15e, 19647-48-4; **15f**, 19713-70-3; **17a**, 18819-63-1; **17b**, 705-55-5; **17c**, 18819-66-4; **17d**, 705-54-4; **17e**, 19647-53-1; **17f**, 19647-54-2; **20** (*cis*), 14533-87-0; **20** (*trans*), 2169-69-9; **21** (*cis*), 19713-73-6; **21** (*trans*), 1754-62-7; *cis*-methyl α-cyanocinnamate, 14533-85-8; *trans*-methyl α-cyanocinnamate, 14533-86-9.

Acknowledgments.—The author wishes to thank the National Institutes of Health for a Predoctoral Fellowship at the University of Wisconsin, and the several donors of unpublished nmr data used in the tables. Numerous helpful discussions were held during the course of this work with Professors Robert West of the University of Wisconsin, Norbert Muller of Purdue University, David M. Lemal of Dartmouth College, Sidney L. Gordon of Georgia Institute of Technology, and Drs. Francis Johnson and W. Lawrence Parker of the Dow Chemical Co. Eastern Research Laboratory.

Photolyses of Trienes. III. Photoreactions of 2,3,7,7-Tetramethylcycloheptatriene

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Received August 26, 1968

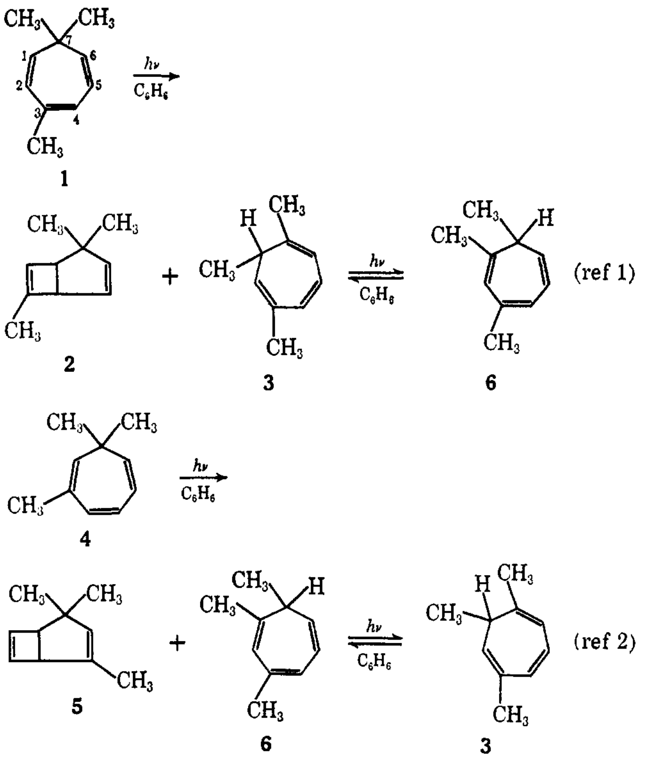
Irradiation of a benzene solution of 2,3,7,7-tetramethylcycloheptatriene (7) in a Pyrex tube with a Hanovia medium-pressure mercury arc lamp yields a complex mixture. The major reaction products were identified as 2,2,6,7-tetramethylbicyclo[3.2.0]hepta-3,6-diene (9) and 1,2,6,7-tetramethylcycloheptatriene (13). Secondary photoproducts (10 and 11) were also produced. These reaction products are the result of a selective (1,7) sigmatropic methyl migration and electrocyclization reaction.

Previous studies[1,2] have indicated that methyl substituents attached to vinyl carbon atoms in various cycloheptatrienes exert a strong directive influence on the course of photochemical cyclization and methyl and hydrogen migration reactions. Specifically, irradiation of 3,7,7-trimethylcycloheptatriene[1] (1) induces an electrocyclization reaction across C_1 and C_4 to give 2 and promotes methyl migration from C_7 to C_1 to give the new cycloheptatriene 3. On the other hand, when 2,7,7-trimethylcycloheptatriene (4) is irradiated,[2] a methyl shift from C_7 to C_6 is observed to give 6, and cyclization occurs across C_3 and C_6 to give 5. Secondary photoproducts were observed in each reaction arising from selective hydrogen migration in the new triene photoproducts to give 6 in the case of 1, and 3 in the case of 4. These reactions are summarized in Chart I. The selectivity noted in the methyl and hydrogen migration reactions was rationalized on the basis of a series of molecular orbital calculations, and the selectivity of the cyclization reactions was accounted for primarily on the basis of steric considerations.[1,2]

Based on our observations that the direction of these photochemical cyclization and migration reactions is dependent upon whether the methyl group is located at C_2 or C_3, it was of interest to prepare a cycloheptatriene with methyl substituents located both at positions 2 and 3 to determine which substituent exerts the stronger effect. It was anticipated that the photochemistry of 2,3,7,7-tetramethylcycloheptatriene (7) would be more complex and that the selectivity would be less than that observed during photolysis of either 1 or 4. With this in mind, we have studied the photolysis of 7 in benzene solution with a 450-W Hanovia medium-pressure mercury arc lamp.

