The Photochemistry of Conjugated *cis*-Bicyclo[5.1.0]octenones, *cis*- and *trans*-Bicyclo[5.2.0]non-2-en-4-ones, and Their Methylene Analogs

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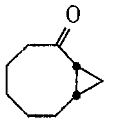
The photochemistry of 1,4,4-trimethyl-*cis*-bicyclo[5.1.0]oct-5-en-2-one, *cis*-bicyclo[5.1.0]oct-2-en-4-one, and their methylene derivatives has been studied. In the first instance, 1,3 shift of the bond common to the two rings occurs, with rearrangement occurring from the singlet manifold. Photoisomerization of its methylene derivative likewise is a singlet state transformation. In sharp contrast, although the 2-en-4-one bicyclic and the derived conjugated diene also undergo excited state vinylcyclopropane–cyclopentene bond reorganization, these reactions proceed readily from the respective triplet states. These differences have been rationalized in terms of conformational factors particularly as they relate to bond overlap in the S_1 or the transoid (*i.e.*, as relates to π-bond overlap) T_1 states. The *cis*- and *trans*-bicyclo[5.2.0]non-2-en-4-ones, as well as their methylene congeners, do not exhibit an analogous propensity for rearrangement. Rather, polymerization was noted in aprotic solvents throughout this latter series.

Recent comparative studies of the photochemistry of medium-ring 2-cycloalkenones and their more highly unsaturated counterparts have revealed that the additional centers of unsaturation present in the latter group of compounds, whether conjugated or not, frequently participate in chemical reaction. For example, although the propensity of *cis*-2-cycloheptenone and *cis*-2-cyclooctenone for rapid intramolecular cis–trans isomerization from their triplet states is known to be exceptionally facile,[3–5] irradiation of the cross-conjugated ketones 2,6-cycloheptadienone and 2,7-cyclooctadienone is more complicated. Under a variety of conditions there are produced intermediates, the nature of which remains to be fully clarified, which can be trapped by both protic solvents and dienes to give bicyclo[3.2.0]heptane and bicyclo[3.3.0]octane derivatives, respectively.[6,7] Also, the straightforward valence isomerization of 2,4-cycloheptadienone (as its 2,6,6-trimethyl derivative)[8] differs notably from the preference of the more flexible 2,4-cyclooctadienone homolog for conversion to its monotrans form and dimerization.[9,10] When 2,6-cyclooctadienone is irradiated in reactive solvents, trapping of the 2-trans-6-cis isomer is found, whereas inert solvents permit photorearrangement to tricyclo[3.2.1.0^{2,6}]octan-2-one.[9,11]

In contrast to the photochemical behavior of *cis*-2-cyclooctenone, the corresponding formally conjugated cyclopropyl analogs **1** and **2** exhibit widely differing stereochemically dependent excited-state reactivities.[12] Bicyclo[6.1.0]nonan-3-one and bicyclo[6.1.0]nonan-4-one, molecules in which the cyclopropane ring is not conjugated with the carbonyl function, also undergo facile photorearrangement.[13,14] Ostensibly, the well-recognized capability of the labile three-membered ring to transmit or extend conjugation and to exhibit many of the reactions of double bonds has encouraged the extensive investigation and delineation of excited-state cyclopropyl ketone reactivities.[15]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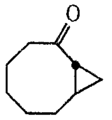
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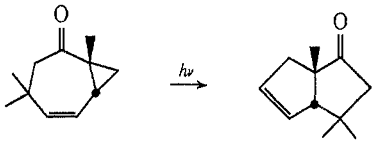
An intriguing question concerned the photochemical behavior of medium-ring ketones which possess a combination of both types of functional groups, *i.e.*, a double bond and a strained fused ring system. The present study had as its goals the elucidation of possible bond reorganization pathways, stereochemistry, and electronic mechanism in a series of bicyclo[5.1.0]octenones and bicyclo[5.2.0]nonenones. Because the exocyclic methylene derivatives of these ketones lack an in-plane unshared electron pair and consequently have no comparable $n \rightarrow \pi^*$ excited states from which to react, elucidation of the reactivity of the $\pi \rightarrow \pi^*$ states in these related hydrocarbons was considered to be of considerable intrinsic interest as well, and such have also been examined.[16]

1,4,4-Trimethyl-*cis*-bicyclo[5.1.0]oct-5-en-2-one (3).—Direct irradiation of **3**[17] [$\lambda_{\max}^{C_2H_5OH}$ 207 nm (ϵ 3710) and 272 (266)] above 250 nm (Corex filter) in ether solution resulted in gradual transformation into a single



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[1] Ohio State University Postdoctoral Fellow, 1967–1969.

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[3] P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964); **87**, 2052 (1965); P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

[4] E. J. Corey, M. Tada, R. LeMahieu, and L. Libit, *J. Amer. Chem. Soc.*, **87**, 2051 (1965).

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[7] J. K. Crandall and R. P. Haseltine, *J. Amer. Chem. Soc.*, **90**, 6251 (1968).

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

[10] G. L. Lange and E. Neidert, *Tetrahedron Lett.*, 4215 (1971); 1349 (1972).

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[12] L. A. Paquette and R. F. Eizember, *J. Amer. Chem. Soc.*, **91**, 7108 (1969).

[13] J. K. Crandall, J. P. Arrington, and C. F. Mayer, *J. Org. Chem.*, **36**, 1428 (1971).

[14] S. Moon and H. Bohm, *J. Org. Chem.*, **36**, 1434 (1971).

[15] For leading references to this vast field, see (a) W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Amer. Chem. Soc.*, **92**, 6273 (1970); (b) H. E. Zimmerman and C. M. Moore, *ibid.*, **92**, 2023 (1970); (c) A. J. Bellamy and G. H. Whitham, *Tetrahedron*, **24**, 247 (1968); (d) D. C. Heckert and P. J. Kropp, *J. Amer. Chem. Soc.*, **90**, 4911 (1968); (e) L. D. Hess and J. N. Pitts, Jr., *ibid.*, **89**, 1973 (1967).

