final pressure was 1.1 atm at 23 °C. Hydrochloric acid (2.4 M) was added to the viscous orange-brown reaction mixture in four 2-mL portions with constant agitation. The crude yield of **2f** which separated (95% pure by NMR) was 1.63 g (94%). Recrystallization from ethanol–water gave 1.35 g (78%) of a light yellow solid: mp 167–170.5 °C; NMR ($CDCl_3$–Me_2SO) δ 1.22 (d, 6, $CH(CH_3)_2$, 2.21 (s, 3, $NHCH_3$), 2.88 (m, 1, $CH(CH_3)_2$), 7.34, 7.89, 8.51 (3 d, 3, Ar H), 9.62 (br, 1, NH), 11.13 (br, 1, CO_2H); IR ($CDCl_3$) 3340 (NH), 2630 (associated OH of CO_2H), 1690 (CO of CO_2H), 1670, 1520 (secondary amide) cm^{-1}.

Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.29; H, 6.93; N, 6.39.

2-Amino-5-(1-methylethyl)benzoic Acid (3f). A 300-mL glass autoclave liner was charged with 0.37 g of $Pd(PPh_3)_2(Cl)_2$, 1.8 g (0.0069 mol) of triphenylphosphine and 88.8 g (0.347 mol) of **1f** and then deoxygenated by evacuation/argon refill cycles. The liner was then further charged with 97.7 mL (0.41 mol) of tri-*n*-butylamine and 22.2 mL of water. Carbonylation of this mixture was carried out in a rocking autoclave under ca. 3 atm of CO pressure for 22 h at 115–120 °C. After the autoclave was cooled and vented, the reaction mixture was a viscous oil which was washed from the liner with a total of 900 mL of 10% aqueous NaOH, followed by 95% ethanol (3 × 10 mL). The combined washes are heated 18 h at ca. 95 °C with stirring under argon. The resulting two-phase system was allowed to cool and was then washed with dichloromethane (3 × 100 mL). The combined washings were extracted with 100 mL of 10% NaOH, and the pH of the combined aqueous layers was brought to 3.0–3.5 by addition of aqueous HCl. The acidified aqueous layer was extracted with ethyl acetate (3 × 200 mL), and the extract was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford 53.4 g of crude, crystalline **3f**. Recrystallization from dichloromethane–hexane gave 45.2 g (72%) of **3f**, mp 130–132 °C (lit.[19] mp 130–131 °C). Evaporation of the mother liquors and crystallization of the residue from dichloromethane–hexane gave an additional 7.0 g of **3f**, mp 125–128 °C. According to NMR analysis, the purity of the first crop was 97% and that of the second crop was 95%.

Acknowledgment. We thank Mrs. P. McGarry, Mr. M. Carson, Mr. J. Kudless, and Mr. D. Wagner for technical assistance, Dr. F. Scheidl for microanalyses, and Dr. T. Williams for NMR analyses.

Registry No. 1a, 614-76-6; **1b**, 79069-35-5; **1c**, 79069-36-6; **1d**, 79069-37-7; **1e**, 79083-83-3; **1f**, 68748-07-2; **2a**, 89-52-1; **2d**, 38985-80-7; **2f**, 79069-38-8; **3b**, 18331-74-3; **3c**, 79069-39-9; **3d**, 6705-03-9; **3e**, 79069-40-2; **3f**, 68701-22-4; 1-bromo-2-methoxybenzene, 578-57-4; 1-bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; 2-hydroxybenzoic acid, 69-72-7; 1-naphthalenecarboxylic acid, 86-55-5; 2-naphthalenecarboxylic acid, 93-09-4; *N*-[4-(1-methylpropy)-phenyl]acetamide, 20331-25-3; *N*-[4-(2-methylpropyl)phenyl]acetamide, 40784-94-9; 2,4-bis(1-methylethyl)aniline, 79069-41-3; 2-bromo-4,6-bis(1-methylethyl)aniline, 79069-42-4; 4-(1-methylethyl)-aniline, 99-88-7; 1-(acetylamino)-4-(1-methylethyl)benzene, 5702-74-9.

