benzene-d_6, relative to Me_4Si) 142.0 (s), 116.4 (d), 70.4 (s), 68.5 (d), 48.1 (d), 43.1 (t), 42.5 (t), 38.6 (s), 34.9 (d), 30.5 (t), 29.6 (q), 24.6 (t), 21.9 (q), 21.3 (q), and 14.2 ppm (q); ^1H NMR (220 MHz, $CDCl_3$, relative to Me_4Si) δ 5.32 (1 H, bd, J = 6 Hz), 4.00 (1 H, dd, J = 12, 4 Hz), 2.43 (1 H, dddd, J = 13, 13, 13, 4 Hz), 2.16 (1 H, heptet, J = 7 Hz), 1.64 (1 H, m), 1.16 (3 H, s), 1.09 (3 H, s), and 1.00 ppm (6 H, d, J = 7 Hz).

Dehydration of 1. Compound 1 (70 mg) was dissolved in benzene (10 mL) and a catalytic amount of *p*-toluenesulfonic acid monohydrate was added (~5 mg). The mixture was refluxed for 30 min, after which time diethyl ether (75 mL) was added and the organic phase neutralized with $NaHCO_3$. The ether phase was separated and dried with anhydrous $MgSO_4$, and the ether was removed in vacuo to yield a light, mobile oil (50 mg). Silica gel TLC showed the production of two relatively nonpolar products, one UV active at R_f 0.7 (petroleum ether) and one non-UV-active at R_f 0.8. Preparative layer chromatography (petroleum ether) gave pure samples of **2** and **3** in a 3:2 ratio. For compound **2:** NMR (60 MHz, CCl_4) δ 6.00 (1 H, s), 4.03 (1 H, dd, J = 12, 5 Hz), 1.67 (3 H, s), 1.05 (6 H, d, J = 7 Hz), 1.03 (3 H, s); UV λ_{max} (CH_2Cl_2) 240, 247, 257 nm; mass spectrum m/e 282/284 (M^+), $C_{15}H_{23}Br$. For compound **3:** NMR (220 MHz, CCl_4) δ 5.39 (1 H, bs), 5.27 (1 H, bs), 4.23 (1 H, dd, J = 11, 5 Hz), 1.66 (3 H, s), 1.02 (6 H, d, J = 8 Hz), 0.86 (3 H, s); mass spectrum M^+ m/e 282/284 (1:1) for $C_{15}H_{23}Br$.

(−)-δ-Selinene (4) from 2. A solution of 20 mg of **2** in 5 mL of anhydrous THF containing excess $LiAlH_4$ was refluxed in a nitrogen atmosphere for 4 h. Standard hydrolytic workup gave 5 mg of (−)-δ-selinene (**4**): NMR (60 MHz, CCl_4) δ 6.02 (1 H, s), 1.67 (3 H, s), 1.05 (6 H, d, J = 7 Hz), 0.92 (3 H, s); UV λ_{max} (CH_3OH) 237, 244, 255 nm; IR (film) ν 2900, 1645, 1620, 1385, 1375, 1295, 1270, 1215, 1175, 1065, 1030, 995, 955, 876, and 805 cm^{-1}; $[\alpha]^{22}_D$ −188° (c 0.08, $CHCl_3$); mass spectrum M^+ m/e 204 for $C_{15}H_{24}$.

1(*S*)-Bromo-4(*R*),7(*R*),8(*R*)-trihydroxy-(−)-selinane (5). A solution of 57 mg of **1** and 50 mg of OsO_4 in 5 mL of anhydrous ether containing 5 drops of pyridine was stirred for 48 h at 25 °C. The reaction was quenched by adding 15 mL of pyridine followed by 20 mL of a 5% solution of $NaHSO_3$. After stirring for 2 h, the reaction mixture was extracted with ether. The ether solution was washed five times with 5% HCl solution and once with saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Filtration and evaporation gave a single product (50 mg), an oil (**5**): NMR (220 MHz, $CDCl_3$) δ 4.02 (1 H, dd, J = 12, 4 Hz), 3.92 (1 H, dd, J = 12, 5 Hz), 2.39 (1 H, dddd, J = 13, 13, 13, 4 Hz), 1.93 (1 H, dd, J = 12, 5 Hz), 1.23 (3 H, s), 1.18 (3 H, s), 1.04 (3 H, d, J = 8 Hz), 0.99 (3 H, d, J = 8 Hz); mass spectrum m/e 291/293 (M^+ − 43), 273/275 M^+ − (43 + H_2O), 255/257 M^+ − (43 + 2H_2O), 237 M^+ − (43 + Br).