[16] For early preliminary reports of a portion of this investigation, see (a) L. A. Paquette, G. V. Meehan, and R. F. Eizember, *Tetrahedron Lett.*, 995 (1969); (b) *ibid.*, 999 (1969).

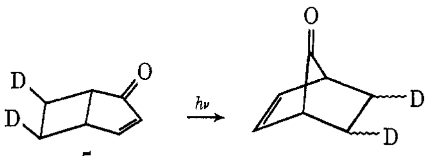
[17] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1354 (1965).

monomeric photoproduct (10% yield after 5 hr, cyclooctane as internal standard). The concurrent production of substantial quantities of polymeric material was also evident. Preparative scale gas chromatographic isolation gave an isomeric ketone identified as **4** chiefly on the basis of its spectral properties. Its infrared spectrum showed a carbonyl stretching band at 1745 cm^{-1} indicative of a five-membered ring ketone and double bond absorption at 1680 cm^{-1}. The virtually negligible electronic spectrum [$\lambda_{max}^{C_2H_5OH}$ 286 nm (ϵ 40)] attested to the absence of the original chromophore. This information, when taken together with the two-proton olefinic signal at δ 5.68 (br s), the two distinct allylic hydrogen multiplets at 2.72 (1 H, H_5) and 2.40 (2 H, H_8), the AB quartet for the α-carbonyl methylene group (2.12, J_{AB} = 16 Hz, Δ_{AB} = 19.5 Hz), and the methyl singlets at 1.29 (CH_3 group at C_1) and 1.10 (CH_3 groups at C_4), is considered to support unequivocally the structural assignment.

When the irradiation was repeated using methanol as solvent, the rate of production of **4** was significantly enhanced; this effect was not found with pentane. The photorearrangement was seen not to be completely quenchable with varying concentrations of piperylene (E_T^{trans} = 59 kcal/mol; E_T^{cis} = 57 kcal/mol) or naphthalene (E_T = 61 kcal/mol) in ether solution. Ketone **3** again polymerized slowly under these conditions. Attempts to generate the triplet of **3** by making recourse to sensitization with benzophenone (E_T = 68.8 kcal/mol) or acetone (E_T = 82 kcal/mol) under conditions where the sensitizer absorbed the major portion of the incident radiation was found to be ineffective in achieving enhanced rearrangement to **4**. Irradiations of tubes containing the sensitizers were performed competitively with direct irradiation of solutions with the identical concentrations of **3** but lacking sensitizer. After adjustment was made for the differences in light capture, sensitization was considered not to be operative.

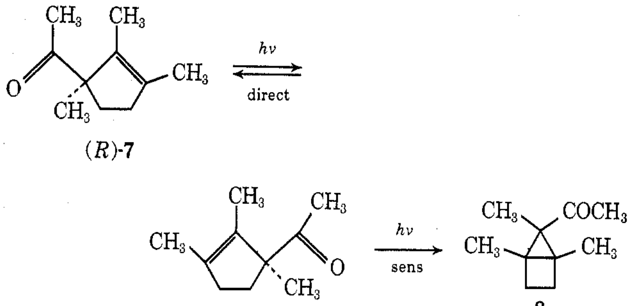
Assuming that the triplet state of **3** lies at a level capable of sensitization by one of these ketones, it can be concluded that T_1 does not rearrange. We cannot rule out the possibility that a higher triplet of **3** is responsible for the rearrangement. However, it is more likely either that the n → π^* singlet state (S_1) is involved or that an electronically excited state relaxes to a ground-state species (speculation would of course center about the C_2–C_3 trans isomer of **3**) which subsequently undergoes the intramolecular rearrangement. Although we have not distinguished between these alternatives, the behavior of the bicyclo[5.2.0]nonenones (see below) and the thermal reactivity of **3**[18] suggest that the former is the more realistic pathway.

On this basis, we are left with the first excited singlet of **3** as responsible for the observed photochemical 1,3 shift. Cargill has suggested that such processes tend to be nonconcerted reactions as evidenced by the stereorandomization of deuterium label noted in the conversion of **5** to **6**, a result inconsistent with a [${}_\sigma 2_s + {}_\pi 2_s$] pathway.[19] However, there are conflicting opinions on this point. For example, Baggiolini, Schaffner,



5 **6**

and Jeger[20] have observed that direct irradiation of optically active **7** proceeds intramolecularly to give racemic material of the same gross structure. Because triplet quenchers were ineffective and sensitization gave rise to the oxadi-π-methane product **8**, a concerted



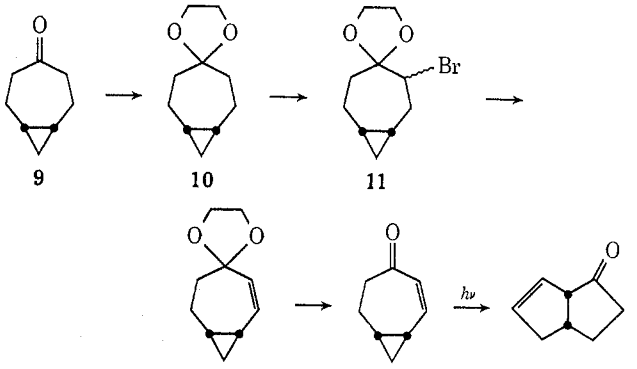
(*R*)-**7**

(*S*)-**7**

8

reaction was considered to be operative. These apparently divergent results can be understood if electronic relaxation to ground-state diradicals operates in certain systems (*e.g.*, **5**) but not in others such as **7**. Unfortunately, because the retention of stereochemistry which accompanies the bond relocation in **3** may be the result of control by thermodynamic factors (the trans isomer of **4** would be highly strained), no definitive conclusions relating to the timing of the **3** → **4** rearrangement can be drawn at this time.

