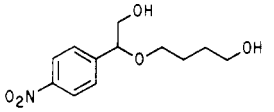

(ii)

mg of 18-crown-6 and 360 mg of potassium hydroxide. The solution was stirred under N_2 for 48 h, then quenched with acetic acid (pH ~6), and diluted with water and ethyl acetate. The organic phase was separated, washed with water and brine, and dried over sodium sulfate. Chromatography of the concentrated multicomponent residue on silica gel (40% EtOAc/hexane) yielded 55 mg of the known product (12% yield): ^{1}H NMR ($CDCl_3$) δ 8.13 and 7.38 (4 H, A_2B_2), 3.88 (t, J = 6 Hz, 2 H), 2.93 (t, J = 6 Hz, 2 H), 2.3 (br s, 1 H).

X-ray Study of 7. Crystal data for 7 ($C_8H_7NO_3$) were as follows: triclinic, space group $P\bar{1}$, Z = 2, a = 7.038 (1) Å, b = 7.718 (2) Å, c = 7.556 (1) Å, α = 104.50 (2)°, β = 83.11 (1)°, γ = 115.10 (5)°, D_{measd} = 1.45 g cm^{-3}, D_{calcd} = 1.52 g cm^{-3}, μ(Cu Kα) = 9.0 mc^{-1}, 1087 reflections, of which 1033 were greater than one standard deviation. Intensity data for all reflections with 2θ 138° were collected by using the step-scan technique at −150 °C on a Syntex $P2_1$ diffractometer controlled by a Harris computer using graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). Standard deviations in observed intensities were approximated by the function $\sigma^2(I) = \sigma^2$(counting statistics) + $(0.017I)^2$, where the coefficient of I was calculated from intensities of 10 reflections monitored throughout the data collection, considering deviations in intensities that were not explained by counting statistics.[19] The structure was solved by direct methods by using DIREC.[20]

Coordinates, hydrogen coordinates, and anisotropic thermal parameters of non-hydrogen atoms were refined minimizing the function $\sum w(F_o^2 - F_c^2)^2$ where weights w were taken as the reciprocals of the variances $\sigma^2(F_o^2)$. Atomic form factors were from "International Tables for X-Ray Crystallography"[21] except hydrogen form factors which were taken from Stewart et al.[22] The final agreement index R, ($R = \sum||F_o| - |F_c||/\sum F_o$), was 0.035. All calculations were carried out on an IBM 3033 computer using the CRYM system of crystallographic programs.[20]

Registry No. 1, 51673-59-7; 3, 6851-99-6; 4, 88057-15-2; 5, 39830-70-1; 6, 88057-17-4; 7, 88057-16-3; 9, 15121-84-3; 9 (benzoate), 88057-18-5; 12, 6388-74-5; 12 (bromohydrin), 19922-82-8; ii, 88057-20-9; (*p*-nitrophenyl)ethylene glycol, 88057-19-6; 2′-nitroacetophenone, 577-59-3; methyl 2-nitrobenzoate, 606-27-9; *p*-nitrophenacyl bromide, 99-81-0; 4′-nitroacetophenone, 100-19-6; 4-nitrobenzeneethanol, 100-27-6.

Supplementary Material Available: Tables II–VII, anisotropic thermal parameters, hydrogen coordinates, bond distances, bond angles, torsion angles, and short intermolecular distances (5 pages). Ordering information is given on any current masthead page.

Regiospecific Two-Step Synthesis of Optically Active Allylic Terpenyl Thiols

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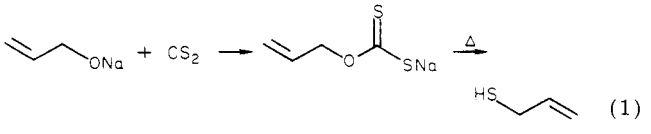
Allylic thiols were prepared in 70–90% yields by treatment of mono- and sesquiterpenes with $C_6H_5SO_2N{=}S{=}O$ followed by $LiAlH_4$ reduction of the ene adducts.

