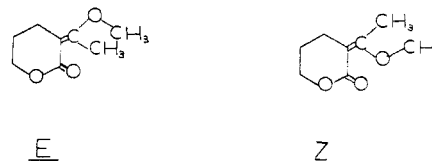
### Dipole Moment and Spectral Data of the (*Z*)- and (*E*)-Enol Ethers, 2-(1-Methoxyethylidene)-5-hydroxypentanoic Acid Lactone<sup>1</sup>

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The observation of certain spectral anomalies associated with the rather flexible structures of the β-alkoxy derivatives of α,β-unsaturated esters<sup>2</sup> prompted the synthesis and study of model compounds of fixed conformation.<sup>3</sup> Two of these, the methyl enol ethers of α-acetyl-δ-valerolactone [2-(1-methoxyethylidene)-5-hydroxypentanoic acid lactone], are the subjects of this report. The *E* isomer has the fixed conformation, trans-*s*-cis, the *Z* isomer, cis-*s*-cis.

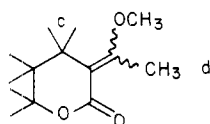


(1) Presented in part at the Rocky Mountain Regional Meeting, American Chemical Society, Laramie, WY, June 1976.

(2) (a) Rhoads, S. J.; Hasbrouck, R. W.; Pryde, C.; Holder, R. W. *Tetrahedron Lett.* 1963, 10, 669. (b) Rhoads, S. J.; Gilbert, J. C.; Decora, A. W.; Garland, T. R.; Spangler, R. J.; Urbigkit, M. J. *Tetrahedron* 1963, 19, 1625. (c) Rhoads, S. J.; Decora, A. W. *Ibid.* 1963, 19, 1645. (d) Rhoads, S. J.; Pryde, C. *J. Org. Chem.* 1965, 30, 3213. (e) Rhoads, S. J. *Ibid.* 1966, 31, 171.

(3) The initial work on this problem is detailed in Harrod, C. E. M.S. Thesis, University of Wyoming, June, 1969. Other information comes from undergraduate research reports of D.R.B. and the Honors Thesis of T.G.B.

(20) E. Hanschke, *Chem. Ber.*, 88, 1053 (1955).

Table I. Spectroscopic Data for the Methyl Enol Ethers of  $\alpha$ -Acetyl- $\delta$ -valerolactone

	A	B
UV max (MeOH), nm ( $\epsilon$ )	260 (11 800)	272 (15 900)
(isooctane), nm ( $\epsilon$ )	246 (11 500)	257 (13 300)
IR, $\nu_{C=O}$ , $\nu_{C=C}$ , $\text{cm}^{-1}$	1692, 1595	1618 (sh), 1576
MS, $m/z$ (rel intensity), fragment	156 (66.7), $M^+$ 141 (33.3), $M - \text{CH}_3$ 43 (100), $\text{COCH}_3$	156 (39.4), $M^+$ 141 (48.5), $M - \text{CH}_3$ 43 (100), $\text{COCH}_3$
NMR, allylic protons in methyl enol ethers c, area 2, $\text{CH}_2$ ; d, area 3, $\text{CH}_3$	c + d, 2.39 (m, 5 H)	c, 2.18 (t, 2 H) d, 2.14 (s, 3 H)

The ethyl acetate acylation of the sodium salt of  $\delta$ -valerolactone yielded  $\alpha$ -acetyl- $\delta$ -valerolactone which exists largely in the enolic form. Its addition to an ethereal diazomethane solution resulted in the isolation of the two methyl enol ethers, which were separable by fractional distillation. The major isomer, B, was a white crystalline solid, mp 48–49 °C, bp 69 °C (0.09 torr). About one-third as much of isomer A was obtained: a colorless, viscous liquid, bp 80–82 °C (0.06 torr). The studies of the physical properties were carried out on carefully purified (VPC) samples.

