Photochemistry of Cyclopentenones: Tricyclo[4.3.2.0]undecenones and Tricyclo[3.3.3.0]undecenones[1]

Robert L. Cargill,* Norton P. Peet, David M. Pond, William A. Bundy, and A. Bradford Sears

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

The irradiation of the tricyclo[4.3.2.0]undecenones **6a–c**, even in cyclohexene as solvent, results only in a quantitative isomerization to **7a–c**, whereas irradiation of the tricyclo[3.3.3.0]undecenones **11** and **18** in cyclohexene gives primarily cycloadducts and products of "frustrated" cycloaddition.

Cyclopentenones are known to undergo a variety of structural reorganizations and/or intermolecular reactions under the influence of ultraviolet irradiation. The effects of substrate structure on the competition among the various paths available to excited cyclopentenones have been discussed.[2] In this paper we compare the photochemistry of some tricyclic cyclopentenones with that of related bicyclic enones.

We have shown that irradiation of bicyclo[3.2.0]hept-3-en-2-ones in pentane or methylene chloride provides the isomers **2** and **3** in low yield, along with varying amounts of dimer **4**.[3,4] On the other hand, **1** undergoes efficient cycloaddition when irradiated in the presence of olefins.[5] When the ordering of triplet states was reversed by substitution on the double bond,[6] as in **5**, the relative rates of the photoisomerizations were only slightly affected.[3]

1   2   3

a, R = H; b = CH₃

4   5
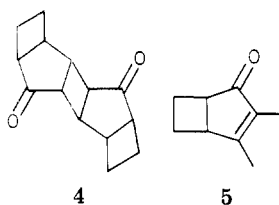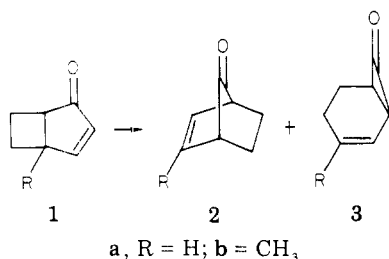
Now we report that none of the related tricyclic cyclopentenones **6**[6] undergoes photochemical cycloaddition. Each undergoes quantitatively an isomerization to **7**, analogous to the **1 → 2** change, even when the irradiation is conducted in cyclohexene.[7] In these cases, again, there is no evident effect on the photochemistry of the substrate when the substitution on the double bond changes the
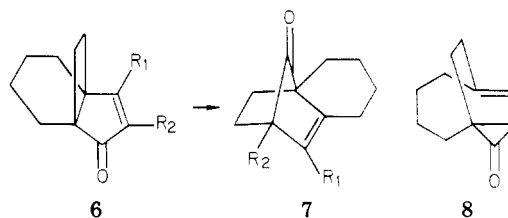
a, R₁ = R₂ = H; b, R₁ = CH₃, R₂ = H; c, R₁ = R₂ = CH₃

relative positions of n,π* and π,π* triplet states. Although the isomerization **1 → 2** is clearly a nonconcerted, triplet-state reaction that does not compete very well with cycloaddition (dimerization), the addition of a tetramethylene bridge results in a marked enhancement in efficiency of the "[1,3] sigmatropic shift" relative to cycloaddition and cyclopropanone formation. The latter reaction may be expected to be inhibited by the excessive strain inherent in the transition state leading to **8**. The inhibition of cycloaddition by the ethano or butano bridges may be greater than that by a propano bridge (see below) as a result of subtle geometric differences.

Structure **7** rests on spectroscopic analysis and the ready thermal decarbonylation of **7a** to diene **9**. The latter was identified by comparison of its spectra with those of authentic material,[8] as well as by independent synthesis from octalone **10** via the tosylhydrazone.[9]

9   10
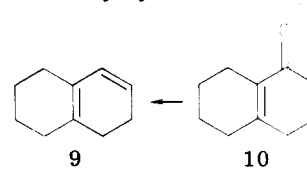
The photochemistry of the cyclopentenones in the [3.3.3]propellane series is more complex. Thus, although the [4.3.2]propellenones refused to undergo cycloaddition to cyclohexene, irradiation of **11**[10] in cyclohexene gave several products of reaction with that olefin. The products of this irradiation could be divided into two gas chromatographically distinguishable groups of approximately equal size. The early-eluting fraction contained a trace of **11** and was mainly saturated ketone **12**.[11] A third component was insufficiently available for complete analysis, but solely on the basis of IR evidence (no vinyl C–H and a 1735 cm⁻¹ C=O stretch) we tentatively assign structure **13**. No attempt was made to isolate the obviously

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

(2) See: Agosta, W. C.; Smith, A. B., III. *J. Am. Chem. Soc.* 1971, *93*, 5513 and references cited therein.

