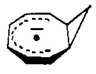
became diamagnetic as 2 mol of potassium was added. Similar results were obtained in samples of 0.01 and 0.005 *M* in I without concomitant precipitation of V. The lithium and sodium reductions of I behaved similarly.

V



VI

Alkali metal reduction of I gives the anion radical II whose esr spectral parameters are relatively insensitive to changes in experimental conditions. Likewise, no appearance of new lines or disappearance of old lines is noted for II for the systems studied. Thus, the presence of a valence tautomer anion radical such as VI cannot be detected, and the anion radical II having more extensive delocalization is favored.[14]

Acknowledgments. The authors are indebted to Professors S. Winstein and R. M. Hedges for helpful discussion. We are indebted to Mr. T. Atkinson for calibration spectra. The esr spectrometer was made available by National Science Foundation Grant GP-3767. Support from the Robert A. Welch Foundation and The Research Council of Texas A&M University are gratefully acknowledged. We also acknowledge the computer facilities made available by the Data Processing Center of Texas A&M University.

(14) NOTE ADDED IN PROOF. Methylcyclooctatetraene anion radical (VII) is observed during the electrolytic reduction of I in liquid ammonia[2b] and during the alkali metal reduction of I in liquid ammonia (R. M. Owens, unpublished results). For the systems I–DME–M and I–THF–M for M = Li, Na, K over the temperature range −130 to +30°, VII is not observed, either alone or concurrently with anion radical II.

Photolyses of Trienes. II. Selective Photoreactions of 2,7,7-Trimethylcycloheptatriene[1]

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Abstract: Irradiation of a benzene or cyclohexane solution of 2,7,7-trimethylcycloheptatriene (**1**) in a Pyrex tube with a Hanovia medium-pressure mercury arc lamp yields a mixture containing 2,2,4-trimethylbicyclo[3.2.0]hepta-3,6-diene (**5**), 1,3,7-trimethylcycloheptatriene (**4**), 1,5,7-trimethylcycloheptatriene (**3**), and recovered starting material. Compounds **4** and **5** are primary photoproducts while **3** arises from further irradiation of **4**. The new trienes arise from highly selective [1,7] sigmatropic methyl and hydrogen migrations, and the bicyclic product arises from a selective electrocyclization reaction. The origin of these highly selective transformations and sensitization studies of these reactions are discussed.

Photoisomerization reactions of a number of cycloheptatrienes have been investigated. Irradiation of cycloheptatriene in solution[2] gives bicyclo[3.2.0]-hepta-2,6-diene as the major product, while the gas phase reaction[3] yields predominantly toluene. Photochemical studies of certain substituted cycloheptatrienes have shown highly selective [1,7] sigmatropic hydrogen migrations.[4-6] Examples of methyl migrations have also been reported[1,7] in studies involving methyl-substituted cycloheptatrienes.

As a continuation of our study of the photoisomerization reactions of cyclic conjugated trienes,[1] we now wish to report the results of a study of the photolysis of 2,7,7-trimethylcycloheptatriene (**1**). As was demonstrated by the photolysis of 3,7,7-trimethylcycloheptatriene (**2**),[1] the methyl group situated at carbon atom 3 in **2** exerts a strong directive influence on the course of both the methyl migration and electrocyclization reactions. It seemed of interest to determine the effect of a methyl group at position 2 on the course of reaction under photolytic conditions and to compare the results with those previously observed[1] for the photolysis of **2**.

2,7,7-Trimethylcycloheptatriene (**1**) has been identified as one of the products of the gas phase pyrolysis of 3,7,7-trimethylcycloheptatriene (**2**).[8] Because of the complexity of this reaction, the pyrolysis did not appear to be a convenient method for the synthesis of **1**. We therefore prepared 2,7,7-trimethylcycloheptatriene (**1**) by the lithium aluminum hydride reduction of 3,3,5-trimethylcycloheptadien-1-one, prepared as described by Büchi and Burgess,[9] followed by acid-catalyzed dehydration.

