

VII (0.475 g) as a viscous light yellow oil. Purification was achieved by short column chromatography (24 g, ca. 13 × 2.5 cm, hexane/ethyl acetate, v/v, 6:1), giving chromatographically homogeneous VII (0.204 g, 43%) as a thick (very viscous) colorless oil. An analytical sample was prepared by Kugelrohr distillation at 0.001 mm (air bath temperature ca. 150 °C): NMR (CDCl_3) 1.33 (s, 1 CH_3), 1.46 (s, 1 CH_3), 1.7 (m, 2 CH_3), 3.30 (d, J = 11.5 Hz, CHS), 5.21 (v br t, J = 7 Hz) and 5.65 (br d, J = 11.5 Hz, 2 CCH), 7.0–7.6 (m, aromatic CH); mass spectrum, m/e (relative intensity) 330 (2), 220 (7), 203 (25), 202 (34), 187 (32), 174 (13), 163 (70), 162 (51), 161 (11), 160 (11), 159 (59), 147 (51), 145 (12), 134 (14), 133 (12), 131 (10), 121 (10), 120 (12), 119 (23), 110 (100), 109 (25), 107 (27), 95 (17), 94 (21), 93 (17), 91 (25), 81 (36), 79 (19), 77 (22), 69 (13), 66 (30), 65 (15), 59 (75), 55 (15), 51 (11), 43 (25), 41 (24), 39 (14). Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{SO}$: C, 76.31; H, 9.15; S, 9.70. Found: C, 76.39; H, 9.19; S, 9.83.

Reduction of VII. A mixture of 0.110 g of VII (0.29 mmol) in ca. 1 mL of tetrahydrofuran and 20 mL of liquid ammonia, cooled in dry ice–2-propanol, was treated with 0.020 g of lithium wire (3 mmol), a deep blue color ensuing. The cooling bath was removed, and the reaction mixture maintained at under reflux for 0.5 h. Thereafter, ammonium chloride was added (discharging the blue color) and the condenser removed to allow evaporation of the ammonia. The residue was partitioned between water and hexane, the organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed in vacuo, giving 0.077 g of colorless oil (theoretical 0.074 g). TLC analysis (hexane/ethyl acetate, v/v, 4:1) indicated only one significant product, characterized by R_{st} 0.8. Preparative TLC furnished 0.0625 g of pure VIII (85%); an analytical sample was prepared by Kugelrohr distillation at 0.001 mm (air bath temperature ca. 110 °C): NMR (CDCl_3) 1.18 (s, 1 CH_3), 1.21 (s, 1 CH_3), 2.72 (br s, 2 CH_3), 5.32 (br t, J = 8 Hz, 2 C=CH); IR (CCl_4) 3615, 1665, 1155, 880, 860 cm^{-1} ; mass spectrum, m/e (relative intensity) 222 (1), 204 (43), 189 (43), 164 (12), 162 (13), 161 (74), 149 (17), 147 (14), 135 (22), 133 (17), 123 (10), 122 (10), 121 (38), 109 (19), 108 (16), 107 (56), 105 (34), 95 (34), 94 (207), 93 (76), 91 (20), 82 (11), 81 (47), 80 (12), 77 (12), 71 (14), 69 (24), 68 (18), 67 (35), 59 (100), 55 (26), 53 (15), 44 (16), 43 (38), 41 (44), 39 (12), 29 (12), 18 (78), 17 (15). Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}$: C, 81.02; H, 11.785. Found: C, 80.88; H, 11.83.

