is to lower the energy of the π,π^* transition below that of the n,π^* transition. This would decrease singlet–triplet crossover and decrease phosphorescence. Since strong phosphorescence was always observed, none of the substitutions examined accomplished this energy inversion.

Compounds **11** and **27** in particular show large red shifts, which suggest that the axis of L in eq 1 goes near the 4 position. This axis must be for an n,π^* transition based on the argument in the foregoing paragraph. There should be another axis for the π,π^* transition which presumably goes near the 6 position. It is unfortunate that a 6-amino compound was not available for testing this idea.

These two amino compounds, **11** and **27**, are much more strongly quenched by oxygen than is **3**. The Stern–Volmer constant $K = k_q\tau$, where k_q is the quenching rate constant and τ the excited-state lifetime. It is possible that the amino compounds have a longer lifetime, τ, than **3**. However, it would be expected that they would form stronger charge transfer complexes with O_2 and thus have a larger k_q and no change of τ.

There are some differences between **11** and **27**. For example, the dimethylamino group in **27** effects a smaller red shift in fluorescence than does the amino group in **11** (both compared with **3**) but at the same time causes less of a decrease in quantum yield.

Acknowledgment. We wish to thank Dr. J. G. Lombardino for a sample of 4-hydroxy-2-methyl-1-isoquinolone and Mr. D. E. Horning for the one of 4-benzoyl-2-methyl-1-isoquinolone. Dr. T. Pavlopoulos and Professor M. El-Sayed discussed the effects of substituents on fluorescence and phosphorescence with us.

Registry No.—**3**, 4594-71-2; **4**, 54931-49-6; **5**, 21640-33-5; **5** monotosylhydrozone, 54931-50-9; **6**, 33930-79-9; **7**, 42792-96-1; **8**, 54931-51-0; **9**, 54931-52-1; **10**, 54931-53-2; **11**, 54931-54-3; **11** salicyl derivative, 54931-55-4; **12**, 54931-56-5; **13**, 54931-57-6; **16** HCl, 54931-58-7; **16** picrate, 54931-60-1; **17**, 33930-63-1; **18**, 27187-01-5; **19**, 54931-61-2; **20**, 20334-97-8; **21**, 54931-62-3; **22**, 54931-63-4; **22** phenylthiourea derivative, 54931-64-5; **23**, 42792-97-2; **24**, 54931-65-6; **25**, 54931-66-7; **26**, 54931-67-8; **27**, 54931-68-9; **28**, 54931-69-0; **29**, 54931-70-3; **30**, 54931-71-4; **31**, 54931-72-5; **32**, 1710-20-9; **33**, 4594-73-4; 2-methylisoquinolinium iodide, 3947-77-1; 1,2,3,4-tetrahydro-4-diazo-1,3-dioxo-2-methylisoquinoline, 6075-60-1; *N*-bromosuccinimide, 128-08-5; 4-bromo-2-methylisoquinolinium iodide, 54931-73-6; *N*-chlorosuccinimide, 128-09-6; trimethyl(3,4-dihydro-2-methyl-1-isoquinolonyl-4)ammonium iodide, 54931-74-7; trimethyl(3,4-dihydro-2-methyl-1-isoquinolonyl-4)ammonium picrate, 54931-76-9; 2,3-dimethylisoquinolinium iodide, 32431-36-0; 2,3-dimethyl-1-isoquinolone, 7114-78-5; tris(2-methyl-1-isoquinolonyl-4)phenylmethane, 54931-77-0; bis(2-methyl-1-isoquinolonyl-4)phenylmethane, 17054-56-7; bis(2-methyl-1-isoquinolonyl-4)methane, 27330-16-1

Miniprint Material Available. Full-sized photocopies of the miniprinted material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the miniprinted and supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JOC-75-1760.

References and Notes

(1) S. F. Mason and D. R. Roberts, *Chem. Commun.*, 476 (1967).
(2) R. A. Henry and C. A. Heller, *J. Lumin.*, **4**, 105 (1971).
(3) C. A. Heller, R. A. Henry, and J. M. Fritsch, "Chemiluminescence and Bioluminescence", M. J. Cormier, D. M. Hercules, and J. Lee, Ed., Plenum Press, New York, N.Y., 1973, p 249.
(4) Reference 3, p 244.
(5) H. Decker, *J. Pract. Chem.*, **47**, 28 (1893).
(6) N. J. Mruk and H. Tieckelmann, *Tetrahedron Lett.*, 1209 (1970).
(7) I. G. Hinton and F. G. Mann, *J. Chem. Soc.*, 599 (1959).
(8) D. E. Horning, G. Lacasse, and J. M. Muchowski, *Can. J. Chem.*, **49**, 2785 (1971).
(9) Y. Kawazoe and Y. Yoshioka, *Chem. Pharm. Bull.*, **8**, 24 (1960).
(10) S. F. Dyke, *Adv. Heterocycl. Chem.*, **14**, 279 (1972).
(11) W. J. Gensler, "Heterocyclic Compounds", Vol. 4, R. C. Elderfield, Ed., Wiley, New York, N.Y., 1952, p 405.
(12) J. M. Muchowski, *Tetrahedron Lett.*, 1773 (1966).
(13) A. L. Henne and W. F. Zimmer, *J. Am. Chem. Soc.*, **73**, 1362 (1951).
(14) L. Friedman and H. Schecter, *J. Org. Chem.*, **26**, 2522 (1961).
(15) A GLC on the benzyl bromide, after this experiment had been performed, indicated a mixture.
(16) Y. I. Rozhinskii and M. A. Mostoslavskii, *Zh. Org. Khim.*, **8**, 2177 (1972).
(17) A. Pictet and E. Patry, *Ber.*, **26**, 1962 (1893).
(18) G. K. Turner, *Science*, **146**, 183 (1964).
(19) C. A. Heller, R. A. Henry, B. A. McLaughlin, and D. E. Bliss, *J. Chem. Eng. Data*, **19**, 214 (1974).
(20) F. P. Schäfer, Ed., "Dye Laser", Springer-Verlag New York, New York, N.Y., 1973.
(21) T. Okano and H. Matsumoto, *Yakugaku Zasshi*, **89**, 510 (1969).