cis-**Bicyclo[5.1.0]oct-2-en-4-one (13).**—Treatment of ketal **10**, available in 92% yield from the known ketone **9**, with excess bromine in ether at room temperature gave monobromide **11**, which without further purification was dehydrobrominated by means of potassium *tert*-butoxide in dry dimethyl sulfoxide at room temperature (50% overall yield). Hydrolysis of the resulting monounsaturated ketal **12** with 3% sulfuric



9 **10** **11**

12 **13** **14**

acid afforded the desired **13** in 95% yield. This material exhibits an infrared carbonyl stretching frequency at 1665 cm^{-1} and an electronic spectrum (isooctane solution) characterized by maxima at 237 (ϵ 7700) and 322 nm (50) and a shoulder at 337 nm (40). Its nmr spectrum (in CCl_4) consists of a one-proton multiplet at δ 0.57, a broad absorption of area 7 at 0.9–3.05, and

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[18] L. A. Paquette, R. P. Henzel, and R. F. Eizember, *J. Org. Chem.*, **38**, 3257 (1973).

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

[20] E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).

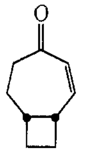
doublets ($J = 12.5$ Hz) at 5.83 and 6.83 due to H_3 and H_2, respectively.

The photolysis of pentane solutions of **13** through a Pyrex filter ($\lambda > 280$ nm) led to the formation of a lone photoproduct in 60% yield after 1 hr. Spectral data on a purified sample of this compound revealed it to be a β,γ-unsaturated cyclopentanone (see Experimental Section). Unequivocal proof of structure **14** was achieved by direct comparison with an authentic sample of *cis*-bicyclo[3.3.0]oct-7-en-2-one.[21]

In apparent contrast to **3**, the photorearrangement of **13** in acetone solvent provided a yield of **14** (82% after 1 hr) greater than that realized in the direct irradiation. Although these observations might be considered superficial since the acetone runs generated measurably less polymer than the pentane experiments, sensitization is operative since the rate of conversion to **14** remains unabated despite absorption by acetone of greater than 90% of the incident radiation. Finally, although benzophenone was expectedly ineffective as a sensitizer, the isomerization was not quenched by concentrations of naphthalene and piperylene as high as 1 *M*.

These results support the conclusions that under the conditions of direct irradiation either $n \rightarrow \pi^*$ singlet states are primarily involved or rates of intramolecular rearrangement of the corresponding triplet states are faster than diffusion control. Whatever the case, the formation of the same product from the preformed triplet reveals that rearrangement by the respective triplet state is possible in this instance. That the singlet state of **13** can undergo cyclopropyl bond cleavage and allylic rearrangement is suggested by the thermal behavior of this ketone.[18]

***cis*- and *trans*-Bicyclo[5.2.0]non-2-en-4-ones (15 and 16).**[22]—This aspect of the work was concerned with the behavior of the structurally less constrained epimeric bicyclo[5.2.0]nonenyl ketones **15** and **16**. Although these systems no longer have the latent potential for vinylcyclopropane rearrangement, which generally is thermodynamically exothermic by about 25 kcal/mol,[23] they are free to undergo an analogous vinylcyclobutane bond reorganization. Moreover, relatively ready accessibility[22] to both the cis and trans isomers in this series promised potential solution to the question of whether concerted 1,3 carbon shifts or stepwise pathways were operative. The ground-state energy difference between **17** and **18** did not appear to be sufficiently great to deter their direct formation from **15** and **16**, respectively, should synchronous processes be operational. On the other hand, the difference was deemed adequate to guarantee the favored production of **17** should dipolar or diradical intermediates intervene.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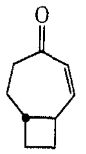
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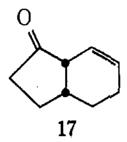
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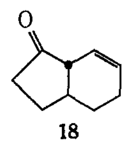
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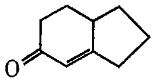
It was soon discovered, however, that these *a priori* considerations were not to apply because **15** and **16** do not follow the photochemical precedent established by **13**. Thus, upon photolysis (200-W Hanovia lamp) of **15** in dilute pentane solution through Pyrex, rapid disappearance of starting material was observed ($t_{1/2}$ ~30 min) but no new volatile products were generated. After 1 hr, little **15** remained (cyclododecane as internal standard) and a white, insoluble material had deposited on the walls of the vessel. Similar results were realized in dilute acetone solution, in which case complete reaction was noted after only 30 min.

Comparable photolysis of **16** in acetone, glyme, or pentane solution likewise resulted only in rapid conversion to polymeric substances. No monomeric products in significant quantity (>1%) were detected. In contrast, when methanol was employed as solvent, a mixture of five major components was formed. Four of these substances were identified as methoxy ketones and were not further characterized. The fifth component, amounting to 9% of the mixture, was identified as **19** by comparison with an authentic sample.[24] Since this conjugated ketone was a minor product, mechanistic considerations of its origin were not given further attention.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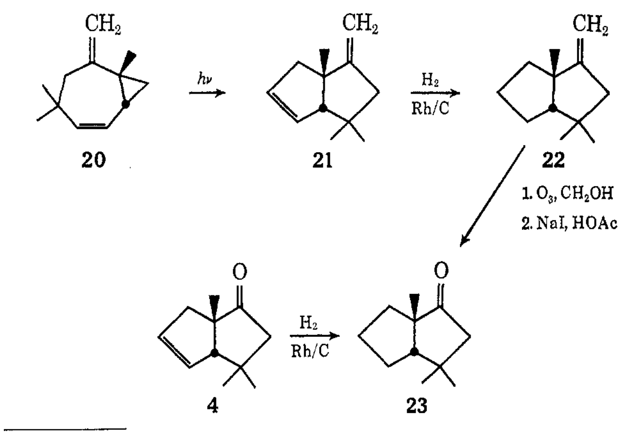
2-Methylene-1,4,4-trimethyl-*cis*-bicyclo[5.1.0]oct-5-ene (20).—The divinylcyclopropane **20** was conveniently prepared by the Wittig reaction of **3** with methylenetriphenylphosphorane. This colorless liquid exhibited only intense end absorption (C_2H_5OH solution) in the ultraviolet region. Upon direct irradiation of **20** in pentane or methanol through Vycor ($\lambda > 220$ nm), an isomeric hydrocarbon was produced in 24 and 56% yields, respectively, after 10 hr. There was also formed 1–3% of an unidentified volatile substance. The primary photoproduct showed nmr features entirely compatible with structure **21**. Corroborative evidence for this assignment was gained ultimately by selective hydrogenation to **22** over 5% rhodium on carbon and