(3) Cargill, R. L.; Sears, A. B.; Boehm, J.; Willcott, M. R. *J. Am. Chem. Soc.* 1973, *95*, 4346.

(4) The structure of dimer 4 was determined by Professor R. E. Davis, University of Texas at Austin, by single-crystal X-ray analysis. We thank Professor Davis for communicating this structure to us.

(5) Cargill, R. L.; King, T. Y.; Sears, A. B. *J. Org. Chem.* 1971, *26*, 1423.

(6) Cargill, R. L.; Bundy, W. A.; Pond, D. M.; Sears, A. B.; Saltiel, J.; Winterle, J. *Mol. Photochem.* 1971, *3*, 123.

(7) For a preliminary report, see: Cargill, R. L.; Gimarc, B. M.; Pond, D. M.; King, T. Y.; Sears, A. B.; Willcott, M. R. *J. Am. Chem. Soc.* 1970, *92*, 3809.

(8) Bates, R. B.; Carnighan, R. H.; Staples, C. E. *J. Am. Chem. Soc.* 1963, *85*, 3030. We thank Professor Bates for this comparison. The ¹H NMR spectrum of 8 contains a sharp two-proton singlet at δ 5.68, a fact that initially confused the identification of the diene.

(9) Shapiro, R. H. *Org. React.* 1976, *23*, 405.

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

(11) Peet, N. P.; Cargill, R. L.; Bushey, D. F. *J. Org. Chem.* 1973, *38*, 1218.

11   12   13

15   17

14   16
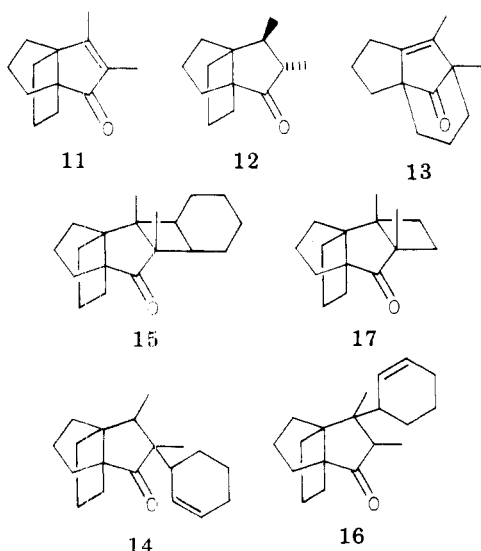
produced bicyclohexenyl. The slower eluting fraction contained three C_{19} ketones in a ratio of 2:1:1. The major component and one of the minor ones are assigned epimeric structures 14, and the other is cycloadduct 15. The stereochemistry at the new quaternary centers of 15 is most likely that shown (cis), for which there is ample precedent, but whether the remaining two centers are cis or trans, as recently observed in a related case by Tobe,[12] remains to be determined. The assignment of structures 14 is based primarily on interpretation of the mass spectra. In particular, the mass specta of both isomers 14 are nearly identical, and they exhibit large peaks at m/e 192 (M – 80) and 177 (M – 80 – 15) and no significant peak at m/e 190 (M – 82) or 191 (M – 83). These data rule out structure 16 and are consistent with structure 14.

Irradiation of 11 in methylene chloride saturated with ethylene gave cycloadduct 17 in high yield, but no cycloaddition with 2-butyne could be induced (only 11 was recovered).

When the unsubstituted enone 18[10] was irradiated in cyclohexene, the results were similar to those already described for 11 (GC analysis), but the cycloadduct 19 (43% isolated yield) was the only well-characterized product.