Dehydrogenation of Amines. An Approach to Imines and Aldehydes

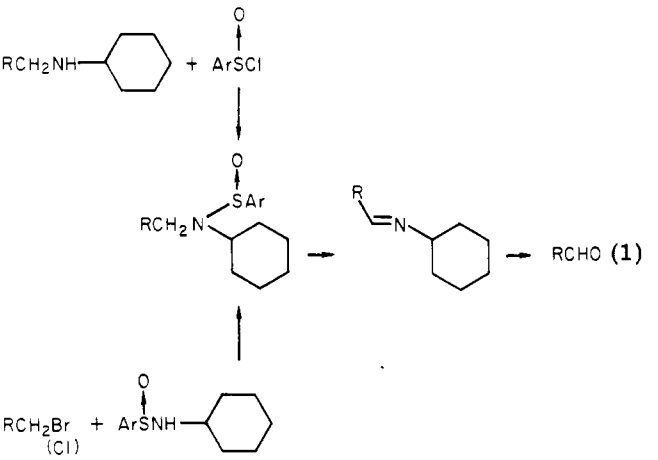
Barry M. Trost* and Guang-jian Liu

McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received April 7, 1981

Whereas the sulfenylation–dehydrosulfenylation method has proved useful for the formation of carbon–carbon double bonds,[1] the use of such a method for the introduction of unsaturation to a heteroatom has been almost unexplored. Among the most important is the formation of imines, in part because of their intrinsic importance (such as in cycloadditions to β-lactams) and in part because of their hydrolysis to carbonyl compounds. Contrary to the thiosulfinates[2a] and the sulfinimines[2b] which have relatively labile S–X bonds, the sulfinimide bond is quite strong. While sulfinamides normally are thought to be very stable, their tendency to have a decomposition point rather than a melting point was promising. We report that such a dehydrogenation proceeds well and serves as a convenient method to convert benzylic and allylic halides to imines and aldehydes.[3]

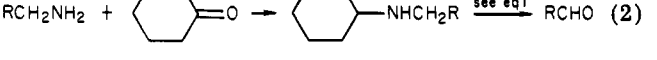
Two approaches to the sulfinamides were employed (eq 1 and Tables I and II). The direct sulfinylation of an



amine proceeded in high yield in ether containing triethylamine. Alternatively, allyl or benzyl bromides (or chlorides) smoothly alkylate *N*-cyclohexylbenzenesulfinamide. While use of sodium hydride as base and DMF as solvent is satisfactory, phase-transfer conditions are preferred. Attempts to use *N*-cyclohexyl-4-nitrobenzenesulfinamide in direct alkylations failed.

Thermolysis of the sulfinamide required use of refluxing xylene. As summarized in Table III, yields were good to excellent. The imine could be isolated by distillation. Chromatographic purification normally effected hydrolysis to the aldehyde. While virtually all of the examples utilized Ar = Ph, a rate enhancement is expected[4] and observed by employing *p*-nitrophenyl.

The regioselectivity of the elimination restricts the method to those cases which contain at least one group which facilitates the elimination. For the present study, the presence of benzylic and allylic activation served such a purpose. The choice of the cyclohexyl substituent was based on (1) the ready availability of cyclohexylamine and cyclohexanone and (2) the minimization of steric hindrance at nitrogen while maximizing the regioselectivity of the elimination away from this substituent. For conversion of a primary amine to an aldehyde, reductive amination (eq 2) produces the requisite cyclohexylamine for dehydrogenation according to eq 1.



