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CYCLOPROPANE FORMATION FROM 4,5-UNSATURATED THIOPHENYLETHERS

CONVERSION OF LIMONENE INTO CAR-2-ENE

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Abstract—Strong bases can abstract a proton α to a double bond. A phenylthio group γ to that double bond can be eliminated at the same time leading to a cyclopropane ring. The procedure is illustrated by a conversion of limonene into car-2-ene.

A biomimetic synthesis of chrysanthemol **1a** has recently been reported.[1] The closure of the cyclopropane ring could be carried out by action of suitable bases on the phenylthioalcohol **2a**. The choice of the "poor" leaving group phenylthiolate ensured 1,3 elimination with an allylic proton rather than 1,2 elimination.

The question arose as to whether the hydroxyl goup in **1a** (or the alkoxide derived thereof) played any role in the ring closure. It is well known that suitably placed coordinating group have a favorable influence on the metalation of organic substrates.[2] It has recently been shown[3] that α-cyclopropane alcohols can be metalated in the ring due to the assistance of the alkoxide group.

It was, therefore, of interest to investigate the corresponding desoxy compound **2b**. This has been obtained by lithium aluminium hydride reduction of the corresponding tosylate. An authentic sample of the cyclization product: desoxychrysanthemyl alcohol **1b** was secured by reaction of ethyl diazoacetate with 2-methyl 2-butene,[4] reduction[6] of the cyclopropane ester **5a** (*ct*)[5] to the corresponding alcohols **5b** (*ct*), reoxidation[6] to the aldehydes **5c** (*ct*) and Wittig reaction with isopropyltriphenylphosphonium bromide.[7]

The sulphide **2b** was then submitted to the same reaction conditions which had converted **2a** into chrysanthemol. The results are shown in Table 1. Removal of the hydroxyl group in **2a** results in a marked decrease in reactivity (compare lines 2 and 4). However, under the more vigorous reaction conditions (heating at 50°C), a much higher conversion and yield are observed with **2b** than with **2a**. The fact that conversion of **2a** stops at about 50% is puzzling. The ring closed product, chrysanthemyl alcohol, on the other hand, is not very stable under the reaction conditions; it disappears if the basic treatment is prolonged. After quenching with D_2O no deuterium is found in it by mass spectrometry.

Encouraged by the fair yields obtained in the cyclisation of unsaturated phenylsulphides **2b** and **4**[1] we next turn to the conversion of limonene **6** into car-2-ene **7** by way of the phenylsulphide **9**.

The relative reactivity of the two double bonds of limonene vary with the electrophilic reagents used. Acid catalysed addition of thiophenol[9] on the exocyclic one proved possible with perchloric acid as catalyst. The addition product **9**, formed in 40% yield, was, however, difficult to purify to a state of more than 82% purity owing to the presence of three impurities which proved difficult to remove by distillation or chromatography. Another, more roundabout route was, therefore, selected.

Treatment of (+) limonene ($[\alpha]_D^{21} = 124°$; o.p. = 99%; recorded value[13] $[\alpha]_D^{20} = 125.6°$) with *N*-bromosuc-

Table 1. Base treatment of sulphides **2a**, **2b**, **4** with *n*-Buli/TMEDA[18] in hexane

	n-Buli/ TMEDA eqn	t°C	Time (h)	Sulphide % recovered	Cuclopropane % formed
2a(X = OLi)[a]	1	20	24	85(b)	5
	2	20	24	50(b)	15
	2(d)	50	18	45(bc)	22
2b(X = H)	1	20	24	95(b)	2
	2	20	24	83(b)	5
	2(d)	50	18	16(b)	54
4	1.6	20	24	8(b)	87 (Ref. 1)

(a) In the three runs with **2a** one more equivalent of base was added to convert the OH group into OLi.
(b) Deuterated on the aromatic portion of the molecule when quenching was carried out with D_2O.
(c) Deuterated in the aliphatic portion of the molecule.
(d) The second equivalent of base is added after 6 hr.

cinimide in methanol[8] gave (70% yield) a mixture of two isomeric bromo ethers (85/15), the major constituent of which could be isolated in a state of purity. The mixture was treated with thiophenol and perchloric acid[9] to give (94%) a mixture (90/10) of two isomeric sulphides which could be separated by column chromatography on silicagel.