Lithium Aluminum Hydride Reduction of Terpene Sultones

Joseph Wolinsky* and Ronald L. Marhenke[1]

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

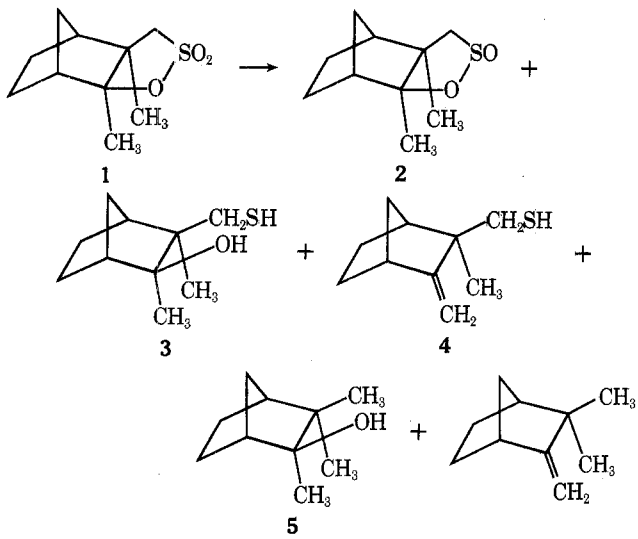
Received February 3, 1975

Lithium aluminum hydride reduction of camphene sultone, 10-isobornyl sultone, and 6-bornyl sultone yield, depending on exact conditions, sulfinate esters, mercapto alcohols, or sulfur-free alcohols. Mercaptans are slowly, and sulfides even more slowly, converted to hydrocarbons by lithium aluminum hydride at 100°.

During an investigation of the chemistry of camphene sultone (**1**)[2] it was discovered that desulfurization to camphene hydrate (**5**) took place on reduction with lithium aluminum hydride. The desulfurization reaction not only provided a powerful method for structural and stereochemical elucidation,[2] but also permitted the facile synthesis of bornane derivatives[3] and the selective introduction of a deuterium atom into the bornane and camphane ring systems.[2] We have now examined the lithium aluminum hydride reduction of terpene sultones in greater detail and wish to report that in addition to the sulfur-free alcohol, cyclic sulfinate esters and mercapto alcohols are also produced.

Camphene Sultone. Treatment of camphene sultone (**1**) with an excess of lithium aluminum hydride in THF at reflux for 6 hr, followed by work-up with aqueous hydrochloric acid, gave 33% of camphene sulfinate ester (**2**), 18% 9-mercaptocamphene hydrate (**3**), 45% of 9-mercaptocamphene (**4**), 1% of camphene hydrate (**5**), and 3% of camphene. Camphene and 9-mercaptocamphene (**4**) were not present to any appreciable extent in the crude product, but were formed in varying amounts by dehydration of **3** and **5** during GLC isolation.

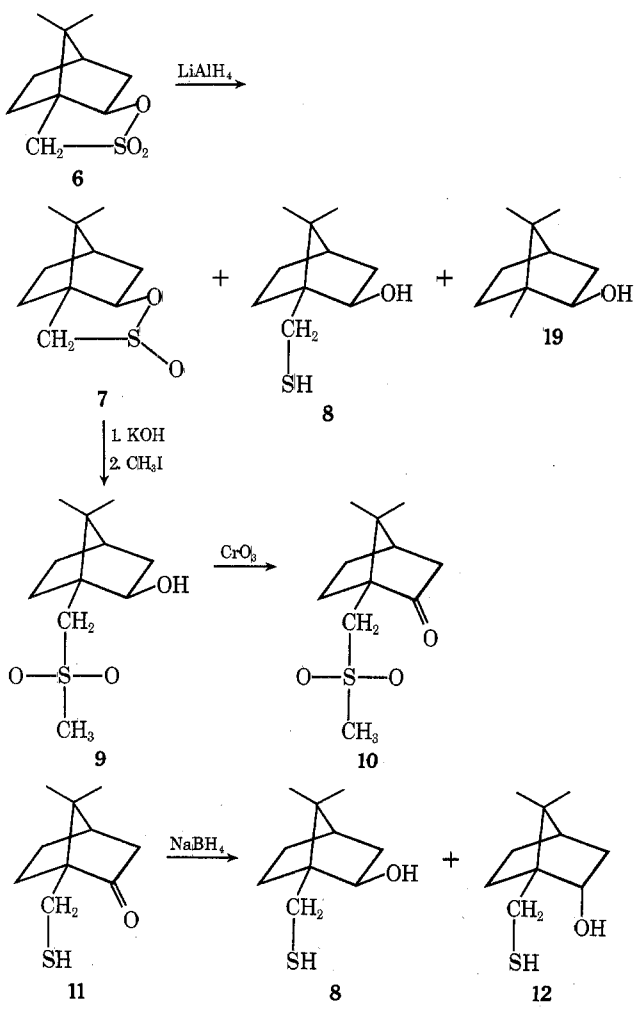
The structure assigned camphene sulfinate **2** was based on elemental and mass spectral analysis, which confirmed a



molecular formula of $C_{10}H_{16}O_2S$. Characteristic sulfinate ester[4] absorption was shown at 8.80 μ,[5] while the NMR spectrum was similar to that of camphene sultone (1). Chromic acid oxidation of 2 using the Jones procedure[7] gave camphene sultone (1).