Our investigation[1] of the photolysis of **2** demonstrated that a new triene, 1,5,7-trimethylcycloheptatriene (**3**), arose from a selective [1,7] sigmatropic methyl migration, and that a second triene, 1,3,7-trimethylcycloheptatriene (**4**), arose from a selective [1,7] sigmatropic hydrogen migration. In addition, 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene was formed as a result of a selective electrocyclization reaction.

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(1) For Part I see: L. B. Jones and V. K. Jones, *J. Am. Chem. Soc.*, **89**, 1880 (1967).

(2) W. G. Dauben and R. L. Cargill, *Tetrahedron*, 12, 186 (1961).

(3) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432 (1962).

(4) A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim.*, **84**, 241 (1965).

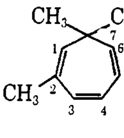
(5) R. W. Murray and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 3527 (1966).

(6) G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *ibid.*, **89**, 2979 (1967).

(7) O. L. Chapman and S. L. Smith, *J. Org. Chem.*, 27, 2291 (1962).

(8) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **88**, 2494 (1966).

(9) G. Büchi and E. M. Burgess, *ibid.*, 82, 433 (1960).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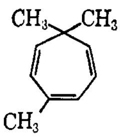
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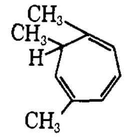
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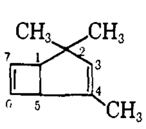
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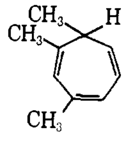
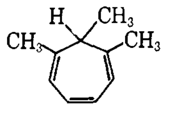

4

Irradiation of **1** in benzene (or cyclohexane) solution with a 450-W Hanovia medium-pressure mercury arc lamp for 2–3 hr results in the formation of 1,3,7-trimethylcycloheptatriene (**4**), 1,5,7-trimethylcycloheptatriene (**3**), and 2,2,4-trimethylbicyclo[3.2.0]hepta-3,6-diene (**5**). Structural assignments of the trienes were made on the basis of comparisons with authentic samples.[1] The bicyclic compound **5** was identified from uv and nmr data and elemental analysis.

Analysis of the photolysis mixture at various time intervals indicates that **4** and **5** are primary photoproducts. Cycloheptatriene **3** arises from **4** in a secondary photochemical reaction. The bicyclic product **5** is inert to further reaction under the conditions employed. If the irradiation is allowed to proceed for several hours the reaction mixture shows 13% of unreacted starting material, 35% of bicyclic product (**5**), and 52% of the product trienes (**3** and **4**). The two new trienes approach an apparent photoequilibrium (as observed previously[1]) of *ca.* 40% of **3** and 60% of **4**. Vapor phase chromatography indicated the possibility that another product triene (conceivably **6**) could have formed in very small amounts. However, we were not able to isolate enough of this material for characterization.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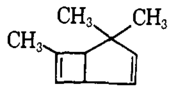

7

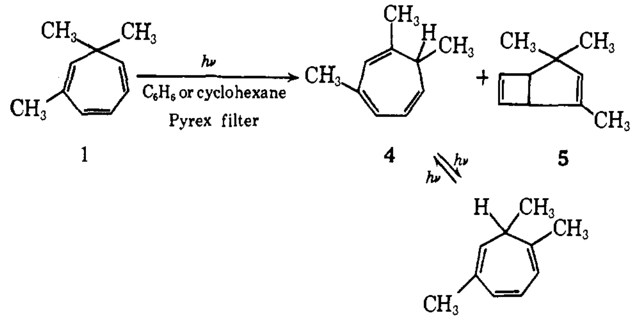
Attempts to photosensitize the migration and cyclization reactions of compounds **1** and **2** were unsuccessful. Acetophenone ($E_T \sim 74$ kcal/mol)[10] and benzophenone ($E_T = 69$ kcal/mol)[11] were used for these reactions. It is doubtful that the triplet energies of the substituted cycloheptatrienes lie above these values. Evans[12] has shown that *trans*-1,3,5-hexatriene has a triplet energy of 47 kcal/mol. This is a planar molecule and this value is, therefore, probably a lower limit for the triplet energy of cycloheptatrienes.

