until TLC monitoring indicated completion (~2 h). Removal of the precipitate by filtration and concentration in vacuo gave the crude sulfinamide which was purified by recrystallization. The experimental details for the individual runs are summarized in Table II.

**Method B.** To a solution of 3 mmol of *N*-cyclohexylbenzenesulfinamide and 0.9 mmol of tetrabutylammonium chloride in 20 mL of benzene was added 4 mL of a 50% (by weight) aqueous solution of sodium hydroxide. After 20 min at room temperature, 3.1 mmol of the halide in 2 mL of benzene was added and stirring continued 2 days at room temperature. The benzene layer was separated and diluted with 15 mL of fresh benzene. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated in vacuo to give the crude sulfinamide which was purified by recrystallization. Table II summarizes the experimental details for each run. In the case of entry 4, the product was purified by silica gel chromatography, with elution with 4:1 hexane–ethyl acetate.

**Spectral Data of Sulfinamides. *N*-Benzyl-*N*-cyclohexylbenzenesulfinamide:** IR ($CCl_4$) 1445, 1343, 1150, 930, 690 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.68–7.12 (10 H, m), 4.12 and 4.00 (2 H, AB, $J$ = 15.5 Hz), 2.96–1.12 (11 H, m).

***N*-Benzyl-*N*-cyclohexyl-4-nitrobenzenesulfinamide:** IR ($CCl_4$) 1600, 1528, 1453, 1345, 1100, 1084, 1065, 925 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 8.16 (2 H, d, $J$ = 9 Hz), 7.74 (2 H, d, $J$ = 9 Hz), 7.05 (5 H, m), 4.02 (2 H, s), 3.00–1.12 (11 H, m).

***N*-Cyclohexyl-*N*-(1-naphthylmethyl)benzenesulfinamide:** IR ($CCl_4$) 1627, 1595, 1475, 1445, 1090, 1060, 800, 780 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.50–7.16 (12 H, m), 4.44 (2 H, s), 2.92–1.04 (11 H, m).

***N*-Cyclohexyl-*N*-(1-naphthylmethyl)-4-nitrobenzenesulfinamide:** IR ($CCl_4$) 1600, 1530, 1448, 1343, 1100, 1083, 1062, 844, 710 $cm^{-1}$. NMR ($CDCl_3$) $\delta$ 8.00–7.33 (11 H, m), 4.64 and 4.52 (2 H, AB, $J$ = 16 Hz), 3.10–1.12 (11 H, m).

***N*-Cyclohexyl-*N*-[(2-methyl-1-naphthyl)methyl]benzenesulfinamide:** IR (KBr pellet) 1475, 1450, 1180, 1155, 1083, 813 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.60 (11 H, m), 4.82 and 4.42 (2 H, AB, $J$ = 12 Hz), 3.50–1.10 (14 H, m).

***N*-Cyclohexyl-*N*-farnesylbenzenesulfinamide:** IR ($CCl_4$) 1665, 1471, 1450, 1380, 1090, 1062, 922, 815, 720, 698 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.61 (2 H, m), 7.36 (3 H, m), 5.02 (3 H, br), 3.61 and 3.45 (2 H, AB, $J$ = 18 Hz), 3.10–1.20 (m).

**Dehydrosulfenylation.** A solution of the sulfinamide in *o*-xylene containing anhydrous potassium carbonate was refluxed for the specified time. After the mixture was cooled to room temperature and the precipitate removed by filtration, the solution was concentrated in vacuo. For isolation of the imine, the resultant oil was distilled on a Kugelrohr apparatus. For isolation of the aldehyde, the resultant oil was purified by chromatography on silica gel with elution with methylene chloride or 4:1 hexane–ethyl acetate which also effected hydrolysis. Table III summarizes the details for the individual runs.

**One-Pot Alkylative Elimination–Hydrolysis Preparation of 1-Bromo-2-naphthaldehyde.** According to method A, a mixture of 408 mg of a 50% dispersion of sodium hydride in mineral oil (8.5 mmol, washed free of mineral oil), 1.016 g (4.55 mmol) of N-cyclohexylbenzenesulfinamide, and 1.380 g (4.6 mmol) of 1-bromo-2-(bromomethyl)naphthalene in 20 mL of anhydrous DME was stirred overnight at 80 °C. After the usual workup, a NMR spectrum of the crude oil revealed a sharp singlet at $\delta$ 9.04 indicative of the imine. Purification by preparative TLC with methylene chloride gave 729 mg (68% yield) of 1-bromo-2-naphthaldehyde: mp 116–118 °C; IR ($CCl_4$) 2740, 1750, 1625, 1600; NMR ($CDCl_3$) $\delta$ 10.68 (1 H, s), 8.46 (1 H, m), 7.72 (5 H, m).