10-Isobornyl Sultone. Reduction of 10-isobornyl sultone (6) with 1.1–2.0 equiv of lithium aluminum hydride in ether, followed by an acidic work-up, gave 10-isobornyl sulfinate (7) in good to excellent yield. When the reduction was carried out for 44 hr in THF at reflux, 10-mercaptoisoborneol (8) became the major product.

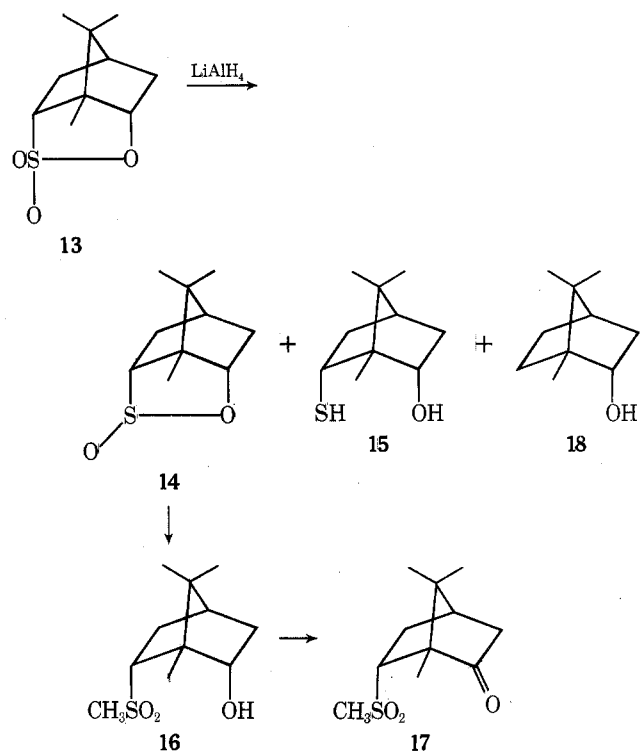
10-Isobornyl sulfinate (7) displayed sulfinate ester absorption at 8.80 μ and an NMR spectrum similar to that of



sultone 6. Treatment of 7 with potassium hydroxide and then methyl iodide afforded 10-methylsulfonylisoborneol (9) which was converted by Jones oxidation[7] to 10-methylsulfonylcamphor (10).

10-Mercaptoisoborneol (8) proved to be identical with one of the alcohols obtained by sodium borohydride reduction of 10-mercaptocamphor (11). The NMR spectrum of 10-mercaptoisoborneol (8) showed an apparent triplet at 3.88 ppm for the 2-endo hydrogen and singlet methyl signals at 0.83 and 1.03 ppm. 10-Mercaptoborneol (12) displayed a characteristic eight-line pattern for the 2-exo proton at 4.25 ppm and a singlet at 0.90 ppm for the *gem*-dimethyl group.

6-Bornyl Sultone. Lithium aluminum hydride reduction of 6-bornyl sultone (13)[3] gave, depending on the exact conditions, 6-bornyl sulfinate (14), 6-*endo*-mercaptoborneol (15),[3] and borneol (18). Oxidation of sulfinate 14 afforded sultone 13, while treatment with base and methyl iodide gave 6-*endo*-methylsulfonylborneol (16), which was oxidized to 6-*endo*-methylsulfonylcamphor (17).

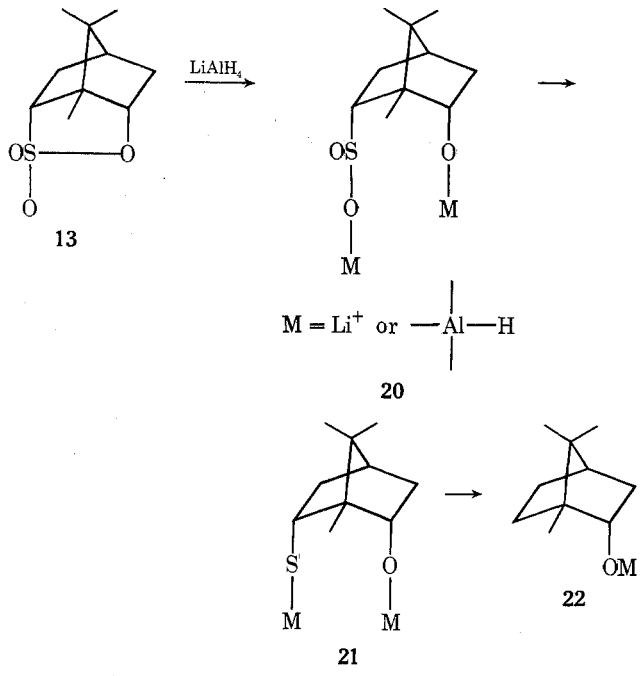


Discussion

Lithium aluminum hydride reduction of terpene sultones, followed by an acid work-up, affords a mixture of sulfinate ester, mercapto alcohol, and sulfur-free alcohol. Reduction of 6-bornyl sultone (13) with an excess of hydride was followed by removing, hydrolyzing, and analyzing aliquots at different time intervals. Sulfinate ester 14 forms initially, but is then consumed as the proportion of mercapto alcohol 15 rises to a maximum and then diminishes as the amount of borneol (18) increases. By controlling the concentration of hydride, temperature, and reaction time, any one of the three products can be made to predominate.