(1) Trost, B. M. *Chem. Rev.* **1978**, *78*, 363. Trost, B. M. *Acc. Chem. Res.* **1978**, *11*, 453. Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

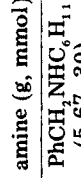
(2) (a) Chow, T. S.; Koppel, G. A.; Dorman, D. E.; Paschal, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 7864. Also see: Bachi, M. D.; Vaya, J. *Ibid.* **1976**, *98*, 7825. (b) Davis, F. A.; Friedman, A. J.; Kluger, E. W. *Ibid.* **1974**, *96*, 5000. Davis, F. A.; Friedman, A. J.; Nadir, U. K. *Ibid.* **1978**, *100*, 2844.

(3) For dehydrogenation of primary amines with selenium reagents see: Czarny, M. R. *J. Chem. Soc., Chem. Commun.* **1976**, *81*.

(4) Emerson, D. W.; Kornski, T. J. *J. Org. Chem.* **1969**, *34*, 4115. Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 197.

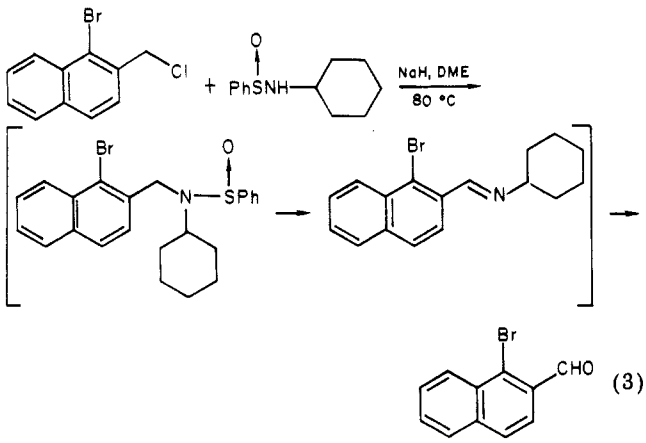
0022-3263/81/1946-4617$01.25/0

Table I. Sulfinylation of Secondary Amines

entry	amine (g, mmol)	ArSCl (g, mmol)	wt of $(C_2H_5)_3N$, g (mmol)	wt of sulfinamide, g (% yield)	mp, °C	anal. calcd (found) C	H	N	S
1	$PhCH_2NHC_6H_{11}$ (5.67, 30)	PhS(O)Cl (5.3, 33)	4.05 (40)	8.67 (92)	81.5–82.5	72.80 (72.83)	7.40 (7.41)	4.47 (4.58)	10.23 (10.17)
2	$PhCH_2NHC_6H_{11}$ (2.83, 15)	p-$O_2NC_6H_4S(O)Cl$ (3.08, 15)	2.02 (20)	3.8 (71)	103.5–104.5	63.66 (63.63)	6.17 (6.17)	7.82 (7.75)	8.95 (8.96)
3	(3.97, 16.6)	PhS(O)Cl (2.99, 18.6)	2.69 (26)	4.53 (75)	150–151	75.99 (76.08)	6.93 (7.01)	3.85 (3.85)	8.81 (8.76)
4	 (2.413, 10)[a]	p-$O_2NC_6H_4S(O)Cl$	1.518 (15)	2.96 (73)	117–119	67.62 (67.46)	5.92 (5.87)	6.86 (6.74)	7.85 (7.74)

[a] CH_2Cl_2 used as solvent instead of ether.

The conversion of alkyl halides to imines (eq 1) complements the more normal approach to imines from ketones and primary amines. The conversion of such halides to aldehydes serves as a convenient alternative to methods based on Me_2SO,[5] nitroalkanes,[6] aryl nitroso compounds,[7] amine oxides,[8] or the Sommelet reaction.[9] For example, the conversion of 1-(bromomethyl)-2-methylnaphthalene to 2-methyl-1-naphthaldehyde proceeded in better yield by this method than by the Sommelet reaction.[10] For the case of 1-bromo-2-(chloromethyl)naphthalene, the intermediate sulfinamide suffered dehydrosulfenylation under the conditions of the alkylation to give the imine. Hydrolysis during workup gave the aldehyde in 68% overall yield in a one-pot operation (see eq 3).



