droxybicyclo[4.3.0]nonan-3-one ethylene ketal: ir (CCl_4) 3600–3400 (OH) and 1735 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.25–3.45 (m, 6, OCH_2CH_2O and CH_2OAc), 3.25 (broad s, 1, OH), 2.5–1.5 (m, 14, remaining protons).

A solution of 0.111 g (0.390 mmol) of the above acetate in methanol (10 ml), water (10 ml), and concentrated HCl (1 ml) was stirred for 30 min and worked up as above to yield 0.0771 g (82.3%) of 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]nonan-3-one: ir (CCl_4) 3600–3300 (OH), 1735 (ester C=O), and 1720 cm^{-1} (C=O).

A solution of 0.0771 g (0.321 mmol) of the ketol acetate and 50 mg of $TsOH \cdot H_2O$ in benzene (60 ml) was heated at reflux for 2 hr with azeotropic removal of water. The benzene solution was cooled, washed with 10% K_2CO_3 (30 ml), dried ($MgSO_4$), and concentrated to leave 0.0713 g (theory) of crude (80% pure by glpc) enone acetate **1a**.

Registry No.—**1a,** 38312-34-4; **2,** 20826-94-2; **3,** 24054-04-4; **4,** 24109-44-2; **7,** 38312-38-8; **8,** 38312-39-9; **9,** 38312-40-2; **11,** 38312-41-3; **12,** 38312-42-4; 9-oxatricyclo[4.3.3.0]dodecane-3,8-dione ethylene ketal, 38312-43-5; 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]non-3-one ethylene ketal, 38312-44-6; 6-(2-acetoxyethyl)-1-hydroxybicyclo[4.3.0]nonan-3-one, 38312-45-7.

Acknowledgment.—The authors are grateful to Dr. P. D. Ellis for determining the ^{13}C nmr spectra.

Synthesis and Acid-Catalyzed Rearrangements of Tricyclo[4.3.2.0]undecanones[1]

NORTON P. PEET, ROBERT L. CARGILL,* AND DEAN F. BUSHEY

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

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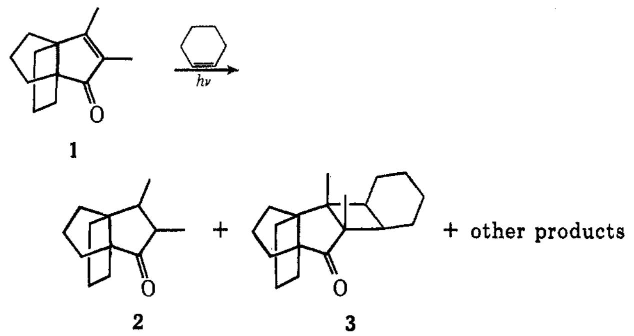
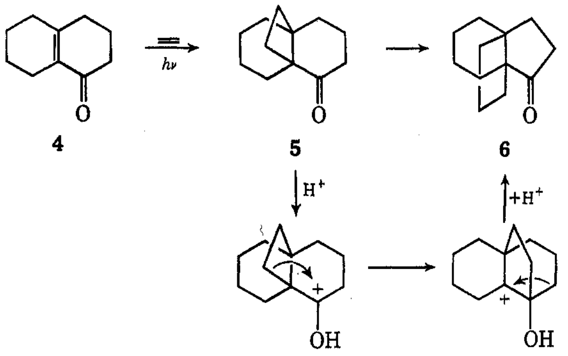
A novel synthesis of 3,4-dimethyltricyclo[3.3.3.0]undecan-2-one (**2**) from bicyclo[4.3.0]non-1(6)-en-2-one (**7**) is reported. A mechanistic interpretation for the different ratio of the three cycloadducts (**8a–c**) obtained from irradiation of **4** with *cis*- and *trans*-2-butene is presented. Cycloadducts **8a** and **8b** were found to undergo rearrangement to **2** at different rates. A synthesis of tricyclo[4.3.3.0]dodecan-7-one (**6**) is also reported.

