Photochemistry of Bicyclo[3.2.0]hept-3-en-2-ones[1a]

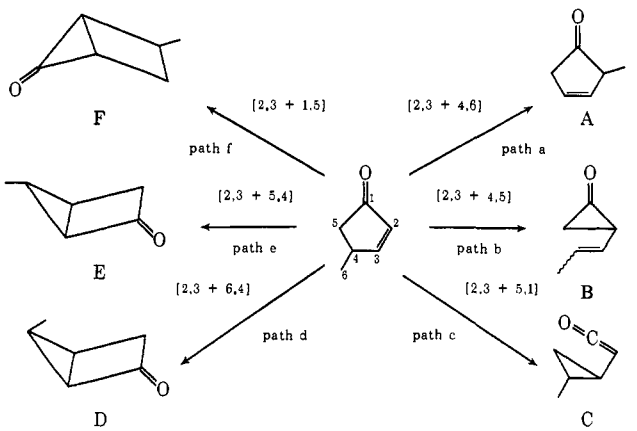
Robert L. Cargill,*[1b] A. Bradford Sears,[1b] Jeffrey Boehm,[1b] and M. Robert Willcott[1c]

Contribution from the Departments of Chemistry, University of South Carolina, Columbia, South Carolina 29208, and University of Houston, Houston, Texas 77004. *Received November 17, 1972*

Abstract: Irradiation of bicyclo[3.2.0]hept-3-en-2-ones yields 7-ketonorbornenes *via* a nonconcerted, diradical path which is superficially a [1,3] sigmatropic change. When the irradiation solvent is methanol an additional set of products, methyl 2-cyclohexenecarboxylates, are formed. These esters arise *via* a concerted, intramolecular [2 + 2] cycloaddition leading to a cyclopropanone and subsequent decomposition of the hemiketal of the cyclopropanone. Evidence upon which the mechanistic conclusions are drawn is presented.

Although cyclopentenones commonly undergo a variety of bimolecular cycloaddition reactions,[2] the mechanisms of which have been studied extensively,[3] the intramolecular cycloadditions of cyclopentenones have received much less attention. There are six possible intramolecular [2 + 2] cycloadditions (excluding hydrogen transfer processes) of γ-substituted cyclopentenones such as 4-methyl-2-cyclopentenone. The olefinic π bond may in principle undergo cycloaddition in either of two directions with each of three allylic σ bonds, C-1–C-5, C-4–C-5, and C-4–C-6. For example, in path a (2,3 + 4,6) new bonds are formed between C-2 and C-6, and between C-3 and C-4, whereas in path d (2,3 + 6,4) new bonds are formed between C-2 and C-4, and between C-3 and C-6. These processes are illustrated in Scheme I.

Scheme I



Numerous examples of isomerization *via* path a are known in both cyclopentenones and cyclohexenones, the most famous example being the verbenone–chrysanthenone rearrangement.[4] One isomerization of a cyclopentenone *via* path b has been demonstrated by Chapman,[5] and Agosta and Kende have found appropriately substituted cyclopentenones to rearrange *via* path c.[6] Path d is followed by several substituted cyclopentenones,[7] but we are unaware of any cyclopentenones which undergo isomerization *via* paths e or f. We describe here our studies of the photochemistry of bicyclo[3.2.0]hept-3-en-2-ones which undergo intramolecular [2 + 2] cycloadditions *via* both paths a and b.[8] We shall discuss first evidence which establishes the nonconcerted nature of path a, then experiments which indicate the concerted nature of path b.

Irradiation of ketone **1a** in pentane, methylene chloride, or methanol gave the anti-head-to-tail dimer[9] and 7-ketonorbornene (**3a**) in 10–20% yield. The photoisomerization of **1** to **3** is a simple example of an allylic shift in which the migrating atom is carbon and which is restricted to being suprafacial.[4] If this transformation is concerted the conservation of orbital symmetry requires that the stereochemistry of the migrating carbon be retained.[10] On the other hand, isomeriza-

(1) (a) Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research; (b) University of South Carolina; (c) University of Houston.

(2) (a) E. J. Corey, J. D. Bass, R. LeMahiew, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); (b) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966); (c) P. G. Bauslaugh, *Synthesis*, **2**, 287 (1970); (d) P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971).

(3) (a) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970); (b) P. de Mayo, J. P. Pete, and M. F. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (c) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968); (d) R. L. Cargill, A. C. Miller, D. M. Pond, P. de Mayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969).

(4) (a) J. J. Hurst and G. W. Whitham, *J. Chem. Soc.*, 2464 (1960); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967); see also (c) H. E. Zimmerman and D. J. Sam, *ibid.*, **88**, 4905 (1966); (d) H. E. Zimmerman and R. L. Morse, *ibid.*, **90**, 964 (1968); (e) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Chem. Commun.*, 823 (1967); (f) R. C. Cookson and D. C. Warrell, *J. Chem. Soc. C*, 1391 (1967); (g) R. C. Cookson, *Quart. Rev., Chem. Soc.*, **22**, 423 (1968); (h) L. A. Paquette, G. V. Meehan, and R. F. Eizember, *Tetrahedron Lett.*, 995, 999 (1969); (i) H. Prinzbach, H. Hagemann, J. H. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965); (j) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 1126 (1967).

(5) L. L. Barber, O. L. Chapman, and J. D. Lassila, *J. Amer. Chem. Soc.*, **91**, 3664 (1969).

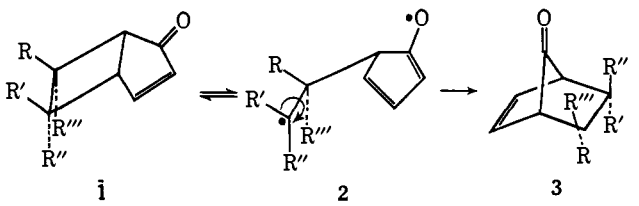
(6) (a) W. C. Agosta, A. B. Smith, A. S. Kende, R. G. Eilerman, and J. Benham, *Tetrahedron Lett.*, 4517 (1969); (b) W. C. Agosta and A. B. Smith, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

(7) (a) D. A. Plank and J. C. Floyd, *Tetrahedron Lett.*, 4811 (1971); (b) T. Matsura and K. Ogura, *Bull. Chem. Soc. Jap.*, **43**, 3187 (1970); (c) T. Matsura and K. Ogura, *J. Amer. Chem. Soc.*, **89**, 3850 (1967); (d) T. Matsura and K. Ogura, *Chem. Commun.*, 1247 (1967); (e) G. F. Burkinshaw, B. R. Davis, and P. D. Woodgate, *J. Chem. Soc. C*, 1607 (1970); (f) S. Wolff and W. C. Agosta, *J. Chem. Soc., Chem. Commun.*, 226 (1972); and (g) H. E. Zimmerman and R. D. Little, *ibid.*, 698 (1972).

(8) Preliminary communications concerning this work have appeared: (a) 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); (b) R. L. Cargill and A. B. Sears, *ibid.*, **92**, 6084 (1970).

(9) The structure and stereochemistry of this dimer have been secured in a crystallographic study and will be reported separately by Professor R. E. Davis.

(10) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). Retention is expected if isomerization occurs in an excited state; a concerted ground-state reaction should proceed with inversion of configuration: J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).



1 2 3

a, R = R′ = R″ = R‴ = H
b, R = R′ = D; R″ = R‴ = H
c, R = R″ = D; R′ = R‴ = H
d, R = R′ = H; R″ = R‴ = D

tion *via* a nonconcerted path, *e.g.*, *via* diradical **2**, should proceed with loss of stereochemistry of the migrating atom. The isomerization of **1** is an ideal case for a stereochemical study since: (a) no isomeric products interfere with the isolation of **3**;[11] (b) the simplicity of the nmr spectra of the 5,6-dideuterio derivatives of **1** and **3** makes determination of the stereochemistry of these derivatives merely a matter of integration of widely separated signals; and (c) no groups which might complicate interpretation of the results are attached to the migrating carbon.

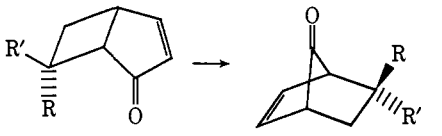
The ethylene ketal of bicyclo[3.2.0]hept-6-en-2-one was reduced with deuteriodiimide and the resulting deuterated product converted by standard methods into *exo*-6,7-bisdeuteriobicyclo[3.2.0]hept-3-en-2-one (**1b**). Analysis of the resulting ketone by nmr and mass spectrometry established exclusive exo deuteration, as expected, and a deuterium content of 87% d_2, 10% d_1, and 3% d_0. We assume that in the monodeuterated species C-6 and C-7 are equally deuterated. The nmr spectra of both **1a** and **3a** exhibit complex absorptions at δ 1.7 and 2.5 and at δ 1.1 and 1.9, respectively. In each case the higher field signal is assigned to the endo methylene protons (shielding by the double bond), and the lower field signal to the exo methylene protons. The deuterium-decoupled spectrum of **1b** contains a finely split singlet at δ 1.7. The high field limit of the higher field bridgehead absorption is δ 2.65. The spectrum of **3d** exhibits a singlet at δ 1.1; the bridgehead protons absorb at δ 2.7.

If we assume (as is demonstrated later) that the stereochemistry at C-7 is unchanged in the isomerization of **1** to **3**, we may calculate, using the above deuterium analysis of **1b**, the ratio of exo to endo protons in the product **3** for each of three limiting cases. For rearrangement occurring with complete retention of stereochemistry at the migrating carbon this ratio will be 12.5; for migration with complete inversion, 1.0; and for migration with complete loss of stereochemistry, 2.5.

In the nmr spectrum of 7-ketonorbornene obtained from irradiation of **1b**,[12] the ratio of the integrated areas of the signals at δ 1.90 and 1.13 (exo and endo, respectively) is 2.5 ± 0.1 and is unchanged whether determined at 25, 70, or 100% reaction. Formation of **3** from **1** is, therefore, accompanied by complete loss of stereochemistry at the migrating carbon.

Similar analysis of the nmr spectrum of recovered starting ketone showed that stereochemistry at C-6 is *ca.* half lost at 25% reaction and is completely lost at 70% reaction. Irradiation of **3d** (0.040 *M* in pentane) produced no loss of **3d**[13] and no change in its nmr spectrum.

Irradiation of **4a** in methanol gave *exo*-5-methyl-7-ketonorbornene (**5a**) (doublet at δ 1.10)[14] which contained neither endo isomer **5b** nor **4b**. Similar irradiation of **4b** gave only **5b** (doublet at δ 0.90). Thus,



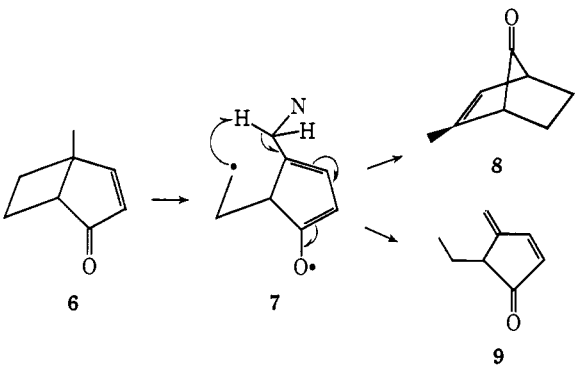
4 5

a, R = CH_3; R′ = H
b, R = H; R′ = CH_3

stereochemistry at C-7 is preserved in this isomerization.