Dehydration of VIII. A solution of 0.169 g of VIII (0.75 mmol) in 3.0 mL of pyridine cooled in an ice–water bath was treated with 0.22 g of thionyl chloride (1.85 mmol). The reaction mixture was stirred and cooling of the mixture was maintained for ca. 15 min. The reaction mixture was poured into chilled aqueous bicarbonate, extracted with hexane, washed with dilute hydrochloric acid and saturated bicarbonate, and dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure furnished a slightly cloudy oil, 0.097 g (theoretical 0.153 g). TLC analysis (hexane/ethyl acetate, v/v, 4:1) indicated the absence of VIII and products at R_{st} ca. 1.6 as well as significant material at the origin; GLC analysis (122 °C) indicated two major volatile components in a somewhat variable ratio, initially ca. 10:1 but only 4:1 for samples standing for sometime. On chromatography over silver nitrate impregnated silica gel (hexane/ethyl acetate, v/v, 1:1), the major component appeared as the slower moving. Preparative TLC over argonated silica gel furnished this component (0.044 g, ca. 20%) as homogeneous: NMR (CDCl_3) 1.68 (m, 1 CH_3), 1.71 (m, 2 CH_3), 4.68 (br s, 2 CCH), 5.27 (br, C=CH₂); IR (CCl_4) 3075, 3030, 1645, 890 cm^{-1} ; mass spectrum, m/e (relative intensity) 204 (50), 189 (56), 162 (10), 161 (57), 148 (16), 147 (49), 135 (16), 134 (11), 133 (23), 122 (13), 121 (43), 120 (10), 119 (28), 109 (15), 108 (28), 107 (54), 106 (11), 105 (36), 95 (29), 94 (28), 93 (87), 92 (11), 91 (29), 81 (29), 81 (62), 80 (12), 79 (41), 77 (19), 69 (20), 68 (100), 67 (56), 65 (10), 55 (34), 53 (36), 43 (15), 41 (64), 40 (11), 39 (29), 29 (20), 27 (16), high-resolution mass spectrum, calcd for $\text{C}_{15}\text{H}_{24}$ 204.1878, found 204.1877.

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Registry No. IV, 75023-40-4; V, 28413-58-3; VIa, 74986-29-1; VIb, 60441-27-2; VII, 60441-28-3; VIII, 60479-01-8; *cis,trans*-farnesol, 61764-67-8; thiophenol, 108-98-5; 10-bromo-*cis,trans*-farnesyl sulfide, 74986-30-4; *cis,trans*-8-(1-methylethenyl)-18-dimethyl-1,5-cyclo-decadiene, 69460-22-6.

Novel Cyclization Reaction of Methyl Styryl Sulfone with Ketone Enolates

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α,β -Unsaturated sulfur compounds have been used as important reagents in synthetic chemistry,¹ for example, vinyl sulfides as carbonyl synthons² and vinylsulfonium salts as precursors of cyclopropanes.³ However, application of vinyl sulfones has been restricted since conversion of the sulfonyl group to another functional moiety is generally difficult. Posner demonstrated that the addition reaction of organocuprates to methyl vinyl sulfones was unsuccessful or gave low yields due to predominant proton abstraction from the methyl group.⁴ In a previous communication, we reported the synthesis of 2-thiadecalain derivatives from cyclohexanone enolates and dimethylstyrylsulfonium salts.⁵ If this annelation reaction was applicable to methyl styryl sulfone, it would be expected to introduce two alkyl groups into the carbonyl substrate by removal of the sulfonyl group from the resulting cyclic sulfones. We report herein the reaction of methyl styryl sulfone with lithium ketone enolates and desulfonylation of the products.

Methyl styryl sulfone (1) was allowed to react with lithium cyclohexanone enolate in THF–DMF (1:2) at 80 °C to give 8a-hydroxy-4-phenyl-2-thiadecalain 2,2-dioxide (2) in quantitative yield. A similar reaction between 1 and other lithium ketone enolates gave the corresponding cyclic sulfones in fairly good yields (Table I).⁶