4(*R*)-Hydroxy-(−)-selin-7-ene (6). To a solution of excess Li in liquid ammonia (dry ice–acetone bath) and diethyl ether, 30 mg of **1** in 2 mL of ether was added with stirring. After 2 h, NH_4Cl was added slowly and the reaction mixture was allowed to warm to room temperature. When the ammonia had evaporated, the reaction mixture was washed with 5% HCl followed by saturated $NaHCO_3$, dried ($MgSO_4$), filtered, and evaporated to give, after thick layer chromatography, 20 mg of **6** as a colorless oil: $[\alpha]^{21}_D$ +57.1° (c 1.37, dioxane); NMR (220 MHz, $CDCl_3$) δ 5.32 (1 H, bs), 2.22 (1 H, hep, J = 7 Hz), 1.17 (3 H, s), 1.02 (6 H, d, J = 7 Hz), 0.96 (3 H, s); IR (film) ν 3350, 2900, 1625, 1140 cm^{-1}; mass spectrum m/e 204 (M^+ − H_2O) $C_{15}H_{24}$, 189 (M^+ − H_2O − CH_3) $C_{14}H_{21}$.

Conversion of 6 to (−)-δ-Selinene. A solution of 20 mg of **6** in 5 mL of benzene containing a catalytic amount of *p*-toluenesulfonic acid monohydrate was refluxed for 1 h. Workup yielded two olefins as judged by NMR, one of which was **4**. The mixture was dissolved in 2 mL of acetic acid containing 2 drops of H_2SO_4 and stirred for 30 min. Workup gave 15 mg of a single olefin, **4**, which was identical with that produced from **2**.

Silver Acetate Rearrangement of 1. A solution of 100 mg of **1** in glacial acetic acid was added slowly with stirring to a suspension of excess AgOAc in glacial acetic acid. The reaction mixture was stirred at 60 °C for 2 h and filtered, and the filtrate was washed with ether. The ether–acetic acid was washed with water, followed by $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated to give a yellow oil. TLC of the reaction mixture indicated two major products which were less polar than **1**. TLC (ether–petroleum ether, 1:1 v/v), R_f 0.4 (**7**) and R_f 0.5 (**8**). Thick layer chromatography gave pure samples of **7** (30 mg) and **8** (20 mg). For compound **7:** ^{13}C NMR (20 MHz, $CDCl_3$) 143.0 (s), 117.7 (d), 86.1 (s), 80.0 (s), 50.3 (d), 49.1 (d), 42.8, 37.2, 36.3, 27.5, 27.1, 24.2, 21.9, 21.7, 17.2 ppm; ^1H NMR (220 MHz, $CDCl_3$) δ 5.23 (1 H, dd, J = 5, 5 Hz), 1.26 (3 H, s), 1.23 (3 H, s), 1.02 (6 H, d, J = 8 Hz); mass spectrum m/e 220 (M^+) $C_{15}H_{24}O$. For compound **8:** ^{13}C NMR (20 MHz, $CDCl_3$) 92.0, 86.1, 53.0, 42.1, 35.7, 31.2, 30.7, 31.0, 27.3, 27.1, 26.2, 25.0, 24.5, 24.2, 17.4 ppm; ^1H NMR (220 MHz, $CDCl_3$) δ 1.20 (3 H, s), 0.95 (3 H, s), 0.94 (3 H, d, J = 7 Hz), 0.92 (3 H, d, J = 7 Hz), 0.45 (1 H, bs), 0.43 (1 H, dd, J = 7, 3 Hz); mass spectrum m/e 220 (M^+) $C_{15}H_{24}O$.

Guaiazulene. A solution of 20 mg of **7** in xylene was refluxed in the presence of 10% Pd on charcoal for 48 h. Filtration and evaporation left a blue residue. TLC (petroleum ether) purification of this mixture gave approximately 1 mg of a blue hydrocarbon which was determined to be identical with guaiazulene by TLC and visible spectra.

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Registry No.—**1,** 62264-66-8; **2,** 62264-67-9; **3,** 62264-68-0; **4,** 28624-23-9; **5,** 62288-63-5; **6,** 62264-69-1; **7,** 62264-70-4; **8,** 62264-71-5.