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[21] N. A. Lebel and L. A. Spurlock, *Tetrahedron*, **20**, 215 (1964). We thank Professor Lebel for generously providing us with a sample of **14**.

[22] Discussion of the synthesis of these compounds is deferred to the accompanying paper.

[23] W. von E. Doering and E. K. G. Schmidt, *Tetrahedron*, **27**, 2005 (1971), and relevant references cited therein.

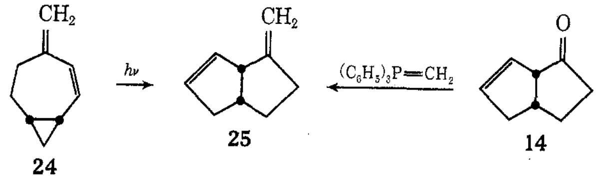
[24] G. S. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

ozonolysis of this dihydro derivative to the cyclopentanone derivative **23**. This compound was identical with that obtained from independent hydrogenation of **4**. The attempted conversion of **4** to **21** under Wittig conditions was not successful, perhaps because of steric factors.

In additional studies, it was observed that photolysis of **20** in dilute acetone solution through either Vycor or Pyrex afforded only minute amounts of **21**. However, extensive polymerization was noted. A similar result was obtained when we sought to generate the triplet of **20** by benzophenone sensitization (*tert*-butyl alcohol solution) under conditions where this ketone absorbed over 97% of the incident light. The efficiency of the triplet transfer to **20** was unequivocally established in the latter series of experiments by its effective quenching of benzopinacol formation when benzhydrol was added. Since **21** was independently found to be stable to these conditions, the polymerization cannot be construed as arising from the excited triplet state of **21**.

Accordingly, there exists a marked reluctance of the **20** triplet to rearrange to **21**. Since intersystem crossing of $S_1 \rightarrow T_1$ is not generally observed in olefinic systems, it appears that, in the case of **20**, S_1 leads to rearrangement but the triplet is ineffective in this regard and engenders only polymerization. This gross behavior parallels the photochemistry of structurally related ketone **3**, despite the fact that different excited states are quite likely involved ($n \rightarrow \pi^*$ for **3** and $\pi \rightarrow \pi^*$ for **20**).

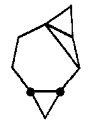
4-Methylene-*cis*-bicyclo[5.1.0]oct-2-ene (24).—The synthesis of **24** required only a Wittig reaction on ketone **13**. The electronic spectrum of this diene (isooctane) consisted of a lone maximum at 237 nm (ϵ 17,030). Sensitized photolysis of **24** in dilute acetone solution (Pyrex optics) resulted in rapid conversion in high (95+%) yield to a single photoproduct. The resulting colorless oil was readily identified as **25** by virtue of its spectral characteristics and unequivocal synthesis from **14**. When pentane was employed as solvent (Vycor filter), the process became more complex; bicyclic diene **25** was again formed as the major product (53% yield), but four additional minor components (not characterized) were also observed. A separate experiment clearly showed that these lesser products were not derived from **25** since, except for a small amount of polymer formation, the latter methylene derivative was stable to the irradiation conditions. Since the triplet-sensitized process afforded only **25** and no side products, the occurrence of singlet transfer to **24** in acetone solution is highly remote.



24 **25** **14**

Consequently, the reactivity profile of **24** lies in marked contrast to the photochemical behavior displayed by **20**, two conjugated methylenecyclohexenes,[25] and a 1-methylene-2,5-cyclohexadiene derivative.[26] In these latter examples, there is seen a complete absence of monomeric products in the sensitized experiments, the di-π-methane rearrangements occurring preferentially from the respective singlet excited states. Owing to observations of efficient triplet bond reorganization in certain rigid bicyclic polyene hydrocarbons lacking exocyclic methylene groups, the absence of triplet rearrangement in molecules such as **31** was attributed to a "free rotor" effect.[27] According to this concept, triplet energy was capable of efficient dissipation as a result of free rotation about bonds of low π order, particularly that to the exocyclic carbon atom. However, Kende's recent finding that 2-methylene-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene, a "free rotor" polyene, exhibits highly regiospecific rearrangement, preferentially *via* a triplet excited state,[28] points to limitations of the "free rotor" hypothesis.[27c]

A possible alternative explanation for the differing behavior of **20** and **24** may be that the energy of the triplet $\pi \rightarrow \pi^*$ excitation of **24** is heavily concentrated in the conjugated diene moiety, a phenomenon which is expected to facilitate migration of the stereoelectronically favored internal cyclopropyl bond. Reaction products which are to be expected[29] from bicyclobutane intermediate **26** were carefully sought but could not be found when **24** was irradiated in methanol. Under these conditions, no solvent-incorporated products were found and the results were approximately the same as those realized in pentane solution. Therefore, the cyclopropyl function appears to exert a significant influence on the reactivity of the transoid diene moiety in the excited states of **24**.