The sulfone 2 was identified with an authentic sample prepared from 8a-hydroxy-4-phenyl-2-thiadecalain and *m*-chloroperbenzoic acid. Although 2 was proved to be single isomer by TLC and NMR, its stereochemistry could not be settled with certainty because five protons at C¹, C³, and C⁴ appeared as a multiplet at δ 3.10–3.20. Four protons at C¹ and C³ were easily deuterated by treatment with sodium carbonate and deuterium oxide.⁷ The NMR of the deuterated sulfone showed a doublet at δ 3.20, assignable to C⁴ proton, and its coupling constant was 6.8 Hz, indicating an axial–axial relationship between the protons at C⁴ and C^{4a}. This structural assignment is in agreement with the annelation reaction of butadienylsulfonium salts and cyclohexanone.⁸ Structures of other cyclic sulfones were confirmed by NMR data, similar to that of 2. In the reaction of 2-decalone and cycloheptanone, dehydrated products (6, 11) were obtained in addition to β -hydroxy sulfones in 18 and 44% yields, respectively. Methyl vinyl sulfone (1) reacted with acetone enolate also to give cyclic sulfone 12 in a relatively low yield. On the basis of these results, it is clear that methyl vinyl sulfone (1) is predominantly transformed into cyclic sulfones by the addition of ketone enolates and subsequent

(1) B. M. Trost, *Chem. Rev.*, 78, 363 (1978).

(2) D. Seebach and M. Kolb, *Chem. Ind. (London)*, 687, (1974).

(3) (a) C. R. Johnson and J. P. Lockard, *Tetrahedron Lett.*, 4589 (1971); (b) K. Takaki and T. Agawa, *J. Org. Chem.*, 42, 3303 (1977).

(4) G. H. Posner and D. J. Brunelle, *J. Org. Chem.*, 38, 2747 (1973).

(5) K. Takaki, H. Takahashi, Y. Oshiro, and T. Agawa, *J. Chem. Soc., Chem. Commun.*, 675 (1977).

(6) In the reaction of 1 with 2-methylcyclohexanone, a byproduct assignable to 15 was traced in the first fraction of chromatography.

(7) H. O. House and B. M. Trost, *J. Org. Chem.*, 30, 1341 (1965).

(8) M. E. Garst, *J. Org. Chem.* 44, 1578 (1979).

Table I. Reaction of Methyl Styryl Sulfone (1) with Lithium Ketone Enolates

ketone	products	% yield ^a
cyclohexanone	2	100
cyclohexanone	3	100
cyclohexanone	4	78
2,2-dimethylcyclohexanone	5 + 6	73 + 18
2,2-dimethylcyclohexanone	7 + 8	43 + 18
cyclopentanone	9	89
cyclopentanone	10 + 11	32 + 44
cyclopropane	12	57

^a Yield of products purified by chromatography or distillation. ^b Mixture of cis and trans (52:48).

condensation reactions, contrasting with the dimethylstyrylsulfonium salt where a cyclization reaction competes with spirocyclopropanation, depending on the ring size and electrophilicity of the ketones.⁵

Then, we studied Ramberg-Bäcklund reaction of the resulting cyclic sulfones to examine the possibility of the synthesis of cyclopentene derivatives. This effort was unfortunately unsuccessful, since sulfone 2 was not halogenated under various conditions, even by the treatment with *n*-butyllithium and iodine.⁹ Although a number of methods for hydrogenolysis of alkyl or aryl sulfones have been reported, most of them resulted in the fission of

Table II. Desulfonylation of the Cyclic Sulfones

sulfone	product	% yield ^a
2	13	70
3	14	74
4	15	50
9	16	54
10	17	81

^a Yield of products purified by distillation.

carbon-sulfur bond only.¹⁰ Therefore, we have undertaken a study of desulfonylation of the cyclic β -hydroxy sulfones which are potentially useful for olefin synthesis.¹¹

The sulfone 2 was treated with sodium (5.0 equiv) and absolute ethanol (5.8 equiv) in dry THF¹² under reflux for 7.5 h to yield 1-methylene-2-(α -styryl)cyclohexane (13) in 70% yield (Table II). On the other hand, similar treatment of 9 and 10 gave monoolefins 16 and 17 in 54 and 81% yields, respectively. Part of the difference mentioned above may be attributed to the different size of the cyclic sulfones; however, this process is mechanistically unclear at this stage.