In our recent investigation of cycloaddition reactions of crowded enones and olefins,[2] we irradiated 3,4-dimethyltricyclo[3.3.3.0]undec-3-en-2-one (**1**) in cyclohexene. In addition to the [2 + 2] cycloadduct **3** (and other products isomeric with **3**) was formed a product suspected to be 3,4-dimethyltricyclo-[3.3.3.0]undecan-2-one (**2**), derived from photoreduction. In order to confirm this suspicion we chose to synthesize **2** independently. Although the saturated ketone **2** could undoubtedly be generated from enone **1** by reduction with lithium in ammonia,[3] we chose to use a less obvious approach which was suggested by some other work which will be described shortly. This decision led not only to a novel synthesis of **2**, but also yielded some mechanistic information on enone photoannulation (an area of study where information is sparse[4]) as well as interesting relative rate differences of Wagner–Meerwein shifts in isomeric systems.



The earlier results which suggested this alternate approach to **2** are shown in Scheme I. Although bicyclo[4.3.0]non-1(6)-en-2-one (**7**) undergoes photocycloaddition with 1,2-dichloroethylene readily,[5] preliminary results from our laboratory indicated that cycloaddition reactions of bicyclo[4.4.0]dec-1(6)-en-2-one (**4**) with olefins (other than ethylene) were not successful.[6] Enone **4**, however, does undergo sluggish photoannulation with ethylene to yield tricyclo[4.4.2.0]-dodecan-2-one (**5**). Ketone **5**, when treated with *p*-toluenesulfonic acid (TsOH) in benzene at reflux, undergoes two Wagner–Meerwein shifts to yield tricyclo[4.3.3.0]dodecan-7-one (**6**), quantitatively.

SCHEME I



The efficiency of the acid-catalyzed rearrangement of **5** to **6** suggested that the photoannulation of enone **7** with 2-butene, followed by acid-catalyzed rearrangement of the resulting isomers **8**, should comprise a good synthesis of ketone **2** (Scheme II). Execution of this reaction sequence (using *cis*-2-butene) resulted in the production of ketone **2** from a mixture of isomers **8**, in an overall yield of 82%. This product was identical with the photoreduced product obtained from the irradiation of enone **1** in cyclohexene. The trans relationship of the methyl groups in **2** was ascertained

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(1) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

(2) R. L. Cargill, N. P. Peet, D. M. Pond, A. B. Sears, W. A. Bundy, and M. G. Rosenblum, to be published.

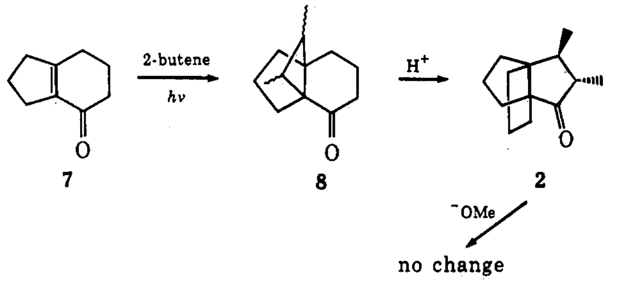
(3) (a) T. G. Halsall, D. W. Theobald, and K. B. Walshaw, *J. Chem. Soc.*, 1029 (1964); (b) H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 360 (1963).

(4) (a) R. M. Bowman, C. Calvo, J. J. McCullough, P. W. Rasmussen, and F. F. Snyder, *J. Org. Chem.*, **37**, 2084 (1972); (b) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

(5) R. L. Cargill and J. W. Crawford, *J. Org. Chem.*, **35**, 356 (1970).

(6) One explanation for this difference holds that the excited state of **4** is not as long-lived as the excited state of **7**, owing to rigidity differences, which would make decay of excited **4** to ground state a more favorable process than decay of **7** to ground state.