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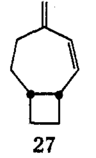
***cis*- and *trans*-4-Methylenebicyclo[5.2.0]non-2-enes (27 and 28).**—In an effort to derive added significance from the highly stereoselective conversion of **24** to **25**, our study was expanded to include the photochemistry of dienes **27** and **28**. Photochemical shifts of a cyclo-



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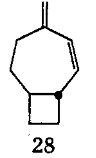

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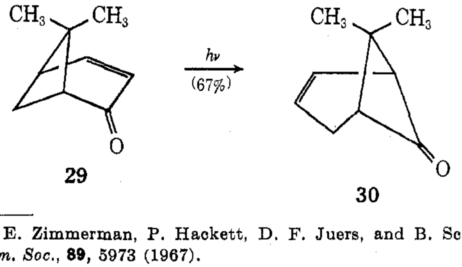

29 **30**

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[25] (a) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **89**, 5971 (1967); (b) W. G. Dauben and W. A. Spitzer, *ibid.*, **90**, 802 (1968).

[26] H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schröder, *J. Amer. Chem. Soc.*, **89**, 5973 (1967).

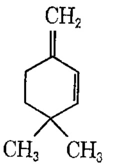
[27] (a) J. S. Swenton, A. R. Crumrine, and T. J. Walker, *J. Amer. Chem. Soc.*, **92**, 1406 (1970); (b) H. E. Zimmerman and G. R. Epling, *ibid.*, **92**, 1411 (1970); (c) *ibid.*, **94**, 8749 (1972).

[28] Z. Goldschmidt and A. S. Kende, *Tetrahedron Lett.*, 4625 (1971).

[29] W. G. Dauben and C. D. Poulter, *Tetrahedron Lett.*, 3021 (1967); W. G. Dauben and J. S. Ritscher, *J. Amer. Chem. Soc.*, **92**, 2925 (1970).

butane bond are rare, but nevertheless known, as exemplified by the conversion of verbenone (**29**) to chrysanthenone (**30**).[30] Comparable migrations in purely olefinic systems have, however, not been reported.

Upon direct irradiation in pentane through Pyrex, both **27** and **28** were found to be slowly consumed with concomitant generation of polymeric substances. Sensitized irradiation in acetone solution gave comparable results. This behavior is exceedingly reminiscent of the case of **31**.[25b] In this example, sensitized photolysis in pentane and methanol as well as direct irradiation in pentane gave only higher molecular weight products. Only when irradiated directly in methanol did **31** form monomeric products. These were identified as methyl ethers derived from solvent capture of intermediate bicyclobutane **32**.



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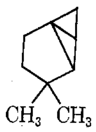


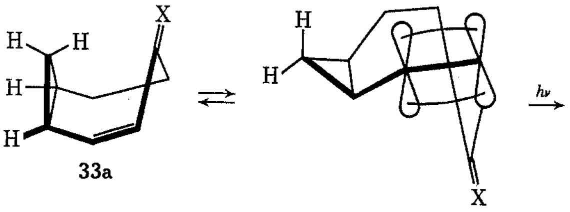
32

When **27** and **28** were photolyzed directly in methanol, slow disappearance of the dienes was again observed. However, volatile products were not in evidence. Thus we conclude tentatively that these dienes probably do not experience comparable electronic reorganization to give bicyclobutane derivatives.

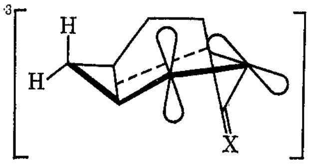
Discussion

A most striking aspect of the photochemistry of the *cis*-bicyclo[5.1.0]octenones and their methylene derivatives is the dramatic difference in behavior of the "cross-functionalized" (**3** and **20**) and linearly conjugated systems **13** and **24**. Although relocation of the strained internal bond operates in all four examples, the vinylcyclopropane rearrangements occur uniquely by way of the singlet excited states of **3** (n → π^*) and **20** ($\pi \rightarrow \pi^*$). In contrast, the isomerizations of **13** and **24** are efficient from their triplet manifolds. That bicyclic product (*i.e.*, **14**) was also found in the direct irradiation of **13** leaves unproven whether this ketone is formed from the singlet state as well. The presence of a cyclopropane ring is essential to photorearrangement of **13** and **24**, since the homologous cyclobutane derivatives **15**, **16**, **27**, and **28** do not give any evidence of isomerization.

Examination of Dreiding models of **13** and **24** has indicated the two more stable ground-state conformations of these molecules to be as shown in **33** with **33b** enjoying fewer nonbonded interactions. In neither structure is the C_2–C_3 π bond seen to be aligned stereoelectronically for favorable overlap with the strained C–C bond common to the two rings. The difference in behavior of the singlet and triplet states of **33** may arise not only as a consequence of spin pairedness but perhaps as importantly because of geometry and energy dissipation considerations. Thus, when the energies of ethylene electronic states *vs.* angle of twist as calculated by several methods[31] are considered, crossing of ground state (S_0) and T_1 potential energy surfaces, but not that of the first excited singlet state (S_1), is indicated. This fact, coupled with the favored transoid nature of triplets (see, for example, **34**), suggests the



33a **33b**



34

possibility of allowed adiabetic conversion of the T_1 states of the linear conjugated molecules to the [3.3.0] bicyclic products. Hence, intersystem crossing in ketone **13** may well be facilitated because crossing from its triplet state potential energy surface to product ground state may be of high efficiency.

When inquiry is made into the conformational features of **3** and **20**, Dreiding models provide evidence for the increased flexibility of these bicyclics relative to **33**. Quite suitable overlap of the exocyclic π network with the internal cyclopropane bond is attainable with little dihedral angle torsion of the relevant orbitals. As a direct consequence of the continuous interaction realizable with this ever lengthening σ bond, the singlet excited states of **3** and **20** proceed with significant usage of this mechanism. The facility of internal bond fission which operates in these examples seemingly precludes intersystem crossing of the singlet n → π^* state of **3** to the triplet manifold.