Finally, methyl styryl sulfone (1) is a useful annelation reagent, providing cyclic β -hydroxy sulfones in good yields. The resulting sulfones are readily desulfonylated by treatment with sodium and ethanol to give olefins. From a synthetic point of view, these total reactions would be available for vicinal dialkylation of cyclic ketones.

Experimental Section

General. All melting points were determined with a Yanagimoto micro melting point apparatus and were uncorrected. The NMR spectra were obtained on JEOL JNM-PMX-60 and JNM-PS-100 spectrometers with tetramethylsilane as an internal standard. The IR spectra were recorded with a Hitachi 215 spectrometer. The mass spectra were taken with Hitachi RMU-6E and Hitachi RMU-6D spectrometers.

Reaction of Methyl Styryl Sulfone (1) with Lithium Ketone Enolates. General Procedure. To a stirred solution of lithium diisopropylamide (12 mmol) in dry THF (40 mL) was

(10) (a) G. H. Posner and D. J. Brunelle, *Tetrahedron Lett.*, 935 (1973); (b) V. Pascali and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 351 (1973); (c) J. F. Biellmann and J. B. Ducep, *Tetrahedron*, 27, 5861 (1971); (d) P. T. Lansbury, R. W. Erwin, and D. A. Jeffrey, *J. Am. Chem. Soc.*, 102, 1602 (1980).

(11) (a) T. Shono, Y. Matsumura, S. Kashimura, *Chem. Lett.*, 69 (1978); (b) P. J. Kocienski, B. Lythgoe, and S. Ruston, *J. Chem. Soc., Perkin Trans. 1*, 829 (1978).

(12) D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 123 (1977).

added an equimolar amount of ketone under nitrogen at -70 °C. After 3 h, methyl styryl sulfone (1.10 mmol) in dry DMF (80 mL) was added. The reaction mixture was warmed to room temperature and then heated at 80 °C for 12 h. Water (40 mL) was added after cooling and the mixture was acidified with aqueous hydrochloric acid until neutral pH. The organic layer was extracted with chloroform (3 × 40 mL), washed with saturated brine, and dried over sodium sulfate. After concentration of the solvent in vacuo, the residue was chromatographed on silica gel with benzene and benzene-ethanol.

8a-Hydroxy-4-phenyl-2-thiadecalin 2,2-dioxide (2): mp 177–178 °C (benzene–hexane); IR (Nujol) 3500, 1300, 1140 cm⁻¹; mass spectrum (70 eV), *m/e* 280 (M⁺); NMR (CDCl₃) δ 1.10–1.90 (m, 9 H), 3.10–3.20 (m, 5 H), 4.00 (s, 1 H, OH), 7.05–7.50 (m, 5 H, aromatic).

Anal. Calcd for C₁₅H₂₀O₃S: C, 64.27; H, 7.19; S, 11.42. Found: C, 64.35; H, 7.09; S, 11.45.

A solution of 2 (250 mg) and sodium carbonate (8 mg) in deuterium oxide (2 mL) and 1,2-dimethoxyethane (8 mL) was refluxed for 18 h. After concentration of the solvent, the sulfone was recovered by extraction with chloroform followed by washing with brine, drying over sodium sulfate, and concentration of the extract. Such treatment was repeated three times. The sulfone (87 mg) was recovered finally, containing 14% *d*₂, 49% *d*₃, and 29% *d*₄ species by mass spectroscopy; NMR (CDCl₃) δ 0.91–1.94 (m, 9 H), 3.20 (m and d, *J* = 6.8 Hz, 1.7 H), 3.68 (br, 0.9 H, OH), 7.02–7.45 (m, 5 H, aromatic).

