CH_2Cl_2 in hexane) showed no spot for Ph_3P at R_f 0.54, along with the appearance of a new spot near the origin (R_f 0.04); the R_f values of **6a** and **3a** were too close to provide useful guides to completion of the reaction. Removal of solvent and preparative TLC gave 0.010 g (24% yield) of **3a** (R_f, IR, and NMR spectra identical with those of authentic **3a**),[1a] together with 0.024 g (82% yield) of triphenylphosphine sulfide (mp 159–161.5 °C; lit.[16] mp 159–162 °C).

1-[[(2,3-Dihydroxypropyl)dithio]methyl]-2-[[(2,3-dihydroxypropyl)trithio]methyl]benzene (6b). The general method gave 0.019 g (8%) of **6b**, from **5** (0.117 g, 0.54 mmol) and **16** (0.117 g, 1.08 mmol), as thick oil: TLC R_f 0.36 (10% MeOH in CH_2Cl_2; the single spot when removed and rechromatographed gave three spots). By the time the ^1H NMR spectrum could be obtained, it showed the material to be almost entirely **3b**, with quite small reasonably placed peaks attributed to **6b**. The disulfide **6b** thus was much less stable than the tolyl derivative **6a**, and attempts to purify it by TLC led only to loss of sulfur and disproportionation.

***erythro*-1,4-Bis(*p*-tolyldithio)-2,3-butanediol (10a). (a) From the *c*-4,*c*-5-Diol *r*-1-Oxide 9.** A solution of *p*-toluenethiol (**15**, 0.066 g, 0.53 mmol) in MeOH (2 mL) was added (5 min) to the stirred solution of **9** (0.035 g, 0.21 mmol) in MeOH (2 mL) under Ar in the dark at 15 °C. After 25 min, TLC (5% MeOH–CH_2Cl_2) showed a new spot and no **9**. Removal of MeOH and chromatography on a silica gel column using 100% CH_2Cl_2 as eluant gave 0.067 g (80%) of **10a** as a white crystalline solid: mp 91–93 °C; TLC R_f 0.50 (1.5% MeOH in CH_2Cl_2); IR (Nujol) 3350–3275 s, 1600, 1490 s, 1300, 1120, 1090, 1060 s, 1025, 1015, 1000, 900, 850, 800 s, 755, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41 (d, J = 8.1 Hz, 4 H, Ar), 7.12 (d, J = 8.1 Hz, 4 H, Ar), 3.94–3.86 (m, 2 H, CH), 3.02–2.97 (dd, J = 13.9 and 3.7 Hz, 2 H), and 2.77–2.74 (dd, J = 13.9 and 8.5 Hz, 2 H) CH_2, 2.41 (d, J = 3.6 Hz, 2 H, OH), 2.32 (s, 6 H, CH_3); MS(EI), exact mass found 398.0479 (0.2), $C_{18}H_{22}O_2S_4$ requires 398.0503; 275.0231 (91) (M – C_7H_7S requires 275.0234) and 246.0547 (100) ($C_{14}H_{14}S_2$ requires 246.0537). Anal. Calcd for $C_{18}H_{22}O_2S_4$: C, 54.24; H, 5.56; S, 32.17. Found: C, 53.87; H, 5.62; S, 32.58.

(b) From the *t*-4,*t*-5-Diol *r*-1-Oxide 8. The procedure for **10a** used with monooxide **8** (0.076 g, 0.45 mmol) and thiol **15** (0.140 g, 1.13 mmol) furnished 0.145 g (81%) of **10a**: mp and mmp 91–93 °C; the R_f, IR, and NMR data were identical with those of **10a** obtained from **9**.