Examination of the Dreiding and space-filling models shows that the conformationally fixed nature of these isomers introduces considerable steric congestion about the structural unit of interest, especially in the *E* isomer. The UV, IR, mass, and NMR spectra were measured in order to secure information about these structures. Table I summarizes these spectral data which provide some evidence for assigning the *E* and *Z* structures to isomers A and B.

The UV data suggest, as did the space-filling models, that the larger bulk of  $\text{CH}_3$  vs.  $\text{OCH}_3$  results in a degree of nonplanarity and, hence, a shorter resonance pathway (shorter  $\lambda_{\text{max}}$  and lower  $\epsilon$  value) in isomer A, which was independent of solvent change. The electron delocalization in the B isomer, where the  $-\text{O}-\text{C}=\text{C}-\text{C}=\text{O}$  atoms lie in a plane, leads to larger wavelength maxima and  $\epsilon$  values. Similar differences in  $\epsilon$  values attributed to steric hindrance were reported by Turner and Voitle<sup>4</sup> for 2-methyl-1-acetylcyclohexene and 1-acetylcyclohexene.

The explanation of the coplanar-extended conjugation for isomer B is also supported by the contrasting IR results. Unlike the findings of Rhoads and Waali<sup>5</sup> with open-chain enol ether esters, the coplanarity in this portion of the conformationally fixed B isomer lends itself to an electronic interaction in a way that has decreased the carbonyl frequency to the point that it blends with the correspondingly lowered carbon-carbon double bond frequency. This is in reasonable agreement with the IR frequencies observed by Awang<sup>6</sup> for the *E* and *Z* isomers of Eistert's open-chain methyl enol ethers of acetylacetone.

The mass spectral data confirm the isomeric nature of the two compounds.

The proton magnetic resonance spectra of the isomers differ only at one possibly useful point.<sup>7</sup> The allylic ring protons, c, appear to be slightly deshielded by the oxygen of the methoxy group in the A isomer. The similarly shifted d ( $\text{CH}_3$ ) protons are influenced by their proximity to the carbonyl group. Spectral data suggest that the *E* configuration be assigned to A and the *Z* configuration to B.

The electric dipole moments of these isomers were determined in order to confirm these tentatively assigned structures. The orientation of the added polar structural feature did produce the expected effects on the  $\delta$ -valerolactone dipole moment, which was found to be 4.26 D.<sup>8</sup> Duplicate measurements of the dielectric constants and refractive indices of the appropriate benzene solutions of the purified ether samples were made. The standard procedures,<sup>9</sup> including Guggenheim's<sup>10</sup> method, along with calculations based on a combination of the Clausius-Mossotti equation, the Lorentz relation, and the Smith<sup>11</sup> assumption, were used. The dipole moments obtained were as follows: A,  $4.44 \pm 0.01$  D; B,  $4.65 \pm 0.02$  D. The methoxy group in the *E* isomer would be expected to contribute very little to the total polarity of the enol ether molecule as compared with the parent lactone. The increase in polarity is twice as much in the *Z* isomer where the methoxy lies in the planar portion of the molecule and nearer to the oxygens of the lactone structure. These values are consistent with the structures proposed and serve to confirm the assignment of the *E* configuration to compound A and the *Z* configuration to compound B.

### Experimental Section

Melting points were taken with a Mel-Temp capillary apparatus. For VPC identification and purity determinations, the instrument used was a Varian Aerograph, Model A-90-P, fitted with either a 4-m column, 1% Reoplex on Fluoropak, or 3 m of 10% SE-30 on Gas Chrom P. Ultraviolet spectra were measured in methanol and isooctane in matched 1-cm silica cells at 25 °C with a Beckman DB spectrophotometer. Infrared spectra were determined for thin film samples with a Perkin-Elmer Model 621 instrument. NMR spectra were obtained on  $\text{CCl}_4$  or  $\text{CDCl}_3$  solutions ( $\text{Me}_4\text{Si}$  internal standard) with a Varian HA-100. For the mass spectra a Varian MAT CH-5 spectrometer was employed. The measurements of dielectric constants of solutions were carried out at 25 °C by using a General Radio Capacitance Bridge Type 1620-A and a three terminal capacitance cell, Balsbaugh Model 100T 3 (air capacitance of 100 pF). Refractive indices were measured with a modified Abbe type refractometer, Bausch and Lomb Model 33-45-02.