Reductive elimination was carried out by action of zinc in ethanol[10] on the above mixture of sulphides when the laevorotatory sulphide **9** ($[\alpha]_D^{20} = -16°$) was readily formed (85%). The enantiomeric dextrorotatory sulphide **9** ($[\alpha]_D^{20} = +12°$ was similarly prepared from (−) limonene ($[\alpha]_D^{23} = -92.8°$; o.p. = 76%; recorded value[13] $[\alpha]_D^{20} = 122.1°$).

The cyclisation of sulphide **9** was next attempted on the (−) enantiomer using various basic conditions used in our previous work.[1] With potassium *t*-butoxide, *n*-butyllithium in pentane[11] as well as potassium *t*-butoxide in dimethylsulphoxide, sulphide **9** was rapidly consumed but mixtures of C_{10} hydrocarbons were formed and these were not further investigated. With lithium diethylamide in ether–hexamethyl phosphoric triamide[12] at room temperature a mixture of four olefins is formed in 85% yield. These were identified by glc and glc/ms with car-2-ene **7** (10%), car-3-ene **8** (8%) carvomenthene **12** (72%) and *p*-cymene (10%). The remarkable reduction of sulphide **9** to **12** calls for further investigation.

The sulphide **9** was then treated with *n*-butyllithium–tetramethyl ethylenediamine in hexane (Table 2) with quenching with deuterium oxide. Two equivalents of base were found necessary to achieve efficient conversion (75–90%) of the starting material. Car-2-ene **7** was then the main elimination product (86%) with minor amounts of limonene (2%) and carvomenthene **12** (12%). These products were identified by glc and were not deuterated; about 10–25% of the starting sulphide was recovered, which was deuterated in the aromatic ring as ascertained by mass-spectrometry. Similar treatment of the impure sulphide **9** obtained by direct addition of phenyl thiol on limonene gave the same three olefins in the same relative amounts together with 16% of *p*-cymene.

In a preparative run the olefins were isolated by distillation (56%) and the starting material (13%) by chromatography on a column of silica. Car-2-ene was isolated by gas liquid chromatography. It had $[\alpha]_D^{21} = +71°$ (C = 1.025, $CHCl_3$), $[\alpha]_D^{21} = +78°$ (neat). The rotatory power of car-2-ene has been reported to be $[\alpha]_D^{28.5} = 76.36°$[14] and $[\alpha]_D^{20} = 97.70°$C.[15] Our synthetic sample therefore has an optical purity of 80%.

The (+) sulphide **9** could be similarly converted into (−) car-2-ene.

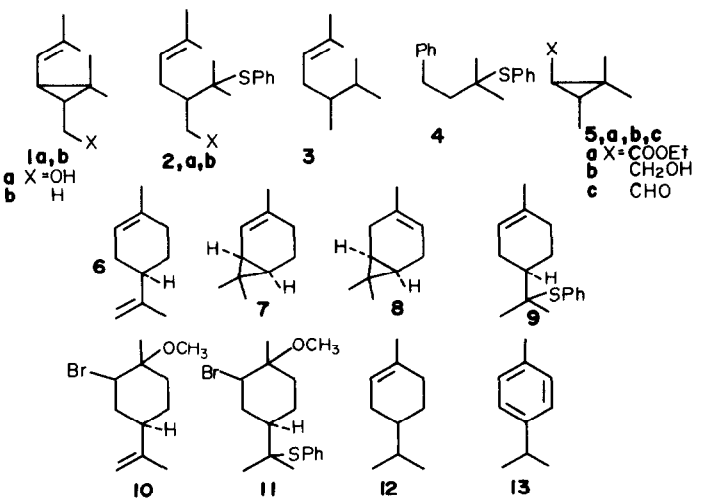
CONCLUSION

Base promoted cyclopropane ring closure in 4,5-unsaturated phenylsulphides thus seems to be a general reaction. It might be use ful for synthesis of a variety of natural products. Good results have been reported recently in cyclopropane ring formation by intramolecular displacement of phenylthiolate ion by sulphur stabilized carbanions.[16,17]