18   20   19
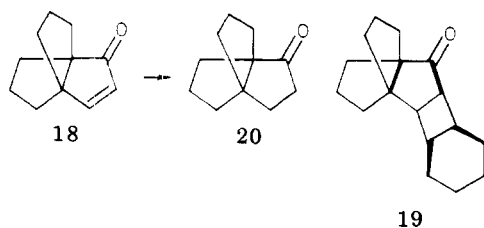
Saturated ketone 20[13] was identified by GC retention time as a minor product. All other products were present in insufficient amounts for collection and characterization, although minor products analogous to 13, 14, and/or 16 may be presumed from the GC trace.

These results may be compared with those reported earlier for the irradiation of the related tricyclic enone 21 in cyclohexene.[14] In that case a mixture of adducts was

obtained, mostly cycloadduct(s) and possibly some "ene" products.

21   22

23   24
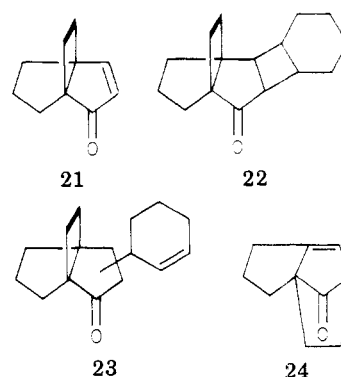
Our present results illustrate the marked effect of changes in the substrate structure on the photochemistry of a given chromophore. Thus, the [3.3.3]propellenones undergo cycloaddition or attempted cycloaddition, e.g., 11 → 15, but little, if any, isomerization; the [3.3.2]propellenone undergoes cycloaddition and no isomerization, probably because the strain of the isomer 24 is reflected in the transition state, and reclosure of the intermediate biradical to give back 21 is favored. On the other hand, all the [4.3.2]propellenones undergo efficient rearrangment to the exclusion of all other processes. Here, relief of cyclobutane strain in going from 6 to 7 is significant and is reflected in the transition state for closure of the biradical intermediate.

Experimental Section[16]

The syntheses of ketones 6b,[6] 6c,[6] 11,[10] 12,[11] 18,[10] and 20[13] have been described in the indicated references.

Tricyclo[4.3.2.0]undec-8-en-7-one (6a). This enone was prepared from bicyclo[4.3.0]non-1(6)-en-7-one by photochemical cycloaddition of 1,2-dichloroethylene followed by ketalization, dehalogenation, hydrogenation, bromination, dehydrohalogenation, and hydrolysis of the resulting ketal (52% overall) as reported for similar enones:[6] bp 59–60 °C (0.2 mm); UV (95% EtOH) 240 nm (ϵ 5200), 321 (73); IR (CCl$_4$) 1715 cm^{-1} (C=O); NMR (CCl$_4$) δ 7.48 (d, J = 6.0 Hz, 1), 6.19 (d, J = 6.0 Hz, 1), 2.5–1.1 (m, 12); mass spectrum (70 eV), m/e 162 (molecular ion). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.33; H, 8.73.

Tricyclo[6.2.1.0^{1,6}]undec-6-en-11-one (7a). A 0.388-g (2.08 mmol) quantity of ketone 6a in methylene chloride (25 mL) was irradiated with ten 15-W black lights for 4 h. The progress of the reaction was monitored by GLC (3% DEGS, 8 ft × 0.125 in. column, 120 °C, 20 cm^3/min of He, injection port 140 °C, detector 150 °C). Removal of the solvent by distillation left 0.371 g (96%) of ketone 7a as a clear oil, which was separated from a minor amount of impurity by preparative GLC (20% SE-52, 10 ft × 0.25 in. column, 140 °C, 85 cm^3/min of He): UV max (95% EtOH) 270 nm (ϵ 21); IR (CCl$_4$) 3020, 1785, 1665 cm^{-1}; NMR (CCl$_4$) δ 6.00 (t, J = 2.8 Hz, 1), 2.8–0.70 (m, 13, remaining protons, with t, J = 3.0 Hz, 1, bridgehead); mass spectrum (70 eV), m/e (relative intensity) 162 (0), 134 (96), 132 (10), 117 (10), 104 (12), 92 (48), 91 (100), 77 (23).

The semicarbazone of 7a [mp 215–216 °C (ethanol–water)] was submitted for analysis.

(12) Tobe, Y.; Hoshino, T.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* 1978, *43*, 4334.

(13) Cargill, R. L.; Dalton, J. R.; O'Connor, S.; Michels, D. G. *Tetrahedron Lett.* 1978, 4465.

