and furan **4** (1.00 g) in benzene (10 ml) was refluxed for 5 hr. Crystallization from benzene–hexane yielded adduct **17** (1.50 g, 75%): mp 222–224° dec; nmr δ 4.1 (s, 1 H), 6.1–7.1 (m, 13 H), and 7.15–7.4 (m, 16 H).

Anal. Calcd for $C_{41}H_{30}O$: C, 91.41; H, 5.61. Found: C, 91.67; H, 5.90.

Reaction of Adduct 17 with Acetic Acid and Hydrochloric Acid.—Adduct **17** (100 mg) was dissolved in 2 ml of glacial acetic acid; two drops of concentrated hydrochloric acid were added, and the solution was heated under reflux for 3 hr. The solvent was removed *in vacuo* and the residue, which had a strong odor of benzaldehyde, was diluted with water. Isolation in the usual manner (ether) and separation by preparative tlc gave 1,2,3,4-tetraphenylnaphthalene (**21**), 64 mg (80%), mp 198–200°, identical with an authentic sample.

In another run, before extraction with ether, the reaction mixture was treated with 40 mg of 2,4-dinitrophenylhydrazine in ethanol solution. After stirring for 10 min, the precipitated hydrazone was filtered and washed with hexane to give 52 mg of 2,4-dinitrophenylhydrazone, mp 220–250°. Recrystallization from ethanol gave the pure derivative, mp 237–238°, identical with an authentic sample.

Registry No.—**5**, 28273-58-7; **9**, 28273-59-8; **10**, 28273-60-1; **16**, 28273-66-7; **17**, 28312-69-8; **18**, 28273-61-2; **19**, 28273-62-3.

Acknowledgment.—We thank the National Science Foundation for a grant in support of this research.

The Tricyclo[5.2.0.0^{2,5}]nonane System[1,2]

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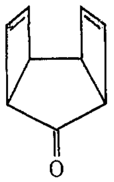
This paper describes the synthesis of *anti*-tricyclo[5.2.0.0^{2,5}]nonan-6-one (**6**), *syn*- and *anti*-tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**4** and **5**), and *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (**21**), as well as some methylated derivatives of these tricyclic ketones. Irradiation of dienone **21** leads efficiently to homocubanone (**2**) *via* the syn dienone **1**. Some transformations of the above tricyclic ketones, especially the β,γ-unsaturated ketones, are discussed.

The obvious relationship of *syn*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (**1**) and homocubanone (**2**) led us to explore synthetic approaches to **1**. In this paper we report syntheses of several members of the tricyclo[5.2.0.0^{2,5}]nonane family as well as some of the transformations of these compounds.[3] In particular, the details of an efficient synthesis of homocubanone from cyclopentenone (14% overall yield) are presented.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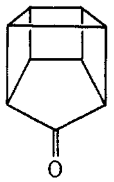
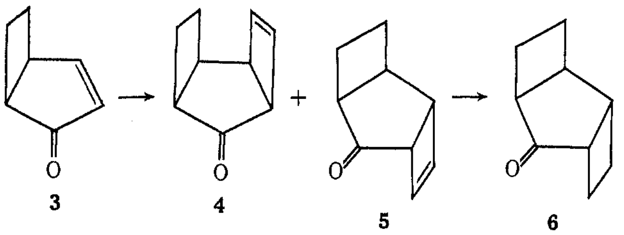
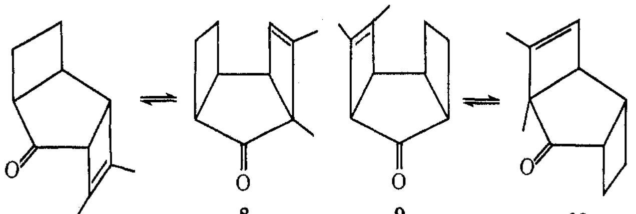

2

Irradiation of bicyclo[3.2.0]hept-3-en-2-one (**3**)[4] with 1,2-chloroethylene followed by ketalization of the cycloadducts, dehalogenation, and hydrolysis provided a mixture of tricyclic ketones **4** and **5**, ratio 2:98, in 75% overall yield.[5] The major isomer is assigned the anti configuration **5**, since cycloaddition should occur predominantly from the less hindered face of **3**. This assignment was confirmed by the identity of the hydrogenation product of the major enone and an authentic sample of *anti*-tricyclo[5.2.0.0^{2,5}]nonan-6-one (**6**) obtained as outlined later in this paper.


3 **4** **5** **6**

Photocycloaddition of ketone **3** and 2-butyne in methylene chloride produced a mixture of four isomeric tricyclic ketones **7**–**10** in 66% yield. The primary adducts **7** and **9** undergo subsequent photisomerization *via* the well-known allylic shift of carbonyl[6] to the isomeric ketones **8** and **10**, respectively. Separate irradiation of pure **7** and of pure **8** gave the same photostationary-state mixture containing 73% of **7** and 27% of **8**. Lack of material precluded similar experiments with **9** and **10**.


7 **8** **9** **10**

In contrast to the photoisomerizations of the substituted enones **7**–**10**, irradiation of the unsubstituted anti enone **5** in methylene chloride yielded the saturated

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

(2) A preliminary report of a portion of this work has appeared: R. L. Cargill and T. Y. King, *Tetrahedron Lett.*, 409 (1970).

(3) The tricyclo[5.2.0.0^{2,5}]nonane system has previously been described by L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Amer. Chem. Soc.*, **61**, 7 (1939); R. Criegee, J. Dekker, and H. A. Brune, *Chem. Ber.*, **96**, 2368 (1963).

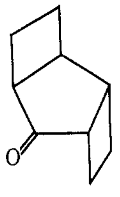
(4) R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

(5) Spectroscopic data for all new compounds are presented in the Experimental Section.