These results conclusively demonstrate the nonconcerted nature of the photoisomerization of **1** to **3** and suggest reversible formation of an intermediate diradical **2**. Diradical **2** must have a lifetime sufficient to permit several rotations about the C-6–C-7 bond before closure to **1** or to **3**.

Further evidence for a diradical intermediate was obtained when irradiation of **6** at −70° in pentane



6 7 8 9

yielded, in addition to the expected ketone **8**, a small amount of a new dienone **9**,[15] which could arise *via* intramolecular hydrogen transfer in diradical **7** as shown.

We conclude that the photochemical allylic shifts in cyclopentenones and cyclohexenones (path a) proceed, in general, *via* a reversibly formed diradical intermediate. The apparently concerted allylic shifts in a series of dicyanoethylenes[16] differ sufficiently from these (in electronic nature and geometrical restrictions upon the chromophore) that meaningful comparison of the two is difficult.

We now turn to a discussion of photoisomerization *via* path b. Irradiation of **1a** in methanol gave, in addition to dimer and **3a**, ester **10**. Similar irradiation of

(11) Compare with the large number of products and the evident duality of mechanisms in the verbenone–chrysanthenone rearrangement.[4a,b]

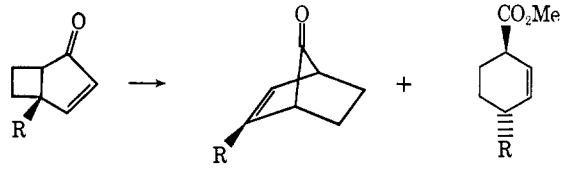
(12) Mass spectrometric analysis showed that no deuterium was lost in the reaction.

(13) From analysis of the deuterium-decoupled 100-MHz nmr spectrum of labeled photoproduct **3**, it is possible to rule out the presence of *cis-exo*-5,6-bisdeuterio-7-ketonorbornene (**3d**). A mechanism for isomerization of **1** involving dissociation into ethylene and cyclopentadienone followed by recombination in a Diels–Alder reaction is thereby excluded.

(14) Compare with δ 0.69 for the methyl absorption of *cis-endo*-5,6-dimethylnorbornene: B. D. Kramer and P. D. Bartlett, *J. Amer. Chem. Soc.*, **94**, 3934 (1972).

(15) See Experimental Section for spectral data.

(16) (a) R. C. Cookson, J. Hudec, and M. Sharma, *Chem. Commun.*, 107, 108 (1971); (b) R. C. Cookson and J. E. Kemp, *ibid.*, 385 (1971).



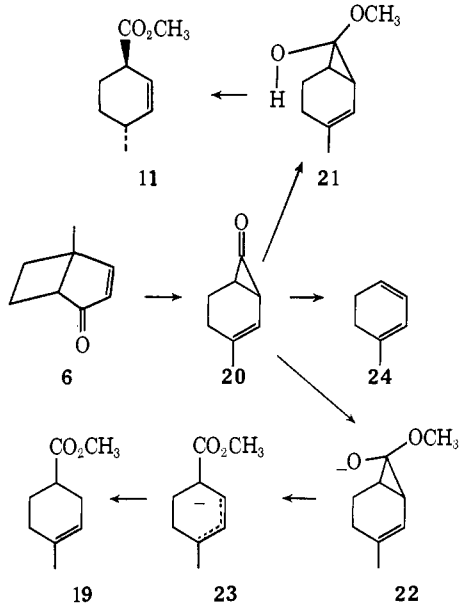
1a, R = H
6, R = CH_3

3a, R = H
8, R = CH_3

10, R = H
11, R = CH_3

6 likewise gave 8 and trans ester 11. In each case the yield of ester was 10–15% and the yields of 7-ketonorbornenes (10–20%) were unaffected by the change in solvent from pentane to methanol.

The nmr spectrum of 10 shows the presence of two vinyl protons and differs from that of the isomeric methyl 3-cyclohexenecarboxylate. Catalytic hydrogenation of 10 gave methyl cyclohexanecarboxylate. Identification of ester 11 was secured by comparison with an authentic sample. Reduction of *p*-toluic acid (12) with lithium–ammonia gave the nonconjugated acid 13 which, after isomerization in the presence of ethoxide ion to the conjugated isomer 14, was further reduced with lithium–ammonia to a mixture of cis and trans acids 15.[17] Separation of the epimeric esters 16a,b by glpc provided samples for comparison. The



11 21 6 20 24 19 23 22

major ester obtained in this sequence was identical with that obtained from irradiation of 6. The trans stereochemistry of this ester was established by catalytic hydrogenation to the saturated ester 18b and hydrolysis to the known trans acid 17b.[18] Since the epimeric esters 16a,b were partially separable by glpc, the absence of the cis ester in the irradiation mixture could be established. Thus, the stereospecificity of the photoisomerization of 6 to 11 = 16b is demonstrated.

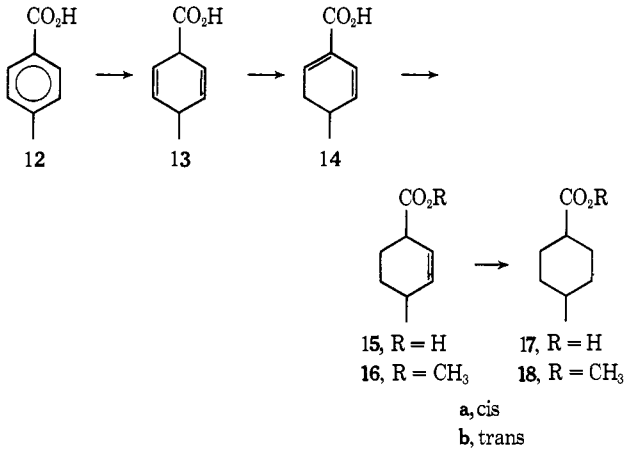
That esters 10 and 11 do not arise from the 7-ketonorbornenes is clear from the facts that (a) irradiation of 3a in methanol through Pyrex caused no detectable change;[13] and (b) addition of methanol to 8 would not produce 11. The stereospecific formation of 11 is inconsistent with the intermediacy of the corresponding ketene.

(17) F. Camps, J. Coll, and J. Pasqual, *J. Org. Chem.*, 32, 2563 (1967).

(18) A. A. B. Kleis, A. A. Massier, D. Medema, P. E. Verkada, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 80, 595 (1961).

Irradiation of 6 in deuteriomethanol containing a trace of dideuteriosulfuric acid followed by dilution with water, extraction with pentane, and isolation by preparative glpc gave 11 containing no deuterium (<5%). A similar experiment using methanol and deuterium oxide gave 11 containing deuterium (23%) at C-4 (mass spectrometry and partial collapse of the doublet at δ 0.97 to a singlet). The obvious control experiments showed that the acid had no effect on the yields of 8 or 11. When the acid was replaced with sodium methoxide, however, 11 was replaced in the product mixture by the isomeric ester 19. These results require the intermediacy of a species containing one readily exchangeable proton and are accommodated in the mechanism outlined in Scheme II. The enone

Scheme II



12 13 14

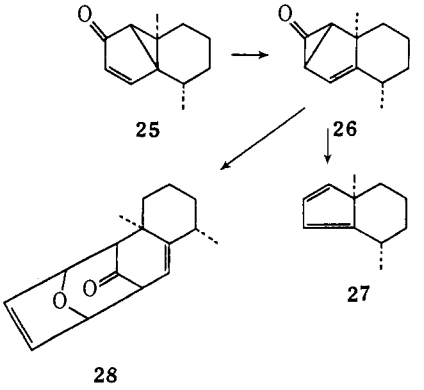
15, R = H
16, R = CH_3

17, R = H
18, R = CH_3

a, cis
b, trans

undergoes photoisomerization to cyclopropanone 20 (path b); in neutral or acidic methanol 20 is immediately trapped as the hemiketal 21 by attack from the less hindered side of the cyclopropanone,[19] and 21 is converted into 11 by thermal isomerization.[20] Reaction of cyclopropanone 20 with methoxide ion leads *via* ion 22 to allyl anion 23 which accepts a proton from solvent at the less substituted end[21] to yield 19.

The photochemical formation of cyclopropanone 26 from 25 at −190° was demonstrated by three methods:[5]



25 26 27 28

(a) the infrared spectrum of 26 was observed (1812 cm^{-1}); (b) further irradiation of 26 caused decarbonyla-

(19) N. J. Turro, *Accounts Chem. Res.*, 2, 25 (1969).

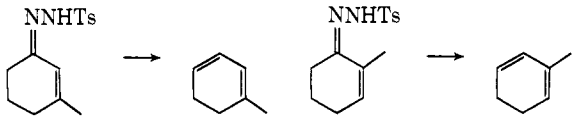
(20) The analogous intramolecular hydrogen transfer in the carene series, $\Delta H^{\ddagger}$ 27 kcal/mol, $\Delta S^{\ddagger}$ −17 eu, has been discussed: (a) G. Ohloff, *Tetrahedron Lett.*, 3795 (1965); (b) K. Gollnick, *ibid.*, 327 (1966); K. Gollnick and G. Schade, *Tetrahedron*, 22, 123 (1966).

(21) See D. J. Cram "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 5, and references cited therein.

tion leading to diene **27**; and (c) irradiation of **25** in furan gave the Diels–Alder adduct **28**.

All of our efforts to detect a cyclopropanone intermediate by infrared spectroscopy under a variety of conditions and with several different substrates failed,[22] presumably because of rapid decarbonylation. We have, therefore, resorted to indirect methods.

Careful examination of the volatile material from irradiation of **6** in methylene chloride revealed the presence of 1-methyl-1,3-cyclohexadiene (**24**). The latter was identified by comparison with authentic samples of both dienes **24** and **29**; each was obtained



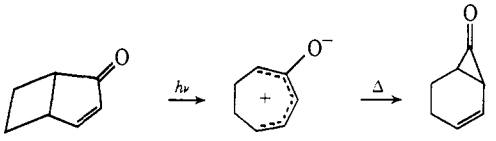
24 **29**

by decomposition of the tosylhydrazones of 3-methylcyclohexenone and 2-methylcyclohexenone, respectively, with methyllithium.[23,24]

The isolation of **24** coupled with the previously discussed findings leave no doubt that the cyclohexene carboxylate esters arise *via* photoisomerization of the bicycloheptenones to the corresponding bicyclo[4.1.0]-hept-2-en-7-ones (**6** → **20**, Scheme II), followed by opening of the cyclopropanone as depicted.