***threo*-1,4-Bis(*p*-tolyldithio)-2,3-butanediol (14a). (a) From the *t*-4,*c*-5-Diol *r*-1-Oxide 12.** The procedure for **10a** used with monooxide **12** (0.040 g, 0.24 mmol) and thiol **15** (0.060 g, 0.48 mmol) gave 0.064 g (67% yield) of **14a** as a white crystalline solid: mp 103–105 °C; TLC R_f 0.75 (5% MeOH in CH_2Cl_2); IR (Nujol) 3350 s (br), 1600, 1490 s, 1400, 1300, 1275, 1160, 1110, 1090 s, 1050, 1015, 915, 890, 850, 835, 810, 800 s, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41, (d, J = 8.1 Hz, 4 H, Ar), 7.11 (d, J = 8.1 Hz, 4 H, Ar), 3.90–3.83 (m, 2 H), 2.87–2.85 (dd, J = 3.4 Hz, 4 H), 2.35 (d, J = 6.0 Hz, 2 H), 2.31 (s, 6 H); MS(EI), exact masses found were similar to those of **10a** above; exact masses found m/z (relative intensity), mmu error were 275 (85), 0.2 and 246 (100), 1.1. Anal. Calcd for $C_{18}H_{22}O_2S_4$: C, 54.24; H, 5.56; S, 32.17. Found: C, 54.20; H, 5.64; S, 32.23.

(b) From the *c*-4,*t*-5-Diol *r*-1-Oxide 13. From monooxide **13** (0.400 g, 2.38 mmol) and thiol **15** (0.739 g, 5.95 mmol), 0.750 g (79% yield) of **14a** was obtained: mp and mmp 103–105 °C; R_f, IR, and NMR data were identical with those of **14a** from **12**.

***erythro*-1,4-Bis[(2,3-dihydroxypropyl)dithio]-2,3-butanediol (10b). (a) From the *c*-4,*c*-5-Diol *r*-1-Oxide 9.** Essentially as described for **10a**, except for 1 h of stirring, **9** (0.040 g, 0.24 mmol) and 3-mercapto-1,2-propanediol (**16**; 0.052 g, 0.48 mmol) gave 0.064 g (73% yield) of **10b** after chromatographic separation on a silica gel column with 7–10% MeOH in CH_2Cl_2, as white crystalline solid: mp 71–73 °C; TLC R_f 0.30 (15% MeOH in CH_2Cl_2); IR (Nujol) 3300 s (br), 1400, 1320, 1220, 1130, 1100 s, 1070 s, 1050 s, 1020 s, 970, 925, 905, 880, 850 cm^{-1}; ^1H NMR (D_2O) δ 3.92–3.77 (m, 4 H, CH), 3.58–3.54 (dd, J = 15.8 and 4.1 Hz, 2 H) and 3.47–3.43 (dd, J = 11.8 and 6.1 Hz, 2 H) terminal CH_2 of side chain, 3.01–2.82 (4 t, 4 H, CH_2 of center), 2.74–2.59 (m, 4 H, $SSCH_2$ of side chain) (the solution was unchanged after 10 days); MS(EI), exact mass found 273.9834 (2.6), $C_7H_{14}O_3S_4$ (M – $C_3H_6O_2$ – H_2O) requires 273.9826; 214.0334 (37), $C_6H_{14}O_4S_2$ requires 214.0334; 165.0045 (100), $C_5H_9O_2S_2$ requires 165.0044; 151.9966 (60), $C_4H_8O_2S_2$ requires 151.9966; and 107.9694 (68), $C_2H_4OS_2$ requires 107.9703. Anal. Calcd for $C_{10}H_{22}O_6S_4$: C, 32.77; H, 6.05; S, 34.99. Found: C, 32.52; H, 6.12; S, 34.87.

(b) From the *t*-4,*t*-5-Diol *r*-1-Oxide 8. The procedure for **10b** from **9** gave 0.102 g (77%) of **10b** from **8** (0.061 g, 0.36 mmol) and the thiol **16** (0.078 g, 0.72 mmol): mp 71–73 °C; the R_f, IR, and NMR data of **10b** were identical with those of authentic **10b**.

***threo*-1,4-Bis[(2,3-dihydroxypropyl)dithio]-2,3-butanediol (14b). (a) From the *t*-4,*c*-5-Diol *r*-1-Oxide 12.** The procedure for **10b** with monooxide **12** (0.071 g, 0.42 mmol) and thiol **16** (0.091 g, 0.84 mmol) afforded 0.107 g (69%) of **14b** as white solid: mp 108–110 °C; TLC R_f 0.30 (15% MeOH in CH_2Cl_2); IR (Nujol) 3275 s (br), 1415, 1400, 1330, 1245, 1155, 1085 s, 1030 s, 935, 910, 885, 870, 850, 815 cm^{-1}; ^1H NMR (D_2O) δ 3.93–3.81 (m, br, 4 H), 3.56–3.43 (4 d, 8 lines, 4 H), 2.93–2.82 (3 d, 6 lines, 4 H), 2.81–2.61 (sharp m, 10 lines, 4 H) (the solution was unchanged after 10 days); MS(EI) similar to **10b**; exact masses found m/z (relative intensity), mmu error were 214 (61), 0.0; 165 (10), 0.5; 152 (100), 0.2 and 108 (61), 0.2. Anal. Calcd for $C_{10}H_{22}O_6S_4$: C, 32.77; H, 6.05; S, 34.99. Found: C, 32.37; H, 6.07; S, 34.47.