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Carbonyl Homologation with α-Substitution. A New Synthesis of 4,4-Disubstituted 2-Cyclopentenones

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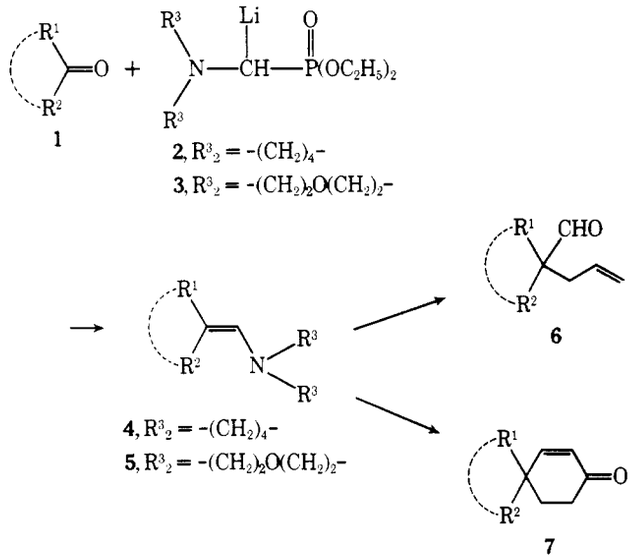
One of the most difficult tasks in organic synthesis is the creation of a quaternary carbon center. Since ketones are among the most accessible compounds in organic chemistry, a procedure for the geminal alkylation at a carbonyl carbon with functionally dissimilar substituents would be very attractive. We have recently described a new approach to this problem which involved the conversion of ketone carbonyl groups into either the pyrrolidine enamines **4** or the morpholine enamines **5** of the homologous aldehydes, and the necessary reagents for effecting these conversions were diethyl lithiopyrrolidinomethylphosphonate (**2**) or diethyl lithiomorpholinomethylphosphonate (**3**), respectively.[1,2] The inherent advantage of these procedures for carbonyl homologation is that the enamines **4** and **5,** which are useful functional derivatives of the corresponding aldehydes, are obtained

directly. Furthermore, these enamines may be employed in subsequent reactions with electrophilic reagents without purification. For example, treatment of the pyrrolidine enamines **4** with allyl bromide gave the α-allyl dialkylaldehydes **6** in good overall yields,[1] and the reaction of the morpholine enamines **5** with methyl vinyl ketone, followed by aldol cyclodehydration, gave the 4,4-disubstituted 2-cyclohexenones **7** in moderate overall yields.[2] This latter procedure constitutes a facile method for the spiroannelation of six-membered rings.



We have, in the course of our synthetic investigations of the acorane sesquiterpenes, developed a need for a method which allows the spiroannelation of a functionalized five-membered ring. Although the geminal allyl–formyl moiety of **6** could be modified for the eventual conversion to a substituted cyclopentane, a number of steps would obviously be required. Consequently, a procedure for the geminal alkylation with substituents which could be directly converted to the cyclopentane ring system would have obvious advantages. We now wish to report a useful modification of our original procedures whereby ketones may be readily converted to 4,4-disubstituted 2-cyclopentenones. The application of this reaction sequence to cyclic ketones constitutes a new method for the spiroannelation of five-membered rings which are suitably functionalized for further synthetic transformations.

The base-catalyzed cyclization of 1,4-dicarbonyl compounds is a useful method for the construction of cyclopentenones.[3] We envisioned, therefore, that the reaction of the enamines **4** with an electrophilic, 2-oxopropyl synthon would afford the requisite γ-ketoaldehydes which could then be cyclized to the desired 2-cyclopentenones. Since the reaction of the enamines of α,α-disubstituted aldehydes with α-bromo ketones is plagued by side reactions such as N-alkylation and polymerization,[4-6] we decided that the introduction of the necessary 2-oxopropyl group would be better achieved by the alkylation of the enamines **4** with 2,3-dibromopropene.[7] Although the latent γ-ketoaldehyde could be unmasked by acid-catalyzed hydrolysis, we anticipated that the 2-(2-bromo-2-propenyl) aldehydes **8** would undergo *direct* acid-catalyzed cyclization to give, after aqueous workup, the desired 4,4-disubstituted 2-cyclopentenones **9**.[8]