(14) Cargill, R. L.; Miller, A. C.; Pond, D. M.; deMayo, P.; Tchir, M. F.; Neuberger, K. R.; Saltiel J. *Mol. Photochem.* 1969, *1*, 301.

(15) On the other hand, 14 may arise via hydrogen abstraction by 11* from cyclohexene at the β-position, followed by radical combination at the α-position.

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.81; N, 19.16. Found: C, 65.74; H, 7.78; N, 19.40.

Analysis of ketone **7a** by GLC under normal conditions (20% SE-52, 10 ft × 0.25 in. column, 150 °C, 85 cm³/min of He, injection port 225 °C, detector 240 °C) led to the isolation of a considerable quantity of diene **9**.

Bicyclo[4.4.0]dec-1(6)-en-2-one p-Toluenesulfonylhydrazone. A solution containing 1.044 g (6.943 mmol) of bicyclo[4.4.0]dec-1(6)-en-2-one (**10**) and 1.310 g (7.034 mmol) of p-toluenesulfonylhydrazine in 100 mL of methanol was refluxed with rapid stirring for 2 h. Distilled water (100 mL) was then added to the hot solution, and the resulting solution was allowed to sit in a refrigerator overnight. The crude product was collected by suction filtration, recrystallized three times from methanol-water, and dried at reduced pressure (0.1 torr) on a steam bath to give 1.925 g (79.12%) of bicyclo[4.4.0]dec-1(6)-en-2-one p-toluenesulfonylhydrazine, mp 136–137 °C dec.

Anal. Calcd for $C_{17}H_{22}N_2O_2S$ (mol wt 350.51): C, 64.15; H, 6.92; N, 8.81. Found: C, 64.28; H, 6.82; N, 8.75.

Bicyclo[4.4.0]deca-1(6),2-diene (9). To a rapidly stirred solution of 0.935 g (0.00267 mol) of bicyclo[4.4.0]dec-1(6)-en-2-one p-toluenesulfonylhydrazone in 5 mL of dry ether was added 3 mL of an ethereal solution containing 0.193 g (8.80 mmol) of methyllithium. The resulting light brown solution was allowed to stir under a nitrogen atmosphere for 14 h at 25 °C. Water was carefully added to quench the reaction, and the resulting two-layer mixture was extracted with four 100-mL portions of pentane. The extracts were combined, dried (Na_2SO_4), and concentrated, and from the resulting colorless oil, preparative GLC (20% SE-52, 10 ft × $^1/_4$ in. column, 130 °C, flow rate 100 mL/min of He) gave 0.271 g (75.6%) of bicyclo[4.4.0]deca-1(6),2-diene (**9**): UV max (95% C_2H_5OH) 266 nm (ϵ 5235); IR (CCl_4) 3030, 1675, 1610, 705 cm⁻¹ (C=C); NMR (CCl_4) δ 5.68 (s, 2, CH=CH), 1.62 (m, 4); mass spectrum (70 eV), m/e (relative intensity) 134 (59), 132 (40), 117 (26), 104 (46), 92 (34), 91 (100), 77 (30).

Anal. Calcd for $C_{10}H_{14}$ (mol wt 134.22): C, 89.49; H, 10.51. Found: C, 89.33; H, 10.41.

Irradiations of 6b and 6c were carried out as described above for **6a**.

7-Methyltricyclo[6.2.1.0¹·⁶]undec-6-en-11-one (7b): yield 100% (from **6b**); clear oil; IR (CCl_4) 1780, 1650 cm⁻¹; NMR (CCl_4) δ 2.47 (d, 1, J = 3.5 Hz), 1.75 (s, 3).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.63; H, 9.05.

7,8-Dimethyltricyclo[6.2.1.0¹·⁶]undec-6-en-11-one (7c): yield 96% (from **6c**); clear oil; IR (CCl_4) 1780 (shoulders 1800, 1765) cm⁻¹; ¹H NMR (CCl_4) δ 1.62 (s, 3), 1.10 (s, 3).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.22; H, 9.59.