2,3,7,7-Tetramethylcycloheptatriene (7) was prepared by the addition of methylmagnesium bromide to eucarvone, followed by acid-catalyzed dehydration.[3,4]

Chart I



As observed by Conrow,[4] this procedure gives rise to a mixture of 7 (the predominant component) and 2-methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8). These materials are readily separable by vapor phase chromatography (vpc).

As anticipated, the photoisomerization reactions of 7 proved to be extremely complex. Irradiation of a benzene solution of 7 to 40% reaction gave a mixture which upon vpc[5] was shown to consist of 1% a group of minor bicyclic products, 11% a group of major bicyclic

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[1] L. B. Jones and V. K. Jones, *J. Amer. Chem. Soc.*, **89**, 1880 (1967).

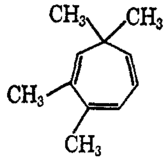
[2] L. B. Jones and V. K. Jones, *ibid.*, **90**, 1540 (1968).

[3] E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).

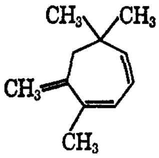
[4] K. Conrow, *ibid.*, **83**, 2958 (1961).

[5] A column packed with SE-30 suspended on base-washed Chromosorb P was employed.

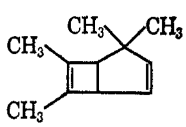
products, 60% unreacted **7**, and 9% new cycloheptatrienes (determined using an internal standard and known thermal conductivity ratios). Further analysis[6] showed the major bicyclic products to consist of three peaks in the relative amounts of 84, 9, and 7%, in order of elution. The structures **9**, **10**, and **11**, respectively, have been assigned to these peaks on the basis of arguments presented below. Further analysis[7] of the new trienes showed four peaks in the relative amounts of ~3%, 13% A, 64% B, and 3% C, in order of elution.[8] Irradiation of **7** to almost complete reaction gave a mixture which vpc[5] showed to consist of 7% minor bicyclic products, 35% major bicyclic products, 6% unreacted starting material, and 10% new cycloheptatrienes (determined using an internal standard and known thermal conductivity ratios). Further analysis[6] showed the major bicyclic products to consist of 64% **9**, 20% **10**, and 16% **11**. Analysis[7] of the new trienes showed four peaks in the relative amounts of ~2%, 34% A, 58% B,[9] and 6% C, in order of elution. As A and B are the major new trienes formed, we centered our attention on the elucidation of their structures. Peak C shows aromatic hydrogen absorptions in the nmr spectrum (7 ppm) and no absorption above 2 ppm. Because of its apparent aromatic nature and the absence of alkyl groups attached to saturated carbon atoms, it is felt that this material is not a photoproduct, but arises from either an acid-catalyzed isomerization or a thermal reaction (reaction temperature 35–40°) during the irradiation.



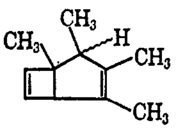
7



8

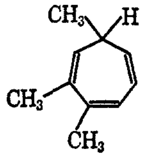


9

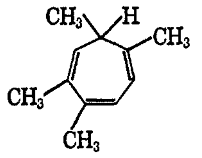


10,11

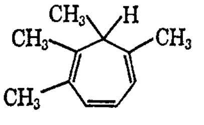
The nmr spectrum of a sample of A shows a three-hydrogen doublet at 0.88 (J = 7.5 Hz), a multiplet at 1.30–2.0 (10 H), a multiplet at 4.50–4.90 (1 H), a multiplet at 5.30–5.60 (1.3 H), and a multiplet at 5.80–6.70 ppm (0.7 H). This spectrum would be consistent with a cycloheptatriene such as **12a** or **12b**, which has one upfield, one midfield, and one low field hydrogen. The ultraviolet (uv) spectrum of the material having this nmr spectrum shows λ_{max} 265 mμ (log ε 3.65), which is typical of cycloheptatrienes.[10] The nmr spectrum of a sample of B shows absorption at 0.75–1.20 ppm on which is superimposed a doublet at 0.96 (J = 7.5 Hz, total integration 3 H), absorption at 1.4–2.1 (10 H), a multiplet at 4.8–5.2 (0.5 H), a multiplet at 5.6–5.9 (1 H), and a multiplet at 6.18–6.38 ppm (1.5 H). This spectrum would be consistent with a cycloheptatriene such as **13**, which would have no upfield, one midfield, and two downfield hydrogens. The uv spectrum of this material shows λ_{max} 266 mμ (log ε 3.59).