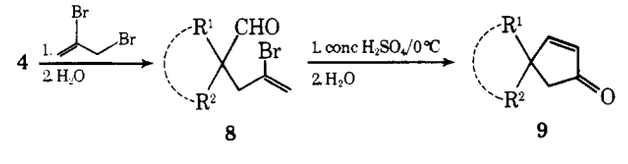


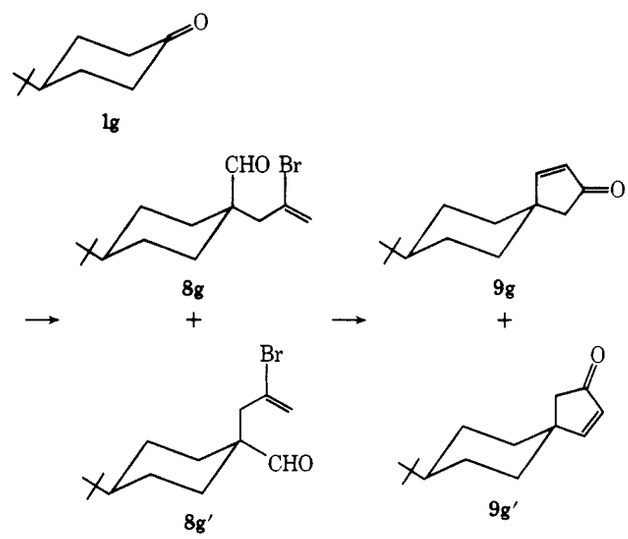
Table I

Starting ketone	% yield of **8**[a]	% yield of **9**[a]
3-Heptanone (**1a**)	40	72
4-Heptanone (**1b**)	43	85
4-Methyl-2-pentanone (**1c**)	33	77
Cyclohexanone (**1d**)	24	78
2-Methylcyclohexanone (**1e**)	32[b]	63[c]
4-Methylcyclohexanone (**1f**)	29[d]	75[e]
4-*tert*-Butylcyclohexanone (**1g**)	28[f]	54[g]

[a] Yields are of isolated product but are not optimized. [b] Obtained as a 83:17 mixture of diastereomers. [c] Obtained as a 82:18 mixture of diastereomers. [d] Obtained as a 83:17 mixture of diastereomers. [e] Obtained as a 78:22 mixture of diastereomers. [f] Obtained as a 82:18 mixture of diastereomers. [g] Obtained as a 78:22 mixture of diastereomers.

In the event, a solution of the enamines **4**, generated in situ from the ketones **1**, and an excess of 2,3-dibromopropene in tetrahydrofuran were heated at reflux for 48 h, and the resultant mixture was hydrolyzed with water at room temperature to give the 2-(2-bromo-2-propenyl) aldehydes **8**. When the aldehydes **8** were treated with concentrated sulfuric acid at 0 °C for 2 h, the 2-cyclopentenones **9** were obtained in acceptable overall yields (Table I).

Preliminary results have also indicated that this new synthetic procedure for geminal alkylation and spiroannelation proceeds with a reasonable degree of stereoselectivity. For example, 4-*tert*-butylcyclohexanone (**1g**) was smoothly converted to a diastereomeric mixture of the 2-(2-bromo-2-propenyl) aldehydes **8g** and **8g'** in about a 4:1 ratio. The assignment of the relative stereochemistry at the newly created chiral center is based upon the observed chemical shifts of the formyl proton (**8g**, δ_{CHO} = 9.67 and **8g'**, δ_{CHO} = 9.63). It is well known in similar systems that the axial formyl proton is deshielded relative to the equatorial one by steric crowding.[9] Furthermore, the methylene of the axial 2-bromo-2-propenyl group in **8g'** (δ_{CH_2} 2.90) is deshielded relative to the methylene of the equatorial 2-bromo-2-propenyl group in the major diastereomer **8g** (δ_{CH_2} 2.64). Sulfuric acid promoted cyclization gave the spiro[4.5]decenones **9g** and **9g'** in approximately a 4:1 ratio. The relative stereochemistry in **9g** and **9g'** may again



be easily confirmed from an analysis of the ^1H and ^{13}C NMR spectra of the mixture. The β-vinyl proton of the major isomer **9g** (δ_{CH} = 8.00, J = 5.5 Hz) is deshielded relative to the β-vinyl proton of the minor isomer **9g'** (δ_{CH} 7.42, J = 5.5 Hz). Owing

to steric compression, the β-vinyl carbon of **9g** (δ 169.5) appears upfield from the β-vinyl carbon of **9g'** (δ 174.3).[10]

We are presently investigating the scope and limitations of this new synthetic sequence as well as its application to the total synthesis of spirosesquiterpene natural products.