(6) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

ketone **6** and tetrachloroethane. No evidence for isomerization of **5** to the syn isomer **4** could be obtained. Photoreduction of the olefinic bond in β,γ-unsaturated ketones is not uncommon when mixing of carbonyl and olefinic orbitals is relatively inefficient, $\epsilon_{\max} < 150$.[7,8] Here it appears that intramolecular triplet energy transfer from carbonyl to olefin yields the olefin triplet, the presumed reactive species in the photoreduction.[9] The Büchi rearrangement ($\mathbf{7} \rightleftarrows \mathbf{8}$), on the other hand, appears to be a singlet reaction since sensitized irradiations of β,γ-unsaturated ketones result in oxadi-π-methane reactions,[10] and quenching of the rearrangement has been impossible.[11,12]

Irradiation of the saturated tricyclic ketone **6** in methanol yielded the acetal **12**. Presumably the acetal arises from the aldehyde **11** in a nonphotochemical step. Sufficient acidic material to catalyze acetal formation could be generated from photolysis of methanol.[13] The absence of any ester in the photolysate reflects the relative energy contents of transition states **13** and **14** which lead to aldehyde **11** and ketene **15**, respectively.



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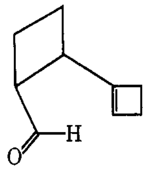

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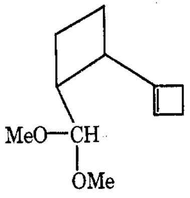

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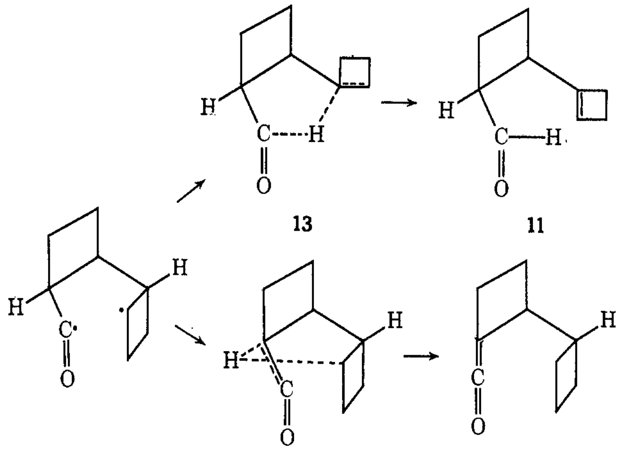
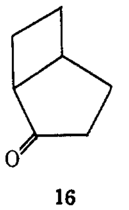


14 **15**

Similar irradiation of bicyclo[3.2.0]heptan-2-one (**16**) in methanol yielded only aldehyde **17** and the corresponding acetal **18**.[14] The absence of ester (from ketene) in this case is more difficult to rationalize.



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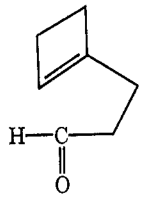

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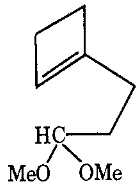
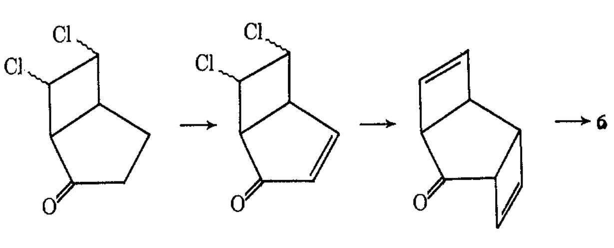


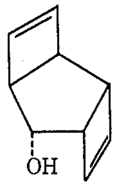
18

We turn now to the tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ones. Attempts to induce cycloaddition of dichloroethylene and bicyclo[3.2.0]hepta-3,6-dien-2-one were unsuccessful. Therefore, a bicyclo[3.2.0]hept-3-en-2-one having a potential double bond in the cyclobutane ring was clearly necessary, dichloro ketone **19**, for example. Attempts to produce **19** by α bromination–dehydrobromination of **20** or its ethylene ketal gave only recovered starting material or products of double dehydrohalogenation. Dehydrogenation of **20** with selenium dioxide in *tert*-butyl alcohol,[15] on the other hand, gave **19** in 51% yield.

Photocycloaddition of ketone **19** and 1,2-dichloroethylene followed by ketalization of the adducts, dechlorination, and removal of the ketal function gave the anti dienone **21** in 46% yield from **19**. Confirmation of the anti stereochemistry in **21** was obtained by reduction to the corresponding alcohol **22**. In passing from ketone **21** to alcohol **22** the C_2 symmetry of **21** is destroyed, rendering the two sets of vinyl protons in **22** nonequivalent. Had the syn ketone **1** been obtained, reduction could have given either or both of two alcohols, **23** and **24**, both of which retain the plane of symmetry present in ketone **1**. The nmr spectrum of alcohol **22** exhibits two two-proton AB quartets[5] establishing the anti stereochemistry in ketone **21**. Catalytic hydrogenation of **21** provided the previously described saturated ketone **6**; therefore, the stereochemistry of **6** and enone **5** are firmly established



20 **19** **21**



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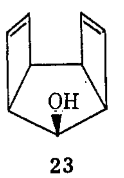

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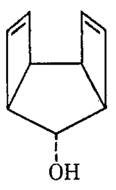

24

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[7] (a) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (b) P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969).

[8] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967), and references cited therein.

[9] Hydrogen abstraction by the triplets of cyclopentene and norbornene has been noted: P. J. Kropp, *J. Amer. Chem. Soc.*, **91**, 5783 (1969), and references cited therein.

[10] W. G. Dauben, M. S. Kellog, J. I. Seeman, and W. A. Spitzer, *ibid.*, **92**, 1786 (1970), and references cited therein.

[11] (a) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969); (b) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Amer. Chem. Soc.*, **92**, 4906 (1970).

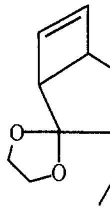
[12] Schuster has reported that the Büchi rearrangement has a quantum yield of 0.04 at 313 nm in benzene and that the reaction can be sensitized with compounds having $E_T > 65$ kcal/mol, but compounds having $E_T < 62$ kcal/mol quench the rearrangement. He concludes, however, that at least 75% of the reaction occurs in the singlet state with the remainder occurring in a quenchable triplet state: D. I. Schuster and D. H. Sussman, *Tetrahedron Lett.*, 1661 (1970); see also J. Ipaktschi, *ibid.*, 3179 (1970).