12a



12b



13

The proposed structures **12a** and **13** for A and B would be logical if, upon irradiation of **7**, a selective (1,7) sigmatropic methyl shift occurred from C_7 to C_1 to give **13**, which could then undergo a selective (1,7) sigmatropic hydrogen shift to give **12a**. If this were the case, then B would be expected to equilibrate upon photolysis to A. In fact, no noticeable equilibration of either A or B could be detected.

On the other hand, structure **12b** would not be expected to photoequilibrate with **13**. The formation of **12b** upon irradiation of **7** could be rationalized as follows: methyl migration from C_7 to C_6 followed by hydrogen migration. This result would be consistent with our previous results.[1,2] The predominant methyl migration reaction of **7** leads to **13**, while methyl migration in the opposite direction transforms **7** into the carbon skeleton of **12b**.

In view of these inconclusive data, it would appear that A and B, as they appear upon vpc, are in fact a mixture of trienes, the major component of B which is structure **13**. This conclusion is further substantiated by other evidence presented below. A control experiment indicated that trienes A and B do not isomerize under the analytical conditions employed (see Experimental Section). It has been reported[11] that certain column materials cause rearrangement of substituted cycloheptatrienes during their gas chromatographic analysis, either by way of an acid-catalyzed mechanism or *via* hydride exchange. The columns used in our work do not fall in the category of columns which cause this type of rearrangement. It has also been demonstrated that thermally induced 1,5-hydrogen migrations occur in cycloheptatrienes.[12] In our system, this possibility is excluded both by the control experiment and by the apparent structure of the new cycloheptatrienes. In our previous work,[1,2] 1,5-hydrogen shifts were not observed in the glpc analyses of the trienes **3** and **6**, which were carried out at detector temperatures of *ca.* 200°. In addition, activation energies determined for thermal 1,5-hydrogen migrations in several substituted cycloheptatrienes are much too high[12] to permit such isomerizations to take place at the temperatures employed for our analyses.

The identification of the bicyclic compound **9** was straightforward. The nmr spectrum shows two three-hydrogen singlets at 0.70 and 0.77 (*gem*-dimethyl), a broadened six-hydrogen singlet at 1.30 (vinyl CH$_3$), a broadened one-hydrogen singlet at 2.30 (monoallylic bridgehead hydrogen), a broadened one-hydrogen singlet at 3.06 (doubly allylic bridgehead hydrogen), a one-hydrogen doublet at 5.04 (J = 6 Hz) further split

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[6] A column packed with Carbowax 20M suspended on base-washed Chromosorb P was employed.

[7] A column packed with 1,2,3-tri-(β-cyanoethoxy)propane (TCEP) suspended on Chromosorb P was employed.

[8] Peaks A and B are not completely resolved.

[9] Here, peak B has a small shoulder.

[10] J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **88**, 2494 (1966).

[11] K. Conrow and L. L. Reasor, *J. Org. Chem.*, **30**, 4368 (1965).

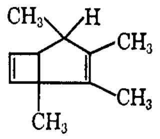
[12] A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **82**, 741 (1963); R. W. Egger, *J. Amer. Chem. Soc.*, **89**, 3688 (1967).

by the bridgehead hydrogen (J = 1.5 Hz), and a one-hydrogen doublet of doublets at 5.36 and 5.45 ppm (J = 2 Hz). The uv spectrum shows only end absorption [210 mμ (ϵ 3397)].

The 100-Mc nmr spectrum of **10** shows a three-hydrogen doublet at 0.96 (J = 7 Hz), a three-hydrogen singlet at 1.30 (bridgehead methyl), a six-hydrogen absorption at 1.45–1.90 (vinyl CH_3), a broadened one-hydrogen quartet at 2.15 (J = 7 Hz), a one-hydrogen singlet at 2.88, and two one-hydrogen doublets at 6.02 and 6.45 ppm (J = 2.5 Hz). Double irradiation at 0.96 ppm caused the broad quartet at 2.5 ppm to collapse to a singlet.