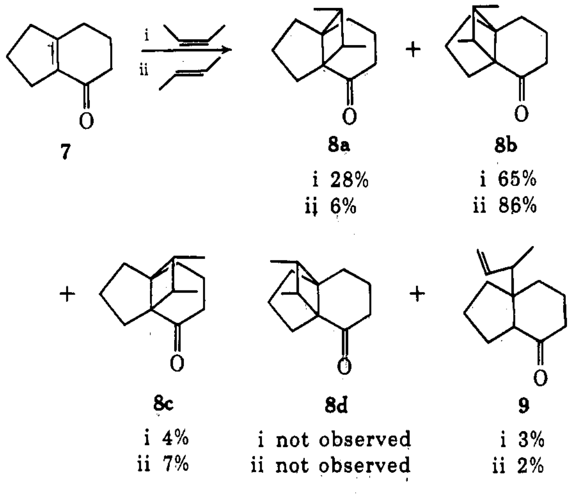
SCHEME II



by recovering **2** unchanged from NaOMe–MeOH at reflux. Had **2** been the cis isomer, base treatment would certainly have converted all or most of it into the thermodynamically more stable trans isomer.

By monitoring the conversion of **8** into **2** by glpc, we noticed that the two major isomers of **8** underwent the skeletal rearrangement at markedly different rates. In order to gain further insight into this difference in behavior, we first had to determine the stereochemistry of the isomers of **8** which were formed. At this point we suspected that the two major isomers of **8**, in the cycloaddition of enone **4** and *cis*-2-butene, were the two trans isomers, as one would predict from a nonconcerted cycloaddition process.[7] In order to confirm this suspicion we performed the cycloaddition with *trans*-2-butene as well, to determine whether the same two products were formed preferentially. The product ratios from photoannulations of enone **7** with *cis*-2-butene and *trans*-2-butene are shown in Scheme III. In each case, the same three cycloadducts (**8a**, **8b**, and **8c**) were formed, as well as small amounts of a keto olefin, thought to be **9**.

SCHEME III



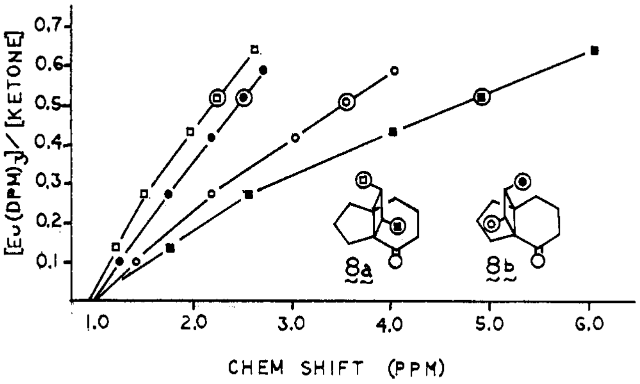
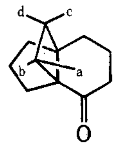
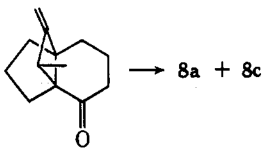


Figure 1.—Effect of nmr shift reagent on methyl groups at varying distances from binding site.

In order to further establish that the two major isomers produced from cycloaddition of **7** with *cis*-2-butene were the trans isomers, and to determine which was which, an nmr study of these two adducts with a shift reagent [Eu(DPM)$_3$] was undertaken. Since the degree of deshielding suffered by a proton or group of protons is inversely proportional to r^3 [r being the average internuclear distance between the proton(s) and the bound Eu^{3+}],[8] it is evident that for the four possible positions of a methyl group, the degree of deshielding should decrease, going from a to d, as shown in the structure below. To carbon tetrachloride solutions of known concentrations of the two major cycloadducts from **7** and *cis*-2-butene were added known amounts of Eu(DPM)$_3$, incrementally. A plot of methyl group chemical shift against [Eu(DPM)$_3$]/[ketone] for the two ketones is shown in Figure 1. This graph shows that the structures given for these two ketones in Scheme III (**8a** and **8b**) are correct, since (i) no two lines in the plot coincide and (ii) the two inner lines correspond to the methyl groups in one ketone and the two outer lines correspond to the methyl groups in the other ketone.