[13] P. Yates, *Pure Appl. Chem.*, **16**, 93 (1968). In other experiments addition of solid potassium carbonate to the irradiation mixture prevented acetal formation.

[14] T. S. Cantrell and J. S. Soloman, *J. Amer. Chem. Soc.*, **92**, 4656 (1970).

[15] M. Heller and S. Bernstein, *J. Org. Chem.*, **26**, 3876 (1961).

Photocycloaddition of ketone **19** with 2-butyne, followed by the sequence outlined above, provided ketone **25** in 45% yield. Although two ketals were obtained in this series, presumably **26** and **27**, hydrolysis of the ketal mixture gave a single ketone **25**. Whether the syn ketone **28** was formed and subsequently underwent acid-catalyzed isomerization to **25**[6] was not ascertained.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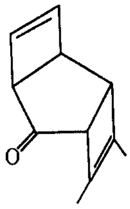
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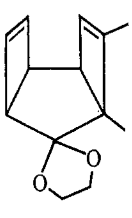
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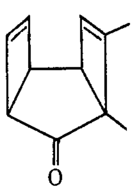
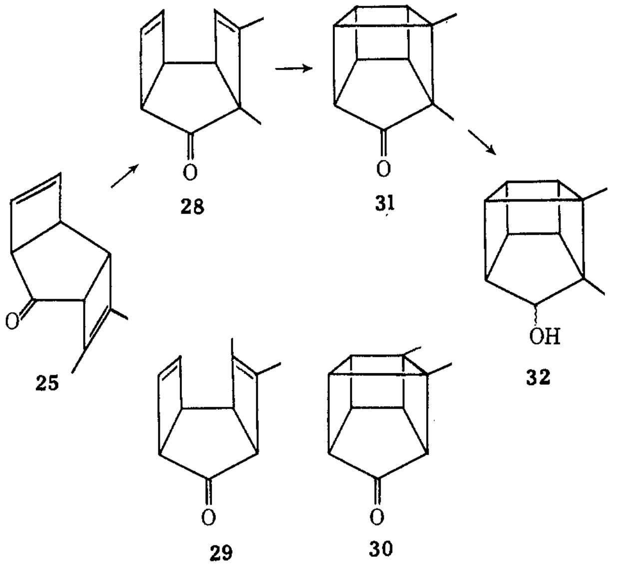

28

Irradiation of anti dienone **21** in methylene chloride with "blacklights" gave homocubanone **2** in 68% yield.[16] Similar irradiation of **25** gave a single dimethylhomocubanone. The formation of homocubanones from the anti dienones most likely involves isomerization of the latter to the corresponding syn isomers *via* the Büchi rearrangement (see above), followed by photocycloaddition of the two olefinic bonds. An alternative route is isomerization of starting anti dienone to cyclononatetraenone which could conceivably undergo cyclization to homocubanone.[17] Isomerization of **25** *via* the latter route could produce only homocubanone **30**, whereas cyclization after isomerization of **25** to one of the syn isomers, **28** or **29**, could yield either **30** or **31**.



We have already noted above that the Büchi rearrangement appears to be a singlet-state reaction. Further, we find that all those bicyclo[3.2.0]hept-6-en-2-ones which undergo the photoinduced allylic shift of carbonyl to the near exclusion of all competing processes exhibit efficient mixing of olefinic and carbonyl orbitals in the spectroscopically observed n,π* singlet state,[8] $\epsilon_{max} > 150$. Since orbital mixing increases with increased substitution of electron donors on the double bond,[8] we expect that Büchi rearrangement will occur most efficiently when the double bond involved is most highly alkyl substituted. Irradiation of **25** should therefore produce **28** rather than **29** as the major (or sole) syn isomer. If homocubanone formation proceeds *via* isomerization of anti to syn dienone followed by cyclization in the syn dienone, we expect homocubanone **31** rather than **30**.

In order to establish whether dienone **25** yields homocubanone **30** or **31**, the product was reduced with lithium aluminum hydride to an epimeric mixture of secondary alcohols **32** in a ratio of *ca.* 2:1. The 100-MHz nmr spectrum of the mixture exhibits two doublets (relative areas, *ca.* 2:1)[5] for the carbinol hydrogens. The presence of a single α proton in the homocubanone is thus established and structure **30** is eliminated. The data are consistent with, but do not prove, the formation of **31** in the irradiation of **25**. We conclude that homocubanone formation is a two-photon process involving first Büchi rearrangement of the anti dienone to the syn isomer followed by photocycloaddition of the double bonds in the latter. The final ring closure probably results from excitation of the carbonyl, intersystem crossing to the n,π* triplet, energy transfer to the π system of the diene, and ring closure in the extended π,π* triplet.

Experimental Section[18]

Bicyclo[3.2.0]hept-3-en-2-one (3).—This ketone was prepared in 47% yield from cyclopentenone by the previously described procedure:[19] bp 58–62° (4 Torr); uv max (95% C_2H_5OH) 226 nm (ε 12,600), 321 (70); ir (CCl_4) 1710 and 1575 cm^{-1}; nmr (CCl_4) δ 7.57 (q, 1, $J_{\alpha,\beta}$ = 5.5 Hz, $J_{\beta,\gamma}$ = 3.0 Hz, OCCH=CH-CH), 6.18 (d, 1, $J_{\alpha,\beta}$ = 5.5 Hz, OCCH=CH), 3.33 (m, 1, C-5 bridgehead), and 1.62–3.00 (m, 5).