(b) From the *c*-4,*t*-5-Diol *r*-1-Oxide 13. The procedure for **10b** with 0.051 g (0.30 mmol) of **13** and 0.065 g (0.60 mmol) of thiol **16** furnished 0.078 g (71% yield) of **14b**: mp 108–110 °C; the R_f, IR and NMR data were identical with those of **14b** from **12**.

Notes

Laser-Driven Thermolysis of Spirohexane

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There is continuing research interest in chemistry of strained organic molecules.[2–4] Spiropentanes are, however, the only members of spiroalkanes whose thermal behavior has been studied thus far.[5–7] Although the thermolysis of three-membered rings is expected[2] to yield ethylene and carbenes, both cyclopropane[8] and spiropentane[5–7] deriva-

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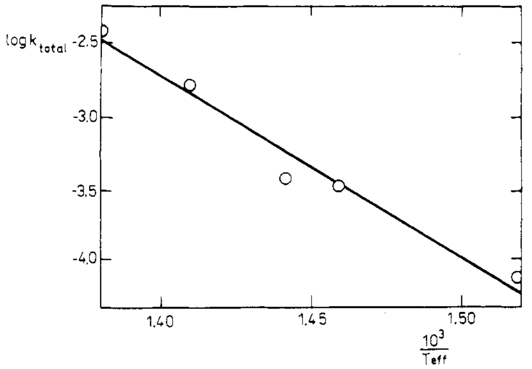
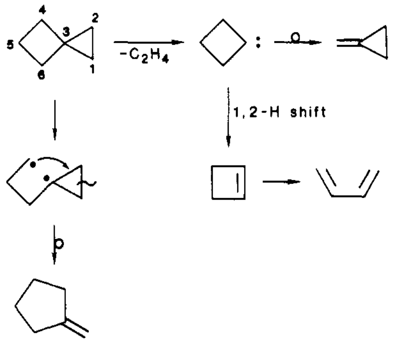


Figure 1. The dependence of the rate coefficient of the spirohexane decomposition on the effective temperature.

Scheme I



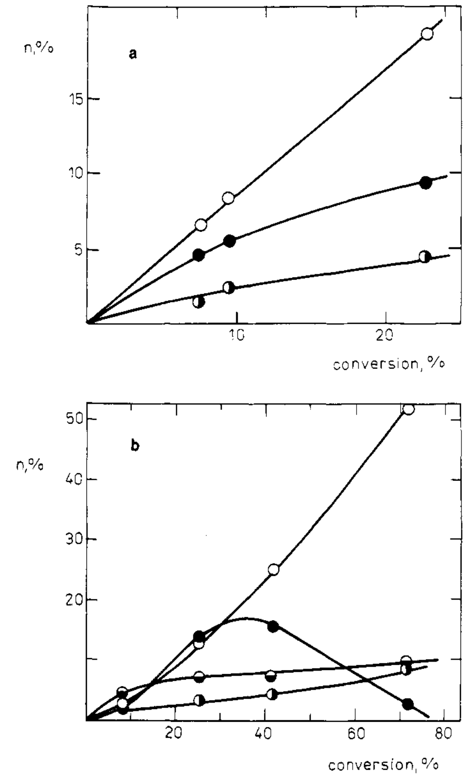


Figure 2. The reaction progress of the laser-driven spirohexane decomposition carried out with laser output of 5 W (a) and 8 W (b). The circles relate to molar percentage (n, %) of ethylene (○), 1,3-butadiene (●), methylenecyclopropane (◑) and methylenecyclopentane (◒).