These observations suggest that hydride initially attacks at the sulfur atom of the sultone to produce an alkoxy sulfinate 20, which is slowly reduced to an alkoxy mercaptide 21. The mercaptide 21 is reduced even more slowly to 22.

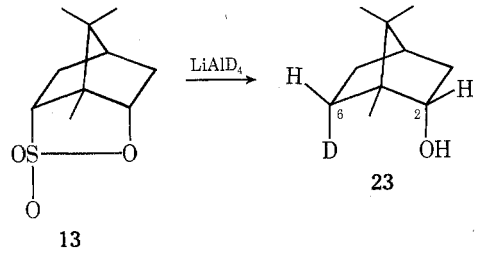
The neighboring alkoxide appears to play a role in facilitating the desulfurization step,[8] since under comparable conditions the desulfurization of mercaptans is extremely slow. For example, the conversion of dodecylmercaptan to



dodecane using lithium aluminum hydride in THF at 65° has a half-time of approximately 115 hr. In dioxane at 100° complete desulfurization requires 96 hr.

Sulfides are also desulfurized by lithium aluminum hydride at 100° using dioxane as a solvent, albeit the rate is extremely slow (70% conversion to hydrocarbons after 19 days).

The participation of the neighboring alkoxide is also inferred by the production of 6-*endo*-deuterioborneol (**23**) in low yield on reduction with lithium aluminum deuteride.



The endo configuration of the deuterium was indicated by the presence of an eight-line NMR signal for the exo C-2 proton. This observation requires the presence of an exo C-6 proton which has the proper "W" relationship for long-range spin coupling.

Experimental Section[9]

Lithium Aluminum Hydride Reduction of Camphene Sultone (1). A solution of 2.88 g (13.4 mmol) of camphene sultone (**1**)[10] in 20 ml of dioxane was added to a slurry of 2.0 g (51 mmol) of lithium aluminum hydride in 20 ml of dioxane. The mixture was heated at reflux for 6 hr and cooled, and water was added carefully. The precipitated salts were dissolved by adding 10% hydrochloric acid and the mixture was extracted with ether. The ether was removed and the products were separated by GLC. Camphene (3%) and camphene hydrate (1%)[11] were not isolated, but their presence was indicated by coincidence of GLC retention times with those of authentic samples. 9-Mercaptocamphene (**4**, 45%) was a liquid: ir 3.9, 6.05, and 11.35 μ; NMR (CCl_4) 1.10 (s, 3, CH_3), 4.52, and 4.75 ppm (s, C=CH_2); mass spectrum *m/e* (rel intensity) 168 (37), 153 (9), 140 (12), 135 (14), 121 (100), 93 (89), 79 (55).

Anal. Calcd for $C_{10}H_{16}S$: C, 71.36; H, 9.58; S, 19.05. Found: C, 71.48; H, 9.78; S, 19.11.

3-Mercaptocamphene hydrate (**3**, 18%) was a liquid: ir 2.85, 3.9, and 9.05 μ; NMR (CCl_4) 0.99 (s, 3, CH_3), 1.21 (s, 3, CH_3), 1.40 (X of ABX, 1, -CH_2**SH**), 1.72 (d, 1, OH), 2.36 and 2.92 ppm (A and B portions of ABX, 2, J_{AX} = 8, J_{BX} = 7, J_{AB} = 13 Hz, -CH_2SH); mass spectrum *m/e* (rel intensity) 168 (12), 153 (27), 152 (56), 135 (20), 121 (14), 109 (73), 93 (24), 43 (100).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.69; H, 9.56.

Camphene sulfinate (**2**, 33%) was further purified by sublimation in vacuo and showed mp 145°; ir 8.8 μ (-SO_2-); NMR (CCl_4) 1.33 (s, 3, CH_3), 1.50 (s, 3, CH_3), and 2.98 ppm (s, 2, -CH_2SO_2); mass spectrum *m/e* (rel intensity) 200 (9), 136 (43), 121 (79), 109 (30), 107 (46), 95 (46), 93 (100), 67 (46), and 43 (65).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.92; H, 8.05; S, 16.01. Found: C, 59.99; H, 8.14; S, 15.77.