The effect of oxygen on the photoreactions of **1** and **2** (both direct and sensitized irradiations) was shown to be negligible.

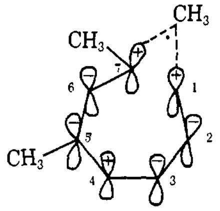
Discussion

The reaction course of **1** under photolytic conditions is summarized in Scheme I. The reaction is highly selective. Methyl migration occurs exclusively in one direction to yield **4**. This triene upon further irradiation undergoes a selective [1,7] hydrogen migration to yield **3**. Similarly, **3** under these reaction conditions exhibits a selective hydrogen migration to yield **4**.[1] The electrocyclization reaction is also observed to be quite selective. The only bicyclic compound produced is **5**. These results clearly demonstrate that a methyl group on carbon atom 2 of the starting triene (**1**) exerts a strong directive influence on the course of both the migration and electrocyclization reactions.

Scheme I



These selective photochemical transformations can be explained using arguments presented earlier.[1] Woodward–Hoffmann orbital symmetry arguments predict sigmatropic [1,7] suprafacial methyl migrations for photochemical reactions in this triene system.[1,13] As a result methyl migration may be expected to occur with either carbon atoms 1 or 6 as the migration terminus. Molecular orbital calculations allow a distinction to be made between these two reaction paths (*i.e.*, transition states **8** and **9**). HMO calculations[14] employing a hyperconjugation model[15] to describe the effect of the methyl substituents indicate that the π energy of **8** (electronically excited seven-electron, seven-atom linear π framework) is less than that of **9** by at least 1.5–2 kcal/mol. Such an energy difference is sufficient to account for the selective formation of **4** *via* the lower energy transition state **8**. In a similar manner molecular orbital calculations[14] also account for the selective hydrogen migrations observed for **3** and **4**.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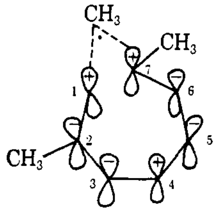
9

The selectivity noted in the cyclization reaction of **1** is most readily rationalized on the basis of steric considerations. The ring fusion in the product **5** must be *cis*. A consideration of a Dreiding model of **5** reveals that there are no serious nonbonded interactions in this molecule. However, compound **7** (the other possible

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(10) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(11) D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087 (1966).

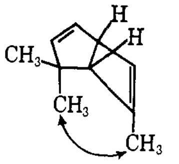
(12) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(13) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(14) L. B. Jones and T. M. Sloane, unpublished calculations. The most consistent results are obtained using a linear rather than a cyclic model for the C-7 radical. Similar models[6,13] have been employed for reactions involving hydrogen migrations.

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1963, p 131.

bicyclic product) has one serious interaction between the methyl group on carbon 7 and one of the *gem*-dimethyl groups at carbon 2. Dreiding models indicate that these two methyl groups are crowded to about the same extent in **7** as are the diaxial methyl substituents in *cis*-1,3-dimethylcyclohexane (**10**). This interaction in **10** leads to an unfavorable energy term of about 5 kcal/mol[16] and should, therefore, strongly favor the formation of **5** (over **7**) in the electrocyclization reaction.



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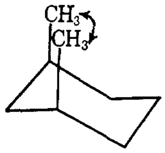

10

Attempts to photosensitize the reactions of **1** and **2** with benzophenone (E_T = 69.5 kcal/mol)[11] and acetophenone (E_T = 74.0 kcal/mol)[10] were unsuccessful. Such results provide a strong indication that neither the migration nor cyclization process occurs from an excited triplet state since it is highly doubtful that the triplet energies of cycloheptatrienes are higher than the energies of these two sensitizers. The observation that oxygen has no effect on these reactions is also consistent with this conclusion. While one cannot completely rule out the possibility that these reactions are occurring from a vibrationally excited ground state, all indications are that the migration and cyclization reactions are occurring from an excited singlet-state species. Both processes are consistent with Woodward–Hoffmann orbital symmetry arguments[1,3,17] only if they are excited-state reactions. Similarly, thermal reactions of **1** lead to a complicated mixture of products[8] which differs considerably from that obtained from the photolysis of **1**. While this latter fact does not preclude reaction from a vibrationally excited ground state we feel that the methyl and hydrogen migration reactions, as well as the electrocyclization processes, are most likely excited singlet-state reactions.