Table 2. Reaction of sulphide **9** with *n*-Buli-TMEDA

Run No.	Eqn base	Temp (°C)	Time (h)	**9** Recovered	car-2-ene %	Other hydrocarbons
1	1	20	67	85	11	1.5
2	1.5	20	67	61	25	4
3	2	20	67	23	66	8.6
4	2[a]	20	67	26	65	8.6
5	2.5	20	67	35	54	7.3
6	2	50	24	15	70	10
7	2[a]	50	24	11	70	9.2

[a]The second equivalent of base was added after 6 hr.



EXPERIMENTAL

Ir spectra were recorded on a Perkin–Elmer 599 spectrometer, Mass spectra on a Ribermag R 10.10 Apparatus coupled with a glc capillary column (25 m × 0.3 mm; SE 52). ^{1}H NMR spectra were recorded with a Varian 390 at 90 MHz and a Cameca 250 at 250 MHz. A Bruker VP 90 was used for the ^{13}C NMR spectra. Chemical shifts δ are given in ppm with respect to tetramethylsilane, in deuteriochloroform. Glc analyses were performed on a Girdel 30 chromatograph with a glass capillary column (30 m × 0.3 mm; Carbowax 600 M, 120°) or on a Varian 1450 apparatus with two columns: FFAP, 3 m, 5% on chromosorb Q or DC 550, 5 m, 15% on chromosorb Q. Peak areas were measured with a Spectraphysic Systems 1 integrator. Optical rotations were measured with a Perkin–Elmer 141 polarimeter.

Phenyl 2,3,6-*trimethyl hept-5-en-2-ylsulphide* **2c**. A solution of phenylthioalcohol **2a**[1] (0.8 g; 3 mmoles) and tosyl chloride (1.2 g; 6.3 mmoles) in dry pyridine (12 ml) after standing 12 hr at 0°C gave 1.24 g (98%) crude tosylate; after precipitation from pentane at −78°C the tosylate of **2a** was obtained (0.578 g; 45%) as a colourless gum: ^{1}H NMR (90 MHz): 1.2 (s, 6H); 1.53 (s, 3H); 1.6 (s, 3H); 2.4 (s, 3H); 4.1 (d, J = 4.5 Hz, 2H); 4.86 (t, J = 7.5 Hz, 1H); 7.0–7.9 (m, 9H). *m/e*: 418 (M^+), 308, 246, 239, 226, 177, 150, 137, 123, 110, 91, 81, 69.

Reduction of the above tosylate (790 mg, 1.9 mmole) with excess lithium aluminium hydride in ether and chromatography on a column of silica gave sulphide **2b**. (179 mg, 43%). $C_{16}H_{24}S$. IR (film) 3020, 1130, 1030, 760, 710 cm^{-1}. ^{1}H NMR (90 MHz): 0.95 (d, J = 6 Hz, 3H); 1.16 (s, 3H); 1.6 (s, 3H); 1.7 (s, 3H); 5.06 (t, J = 7 Hz, 1H); 7.0–7.6 (m, 5H). *m/e*: 248 (M^+, 8), 151 ($PhSC_3H_6$, 16), 138 (M–PhS, 57); 123 (M–PhS–Me, 39), 110 (PhSH, 43); 109 (PhS, 27), 97 (C_7H_{13}, 25); 69 (C_5H_9, 100).