Experimental Section

General Procedure for the Conversion of Ketones 1a–g into 2-(2-Bromo-2-propenyl) Aldehydes 8a–g. To a well-stirred solution of diethyl pyrrolidinomethylphosphonate (4.0 g, 18.0 mmol) in anhydrous THF (60 mL) under dry nitrogen at −78 °C was slowly added *n*-butyllithium (7.5 mL of a 2.40 N solution in hexane, 18.0 mmol), and the stirring was continued at −78 °C for 1 h. A solution of the appropriate ketone **1a–g** (15 mmol) in anhydrous THF (5 mL) was then added, and the stirring was continued at −78 °C for 4 h and at room temperature overnight to give a solution of the enamine **4a–g**. 2,3-Dibromopropene (15.0 g, 75 mmol) was added, and the mixture was heated at reflux for 48 h. Upon cooling to room temperature, water (30 mL) was added, and the resulting mixture was stirred vigorously at room temperature for 4 h. The reaction mixture was diluted with saturated brine (50 mL), the layers were separated, and the aqueous layer was extracted with ether (3 × 75 mL). The combined organic layers were washed with 1 N HCl (2 × 50 mL) and saturated sodium bicarbonate (2 × 50 mL). After drying ($MgSO_4$), the excess solvent was removed under reduced pressure to give the crude 2-(2-bromo-2-propenyl) aldehyde **8a–g** which was distilled and used in the next step without further purification.

4-Bromo-2-ethyl-2-*n*-butyl-4-pentenal (8a): 40%, bp 85–87 °C (1.0 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.60 (s, 1 H), 5.60 (m, 2 H), 2.78 (s, 2 H), 0.65–1.95 (m, 14 H); mass spectrum *m/e* 248, 246, 167 (base), 85, 57, 55, 41. 2,4-Dinitrophenylhydrazone: mp 124.5–126 °C (from ethanol).

Anal. Calcd for $C_{17}H_{23}O_4N_4Br$: C, 47.78; H, 5.42. Found: C, 48.10; H, 5.17.

4-Bromo-2,2-di-*n*-propyl-4-pentenal (8b). 43%, bp 110–112 °C (3.3 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.57 (s, 1 H), 5.60 (m, 2 H), 2.82 (m, 2 H), 0.70–2.00 (m, 14 H); mass spectrum *m/e* 248, 246, 167 (base), 95, 55, 43, 41.

4-Bromo-2-methyl-2-isobutyl-4-pentenal (8c): 33%, bp 140–142 °C (4.2 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.73 (s, 1 H), 5.63 (m, 2 H). 2.78 (d, 2 H, *J* = 6 Hz), 0.63–2.00 (m, 12 H); mass spectrum *m/e* 234, 232, 153 (base), 112, 97, 83, 69, 43, 41.

1-(2-Bromo-2-propenyl)cyclohexanecarboxaldehyde (8d): 24%, bp 145–147 °C (6.0 mm); IR ($CHCl_3$) 1725 cm^{-1} (C=O); NMR ($CDCl_3$) δ 9.65 (s, 1 H), 5.58 (m, 2 H), 2.73 (s, 2 H), 1.20–2.10 (m, 10 H); mass spectrum *m/e* 232, 230, 151 (base), 110, 81, 79, 41.

1-(2-Bromo-2-propenyl)-2-methylcyclohexanecarboxaldehyde (8e): 32% as an 83:17 mixture of diastereomers, bp 146–148 °C (6.0 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 9.83 (s, 0.83 H), 5.62 (m, 2 H), 2.90 (d, 2 H, *J* = 10 Hz), 0.78–2.15 (m, 12 H), (minor diastereomer) δ 9.70 (s, 0.17 H); mass spectrum *m/e* 246, 244, 165 (base), 124, 95, 81, 79, 67, 55, 41.

1-(2-Bromo-2-propenyl)-4-methylcyclohexanecarboxaldehyde (8f): 29% as an 83:17 mixture of diastereomers, bp 148–150 °C (6.0 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 9.75 (s, 0.83 H), 5.55 (m, 2 H), 2.65 (s, 1.66 H), 0.75–2.40 (m, 12 H), (minor diastereomer) δ 9.73 (s, 0.17 H), 2.90 (s, 0.34 H); mass spectrum *m/e* 246, 244, 165 (base), 124, 95, 81, 79, 67, 55, 41.

1-(2-Bromo-2-propenyl)-4-*tert*-butylcyclohexanecarboxaldehyde (8g): 28% as an 82:18 mixture of diastereomer, bp 137–140 °C (1.5 mm); IR ($CHCl_3$) 1720 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 9.67 (s, 0.82 H), 5.53 (m, 2 H), 2.64 (s, 1.64 H), 0.72–2.36 (m, 18 H), (minor diastereomer) δ 9.63 (s, 0.18 H), 2.90 (s, 0.36 H); mass spectrum *m/e* 288, 286, 207 (base), 166, 81, 79, 67, 57, 41. 2,4-Dinitrophenylhydrazone: mp 168–170 °C (from ethanol).