**$\alpha$ -Acetyl- $\delta$ -valerolactone (1).**<sup>12</sup> To a 1000-mL Morton flask fitted with a nitrogen inlet tube, 125-mL dropping funnel, thermometer, and reflux condenser was added 24.48 g of a 50% NaH-mineral oil dispersion (Metal Hydrides, Inc.). After the removal of the mineral oil with successive dry ether washes, the NaH was slurried with 210 mL of redistilled ethyl acetate and stirred mechanically under anhydrous conditions. A solution of 47.66 g of  $\delta$ -valerolactone (Aldrich) in 75 mL of ethyl acetate was added slowly to the stirring mixture. Four drops of absolute ethanol initiated the rapid evolution of hydrogen and the reaction

(7) Attempts to magnify the spectral differences with changes in solvent and the addition of a shift reagent  $[\text{Eu}(\text{fod})_3]$  were unsuccessful.

(8) Huisgen and Ott [Huisgen, R.; Ott, H. *Tetrahedron* 1959, 6, 253] reported 4.22 D.

(9) Detailed discussions of such dipole moment measurements are found in: (a) Thompson, H. B. *J. Chem. Educ.* 1966, 43, 66. (b) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I. "Experiments in Physical Chemistry", 3rd ed.; McGraw-Hill: New York, 1974; p 411.

(10) Guggenheim, E. A. *Trans. Faraday Soc.* 1949, 45, 714.

(11) Smith, J. W. *Trans. Faraday Soc.* 1950, 46, 394.

(12) Korte, F.; Büchel, K. H.; Scharf, D.; Zschocke, A. *Chem. Ber.* 1959, 92, 884.

(4) Turner, R. B.; Voitle, D. M. *J. Am. Chem. Soc.* 1951, 73, 1403.

(5) Rhoads, S. J.; Waali, E. E. *J. Org. Chem.* 1970, 35, 3358.

(6) Awang, D. V. C. *Can. J. Chem.* 1971, 49, 2672.

mixture was stirred for 2 h at 5 °C in an ice bath. Room temperature stirring for 1 h was followed by overnight standing. The solution was diluted with 150 mL of ice water and extracted with four 50-mL portions of ether. This ether solution was dried ( $\text{Na}_2\text{SO}_4$ ), concentrated, and fractionally distilled, giving a 30% yield<sup>13</sup> of 1, in four fractions, bp 92–98 °C (0.2 torr), as clear liquid and white crystals, 80–97% pure by VPC. The instantaneous positive  $\text{FeCl}_3$  test (purple) showed the highly enolic character,<sup>14</sup> estimated at ~95% via NMR integrals.

**Methyl Enol Ethers of  $\alpha$ -Acetyl- $\delta$ -valerolactone (A and B).**<sup>15</sup> Diazomethane<sup>16</sup> was prepared in ethereal solution, 76% yield, from the reaction of  $N,N'$ -dinitroso- $N,N'$ -dimethylterephthalamide in mineral oil with sodium hydroxide in Carbitol and ether. To the ether solution of diazomethane, at room temperature, was added 6.02 g of 1 dissolved in methanol. The solution was protected from light and moisture for the 5 days of reaction time. Excess  $\text{CH}_2\text{N}_2$  was destroyed with 2 N HOAc. The colorless solution, washed with cold 2 N NaOH followed by  $\text{H}_2\text{O}$ , was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Flash distillation, followed by repeated fractional vacuum distillations, yielded the A and B isomers in a 1:3 ratio, 56% total yield. A: bp 80–82 °C (0.06 torr);  $\lambda_{\text{max}}$  (MeOH) 260 nm (11 800); IR 2950, 1692, 1595, 1285, 1097  $\text{cm}^{-1}$ ; NMR  $\delta$  1.76 (m, 2 H), 2.39 (m, 5 H), 3.76 (s, 3 H), 4.07 (t, 2 H); MS 156 ( $\text{M}^+$ ), 141 ( $\text{M} - \text{CH}_3$ ), 43 (base,  $\text{CH}_3\text{CO}$ ). B: bp