The structure of the minor cycloadduct was established as **8c** by its identity (glpc and mass spectrum) with one of the products obtained from catalytic hydrogenation of **10**.[9]



10

The results of these photoannulations of enone **7** with *cis*- and *trans*-2-butene agree well with the theory proposed by Dilling[10] in his study of cycloaddition reactions of *cis*- and *trans*-dichloroethylenes with cyclopentenone. Schemes IV and V show the mechanistic interpretations for initial β bonding and initial α bonding, respectively, where the diradical intermediates (**11** and **13**, **12** and **14**, **15** and **17**, and **16** and **18**) are rotationally equilibrated before ring closure. Percentages directly above and below the ketones **8a–d** are the observed yields of the products (from Scheme

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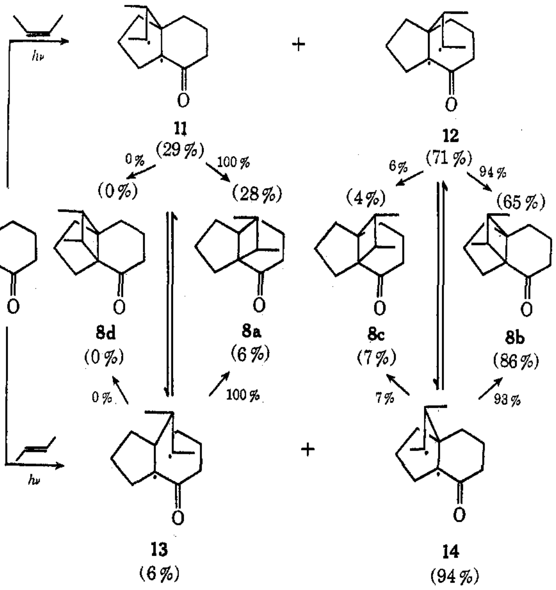
[7] It seemes reasonable to conclude that the 1,2 interactions of the methyl groups on the cyclobutane ring would have more to do with the resulting product stereochemistry than whether a methyl group lay over a five- or six-membered ring.

[8] M. R. Willcott, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, **94**, 1742 (1972).

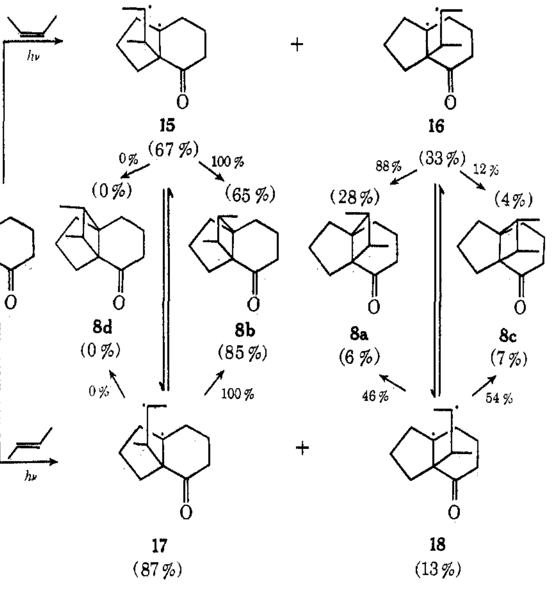
[9] The structure and stereochemistry of ketone **10** have been established: N. P. Peet, R. L. Cargill, and J. W. Crawford, *J. Org. Chem.*, **38**, 1222 (1973).

[10] W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

SCHEME IV



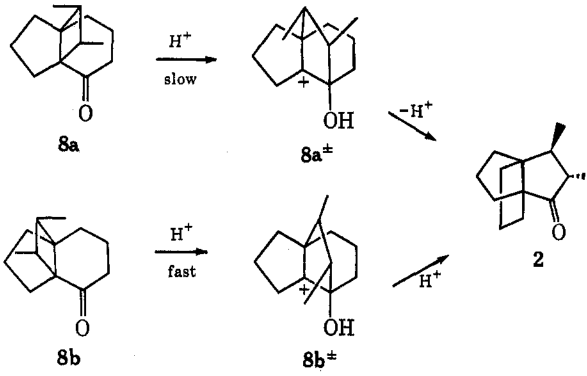
SCHEME V



III). Percentages under the diradical intermediates (**11**–**18**) represent relative amounts of each which must be formed to produce the ratios of ketones to which they close. Finally, the percentages over the arrows indicate the amounts of each diradical which close to each ketone. If α bonding occurs initially (Scheme V), a majority (88%) of diradical **16** from *cis*-2-butene must close to **8a**, whereas a majority (54%) of diradical **18** (in rotational equilibrium with **16**) from *trans*-2-butene must close to **8c**. Such an inconsistency does not arise in the mechanistic pathway involving initial β bonding (Scheme IV). For this reason, we favor the mechanistic pathway shown in Scheme IV.