(3)

Experimental Section

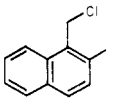
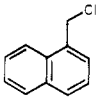
General Methods. Most of the reactions were run under a nitrogen atmosphere. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Beckman Acculab 7 spectrometer. Proton NMR spectra were recorded on JEOL MH-100 instruments using $CDCl_3$ as the solvent and Me_4Si as an internal standard. Chemical shifts are given in parts per million and coupling constants are in hertz. Analytical TLC was performed on Merck silica gel sheets. Preparative TLC was performed on 1.5-mm-thick 20 × 20 or 20 × 40 cm plates coated with Macherey-Nagel silica gel. Elemental analyses were performed by Spang Microanalytical Laboratory.

Sulfinylation of Amines. To a solution of 33 mmol of benzenesulfinyl chloride in 40 mL of ether at −15 °C was added dropwise over 40 min a solution of 30 mmol of secondary amine and 40 mmol of triethylamine in 30 mL of ether. Upon completion of the addition, the mixture was stirred 3 h at room temperature. The white precipitate was removed by filtration and washed with an additional small volume of ether. The combined ether layers were concentrated in vacuo to give the crude product which was purified by recrystallization. The experimental details are summarized in Table I.

***N*-Alkylation of *N*-Cyclohexylbenzenesulfinamide. Method A.** To a suspension of sodium hydride (12 mmol) washed free of mineral oil with hexane in 6 mL of DME or DMF was added dropwise a solution of 7.3 mmol of *N*-cyclohexylbenzenesulfinamide in 25 mL of anhydrous DME or DMF. After being stirred 1 h at room temperature and 3 h at 50–70 °C, the mixture was cooled to room temperature. A solution of 8 mmol of the halide in 20 mL of anhydrous DME or DMF was added and the resulting mixture heated at 60 (DMF) or 80 °C (DME)

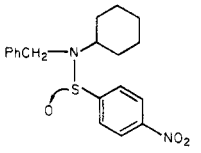
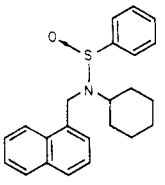
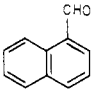
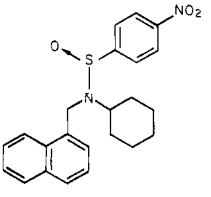
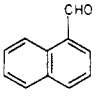
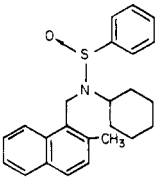
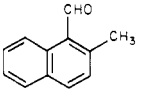
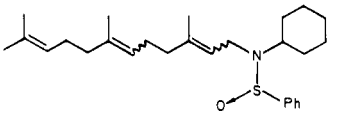
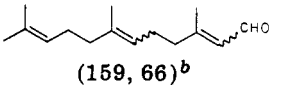
(5) Kornblum, N.; Jones, W. J.; Anderson, G. J. *J. Am. Chem. Soc.* **1959**, *81*, 4113. Epstein, W. W.; Sweat, F. W. *Chem. Rev.* **1967**, *67*, 247.
(6) Hass, H. B.; Bender, M. L. *J. Am. Chem. Soc.* **1949**, *71*, 1767.
(7) Karrer, P.; Epprecht, A. *Helv. Chim. Acta* **1941**, *24*, 1039.
(8) Franzen, V.; Otto, S. *Chem. Ber.* **1961**, *94*, 1360.
(9) Angyal, S. J. *Org. React.* **1954**, *8*, 197.
(10) Hall, D. M.; Turner, E. E. *J. Chem. Soc.* **1955**, 1242.