Although other investigators have emphasized models in which ground-state geometry serves as a stereochemical determinant,[32] it is also entirely possible that these same characteristics dictate from which of the excited state manifolds bond relocation can occur most readily. In this regard, it is interesting that the fused cyclobutane derivatives **15**, **16**, **27**, and **28** do not partake of similar reactions. This absence of an inducement for rearrangement, which likely has its origins in the obvious diminution of ring strain, supports the proposition that a composite of factors determines the suitability of a molecule for excited state transformation.

Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer and apparent coupling constants are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. All photolyses were conducted in the absence of oxygen and continuous introduction of O_2-free nitrogen was accomplished where possible.

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(30) (a) J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960); (b) W. F. Erman, *J. Amer. Chem. Soc.*, **89**, 3828 (1967).

(31) R. S. Mulliken and C. C. J. Roothan, *Chem. Rev.*, **41**, 219 (1947); U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968); N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 4427 (1971).

(32) W. G. Dauben, *Chem. Weekbl.*, **60**, 381 (1964); J. P. Malrieu, *Photochem. Photobiol.*, **5**, 291, 301 (1966); J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 6444 (1969).

Irradiation of 1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-one (3).—A solution of 2.0 g of **3**[17] in 450 ml of reagent-grade acetone was irradiated with a 450-W Hanovia mercury vapor lamp in a standard quartz immersion well fitted with a Corex filter. The progress of the reaction was followed by withdrawal of small aliquots at periodic intervals and analyses of these by vpc methods.[33] After 5 hr, the solvent was carefully evaporated and the nonpolymeric residue (1.9 g) was submitted to preparative vpc purification.[33] The lone photoproduct, isolated as a colorless liquid in 10% yield, was identified as **4**: $\nu_{\text{max}}^{\text{neat}}$ 1745 and 1680 cm^{-1}; $\lambda_{\text{max}}^{C_2H_5OH}$ 286 nm (ϵ 40); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.10 (s, 6, methyls), 1.29 (s, 3, methyl at C$_1$), 2.12 (AB pattern, $J_{AB} = 16$ Hz, $\Delta_{AB} = 19.5$ Hz, –CH$_2$CO–), 2.40 (m, 2, H$_8$), 2.72 (m, 1, H$_5$), and 5.68 (br s, 2, olefinic). The semicarbazone derivative melted at 202–204°.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.50; H, 9.84.

For quantitative work, accurately weighed amounts of **3** and cyclooctane were dissolved in 3 ml of the solvent of choice and placed in quartz test tubes which were affixed in vertical array around the immersion well. Each tube was then tightly stoppered with a serum cap which permitted the withdrawal of aliquots with a microsyringe for vpc analysis. Percentage compositions (Table I) were calculated according to established procedures.[34]

TABLE I

PERCENTAGE COMPOSITION RATIOS FOR THE IRRADIATION OF **3** UNDER VARIOUS CONDITIONS

Solvent (filter)	Time, hr	Composition, %^{a}		Solvent (filter)	Time, hr	Composition, %^{a}	
		3	**4**			**3**	**4**
Methanol (Vycor)	1	33	5	Pentane (Vycor)	1	31	Trace
	2	13	10		2	9	Trace
	3	8	8				
Ether (Corex)	1	61	8	Acetone (Corex)	1	87	4
	2	53	10		2	74	7
	3	35	8		3	70	9
	4	31	8		4	61	9
	5	27	8		5	58	10
Naphthalene (0.1 *M*) in ether (Corex)	28	15	2	Piperylene (0.1 *M*) in ether (Corex)	37	10	3
	32	13	Trace		40	10	3
	49	7	Trace		53	9	2
	70	5	Trace		68	10	
	100				100		

^{a} Cyclooctane was used as the internal standard.

cis-**Bicyclo[5.1.0]octan-4-one Ethylene Ketal (10).**—A mixture of 4.00 g (32.2 mmol) of **9**,[35] 2.20 g (34.5 mmol) of ethylene glycol, and 60 mg of *p*-toluenesulfonic acid monohydrate in 250 ml of benzene was heated under reflux for 12 hr with azeotropic removal of water. The benzene solution was washed with saturated aqueous sodium bicarbonate (2 × 50 ml), water (2 × 50 ml), and saturated sodium chloride (1 × 50 ml) and dried, and the solvent was removed *in vacuo*. The residual oil was distilled to give 4.98 g (92%) of **10**: bp 62–64° (1.0 mm); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.79 (s, 4, –CH$_2$O–), 0.3–2.3 (br m, 11), and −0.06 (m, 1, H$_8$).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.66; H, 9.63.

cis-**Bicyclo[5.1.0]oct-2-en-4-one Ethylene Ketal (12). A. Bromination of 10.**—Bromine was added dropwise to a stirred solution of 2.85 g (17.0 mmol) of **10** in 100 ml of anhydrous ether at such a rate as to maintain the bromine coloration. After 3.73 g (23.3 mmol) of bromine had been added the uptake ceased. Twenty milliliters of a solution of monosodium ethyleneglycolate [from 880 mg (38 mg-atoms) of sodium in 20 ml of ethylene glycol] was added and the two-phase system was stirred for 5 min at room temperature. The reaction mixture was poured into 100 ml of water, the ether layer was separated, and the aqueous phase was extracted with a further 150 ml of ether. The combined ether extracts were washed with water and saturated sodium chloride, dried, and evaporated *in vacuo* to give 4.14 g of the crude bromination product **11** as a viscous yellow oil.