Small amounts of a keto olefin, assigned structure **9**, were also formed in the photoannulations of enone **7** with both *cis*- and *trans*-2-butene. This photoproduct was not considered in the mechanistic interpretations of Schemes IV and V, but can be envisioned as arising from diradical intermediate **11** or **12** by intramolecular hydrogen abstraction.

As was previously mentioned, ketone **8b** rearranged to **2** much more rapidly than did ketone **8a** (see Experimental Section). These results are best interpreted by comparing the energetics of the processes leading to the intermediates **8a**$^{\pm}$ and **8b**$^{\pm}$ from the respective



ketones. In the formation of intermediate **8a**$^{\pm}$, both methyl groups are being positioned over the planes of the rings, or into sterically crowded environments. However, in the formation of intermediate **8b**$^{\pm}$, both methyl groups are being twisted away from these sterically crowded regions. Thus, since the ground-state energies of **8a** and **8b** must be similar, the activation energies for conversion of these two ketones into **2** should differ with that for **8a** → **2** being the larger.

Experimental Section[11]

Tricyclo[4.4.2.0]dodecan-2-one (5).—A solution of 1.01 g (6.72 mmol) of bicyclo[4.4.0]dec-1(6)-en-2-one (4)[12] in methylene chloride (150 ml) saturated with ethylene was irradiated (Pyrex filter) at low temperature[13] for 20.5 hr. Progress of the reaction was monitored by glpc (10% Carbowax 1000M, 6 ft × 0.125 in., 150°, 30 cc/min of He); the addition was 50% complete after 5 hr, and 95% complete when irradiation was terminated. The reaction solution was warmed to room temperature and dried ($MgSO_4$), and the solvent was removed by distillation to leave a clear oil which was short path distilled to yield 0.939 g (78%) of 95% pure 11. Separation from the small amount of starting enone present by preparative glpc (10% Apiezon M, 8 ft × 0.25 in., 175°, 85 cc/min of He) afforded pure **5**: bp 69° (0.6 mm); uv max (95% EtOH) 292 nm (ε 14); ir (CCl_4) 1705 cm^{-1} (C=O); nmr δ 2.5–1.1 (m); mass spectrum (70 eV) *m/e* 178 (molecular ion).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.82; H, 10.04.

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[11] All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Infrared spectra were recorded using a Perkin-Elmer Model 257 grating spectrophotometer. All nmr spectra were determined using tetramethylsilane as an internal standard, with a Varian A-60 nmr spectrometer. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer. Analytical gas–liquid partition chromatograms were determined using a Varian Aerograph 1200 flame ionization chromatograph, and preparative glpc separations were conducted using a Varian Aerograph 90-P-3 chromatograph. Irradiations were carried out using a Hanovia high-pressure mercury arc (450 W), internal probe, type L, with the filter specified.

[12] Enone **4** was prepared by G. W. Hanwell using the method of H. O. House and H. W. Thompson, *J. Org. Chem.*, **36**, 3729 (1971). For alternate methods, see R. K. Hill and R. T. Conley, *J. Amer. Chem. Soc.*, **82**, 645 (1970), and R. G. Carlson and E. G. Zey, *J. Org. Chem.*, **37**, 2468 (1972).

[13] Low temperature was maintained by immersing the irradiation vessel in a Dry Ice–isopropyl alcohol bath, and circulating isopropyl alcohol, cooled indirectly with Dry Ice, through the probe.