Ethyl 2,2,3-*trimethyl cyclopropane carboxylate* **5a**. A solution of ethyl diazoacetate (23 g, 0.2 mole) in 2-methyl-2-butene (25 ml) is carefully added over 5 minutes to a solution of CuI, $P(OEt)_3$[4](1 g) in 2-methyl-2-butene (25 ml). Nitrogen is violently evolved after 10–15 min; the reaction vessel is cooled in ice. When the gas evolution has subsided the brown heterogenous reaction mixture is distilled to give a colourless oil. B.p.: 82–84°C (30 mm Hg); lit.[5] B.p.: 75–80°C (11 mm Hg); 5.70 g, 18% calculated on ethyl diazoacetate). IR (film): 1710 cm^{-1}. Glc/mass: 2 peaks (40/60) with identical mass spectra: *m/e*: 156, 141, 111, 95, 85, 83. ^{1}H NMR (90 MHz) singlets at 1.1; 1.13; 1.16; 1.23; 1.3; multiplet at 3.8–4.4.

2,2,3-*trimethyl cyclopropane methanol* **5b**. The above mixture of esters (5.65 g; 36.2 mmoles) is reduced[6] with an excess of lithium aluminium hydride in dry ether (200 ml) 24 hr at 19° to give a colourless oil 2.23 g; 54%; B.p.: 65–75°C (25 mm Hg). IR (film): 3310 cm^{-1}. Glc/mass: two peaks (40/60) with identical mass spectra; *m/e*: 99 ($M-CH_3$); 96 ($M-H_2O$); 83; 81; 55; ^{1}H NMR (90 MHz) singlets between 0.93 and 1.1; multiplet at 3.3–3.7.

2,2,3-*Trimethyl cyclopropane carboxaldehyde* **5c**. The above mixture of *cis* + *trans* alcohols (2.2 g; 1.9 mmole) is oxidised[6] with the complex prepared from chromium trioxide (24 g) and pyridine (20 ml). The aldehydes (*c*, *t*) are isolated by distillation 0.6 g; 28%; B.p.: 75–80°C (25 mm Hg) IR (film): 2950; 2860; 2730; 1685; 800 cm^{-1}. Glc/mass: 2 peaks (40/60) with identical mass spectra; *m/e*: 112 (M^+); 97 ($M-CH_3$); 83; 55. ^{1}H NMR (90 MHz) 0.75–0.9 (m, 1H); 1.07 (s); 1.10 (s); 1.25 (d, J = 3.5 Hz); 1.27 (d, J = 3.5 Hz) 1.45–1.75 (m, 1H); 9.15–9.30 (m); 9.38 (m). Dinitrophenyl hydrazone (mixture) m.p.: 161–163°C (EtoAc, MeOH) $C_{13}H_{16}N_4O_4$.

2,2,3-*Trimethyl*-1-(2′-*methylprop*-1′-*en*-1′-*yl cyclopropane*; *desoxychrysanthemol* **1b**. A solution of methyllithium in ether (1.8 *M*; 2.7 ml; 4.9 mmoles) is added under nitrogen to a stirred suspension of isopropyl triphenyl phosphonium bromide[7] (2.16 g, 5 mmol) in dry ether (10 ml) at 0°. A solution of the above aldehydes (*c*, *t*) (537 mg, 4.8 mmoles) in dry ether (5 ml) is added after 1.5 hr. The orange colour rapidly fades away. After 30 min, the mixture is filtered and the solvent evaporated. The oily residue is dissolved in pentane and filtered on a column of silica. The column is washed with the same solvent and the pentane solutions evaporated to give olefins **2b** 62 mg: 10%. Glc/mass, 2 peaks = 50% and 30% with identical mass spectra: *m/e*: 138 (M^+, 50); 123 ($M-CH_3$, 100); 95 (29); 81 (83); 67 (44); 55 (49). Two minor peaks (10 and 10%) give different mass spectra with the same M = 138. ^{1}H NMR (90 MHz), 0.25–0.55 (m, 1H); 0.65–0.9 (m, 1H); 0.85 (s); 0.97 (s); 1.0 (s); 1.02 (s); 1.07 (s); 1.67 (s, 3H); 1.7 (s, 3H); 4.80 (d, J = 7.5 Hz, 1H).