Anal. Calcd for $C_{20}H_{27}O_4N_4Br$: C, 51.39; H, 5.82. Found: C, 51.26; H, 5.52.

General Procedure for the Cyclization of 2-(2-Bromo-2-propenyl) Aldehydes 8a–g to 4,4-Disubstituted 2-Cyclopentenones 9a–g. While a rapid stream of dry nitrogen was bubbled through concentrated sulfuric acid (4 mL) cooled to 0 °C, the 2-(2-bromo-2-propenyl) aldehyde (**8a–g** 1.0 g) was added dropwise. After completion of the addition, the dark mixture was stirred under dry nitrogen at 0 °C for 2 h, whereupon it was poured slowly onto crushed ice. The aqueous mixture was extracted with methylene chloride (3 × 100 mL), and the combined extracts were washed with saturated sodium bicarbonate (2 × 50 mL) and then dried (Na_2SO_4). Evaporation of the excess solvents under reduced pressure afforded the crude 4,4-disubstituted 2-cyclopentenone **9a–g** which was purified by vacuum distillation.

4-*n*-Butyl-4-ethyl-2-cyclopentenone (9a): 72%, bp 77–80 °C (0.7 mm); IR ($CHCl_3$) 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.45 (d, 1 H, *J* = 5.5 Hz), 6.05 (d, 1 H, *J* = 5.5 Hz), 2.16 (s, 2 H), 0.66–1.85 (m, 14 H); mass spectrum *m/e* 166, 110 (base), 109, 96, 95, 81. Exact mass: calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1350. 2,4-Dinitrophenylhydrazone: mp 134–135 °C (from ethanol).

4,4-Di-*n*-propyl-2-cyclopentenone (9b): 85%, bp 114–116 °C (6.0 mm); IR ($CHCl_3$) 1715 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.43 (d, 1 H, *J* = 5.5 Hz), 6.07 (d, 1 H, *J* = 5.5 Hz), 2.18 (s, 2 H), 0.84–1.60 (m, 14 H); mass spectrum *m/e* 166, 124, 96, 95 (base), 81. Exact mass: calcd for $C_{11}H_{18}O$, 166.1358; found, 166.1355. 2,4-Dinitrophenylhydrazone: mp 114.5–116 °C (from ethanol).

Anal. Calcd for $C_{17}H_{22}O_4N_4$: C, 58.94; H, 6.40. Found: C, 59.21; H, 6.13.

4-Isobutyl-4-methyl-2-cyclopentenone (9c): 77%, bp 84–86 °C (2.4 mm); IR ($CHCl_3$) 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.55 (d, 1 H, *J* = 5.5 Hz), 6.08 (d, 1 H, *J* = 5.5 Hz), 2.27 (d, 2 H, *J* = 4 Hz), 0.70–1.85 (m, 12 H); mass spectrum *m/e* 152, 96 (base), 95, 67, 41. Exact mass: calcd for $C_{10}H_{16}C$, 152.1201; found, 152.1196. 2,4-Dinitrophenylhydrazone: mp 98–99.5 °C (from ethanol).

Spiro[4.5]dec-3-en-2-one (9d): 78%, bp 115–117 °C (6.0 mm); IR ($CHCl_3$) 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.57 (d, 1 H, *J* = 5.5 Hz), 6.05 (d, 1 H, *J* = 5.5 Hz), 2.22 (s, 2 H), 1.15–1.81 (m, 10 H); mass spectrum *m/e* 150 (base), 107, 95, 82, 79. Exact mass: calcd for $C_{10}H_{14}O$, 150.1045; found, 150.1046. Semicarbazone: mp 198–200 °C (from aqueous ethanol) which was identical (IR, mp, mmp) with an authentic sample.[11]

6-Methylspiro[4.5]dec-3-en-2-one (9e): 63% as an 82:18 mixture of diastereomer, bp 90–92 °C (0.5 mm); IR ($CHCl_3$) 1705 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 7.80 (d, 0.82 H, *J* = 5.5 Hz), 6.17 (d, 0.82 H, *J* = 5.5 Hz), 2.15 (d, 1.64 H, *J* = 7.0 Hz), 0.63–2.00 (m, 12 H), (minor diastereomer) δ 7.37 (d, 0.18 H, *J* = 5.5 Hz), 6.07 (d, 0.18 H, *J* = 5.5 Hz), 2.22 (d, 0.36 H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 209.0 (C_2), 168.5 (C_4), 133.9 (C_3), (minor diastereomer) δ 209.9 (C_2), 173.7 (C_4), 131.8 (C_3); mass spectrum *m/e* 164, 122, 95, 94 (base), 66. Exact mass: calcd for $C_{11}H_{16}O$, 164.1201; found, 164.1196. 2,4-Dinitrophenylhydrazone: mp 147–148 °C (from ethanol).