Oxidation of Camphene Sulfinate (2) to Camphene Sultone (1). A solution of 144 mg (0.72 mmol) of camphene sulfinate (**2**) in acetone was titrated with 0.30 ml (0.80 mmol) of Jones reagent.[7] After 1 hr several drops of isopropyl alcohol were added, the mixture was filtered, and the filtrate was diluted with water and extracted with ether. The ether was dried ($MgSO_4$) and removed, leaving an oil which was sublimed to give 86 mg (55%) of crystalline camphene sultone (**1**), mp 133–135°.[2]

10-Isobornyl Sulfinate Ester (7). A solution of 8.0 g (37 mmol) of 10-isobornyl sultone (**6**) in diethyl ether was added slowly to a stirred slurry of 2.88 g (74 mmol) of lithium aluminum hydride in ether. The mixture was refluxed for 45 hr and cooled, and the excess hydride was decomposed by the slow addition of saturated sodium chloride solution. The salts were separated by filtration, washed with ether, and dissolved in dilute hydrochloric acid. The acidic solution was extracted with ether. The ether extract was dried and evaporated to leave 5.26 g of crude sulfinate ester. An analytical sample of **7** was obtained by preparative TLC (silica gel PF-254, 10% ether–hexane) followed by GLC using a SE-30 column at 190°: mp 145–148°; ir (CCl_4) 8.80 (-SO_2-), 9.08, 10.1, and 11.65 μ; NMR (CCl_4) 0.89 and 0.92 (s, 6, CH_3), 1.0–2.25 (m, 7), 2.50 and 3.33 (AB q, 2, J = 14.2 Hz, -CH_2SO_2-), and 5.08 ppm (m, 1, J_{AX} = 7.5, J_{BX} = 3.8 Hz, -CHOSO-); mass spectrum *m/e* (rel intensity) 200 (1.4), 136 (33), 121 (72), 107 (46), 93 (100), 79 (44), 67 (40), and 41 (73).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.92; H, 8.05; S, 16.01. Found: C, 59.89; H, 8.01; S, 15.67.

GLC analysis of the material isolated from the original ether filtrate, as well as the sulfinate ester isolated from the salts as described above, indicated the formation of 70% of sulfinate ester **7**, 9% of 10-mercaptoisoborneol (**8**), and 21% of isoborneol (**19**).

10-Methylsulfonylisoborneol (9). A 4.1-g sample of a mixture of sulfinate ester **7**, sultone **6**, 10-mercaptoisoborneol (**8**), and isoborneol (**19**) was suspended in water and treated with 1.2 g of potassium hydroxide and 2.9 g of methyl iodide. The mixture was extracted after 2 hr with ether and the ether was removed to leave a small amount of oil whose ir spectrum indicated the presence of isoborneol and sultone **6**. Another 100 mg of potassium hydroxide and 3 g of methyl iodide were added to the aqueous phase, which was then stirred at ambient temperature for 24 hr and extracted with ether. The ether extract was washed with saturated sodium bisulfite and saturated salt solutions, dried, and evaporated to give 1.3 g (27%) of 10-methylsulfonylisoborneol (**9**). An analytical sample was obtained by sublimation in vacuo: mp 95–97°; ir (CCl_4) 2.8, 7.65, 8.85, 9.3, 9.5, 10.4, and 11.4 μ; NMR ($CDCl_3$) 0.84 and 1.08 (s, 6, CH_3), 1.3–2.0 (m, 7), 2.98 (s, 3, SO_2CH_3), 3.12 (s, 1, OH removed by addition of trifluoroacetic acid), 2.93 and 3.48 (AB q, 2, J = 13.5 Hz, -CH_2SO_2), and 4.12 ppm (broad t, 1, -CHO); mass spectrum *m/e* (rel intensity) 232 (0.1), 153 (74), 135 (83), 109 (100), 108 (100), 107 (71), 94 (49), 93 (99), and 41 (90).

Anal. Calcd for $C_{11}H_{20}O_3S$: C, 56.86; H, 8.68; S, 13.80. Found: C, 57.20; H, 8.64; S, 14.05.

10-Methylsulfonylcamphor (10). To a solution of 430 mg of 10-methylsulfonylisoborneol (**9**) in 5 ml of purified acetone was added 0.7 ml of Jones reagent.[7] The excess oxidant was destroyed with isopropyl alcohol, the solution was diluted with 15 ml of ether, and anhydrous sodium sulfate was added. The ether solution was separated and distilled in vacuo to give 425 mg of solid. Recrystallization from hexane gave 318 mg (74%) of 10-methylsulfonylcamphor (**10**): mp 79.5–80.5°; ir (CCl_4) 5.75, 7.6, and 8.8 μ; NMR (CCl_4) 0.90 and 1.08 (s, 6, CH_3), 1.3–2.7 (m, 7), 3.02 (s, 3, -SO_2CH_3), and 2.77 and 3.38 ppm (AB q, 2, J = 16 Hz, -CH_2SO_2-); mass spectrum *m/e* (rel intensity) 230 (0.6), 151 (75), 123 (49), 109 (100), 107 (30), 93 (29), 81 (80), 67 (49), 55 (36), 43 (34), and 41 (57).

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88; S, 13.92. Found: C, 57.08; H, 8.00; S, 13.84.

10-Mercaptoisoborneol (8). To a solution of 502 mg (2.3 mmol) of 10-isobornyl sultone (**6**) in 8 ml of dry THF was added

2.55 ml of a 1.0 *M* (2.55 mmol) solution of lithium aluminum hydride in THF. The solution was heated at reflux and aliquots were periodically withdrawn, treated with water and dilute hydrochloric acid, and extracted with ether, and the ether solution was then analyzed by GLC (SE-30 column). The yield of 10-mercaptoisoborneol rose to 40% after 44 hr. A sample of 8 isolated by GLC proved identical with an authentic sample of 8 prepared by reduction of 10-mercaptocamphor (11) as described below.