(−)*p-Menth*-1-*en*-8-*yl phenylsulphide*; *α-terpinylphenylsulphide*; 8-*phenylthio-p-menth*-1-*ene* **9** (a) Aqueous perchloric acid (70%, 1 ml) is slowly added to a stirred solution of (+)R-limonene $[\alpha]_D^{23} = 124°$, o.p. = 99% 13.6 g; 0.1 mole in thiophenol (30 ml) at −20°C. The temperature was kept below −15° for 1 hr, after which time the mixture was poured in 6 *M* sodium hydroxide (500 ml) and extracted with pentane. Usual work up gave 18 g crude product, which was chromatographed on silica: hydrocarbons (2.6 g) were eluted with hexane; phenyl sulphides (10 g, 40%) were eluted with 5% ether in hexane; a cristalline compound was not further examined. Glc analysis of the sulphide fraction showed the presence of four compounds (6, 6, 6, 82%). The ^{1}H NMR spectrum at 250 MHz showed the major component to be the sulphide **9**. It proved however difficult to free it from the accompanying impurities.

2-*Bromo*-1-*methoxy-p-menth*-8-*ene* **10**. (b) (+)R-Limonene (27.2 g; 0.2 mole) was added to a suspension of *N*-bromo succinimide (35.6 g; 0.2 mole) in anhydrous methanol (100 ml) at 0°C, and the solution stirred at 0°C for 1 hr then at 19°C for another 2 hr. Distillation of the crude product (50 g) gave bromoether **10**: 33 g, (71%), B.p.: 88–92° (2 mm Hg); 2 peaks on glc (85/15). The major isomer was isolated by chromatography of 1 g of the mixture on a column of silica (5% ether in hexane). $C_{11}H_{19}OBr$. $[\alpha]_D^{23} = 69°$ (c = 1,; $CHCl_3$). IR (film): 3080, 1632, 1370, 1180, 1075, 900, 725, 680 cm^{-1}. ^{1}H NMR (250 MHz): 1.3 (s, 3H): 1.54 (m, 2H); 1.74 (s, 3H); 1.9 (m, 3H); 2.2 (m, 1H); 2.46 (m, 1H); 3.2 (s, 3H); 4.32 (m, 1H); 4.72 (s, 2H).

2-*Bromo*-1-*methoxymenth*-8-*yl phenylsulphide* **11**. Using the technique described under (a) 20° 1 hr, the above mixture (85/15) of bromoethoxy olefins (5 g, 20 mmoles) gave 6.8 g (24%) crude bromomethoxysulphide, 1 g of which was chromatographed on a column of silica with 70% ether in pentane.

Major constituant (less polar): $C_{17}H_{25}OSBr$; $[\alpha]_D^{23} = 88.6°$ (c 2.57; $CHCl_3$). IR (film): 1450, 1370, 1070, 760, 710 cm^{-1}. ^{1}H NMR (250 MHz) = 1.22 (s, 6H); 1.3 (s, 3H); 3.22 (s, 3H); 4.4 (m, 1H); 7.34 (m, 3H); 7.48 (m, 2H).

Minor constituant (more polar) $C_{17}H_{25}OSBr$; $[\alpha]_D^{23} = -28°$ (C 2.98; $CHCl_3$). IR identical with that of the major isomer. ^{1}H NMR (250 MHz): 1.18 (s, 3H); 1.2 (s, 3H); 1.32 (s, 3H); 3.26 (s, 3H); 4.14 (dd, J = 13 and 4 Hz, 1H); 7.34 (m, 3H); 7.48 (m, 2H).