B. Dehydrobromination of 11.—To a solution of the above material in 60 ml of anhydrous dimethyl sulfoxide was added 4.30 g (38.4 mmol) of potassium *tert*-butoxide. After the initial exothermic reaction had subsided, the dark red solution was stirred at room temperature for 1.5 hr, poured into saturated sodium chloride solution (120 ml), and extracted with pentane (4 × 130 ml). The combined pentane layers were washed with water (2 × 100 ml) and saturated aqueous sodium chloride (1 × 100 ml), dried, and evaporated *in vacuo* to give 2.10 g of a yellow oil consisting of two components in a ratio of 86:14.[36] Preparative vpc separation of this mixture at 120° afforded 1.35 g (48% from **10**) of **12**: $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.75 (d with additional splitting, $J = 12$ Hz, 1, olefinic), 5.16 (d, $J = 12$ Hz, 1, olefinic), 3.83 (s, 4, –CH$_2$O–), 0.6–2.6 (br m, 7), and 0.19 (m, 1, H$_8$). The analytical sample was prepared by molecular distillation [55° (1 mm)].

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.05; H, 8.45.

The minor component (14%) was subsequently identified as the corresponding ketone (**13**).

cis-**Bicyclo[5.2.0]oct-2-en-4-one (13).**—A mixture of 1.44 g (8.7 mmol) of **12** and 3.5 ml of 3% sulfuric acid was shaken at room temperature for 15 min. Water (15 ml) was added and the product was extracted with ether (2 × 50 ml). The ethereal solution was washed with saturated aqueous sodium bicarbonate (1 × 20 ml) and sodium chloride solutions (1 × 20 ml), dried, and evaporated *in vacuo* at 0° to give 1.02 g (95%) of colorless oil which was homogeneous by vpc. Distillation afforded 845 mg (78.5%) of pure **13**: bp 55–57° (1.2 mm); $\nu_{\text{mnx}}^{\text{CCl}_4}$ 1665 cm^{-1}; $\lambda_{\text{max}}^{\text{isooctane}}$ 237 nm (ϵ 7700), 322 (50), and 337 (sh, 40); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 6.83 (d with additional coupling, $J = 12.5$ Hz, 1, olefinic), 5.83 (d, $J = 12.5$ Hz, 1, olefinic), 0.9–3.05 (br m, 7), and 0.57 (m, 1, H$_8$).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.60; H, 8.27.

Photorearrangement of 13.—A solution of 300 mg of **13** in 20 ml of pentane was irradiated for 2.5 hr under nitrogen in a quartz test tube attached to a quartz immersion well fitted with a 200-W Hanovia mercury arc and Pyrex filter. Removal of the solvent *in vacuo* at 0° gave 250 mg of a yellow oil. The photoproduct (116 mg, 39%) was isolated by preparative vpc at 90°: $\nu_{\text{max}}^{\text{CCl}_4}$ 1742 cm^{-1}; $\lambda_{\text{max}}^{\text{isooctane}}$ 284 nm (sh, ϵ 45), 293 (60), 302.5 (70), 312.5 (60), and 323 (sh, 30); $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.58 (symmetrical 14-line m, 2, olefinic) and 1.2–3.45 (br, 8 H). This ketone was identical in all respects with an authentic sample of **14**.[21]

The semicarbazone of **14** was prepared in the usual manner and after recrystallization from aqueous ethanol showed mp 165.5–166.5° (lit.[21] mp 166.5–167.2°).

Analytical studies were conducted with accurately weighed mixtures of *ca.* 30 mg of **13** and *ca.* 10 mg of cyclooctane in 3 ml of purified pentane. Product composition data (Table II) were obtained as before and the photolyses were conducted as described above (Pyrex filter).

2-Methylene-1,4,4-trimethyl-*cis*-bicyclo[5.1.0]oct-5-ene (20).—To a suspension of 3.6 g (0.011 mol) of methyltriphenylphosphonium bromide in 50 ml of anhydrous ether under nitrogen was added dropwise 4.3 ml (0.011 mol) of 1.6 *M* *n*-butyllithium in hexane. After this mixture was stirred for 3 hr, a solution of 1.64 g (0.01 mol) of **3** in 10 ml of anhydrous ether was added dropwise and the resulting suspension was refluxed for 12 hr. Water (75 ml) was added, the ether layer was separated, and the aqueous layer was extracted with ether. The combined ethereal layers were washed with brine, dried, and carefully concentrated. The oily residue was taken up in pentane and the insoluble solids were separated by filtration. The filtrate was carefully concentrated and distilled to afford 0.8 g (50%) of **20**: bp 72–75° (1 mm); n^{24}D 1.4887; $\lambda_{\text{max}}^{C_2H_5OH}$ 275 nm (ϵ 140); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.20 (m, 4, vinyl), 2.17 (m, 2, allylic), 1.20, 0.95, 0.83 (s, 3 each, methyls), and 0.9 (m, 3, cyclopropyl).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.19. Found: C, 88.90; H, 11.18.

Irradiation of 20.—A solution of 2.0 g of **20** in 450 ml of anhydrous methanol was irradiated with a 450-W mercury arc placed in a quartz immersion well fitted with a Vycor filter. Progress of the reaction was followed by withdrawal of small aliquots at periodic intervals. After 10 hr, the solution was carefully concentrated and the residual oil was subjected to

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[33] A 6 ft × 0.25 in. aluminum column packed with 5% SF-96 on 60–80 mesh Chromosorb G was employed.

[34] L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).

[35] A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4843 (1962).

[36] This vpc analysis was performed with the aid of a 5.5 ft × 0.25 in. aluminum column packed with 20% SE-30 on 60–80 mesh Chromosorb W.