6-*tert*-Butyl-8a-hydroxy-4-phenyl-2-thiadecalin 2,2-dioxide (3): mp 205.5–206.5 °C (benzene–hexane); IR (Nujol) 3500, 1300, 1110 cm⁻¹; mass spectrum (70 eV), *m/e* 336 (M⁺); NMR (Me₂SO-*d*₆) δ 0.68 (s, 9 H, 3 CH₃), 0.78–2.17 (m, 8 H), 2.80–4.07 (m, 6 H), 7.10–7.50 (m, 5 H, aromatic).

Anal. Calcd for C₁₉H₂₈O₃S: C, 67.83; H, 8.39. Found: C, 67.84; H, 8.72.

8a-Hydroxy-8-methyl-4-phenyl-2-thiadecalin 2,2-dioxide (4): bp 155–160 °C (1 mm, bath temperature); IR (Nujol) 3500, 1295, 1120 cm⁻¹; mass spectrum (70 eV), *m/e* 294 (M⁺); NMR (CDCl₃) δ 0.73–2.57 (m, 12 H), 2.77–3.93 (m, 5 H), 6.97–7.47 (m, 5 H, aromatic).

9a-Hydroxy-4-phenyl-2-thiaperhydroanthracene 2,2-dioxide (5): mp 201–203 °C (ethanol); IR (Nujol) 3500, 1310, 1125 cm⁻¹; mass spectrum (70 eV), *m/e* 334 (M⁺); NMR (CD₃CN) δ 0.50–2.40 (m, 16 H), 2.77–4.13 (m, 5 H), 7.00–7.53 (m, 5 H, aromatic). Anal. Calcd for C₁₉H₂₆O₃S: C, 68.24; H, 7.84; S, 9.57. Found: C, 68.35; H, 7.78; S, 9.40.

4-Phenyl-2-thia-1,3,4,5,6,7,8,8a,9,10,10a-undecahydroanthracene 2,2-dioxide (6): mp 180–182 °C (ethanol); IR (Nujol) 3500, 1300, 1140 cm⁻¹; mass spectrum (70 eV), *m/e* 316 (M⁺); NMR (CD₃CN) δ 0.67–2.43 (m, 15 H), 3.00–4.27 (m, 4 H), 7.20–7.53 (m, 5 H, aromatic).

Anal. Calcd for C₁₉H₂₄O₂S: C, 72.12; H, 7.65; S, 10.12. Found: C, 72.23; H, 7.67; S, 9.83.

4a-Hydroxy-1-phenyl-3-thia-1,2,4,9,10,10a-hexahydrophenanthrene 3,3-dioxide (7): mp 208–209 °C (benzene–hexane); IR (Nujol) 3500, 1300, 1115 cm⁻¹; mass spectrum (70 eV), *m/e* 328 (M⁺); NMR (Me₂SO-*d*₆) δ 1.00–4.50 (m, 10 H), 5.50–5.73 (s, 1 H, OH), 6.83–7.43 (m, 8 H, aromatic), 7.50–7.83 (m, 1 H, aromatic).

Anal. Calcd for C₁₉H₂₀O₃S: C, 69.50; H, 6.14; S, 9.74. Found: C, 69.77; H, 5.88; S, 9.57.

2-(2-(Methylsulfonyl)-1-phenylethyl)-3,4-dihydro-1-(2*H*)-naphthalenone (8): mp 153–154 °C (benzene–hexane); IR (Nujol) 1680, 1300, 1115 cm⁻¹; mass spectrum (70 eV), *m/e* 328 (M⁺); NMR (Me₂SO-*d*₆) δ 1.40–3.13 (m, 5 H), 2.60 (s, 3 H, CH₃), 3.43–4.13 (m, 3 H), 6.83–7.67 (m, 8 H, aromatic), 7.85–8.20 (m, 1 H, aromatic).