It is of some interest that the yield of isolated diene **24** in the above experiment was 9% and that of norbornenone **8** was 34%. These data coupled with the rapid resinification of **24** upon standing (presumably *via* dimerization and polymerization) indicate that the efficiency of cyclopropanone formation from bicycloheptenones is probably greater than previously indicated and that photodimerization is probably less important.[8]

We may now discuss the pathway by which cyclopropanone formation occurs. The change may be concerted or nonconcerted. A suitable model for the nonconcerted path comprises electrocyclic ring opening to a seven-membered ring zwitterion[26] followed by thermal cyclization to the cyclopropanone (**1a** → **30** → **31**). Disrotatory ring closure in the ground-state



1a **30** **31**

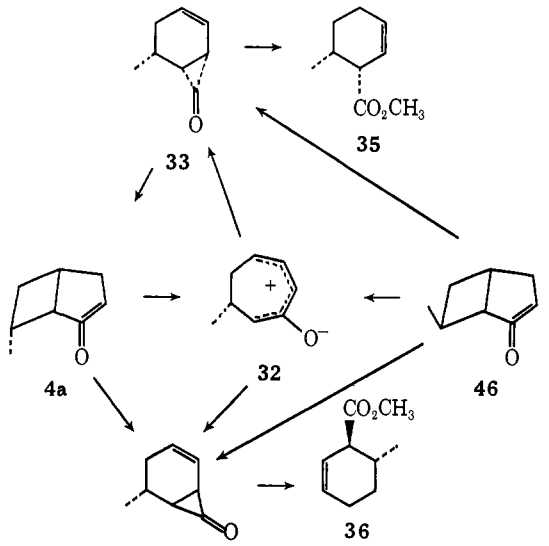
zwitterion preserves orbital symmetry. Alternatively, the cyclopropanone may be formed *via* a concerted $[_{\sigma}2 + _{\pi}2]$ cycloaddition.[5,10]

In order to distinguish between concerted and nonconcerted routes we have incorporated a stereochemical label at C-7 of the bicycloheptenone nucleus. The choice of C-7 for the stereolabel follows from two facts: (1) ketones **4a** and **4b** are available from the allene–cyclopentenone photoadduct[27] by reduction as described below; and (2) the stereochemistry at C-7 of the bicyclo[3.2.0]heptenones is preserved during irradiation (see above).

Because of the requirement that the cyclopropanone contain a cis double bond and a cis ring fusion, the only concerted paths which are geometrically allowed are $[_{\sigma}2_s + _{\pi}2_s]$ and/or $[_{\sigma}2_a + _{\pi}2_a]$ cycloadditions. These are the paths which conserve orbital symmetry if the reaction proceeds from an excited state.[10]

We now predict the stereochemical outcome of irradiation of **4a** and **4b**. If the reaction proceeds *via* the nonconcerted path described above, the planar (or nearly so) zwitterion **32** may close to yield both cyclopropanones **33** and **34**, which would be converted into the cis and trans esters **35** and **36**, respectively. Both **4a** and **4b** should yield the same mixture of esters **35** and **36**. Furthermore, there appears to be little difference in strain energy from nonbonded interactions or from bond torsions between the two cyclopropanones; therefore, the nonconcerted path should lead eventually to a mixture containing nearly equal amounts of cis and trans esters (see Scheme III).

Scheme III



34

In the concerted formation of the cyclopropanone from **4a**, the path leading to **33** should be favored over that leading to **34** because the former requires much less nuclear motion than the latter.[28,29] Thus, if the photoisomerization is concerted the mixture of esters obtained from **4a** should be significantly enriched in the

(22) Most of these experiments were carried out in the laboratories of Professor O. L. Chapman at Iowa State University and will be published separately by that group. We are very grateful to Professor Chapman and Dr. Jean Lassila for their interest and generous collaboration in this project.

(23) (a) R. H. Shapiro and J. H. Duncan, *Org. Syn.*, **51**, 66 (1971); (b) W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

(24) The previously reported syntheses of **24** and **29**[25] are not without some ambiguity, nor can **24** and **29** be distinguished by inspection of their spectra, separately or together. The formation of only **24** from 3-methylcyclohexenone and of only **29** from 2-methylcyclohexenone confers total lack of ambiguity upon these results.[23]

(25) (a) H. Plieniger, L. Arnold, and W. Hoffman, *Chem. Ber.*, **98**, 1399 (1965); (b) M. A. M. Mandron, P. Potin, and R. Wylde-Lachazette, *Bull. Soc. Chim. Fr.*, 1549 (1962); (c) K. W. Egger and T. L. James, *Trans. Faraday Soc.*, **66**, 411 (1970); (d) H. Babad, W. Flenion, and J. Wood, *J. Org. Chem.*, **32**, 2871 (1967); (e) C. W. Spangler and N. Johnson, *ibid.*, **34**, 1444 (1969); (f) W. A. Thomas, *J. Chem. Soc. B*, 127 (1966).

(26) For example, see H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **86**, 1436 (1964), and other papers of Zimmerman.

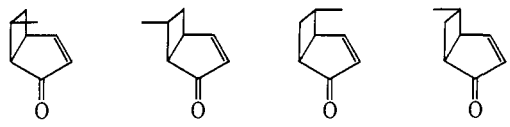
(27) P. E. Eaton, *Tetrahedron Lett.*, 3695 (1964).

(28) For a recent discussion of the Principle of Least Motion, see O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972), and references cited therein.

(29) Studies with molecular models show that the change **4a** → **33** requires very little motion of the carbon framework; however, the change **4a** → **34** requires considerable motion, mostly in swinging the carbonyl group through a large arc. The former process should be favored, but probably not to the exclusion of the latter.

cis ester **35**. Conversely, **4b** should provide *via* the concerted path a mixture of esters in which the trans ester **36** predominates. Because of the differences in overall geometry of **4a** and **4b**, however, the ratios of esters obtained from the irradiations of **4a** and **4b** need not be reciprocals.

The syntheses of ketones **4a** and **4b** are straightforward, if laborious. Catalytic hydrogenation of the mixture of photoadducts obtained from cyclopentenone and allene[27] provided an inseparable (by glpc) mixture of three of the four possible 6- and 7-methylbicyclo-[3.2.0]heptan-2-ones. This mixture was carried to the enone stage by the method of Garbisch.[30] The enone mixture was separated into three fractions by glpc, ratio 83.5:11.5:5.0. The nmr spectrum of the 83.5% fraction exhibits a methyl doublet at δ 0.95, that of the 11.5% fraction a doublet at δ 1.30, and that of the 5.0% fraction a doublet at δ 0.95. These nmr data coupled with the relative amounts of the enones establish the structures of each of the three fractions as **4a**, **4b**, and **37**, respectively.[31]

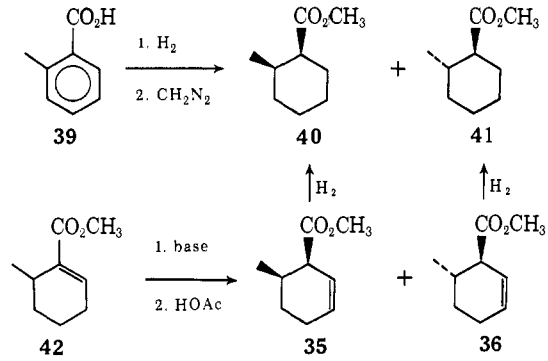


4a **4b** **37** **38**

Reduction of the cyclopentenone–allene adduct mixture with sodium in ammonia,[14] followed by reoxidation of any alcohol present back to the ketone stage, gave a mixture of saturated ketones. These were converted as before into the enones which were separated by glpc. In this case the major products were **4b** and **38**.

Having obtained the necessary starting ketones of rigorously established structure and stereochemistry, we were required to demonstrate that the expected esters **35** and **36** could be identified, separated, and analyzed. Catalytic hydrogenation of *o*-toluic acid (**39**) followed by esterification with diazomethane gave an easily separable (glpc) mixture of cis and trans esters **40** and **41** in a ratio of 9:1, respectively. The stereochemical assignment is based on equilibration of the mixture with sodium methoxide in methanol, which reversed the ratio of the two esters. Thus, the major component in the reduction mixture is the cis isomer.

Attempts to reduce *o*-toluic acid with lithium in ammonia to the tetrahydro stage failed, only dihydro material being obtained.[17,32] However, deconjugation of methyl 6-methylcyclohexenecarboxylate (**42**)[33] by treatment with base and quenching the resulting enolate with acetic acid gave a mixture of esters **35** and **36** in which the former predominated by *ca.* 9:1. Although esters **35** and **36** were only partially separable by glpc, the major component was obtained pure by preparative glpc. Mild catalytic hydrogenation of this pure ester gave only cis ester **40**, establishing its stereochemistry



as cis, and further demonstrating that the conditions of hydrogenation did not disturb the stereochemistry of either the unsaturated or saturated esters. Thus, the best method for analyzing a mixture of unsaturated esters **35** and **36** is to hydrogenate the mixture and analyze the resulting mixture of saturated esters by glpc.

At this point we could determine the stereochemical course of the cyclopropanone-forming reaction. Irradiation of **4a** in methanol as above gave three volatile products, norbornenone **5a** (7%) and esters **35** and **36** (5% total). The mixture of esters was collected, care being taken to trap all the effluent, and hydrogenated as above. The mixture of saturated esters thus obtained contained 93% of the cis isomer **40** and 7% of the trans isomer **41**. Similar irradiation of **4b** followed by similar work-up gave a mixture of esters **40** and **41** in a ratio of 20:80, respectively. We conclude that the ratios of saturated esters **40** and **41** obtained here accurately reflect the ratios of esters **35** and **36** obtained in the irradiations. These data clearly rule out any major contribution of the zwitterionic pathway to the mechanism of cyclopropanone formation, and are consistent with the concerted paths already discussed. Although a small portion of the reaction could occur *via* the nonconcerted path, we conclude that all cyclopropanone formation occurs *via* the concerted $[_{\sigma}2 + _{\pi}2]$ cycloaddition, and that the different ratios of esters **35** and **36** formed (and therefore cyclopropanones **33** and **34**) reflect the relative energetics of ring closure across the convex face of the molecule, *e.g.*, **4a** → **33** *vs.* closure across the concave face **4a** → **34**.

In addition to showing that cyclopropanone formation occurs in concert with one mode of cyclobutane ring opening, these results also demonstrate that the interconversion of ketones **4a** and **4b** by a process similar to the thermal inversions of bicyclo[2.1.0]pentanes[34] does not occur.[35]

The simultaneous occurrence of one nonconcerted $[_{\sigma}2 + _{\pi}2]$ cycloaddition and one concerted $[_{\sigma}2 + _{\pi}2]$ cycloaddition in the same molecule raises a question. Do the two reactions occur from the same or different electronic states? All the photochemistry of the bicyclo[3.2.0]hept-3-en-2-ones is quenched by 1 *M cis*-1,3-pentadiene; therefore, we presume that both isomerizations described above occur from a triplet state.[37]

(30) E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965).