Irradiation of 11 in Cyclohexene. A solution of 0.872 g (4.58 mmol) of **11** and freshly distilled cyclohexene (250 mL) in 140 mL of spectral grade hexane was irradiated (uranium-glass filter) at ambient temperature for 10 h. The progress of the reaction was followed by GLC (SE-30, 200 °C); disappearance of **11** was accompanied by development of two sets of peaks (relative areas 1:1.2). The solvent was removed, and the residue, 1.5 g of clear oil, was subjected to preparative GLC (Apiezon M, 230 °C). Collection of the more abundant, slower eluting set of peaks gave

14a, 14b, and 15 (2:1:1 respectively, retention times 26.0, 27.8, and 31.2 min, respectively).

Adduct 14a: IR (CCl_4) 3010, 1720 cm⁻¹; ¹H NMR (CCl_4) δ 5.65 (m, 2), 2.55–0.70 (m, 26); in C_6D_6 the methyl signals resolved into δ 0.97 (s) and 0.88 (d, J = 5 Hz); mass spectrum (70 eV), m/e 272 (7), 192 (67), 190 (3), 178 (14), 177 (91), 81 (100).

Adduct 14b: IR (CCl_4) 3010, 1720 cm⁻¹; ¹H NMR (CCl_4) δ 5.62 (m, 2), 2.8–0.70 (m, 26, with peaks at 1.27 and 0.85); in C_6D_6 the methyl signals appear at δ 0.97 (s) and 1.02 (d, J = 6 Hz); mass spectrum (70 eV), m/e 272 (15), 192 (63), 190 (12), 178 (19), 177 (100), 81 (92).

Cycloadduct 15: IR (CCl_4) 1720 cm⁻¹; ¹H NMR (CCl_4) δ 2.5–0.8 (m, singlets at 1.24 and 0.99); in C_6D_6 the methyl signals appear at δ 1.03 and 0.95; mass spectrum (70 eV), m/e 272 (13), 192 (13), 190 (100), 177 (4).

The mixture of isomers was collected for analysis.

Anal. Calcd for $C_{19}H_{28}O$: H, 83.77; H, 10.36. Found: C, 83.71; H, 10.16.

Collection of the more volatile components and recollection (SE-30, 150 °C) gave 12, 13 (?), and 11 (60:25:15, respectively, retention times 5.0, 7.2, 8.6 min, respectively). Products 11 and 12 were identified by comparison with authentic samples.[11] The center peak could not be obtained in sufficient quantity for complete analysis. The IR spectrum exhibits absorption at 1735 cm⁻¹.

3,6-Dimethyltetracyclo[5.3.3.0.0³·⁶]tridecan-2-one (17). A solution of 0.978 g (5.14 mmol) of enone **11** in 150 mL of methylene chloride saturated with ethylene was irradiated (Pyrex filter) at −70 °C for 2 h. The progress of the reaction was monitored by GLC (20% SE-30, 5 ft × 0.125 in. column, 150 °C, 30 cm³/min of He); at the end of 2 h the ratio of enone **11** and cycloadduct **17** was 15:85. Removal of the solvent left 1.11 g of clear oil, from which cycloadduct **17** was collected as a white, waxy, volatile solid by using GLC (20% SE-30, 5 ft × 0.25 in. column, 165 °C, 30 cm³/min of He): mp 173.5–174.5 °C; UV (95% EtOH) 306 nm (ϵ 34); IR (CCl_4) 1725 cm⁻¹; NMR (CCl_4) δ 2.15–1.25 (m, 16 H), 1.15 (s, 3 H), 1.00 (s, 3 H); mass spectrum (70 eV), m/e 218 (molecular ion).

Anal. Calcd for $C_{15}H_{22}O$: C, 82.51; H, 10.16. Found: C, 82.51; H, 10.17.

Irradiation of 18 in cyclohexene was carried out as described for **11**. After 4 h the starting enone (4.13 g, 25.5 mmol) had disappeared. Removal of solvent gave 5.03 g of clear oil. Elution of 1.00 g of the oil through alumina (Woelm basic) with hexane-ether (9:1) gave 540 mg of oily **19**. Further purification by GLC (SE-30, 190 °C) gave pure **19**: UV (95% EtOH) 295 nm (ϵ 153); IR (CCl_4) 1730 cm⁻¹; ¹H NMR (CCl_4) δ 2.61–2.44 (m, 1), 2.30–0.95 (m, 23).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.37; H, 9.84.