Table I. Representative Methylenecyclopropane:1,3-Butadiene Ratios

laser output, W	convrsn, %	ratio
5	7.3	0.20
	9.5	0.35
	22.4	0.30
8	34.3	0.28
	42.7	0.26
	87.9	0.27

tives cleave via diradicals into propenes or methylenecyclobutanes. The expulsion of ethylene was, in fact, observed only as a very minor pathway occurring simultaneously with the isomerization of spiropentane.[5]

We report that the thermal decomposition of spirohexane in the gas phase noticeably differs from the thermal decomposition of spiropentanes in that it can be explained to occur exclusively via the expulsion of ethylene and intermediary formation of cyclic carbene. The reaction was carried out as truly homogeneous, laser-photosensitized (SF_6) process in order to avoid possible heterogeneous reactions on hot reactor walls that were observed with the four- and three-membered cyclic hydrocarbons.[9-11]

Results and Discussion

The CW CO_2 laser-induced decomposition of spirohexane was carried out in the presence of energy conveying SF_6, since spirohexane is not good absorber of the IR radiation at 10 μm. With the laser outputs as low as 4–6 W the reaction yields ethylene, 1,3-butadiene, and methylenecyclopropane. At higher laser outputs (8 W) small amounts of methylenecyclopentane can be observed as well. The decomposition (k_{total}, ref 12) obeys the first-order kinetics and its study in the presence of marker reaction[13] (isopropyl acetate → propene + acetic acid) allows the estimation of the effective temperatures.[12] The temperature dependence of the rate coefficient (Figure 1) is given by the Arrhenius equation (eq 1), where the E_a value is

$$\log k_{total} = 15.1 - (243\ \mathrm{kJ{\cdot}mol^{-1}})/2.3RT_{eff} \qquad (1)$$

very similar to that observed for the cleavage of the three-membered spiropentane (241 kJ·mol^{-1}, ref 5). The product distributions at different reaction progress are seen in Figure 2 and they can be consistent with a reaction scheme shown in Scheme I.

We assume that an intermediary cyclobutylidene, formed via a concerted or nonconcerted (the C_1–C_3 bond cleavage) elimination of ethylene, can be a common precursor of methylenecyclopropane and cyclobutene. Similar pathways of cyclobutylidene, i.e., its ring-contraction rearrangement to methylenecyclopropane and its 1,2-hydrogen shift to cyclobutene and further reaction to 1,3-butadiene, were also claimed to take place in the thermal liquid-phase decomposition of cyclobutanone[14,15] and bicyclo[3.1.1]heptan-6-one[16] tosylhydrazones. There are also other reasonable mechanisms leading to 1,3-butadiene as a sequence of the C_1–C_3 cleavage, a migration to form vinylcyclobutane and allylic stabilized cyclobutane decomposition. The intermediacy of the cyclobutylidene as a precursor of both methylenecyclopropane and cyclobutene seems, however, to get kinetic support from the almost constant methylenecyclopropane:1,3-butadiene ratio at different reaction progress, which might reflect that

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the decomposition of spirohexane is controlled by the stage of the C_2H_4 elimination. The liquid-phase decompositions favor the ring contraction over the 1,2-hydrogen shift. The opposite situation is encountered under our conditions, where the methylenecyclopropane:1,3-butadiene ratio (Table I) ranges between 0.2 and 0.4. The observed invariance of this ratio at different laser outputs (different T_{eff}'s) can be consistent with very similar activation energies of both cyclobutylidene pathways.

The closeness in the E_a values for the decomposition of spiropentane and spirohexane seems to be supportive of the suggested reaction scheme in which the three-membered ring is cleaved first. Low yields of methylenecyclopentane at only higher temperatures can, however, indicate that this product arises via a higher energy process which can be initiated by a cleavage of the four-membered ring and consecutive migration and peripheral C_1–C_2 cleavage (see Scheme I).

The yield of ethylene is always higher than the total of yields of methylenecyclopropane and 1,3-butadiene. This indicates that 1,3-butadiene partly polymerizes. The 1,3-butadiene depletion upon the irradiation (8-W output) of 1,3-C_4H_6 (3.7 kPa)–SF_6 (1.9 kPa) mixture is, indeed, corroborating such a statement, since only traces of ethylene and a few percent of propene are formed after the expositions 7–10 times longer than those needed to drive the decomposition of spirohexane to completion.

Triplet carbenes can be detected via their conversion into long-lived iminoxyl radical by reaction with nitric oxide[17] or via their fast exothermic dimerization.[18,19] Our attempts to detect intermediary cyclobutylidene failed. No traces of dicyclobutyleneethylene were found among the reaction products. We also observed that spirohexane reacts with nitric oxide at ambient temperatures to produce liquid polymeric substance.