***syn*- and *anti*-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (4 and 5).**—A solution of 1.56 g (11.6 mmol) of bicyclo[3.2.0]hept-3-en-2-one (**3**) and 30 ml of a mixture of *cis*- and *trans*-1,2-dichloroethylene in 100 ml of purified methylene chloride was irradiated (Corex) for 2 hr. Progress of the reaction was followed by glpc [3% diethylene glycol succinate (DEGS), 8 ft × 0.125 in., 120°, 25 cc/min of He]. Removal of the methylene chloride and excess dichloroethylene by distillation resulted in a brown oil. To the crude mixture of cycloadducts were added 70 ml of ethylene glycol, 120 ml of benzene, and 5 drops of concentrated sulfuric acid. The solution was refluxed for 48 hr with removal of water. A 5% solution of sodium bicarbonate (200 ml) was added and the dichloro ketal isomers were extracted with three 200-ml portions of ether. The extracts were combined and dried ($CaCl_2$). Approximately 300 ml of the ether was removed by distillation and to the remaining solution was added 300 ml of ammonia in a 1-l. three-necked flask. Sodium metal was added until the solution remained dark blue for 30 min. Ammonium chloride was added to destroy the excess sodium. Water (300 ml) was added after the ammonia had evaporated and the aqueous layer was extracted with two 200-ml portions of ether. To the combined extracts was added 100 ml of 3 *M* hydrochloric acid, and this mixture was allowed to stir at room temperature for 12 hr.

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[16] Homocubanone was identified by comparison of ir and nmr spectra of authentic material. We thank Professor W. G. Dauben for these spectra.

[17] We thank Professor J. A. Berson for calling this possibility to our attention.

[18] All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Miroanalytisches Laboratorium, Elbach uber Engelskirken, Germany, or by Gailbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were determined in carbon tetrachloride unless otherwise stated, using a Perkin-Elmer Model 337 or 257 grating spectrophotometer. All nmr spectra were determined in carbon tetrachloride containing tetramethylsilane as an internal standard using a Varian A-60 nmr spectrometer. Analytical gas-liquid partition chromatograms were determined using a Varian Aerograph Model 1200 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, and the filter specified.

[19] R. L. Cargill, A. C. Miller, D. M. Pond, P. deMayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969); see ref 4 also.

Sodium bicarbonate (200 ml of 15% solution) was added to destroy the acid, the resulting solution was washed with 200 ml of water, and the aqueous layer was extracted with two 100-ml portions of ether. The extracts were combined and dried ($CaCl_2$) and the ether was removed by distillation. The remaining brown residue was distilled, bp 39–41° (0.50 Torr), yielding 1.46 g (75.3% based on **3**) of **4** and **5** as a colorless oil. Analysis by preparative glpc (20% DEGS, 5 ft × 0.25 in., 115°, 30 cc/min of He) showed this oil to be a mixture of *syn*- and *anti*-tricyclo-[5.2.0.0^{2,5}]non-3-en-one (**4** and **5**) in the ratio 2:98, respectively.

syn-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**4**): uv max (95% C_2H_5OH) 310 nm (ϵ 102); ir (CCl_4) 3110 and 3035 (CH═CH), and 1725 cm^{-1} (C═O); nmr (CCl_4) δ 6.37 (AB q, 2, J_{AB} = 2.5 Hz, Δ_{AB} = 10.0 Hz, CH═CH; each peak of the upfield doublet is split further into a doublet by J_{BX} = 1.4 Hz) and 1.0–3.7 (m, 8).

Anal. Calcd for $C_9H_{10}O$ (134.11): C, 80.56; H, 7.51. Found: C, 80.40; H, 7.55.

anti-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**5**): uv max (95% C_2H_5OH) 310 nm (ϵ 146); ir (CCl_4) 3110 and 3035 (CH═CH) and 1725 cm^{-1} (C═O); nmr (CCl_4) δ 6.13 (AB q, 2, J_{AB} = 2.5 Hz, Δ_{AB} = 10.0 Hz, CH═CH; each peak of the upfield doublet is split further into a doublet by J_{BX} = 1.4 Hz), 3.39 (d, br, 1, bridgehead, spacing 2.5 Hz), 3.02 (d, 1, bridgehead, spacing 2.5 Hz), and 1.40–2.95 (m, 6); mass spectrum (70 eV) *m/e* molecular ion 134.

Anal. Calcd for $C_9H_{10}O$ (134.11): C, 80.56; H, 7.51. Found: C, 80.52; H, 7.57.

Irradiation of Bicyclo[3.2.0]hept-3-en-2-one (3) with 2-Butyne.—A solution of 1.09 g (10.1 mmol) of **3** in 80 ml of methylene chloride and 15 ml of 2-butyne was irradiated (Corex) for 1.5 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 128°, 25 cc/min of He). The solvent and excess 2-butyne were removed by distillation leaving a pale yellow residue. Distillation, bp 39–60° (0.24 Torr), gave 1.07 g (65.6%) of a colorless oil. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 114°, 25 cc/min of He) showed the distillate to be a mixture of four components (**10**, **8**, **7**, and **9**) in a ratio of 1:10:7.5:1, respectively. Pure samples of **10**, **8**, **7**, and **9** were obtained by preparative glpc (20% Carbowax, 8 ft × 0.25 in., 152°, 100 cc/min of He).

anti-3,4-Dimethyltricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**7**): uv max (95% C_2H_5OH) 311 nm (ϵ 349); ir (CCl_4) 1730 (CO) and 1700 cm^{-1} (C═C); nmr (CCl_4) δ 1.5–3.2 (m, 8) and 1.57 (s, 6, $CH_3C{=}CCH_3$); mass spectrum (70 eV) *m/e* molecular ion 162.

Anal. Calcd for $C_{11}H_{14}O$ (162.22): C, 81.44; H, 8.70. Found: C, 81.36; H, 8.72.

syn-4,5-Dimethyltricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**8**): uv max (95% C_2H_5OH) 319 nm (ϵ 140); ir (CCl_4) 3030 (>C═CH), 1725 (C═O), and 1650 cm^{-1} (C═C); nmr (CCl_4) δ 6.02 (d, 1, J = 2.0 Hz, >C═CH), 2.91 (m, 3, bridgehead), 2.12 (m, 4), 1.65 (s, br, 3, $CH_3C{=}CH$), and 1.17 (s, 3, CH_3C); mass spectrum (70 eV) *m/e* molecular ion 162.