Anal. Calcd for C₁₉H₂₀O₃S: C, 69.50; H, 6.14; S, 9.74. Found: C, 69.40; H, 6.01; S, 9.80.

3a-Hydroxy-7-phenyl-5-thiaperhydroindan 5,5-dioxide (9): mp 184.5–185.5 °C (benzene–hexane); IR (Nujol) 3450, 1295, 1115 cm⁻¹; mass spectrum (70 eV), *m/e* 266 (M⁺); NMR (CDCl₃) δ 1.28–2.05 (m, 7 H), 3.03–3.90 (m, 5 H), 4.20 (s, 1 H, OH), 6.98–7.63 (m, 5 H, aromatic).

Anal. Calcd for C₁₄H₁₈O₃S: C, 63.14; H, 6.81; S, 12.02. Found: C, 63.30; H, 6.84; S, 11.92.

1-Hydroxy-8-phenyl-10-thiabicyclo[5.4.0]undecane 10,10-dioxide (10): mp 158.5–159.5 °C (benzene–hexane); IR (Nujol) 3450, 1300, 1120 cm⁻¹; mass spectrum (70 eV), *m/e* 294 (M⁺); NMR (CDCl₃) δ 0.80–2.20 (m, 11 H), 2.83–3.52 (m, 5 H), 3.95 (br, 1 H, OH), 6.97–7.55 (m, 5 H, aromatic).

Anal. Calcd for C₁₆H₂₂O₃S: C, 65.29; H, 7.53. Found: C, 65.26; H, 7.44.

8-Phenyl-10-thiabicyclo[5.4.0]undec-1(7)-ene 10,10-dioxide (11): mp 134–135 °C (benzene); IR (Nujol) 1295, 1105 cm⁻¹; mass spectrum (70 eV), *m/e* 276 (M⁺); NMR (CDCl₃) δ 0.93–2.43 (m, 10 H), 2.93–4.27 (m, 5 H), 6.93–7.67 (m, 5 H, aromatic).

Anal. Calcd for C₁₆H₂₀O₂S: C, 69.54; H, 7.30. Found: C, 69.32; H, 7.23.

3-Hydroxy-3-methyl-5-phenylthiane 1,1-dioxide (12): mp 118–120 °C (benzene–hexane); IR (Nujol) 3450, 1300, 1140 cm⁻¹; mass spectrum (70 eV), *m/e* 240 (M⁺); NMR (CDCl₃) δ 1.40 (s, 3 H, CH₃), 1.60–2.33 (m, 2 H), 3.00–3.28 (m, 4 H), 3.33–3.95 (m, 2 H), 7.03–7.60 (m, 5 H, aromatic).

Anal. Calcd for C₁₂H₁₆O₃S: C, 59.99; H, 6.71. Found: C, 60.28; H, 6.61.

Desulfonylation of the Cyclic β -Hydroxy Sulfones.

General Procedure. A solution of the cyclic β -hydroxy sulfone (5.36 mmol) and sodium (0.62 g, 27 mmol) in absolute ethanol (1.81 mL, 31 mmol) and dry THF (22 mL) was refluxed for 7.5 h. After the solution was cooled, methanol (18 mL) and then water (30 mL) were added cautiously, followed by extraction with chloroform, drying over sodium sulfate, and concentration of the solvent. The residue was purified by short-path distillation in vacuo.

1-Methylene-2-(α -styryl)cyclohexane (13): bp 64.5–65.5 °C (1.5 mm, bath temperature); IR (neat) 1640, 1620, 890 cm⁻¹; mass spectrum (70 eV), *m/e* 198 (M⁺); NMR (CDCl₃) δ 1.00–2.67 (m, 8 H), 3.00–3.33 (m, 1 H), 4.57–4.83 (m, 2 H, vinylic), 5.08 (d, *J* = 1.3 Hz, 1 H, vinylic), 5.45 (d, *J* = 1.3 Hz, 1 H, vinylic), 7.00–7.67 (m, 5 H, aromatic).