The 100-Mc nmr spectrum of **11** shows a three-hydrogen doublet at 0.95 (J = 7 Hz), a three-hydrogen singlet at 1.18, a six-hydrogen absorption at 1.40–1.80, a broadened one-hydrogen absorption at 2.1–2.4, a one-hydrogen singlet at 2.92, and two one-hydrogen doublets at 6.08 and 6.30 ppm (J = 2.5 Hz). Double irradiation of the broad absorption at 2.1–2.4 ppm caused the doublet at 0.95 ppm to collapse to a singlet and caused the absorption at 2.92 ppm to sharpen slightly. Double irradiation at 2.92 ppm caused the broad absorption at 2.1–2.4 ppm to collapse to a singlet resembling the singlet at 2.92 ppm.

Thus, the nmr spectra of **10** and **11** are in agreement with the structure of 2,3,4,5-tetramethylbicyclo[3.2.0]-hepta-3,6-diene, epimeric at C_2. The strongest evidence against the isomeric structure **14** is the almost identical chemical shift of the bridgehead hydrogen in **10** and **11**. In compound **9**, the difference in the chemical shifts of the monoallylic and doubly allylic bridgehead hydrogens corresponds to *ca.* 40 Hz. In 2,2,6-trimethylbicyclo-[3.2.0]hepta-3,6-diene (**2**),[1] the difference in chemical shifts between the double allylic and monoallylic hydrogens also amounts to *ca.* 40 Hz. In addition, the ratio of **10** and **11** stays approximately the same at various stages of photolysis. The most consistent interpretation of these data is that both **10** and **11** arise from the same triene. If they were arising from electrocyclization of two tautomeric trienes, their ratio should change during the course of the irradiation, because the ratio of tautomeric trienes would change.



14

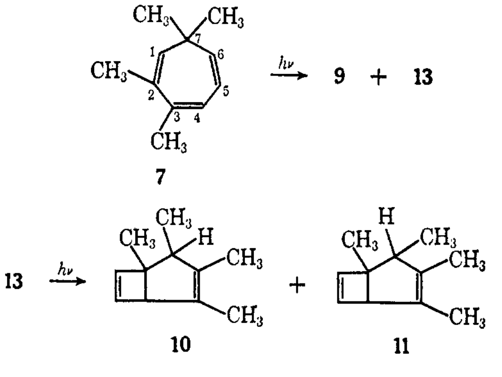
To help to elucidate the structures of the photoproducts of **7**, 1-deuterio-2,3,7,7-tetramethylcycloheptatriene (**7**-d_1) was synthesized from eucarvone-d_2.[1] The nmr spectra of the new trienes, A-d_1 and B-d_1, were inconclusive (see Experimental Section). In the nmr spectrum of **9**-d_1, the singlet at 2.30 ppm has disappeared. The remainder of the spectrum is virtually unchanged. The 60-Mc nmr spectra of **10**-d_1 and **11**-d_1 each show a broadened singlet at 0.97 ppm. The absorption at 2.0–2.4 ppm has disappeared, and the remainder of the spectra are unchanged. Thus, **10** and **11** can only arise from electrocyclization of the cycloheptatriene **13**, which must result from a (1,7) sigmatropic methyl shift from C_7 to C_1 in compound **7**.

As evidence that photoproduct B must consist predominantly of **13**, a sample consisting of *ca.* 10% A and 90% B was irradiated to complete disappearance of A and B. Analysis of the bicyclics showed the presence of six peaks in the relative amounts of 2, 10 (two peaks), 6, 49, and 33%. The 49 and 33% peaks had the retention times of **10**, and **11**, respectively. Irradiation of a sample consisting of *ca.* 25% A and 75% B was carried out to 75% reaction. Analysis of the bicyclic mixture showed seven peaks in the relative amounts of 1, 6, 3, 9, 12, 39, and 25%. The 39 and 25% peaks had the retention times of **10** and **11**.

The bicyclic compounds **10** and **11** were further subjected to selective catalytic hydrogenation. Both **10** and **11** could be selectively reduced at the cyclobutenyl double bond to give the corresponding bicyclo[3.2.0]-hept-3-ene, as indicated by the loss of the cyclobutenyl hydrogen absorption in the nmr spectrum. The nmr spectra of the reduced compounds are very similar. The mass spectra of the reduced compounds are virtually identical and show highest m/e at 150, with the base peak at m/e 122. This is in agreement with the 1,2,3,4-tetramethylbicyclo[3.2.0]hept-3-ene structure, the positive ion of which could easily split out ethylene to give a stable C_9 fragment corresponding to m/e 122.

It is interesting to compare the hydrogenation results of **10** and **11** with those obtained for **9**. After the uptake of 1 mol of hydrogen, the nmr spectrum shows loss of the cyclopentenyl hydrogen absorption. Selective reduction of the cyclopentenyl double bond is reasonable, as *cis* reduction of the cyclobutenyl double bond would result in serious steric interactions of the methyl substituents.