Anal. Calcd for $C_{11}H_{14}O$ (162.22): C, 81.44; H, 8.70. Found: C, 81.33; H, 8.60.

syn-3,4-Dimethyltricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**9**): uv max (95% C_2H_5OH) 310 nm (ϵ 229); ir (CCl_4) 1720 (C═O) and 1675 cm^{-1} (C═C); nmr (CCl_4) δ 3.05 (m, 4, bridgehead protons), 2.08 (m, 4), and 1.70 (s, 6, $CH_3C{=}CCH_3$); mass spectrum (70 eV) *m/e* molecular ion 162.

Anal. Calcd for $C_{11}H_{14}O$ (162.22): C, 81.44; H, 8.70. Found: C, 81.56; H, 8.77.

anti-4,5-Dimethyltricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**10**): uv max (95% C_2H_5OH) 309 nm (ϵ 301); ir (CCl_4) 3045 (CH═CH), 1725 (C═O), and 1640 cm^{-1} (C═C); nmr (CCl_4) δ 5.71 (s, poorly resolved, >C═CH), 1.8–3.2 (m, 7, bridgehead and methylene protons), 1.53 (s, br, 3, $CH_3C{=}CH$), and 1.30 (s, 3, $CH_3C<$); mass spectrum (70 eV) *m/e* molecular ion 162.

Anal. Calcd for $C_{11}H_{14}O$ (162.22): C, 81.44; H, 8.70. Found: C, 81.39; H, 8.76.

Photoequilibration of 7 and 8.—A solution of 52 mg of **7** in 25 ml of methylene chloride was irradiated through Pyrex with ten "blacklights" for 8.5 hr, at which time a photostationary-state mixture containing 73% of **7** and 27% of **8** was obtained. Similar irradiation of 64 mg of **8** for 10 hr provided an identical photostationary-state mixture.

Irradiation of *anti*-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (5).—A solution of 339 mg (2.53 mmol) of **5** in 90 ml of methylene chloride was irradiated (Pyrex) for 7 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 128°, 25 cc/min of He). The solvent was removed by distillation to give 325 mg of a yellow oil. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in. 128°, 25 cc/min of He) showed the presence of three products, **6**, **11**, and tetrachloroethane, in a ratio of 3.8:3.4:1.0, respectively. Pure samples were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 110°, 50 cc/min of He). Nmr and ir spectra of **6** and tetrachloroethane were compared with those of authentic samples. The third product, which decomposed upon attempted collection, was presumed to be **11**.

***anti*-Tricyclo[5.2.0.0^{2,5}]nonan-6-one (6).**—A solution of 1.464 g (10.92 mmol) of a mixture of **4** and **5** (ratio 2:98) in 50 ml of absolute methanol and 30 mg of platinum oxide was hydrogenated in a Parr shaker for 10 hr. The solution was filtered and the solvent was removed leaving 966 mg (65.0%) of a pale yellow oil. A pure sample of **6** was obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 125°, 60 cc/min of He). *anti*-Tricyclo[5.2.0.0^{2,5}]-nonan-6-one (**6**): uv max (95% C_2H_5OH) 306 nm (ϵ 22); ir (CCl_4) 1730 cm^{-1}; nmr (CCl_4) δ 1.3–3.2 (m, 12); mass spectrum (70 eV) *m/e* molecular ion 136.

Anal. Calcd for $C_9H_{12}O$ (136.12): C, 79.37; H, 8.88. Found: C, 79.30; H, 8.93.

Irradiation of *anti*-Tricyclo[5.2.0.0^{2,5}]nonan-6-one (6) in Methanol.—A solution of 432 mg (3.18 mmol) of **6** in 80 ml of absolute methanol was irradiated (Corex) for 1.75 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 123°, 25 cc/min of He). Two products, **12** and **11** (13:1), were formed. The solvent was removed at atmospheric pressure resulting in 547 mg of a pale yellow oil. Pure samples of **12** were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 113°, 30 cc/min of He). The minor component of the mixture was presumed to be **11**. 2-(1-Cyclobutenyl)cyclobutanecarboxaldehyde dimethyl acetal (**12**): ir (CCl_4) 3045 (>C═CH) and 1605 cm^{-1} (C═C); nmr (CCl_4) δ 5.70 (s, br, 1, >C═CH), 4.30 (d, 1, J = 8.0 Hz, $>CHC\mathbf{H}(OCH_3)_2$), 3.10 (s, 3, $>CHOCH_3$), 3.15 (s, 3, $>CHOC\mathbf{H}_3$), and 1.7–3.0 (m, 10); mass spectrum (70 eV) *m/e* molecular ion 182.

Anal. Calcd for $C_{11}H_{18}O_2$ (182.27): C, 72.49; H, 9.96. Found: C, 72.47; H, 9.92.

Irradiation of Bicyclo[3.2.0]heptan-2-one (16) in Methanol.—A solution of 1.47 g (13.4 mmol) of **16** in 90 ml of absolute methanol was irradiated (Corex) for 3 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 109°, 25 cc/min of He). The solvent was removed and the pale yellow residue was distilled, bp 60–70° (8 Torr), yielding 1.21 g of a colorless oil. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 109°, 25 cc/min of He) showed two products, **17** and **18**, and a small amount of starting material. Pure samples of **17** and **18** in the ratio 3:2 were obtained by preparative glpc (20% Carbowax, 8 ft × 0.25 in., 122°, 86 cc/min of He).

3-(1-Cyclobutenyl)propionaldehyde (**17**): ir (CCl_4) 3025 (>C═CH), 2705 (CHO), 1725 (C═O), and 1625 cm^{-1} (C═C); nmr (CCl_4) δ 9.87 (t, 1, J = 1.5 Hz, CHO), 5.58 (t, 1, J = 1.5 Hz, >C═CH), and 2.33 (m, 8); mass spectrum (70 eV) *m/e* molecular ion 110.