Anal. Calcd for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85. Found: C, 59.19; H, 5.91.

8-Methylspiro[4.5]dec-3-en-2-one (9f): 75% as a 78:22 mixture of diastereomers, bp 86–88 °C (0.6 mm); IR ($CHCl_3$) 1710 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 7.92 (d, 0.78 H, *J* = 5.5 Hz), 6.08 (d, 0.78 H, *J* = 5.5 Hz), 2.19 (s, 2 H), 0.82–1.88 (m, 12 H), (minor diastereomer) δ 7.43 (d, 0.22 H, *J* = 5.5 Hz), 6.03 (d, 0.22 H, *J* = 5.5 Hz); mass spectrum *m/e* 164 (base), 136, 107, 95, 82. Exact mass: calcd for $C_{11}H_{16}O$, 164.1201; found, 164.1194. 2,4-Dinitrophenylhydrazone: mp 183–184 °C (from ethanol).

8-*tert*-Butylspiro[4.5]dec-3-en-2-one (9g): 54% as a 78:22 mixture of diastereomers, bp 129–131 °C (0.4 mm); IR ($CHCl_3$) 1705 cm^{-1} (C=O); NMR ($CDCl_3$) (major diastereomer) δ 8.00 (d, 0.78 H, *J* = 5.5 Hz), 6.12 (d, 0.78 H, *J* = 5.5 Hz), 2.19 (s, 2 H), 0.81–2.07 (m, 18 H), (minor diastereomer) δ 7.42 (d, 0.22 H, *J* = 5.5 Hz), 6.02 (d, 0.22 H, *J* = 5.5 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 209.0 (C_2), 169.5 (C_4), 132.5 (C_3), (minor diastereomer) δ 209.7 (C_2), 174.3 (C_4), 131.5 (C_3); mass spectrum *m/e* 206, 151, 150, 107, 95, 57 (base). Exact mass: calcd for $C_{14}H_{22}O$, 206.1671; found, 206.1669. 2,4-Dinitrophenylhydrazone: mp 197–199 °C (from ethanol).

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Registry No.—**1a,** 106-35-4; **1b,** 123-19-3; **1c,** 108-10-1; **1d,** 108-94-1; **1e,** 583-60-8; **1f,** 589-92-4; **1g,** 98-53-3; **4a,** 58712-03-1; **4b,** 62167-26-4; **4c,** 62167-27-5; **4d,** 6815-55-0; **4e,** 62167-28-6; **4f,** 62167-29-7; **4g,** 62167-30-0; **8a,** 62167-31-1; **8a** DNP, 62167-32-2; **8b,** 62167-33-3; **8c,** 62167-34-4; **8d,** 62167-35-5; *cis*-**8e,** 62167-36-6; *trans*-**8e,** 62167-37-7; *cis*-**8f,** 62167-38-8; *trans*-**8f,** 62167-39-9; *cis*-**8g,** 62167-40-2; *trans*-**8g,** 62167-41-3; *cis*-**8g** DNP, 62167-42-4; *trans*-**8g** DNP, 62167-43-5; **9a,** 62167-44-6; **9a** DNP, 62167-45-7; **9b,** 62167-46-8; **9b** DNP, 62167-47-9; **9c,** 59346-67-7; **9c** DNP, 62167-48-0; **9d,** 62167-49-1; **9e** α-methyl, 62167-50-4; **9e** DNP α-methyl, 62167-51-5;

9f α-methyl, 62167-52-6; **9f** DNP α-methyl, 62167-53-7; **9g** α-methyl, 62167-54-8; **9g** DNP α-methyl, 62197-67-5; diethyl pyrrolidinomethylphosphonate 51868-96-3; 2,3-dibromopropene, 513-31-5; **9e** β-methyl, 62167-55-9; **9e** DNP β-methyl, 62167-56-0; **9f** β-methyl, 62167-57-1; **9f** DNP β-methyl, 62167-58-2; **9g** β-methyl, 62167-59-3; **9g** DNP β-methyl, 62197-69-7.