69 °C (0.09 torr);  $\lambda_{\text{max}}$  (MeOH) 272 nm (15 900); IR 2958, 1618 (sh), 1576, 1377, 1160  $\text{cm}^{-1}$ ; NMR  $\delta$  1.78 (m, 2 H), 2.14 (s, 3 H), 2.18 (t, 2 H), 3.77 (s, 3 H), 4.18 (t, 2 H); MS 156 ( $\text{M}^+$ ), 141 ( $\text{M} - \text{CH}_3$ ), 113, 109, 43 (base,  $\text{CH}_3\text{CO}$ ).

**Dipole Moment Measurements.**<sup>9b-11</sup> Repeated vacuum distillations provided pure samples of the isomeric enol ethers, A and B. For the quantitatively prepared 100-mL solutions, in benzene, approximately 4, 3, 2, and 1 mol % carefully measured solute weights and densities were used in the mole fraction determinations. Capacitance of solution measurements,  $C$ , were compared with that of air,  $C_0$ , for the dielectric constant values,  $\epsilon = C/C_0$ . Refractive indices of the solvent,  $n_1$ , and the solutions were measured. With these data, calculations of the molar orientation polarization at infinite dilution,  $P_{2\mu}^\circ$ , and the dipole moments,  $\mu$ , were made using the equations  $P_{2\mu}^\circ = Ca - 3Bc/(n_1^2 + 2)^{217}$  and  $\mu = 0.0128 (P_{2\mu}^\circ T)^{1/2} \times 10^{-18}$  D, where  $a$  = slope of plot of dielectric constants vs. mole fraction of solute,  $c$  = slope of plot of squares of indices of refraction vs. mole fraction of solute,  $B$  = molecular weight of solvent/ $\rho_{\text{solvent}}$ , and  $C = 3$  (molecular weight of solvent)/(dielectric constant + 2)<sup>2</sup>  $\times \rho_{\text{solvent}}$ . The averages of the results for duplicate determinations of the dipole moments were as follows: (*Z*)-ether, B,  $P_{2\mu}^\circ = 443 \text{ cm}^3/\text{m}$ ,  $\mu = 4.65 \pm 0.02$  D; (*E*)-ether, A,  $P_{2\mu}^\circ = 404 \text{ cm}^3/\text{m}$ ,  $\mu = 4.44 \pm 0.01$  D.

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**Registry No.** 1, 63872-58-2; 1, *Z* methyl enol ether, 72525-31-6; 1, *E* methyl enol ether, 72525-32-7;  $\delta$ -valerolactone, 542-28-9.

(13) The separation of the self-condensation product, ethyl acetate, as well as the removal of unreacted  $\delta$ -valerolactone required repeated procedures and purifications before the ether preparations were carried out.

(14) This intermediate had not previously been prepared. White platelets: mp 42–43 °C from petroleum ether (bp 50–60 °C); IR broad OH band characteristic of chelated enol, 1735 (ester C=O), 1717 (ketone C=O), 1636 (str, enol C=O), 1610  $\text{cm}^{-1}$  (str, enol C=C); NMR ( $\text{CCl}_4$ )  $\delta$  13.73 (enolic H).