Table II. N-Alkylation of *N*-Cyclohexylbenzenesulfinamide

entry	halide (wt, mmol)	wt of $C_6H_{11}NHS(O)Ph$, (mmol)	method[a]	base (amt)	solvent (mL)	wt of sulfinamide (% yield)
1	$PhCH_2Cl$ (265 mg, 2.1)	405 mg (1.82)	A	NaH[b] (115 mg, 2.4 mol)	DMF (8)	432 mg (76)[c]
2	 (1.527 g, 8)	1.626 g (7.28)	A	NaH[b] (571 mg, 12 mmol)	DME (45)	2.384 g (86)[d]
3	 (547 mg, 3.1)	670 mg (3)	B	NaOH (4 mL)[e]	PhH (22)	997 mg (92)[c]
4	 (825.4 mg, 3.1)	670 mg (3)	B	NaOH (4 mL)[e]	PhH (20)	728.2 mg (76)[f]

[a] See the experimental procedure. [b] Weight of 50% dispersion in mineral oil. [c] For analytical data see Table I. [d] Mp 172–174 °C. Calcd for $C_{24}H_{27}NOS$: C, 76.35; H, 7.21; N, 3.71; S, 8.49. Found: C, 76.37; H, 7.20; N, 3.64; S, 8.56. [e] Volume of 50% aqueous solution. [f] Oil. Calcd for $C_{27}H_{41}NOS$: C, 75.82; H, 9.66; N, 3.27; S, 7.49. Found: C, 75.79; H, 9.65; N, 3.32; S, 7.43.

Table III. Preparation of Imines and Aldehydes via Regioselective Dehydrosulfenylations

entry	sulfinamide (wt, mmol)	mL of *o*-xylene	time, h	wt of K_2CO_3, mg (mmol)	product (mg, % yield)
1	 (716 mg, 2.0)	50	8	553 (4.0)	$PhCH{=}NC_6H_{11}$[a,b]
2	 (908 mg, 2.5)	40	10	691 (5.0)	 (319, 82)[b]
3	 (817 mg, 2.0)	40	6	553 (4.0)	 (279, 89)[b]
4	 (715 mg, 1.89)	15	48	552 (4.0)	 (226, 70)[b]
5	 (450 mg, 1.1)	6	13	304 (2.2)	 (159, 66)[b]

[a] Bp 93–95 °C (bath temperature at 0.65 torr). [b] Identical with an authentic sample.

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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 δ 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 ($CDCl_3$) δ 10.68 (1 H, s), 8.46 (1 H, m), 7.72 (5 H, m).

Acknowledgment. We thank the National Foundation for their generous support of our programs. We thank the University of Nanking and the government of the People's Republic of China for making it possible for Mr. Liu to be a Visiting Scholar.

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.

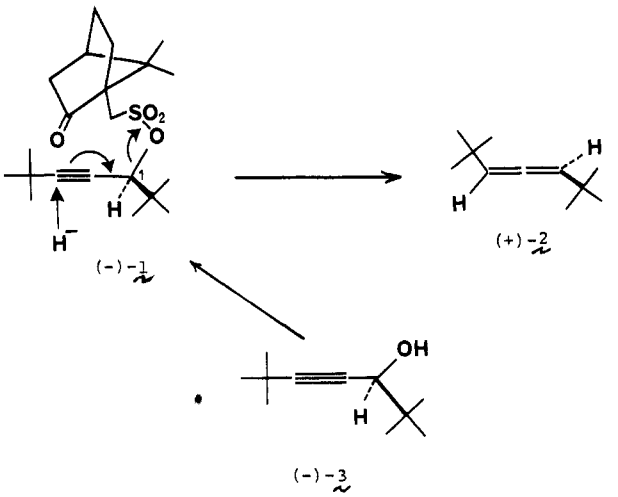
Absolute Configuration of 1,3-Di-*tert*-butylpropargyl Alcohol. Borden–Corey Stereochemistry Confirmed

William M. Butler, Yoshio Tanaka, and Masato Koreeda*

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109

Received August 21, 1980

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