Tricyclo[4.3.3.0]dodecan-7-one (6).—A solution of 0.252 g (1.41 mmol) of ketone **5** and 0.5 g of *p*-toluenesulfonic acid monohydrate (Baker, TsOH·H_2O) in benzene (45 ml) was heated at reflux for 45 min. Progress of the reaction was monitored by glpc (10% Carbowax 1000M, 6 ft × 0.125 in., 150°, 30 cc/min of He). The cool reaction solution was washed with saturated $NaHCO_3$ (25 ml) and water (15 ml), dried ($MgSO_4$), and concentrated to leave 0.243 g (95%) of 95% pure **6**. Separation from the small amount of enone **4** (present initially in **5**) by preparative glpc (10% Apiezon M, 8 ft × 0.25 in., 175°, 85 cc/min of He) afforded pure **6**: mp 121–123°; uv (95% EtOH) 292 nm (ϵ 30); ir (CCl_4) 1735 cm^{-1} (C═O); nmr (CCl_4) δ 2.30 (t, J = 7 Hz, 2, $COCH_2$), 2.1–1.1 (m, 16, remaining protons); mass spectrum (70 eV) *m/e* 178 (molecular ion).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.88; H, 10.10.

Cycloaddition of Enone 7 and *cis*-2-Butene.—A solution of 1.47 g (10.8 mmol) of enone **7**[5] and *ca.* 20 ml of *cis*-2-butene (Matheson, CP grade) in methylene chloride (140 ml) was irradiated (Pyrex filter) for 8 hr at low temperature.[13] Progress of the reaction was monitored by the disappearance of **7** with glpc (3% SE-30, 8 ft × 0.125 in., 140°, 30 cc/min of He). The reaction solution was warmed to room temperature and dried ($MgSO_4$), and the solvent was removed by distillation to leave 2.08 g (theory) of a mixture containing isomeric 10,11-dimethyltricyclo[4.3.3.0]undecan-2-ones **8a** (28%), **8b** (65%), and **8c** (4%), and 6-(1-methylprop-2-enyl)bicyclo[4.3.0]nonan-2-one (**9**) (3%), as determined by glpc. All of these components were collected from glpc (10% Apiezon M, 8 ft × 0.25 in., 160°, 85 cc/min of He) for spectral analysis. Collected samples were reanalyzed on analytical glpc (10% Carbowax 1000M, 6 ft × 0.125 in., 150°, 30 cc/min of He) to ensure purity.

Ketone **8a** had ir (CCl_4) 1690 cm^{-1} (C═O); nmr (CCl_4) δ 2.5–0.8 (m, all protons, with CH_3 doublets, J = 7.2 Hz, at 0.90 and 0.87); mass spectrum (70 eV) *m/e* (rel intensity) 192 (1), 137 (92), and 108 (100).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.81; H, 10.28.

Ketone **8b** had ir (CCl_4) 1690 cm^{-1} (C═O); nmr (CCl_4) δ 2.5–0.8 (m, all protons, with CH_3 doublets, J = 7.2 Hz, at 0.99 and 0.93); mass spectrum (70 eV) *m/e* (rel intensity) 192 (15), 137 (70), and 108 (100).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.01; H, 10.36.

Ketone **8c** had ir (CCl_4) 1690 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 192 (6), 137 (94), and 108 (100). Insufficient quantities of **8c** were available for nmr and elemental analyses.

Ketone **9** had ir (CCl_4) 3060 (vinyl CH), 1705 cm^{-1} (C═O); nmr (CCl_4) δ 6.0–4.0 (m, CH_2═CH), 5.03 (m, CH_2═CH), 2.5–0.7 (m, remaining protons, with CH_3 d, J = 7.2 Hz, at 0.93); mass spectrum (70 eV) *m/e* 192 (molecular ion).

Cycloaddition of Enone 7 and *trans*-2-Butene.—A solution of 0.833 g (6.11 mmol) of enone **7**[5] and *ca.* 20 ml of *trans*-2-butene (Matheson, CP grade) in methylene chloride (140 ml) was irradiated (Pyrex filter) for 2.5 hr at low temperature.[13] Reaction progress was monitored as above and the reaction solution was worked up as above to leave 1.17 g (theory) of isomeric ketones **8a** (6%), **8b** (86%), **8c** (7%), and **9** (2%).