(31) No indication of the presence of **38** in this mixture was obtained. Subsequently, analysis of the reduction products of the cyclopentenone–allene adducts showed that **4a** and **38** have identical retention times on the column used; however, the spectra of **4a** collected from this column gave no detectable signals attributable to **38**. Irradiation of **4a**, purified in this manner, gave no detectable products derivable from **38** or **37**.

(32) M. E. Kuehne and B. F. Lambert, *J. Amer. Chem. Soc.*, **81**, 4278 (1959).

(33) (a) T. Holm, *Acta Chim. Scand.*, **18**, 1577 (1964); (b) W. S. Rapson and R. G. Schuttleworth, *J. Amer. Chem. Soc.*, 62, 636 (1940).

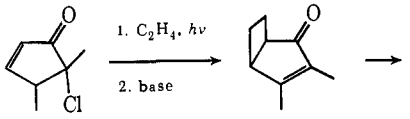
(34) (a) J. P. Chesick, *ibid.*, **84**, 3250 (1962); (b) M. J. Jorgenson, T. J. Clark, and J. Corn, *ibid.*, **90**, 7020 (1968).

(35) Zwitterion **32** may not undergo disrotatory cyclization to yield either **4a** or **4b** without destruction of orbital symmetry. The symmetry of the pentadienyl cation is not significantly altered by the negatively charged oxygen.[36]

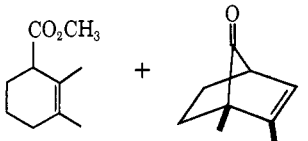
(36) (a) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5613 (1968); (b) T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

(37) The spectroscopic studies already reported[38] show that in rigid cyclopentenones, the n,π^* singlet, the n,π^* triplet, and the π,π^* triplet

If the electronic configuration of the reactive state is of prime importance in determining the path followed by the excited ketone, then reversal of the triplet levels should have a pronounced effect on the ratio of path a to path b rearrangement. We have, therefore, investigated the photochemistry of 3,4-dimethylbicyclo[3.2.0]-hept-3-en-2-one (**43**), the lower lying triplet of which is



44 **43**



45 **46**

π,π^* rather than n,π^* as in **1**, **4**, and **6**.[38] This enone was prepared by photo-cycloaddition of ethylene with ketone **44**,[40] followed by dehydrohalogenation in 50% overall yield.

Irradiation of **43** in methanol, as before, gave ester **45** in 4% yield and ketone **46** in 25% yield. Thus, the ratio of ester to ketone is dramatically affected by the presence of methyl groups attached to the double bond. This result may be consistent with isomerization *via* path a in the π,π^* triplet and isomerization *via* path b in the n,π^* triplet, the lower-lying triplet providing the major reaction path.[41] However, all the experiments discussed above, taken with the absence of any products from paths c–f may be better explained as follows. The excited molecule, whether an equilibrium mixture of several electronic states or a single electronic species, *e.g.*, n,π^* triplet, lies some 70 kcal/mol above the ground state. The excited molecule thus possesses sufficient energy to overcome one or more reaction barriers, and the mixture of products obtained in an irradiation merely reflects the relative rates of several competing processes. In the cases at hand, the two reactions observed are two of the possible six which relieve the strain imposed upon the starting ketone by the cyclobutane ring.[42] The presence of electron donating substituents on the double bond should greatly stabilize the radical obtained in path **a** but should have little effect on path b; therefore, irradiation of **43** is expected to yield a greater proportion of 7-norbornenone than ester when compared with the unsubstituted enone. Further experiments are necessary before a distinction between these two explanations may be made.

Experimental Section[43]

exo-**6,7-Bisdeuteriobicyclo[3.2.0]hept-3-en-2-one** (**1b**).[44] A solution of 6.00 g (39.4 mmol) of bicyclo[3.2.0]hept-6-en-2-one ethylene ketal and 45 g (0.23 mol) of potassium azodicarboxylate[45] (dried under vacuum over phosphorus pentoxide) in 70 ml of methanol-d_1 was stirred while 14 ml of acetic acid-d_1 and 30 ml of deuteriomethanol were added very slowly. The reaction was stirred overnight and all the yellow color disappeared. The reaction mixture was filtered and most of the methanol was removed by distillation through a Holzmann column.[46] Water (50 ml) was added to the residue and the aqueous phase was extracted with ether. After the ether extract was dried ($CaCl_2$), the solvent was removed to give 5.54 g of crude ketal, which was shown by nmr analysis to contain no olefinic protons. The crude saturated ketal was brominated, dehydrobrominated, and hydrolyzed to give 2.55 g (58.9%) of distilled **1b**: bp 58–62° (4 Torr); ir (CCl_4) 3030, 2200, and 1715; nmr (CCl_4) δ 1.70 (br s, 2, *endo*-cyclobutane protons), 2.83 (m, 1, bridghead proton), 3.37 (m, 1, bridgehead proton), 6.18 (d, 1, $J_{\alpha,\beta}$ = 5.4 Hz, —COCH=CH—), and 7.61 (q, 1, $J_{\alpha,\beta}$ = 5.4 Hz, $J_{\beta,\gamma}$ = 3.0 Hz, —COCH=C*H*—). The deuterium content of **1b** was found to be 87% d_2, 10% d_1, and 3% d_0 by comparing the mass spectra (70 eV) of **1a**, *m/e* (% rel abundance): 107 (6), 108 (100), and 109 (12), and **1b**, *m/e* (% rel abundance) 108 (3), 109 (18), 110 (100), and 111 (11).

Irradiation of *exo*-**6,7-Bisdeuteriobicyclo[3.2.0]hept-3-en-2-one** (**1b**). A. A solution of 300 mg (0.366 mmol) of **1b** in 190 ml of purified pentane was irradiated with blacklight through Pyrex.[47] The irradiation, the progress of which was followed by analytical glpc (3% Carbowax, 8 ft × 0.125 in., 100°, 25 ml/min), was terminated when essentially all the starting material had disappeared. The solvent was removed by careful distillation[48] and the resulting 5,6-bisdeuterio-7-ketonorbornene (**3b,c**) was purified by preparative glpc (20% DEGS, 10 ft × 0.25 in., 120°, 50 ml/min, injector 145°, detector 150°): nmr (CCl_4) δ 1.13 (m, endo protons), 1.92 (m, exo protons), 2.72 (m, 2, bridgehead protons) and 6.42 (t, 2, $J_{1,3}$ = $J_{3,2}$ = 2.4 Hz). The ratio of endo:exo protons, determined by integration of the appropriate peak areas, was found to be 2.5 ± 0.1. A comparison of the mass spectrum (70 eV) of **3a** [*m/e* (% rel abundance) 78 (3), 79 (12), 80 (100), and 81 (7)] with that of **3b,c** [*m/e* (% rel abundance) 79 (1), 80 (4), 81 (21), 82 (100), 83

lie very near each other. The quenching by pentadiene, therefore, does not rigorously eliminate the n,π^* singlet as a reactive species.[39]

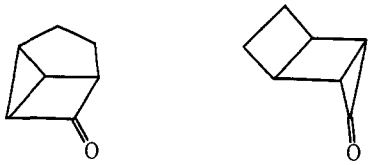
(38) R. L. Cargill, W. A. Bundy, D. M. Pond, A. B. Sears, J. Saltiel, and J. Winterle, *Mol. Photochem.*, 3, 123 (1971).

(39) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

(40) G. J. Martin and G. Daviand, *Bull. Soc. Chim. Fr.*, 3098 (1970).

(41) In the α,β-dimethyl cyclopentenones previously reported[38] the π,π^* triplet lies *ca.* 9 kcal/mol below the n,π^* singlet and is estimated to lie *ca.* 6 kcal/mol lower than the n,π^* triplet. Appropriate spectroscopic measurements for the location of the n,π^* triplet when that state is T^2 are being initiated in collaboration with Professor D. R. Kearns.

(42) The other processes in which cyclobutane cleavage may occur are cycloaddition of the C-1–C-7 bond across the double bond in either of two directions and paths d and e (Scheme I). All of these paths lead, in the bicycloheptenones under discussion, to either i or ii, both



i ii

of which are highly strained tricyclic compounds. Formation of either of these two compounds from **1** would be highly endothermic, and unlikely to compete favorably with paths a and b.

(43) All boiling points and melting points are uncorrected. Microanalyses were performed by Bernhardt Microanalytisches Laboratorium, Elbach uber 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. In the descriptions of nmr spectra s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. 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. Low-temperature irradiations were conducted by immersing the irradiation vessel in a Dry Ice–isopropyl alcohol bath. The probe was cooled by circulation of isopropyl alcohol which was cooled indirectly with Dry Ice.

(44) Ketones **6** and **1a** are described in ref 38.

(45) (a) S. Hunig, H. R. Muller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, **4**, 271 (1965); (b) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, **30**, 3985 (1965); (c) P. F. Fassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **90**, 4748 (1968); (d) J. A. Berson, M. S. Poonian, and W. J. Libbey, *ibid.*, **91**, 5567 (1969); (e) we thank Professor P. G. Gassman for his advice concerning the deuteriodiimide reduction.

(46) A 24 cm × 5 mm column containing a tantalum wire spiral was used.

(47) R. L. Cargill, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Org. Chem.*, **36**, 1423 (1971).

(8), and 84 (1)] indicated that no deuterium was lost during the rearrangement.

B. A pentane solution of **1b** was irradiated and worked up as described above except that the irradiation was terminated when 60–70% of starting material had disappeared. The nmr spectrum of 5,6-bisdeuterio-7-ketonorbornene from this irradiation was identical with that from experiment A. The nmr spectrum of recovered starting material showed all the absorptions characteristic of **1b** and, in addition, a multiplet at δ 2.43 (exo proton). Integration of peak areas corresponding to endo proton (δ 1.70) and exo proton (δ 2.43) absorptions gave a ratio, endo:exo, of 2.5 ± 0.5.

C. Irradiation of **1b** as described above, except that the irradiation was terminated when 25% of starting material had disappeared, gave 5,6-bisdeuterio-7-ketonorbornene, the nmr spectrum of which is identical with those obtained in experiments A and B. The nmr spectrum of recovered starting material was like that of recovered starting material from experiment **B** except that the ratio of endo:exo protons was 6 ± 1.

exo-**5,6-Bisdeuterio-7-ketonorbornene (3d).** *exo*-5,6-Bisdeuteriobicyclo[2.2.1]hept-2-en-7-ol[48] was oxidized by the method of Bly[49] for oxidation of the corresponding protio compound. The crude product was distilled to give **3d**: bp 46–49° (6.0 Torr) in 43% yield; nmr (CCl_4) δ 1.13 (s, 2, endo protons at C-5 and C-6), 2.70 (t, 2, $J_{1,2} = J_{1,3} = 2.4$ Hz, bridgehead protons), and 6.43 (t, $J_{21} = J_{31} = 2.4$ Hz).

Irradiation of *exo*-5,6-Bisdeuterio-7-ketonorbornene (3d). A solution of 110 mg of **3d** was irradiated in 25 ml of pentane and worked up as described for the irradiation of **1b** except that the irradiation time was twice as long (22 hr). The nmr spectrum of recovered **3d** was identical with that before irradiation.