Based on these data, we suggest that the predominant photoreaction of **7** is that indicated in eq 1. The methyl substituent at C_3 in **7** exhibits a stronger directive influence (in the methyl migration reaction) than the C_2 methyl group and, hence, the predominant mode of migration is from C_7 to C_1. This is consistent with the HMO treatment discussed previously.[1,2] The preferred mode of cyclization involves bond formation across C_1–C_4 to produce the more highly substituted olefinic system. This mode of cyclization avoids placing a methyl group at the bridgehead which would be eclipsed with the adjacent bridgehead hydrogen.

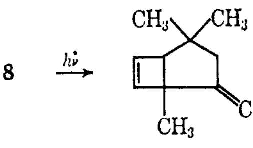


7

10 **11**

(1)

Compound **8** (a by-product in the preparation of **7**) was also irradiated in benzene solution with a Pyrex filter. As anticipated, a single product corresponding to 2,2,5-trimethyl-4-methylenebicyclo[3.2.0]hept-6-ene



15 (2)

(**15**) was produced (eq 2). This diene (**15**) was identified on the basis of spectroscopic data, deuterium labeling, and elemental analysis data (see Experimental Section).

Experimental Section[13]

2,3,7,7-Tetramethylcycloheptatriene (7) and 2-Methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8).—The procedure followed was essentially that described earlier.[4] Following the addition of 10 g (0.067 mol) of eucarvone to an excess of methylmagnesium bromide and decomposition with aqueous ammonium chloride, the crude alcohol was dehydrated by dropwise addition to 1 g of potassium hydrogen sulfate at a bath temperature of 150–160° and water aspirator pressure. The material having bp 110–115° (60–70 mm) was collected. The water layer was removed, and after drying the organic layer amounted to 7 g. Gas chromatography[5] showed the material to consist of two products in the relative amounts of 75 and 25%, in order of retention. Each peak was collected. The nmr spectrum of the major product showed a *gem*-dimethyl group at 0.95, two vinyl methyl groups at 1.88 and 2.01, a two-hydrogen absorption at 4.80–5.1, and a two-hydrogen absorption at 5.6–6.25 ppm, and is in agreement with the spectrum of **3** published by Conrow.[4] The nmr spectrum of the minor product showed a *gem*-dimethyl group at 0.98, a vinyl methyl group at 2.00, the saturated methylene group at 2.05, a one-hydrogen absorption centered at 4.90, a one-hydrogen absorption at 5.25, and a two-hydrogen absorption centered at 5.60 ppm, and is in agreement with the spectrum of **4** published by Conrow.[4]

1-Deuterio-2,3,7,7-tetramethylcycloheptatriene (7-d_1) and 1-Deuterio-2-methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8-d_1).—Eucarvone-d_2 was prepared as previously described[1] from 10 g of eucarvone. The crude eucarvone-d_2 was treated with methylmagnesium bromide and dehydrated as described above. The material boiling at 100–110° (30–40 mm) was collected and, after separation of water and drying of the organic layer, amounted to 3 g of material consisting of 42% **7**-d_1 and 58% **8**-d_1. The compounds were collected by gas chromatography.[6] The nmr spectrum of **7**-d_1 showed a *gem*-dimethyl group at 0.96, two vinyl methyl groups at 1.88 and 2.01, a one-hydrogen absorption at 4.80–5.10, and a two-hydrogen absorption at 5.6–6.25 ppm. The spectrum of **8**-d_1 showed loss of the saturated methylene group at 2.05 ppm. The remainder of the spectrum is unchanged.

Irradiation of 2,3,7,7-Tetramethylcycloheptatriene (7).—A solution of 53.4 mg of **7** in 2 ml of benzene was irradiated in a Pyrex tube with a 450-W Hanovia mercury arc lamp for 16 hr. At the end of irradiation, 31.4 mg of 2-methylene-3,7,7-trimethyl-3,5-cycloheptadiene (**8**) was added as an internal standard, and the mixture was concentrated at room temperature and water aspirator pressure, then analyzed by gas chromatography[5] to show 60% unreacted **7**. The results are presented in the text.

A solution of 59.9 mg of **7** in 0.3 ml of benzene was irradiated in a Pyrex tube for 24 hr. After addition of 16.4 mg of **8** and concentration, analysis[5] showed 6% unreacted **8**. The results are presented in the text.