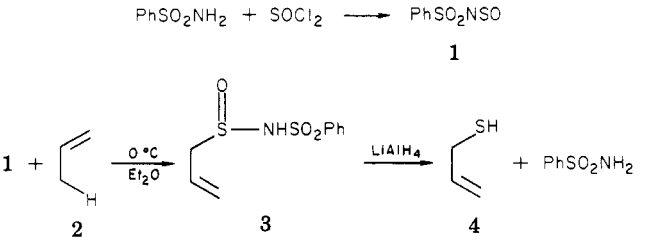
Allylic thiols are of interest as synthesis intermediates because they can be converted into allylic dianions that

react preferentially in the γ-position with a variety of electrophiles.[1] In addition, terpene thiols are constituents of fruit flavors and of perfumes.[2-6] Allylic thiols can be prepared by treating an alkali metal allylic alcoholate with CS_2 followed by thermal degradation of the resulting metal xanthogenate[3] (eq 1).



(1)

Scheme I



This reaction has been applied to the preparation of terpene thiols from geraniol, pulegol, carveol, and myrtenol. However, it is not regioselective (or stereoselective), presumably because of a double rearrangement similar to the one that has been observed with sulfodiimides.[7] We here present a new regiospecific synthesis of optically active terpene thiols in two steps from readily available terpene hydrocarbons.

N-Sulfinylbenzenesulfonamide (1), which is a potent enophile and dienophile,[8-10,16] undergoes an ene reaction

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(8) Dêlêris, G.; Kowalski, J.; Dunoguès, J.; Calas, R. *Tetrahedron Lett.* **1977**, 4211.
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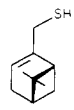
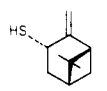
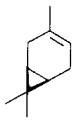
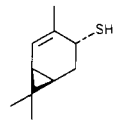
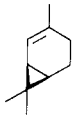
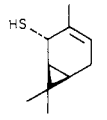
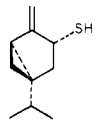
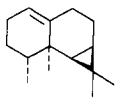
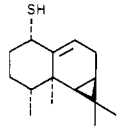
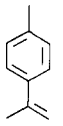
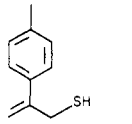
Table I. Synthesis of Allylic Thiols from Hydrocarbons

compd	alkene 2	$[\alpha]^{22}_D$[a] (lit.), deg	reaction time, h	yield of adduct 3,[b] %	thiol 4[c]	yield, % (from 3)	$[\alpha]^{22}_D$,[a] deg
a		−17.46 (−22.6)[11]	0.05	95		84	−42.6
b		−50.1 (−50.1)[11]	16	70		93	+121
c		+16.85 (+17.1)[12]	3	92		86	+519
d		+92.32 (+89.4)[13]	1	85[d]		88	−105.6
e		+20.05 (+20.8)[14]	3	72		72	−78.7
f		+52.20 (+72)[15]	6	50		82	−27.6
g			6	81		75	

[a] $c \approx 0.4$ mol L^{-1}; $CHCl_3$. [b] Adducts **3** have the same carbon skeleton as thiols **4**, with the group $S(O)NHSO_2Ph$ in place of SH. [c] Satisfactory analyses (±0.3%) for C, H, and S and mass spectra have been submitted to the editor. [d] Two diastereoisomers were obtained, which evidently correspond to the two configurations of the chiral S(O) group since reduction of the mixture gave the single allylic thiol **4d**.