Low-Temperature Irradiation of 6. A solution of 299 mg of **6** in 150 ml of pentane was irradiated at *ca.* −70° through Pyrex for 2.75 hr, after which time 95% of **6** had reacted and two new volatile products had been formed in *ca.* 10% yield each. The cold solution was diluted with 60 ml of methanol, allowed to warm to 25°, and further diluted with 25 ml of water, and the organic phase was collected. The dried pentane solution was concentrated to yield two products which were obtained by preparative glpc (20% DEGS, 10 ft × 0.25 in., 125°, 90 ml/min). One was identified as **8**, and the other as **9**. The latter has ir (CCl_4) 3060, 3030, 1715, 1640, 1550, 890 cm^{-1} and nmr (CCl_4) δ 0.83 (t, 3, J = 7 Hz, CH_2CH_3), 1.8 (m, 2, methylene), 2.68 (m, 1, α'-methine), 5.22 (ABq, 2, Δ_{AB} = 8 Hz, J_{AB} = 2 Hz, exo methylene), 6.19 (d, $J_{\alpha,\beta}$ = 7 Hz, each leg of the doublet is further split by $J_{\alpha,\alpha'}$ = 2 Hz, α proton), 7.58 (d, $J_{\alpha,\beta}$ = 7 Hz, each leg of the doublet is further split by $J_{\beta,\alpha'}$ = 1 Hz, β proton). Insufficient sample remained for further analysis.

Irradiation of 5-Methylbicyclo[3.2.0]hept-3-en-2-one (6) **in Methanol.** A solution of 300 mg (2.46 mmol) of **6** in 80 ml of methanol was irradiated through Corex. The reaction, which was monitored by glpc (3% Carbowax, 8 ft × 0.125 in., 110°, 25 ml/min), was terminated when all of **6** had disappeared. After the addition of 100 ml of water, the products were extracted into pentane and dried ($CaCl_2$), and the solvent was removed.[46] Analysis by preparative glpc (20% DEGS, 10 ft × 0.25 in., 115°, 70 ml/min) showed that two volatile products were present. The earlier-eluted product was identified as 2-methylbicyclo[2.2.1]hept-2-en-7-one (**8**): ir (CCl_4) 3045, 1790, and 1620 cm^{-1}; nmr (CCl_4) δ 1.2 (m, 2, endo H), 1.87 (d, 3, J_{AX} = 1.8 Hz, —CH=CCH_3), 1.9 (m, 2, exo H), 2.50 (m, 1, bridgehead H), 2.66 (m, 1, bridgehead H), and 5.97 (m, 1, —CH=CCH_3).

Anal. Calcd for $C_8H_{10}O$ (122.16): C, 78.65; H, 8.25. Found: C, 78.71; H, 8.44.

The slower moving product was identified as methyl *trans*-4-methyl-2-cyclohexencarboxylate (**11** = **16b**): ir (CCl_4) 3020, 1740, 1650, and 1165 cm^{-1}; nmr (CCl_4) δ 0.97 (d, 3, J_{AB} = 7.0 Hz, CHCH_3), 1.88 (m, 5), 2.94 (m, 1, C=CCHCO$_2$CH$_3$), 3.58 (s, 3, OCH_3), and 5.55 (s, 2, —CH=CH—); mass spectrum (70 eV) *m/e* molecular ion 154.

Anal. Calcd for $C_9H_{14}O_2$ (154.20): C, 70.10; H, 9.15. Found: C, 70.13; H, 9.25.

Irradiation of Bicyclo[3.2.0]hept-3-en-2-one (1a) in Methanol. A solution of 580 mg (5.36 mmol) of **1a** in 80 ml of methanol was irradiated as described above for the irradiation of **6** except that a Pyrex filter was employed. The two volatile produts were identified as bicyclo[2.2.1]hept-2-en-7-one (**3a**) by comparison of ir and nmr spectra with those of an authentic sample[49] and methyl 2-cyclohexenecarboxylate (**10**):[50] ir (CCl_4) 3030, 2940, 1745, and 1165 cm^{-1}; nmr (CCl_4) δ 1.75 (m, 6), 2.97 (br s, 1, CH=CHCH-CO$_2$CH$_3$), 3.60 (s, 3, OCH_3) and 5.67 (m, 2, $W_{h/2}$ = 3 Hz, HC=CH).

Hydrogenation of Ester from Irradiation of 1a in Methanol. A solution of 90 mg (0.64 mmol) of **10** in 1.0 ml of methanol was hydrogenated at atmospheric pressure using a 10% Pd/C catalyst. After absorption of hydrogen was complete, the catalyst was removed, 2 ml of water was added, and the aqueous solution was extracted with pentane. The pentane solution was dried and the solvent removed to give a slightly yellow oil. Analysis by preparative glpc (30% DEGS, 10 ft × 0.25 in., 110°, 60 ml/min) indicated that only one compound was present. This compound was identified as methyl cyclohexanecarboxylate:[50] ir (CCl_4) 2840, 1740, 1190, and 1165 cm^{-1}; nmr (CCl_4) δ 1.60 (m, 11) and 3.58 (s, 3, OCH_3).

Authentic Methyl Cyclohexanecarboxylate. An ethereal solution of 50 mg of cyclohexanecarboxylic acid was converted into its methyl ester by treatment with diazomethane. The ir and nmr spectra of this ester were identical with those of the ester resulting from hydrogenation of **10**.

Lithium–Ammonia Reduction of *p*-Toluic Acid.[17] To 16.3 g of *p*-toluic acid in a 1000-ml, three-necked flask, equipped with a Dry Ice–acetone condenser, gas inlet tube, drying tube, and magnetic stirrer, was added 125 ml of dry ether (distilled from $LiAlH_4$). Approximately 400 ml of ammonia was condensed in the flask and 3.3 g of lithium was added in small pieces. The resulting blue solution was stirred for 15 min and then 20 ml of anhydrous ethanol was added dropwise. When the blue color had disappeared the ammonia was evaporated. After the resulting mixture had stood overnight, 350 ml of ammonia was added. The resulting solution was stirred while 2.5 g of lithium was added as before. The blue solution was stirred for 15 min and then 22 ml of ethanol was added over a 10-min period. After 10 min of further stirring, 45 g of ammonium chloride was added and the ammonia was evaporated. The reaction mixture was acidified with 6 *M* hydrochloric acid and extracted with three 300-ml portions of ether. The extracts were washed with saturated sodium chloride and dried with sodium sulfate, and the solvent was removed to give a dark blue liquid. Distillation of this blue material gave 12.2 g (72.8%) of 4-methyl-2-cyclohexenecarboxylic acid (**15**)[32] (mixture of cis and trans isomers) as a colorless liquid, bp 83–86° (0.25 Torr), which crystallized in a refrigerator.

Methyl *cis*- and *trans*-4-Methyl-2-cyclohexenecarboxylate (16a,b). An ethereal solution of 500 mg of **15**, from the lithium–ammonium reduction of *p*-toluic acid, was treated with diazomethane. Preparative glpc analysis (20% DEGS, 10 ft × 0.25 in., 120°, 68 ml-min) of the resulting esters showed the presence of only two compounds which were not separated completely. The major ester, which eluted last, was obtained pure after two collections and was shown, by comparison of ir and nmr spectra, to be identical with the ester **16b** = **11** resulting from irradiation of **6** in methanol. The minor ester was obtained pure after three collections and identified as methyl *cis*-4-methyl-2-cyclohexenecarboxylate (**16a**): ir (CCl_4) 3020, 1740, 1650, and 1170 cm^{-1}; nmr δ 0.99 (d, 3, J_{AB}, = 7.0 Hz, CHCH_3), 1.75 (m, 5), 2.90 (m, 1, CH=CHCHCO$_2$CH$_3$), 3.58 (s, 3, OCH_3), and 5.54 (br, 2, —CH=CH—).

Anal. Calcd for $C_9H_{14}O_2$ (154.20): C, 70.10; H, 9.15. Found: C, 69.93; H, 9.24.

Methyl *trans*-4-Methylcyclohexanecarboxylate (18b)[18] A solution of 295 mg (1.92 mmol) of methyl *trans*-methyl-2-cyclohexenecarboxylate (**16b** = **11**) in 15 ml of methanol was hydrogenated using platinum oxide and an initial pressure of 55 psi. After the uptake of hydrogen was complete, the catalyst was removed and 30 ml of water was added, and the aqueous phase was extracted with pentane. The pentane solution was dried ($CaCl_2$), the solvent removed,[46] and the methyl *trans*-4-methylcyclohexanecarboxylate (**18b**) purified by preparative glpc (20% Carbowax, 8 ft × 0.25 in., 140°, 56 ml min): ir (CCl_4) 2840, 1740, and 1140 cm^{-1}; nmr (CCl_4) δ 0.89 (d, 2, J_{AB} = 5.0 Hz, CHCH_3), 2.50 (m, 10), and 3.54 (s, 3, OCH_3): $n^{20}D$ 1.4404, $n^{25}D$ 1.4383 (lit.[18] $n^{25}D$ 1.4380).

***trans*-4-Methylcyclohexanecarboxylic Acid (17b).**[18] To 1.3 ml of 10% potassium hydroxide was added 90 mg (0.58 mmol) of

(48) B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

(49) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963). We wish to thank Dr. Ruta Bly for her advice concerning this oxidation reaction.

(50) C. G. Overberger and P. Kabasakalian, *J. Org. Chem.*, **21**, 1124 (1956).

methyl *trans*-4-methylcyclohexanecarboxylate (**18b**). The mixture was refluxed for 1 hr. The reaction mixture was cooled and extracted with ether. The aqueous phase (at 0°) was adjusted to pH 2 with 4 *M* sulfuric acid. The white precipitate, which formed immediately, was washed with cold water and dried in a vacuum desiccator over P_2O_5: ir (CCl_4) 1715, 1250, 1210 cm^{-1}; nmr (CCl_4) δ 0.90 (d, 3, J_{AX} = 3.5 Hz, $CHCH_3$), and 11.72 (s, 1, $-CO_2H$); mp 109.5–110.5° (lit.[18] mp 110.5–111.5° and 107.5–108.5°).

Irradiation of 6 in Acidic Methanol. A solution of 150 mg (1.23 mmol) of **6** in 80 ml of methanol containing a few drops of sulfuric acid was irradiated and worked up as described above. Analysis by preparative glpc (as above) showed that four relatively volatile products had been formed. One of the products was identified as **8**, one as **11**, and another as 2-methylbicyclo[2.2.1]hept-2-en-7-one dimethyl ketal: ir (CCl_4) 3040, 2820, 1640, 1095, 1070 cm^{-1}; nmr (CCl_4) δ 0.92 (m, 2, endo H), 1.73 (d, 3, J_{AX} = 1.6 Hz, $CH{=}CCH_3$), 1.8 (m, 2, exo H), 2.40 (m, 1, bridgehead H), 2.54 (m, 1, bridgehead H), 3.02 (s, 3, OCH_3), 3.07 (s, 3, OCH_3), and 5.43 (m, 1, C=CH).