A solution of 1.4 g of **7** in 60 ml of benzene was irradiated in a Pyrex tube for 16 hr. The reaction mixture was concentrated at water aspirator pressure and room temperature and analyzed by gas chromatography[6] to show 78% bicyclic products, 1% **7**, and 21% new trienes as determined from relative peak areas. The bicyclic products and the new trienes were collected. Further chromatography[6] showed the bicyclic products to consist of 16% at least five peaks (minor bicyclics) and 37% **9**, 25% **10**, and 22% **11**, in order of elution as determined from relative peak areas. The peaks corresponding to **9**, **10**, and **11** were collected. Further chromatography[7] of the triene mixture showed three partially resolved peaks in the approximate relative amounts of 8, 42% A, and 50% B, in order of elution, as determined from peak areas. Because of only partial resolution, the central portion of the new triene peaks A and B were collected.

The nmr and uv spectra of **9**, **10**, **11**, and the triene mixtures A and B are described in the text. *Anal.* Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found for **9**: C, 89.28; H, 10.84. Found for **11**: C, 89.05; H, 11.09. The mass spectrum of **10** showed highest *m/e* at 148. Found for a mixture of *ca.* 20% A and 80% B: C, 89.22; H, 10.92. The ir spectrum[14] of **9** showed medium bands at 3010 and 3030 (CH of olefin) and a strong band at 765 cm^{-1}.

Irradiation of 1-Deuterio-2,3,7,7-tetramethylcycloheptatriene (7-d_1).—A solution of 320 mg of **7**-d_1 in 5 ml of benzene was irradiated for 7 hr. Gas chromatography[5] showed *ca.* 80% bicyclics and 20% new trienes as determined from the relative areas of the peaks. Analysis of the collected bicyclics showed 15% minor bicyclics, 43% **9**-d_1, 23% **10**-d_1, and 19% **11**-d_1, as determined from relative peak areas. Analysis[7] of the collected triene mixture showed *ca.* 30% A and 70% B. Samples of **9**-d_1, **10**-d_1, **11**-d_1, A-d_1, and B-d_1 were collected and their nmr spectra were determined using the microcell described previously.[2] The nmr spectra of **9**-d_1, **10**-d_1, and **11**-d_1 are described in the text. A 100-Mc spectrum of a sample of *ca.* 60% A-d_1 and 40% B-d_1 showed absorption at 0.55–1.0 (2.3 H) consisting of two broadened peaks and absorption at 1.25–2.00 (11.3 H), 4.4–4.7 (0.34 H), 5.3–5.6 (0.52 H), and 5.8–6.0 ppm (0.46 H). A 100-Mc spectrum of a sample consisting of 30% A-d_1 and 70% B-d_1 showed multiplet absorption at 0.6–1.0 (2.24 H) and absorption at 1.25–2.00 (11 H), 4.4–4.8 (0.24 H), 5.3–5.6 (0.6 H), and 5.75–6.10 ppm (0.65 H). A 100-Mc spectrum of a sample of B-d_1 showed broad absorption at 0.6–1.0 on which was superimposed a broadened singlet at 0.95 (2.3 H) and absorption at 1.4–1.7 (11 H), 4.7–4.9 (0.14 H), 5.4–5.6 (0.8 H), and 5.8–6.1 ppm (1.07 H).

Irradiation of Trienes A and B to Bicyclics.—A 20-mg sample consisting of *ca.* 90% B and 10% A in 0.2 ml of cyclohexane was irradiated for 24 hr to disappearance of the starting trienes. The mixture was concentrated and analyzed by gas chromatography[15] to show six peaks in the relative amounts of 2, 10 (two peaks), 6, 49, and 33%, in order of elution. The 49 and 33% peaks had the retention times of **10** and **11**, respectively. A 130-mg sample consisting of *ca.* 25% A and 75% B in 1 ml of benzene was irradiated for 19 hr to 75% reaction. Analysis[15] of the bicyclics showed seven peaks in the relative amounts of 1, 6, 3, 9, 12, 39, and 29%, in order of retention. The 39 and 25% peaks had the retention times of **10** and **11**, respectively.

Attempted Photoequilibration of A and B.—A 10-μl sample consisting of *ca.* 90% A and 10% B was irradiated in 0.20 ml of benzene for 10 hr. Analysis showed loss of material but no apparent change in peak composition. A 10-μl sample consisting of *ca.* 90% B and 10% A was irradiated in 0.18 ml of benzene for 10 hr. Analysis showed loss of material, but no apparent change in peak composition.