Sodium Borohydride Reduction of 10-Mercaptocamphor (11). A solution of 10 g of 10-mercaptocamphor,[12] mp 65.5–67°, and 720 mg of sodium borohydride in 50 ml of ethanol was kept at ambient temperature for 24 hr and then poured into water and extracted with ether. The ether was dried and removed to leave 9.2 g of colorless oil which slowly solidified.

A 4.1-g portion of the crude product was chromatographed on 100 g of silica gel using 5% ether–hexane as eluent. 10-Mercaptoisoborneol (8), 1.93 g, eluted first and after sublimation in vacuo showed mp 71.5–73°: ir (mull) 2.9, 3.9 μ; NMR (CCl_4) 0.83 and 1.03 (s, 6, CH_3), 1.11 (X of AMX, 1, J_{AX} = 9, J_{MX} = 6 Hz, SH), 2.25 (s, 1, OH), 2.46 and 2.79 (AM of AMX, 2, J_{AM} = 12.5 Hz, $-CH_2S$), and 3.88 ppm (broad t, 1, –CHO); mass spectrum *m/e* (rel intensity) 186 (0.5), 168 (24), 153 (7), 152 (10), 135 (32), 121 (21), 109 (27), 108 (100), 95 (58), and 93 (42).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74; S, 17.22. Found: C, 64.57; H, 9.64; S, 17.29.

After collecting a mixture of 10-mercaptoisoborneol and 10-mercaptoborneol, 350 mg of pure 10-mercaptoborneol (12) was obtained. The analytical sample was obtained by sublimation in vacuo and showed mp 83–84° (sealed capillary); ir (mull) 2.9 and 4.0 μ; NMR (CCl_4) 0.90 (s, 6, CH_3CCH_3), 2.3 (s, 1, OH which was removed upon addition of trifluoroacetic acid), 2.53 and 2.66 (m, 2, $-CH_2S$), and 4.25 ppm (m, 1, CHO); NMR (benzene) 0.71 (s, 6, CH_3CCH_3), 1.27 (m, 1, SH), 2.38 and 2.40 (AB portion of ABX, 2, $-CH_2S$), 2.57 (s, 1, OH), 4.18 ppm (m, 1, –CHO–); mass spectrum *m/e* (rel intensity) 186 (1.5), 168 (8), 153 (8), 152 (15), 135 (19), 121 (15), 109 (28), 108 (100), 95 (63), and 93 (35).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74; S, 17.22. Found: C, 64.67; H, 9.53; S, 17.12.

6-Bornyl Sulfinate Ester (14). A slurry of 278 mg (7.3 mmol) of lithium aluminum hydride in ether was added slowly to a solution of 1.58 g (7.3 mmol) of 6-bornyl sultone (13) in ether. The mixture was stirred at ambient temperature for 24 hr and then water was carefully added until the aluminum salts coagulated. The salts were removed by filtration and washed with ether. The filtrate was evaporated leaving 545 mg (34% recovery) of sultone 13.

The aluminum salts were dissolved in 10% hydrochloric acid and extracted with ether. The ether extracts were dried ($MgSO_4$) and evaporated, leaving 928 mg (63%) of colorless solid. Recrystallization from hexane gave pure sulfinate ester 14: mp 191–193°; ir ($CHCl_3$) 9.0 μ; NMR (CCl_4) 0.97, 1.00, and 1.41 (s, 9, CH_3), 3.05 (d of d, 1, J = 10.7 and 3.0 Hz, $-CHSO_2-$), and 4.88 ppm (d of d, 1, J = 7.2 and 0.6 Hz, –CHO); mass spectrum *m/e* (rel intensity) 200 (28), 136 (26), 135 (37), 121 (27), 108 (28), 107 (31), 93 (100), 41 (39).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.92; H, 8.05; S, 16.01. Found: C, 60.15; H, 8.24; S, 16.16.

The results illustrated in Table I were obtained by treating 1 mmol of sultone 13 in 5 ml of THF at 0° with 1.0 and 5.0 ml of a 1.0 *M* solution of lithium aluminum hydride in ether. Aliquots were withdrawn, quenched with 5% hydrochloric acid, and extracted with ether. The ether extract was dried ($MgSO_4$), concentrated, and analyzed using an SE-30 column at 170°.

Table I
Lithium Aluminum Hydride Reduction of 6-Bornyl Sultone (13)

$LiAlH_4$, mmol	Time	% sultone 13	% sulfinate ester 14[a]
1	5 min	92	6
1	1 hr	86	12
1	6 hr	18	80
5	5 min	39	61
5	1 hr	13	86
5	5 hr	0	91

[a] Material balance shown is not 100% owing to the formation of small amounts of more highly reduced compounds.

Oxidation of 6-Bornyl Sulfinate Ester (14). A 107-mg sample of pure sulfinate ester 14 was kept overnight in acetone with an excess of chromium trioxide in sulfuric acid–water.[7] Excess reagent was destroyed with isopropyl alcohol and the mixture was diluted with water and extracted with ether. The ether was dried and removed to leave 100 mg of solid whose infrared spectrum indicated that it was mainly sultone 13 contaminated by a small amount of sulfinate ester 14.