Irradiation of 6 in Acidic Methanol. Deuterium Oxide Work-Up. A solution of 205 mg (1.68 mmol) of **6** in 80 ml of ordinary methanol containing sulfuric acid was irradiated and worked up as described above using 120 ml of deuterium oxide (99%). Separation of the products in the above manner gave **11** with 23% deuterium incorporation at C-4 as determined by nmr and mass spectral analysis. The nmr spectrum was similar to that for protio **11** (see above) except that the doublet centered at δ 0.97 was partially collapsed to a broad singlet at δ 0.97. The deuterium content of **11** was found to be 23% d_1 and 0% d_2 by comparing the mass spectrum (70 eV) of **11** obtained from this irradiation [*m/e* (% rel abundance) 152 (2), 153 (11), 154 (100), 155 (47), and 156 (6)] with that of protio **11** [*m/e* (% rel abundance) 152 (3), 153 (11), 154 (100), and 155 (18)].

Irradiation of 6 in Acidic Methanol-d_1. A solution of 305 mg (2.50 mmol) of **6** in 80 ml of methanol-d_1 (99%) containing sulfuric acid-d_2 was irradiated and worked up as above using 120 ml of ordinary water. The nmr spectrum of **11** from this experiment was essentially the same as that for protio **11** except that there was a small singlet peak at δ 0.97 corresponding to some collapse of the doublet centered at δ 0.97. A comparison of this nmr spectrum with the corresponding nmr spectrum of **11** containing 23% d_1 (see above) shows that *ca.* 4% deuterium had been incorporated.

Irradiation of 6 in Basic Methanol. A solution of 153 mg (1.25 mmol) of **6** in 80 ml of methanol which contained enough sodium methoxide to adjust the "pH" to *ca.* 8 was irradiated and worked up as described above. The volatile products were separated and identified as **8** and methyl 4-methyl-3-cyclohexenecarboxylate (**19**): ir (CCl_4) 3040, 3005, 1745, 1165 cm^{-1}; nmr (CCl_4) δ 1.62 (br s, 3, $CH{=}CCH_3$), 2.08 (m, 7), 2.56 (s, 3, OCH_3), and 5.29 (br s, 1, C=CH); mass spectrum (70 eV) *m/e* molecular ion 154.

Irradiation of 6 in Methanol-d_1.[51] A solution of 309 mg (2.53 mmol) of **6** in 80 ml of methanol-d_1 (99%) was irradiated as described above. When glpc analysis (10% XF-1150, 8 ft × 0.125 in., 140°, 25 ml/min) indicated that **6** had disappeared, the irradiation was terminated, the solvent was removed at atmospheric pressure, and the volatile products were purified by preparative glpc as above. There were three minor products (accounting for *ca.* 10% of the product mixture) in addition to **19**: nmr (CCl_4) δ 1.62 (br s, 3, $CH{=}CCH_3$), 2.08 (m, 6), 2.56 (s, 3, OCH_3), and 5.29 (br s, 1, C=CH), and **8**. The **19** obtained in this experiment was shown to contain 99% one deuterium by comparing its mass spectrum (70 eV), *m/e* (% rel abundance) 154 (4), 155 (100), and 156 (11), with that of the protio compound, *m/e* (% rel abundance 154 (100) and 155 (14).

Irradiation of 5-Methylbicyclo[3.2.0]hept-3-en-2-one (6) in Methylene Chloride. A solution of 6.94 g (57.0 mmol) of 5-methylbicyclo[3.2.0]hept-3-en-2-one (**6**) in 1400 ml of methylene chloride was irradiated (Uranium filter) at ambient temperature, for 7 hr. The methylene chloride was removed by careful distillation at 1 atm, through a Nester-Faust spinning-band column (18 in., platinum band). The residual oil was purified by a short path distillation at reduced pressure. The fraction which distilled at 25–35° (75 Torr), 0.28 g, was 1-methyl-1,3-cyclohexadiene (**24**). The next fraction also contained **24** along with **8**. It was estimated, from a consideration of the relative amounts of **24** and **8** in the second fraction (as shown by nmr), that a total of *ca.* 0.5 g (9%) of **24** was obtained from the first and second fractions. Diene **24** was further purified by preparative glpc (20% DC-710, 8 ft × 0.25 in., 80°, 67 ml/min). The collected material formed a viscous oil (presumably dimer) upon standing at room temperature for 24 hr. Pure **24**: ir(CCl_4) 3030, 695 cm^{-1}, nmr (CCl_4) δ 5.90–5.20 (m, 3, olefinic protons), 2.10 (s, 4, methylene protons), 1.75 (s, 3, $-C{=}C(CH_3)-$); uv (isooctane) 264 nm (ϵ 4150).

A total of 2.38 g (34%) of **8**, bp 50° (10 Torr), was isolated from the irradiation.

A residue amounting to 3.3 g of nonvolatile material remained after distillation.

1-Methyl-1,3-cyclohexadiene (24). Conversion of 3-methylcyclohexenone into its *p*-toluenesulfonylhydrazone was effected in 65% yield, mp 129–130°.

The above *p*-toluenesulfonylhydrazone was converted into **24** by the method of Shapiro,[23] bp 117° (1 atm). The nmr spectrum of the distilled material was identical with that of the volatile hydrocarbon obtained from the irradiation of **6** in methylene chloride.

2-Methyl-1,3-cyclohexadiene (29). Conversion of 2-methylcyclohexenone into its *p*-toluenesulfonylhydrazone was effected in 73% yield, mp 156.5–157°.

Anal. Calcd for $C_{14}H_{18}O_2N_2S$ (278.38): C, 60.41; H, 6.52; N, 10.06. Found: C, 60.44; H, 6.42; N, 10.25.

The above *p*-toluenesulfonylhydrazone was converted into **29** by the method of Shapiro[23] in 68.5% yield, bp 44–46° (75 Torr). The distilled material was further purified by glpc (20% DC-710, 8 ft × 0.25 in., 80°, 67 ml/min). The collected material formed a viscous oil (presumably dimer) on standing at room temperature for 24 hr. Pure **29**: ir (CCl_4) 3030, 1450, 725, 665 cm^{-1}; nmr (CCl_4) δ 6.68 (finely split s, 2, $-CH{=}C(CH_3)CH{=}CH-$), 5.35 (m, 1, $-CH{=}C(CH_3)CH{=}CH-$), 2.05 (finely split s, 4, methylene protons) 1.69 (finely split s, 3, $-CH{=}C(CH_3)-$); uv (isooctane) 261 nm (ϵ 3200).

7-Methylenebicyclo[3.2.0]heptan-2-one and 6-Methylenebicyclo[3.2.0]heptan-2-one. A 9.7-g (77 mmol) quantity of cyclopentenone ethylene ketal was dissolved in 30 ml of water containing a trace of sulfuric acid and stirred for 1 hr. The solution was extracted with 3 × 50 ml of methylene chloride, drie d(Na_2SO_4), and then diluted to a total volume of 950 ml with pentane (MCB spectral quality). The solution was cooled to −78° in a low-temperature irradiation apparatus, and *ca.* 50 ml of allene was condensed into the solution. Irradiation was commenced (Corex); the reaction was followed by glpc (3% SE-30, 8 ft × 0.125 in., 85°, 30 ml/min) and was completed within 5 hr. The solution was allowed to return to ambient temperature and the allene removed. The solution was dried (Na_2SO_4), concentrated,[46] and distilled giving 6.8 g (72% of the two isomeric adducts, bp 45–50° (3 Torr)). The nmr and ir spectra were nearly identical with those of the pure head-to-head adduct obtained by Eaton.[27] The isomers were separable by glpc (10% Carbowax 1000, 6 ft × 0.125 in., 100°, 30 ml/min) and were shown (by glpc) to be in the ratio of *ca.* 9:1. Based on the results of Eaton,[27,52] the major isomer is assumed to be the head-to-head isomer.

***endo*-7-Methylbicyclo[3.2.0]heptan-2-one and Isomers.** A 5.41-g (45.5 mmol) quantity of a 95:5 mixture of the above adducts, enriched in the major isomer by distillation through a Nester-Faust spinning band column (18 in. platinum band), was dissolved in 250 ml of ethyl acetate and hydrogenated over platinum at *ca.* 45 psi. The catalyst was filtered and the solution was concentrated.[46] The residual oil was distilled, giving 5.1 g (91%) of the mixture of isomers: bp 75–80° (15 Torr); ir (CCl_4) 1730, 1450 cm^{-1}; nmr (CCl_4) δ 3.00–1.10 (m, 9), 0.90 (d, 3, J = 7 Hz, Me).

***endo*-7-Methylbicyclo[3.2.0]hept-3-en-2-one (4a).** Conversion of 5.0 g (40 mmol) of the above mixture of saturated ketones into the corresponding enones by the method of Garbisch[30] afforded 2.0 g (41%) of distilled product, bp 68–71° (5 Torr). Analysis of this mixture by glpc (10% Carbowax 1000, 6 ft × 0.125 in., 110°, 30 ml/min) showed three peaks in a ratio of 83.5:11.5:5.0. Preparative glpc (20% Carbowax 1000, 5.5 ft × 0.25 in., 125°, 60 ml/min) gave the three pure ketones. Each of the two collected from the 83.5% and the 5% peaks had a methyl doublet centered at 0.95 ppm. The compound collected from the 11.5% peak had a methyl doublet centered at 1.30 ppm. On the basis of these data, a consideration of how the material was synthesized, and the results of Eaton,[27] the 5% peak is assigned as *endo*-6-methylbicyclo[3.2.0]-

(51) P. Yates, *Pure Appl. Chem.*, 16, 93 (1968), has noted that irradiation of a methanol solution of a compound apparently produces a more acidic medium than irradiation of a methanol-d_1 solution of the same compound.

(52) P. E. Eaton, personal communication.

hept-3-en-2-one (**37**), the 11.5% peak as *exo*-7-methylbicyclo[3.2.0]-hept-3-en-2-one (**4b**), and the 83.5% peak as *endo*-7-methylbicylo-[3.2.0]hept-3-en-2-one (**4a**). For **4a**: ir (CCl_4) 3045, 1700, 1600, 805 cm^{-1}; nmr (CCl_4) δ 7.70 (dd, 1, $J_{\alpha,\beta}$ = 5 Hz, $J_{\beta,\gamma}$ = 2 Hz, β vinyl proton), 6.15 (finely split d, $J_{\alpha,\beta}$ = 5 Hz, α vinyl proton), 3.20 (m, 1, C-1 bridgehead proton), 3.05–2.15 (m, 3, exo and C-5 bridgehead protons), 1.35 (m, 1, endo proton), 0.95 (d, 3, J = 6 Hz, endo Me); uv (95% EtOH) 232 nm (ϵ 8160) and 326 (78); mass spectrum (70 eV) *m/e* (rel intensity) 123 (5.5), 122 (56), 108 (24), 95 (34), 80 (100), 67 (22), 54 (31), 53 (69), 52 (32), 42 (30), 40 (64).