Control Experiment to Determine Presence of Triene Isomerization under Conditions of Analysis.—A sample of trienes which glpc[7] showed to consist of A and B in the relative amounts of *ca.* 80 and 20%, respectively, was collected under the following conditions: inlet temperature, 230°; oven temperature, 130°; detector temperature, 210°. The collected material from glpc[7] analysis consisted of *ca.* 80 and 20% A and B, respectively.[16]

The nmr[17] of the collected material showed a multiplet at 0.65–1.0 (2H), absorption at 1.30–1.90 (11 H), a multiplet at

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[13] All boiling points are uncorrected. Magnesium sulfate was employed as a drying agent. Ultraviolet spectra of solutions in 95% ethanol were determined with a Cary Model 14 recording spectrophotometer. Nuclear magnetic resonance spectra of carbon tetrachloride solutions with tetramethylsilane as internal reference were determined at 60 Mc with a Varian Model A-60 spectrometer and at 100 Mc when so indicated with a Varian Model HA-100 spectrometer. Integrations of the 100-Mc spectra were carried out manually with a planimeter. Infrared spectra were determined with a Perkin-Elmer Model 337 ir recording spectrophotometer. Vapor phase chromatography was carried out on an Aerograph Model A-90-P3 gas chromatograph. The mass spectra were determined with a Hitachi Perkin-Elmer RMV-6 E mass spectrometer. The microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

[14] Determined as a film.

[15] A column packed with 4-methyl-4-nitropimelonitrile (NMPN) suspended on Chromosorb P was employed.

[16] A more precise estimate of the relative amounts of these peaks is difficult as they are only partially resolved.

[17] The nmr spectrum was determined at 100 Mc using the microcell described previously[2] with the triene mixture in the capillary and tetramethylsilane in carbon tetrachloride surrounding the capillary.

4.2–4.9 (0.8 H), a multiplet at 5.3–5.5 (1 H), and a multiplet at 5.7–6.0 ppm (1.2 H). This material was reinjected under conditions identical with those above and collected. The nmr of the collected material, which glpc[7] showed to consist of *ca.* 80 and 20% A and B, respectively,[16] was identical and superimposable with the one described above.

Irradiation of 2-Methylene-3,7,7-trimethyl-3,5-cycloheptadiene (8) and (8-d_2).—A solution of 200 mg of **8** in 3 ml of benzene was irradiated in a Pyrex tube for 9 hr. Gas chromatography[5] showed 95% **15** and 5% **8** as determined from relative peak areas. The new product was collected. The nmr spectrum of **15** showed two singlets at 0.58 and 0.74 (6 H, *gem*-dimethyl), a singlet at 1.08 (3 H, bridgehead CH$_3$), two one-hydrogen doublets at 1.64 and 2.44 (J = 15 Hz, $=$CH$_2$), a singlet at 2.18 (1 H, bridgehead H), a two-hydrogen absorption at 4.50–4.60 consisting of two peaks, and a two-hydrogen doublet of doublets at 5.72 and 5.84 ppm (J = 2.5 Hz, cyclobutenyl hydrogens). The uv spectrum of **15** showed only end absorption [210 mμ (ϵ 2476)]. The ir spectrum[18] of **15** showed a weak band at 1645 and a strong band at 885 cm^{-1} ($=$CH$_2$). *Anal.* Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 89.28; H, 10.82.

A solution of 350 mg of **8**-d_1 in 5 ml of benzene was irradiated for 14 hr. Analysis[5] showed 55% **15**-d_1 and 45% **8**-d_1. The mixture was concentrated and a sample of **15**-d_1 was collected. The nmr spectrum of **15**-d_1 showed loss of the doublets at 1.64 and 2.44 ppm. The absorption at 4.50–4.60 ppm had collapsed to a singlet. The remainder of the spectrum is unchanged.

Reduction of 9.—A solution of 172 mg (1.165 mmol) of **9** in 5 ml of carbon tetrachloride containing the catalyst from 40 mg of platinum oxide was permitted to absorb 0.9 equiv of hydrogen. The reaction mixture was filtered and concentrated. Gas chromatography[15] showed one major component (*ca.* 95%) which was collected. The 100-Mc nmr spectrum of this material showed singlets at 0.58 and 0.82 (*gem*-dimethyl), absorption at 1.0–1.5, and singlets at 2.65 and 3.10 ppm (bridgehead hydrogens). The cyclopentenyl absorption at 5.0–5.4 ppm had disappeared. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (15), 135 (80), 122 (38), 107 (100), etc.

Reduction of 10.—A solution of 38 mg (0.27 mmol) of **10** in 1 ml of carbon tetrachloride containing the catalyst from 10 mg of platinum oxide was permitted to absorb 1.1 equiv of hydrogen. The reaction mixture was filtered and concentrated. Gas chromatography[15] showed one major component (*ca.* 85%) which was collected. The nmr spectrum of this material showed loss of the cyclobutenyl hydrogen absorption. The allylic hydrogen could not be distinguished. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (11), 135 (24), 122 (100), 107 (78), etc.