It is of considerable interest to compare the photochemical reactions of 2,7,7-trimethylcycloheptatriene (**1**) and 3,7,7-trimethylcycloheptatriene (**2**). Irradiation of triene **2** induces migration of one of the *gem*-dimethyl groups from carbon atom 7 to carbon atom 1. When triene **1** is subjected to photolysis conditions, one of the *gem*-dimethyl groups migrates from carbon 7 to position 6. Thus, the migration terminus is strongly dependent upon the location of the vinyl methyl substituent. A comparison of the cyclization reactions indicates that the ring closure reaction is also strongly dependent upon the location of the methyl substituent in the starting triene. Placement of the methyl group at position 3 in the cycloheptatriene produces ring closure at carbons 1 and 4. When the methyl substituent is located at position 2, ring closure occurs at carbons 3 and 6 to form **5**.

We are currently investigating the photochemical reactions of 2,3,7,7-tetramethylcycloheptatriene to compare the relative directive influences of the methyl groups at the 2 and 3 positions when present in the same molecule. We hope to report these results in a subsequent paper.

Experimental Section[18]

2,7,7-Trimethylcycloheptatriene (1). 3,3,5-Trimethylcyclohepta-dien-1-one was prepared as described by Büchi and Burgess.[9] A mixture of 4 g of 1,4,4-trimethylbicyclo[3.2.0]hept-6-en-2-one having bp 94–98° (40–50 mm) [lit.[9] bp 95–96° (45 mm)], isolated from the irradiation of eucarvone,[9] and 1 g of *p*-toluenesulfonic acid in 100 ml of benzene was refluxed for 2 hr in the dark. The mixture was cooled, diluted with ether, and washed with aqueous potassium carbonate. The organic layer was dried and concentrated. The crude mixture was pyrolyzed at 400° to give 3 g of a yellow pyrolysate consisting of *ca.* 60% of 3,3,5-trimethylcycloheptadien-1-one.[20] This mixture was used without purification in the subsequent reactions. The mixture was reduced with 0.5 g of lithium aluminum hydride, and the crude alcohols were dehydrated by dropwise addition to 1 g of potassium acid sulfate at 120° and water-aspirator pressure. The crude trienes distilled as formed to give 1 g of material having bp 44–50° (40 mm). Gas chromatography[21] showed the presence of two peaks in the relative amounts of 60 and 40% in order of retention times. The minor peak was shown to be 3,7,7-trimethylcycloheptatriene (**2**) from its nmr spectrum[6] and retention time.[20] The major peak was collected to give 300 mg of 2,7,7-trimethylcycloheptatriene (**1**) containing 10% of **2**. The nmr spectrum[22] of **1** was in agreement with the nmr absorptions (in parts per million, ppm) published by Berson and Willcott,[8] and contained a singlet at 0.96 (6 H, *gem*-dimethyl), a band at 1.88 (3 H, vinyl methyl), and absorptions at 4.7–5.2 (two-hydrogen multiplet, C-1 and C-6 olefinic hydrogens), 5.7–6.2 (one-hydrogen multiplet, C-5 hydrogen), and 6.2–6.4 (two-hydrogen multiplet, C-3 and C-4 hydrogens). The presence of 3,7,7-trimethylcycloheptatriene (**2**) was indicated by the lone methyl absorption at 2.0 ppm. As was also observed by Berson and Willcott,[8] 2,7,7-trimethylcycloheptatriene (**1**) is difficult to obtain free of **2**. Due to overlap of the two compounds on the column, purity of better than 95% could not be achieved despite repeated collections. Since the preparation of the compound is extremely tedious and material is lost upon collection, samples of 90–95% of purity were employed in the photolyses experiments.