Anal. Calcd for $C_8H_{10}O$ (122.16): C, 78.65; H, 8.25, Found: C, 78.45; H, 8.40.

Unambiguous Synthesis of Methyl *cis*- and *trans*-6-Methylcyclohex-2-enecarboxylates (35 and 36). To a solution of lithium cyclohexylisopropylamide[53] prepared from 0.92 g (6.5 mmol) of cyclohexylisopropylamine and 2.8 ml (5.6 mmol) of 2 *M* methyllithium at −78° was added, under nitrogen, 0.74 g (4.8 mmol) of methyl 6-methylcyclohex-1-enecarboxylate (**42**).[38] The resulting yellow solution was stirred at −78° for 15 min, allowed to warm to 0°, and quenched with 5 ml of 20% aqueous acetic acid. Ether (50 ml) was immediately added and the mixture filtered through Celite. The Celite pad was washed with 2 × 50 ml of ether and the aqueous phase extracted with 2 × 50 ml of ether. The combined organic phases were washed with 2 × 50 ml of aqueous $NaHCO_3$, dried ($MgSO_4$), and distilled through an alembic still to give 0.38 g (51%) of a mixture of esters **35** and **36** in a ratio of 9:1, respectively (glpc): bath = 120° (10 Torr), ir (CCl_4) 3030, 1750, 1190, 1160, 1150 cm^{-1}; nmr (CCl_4) δ 5.55 (br s, 2, olefinic protons), 3.60 (s, 3, ester Me), 3.05 (d, J = 7 Hz, $>CHCH_3$); mass spectrum (70 eV), *m/e* (rel intensity) 155 (2), 154 (13), 122 (21), 95 (100), 94 (77), 79 (40), 67 (37), 55 (27), 40 (30), 38 (29).

Anal. Calcd for $C_9H_{14}O_2$ (154.20): C, 70.10; H, 9.15. Found: C, 70.41; H, 9.28.

Authentic Methyl *cis*- and *trans*-2-Methylcyclohexanecarboxylates (40 and 41). *o*-Toluic acid was treated with diazomethane, and the resulting ester reduced over rhodium on alumina at 45 psi, to give methyl *cis*- and *trans*-2-methylcyclohexanecarboxylates[54] in 66.5% overall yield. The ratio of isomers was *ca.* 9:1 [by glpc (3% SE-30, 9 ft × 0.125 in., 80°, 30 ml/min]: bp 88° (7 Torr); ir (CCl_4) 1750, 1175, 1135 cm^{-1}; nmr (CCl_4) δ 3.55 (s, 3, CO_2CH_3), 2.30–1.10 (m, 10), 0.90 (d, 3, J = 6 Hz, $CHCH_3$).

Equilibration of Methyl *cis*- and *trans*-2-Methylcyclohexanecarboxylates (40 and 41). To a solution prepared from 0.25 g of sodium and 25 ml of methanol was added 0.20 g of the mixture of **40** and **41** obtained from *o*-toluic acid. The solution was refluxed for 24 hr under dry nitrogen, poured into 50 ml of water, extracted with 3 × 30 ml of ether, dried ($CaCl_2$), concentrated,[46] and distilled giving a mixture of **40** and **41** which was shown by glpc (3% SE-30, 8 ft × 0.125 in., 80°, 30 ml/min) to be in a ratio of 1:9, respectively: bp 88° (7 Torr); ir (CCl_4); 1750, 1170, 1140 cm^{-1}, nmr (CCl_4) δ 3.54 (s, 3, CO_2CH_3), 2.20–1.00 (m, 10), 0.82 (d, 3, J = 6 Hz, $CHCH_3$).

Catalytic Hydrogenation of Methyl *cis*-6-Methylcyclohex-2-enecarboxylate (35). The major isomer obtained from the deconjugation of **42** was collected by preparative glpc (20% Carbowax 1000, 5.5 ft × 0.25 in., 115°, 88 ml/min) by allowing the half of the peak which overlapped that of the other isomer to elute without being collected. A 50.4-mg (0.328 mmol) quantity was collected and was shown by reinjection (10% Carbowax 1000, 6 ft × 0.125 in., 120°, 30 ml/min) to be free of the minor isomer. This material in 3 ml of methanol containing 3.1 mg of PtO_2 was hydrogenated (1 atm). The catalyst was filtered, and glpc analysis of the solution showed complete disappearance of the unsaturated ester and appearance of a single product, which was shown to be methyl *cis*-2-methylcyclohexanecarboxylate (**40**) by coinjection with an authentic sample.

Irradiation of *endo*-7-Methylbicyclo[3.2.0]hept-3-en-2-one (4a). To 542 mg (4.45 mmol) of **4a** in 110 ml of methanol (0.041 *M*) was added 533 mg of tetradecane as an internal standard. The solution was irradiated with blacklights as previously described[47] for 7 hr. The progress of the reaction was followed by glpc (5% DC-710, 8 ft × 0.125 in., 120°, 30 ml/min). With the aid of the internal standard, the assumption that all response factors are the same, and a knowledge of the retention times of the desired products, yields before work-up were estimated to be 7% of *exo*-5-methyl-7-ketonorbornene (**5a**) and 5% of the mixture of *cis*- and *trans*-methyl-6-methylcyclohex-2-enecarboxylates (**35** and **36**). The reaction mixture was poured into 110 ml of water and extracted with 4 × 50 ml of pentane. The pentane extract was dried ($MgSO_4$) and concentrated.[46] The remaining liquid was collected by preparative glpc (20% DC-710; 8 ft × 0.25 in., 140°, 81 ml/min) in two fractions. The first, 25 mg, was assigned as *exo*-5-methyl-7-ketonorbornene (**5a**) (4.8% isolated yield): ir (CCl_4) 3050, 1790, 700 cm^{-1}; nmr (CCl_4) δ 6.45 (finely split t, 2, olefinic protons), 2.70 (br, s, 1, C-1 proton), 2.40 (m, 1, C-4 proton), 1.85–1.25 (m, 3, endo and exo protons), 1.10 (d, 3, J = 7 Hz, exo Me); mass spectrum (70 eV) *m/e* (rel intensity) 94 (49), (P − CO), 79 (100), 77 (40). The second fraction was a mixture of methyl *cis*- and *trans*-6-methylcyclohex-2-enecarboxylates (**35** and **36**), 69 mg, (10% isolated yield), with the cis isomer shown to be the major ester product by glpc analysis under conditions which partially separated the isomers (10% Carbowax 1000, 100°, 30 ml/min). The spectra of this fraction were essentially identical with those of the mixture of **35** and **36** obtained from the deconjugation of methyl-6-methylcyclohex-1-enecarboxylate (**42**).

In a second irradiation of **4a** it was shown, by glpc analysis using conditions which were known to separate **4a** and *exo*-7-methylbicyclo[3.2.0[hept-3-en-2-one (**4b**) (10% Carbowax 1000, 6 ft × 0.125 in., 100°, 30 ml/min), that no trace of a compound with a retention time similar to that of **4b** was observable at any point during the course of the reaction.

Catalytic Hydrogenation of Methyl *cis*- and *trans*-Methylcyclohex-2-enecarboxylate (35 and 36). A 69-mg (0.45 mmol) quantity of the mixture of methyl *cis*- and *trans*-6-methylcyclohex-2-enecarboxylates (**35** and **36**) obtained from the irradiation of *endo*-7-methylbicyclo[3.2.0]hept-3-en-2-one (**4a**) was dissolved in 3 ml of methanol containing 4.4 mg of PtO_2 and hydrogenated (1 atm). The catalyst was filtered and the methanolic solution was analyzed by glpc (10% Carbowax 1000, 6 ft × 0.125 in., 100°, 30 ml/min). No trace of the unsaturated esters **35** and **36** was detectable and two completely separate products were observed. These products were identified as methyl *cis*- and *trans*-2-methylcyclohexanecarboxylates (**40** and **41**) by coinjection with authentic samples. The ratio of cis to trans ester was shown by glpc to be 93:7. The solution was concentrated by evaporation of the methanol at atmospheric pressure and ambient temperature giving an oil which had an nmr spectrum essentially identical with that of an authentic 9:1 mixture of **40** and **41** obtained from catalytic hydrogenation of methyl *o*-toluate.

***exo*-7-Methylbicyclo[3.2.0]heptan-2-ol and Isomers.**[14] A 7.8-g (64 mmol) quantity of a mixture of adducts obtained from the photochemical cycloaddition of allene to cyclopentenone was dissolved in 12 g (260 mmol) of absolute ethanol in a 1-l., three-necked flask. Approximately 500 ml of ammonia was condensed into the vessel, the ammonia was allowed to reflux, and 9 g (400 mg-atom) of sodium was added in small pieces to the mechanically stirred solution. The resulting blue solution was stirred for 1 hr and then ammonium chloride was added to destroy the excess sodium. The ammonia was evaporated and the salts were dissolved in 200 ml of water. This aqueous solution was extracted with 4 × 75 ml of ether, and the combined organic phases were dried ($MgSO_4$), concentrated[46] and distilled, giving 5.1 g (63%) of the mixture of isomeric alcohols: bp 81–84° (8 Torr); ir (CCl_4) 3600, 3320, 1060 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 126 (3), 108 (17), 83 (38), 82 (97), 81 (36), 69 (33), 67 (60), 57 (30), 55 (67), 53 (33), 43 (41), 41 (100), 40 (64), 39 (76).

***exo*-7-Methylbicyclo[3.2.0]heptan-2-one and Isomers.** To a mechanically stirred solution of 38 g (480 mmol) of pyridine in 600 ml of methylene chloride was added at once 24 g (240 mmol) of chromic anhydride. The resulting reddish solution was stirred for *ca.* 15 min and then 4.8 g (38 mmol) of the above mixture of alcohols (dissolved in 20 ml of methylene chloride) was added and the resulting mixture was stirred for 1 hr. Methylene chloride (300 ml), 19 g (240 mmol) of pyridine, and 12 g (120 mmol) of chromic anhydride were then added, in succession, to the solution. The mixture was stirred for an additional 1 hr, the methylene chloride was decanted, and the tarry residue was washed with 3 × 100 ml of methylene chloride. The combined organic phases were washed with 4 × 200 ml 5% aqueous NaOH, 2 × 200 ml 1 *N* HCl, 400 ml of saturated aqueous $NaHCO_3$, and 400 ml of saturated aqueous NaCl, dried ($MgSO_4$), concentrated,[46] and distilled, giving 3.9 g (83%) of the mixture of saturated ketones: bp 70–76° (9 Torr); ir (CCl_4) 1740 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 125 (5), 124 (45), 83 (64), 82 (97), 81 (42), 69 (94), 48 (42), 67 (64), 55 (61), 54 (64), 53 (42), 41 (83), 39 (100).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.18; H, 9.88.

(53) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).