TABLE II

PERCENTAGE COMPOSITION RATIOS FOR THE IRRADIATION OF **13** UNDER VARIOUS CONDITIONS

Solvent	Time, min	Composition, %[a]		Solvent	Time, min	Composition, %[a]	
		13	**14**			**13**	**14**
Pentane	15	55	27	Acetone	15	66	29
	30	29	48		30	43	52
	45	12	57		45	23	73
	60	4	61		60	13	82
	75	<2	63		75	8	88
Ether (0.67 *M* in benzophenone)	20	51	15	Ether (1.0 *M* in naphthalene)	20	[b]	21
	30	37	19		30	[b]	33
	60	28	33		60	[b]	50
	75	23	37		75	[b]	60
	105	14	47				
	135	9	50	Ether (1.0 *M*)	20	32	29
					30	25	38
					60	6	50
					75	4	54

[a] Cyclooctane was utilized as the internal standard. [b] The concentration of **13** could not be determined in these runs owing to overlapping with the naphthalene peak.

preparative vpc isolation.[37] The lone product formed in 56% yield was identified as **21**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.67 (m, 2, vinyl), 4.77 (m, 2, exo methylene), 2.84 (m, 3), 2.1 (m, 1), 1.27 0.99, and 0.91 (s, 3 each, methyls).

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.19. Found: C, 88.96; H, 11.29.

For the quantitative work in Table III, carefully weighed amounts of **20** and cyclooctane were dissolved in 3 ml of the solvent of choice and placed in quartz test tubes which were affixed in vertical array around the immersion well. Each tube was tightly stoppered with a serum cap and the photolyses were conducted as predescribed (Vycor filter).

TABLE III

PERCENTAGE COMPOSITION RATIOS FOR THE IRRADIATION OF **20** UNDER VARIOUS CONDITIONS

Solvent	Time, hr	Composition, %[a]		Solvent	Time, hr	Composition, %[a]	
		20	**21**			**20**	**21**
Acetone	2	47	4.5	Pentane	2	85	12
	4	21	5		4	70	20
	6	6	3		6	60	25
	8	3	3		8	43	24
Methanol	2	75	19	Acetone (Pyrex)	2	82	1
	4	41	35		4	60	2
	6	31	44		6	41	3
	8	14	47		8	33	2
	10	3	56				

[a] Cyclooctane served as the internal standard.

Hydrogenation of 4.—A solution of 100 mg of **4** in 20 ml of ether containing 30 mg of 5% rhodium on carbon was hydrogenated at 25° and atmospheric pressure. After 20 min, approximately 1 equiv of hydrogen was taken up. The reaction mixture was filtered, carefully concentrated, and subjected to preparative vpc purification[37] to give **23** as a colorless liquid: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 0.85–2.5 (9 H), 1.18, 1.07, and 1.05 (s, 3 each, methyls); $\nu_{\mathrm{max}}^{\mathrm{CCl_4}}$ 1735 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.52; H, 10.94.

Hydrogenation of 21.—A solution of 200 mg of **21** in 30 ml of pentane containing 50 mg of 5% rhodium on carbon was hydrogenated as above for 1 hr, the time required for slightly more than 1 molar equiv of hydrogen to be consumed. Preparative vpc purification[37] afforded 80 mg (40%) of **22**, which showed evidence of an exocyclic methylene group at δ 4.75 (2 H) in its nmr spectrum ($CDCl_3$).

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.48; H, 12.68.

Ozonolysis of 2.—A solution of 150 mg of **22** in 10 ml of methanol cooled to −78° was treated with ozone until the solution was saturated (bluish tint). A solution of 500 mg of sodium iodide and 0.2 ml of acetic acid in 1 ml of methanol diluted with 10 ml of water was added and solid sodium bisulfite was introduced to destroy the resulting iodine. The product was extracted with ether and isolated by preparative vpc.[37] Its infrared and nmr spectra were superimposable with those of **23** isolated above.

4-Methylene-*cis*-bicyclo[5.1.0]oct-2-ene (24).—Reaction of 610 mg (5.0 mmol) of **13** with 2.68 g (7.5 mmol) of methyltriphenylphosphonium bromide and 7.5 mmol of *n*-butyllithium in hexane dissolved in 50 ml of anhydrous ether was carried out in the predescribed fashion. Distillation of the residue *in vacuo* gave 310 mg (52%) of **24**: bp 68–70° (20 mm); $\lambda_{\mathrm{max}}^{\mathrm{isooctane}}$ 237 nm (ε 17,000); $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.88 (s, 2), 4.84 (s, 2), 0.6–2.7 (br, 7), and 0.22 (m, 1).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.66; H, 9.87.

Photorearrangement of 24.—A solution of 200 mg of **24** in 20 ml of acetone was irradiated for 3.25 hr as previously described using a 450-W Hanovia lamp and Pyrex optics. The majority of the solvent was removed by distillation at atmospheric pressure through a small Vigreux column. The residue was submitted to preparative vpc isolation.[38] There was obtained 81 mg (40%) of **25**: $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 5.49 (s, 3), 4.79 (septet, 2), 3.5 (br d, 1) and 1.0–3.0 (br, 7). The analytical sample was prepared by molecular distillation at 50–55° (35 mm).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.86; H, 10.06.

2-Methylene-*cis*-bicyclo[3.3.0]oct-7-ene (25).—Treatment of 100 mg (0.82 mmol) of **14** with 1.64 mmol of methylenetriphenylphosphorane in anhydrous ether as previously outlined afforded, after preparative vpc isolation[38] at 70°, 27 mg (27%) of **25** identical in all respects with the sample isolated above.

Acknowledgment.—Partial financial support of this research has been provided by the Army Research Office (Durham).

Registry No.—**3**, 24217-77-4; **4**, 40905-63-3; **4** semicarbazone, 40905-64-4; **9**, 40905-65-5; **10**, 24217-78-5; **11**, 40905-67-7; **12**, 24217-79-6; **13**, 24217-80-9; **14**, 10095-78-0; **20**, 24217-81-0; **21**, 40905-72-4; **22**, 40905-73-5; **23**, 40905-74-6; **24**, 24217-82-1; **25**, 24217-83-2; ethylene glycol, 107-21-1.

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(37) A 6 ft × 0.25 in. aluminum column packed with 5% Carbowax on 60–80 mesh Chromosorb G was utilized for this separation.

(38) A 5.5 ft × 0.25 in. aluminum column packed with 10% SF-96 on 60–80 mesh Chromosorb G was employed.