6-*endo*-Methylsulfonylcamphor (17). A suspension of 770 mg (3.8 mmol) of 6-bornyl sulfinate ester (14) in 20 ml of water containing 700 mg of potassium hydroxide was heated for 2 hr, cooled, filtered, and then treated with 1.0 ml of methyl iodide. After stirring at ambient temperature for 24 hr, the mixture was heated to drive off excess methyl iodide, cooled, and then extracted with ether. The ether was removed to give 551 mg of crude 6-*endo*-methylsulfonylborneol (16). Two recrystallizations from hexane gave a solid, mp 85–94°, sublimation under vacuum gave a product melting over a range of 70–90°, while preparative thin layer chromatography gave a solid: mp 71–74°; ir (CCl_4) 2.9 and 8.85 μ; NMR (CCl_4) 0.95 (s, 6, CH_3CCH_3), 1.18 (s, 3, CH_3), 3.00 (s, 3, CH_3SO_2-), 3.42 (four broad lines, 1, $CHSO_2-$), 3.72 (s, 1, OH), and 3.97 ppm (four broad lines, 1, –CHO); mass spectrum *m/e* (rel intensity) 232 (0.1), 188 (1), 153 (4), 152 (3), 109 (32), 108 (100), 93 (28), and 41 (34).

6-*endo*-methylsulfonylborneol (16, 368 mg) in 20 ml of acetone was treated with 1 ml of Jones reagent.[7] After 15 min the excess chromic acid was destroyed with ethanol and the mixture was poured into water and extracted with ether. The ether was removed and the residue was recrystallized from dry methanol to give 77 mg of 6-*endo*-methylsulfonylcamphor (17): mp 209–211°; ir (mull) 5.75 and 8.8 μ; NMR ($CDCl_3$) 0.87 (s, 3, CH_3), 1.05 (s, 3, CH_3), 2.88 (s, 3, CH_3SO_2-), and 3.51 (X portion of ABX, 1, J_{AX} = 10.5, J_{BX} = 5.5 Hz, $-CHSO_2$).

Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88. Found: C, 57.15; H, 7.99.

Lithium Aluminum Hydride Reduction of 6-Bornyl Sulfinate ester (14). To a solution of 73 mg (0.36 mmol) of 6-bornyl sulfinate ester (14) in 5 ml of dry THF was added 0.7 ml of a 1.0 *M* solution (0.7 mmol) of lithium aluminum hydride in ether. Aliquots were periodically removed from the refluxing solution, quenched with water, and acidified with 5% hydrochloric acid. The resulting solutions were saturated with sodium chloride and extracted with ether. The ether solutions were dried ($MgSO_4$), concentrated, and analyzed using a SE-30 column at 155°. The yield of 6-*endo*-mercaptoborneol (15)[3] rose to 97% within 2 hr and then dropped to 90% after 44 hr as the amount of borneol (18) increased to 10%.

Reduction of 6-Bornyl Sultone (13) with Lithium Aluminum Deuteride. A solution of 326 mg of 6-bornyl sultone in dry THF was added to a slurry of 650 mg of lithium aluminum deuteride (Alfa Inorganics) in THF. The solution was heated at reflux for 440 hr and cooled and the excess deuteride was decomposed with deuterium oxide. Dilute hydrochloric acid was added until the salts dissolved and the solution was extracted with ether. The ether was dried and removed and GLC analysis of the residue showed that it was composed of 6-*endo*-mercaptoborneol (15) and borneol (18). A pure sample of borneol was obtained by GLC using a SE-30 column at 125°. The NMR spectrum of this sample of borneol was identical with that of authentic material except it integrated for one less proton in the region 1.9–2.6 ppm. The relative abundance of the molecular ion was too low to permit an accurate determination of the deuterium content.

A 25-mg sample of the borneol obtained above was oxidized using a solution of chromium trioxide in pyridine and water. After the usual work-up a mixture of 60% camphor and 40% borneol was obtained. A pure sample of camphor was isolated by GLC using a 20% Carbowax column at 177°; the mass spectrum indicated the presence of 88% of one deuterium atom; the NMR spectrum showed a reduction in peak area in the 1.3–1.4 region.

Lithium Aluminum Hydride Reduction of Dodecyl Mercaptan. A weighed amount of dodecyl mercaptan was added to the solvent, followed by an appropriate amount of 1.0 *M* lithium aluminum hydride solution in ether. The solution was brought to reflux and aliquots were withdrawn at appropriate time intervals, quenched with 5% hydrochloric acid, and extracted with ether. The ether extract was dried, concentrated, and analyzed using a SE-30 column at 140°. The results are displayed in Table II.

Table II
Lithium Aluminum Hydride Reduction of Dodecyl Mercaptan

Solvent	Mmol $LiAlH_4$/ mmol RSH	Time, hr	% dodecane
THF	5.4	3.5	0
THF	5.4	21.0	6
THF	5.4	115	53
Dioxane	5.0	2.0	3
Dioxane	5.0	44	47
Dioxane	5.0	71	92
Dioxane	1.1	40	25
Dioxane	1.1	72	83
Dioxane	1.1	96	98

Lithium Aluminum Hydride Reduction of Decyl Dodecyl Sulfide. Approximately 20 ml of dioxane was distilled into a flask containing 1.002 g (2.93 mmol) of decyl dodecyl sulfide,[13] and then 264 mg of cyclododecane and 230 mg (6.0 mmol) of lithium aluminum hydride were added. The stirred slurry was heated at reflux and aliquots were withdrawn periodically, diluted with ether, quenched with water, and acidified with 5% hydrochloric acid. The organic products were extracted with ether and dried. The concentrated ether solution was analyzed using an SE-30 column at 130°. The yields of dodecane follow, time in hours (% dodecane): 2 (0), 15 (0.2), 82 (24), 278 (56), and 472 (64). At no time was there evidence for the presence of decyl or dodecyl mercaptan.