Table II. Characterization Data

compd	solvent: ^{1}H NMR, δ	IR, cm^{-1}	MS, *m/e* (relative intensity)
4a	CCl_4: 0.83 (s, 3 H, gem CH_3) 1.33 (s, 3 H gem CH_3), 1.23 (t, J = 2 Hz, 1 H, SH) 3.1 (br d, J = 8 Hz, 2 H, CH_2-S) 5.45 (m, 1 H, C=CH)	2565, 1640, 1380, 1360	168 (M^+, 8), 91 (100), 124 (14), 119 (14)
4b	CCl_4: 0.66 (s, 3 H, gem CH_3), 1.23 (s, 3 H, gem CH_3), 3.73-4.13 (m, 1 H, CH-S), 4.66 (br s, 1 H, C=CH), 4.86 (br s, 1 H, C=CH)	3080, 2560, 1640, 1370, 1340	168 (M^+, 5), 134 (27), 119 (23), 92 (62), 91 (100), 79 (23)
4c	CCl_4: 0.87 (s, 3 H, gem CH_3), 1.1 (s, 3 H, gem CH_3), 2.7-3.1 (m, 1 H, CH-S), 5.27-5.5 (m, 1 H, C=CH)	2920, 2560, 1450	168 (M^+, 2), 167 (5), 119 (37), 93 (100), 92 (100), 91 (28)
4d	CCl_4: 0.87 (s, 3 H, gem CH_3), 1.02 (s, 3 H, gem CH_3), 3.13 (br d, 1 H, J = 8 Hz CH-S), 5.02-5.35 (m, 1 H, C=CH)	3000, 2560	168 (M^+, 2), 134 (29), 119 (100), 91 (37)
4e	CCl_4: 0.6 (d, J = 6 Hz, 2 H, C-C-CH_2), 0.7-1.07 (2 d, J = 7 Hz, 6 H, $(CH_3)_2CH$), 2.87-3.5 (m, 1 H, CH-S), 4.95 (d, 2 H, $C=CH_2$)	3080, 2550, 1660, 1390, 1370	168 (M^+, 4), 136 (20), 135 (41), 119 (40), 93 (95), 92 (58), 91 (100)
4f[a]	CCl_4: 3.87-4.17 (m, 1 H, CH-S), 5.27-5.53 (m, 1 H, C=CH)	3000, 1660	236 (M^+, 6), 203 (42), 202 (28), 159 (100), 145 (39), 105 (53), 91 (42)
4g	CCl_4: 1.36 (t, J = 8 Hz, 1 H, SH), 2.33 (s, 3 H, CH_3Ph), 3.53 (d, J = 8 Hz, 2 H, CH_2-S), 5.17-5.43 (m, 2 H, $C=CH_2$)	3030, 2560, 1660, 1620, 1570, 1540	164 (M^+, 74), 149 (90)

[a] Mp 61 °C (hexane).

with terpene hydrocarbons and similar compounds under mild conditions to give an intermediate, **3**, that can be reduced with $LiAlH_4$ to a thiol (Scheme I).

The ene reaction proceeds readily at 0 °C and is re-

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giospecific. Benzenesulfonamide is recovered quantitatively from the reduction step. Results of the application of this reaction sequence to several terpenes and other hydrocarbons are summarized in Table I.

Work is in progress to define the scope and limitations of this route to allylic thiols.

Experimental Section

General Methods. Infrared spectra were run on a Perkin-Elmer 457 spectrophotometer. ^1H NMR spectra were determined in the indicated solvent on a Perkin-Elmer R12 (60 MHz) or a Perkin-Elmer Hitachi R24A (60 MHz) instrument with tetramethylsilane as an internal standard. Mass spectra were obtained at an ionizing current of 200 μA and an ionizing voltage of 70 eV on a Micromass 16F instrument. Elemental microanalyses were performed by Service Central de Microanalyse du CNRS, F-69390 Vernaison, France. Optical activities were obtained in chloroform solutions by using a Perkin-Elmer 141 polarimeter.

The synthesized allylic thiols were not distilled because of their instability but were purified on a silica gel column with hexane or pentane as the eluent.

For reactions requiring dry solvents, tetrahydrofuran and diethyl ether were distilled from potassium and benzophenone. Hexane, pentane, and dichloromethane were distilled from calcium hydride.

N-Sulfinylbenzenesulfonamide was synthesized on a scale of several hundred grams by heating benzenesulfonamide with thionyl chloride; mp 72 °C (toluene).[16]