8-*Phenylthio-p-menth*-1-*ene* **9**. The crude bromomethoxysulphide **11** (4.4 g; 12.3 mmoles) was treated with zinc powder (2.5 g, 38 mat) in refluxing 90% ethanol (33 ml) for 4 hr; after filtration on celite, the solvent was evaporated and the residue taken up in ether. The ethereal solution was washed with water, dried and evaporated. Distillation of the residue gave the sulphide **9** as an oil = 2.6 g (85%); B.p.: 140–141° (1 mm Hg); $C_{16}H_{22}S$; $[\alpha]_D^{23} = -16°$ (c = 1.0; $CHCl_3$); IR (film) 3020, 1430, 1120, 1030, 925, 810, 760, 720, 710 cm^{-1}. ^{1}H NMR (250 MHz): 1.16 (s, 3H); 1.25 (s, 3H); 1.65 (s, 3H); 5.38 (m, 1H); 7.32 (m, 3H); 7.5 (m, 2H). *m/e* (rel. int.) 246 (47); 151 (14); 137 (33); 136 (66); 121 (20); 110 (10); 109 (15); 95 (15); 93 (20); 81 (100). Glc (FFAP, 180°) one peak.

Car-2-ene- by isomerisation of car-3-ene. A solution of commerical car-3-ene (1.36 g; 10 mmoles) and potassium *t*-butoxide (1.34 g) in dimethyl sulphoxide[14] (11 mmoles) was heated for 0.5 hr at 100°C. Reisolation of the hydrocarbons gave (1.25 g; 92%) a mixture of car-2-ene (37%) and car-3-ene (63%). Car-2-ene; *m/e* 136 (74); 121 (100); 93 (79); 91 (43); 80 (9); 79 (48); 77 (49); car-3-ene; *m/e* 136 (35); 121 (23); 93 (100); 91 (43); 80 (32); 79 (43); 77 (48).

Cyclopropane ring closures

Desoxychrysanthemol **1b**. *n*-Butyllithium (1.6 *M* in hexane; 0.63 ml; 1 mmole) is added to TMEDA (0.16 ml, 1 mmole) under nitrogen; after 5 min sulphide **2c** (248 mg, 1.03 mmole) is added together with *n*-tridecane (65 mg as internal standard). After 6 hr at 50° quenching of a sample and glc analysis (DC 550, 100°) showed that less than 5% olefins had been formed. Another equivalent of *n*-Buli/TMEDA is added. After 12 hr at 50° the

mixture is hydrolysed with deuterium oxide. Glc analysis showed sulphide **2b** (16%) together with three olefins (54%; proportions 61, 19, 20%).

The first two peaks have the same retention times and mass spectra as the two major peaks of authentic **1b** prepared above. By repeated chromatography on silica a sample of these two compounds free of the third constituent was obtained and showed an NMR spectrum in agreement with structure **1b** (*ct*). The third component was assigned the structure **3** (desoxylavandulol) by ^{1}H NMR (90 MHz): 4.6 (q, J = 1 Hz) and 5.0 (t, J = 7 Hz). *m/e*: 136 (M^+, 7); 123 ($M-CH_3$, 11); 95 (32); 69 (100).

In the mass spectrum of the recovered sulphide, the peaks of the fragments containing the aromatic ring are split (249/248; 152/151; 111/110) whereas the other ones are not (138, 123, 95, 69).

Car-2-ene **7** *by cyclisation of sulphide* **9**. Preliminary experiments were carried out on samples (308 mg) of sulphide **9** with 1, 1.5, 2, 2.5 equivalent *n*-Buli/TMEDA 67 hr at 19°C or 24 hr at 50°. Quenching was carried out with deuterium oxide and analysis by glc (DC 550, 140° for the hydrocarbons, 240°C for the sulphide) using *n*-tridecane as an internal standard.