Irradiation of 2,7,7-Trimethylcycloheptatriene (1). A solution of 120 mg of **1** containing 5% of **3** in 2.5 ml of benzene was irradiated in a Pyrex tube with a 450-W Hanovia lamp for 2 hr. Gas chromatography[20] showed 35% of **5**, 13% of **1**, and 52% of a mixture of new trienes. Further gas chromatography[21] showed **3** and **4** to be present in the relative amounts of 25 and 69%, respectively, in order of retention times. A small peak present in the relative amount of 6% was eluted last and was not characterized. Compounds **3**, **4**, and **5** were collected.

Compound **3** had the retention time[21] of 1,5,7-trimethylcycloheptatriene.[1] The nmr spectrum (in ppm) shows a three-proton doublet at 1.18 (J = 7 cps). The vinyl methyl groups appear as broadened singlets at 1.80 and 1.87. The olefinic proton absorptions appear at 4.75 (one-hydrogen broadened doublet, J = 6 cps), 5.80 (a broad band corresponding to one hydrogen), and 6.29–6.45 (two-hydrogen multiplet). This spectrum agrees with the spectrum of 1,5,7-trimethylcycloheptatriene.[1]

Compound **4** has the retention time[21] of 1,3,7-trimethylcycloheptatriene.[1] The nmr spectrum shows a three-proton doublet at 1.18 ppm (J = 7 cps). The vinyl methyl groups appear as broad-

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(16) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

(17) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(18) 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 were determinined at 60 Mc with a Varian Model A-60 nmr spectrometer, using a slight modification of the microcell described by Itô and Miura[19] unless otherwise stated. A 5–8-μl sample of the pure liquid made up to 10–15 μl with carbon tetrachloride containing a trace of tetramethylsilane as an internal standard was sealed in a melting point capillary and placed in a standard size nmr tube containing carbon tetrachloride. Microanalyses were performed by Huffman Laboratories, Inc., Wheatridge, Colo.

(19) S. Itô and I. Miura, *Bull. Chem. Soc. Japan*, **38**, 2197 (1965).

(20) A column packed with SE 30 suspended on Chromosorb P was employed.

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

(22) Determined in the normal manner as a solution in carbon tetrachloride and tetramethylsilane as internal reference.

ened singlets at 1.86 and 1.95 ppm. The olefin proton absorptions appear at 4.90–5.05 (one-hydrogen pair of doublets, $J = 6$ cps), 5.70–6.10 (two-hydrogen multiplet), and 6.16–6.40 (one-hydrogen multiplet). This spectrum agrees with the spectrum of 1,3,7-trimethylcycloheptatriene.[1]

The nmr spectrum of **5** shows a *gem*-dimethyl group as two nonequivalent singlets at 0.98 and 1.03 ppm. The vinyl methyl group appears at 1.70 ppm. The bridgehead protons at positions 1 and 5 appear as broad bands at 3.00 and 3.45 ppm, respectively. The cyclopentene hydrogen at position 3 appears as a band at 4.98 ppm containing fine splitting (J = *ca.* 1 cps). The cyclobutene protons appear as a doublet at 6.13 ppm ($J = 3$ cps) containing further splitting (J = *ca.* 1 cps) and as a doublet at 6.55 ppm ($J = 3$ cps) containing further splitting (J = *ca.* 0.5 cps). Trace absorptions (*ca.* 5–10% from the integration) appear at 5.36 and 5.70 ppm. If a sample of **1** containing 10% of **2** is irradiated, the isolated sample of **5**, which appears as a single peak on all gas chromatographic columns tried, contains *ca.* 35% (from the nmr integration) of 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene, the bicyclic photoproduct of **2**, as shown by nmr absorption bands at 2.76 ppm, a doublet at 5.36 ppm ($J = 6$ cps) further coupled with the bridgehead hydrogen (J = *ca.* 1 cps), and a multiplet at 5.64–5.84 ppm. That the trace absorptions at 5.36 and 5.70 in the sample of **5** obtained from the irradiation of **1** containing 5% of **2** arise from the presence of **7** which would have a spectrum very similar to that of 2,2,6-trimethylbicyclo[3.2.0]hepta-3,6-diene cannot be excluded, but the above results seem to indicate that they arise from the bicyclic photoproduct of **2**. However, it can be concluded that at least 90% of the bicyclic product from **1** is **5**, which indicates a very selective photocyclization.