Typical Synthesis Procedure. 3,7,7-Trimethylbicyclo[4.1.0]hept-2-ene-4-thiol (4c). 3,7,7-Trimethylbicyclo[4.1.0]-hept-3-ene (3-carene; 5.71 g, 42 mmol) was added to a solution/suspension of **1** (8.12 g, 40 mmol) in dry ether (40 mL) at 0 °C under an argon atmosphere. After the mixture had been allowed to stand 1 h, the precipitate of **3c** (11.5 g, 85%) was separated by filtration. The solid **3c** (34 mmol) was added under argon to a suspension of $LiAlH_4$ (2.7 g, 71 mmol) in 150 mL of dry ether at 0 °C. The mixture was allowed to warm to room temperature, and acetone (3 mL)[17] and acidified water were added in succession. The mixture was extracted with ether, the ether was evaporated, and the residue was mixed with 50 mL of pentane. The insoluble benzenesulfonamide was separated by filtration (quantitative recovery), and the pentane was evaporated to give crude **4c**. The product was purified by chromatography on silica gel with hexane as the eluent; yield 5.0 g (88% from **3c**); spectroscopic data are in Table II.

Thiols **4a,b,d-g** (Table I) were prepared by the same procedure.

Acknowledgment. We thank Dr. P. Teisseire, Scientific Director, Roure Bertrand Dupont S.A, F 06332 Grasse, France, for generous gifts of terpenes.

Registry No. **1**, 6536-23-8; **2a**, 18172-67-3; **2b**, 7785-26-4; **2c**, 498-15-7; **2d**, 4497-92-1; **2e**, 563-34-8; **2f**, 17334-55-3; **2g**, 1195-32-0; **3a**, 88195-46-4; **3b**, 88195-47-5; **3c**, 88106-16-5; **3d** (isomer 1), 88106-17-6; **3d** (isomer 2), 88106-20-1; **3e**, 88106-18-7; **3f**, 74323-43-6; **3g**, 88106-19-8; **4a**, 88195-44-2; **4b**, 88195-45-3; **4c**, 88106-12-1; **4d**, 88106-13-2; **4e**, 88130-55-6; **4f**, 88106-14-3; **4g**, 88106-15-4.

Supplementary Material Available: Complete NMR spectra of compounds **3a-g** and IR and mass spectra of **4a-g** (5 pages). Ordering information is given on any current masthead page.

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(17) When methyl acetate was added instead of acetone to destroy the excess $LiAlH_4$, terpenyl thioacetates were formed.

Synthesis of Some Azahomodiamantane Derivatives via Acidolysis and Photolysis of 1- and 4-Azidodiamantanes[1]

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Received June 28, 1983

Acidolytic and photolytic ring expansions of 1- (**1**) and 4-azidodiamantane (**2**) have been explored. Symmetrical bridgehead azide **2** afforded 9-substituted 10-aza-2(3)-homodiamantanes **6**, **7**, and **9** by photolysis and acidolysis. Unsymmetrical bridgehead azide **1** gave exclusively 11-hydroxy-12-aza-1(2)-homodiamantane (**12**) on acidolysis; however, photolysis of **1** in MeOH afforded a complex mixture due to anomalous side reactions. The simple MeOH adduct (**17**) to the major ring-expansion product 12-aza-1(2)-homodiamant-11-ene (**15**) was not stable under purification conditions, affording **12** (41%) and O-N Me migration product **19** (27%). An MeOH adduct, **18**, to 11-aza-2(3)-homodiamant-11-ene (**16**) as another possible ring expansion product was not obtained, but 12-methoxy-11-aza-2(3)-homodiamant-10-ene (**20**) was isolated as a minor product (9%). Hydrocyanation under photolytic conditions gave amino nitrile **22** (43%). Some other related conversions of above products such as acetylation and reduction have been reported also.

The azido group is one of the more versatile functional groups for synthesis of nitrogen-containing organic compounds.[2] For example, introduction of azido group into bi- and tricyclic systems followed by acidolytic[3] and/or photolytic[4] ring expansions provides a convenient route to aza-bridged polycyclic systems. Various aza-modified adamantanes and related derivatives have been prepared recently by this methodology.[3,4b,d-f,i,j] As an extension of these studies, we now report the synthesis of 1- and 4-

(1) Synthesis of Adamantane Derivatives. 67. Part 66: Sasaki, T.; Eguchi, S.; Okano, T. *J. Am. Chem. Soc.* **1983**, *105*, 5912.

(2) For a general review, see: Sheradsky, T. "The Chemistry of the Azido Group"; Patai, S., Ed.; Interscience: New York, 1971, Chapter 6.

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