Anal. Calcd for C₁₅H₁₈: C, 90.85, H, 9.15. Found: C, 91.19; H, 8.79.

4-*tert*-Butyl-1-methylene-2-(α -styryl)cyclohexane (14): bp 80–85 °C (1 mm, bath temperature); IR (neat) 1640, 1620, 890 cm⁻¹; mass spectrum (70 eV), *m/e* 254 (M⁺); NMR (CDCl₃) δ 0.88 (s, 9 H, 3 CH₃), 1.03–2.50 (m, 7 H), 2.88–3.27 (m, 1 H), 4.60 (m, 2 H, vinylic), 5.05 (d, *J* = 1.2 Hz, 1 H, vinylic), 5.47 (d, *J* = 1.2 Hz, 1 H, vinylic), 7.02–7.47 (m, 5 H, aromatic).

Anal. Calcd for C₁₉H₂₆: C, 89.70; H, 10.30. Found: C, 89.35; H, 10.59.

1-Methylene-6-methyl-2-(α -styryl)cyclohexane (15): bp 55–57 °C (1 mm, bath temperature); IR (neat) 1640, 1620, 890 cm⁻¹; mass spectrum (70 eV), *m/e* 212 (M⁺); NMR (CDCl₃) δ 1.05 (d, *J* = 6.0 Hz, 3 H, CH₃), 1.18–2.35 (m, 7 H), 2.90–3.30 (m, 1 H), 4.70 (m, 2 H, vinylic), 5.10 (d, *J* = 1.2 Hz, 1 H, vinylic), 5.55 (d, *J* = 1.2 Hz, 1 H, vinylic), 7.10–7.53 (m, 5 H, aromatic).

Anal. Calcd for C₁₈H₂₀: C, 90.50; H, 9.50. Found: C, 90.43; H, 9.25.

1-Methylene-2-(1-phenylethyl)cyclopentane (16): bp 48–52 °C (2 mm, bath temperature); IR (neat) 1645, 1595, 880 cm⁻¹; mass spectrum (70 eV), *m/e* 186 (M⁺); NMR (CDCl₃) δ 1.00–3.07 (m, 11 H), 4.77–5.43 (m, 2 H), 6.97–7.70 (m, 5 H, aromatic).

Anal. Calcd for C₁₄H₁₈: C, 90.26; H, 9.74. Found: C, 90.46; H, 9.36.

1-Methylene-2-(1-phenylethyl)cycloheptane (17): bp 55–60 °C (1 mm, bath temperature); IR (neat) 1630, 1590, 890 cm⁻¹; mass spectrum (70 eV), *m/e* 214 (M⁺); NMR (CDCl₃) δ 0.80–2.57 (m, 15 H), 4.70–4.97 (m, 2 H), 7.00–7.30 (m, 5 H, aromatic).

Anal. Calcd for C₁₈H₂₂: C, 89.65; H, 10.35. Found: C, 89.50; H, 10.29.

Registry No. 1, 5342-84-7; 2, 69263-13-4; 3, 75011-17-5; 4, 75011-18-6; 5, 75011-19-7; 6, 75011-20-0; 7, 75011-21-1; 8, 75011-22-2; 9, 75011-23-3; 10, 75011-24-4; 11, 75011-25-5; 12, 75011-26-6; 13, 75011-27-7; 14, 75011-28-8; 15, 75011-29-9; 16, 75011-30-2; 17, 75011-31-3; cyclohexanone, 108-94-1; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; *cis*- β -decalone, 1579-21-1; *trans*- β -decalone, 16021-08-2; 3,4-dihydro-1(2*H*)-naphthalenone, 529-34-0; cyclopentanone, 120-92-3; cycloheptanone, 502-42-1; acetone, 67-64-1.