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(11) We thank Professor Ernest Wenkert, Rice University, for providing us with a sample of the authentic material for comparison.

Photocycloaddition of Bicyclic Cyclopentenones with Cyclohexene

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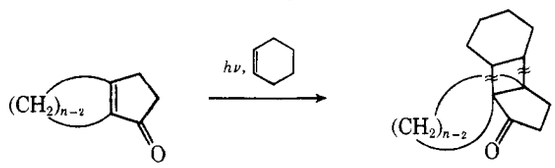
While one of the most important problems in the field of photocycloaddition of cyclic enones to an alicyclic olefin is the stereochemistry of photoannelation adducts, very few studies have been made.[1] We wish to report here the remarkable effect of the fused ring size on the photocycloaddition of a series of bicyclic cyclopentenones **1–4** with cyclohexene.

On irradiation of the enones **1**, **3**, and **4** with 10 molar excess of cyclohexene, the respective cycloadducts **5**,[2] **7**, and **8** were obtained as major products in good yields, but these cycloadducts consisted of three or four stereoisomers.[3] On the other hand, the photoreaction of the enone **2** under a similar condition gave the sole cycloadduct **6** in an 84% yield, along with small amounts of three kinds of other products (Chart I). Concerning the structure of **6**, the absolute configuration

Chart I



1, n = 5	5a, 21%; b, 35%; c, 12%; d, 5%
2, n = 6	6, 84%
3, n = 7	7a, 7%; b, 82%; c, 5%
4, n = 8	8a, 3%; b, 79%, c, 5%

about the cyclobutane ring was established to be cis-anti-trans by means of x-ray analysis[4] (Figure 1).

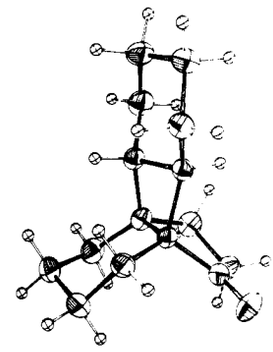


Figure 1. Molecular structure of **6**.

Table I. Phosphorescence Spectra and Lifetimes of the Enones 1–4[a]

Enone	Phosphorescence, cm^{-1} Origin	Max	10%	τ, ms
1[b]	26 000	21 200	24 800	760
2[b]	25 800	20 900	25 100	28
3	26 100	22 200	25 500	64
4	26 200	22 300	25 500	150

[a] Measured at 77 K in EPA matrix. [b] Measured by Cargill et al.[1b,6]

The quantum yield for the formation of **6** was determined to be 0.69. The stereoselective cycloaddition of **2** as well as the high quantum efficiency, compared with 0.25 for **5a–d**[1b] and 0.48 for tricyclo[6.3.0.$0^{2,7}$]undecan-9-ones,[5] suggests that **6** may be formed in a concerted manner via a singlet excited state of **2**. But the formation of **6** was quenched by added piperylene, and, therefore, the participation of triplet species was concluded.

It is obvious, however, from the spectroscopic data listed in Table I that there is no significant difference in the nature of each triplet excited state of **1–4**.

Consequently, it is reasonable that the observed distinction in reactivity among these enones is considered in terms of the steric effect of fused alicyclic rings on the cycloaddition via triplet 1,4-diradical intermediates derived from the enones and cyclohexene. Namely, it may be assumed that nonbonded interaction of hydrogens between ring methylenes plays a key role in the determination of the stereoisomer distribution. In the case of either **1**, having planar cyclopentene ring, or **3** and **4**, having flexible cycloheptene and cyclooctene ones, four or three isomers are formed. It is probably due to little difference in the nonbonded interaction among the four possible stereoisomers. On the other hand, in the case of **2**, having a less flexible cyclohexene ring, the nonbonded interaction may be much severer than in other cases and, as a result, only the cis-anti-trans isomer, having the least interaction, may be produced selectively.

Experimental Section[7]

Materials. The enones **1–3** were prepared according to the procedures reported by Kulkarni and Dev,[8] by Dev,[9] and by Plattner and Büchi,[10] respectively, and **4** was prepared by a method similar to that of **3**.

General Irradiation Procedure. The enones **1–4** were irradiated with 10 molar excess of cyclohexene using a 500-W high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature, and the irradiation was continued until the enones were almost consumed (>95%). After removal of cyclohexene, the residue was distilled under reduced pressure. The products were analyzed by GLC (6 ft × 0.125 in. columns: A, 10% PEG-20M; B, 5% SE-30; C, 10% FFAP; D, 10% DEGS), and isolated by preparative GLC. Yields were