Anal. Calcd for $C_7H_{10}O$ (110.15): C, 76.32; H, 9.15. Found: C, 76.05; H, 9.15.

3-(1-Cyclobutenyl)propionaldehyde dimethyl acetal (**18**): ir (CCl_4) 3025 (>C═CH) and 1630 cm^{-1} (C═C); nmr (CCl_4) δ 5.38 (s, br, 1, >C═CH), 4.07 (t, 1, J = 5.5 Hz, $CH_2C\mathbf{H}(OCH_3)_2$), 3.03 (s, 6, $CH(OC\mathbf{H}_3)_2$), 2.17 (s, 4, cyclobutane protons), and 1.3–2.1 (m, 4); mass spectrum (70 eV) *m/e* molecular ion 156.

Anal. Calcd for $C_9H_{16}O_2$ (156.23): C, 69.19; H, 10.32. Found: C, 69.23; H, 10.32.

6,7-Dichlorobicyclo[3.2.0]hept-3-en-2-one (19).—A solution of 6.492 g (79.19 mmol) of 2-cyclopentenone and 30 ml of a mixture of *cis* and *trans*-1,2-dichloroethylene in 70 ml of methylene chloride was irradiated (Corex) for 6 hr. The progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 105°, 25 cc/min of He). Removal of the solvent and excess dichloroethylene left a mixture of isomeric dichloro ketones. Vacuum distillation of this brown oil afforded 12.050 g of a pale yellow oil. To this was added 10 g of selenium dioxide and 500 ml of *tert*-butyl alcohol. The stirred solution was allowed to reflux for 13 hr under a nitrogen atmosphere. The solution was then cooled to room temperature and filtered twice using a Celite cake. The solvent was removed by distillation at aspirator pressure. The crude, reddish brown viscous residue was then distilled, bp up to 150° (0.07–0.10 Torr), yielding 6.048 g (43.6% from 2-cyclopentenone) of a yellow oil, **19**, which partially crystallized upon standing. Pure samples of **19** obtained by vacuum distillation using a cold finger apparatus had uv max (95% C_2H_5OH) 229 nm (ϵ 3700); ir (CCl_4) 3060 (CH=CH), 1720 (C=O), and 1575 cm^{-1} (C=C); nmr (CCl_4) δ 7.58 (q, 1, $J_{\alpha,\beta}$ = 6.5 Hz, $J_{\beta,\gamma}$ = 3.0 Hz, COCH=CH), 6.32 (q, 1, $J_{\alpha,\beta}$ = 6.5 Hz, $J_{\alpha,\gamma}$ = 2.0 Hz, COCH=CH), 4.58 (q, 1, J = 9.0 Hz, J = 6.0 Hz, CHCl), 4.00 (m, 2, bridgehead and CHCl), and 3.00 (t, 1, J = 5.5 Hz, bridgehead); mass spectrum (70 eV) *m/e* molecular ion 176 and 178.

Anal. Calcd for $C_7H_6OCl_2$ (177.03): C, 47.49; H, 3.32; Cl, 40.04. Found: C, 47.59; H, 3.40; Cl, 40.23.

***anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (21).**—A solution of 3.09 g (16.9 mmol) of 6,7-dichlorobicyclo[3.2.0]hept-3-en-2-one (19) in 50 ml of purified methylene chloride and 40 ml of a mixture of *cis-* and *trans*-1,2-dichloroethylene was irradiated (Corex) for 3.5 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 170°, 25 cc/min of He). Solvent and excess dichloroethylene were removed by distillation leaving a brown oily residue. To this were added 125 ml of benzene, 70 ml of ethylene glycol, and 6 drops of concentrated sulfuric acid. This solution was allowed to reflux for 40 hr with water removal. The solution was cooled to room temperature and 200 ml of 5% sodium bicarbonate solution was added. The aqueous layer was extracted with four 200-ml portions of ether–methylene chloride (1:1), and the extracts were combined and dried ($CaCl_2$). The solvent was removed by distillation. The brown residue was dissolved in 50 ml of dry ether and added to 400 ml of ammonia contained in a 1-l. three-necked flask. Sodium metal was added to this stirred solution until the blue color persisted for 20 min. The reaction was then quenched with ammonium chloride. After complete evaporation of the ammonia 350 ml of water was added. The aqueous solution was extracted with three 200-ml portions of ether. The extracts were combined and 100 ml of 1.5 *M* hydrochloric acid was added to the ethereal solution. The solution was then allowed to stir at room temperature for 4 hr. The organic layer was washed with 100 ml of 5% sodium bicarbonate and then with 100 ml of water. The aqueous layer was extracted with two 100-ml portions of ether and the combined ethereal extract was washed with 50 ml of sodium bicarbonate and 50 ml of water and dried ($CaCl_2$). The ether was removed and the resulting oil was distilled, bp 34° (0.50 Torr), yielding 955 mg (41.8% overall) of a colorless oil, 21. Pure samples of 21 were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 122°, 60 cc/min of He). *anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (21): uv max (95% C_2H_5OH) 306 nm (ϵ 267); ir (CCl_4) 3115 and 3040 (CH=CH) and 1725 cm^{-1} (C=O); nmr (CCl_4) δ 6.07 (AB q, 4, J_{AB} = 2.7 Hz, Δ_{AB} = 7.5 Hz, CH=CH; each peak of the upfield doublet is split further into a doublet by J_{BX} = 1.3 Hz), 3.60 (s, br, 2, bridgehead protons), and 3.12 (m, 2, bridgehead protons); mass spectrum (70 eV) *m/e* molecular ion 132.

Anal. Calcd for C_9H_8O (132.15): C, 81.79; H, 6.10. Found: C, 81.73; H, 6.14.

***anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (22).**—To 205 mg (5.12 mmol) of lithium aluminum hydride in 20 ml of dry ether was added 245 mg (1.85 mmol) of 21 in 10 ml of ether. The resulting mixture was stirred at room temperature for 17 hr and then 10 ml of 10% sodium hydroxide was slowly added to destroy the excess lithium aluminum hydride. The solid was filtered and washed three times with 20-ml portions of ether. The layers were separated and the ethereal solution was washed with 40 ml of saturated sodium chloride solution and dried (Na_2SO_4). The solvent was removed at atmospheric pressure leaving 177 mg of an oil. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 125°, 25 cc/min of He) showed one product, 22. Pure samples of 22 were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in. 133°, 65 cc/min of He). *anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-ol (22): mp 49.7–50.8°; ir (CCl_4) 3600, 3575, and 3350 (broad, >CHOH), 3115 and 3030 cm^{-1} (CH=CH); nmr (CCl_4) δ 6.02 (AB q, 2, J_{AB} = 3.0 Hz, Δ_{AB} = 3.3 Hz, CH=CH), 5.97 (A′B′ q, 2, $J_{A'B'}$ = 2.8 Hz, $\Delta_{A'B'}$ = 17.5 Hz, CH=CH), 3.91 (s, 2, bridgehead), 3.44 (d, 1, J = 3.0 Hz, <CHOH), 3.09 (d, 2, J = 3.0 Hz, bridgehead), and 2.54 (s, 1, >CHOH); mass spectrum (70 eV) *m/e* molecular ion 134.

Anal. Calcd for $C_9H_{10}O$ (134.17): C, 80.56; H, 7.51. Found: C, 80.65; H, 7.42.

Hydrogenation of *anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (21).—A solution of 148 mg (1.12 mmol) of *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (21) in 25 ml of absolute methanol and 20 mg of platinum oxide was hydrogenated in a Parr shaker for 6 hr. The methanolic solution was filtered and concentrated to give 91 mg of an oil. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 125°, 25 cc/min of He) showed a single product. Pure samples of 6 were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 130°, 60 cc/min of He). Nmr and ir spectra of this product were identical with those of *anti*-tricyclo[5.2.0.0^{2,5}]nonan-6-one (6) prepared from the hydrogenation of *anti*-tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (5).

***anti*-3,4-Dimethyltricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (25).**—A solution of 3.28 g (18.5 mmol) of 6,7-dichlorobicyclo[3.2.0]hept-3-en-2-one (19) in 90 ml of purified methylene chloride and 20 ml of 2-butyne was irradiated (Corex) for 2 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 170°, 25 cc/min of He). The solvent and excess 2-butyne were removed by distillation leaving a brown residue. To this were added 125 ml of benzene, 70 ml of ethylene glycol, and 6 drops of concentrated sulfuric acid. This solution was allowed to reflux (110°) for 40 hr with water removal. The solution was cooled to room temperature and 200 ml of a 5% sodium bicarbonate solution was added. The aqueous layer was extracted with three 200-ml portions of ether–methylene chloride (1:1), and the extracts were combined and dried ($CaCl_2$). The solvent was removed by distillation. The brown residue was dissolved in 50 ml of dry ether and added to 400 ml of ammonia contained in a 1-l. three-necked flask. Sodium metal was added to this stirred solution until the blue color persisted for 25 min. The reaction was quenched with ammonium chloride. After evaporation of the ammonia, 350 ml of water was added. The aqueous solution was extracted with three 200-ml portions of ether. The ethereal extracts were combined and stirred overnight with 150 ml of 2.0 *M* hydrochloric acid. The ether layer was separated and the aqueous phase was neutralized with sodium bicarbonate solution and extracted with ether. All the ether extracts were combined and dried ($CaCl_2$). The solvent was removed and the residue was distilled, bp 55–56° (0.27 Torr), yielding 2.32 g of a colorless oil. Analysis by glpc (20% DEGS, 5 ft × 0.25 in., 115°, 70 cc/min of He) showed the presence of one major product, 25, and an impurity, *ca.* 30%, presumed to be bicyclo[3.2.0]hept-6-en-2-one. Pure samples of 25 were obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 115°, 70 cc/min of He). *anti*-3,4-Dimethyltricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (25): uv max (95% C_2H_5OH) 309 nm (ϵ 323); ir (CCl_4) 3085 and 3015 (CH=CH), 1720 (C=O), and 1680 cm^{-1} (weak, $CH_3C{=}CCH_3$); nmr (CCl_4) δ 6.07 (AB q, 2, J_{AB} = 2.5 Hz, Δ_{AB} = 8.5 Hz, CH=CH; each peak of the upfield doublet is split further into a doublet by J_{BX} = 1.3 Hz), 3.47 (m, 1, bridgehead), 3.25 (m, 1, bridgehead), 3.10 (m, 1, bridgehead), 2.78 (m, 1, bridgehead), and 1.60 (s, 6, $CH_3C{=}CCH_3$); mass spectrum (70 eV) *m/e* molecular ion 160.

Anal. Calcd for $C_{11}H_{12}O$ (160.21): C, 82.46; H, 7.55. Found: C, 82.30; H, 7.66.

Irradiation of *anti*-Tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (21).—A solution of 570 mg (4.32 mmol) of 21 in 200 ml of purified methylene chloride was irradiated in a Pyrex tube with ten 15-W "blacklights" for 30 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 128°, 25 cc/min of He) and analysis showed the formation of a single product, 2. Solvent was removed (50–70°) and the resulting oil was distilled to give 390 mg (68.5%) of 2 as a colorless oil which crystallized upon standing. Pure samples of 2 were obtained by preparative glpc (20% SE-30, 5 ft × 0.25 in., 128°, 100 cc/min of He). Homocubanone (2) was identified by comparison of the nmr and ir spectra with those of an authentic sample.[16]

Irradiation of *anti*-3,4-Dimethyltricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (25) in Methylene Chloride.—A solution of 814 mg (5.04 mmol) of 25 in 190 ml of purified pentane was irradiated as above for 50 hr. Progress of the reaction was followed by glpc (3% Carbowax, 8 ft × 0.125 in., 122°, 25 cc/min of He). Two products were evident, one of which diminished upon further irradiation, leaving one final product. Solvent was removed and the product distilled in a short-path still to give 598 mg of 31, bp 50–70° (bath temperature) (0.1 Torr). An analytical sample of 31 was obtained by preparative glpc (20% DEGS, 5 ft × 0.25 in., 105°, 70 cc/min of He). 1,2-Dimethylpentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (31): ir (CCl_4) 1755 cm^{-1} (C=O); nmr (CCl_4) δ 2.2–3.8 (m, 6, methine protons), 1.11 (s, 3, CH_3C<), and 1.07 (s, 3, CH_3C<).