Surprising difference in behavior of intermediary diradicals postulated in the decomposition of both spiroalkanes might be associated with a higher stability of cyclobutylidene compared to cyclopropylidene. The examination of laser-driven decompositions of spiro[2.*n*]alkanes (*n* = 4–6) along with the study of deuterium labeled spiroalkanes are believed to bring more understanding to this problem.

Experimental Section

Experiments were carried out with a 1.4 cm long stainless-steel optical cell (internal diameter, 3.6 cm) equipped with one needle valve, two NaCl windows, and a side arm with a rubber septum. Mixtures of spirohexane (3.7 kPa) and sulfur hexafluoride (1.9 kPa) were prepared directly in the cell by using a standard vacuum line and were irradiated at measured intervals with slightly focused laser beam. A cw CO_2 laser[20] operated at the P(20) line of the 10.6-μm transition with the output covering the range of 4–8 W.

The extent of the spirohexane decomposition was followed by periodical analyses of gaseous mixtures on a Chrom-4 gas chromatograph (flame ionization, 3 m long column packed with alumina deactivated with silicon oil) coupled with a computing integrator (Model CI 100) and on a GC–MS spectrometer (Shimadzu Model QP 1000 equipped with a 3 m long column packed with 10% OV-101 silicone elastomer on Chromaton Super). For the identification of the decomposition products the GC–MS system was used. The products were identified by comparison with authentic samples (methylenecyclopentane (Fluka), methylenecyclopropane (laboratory stock), ethylene and 1,3-butadiene (both Chemapol)) both for the retention time and mass spectrum.

The decomposition progress was calculated as the ratio ethylene + methylenecyclopentane/ethylene + methylenecyclopropane + spirohexane. The amount of 1,3-butadiene formed prior to its polymerization was assessed as the difference between the amounts of ethylene and methylenecyclopropane. For the estimation of the effective mean temperatures and the Arrhenius parameters of the spirohexane decomposition, the technique for noninteracting systems[12] using isopropyl acetate as a chemical thermometer (marker) was used. The mixtures of spirohexane (3.7 kPa)–isopropyl acetate (2.9 kPa) and SF_6 (1.9 kPa) were irradiated with mildly focused laser beam with the output ranging from 4 to 8 W. Prior to the analysis of the reaction mixtures for the products of the spirohexane decomposition, the depletion of isopropyl acetate was monitored by recording the IR spectra at 1240 cm^{-1}. For this purpose a Perkin-Elmer Model 621 infrared spectrometer was used. The effective temperatures were calculated on the grounds of the Arrhenius parameters for isopropyl acetate decomposition taken from ref 21.

Sulfur hexafluoride (Fluka, purum) and isopropyl acetate (Lachema, purum) were commercial samples. Spirohexane[22] and nitric oxide[23] were prepared as reported earlier.

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Registry No. Spirohexane, 157-45-9; ethylene, 74-85-1; 1,3-butadiene, 106-99-0; methylenecyclopropane, 6142-73-0; methylenecyclopentane, 1528-30-9.

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Simple One-Step Synthesis of 1,4-Diketones: A New Approach to Dihydrojasmone

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Many biologically active natural products are characterized by a cyclopentenone moiety as a main structural feature, hence an increasing interest exists in developing new synthetic routes to substituted cyclopentenones.[1] In this context 1,4-diketones represent the most widely employed intermediates and efforts to find new efficient syntheses of these compounds are continuing.[2,3]

Since triorganoalanes (AlR_3 or $AlR_3{\cdot}OEt_2$) react with α-nitro olefins **1** to give the corresponding saturated nitro compounds **2** in high yields (Scheme I),[4] and **2** can be easily converted into carbonyl derivatives[5] **3**, the reaction of AlR_3 or $AlR_3{\cdot}OEt_2$ with a suitable nitro olefin such as **4** could represent a useful approach for the preparation of unsymmetrical 1,4-diketones **6** "via" the saturated nitrocompound **5** (Scheme II).

Results and Discussion

The reaction of 5-hexen-2-one (**7**) with $HgCl_2/NaNO_2$[6] followed by acid-catalyzed (TsOH) ketalization with

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