3,4-Dimethyltricyclo[3.3.3.0]undecan-2-one (2).—A solution of 1.41 g (7.34 mmol) of ketones **8a**, **8b**, **8c**, and **9** (in a ratio of 11:24:1.4:1.0, respectively) and TsOH·H_2O (0.5 g) in benzene (40 ml) was heated at reflux for 8 hr. Progress of the reaction was monitored by glpc (10% Carbowax 1000M, 6 ft × 0.125 in., 150°, 30 cc/min of He) and the four ketones in the initial mixture eluted at 8.0, 9.8, 12.2, and 15.5 min, respectively. After 8 hr the peaks at 9.8 (**8b**), 12.2 (**8c**), and 15.5 min (**9**) were absent,[14] and a new peak at 7.0 min had developed. A substantial amount of the ketone at 8.0 min still remained. The reaction mixture was cooled and 75% of the reaction solution was washed with saturated $NaHCO_3$ (25 ml) and water (20 ml), dried ($MgSO_4$), and concentrated to leave 1.02 g (96%) of a mixture of two ketones at 7.0 and 8.0 min. These ketones were collected from preparative glpc (10% Apiezon M, 8 ft × 0.25 in., 150°, 85 cc/min of He), a system in which the two ketones eluted in the same order. An infrared spectrum (CCl_4) of the smaller peak at 8.0 min was identical with that of ketone **8a**. An infrared spectrum of the large product peak at 7.0 min (ketone **2**) was identical with that of the photoreduction product from **1**. Ketone **2** had ir (CCl_4) 1730 cm^{-1} (C═O); nmr (CCl_4) δ 2.45–0.78 (m, with CH_3 doublets, J = 7.2 Hz, at 1.02 and 0.91); mass spectrum (70 eV) *m/e* 192 (molecular ion).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 80.93; H, 10.39.

The remaining 25% of the reaction mixture was heated at reflux for an additional 24 hr and worked up as above to yield 0.300 g (85%) of *pure* **2**.

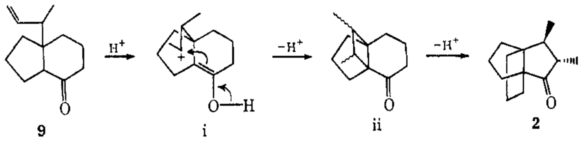
To determine the stereochemical relationship of the methyl groups in ketone **2**, a 0.300-g (1.56 mmol) quantity of **2** in 10 ml of 1.5 *N* NaOMe was heated at reflux under an inert atmosphere for 2 hr. The cool reaction solution was diluted with water (20 ml) and extracted with pentane (3 × 15 ml). The combined extracts were dried ($MgSO_4$) and concentrated to leave 0.208 g (70%) of unchanged **2**, as evidenced by its infrared spectrum. Analysis by glpc (10% Carbowax 1000M, 6 ft × 0.125 in., 150°, 30 cc/min of He) and coinjection with authentic **2** both gave a single peak.

Reduction of Ketone 10.—A solution of 16 mg of ketone **10**[9] (*ca.* 80% pure from preparative glpc) in 5 ml of methanol was hydrogenated at 46 psi for 2 hr using 3.2 mg of platinum oxide catalyst. The catalyst was filtered, and the filtrate was diluted with water, extracted with carbon tetrachloride, dried ($MgSO_4$), and concentrated. Analysis by glpc (coinjection) (DEGS) showed the presence of **8a** and **8c** (ratio *ca.* 2:1, respectively), along with small amounts of two products derived from the original impurity in **10**. The mass spectrum (70 eV) of **8c** obtained from **10** is identical with that obtained in the photoannulation experiments.

Registry No.—**2**, 38312-59-3; **4**, 18631-96-4; **5**, 38312-61-7; **6**, 38312-62-8; **7**, 22118-01-0; **8a**, 38312-64-0; **8b**, 38343-72-5; **8c**, 38312-65-1; **9**, 38312-66-2; **10**, 38312-67-3; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

Acknowledgment.—The authors are grateful to Dr. Wendell L. Dilling of Dow Chemical Company for help with the interpretation of the photoannulation results in a private communication, and for other valuable contributions.

[14] Ketone **9**, as well as ketones **8b** and **8c**, was apparently converted to ketone **2** during this 8-hr period. It is conceivable that **9** was converted to **2** *via* **ii** as follows.



9 **i** **ii** **2**