Anal. Calcd for $C_{11}H_{12}O$ (160.21): C, 82.46; H, 7.55. Found: C, 82.52; H, 7.50.

Reduction of Dimethylhomocubane (31).—Reduction of 31 with lithium aluminum hydride as above gave a mixture of epimeric alcohols **32**. Analysis by glpc (3% Carbowax, 8 ft × 0.125 in., 120°, 25 cc/min of He) showed two peaks in a ratio of *ca.* 2:1. The mixture of carbinols was purified by preparative glpc (20% XF-1150, 10 ft × 0.125 in., 130°, 100 cc/min of He). Carbinols **32** have δ (CCl_4) 3.73 and 3.68 (doublets, J = 2.2 and 2.0 Hz, respectively, relative areas *ca.* 2:1, respectively, carbinol), 1.15, 1.12 (pair of equally intense singlets), and 1.07, 1.03 (pair of equally intense singlets, the former pair having *ca.* twice the area of the latter pair, methyls). The high resolution mass spectrum of **32** exhibits m/e 162.1040 (calcd for $C_{11}H_{14}O$: 162.1045).[20]

Registry No.—**3**, 28256-69-1; **4**, 28256-70-4; **5**, 28256-71-5; **6**, 28256-72-6; **7**, 28256-73-7; **8**, 28256-74-8; **9**, 28256-75-9; **10**, 28256-76-0; **12**, 28256-77-1; **17**, 28256-78-2; **18**, 28256-79-3; **19**, 25995-00-0; **21**, 25995-02-2; **22**, 26121-77-7; **25**, 28256-82-8; **31**, 28256-83-9; **32a**, 28256-84-0; **32b**, 28256-85-1.

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The Photochemistry of Bicyclo[6.1.0]nonanones[1a]

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The solution photochemistry of three bicyclic ketones containing formally nonconjugated chromophores in a medium ring has been examined. Bicyclo[6.1.0]nonan-3-one (**1**) affords *trans*-5,8-nonadienal (**4**), 2-allylcyclohexanone (**5**), and 3-vinylcycloheptanone (**6**). Photolysis in methanol also gives methyl 8-nonenoate (**7**). In addition to photoreduction to the corresponding alcohols, bicyclo[6.1.0]nonan-4-one (**2**) forms aldehydes **15** and **16** and ester **17**. A distinct solvent effect on the product distribution was observed in this system. 4,5-Epoxycyclooctanone (**3**) undergoes simple photoreduction of the ketone function. These results are discussed in relation to similar systems.

As part of a continuing study[2,3] on the photochemical interaction of formally nonconjugated chromophores contained within the same molecule, we have examined the photochemistry of the modified cyclooctanones **1–3**. Compound **1** is the cyclopropyl analog of the β,γ-unsaturated ketone, 3-cyclooctenone, upon which we have reported earlier.[2] The remaining ketones are functionalized in the γ,δ position with a cyclopropane and an epoxide unit. These compounds can be considered as derivatives of 4-cyclooctenone.[3] These specific systems have been chosen in a search for photochemical interplay of remote functional groups, since the medium-ring framework provides the geometrical proximity which has been effective in inducing transannular processes.[4]

Bicyclo[6.1.0]nonan-3-one.—The synthesis of **1** was accomplished from 3-cyclooctenol[5] by the sequence: acetylation, Simmons–Smith reaction, saponification, and chromic acid oxidation. Acetylation was critical to this synthetic scheme since the Simmons–Smith method failed on the alcohol itself. The ultraviolet spectrum of **1** suggests weak interaction of the cyclopropyl moiety with the carbonyl group as evidenced by an enhancement of the extinction coefficient [uv max (hexane) 289 nm (ϵ 44)]. This spectrum is similar to that of 3-cyclooctenone [292 nm (ϵ 47)][2] for which some overlap of the two π bonds seems certain.[6] The ability of a cyclopropane to function in this fashion has only recently been documented.[7]

Irradiation of **1** leads to the rapid formation of three major products in approximately a 1:2:1 ratio in either benzene or cyclohexane. Photoisomer **4** displays spectroscopic properties (detailed in the Experimental Section) which suggest the presence of aldehyde, terminal vinyl, and a nonconjugated trans-disubstituted double bond. The relative position of the double bonds is evidenced by a doubly allylic methylene group at δ 2.7 in the nmr. The carbon skeleton of this compound was shown by the isolation of *n*-nonanal from a photolysis mixture which had subsequently been catalytically hydrogenated. 2-Allylcyclohexanone (**5**) was identified by comparison with a synthetic sample derived from allyl Grignard addition to cyclohexene oxide and subsequent chromic acid oxidation of the resulting alcohol. The structure of **6** rests on spectral data which show a cycloheptanone carbonyl (5.90 μ) and a terminal vinyl group. The absence of a signal at *ca.* δ 3.0 ($CH_2{=}CHCHCO$) in the nmr indicates that the vinyl substituent is not adjacent to the carbonyl group,[2] and, therefore, the presence of an important fragment at m/e 81 in the mass spectrum of **6** establishes the indicated locus of the vinyl substituent.[8]

Irradiation of **1** in methanol solvent gave methyl 8-nonenoate (**7**) in addition to the above three products. Methyl ester and terminal vinyl groups were manifest spectroscopically, and catalytic hydrogenation converted **7** to methyl *n*-nonanoate.

Examination of the photoisomers under the irradiation conditions demonstrated the absence of interconversion. In fact, except for aldehyde **4** which decomposed to an unidentified material of short retention time, the products were surprisingly stable to the photolysis conditions.

These results parallel closely those obtained by Heck-

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