In a preparative run the sulphide **9** (8.22 g; 33 mmoles) is added to a mixture of *n*-Buli (1.6 *M* in hexane; 40 ml) and TMEDA (10 ml); after 18 hr at 50° and quenching with D_2O the organic material is freed from thiophenol and distilled to give olefins (2.5 g, 56%) B.p.: 72–73° (40 mm Hg) $[\alpha]_D^{21} = +67°$ (c = 1: $CHCl_3$). By chromatography of the residue on a silica column sulphide **9** 1.11 g; 13%) is recovered.

Glc analysis of the olefinic material shows three constituents (86, 2, 12%) with the retention times and mass spectra of (non-deuterated) car-2-ene, limonene, and carvomenthene. The major constituent, isolated by preparative glc (SE 30, 6 m, 15%, 120°) had $[\alpha]_D^{21} = 71°$ (c = 1.025; $CHCl_3$) and $[\alpha]_D^{21} = 78°$ (neat). ^{1}H NMR (250 MHz): 0.82 (m, 1H); 0.86 (s, 3H); 0.96 (dd, J = 8 Hz, 5 Hz, 1H); 1.08 (s, 3H); 1.66 (s, 3H); 1.8–2 (m, 2H); 5.54 (s, 1H). On irradiation of the broad singlet at 5.54 ppm, the signal at 0.96 ppm was converted into a doublet J = 8 Hz.

The recovered sulphide **9** had $[\alpha]_D^{21} = -15°$ (c = 1, 2, $CHCl_3$). In its mass spectrum the fragment containing the aromatic ring gave split peaks (247/246; 152/151; 111/110), the other ones did not (137, 136, 121, 95, 93, 81). The recovered thiophenol shows all its peaks split (111/110; 78/77; 67/66). Reaction of sulphide **9** with other bases.

(a) Potassium *t*-butoxide in DMSO and potassium *t*-butoxide/*n*-butyllithium in hexane. Sulphide **9** was completely converted after 24 hr at room temperature. An olefin fraction could be isolated in 75–80% yield; glc analysis, however, showed more than 15 constituents.

(b) Lithium diethylamide in ether-hexamethylphosphoric triamide.[12] Diethylamine (3 ml) and hexamethyl phosphoric triamide (40 ml) are added at 0°C to a solution of *n*-butyllithium (1.6 *M* in hexane, 20 ml, 32 mmoles) in dry ether (20 ml). A solution of sulphide **9** (2.64 g; 10.7 mmoles) in dry ether (5 ml) is then added and the temperature is allowed to rise to 20°C. A deep violet colour develops. After 3 hr the sulphide has disappeared. After work up the crude product (1.35 g) was chromatographed on a column of silica with pentane elution. A hydrocarbon fraction was collected (1.25 g; 85%) which gave 4 peaks on a capillary glc column (10, 8, 72, 10%). Peaks 1.2 and 4 had retention times and mass spectra identical with those of car-2-ene, car-3-ene and *p*-cymene, respectively. The third, major peak was isolated by repeated chromatography on a column of silica eluted with pentane, and identified by its spectral data with racemic carvomenthene.

(−)*Car-2-ene from S(−)limonene.* S(−)Limonene (6.8 g; 50 mmoles; o.p. 76%) was treated as its enantiomer with *N*-bromosuccinimide (9 g; 50 mmoles) in methanol (25 ml). The bromoether (−) **10** was isolated by distillation (8.1 g; 65%).

Addition of thiophenol and zinc reduction gave sulphide (+) **9** (b.p. = 140°C (1 mm Hg); 2.4 g (78%) $[\alpha]_D^{21} = +12°$ (c = 1.2; $CHCl_3$).

The (+) sulphide (2.2 g) on cyclisation with *n*-Buli-TMEDA gave a mixture of olefins, 670 mg; 55%; $[\alpha]_D^{21} = -50°$ (c = 0.98; $CHCl_3$) which had (glc) the same composition as that obtained above.

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