Reduction of 11.—A solution of 65 mg (0.44 mmol) of **11** in 1 ml of carbon tetrachloride containing the catalyst from 30 mg of platinum oxide was permitted to absorb 0.9 equiv of hydrogen. The mixture was filtered and concentrated. Gas chromatography[15] showed one major compound (*ca.* 95%) which was collected. The nmr spectrum of this material showed loss of the cyclobutenyl hydrogen absorption. The allylic hydrogen could not be distinguished, and the spectrum was very similar to that of reduced **10**. Mass spectrum (80 eV) showed m/e (rel intensity) 150 (13), 135 (25), 122 (100), 107 (77), etc.

Registry No.—**7**, 19566-41-7; **8**, 19566-42-8; **9**, 19566-43-9; **10**, 19566-44-0; **11**, 19566-45-1; **13**, 19566-47-3; **15**, 19566-48-4.

Acknowledgment.—The authors are grateful to the National Aeronautics and Space Administration for an institutional grant which was used in part to support this work.

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[18] Determined as a solution in carbon tetrachloride.

Stereochemistry of Radical Additions of Bromotrichloromethane to Some Cyclic Olefins[1]

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Received October 3, 1968

In order to assess the importance of some factors which may influence the stereochemistry of additions of reagents which are sources of carbon radicals to alkenes, we have investigated the photoinitiated additions of bromotrichloromethane to several cycloalkenes. Nmr data have been used to assign stereochemistry to the 1-bromo-2-trichloromethylcycloalkane adducts. Like cyclooctene,[2] cyclohexene affords a mixture of *cis* and *trans* adducts. *trans*-1,4,5,6,7,8,9,10-Octahydronaphthalene, cyclopentene, indene, and norbornene yield only *trans* adducts, and cycloheptene only the *cis* adduct. The over-all stereochemical results are most readily rationalized in terms of addition of both portions of the addend (in separate steps) from an axial-like direction. Abstraction of Br from BrCCl$_3$ by the intermediate 2-trichloromethylcycloalkyl radical may occur before or after ring flipping in flexible systems, but it does not occur to form product with eclipsed Br and CCl$_3$ substituents.

Recent investigation of the photoinitiated addition of bromotrichloromethane to *cis*-cyclooctene demonstrated that the 1,2-addition product consists of a 1:1 mixture of *cis*- and *trans*-1-bromo-2-trichloromethylcyclooctane.[2,3] While a mixture of geometrical isomers was expected for this radical addition reaction, the 1:1 proportion obtained was surprising. Both highly stereoselective and nonselective radical additions of hydrogen bromide, halogens, thiols, and hydrogen sulfide have been reported.[4] Reaction conditions, identity of substituents on the alkene linkage, and steric factors have been found to affect significantly the stereoselectivity of these additions.[4] Few data are available however, on the stereochemistry of additions of carbon tetrahalide (or of other reagents which are sources of carbon radicals) to alkenes.[5] Therefore, in order to assess the importance of some factors which may influence the stereochemistry of such additions, we have

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[1] (a) We gratefully acknowledge partial support of this research by a grant from the National Science Foundation (Grant No. GP 5749). (b) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec 1967, paper 170.

[2] J. G. Traynham, T. M. Couvillon, and N. S. Bhacca, *J. Org. Chem.*, **32**, 529 (1967). Although the addition product appeared to be a single component by gas chromatographic (gc) analysis, nuclear magnetic resonance (nmr) data clearly established it to be a mixture.

[3] The 1,2-addition product formed in minor amounts (3%) from addition of carbon tetrachloride to *cis*-cyclooctene was likewise shown to be a 1:1 mixture of *cis* and *trans* isomers: J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **89**, 3205 (1967).

[4] For brief reviews, with references, see (a) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 206–218; (b) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62**, 599 (1962).

[5] (a) E. S. Fawcett, *ibid.*, **47**, 219 (1950). (b) E. Tobler and D. J. Foster, *J. Org. Chem.*, **29**, 2839 (1964). (c) J. Weinstock (Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., Sept 1955, p 19-20) reported that radical addition of BrCH$_2$COOEt to norbornene appeared to give the *exo-cis* product. (d) NOTE ADDED IN PROOF.—L. H. Gale [*J. Org. Chem.*, **34**, 81 (1969)] has reported radical additions of BrCCl$_3$ to cycloalkenes (ring sizes 5–8, γ radiation). He reports single adducts with cyclopentene and cycloheptene but does not identify them as *cis* or *trans* isomers. He does report *cis* and *trans* adducts with cyclohexene.