(54) J. Klein and G. Levin, *J. Amer. Chem. Soc.*, **80**, 1707 (1958).

exo-7-Methylbicyclo[3.2.0]hept-3-en-2-one (**4b**). A 4.9g- (40 mmol) quantity of *exo*-7-methylbicyclo[3.2.0]heptan-2-one and its isomers was converted to the corresponding enones by the method of Garbisch[30] affording 2.2 g (45%) of distilled product, bp 68–72° (7 Torr). Analysis of the mixture by glpc (20% Carbowax 1000, 5 ft × 0.25 in., 110°, 73 ml/min) showed three peaks. Subsequent isolation and nmr spectra showed the presence of all possible isomers. The first and major peak (*ca.* 60%) was the desired *exo*-7-methylbicyclo[3.2.0]hept-3-en-2-one (**4b**). The second peak was a mixture of *endo*-7-methylbicyclo[3.2.0]hept-3-en-2-one (**4a**) and *exo*-6-methylbicyclo[3.2.0]hept-3-en-2-one (**38**). The last peak was *endo*-6-methylbicyclo[3.2.0]hept-3-en-2-one (**37**).

For *exo*-7-methylbicyclo[3.2.0]hept-3-en-2-one: ir (CCl_4) 3030, 1710, 1590; nmr (CCl_4) δ 7.65 (dd, 1, $J_{\alpha,\beta}$ = 5 Hz, $J_{\beta,\gamma}$ = 2 Hz, β vinyl proton), 6.10 (d, $J_{\alpha,\beta}$ = 5 Hz, α vinyl proton), 3.30 (br s, 1, C-5 proton), 2.42 (m, 1, C-1 proton), 2.30–1.65 (m, 3, C-6 and C-7 protons), 1.28 (d, 3, J = 6 Hz, Me); uv max (95% EtOH) 227 nm (ϵ 5750) and 325 (73); mass spectrum (70 eV) *m/e* (rel intensity) 123 (4), 122 (43), 108 (29), 80 (100), 78 (33), 67 (22), 54 (23), 53 (72), 52 (29), 42 (35), 40 (59).

Anal. Calcd for $C_8H_{10}O$ (122.16): C, 78.65; H, 8.25. Found: C, 78.44; H, 8.46.

Irradiation of *exo*-7-Methylbicyclo[3.2.0]hept-3-en-2-one (4b). A solution of 571 mg (4.68 mmol) of *exo*-7-methylbicyclo[3.2.0]hept-3-en-2-one (**4b**) and 573 mg of tetradecane in 135 ml of methanol (0.034 *M* in enone) was irradiated with blacklights. Upon completion of the reaction, the glpc yields before work-up were shown to be 4% ester and 6% norborenone. The reaction solution was poured into water and extracted into pentane. The pentane extract was dried ($MgSO_4$) and concentrated.[46] The remaining liquid was collected by preparative glpc (20% DC-710; 8 ft × 0.25 in., 140°, 80 ml/min) in two fractions. The first was assigned as *endo*-5-methyl-7-ketonorbornene (**5b**): nmr (CCl_4) δ 6.40 (m, 2, olefinic protons), 2.70 (m, 1, C-1 proton), 2.25 (m, 1, C-4 proton), 1.60–1.15 (m, 3, endo and exo protons), 0.90 (d, J = 6 Hz, endo Me). The second fraction was a mixture of methyl *cis*- and *trans*-6-methylcyclohex-2-enecarboxylate (**35** and **36**). The trans isomer was the major component as shown by glpc coinjection (10% Carbowax 1000, 6 ft × 0.125 in., 100°, 30 ml/min) with an authentic mixture of the cis and trans esters.

Catalytic Hydrogenation of Methyl *cis*- and *trans*-6-Methylcyclohex-2-enecarboxylates. An 18-mg (0.15 mmol) quantity of the mixture of esters obtained from the irradiation of *exo*-7-methylbicyclo[3.2.0]hept-3-en-2-one (**4b**) was dissolved in 1 ml of methanol containing 3 mg of PtO_2 and hydrogenated (1 atm). The catalyst was filtered and the methanolic solution was analyzed by glpc (5% DC-710, 8 ft × 0.125 in., 30 ml/min). No trace of the unsaturated esters **35** and **36** was detectable and two completely separable products were observed. These products were identified as methyl *cis*- and *trans*-2-methylcyclohexanecarboxylates (**40** and **41**) by coinjection with authentic samples. The ratio of the cis to trans ester was shown by glpc to be 20:80.

Irradiation of *endo*-6-Methylbicyclo[3.2.0]hept-3-en-2-one (37). A solution of 35.6 mg (0.296 mmol) of *endo*-6-methylbicyclo[3.2.0]-hept-3-en-2-one (**37**) in 8 ml of methanol (0.037 *M*) was irradiated for 16 hr with blacklights. The reaction was followed by glpc (10% Carbowax 1000, 6 ft × 0.125 in., 115°, 30 ml/min). A product appeared and then disappeared during the course of the reaction. This transient compound is believed to be *exo*-6-methylbicyclo]3.2.0]hept-3-en-2-one (**38**) and its appearance is taken as further evidence that stereochemistry is lost at C-6 of bicyclo[3.2.0]-hept-3-en-2-ones upon irradiation. At the end of the irradiation the sole product detectable by glpc had the same retention time as *exo*-5-methyl-7-ketonorbornene (**5a**).

3-Chloro-3,4-dimethylbicyclo[3.2.0]heptan-2-one. A solution of 2.64 g (18.3 mmol) of 3,4-dimethyl-4-chlorocyclopentenone (**44**)[49] in 450 ml of methylene chloride in the low temperature irradiation apparatus (−78°) was saturated with ethylene and irradiated (Pyrex). Ethylene was bubbled through the solution during the irradiation. The reaction was followed by glpc (3% SE-30, 8 ft × 0.125 in., 110°, 30 ml/min) and was complete within 5 hr. The solution was allowed to warm to room temperature, dried ($MgSO_4$), concentrated, and distilled to give 2.1 g (66%) of 3-chloro-3,4-dimethylbicyclo[3.2.0]heptan-2-one: bp 82° (0.25 Torr); ir (CCl_4) 1750 cm^{-1}; nmr (CCl_4) δ 3.15 (m, 1, C-1 proton), 2.70–2.50 (m, 6), 1.52 (s, 3, C-3 methyl), 1.19 (d, 3, J = 6 Hz, exo C-4 methyl); mass spectrum (70 eV) *m/e* (% rel abundance) 174 (5), 172 (15), 116 (23), 109 (60), 108 (23), 93 (23), 91 (23), 89 (24), 81 (60), 79 (39), 77 (23), 67 (42), 65 (23), 55 (100), 53 (42), 41 (48), 39 (62).

3,4-Dimethylbicyclo[3.2.0]hept-3-en-2-one (43). A 2.23-g (12.4 mmol) quantity of distilled[55] 3-chloro-3,4-dimethylbicyclo[3.2.0]-heptan-2-one was dehydrochlorinated with collidine[56] giving 1.3 g (76%) of 3,4-dimethylbicyclo[3.2.0]hept-3-en-2-one (**43**): bp 65° (1.3 Torr); ir (CCl_4) 1700, 1650 cm^{-1}; nmr (CCl_4) δ 3.20–2.10 (m, 4, exo and bridgehead protons), 1.93 (finely split s, 3, C-4 methyl), 1.75–1.30 (m, 5, endo protons and C-3 methyl with the finely split methyl s at δ 1.65); uv max (95% EtOH) 243 nm (ϵ 11,800) and 311 (134); mass spectrum (70 eV) *m/e* (% rel abundance) 137 (3.8), 136 (35), 108 (100), 93 (66), 91 (30), 80 (79), 79 (53), 77 (35), 53 (25), 51 (24), 41 (23), 39 (53).

Anal. Calcd for $C_9H_{12}O$ (136.19): C, 79.37; H, 8.88. Found: C, 79.03; H, 8.78.

Irradiation of 3,4-Dimethylbicyclo[3.2.0]hept-3-en-2-one (43). A 573-mg (4.20 mmol) quantity of 3,4-dimethylbicyclo[3.2.0]hept-3-en-2-one (**43**) dissolved in 100 ml of methanol (0.042 *M*) was irradiated with blacklights. The reaction was followed by glpc (3% SE-30, 8 ft × 0.125 in., 110°, 30 ml/min) and was determined to be complete after *ca.* 51 hr. The solution was poured into 100 ml of water and extracted with 4 × 75 ml of pentane. The combined organic phases were dried ($MgSO_4$) and concentrated.[46] The concentrated product mixture was collected by preparative glpc (20% Carbowax 1000, 5 ft × 0.125 in., 140°, 104 ml/min) in three fractions. Fraction 1 was assigned as 1,2-dimethyl-7-ketonorbornene dimethyl ketal: ir (CCl_4) 3160, 1185, 1145, 1125, 1080, 1060 cm^{-1}; nmr (CCl_4) δ 5.50 (br s, 1, olefinic proton), 3.18 (s, 3, OMe), 3.10 (s, 3, OMe), 2.54 (finely split t, 1, bridgehead proton), 2.10–1.50 (m, 5, exo protons and C-2 methyl with the methyl doublet, J = 2 Hz, at δ 1.60), 1.13 (s, 3, C-1 methyl), 0.90 (br s, 1, endo proton), 0.80 (br s, 1, endo proton); mass spectrum (70 eV) *m/e* (% rel abundance) 182 (21), 151 (22), 107 (55), 93 (24), 75 (42), 58 (30), 43 (100).

Fraction 2 was a minor product and was assigned as 1,2-dimethyl-7-ketonorbornene (**46**): ir (CCl_4) 3050, 1780 cm^{-1}; nmr (CCl_4) δ 6.08 (br s, 1, olefinic proton), 2.67 (finely split t, 1, J = 3 Hz, bridgehead proton), 2.20–1.55 (m, 5, exo protons and C-2 methyl with the methyl doublet, J = 2 Hz, at 1.77), 1.50–1.00 (m, 5, endo protons and C-1 methyl with the methyl singlet at 1.13).

Fraction 3 was assigned as methyl 2,3-dimethylcyclohex-2-enecarboxylate (**45**): ir (CCl_4) 1740, 1155 cm^{-1}; nmr (CCl_4) δ 3.58 (s, 3, ester methyl), 2.82 (br s, 1, methine proton), 2.20–1.40 (m, 10, methylene and methyl protons with both methyls appearing as a broad singlet at 1.60); mass spectrum (70 eV) *m/e* (% rel abundance) 168 (12), 109 (100), 108 (28), 67 (38), 41 (22), 32 (22).

Anal. Calcd for $C_{10}H_{16}O_2$ (168.23): C, 71.39; H, 9.59. Found: C, 71.25, H, 9.59.

The glpc yields were estimated to be *ca.* 4% **45**, 25% ketal, and less than 1% **46**.

(55) Good yields could not be obtained with undistilled chloroketone.

(56) E. W. Warnhoff, D. G. Martin, and W. S. Johnson, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, pp 162–163.