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**Registry No.** $PhCH_2NHC_6H_{11}$, 4383-25-9; $PhCH_2Cl$, 100-44-7; $p$-$O_2NC_6H_4S(O)Cl$, 13088-17-0; PhS(O)Cl, 4972-29-6; $PhCH{=}NC_6H_{11}$, 2211-66-7; *N*-(1-naphthylmethyl)cyclohexylamine, 14489-84-0; 1-(chloromethyl)-2-methylnaphthalene, 6626-23-9; 1-(chloromethyl)naphthalene, 86-52-2; *N*-cyclohexyl-*N*-(1-naphthylmethyl)-4-nitrobenzenesulfonamide, 78804-11-2; *N*-cyclohexyl-*N*-(1-naphthylmethyl)benzenesulfonamide, 78804-12-3; *N*-benzyl-*N*-cyclohexyl-4-nitrobenzenesulfinamide, 78804-13-4; *N*-benzyl-*N*-cyclohexylbenzenesulfinamide, 78822-59-0; farnesyl bromide, 6874-67-5; *N*-cyclohexylbenzenesulfinamide, 35810-04-9; *N*-cyclohexyl-*N*-[(2-methyl-1-naphthyl)methyl]benzenesulfinamide, 78804-14-5; *N*-cyclohexyl-*N*-farnesylbenzenesulfinamide, 78804-15-6; 1-naphthaldehyde, 66-77-3; 2-methyl-1-naphthaldehyde, 35699-44-6; farnesaldehyde, 19317-11-4; 1-bromo-2-naphthaldehyde, 3378-82-3.

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# Absolute Configuration of 1,3-Di-*tert*-butylpropargyl Alcohol. Borden–Corey Stereochemistry Confirmed

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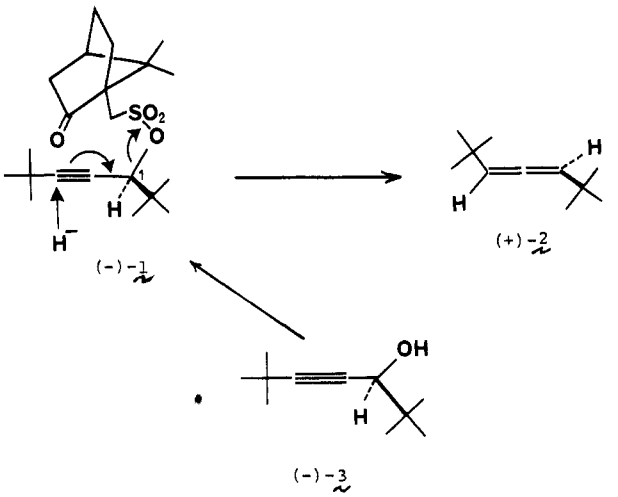
The $S_N2'$ reactions of propargylic derivatives which lead to allenes have attracted considerable attention in recent years from both synthetic and mechanistic standpoints.[1] In particular, the highly stereoselective displacement reaction of optically active propargylic derivatives has provided a convenient means for the preparation of optically active allenes. One of the earliest and most significant contributions along this line was made by Borden and Corey.[2] They converted diastereomerically pure *d*-camphor-10-sulfonate esters of 1,3-di-*tert*-butylpropargyl alcohol (1 and its epimer at C-1) into the optically active 1,3-di-*tert*-butylallenes by using lithium aluminum hydride and other hydride agents.




The overall anti stereochemistry, as indicated above by arrows, for this allene-forming reaction has been proposed[2] on the basis of the allenes **2** and their propargyl alcohol precursors **3**[3] as deduced by following the Lowe–Brewster and the Brewster rules,[4,5] respectively. Subsequently, the

(1) See, for example, the following and the references cited therein: Overton, K. H. *Chem. Soc. Rev.* **1980**, 447.
(2) Borden, W. T.; Corey, E. J. *Tetrahedron Lett.* **1969**, 313.
(3) It should be noted that there is a typographical error in the Borden–Corey manuscript.[2] Namely, although the absolute configurations of the propargylic centers of the camphorsulfonates **1** are correctly drawn, in the text (+)-**3**, which correlates with (+)-**1**, is erroneously designated *S* instead of *R*. See also: Macomber, R. S. *J. Org. Chem.* **1972**, *37*, 1205.
(4) Lowe, G. *Chem. Commun.* **1966**, 411.
(5) Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475.

0022-3263/81/1946-4620$01.25/0 

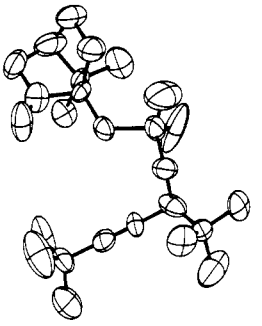


**Figure 1.** Stereodrawing of (−)-1 with thermal ellipsoids.

stereochemistry of 1,3-di-*tert*-butylallene (2) was convincingly discussed by Moore et al.[6] through their extensive ORD studies of various optically active allenes. In contrast, while the stereochemistry of the propargyl alcohols 3 was further corroborated[2] by using Mislow's method[7] of asymmetric induction of sulfoxide optical activity, this alcohol has never been transformed chemically to a compound of known configuration.