Registry No.—**1**, 13131-58-3; **2**, 54934-37-1; **3**, 54934-38-2; **4**, 54934-39-3; **6**, 13131-57-2; **7**, 54934-40-6; **8**, 54934-41-7; **9**, 54934-42-8; **10**, 54934-43-9; **11**, 54984-43-9; **12**, 54934-44-0; **13**, 38359-42-1; **14**, 54934-45-1; **16**, 54934-46-2; **17**, 54934-47-3; lithium aluminum hydride, 16853-85-3; sodium borohydride, 16940-66-2; dodecyl mercaptan, 112-55-0; decyl dodecyl sulfide, 54934-48-4.

References and Notes

(1) Abstracted in part from the Ph.D. Thesis of R. L. Marhenke, Purdue University, Aug 1970.
(2) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).
(3) J. Wolinsky, R. L. Marhenke, and E. J. Eustace, *J. Org. Chem.*, **38**, 1428 (1973).
(4) For the preparation of sulfinate esters see D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969); J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. DeMayo, *Chem. Commun.*, 31 (1969); E. N. Givens and L. A. Hamilton, *J. Org. Chem.*, **32**, 2857 (1967); R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968); K. S. Dhami, *Chem. Ind. (London)*, 1004 (1968); D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969).
(5) It has been suggested[6] that sulfinate esters show characteristic infrared absorption bands at 8.7–9.1 and 10.1–11.0 μ. The sulfinate esters prepared in this study show the first of these peaks. Sulfinates **7** and **14** show a second peak at 10.1 and 10.5 μ, respectively, whereas camphene sulfinate **2** shows only weak absorption in the region 9.1–11.3 μ.
(6) L. F. Field, C. B. Hoelzel, J. M. Locke, and J. E. Lawson, *J. Am. Chem. Soc.*, **83**, 1256 (1961).
(7) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).
(8) For the desulfurization of aminothiols see E. L. Eliel and J. Roy, *J. Org. Chem.*, **30**, 3092 (1965), and references cited therein. See B. Franzen and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965), for the role of a neighoring hydroxyl in the reduction of double bonds by lithium aluminum hydride.
(9) All boiling and melting points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord spectrometer or with a Perkin-Elmer Model 421 spectrometer. NMR spectra were determined with a Varian A-60A spectrometer. Mass spectra were recorded by the Purdue University Spectral Services Department on a Hitachi RMU-6A instrument using a ionizing energy of 70 eV, an inlet temperature of 185°, and a source temperature of 160°. Microanalyses were performed by Dr. C. S. Yeh and associates.
(10) Prepared by thermal rearrangement of 10-isobornyl sultone (**6**).[2]
(11) The amount of camphene, camphene hydrate, 9-mercaptocamphene, and 9-mercaptocamphene hydrate varied from analysis to analysis, presumably owing to dehydration occurring in the injection port of the gas chromatograph.
(12) O. Dimroth, L. Kraft, and K. Aichinger, *Justus Liebigs Ann. Chem.*, **545**, 124 (1940).
(13) Decyl dodecyl sulfide was obtained by the reaction of dodecyl mercaptan with 1-bromodecane using sodium hydroxide and ethanol. The solid sulfide was purified by distillation, bp 171–173° (0.25 mm), mp 27.5–28.5°, *m/e* 242 (35%).

Reactions of Organolithium Compounds and Grignard Reagents with Lithium Carboxylates

Robert Levine,* Marvin J. Karten, and William M. Kadunce

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received July 18, 1974

With the exception of the reaction of equivalents of phenyllithium with lithium acetate for 24 hr, which gives a mixture of acetophenone and diphenylmethylcarbinol, similar reactions involving six other lithium carboxylates give only ketones. The reactions of three lithium carboxylates with phenyllithium for only 0.5 hr give mixtures of ketones and carbinols. These latter results are explained by suggesting that even in the presence of water the unreacted phenyllithium survives for sufficiently long so that it reacts appreciably with the ketone, $RCOC_6H_5$, which arises from the hydrolysis of the intermediate, $R(C_6H_5)C(OLi)_2$. Evidence to support this argument is given. The reactions of two lithium carboxylates with three Grignard reagents give mixtures of ketones and carbinols with the latter products predominating except with methylmagnesium iodide, in which case the reverse is true.

A thorough study of the reactions of carboxylic acids and their lithium salts with phenyllithium has apparently not been reported. In 1933 Gilman and Van Ess[1] made the significant observations that the reaction of benzoic acid (1 equiv) with phenyllithium (2 equiv) gave benzophenone (37.2%) and triphenylcarbinol (14.1%) and that refluxing lithium benzoate (0.136 mol) with phenyllithium (0.1 mol) for 5.5 hr gave benzophenone (70.0%) and no triphenylcarbinol. In contrast to these results Tegnér[2] has shown that the reactions of 2 equiv of methyllithium with 1 equiv of a series of aliphatic and aromatic acids for 1 hr give the corresponding methyl ketones and no tertiary alcohols.

Braude and Coles[3] have also obtained only ketone (30–40%) by stirring a mixture of equivalents of isobutenyllithium and lithium acetate, benzoate, or crotonate for a 24-hr period. Petrov and Sokolova[4] report yields of less than 25% of ketone and no carbinol from the reactions of sodium acetate and sodium *n*-butyrate with primary Grignard reagents in ether.

The present investigation is concerned with a study of