(15) An adaptation of the method of: Arndt, F.; Loewe, L.; Sevrge, T.; Türegün, I. *Chem. Ber.* 1938, 71, 1640.

(16) Moore, J. A.; Reed, D. E. *Org. Synth.* 1961, 41, 16.

## Communications

### Preparation of Benzocyclobutenols from *o*-Halostyrene Oxides

**Summary:** Reaction of several *o*-bromo- and *o*-iodostyrene oxides, dissolved in THF at –78 °C containing a suspension of  $\text{MgBr}_2$ , with *n*-BuLi gave benzocyclobutenols in 50–83% yield.

**Sir:** Our work on the Grignard-reagent-induced cyclization of  $\gamma$ -epoxy sulfones<sup>1,2</sup> and  $\gamma$ -epoxy nitriles<sup>1</sup> (eq 1), coupled with the report by Bradsher and Reames<sup>3</sup> that metalation of the *o*-brominated epoxides 1 with *n*-butyllithium gave the intermediate 2 without interference from the epoxide function, suggested that ortho-halogenated styrene oxides 3 might possibly serve as precursors to benzocyclobutenols 4.<sup>4</sup> As is reported in this communication, this expectation has been realized.

Thus reaction of 3b, dissolved in THF at –78 °C containing 2 equiv of suspended  $\text{MgBr}_2$ , with *n*-BuLi for 30 min, followed by warming to room temperature, afforded

benzocyclobutenol (4) [<sup>1</sup>H NMR<sup>5</sup>  $\delta$  2.28 (OH), 3.30 (dd,  $J = 14$ , 2 Hz, 1 H), 3.59 (dd,  $J = 14$ , 4.5 Hz, 1 H), 5.28 (dd,  $J = 4.5$ , 2 Hz, 1 H), 7.1–7.4 (m, 4 H); mp 56–58 °C (lit.<sup>6</sup> 58 °C)] in yields up to 83%.<sup>7</sup> The formation of 4 was equally successful from *o*-iodostyrene oxide (3c).

Benzocyclobutenol was also obtained from 3b, albeit in only 40% yield, when the metal-halogen exchange was carried out with *n*-BuLi at –78 °C for 5 min followed by addition of 2 equiv of  $\text{MgBr}_2$  (2.5 M in ether). Longer time intervals between the *n*-BuLi and  $\text{MgBr}_2$  additions decreased the yield of 4 even further and gave crude products whose NMR spectrum showed considerable butyl group absorption. No 4 was obtained in the absence of  $\text{MgBr}_2$ .

In contrast to the results obtained with the *o*-bromo and *o*-iodo derivatives, *o*-chlorostyrene oxide (3a) gave no 4 under the above conditions. When 3a was metalated at –95 °C in THF for 15 min and the reaction mixture was allowed to warm to room temperature prior to addition of a saturated  $\text{NH}_4\text{Cl}$  solution, an *E/Z* mixture of the unusual stilbene derivative 5 was formed in about 50% yield. The two isomers were separated by column chromatography

(1) B. Corbel and T. Durst, *J. Org. Chem.*, 41, 3648 (1976).

(2) B. Corbel, J. M. Decesare, and T. Durst, *Can. J. Chem.*, 56, 505 (1978).

(3) C. K. Bradsher and D. C. Reames, *J. Org. Chem.*, 43, 3800 (1978).

(4) Benzocyclobutene derivatives have been shown to be valuable intermediates in the synthesis of steroids and alkaloids: W. Oppolzer, *Synthesis*, 793 (1978).

(5) These values differ from those reported by Arnold et al.: B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, *J. Chem. Soc., Perkin Trans. 1*, 401 (1974). In particular, the vicinal coupling constants were erroneously reported and should be reversed. The hydrogen *cis* to the OH group occurs at lower field than that which is *trans*.

(6) M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, 82, 652 (1960).

(7) In a number of experiments the yield of 4 ranged from 60 to 83%.