In view of this failure, a single-crystal X-ray structure determination was carried out on the camphorsulfonate (−)-1: mp 110.5–111.5 °C; $[\alpha]^{26}_{D}$ −25.8° (*c* 0.460, $CHCl_3$). Figure 1 shows a computer-generated perspective drawing of the final X-ray model less hydrogens. Although this X-ray experimental provides only the relative configuration, since the absolute configuration of the *d*-camphorsulfonyl moiety is known, the *S*-configuration was assigned for the sulfonate ester bearing carbon. This confirms the original structural deduction for 1 by Borden and Corey, thus securing their anti-$S_N2'$ stereochemistry for the allene-forming reaction.

Interestingly, a recent report by Claesson and Olsson[8] points out that either the anti or the syn mechanism may be observed, depending upon the nature of the leaving group in these allene-forming reactions and furthermore the degree of stereochemical integrity may be affected as well by these leaving groups. After completion of this work, we learned that Arigoni[9] confirmed the Borden-Corey stereochemistry by chemical correlation of the alcohol, (−)-3[10] with the allene, (−)-2[10] which proceeded through the ketal intermediate followed by its thermal syn-sigmatropic rearrangement.

(6) Moore, W. R.; Anderson, H. W.; Clark, S. D. *J. Am. Chem. Soc.* **1973**, *95*, 835.
(7) Green, M. M.; Axelrod, M.; Mislow, K. *J. Am. Chem. Soc.* **1966**, *88*, 861.
(8) Claesson, A.; Olsson, L.-I. *J. Am. Chem. Soc.* **1979**, *101*, 7302.
(9) Arigoni, D., personal communication. See also ref 1.
(10) Absolute configurations for these were not assigned.

## Experimental Section

The *d*-camphorsulfonate ester (−)-1 was prepared by the method of Borden and Corey[2] and its single crystals were grown by slow evaporation of a solution in petroleum ether/benzene. A crystal of dimensions 0.23 × 0.21 × 0.33 mm was mounted on a Syntex $P2_1$ diffractometer and found to be tetragonal with $a$ = 12.141 (3) Å and $c$ = 15.500 (4) Å. The density was measured to be 1.135 g/cm$^3$ and calculated to be 1.111 g/cm$^3$ for $Z$ = 4 ($C_{21}H_{34}O_4S$, $M_r$ = 382).

Intensity data were obtained by using Mo K$\alpha$ radiation monochromatized from a graphite crystal whose diffraction vector was perpendicular to the diffraction vector of the sample. A total of 4009 reflections were measured for $2\theta < 60°$, of which 818 were considered observed [$I > 3.0\sigma(I)$].

The data were reduced by procedures previously described.[11] The crystal had less than 5% absorption differences, and no correction was made. The structure was solved in space group $P4_3$ by using MULTAN78. On the basis of chemical evidence, the space group was changed to $P4_1$ in order to obtain the correct isomer. In the least-squares refinement, the agreement indices $R1 = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R2 = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used. The atomic scattering factors are from the literature.[12] Least-squares refinement using anisotropic thermal parameters for all nonhydrogen atoms gave R1 = 0.093 and R2 = 0.106. Difference Fourier calculations then revealed all hydrogen atoms. Refinement to convergence with the hydrogens as fixed contributors gave R1 = 0.070 and R2 = 0.081.

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**Registry No.** (−)-1, 22688-40-0.

**Supplementary Material Available:** Final positional parameters with estimated standard deviations are shown in Table I. Anisotropic thermal parameters with their estimated standard deviations are listed in Table II. Table III lists the crystallographically determined bond distances and angles (listings of observed and calculated structure factor amplitudes are available from the authors). In addition, a figure is given which shows the computer-generated perspective drawing of (−)-1 with the crystallographic numbering scheme (4 pages). Ordering information is given on any current masthead page.

(11) Computations were carried out on an Amdahl 470/V6 computer. Computer programs used during the structural analysis were SYNCOR (data reduction by W. Schmonsees), FORDAP (Fourier refinement by Z. Zalkin), ORFLS (full-matrix, least-squares refinement by Busing, Martin, and Levy), ORFFE (distances, angles, and their esd's by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), HATOMS (hydrogen atom positions by A. Zalkin), PLANES (least squares planes by D. M. Blow), and MULTAN78 (by Peter Main).
(12) Ibers, James A.; Hamilton, Walter C., Eds. "The International Tables for X-ray Crystallography", Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2 and 2.3.1.