A sample of **5** containing 5–10% of the second olefin shows only end absorption (ϵ_{210} 2940) in the ultraviolet, which is in agreement with the bicyclic structure.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found for **5**: C, 89.55; H, 10.45.

Irradiation of 25 mg of **1** containing not more than 5% of **2** in 1 ml of benzene was followed by gas chromatographic analysis[21] at various time intervals to determine the relative amounts of **3** and **4**. These data are presented in Table I.

Table I. Relative Amounts of **3** and **4** during Irradiation of **1**

Time, min	% **3**	% **4**
25	0	100
35	0	100
45	3	97
75	25	75
85	35	65
125	35	65

Irradiation of 3,7,7-Trimethylcycloheptatriene (2) in the Presence of Sensitizer.[23] A solution of 20 mg (0.11 mmol) of **2** in 0.3 ml of benzene was placed in each of two Pyrex nmr tubes. To one of the tubes 30 mg (0.25 mmol) of acetophenone was added. To another nmr tube were added 15 mg (0.22 mmol) of piperylene (75% of the *trans* isomer, 25% of the *cis* isomer) and 30 mg (0.25 mmol) of acetophenone in 0.3 ml of benzene. The nmr tubes were placed in Pyrex tubes and immersed in the filter solution behind plate glass of 0.5-cm thickness. The samples were irradiated for 18 hr. Gas chromatographic analysis[20] of the triene solution without added acetophenone showed 35% of bicyclic product, 47% of unreacted **2**, and 18% of a mixture of new trienes. Analysis[20] of the triene solution with added acetophenone showed only the presence of unreacted **2**. Analysis of the piperylene solution[21] showed 60% of the *trans* isomer and 40% of the *cis* isomer (stationary state of piperylene using acetophenone as sensitizer is reported[24] as 53–55% of the *trans* isomer).

A solution of 70 mg (0.52 mmol) of triene **2** in 5 ml of benzene was placed in each of two Pyrex test tubes. To one of the tubes, 188 mg (1.03 mmol) of benzophenone was added. To another tube were added 34 mg (0.50 mmol) of piperylene (75% *trans*) and 177 mg (0.97 mmol) of benzophenone. The tubes were irradiated in the filter solution behind 0.5 cm of plate glass. After 4.5 days of irradiation, analysis[20] of the triene solution without added benzophenone showed *ca.* 50% photoproducts and *ca.* 50% of unreacted starting material. The sample with added benzophenone showed only the presence of **2**. Analysis[21] of the piperylene solution showed 57% of the *trans* isomer and 43% of the *cis* isomer (photostationary state of piperylene using benzophenone as a sensitizer is reported[24] as 56–57% of the *trans* isomer).

A solution of 68 mg (0.51 mmol) of triene **2** in 5 ml of benzene was placed in each of two Pyrex test tubes. To one of the tubes was added 190 mg (1.0 mmol) of benzophenone, and the mixture was degassed. To another tube was added 35 mg (75% *trans*) of piperylene, 180 mg (1.0 mmol) of benzophenone, and 5 ml of benzene, and the mixture was degassed. After 46 hr of irradiation, analysis[20] of the triene solution without added benzophenone showed complete reaction. Analysis[20] of the degassed triene solution with added benzophenone showed only the presence of **2**. Analysis[21] of the piperylene solution showed 60% of the *trans* isomer.

Irradiation of 2,7,7-Trimethylcycloheptatriene (1) in the Presence of Sensitizers. These irradiations were carried out using 15 mg (0.11 mmol) of triene **1** in 1.0 ml of benzene. After 5-hr irradiation, *ca.* 70% of **1** had rearranged to bicyclics and new triene products. Addition of 2 equiv of acetophenone definitely slowed down the rearrangement, while addition of 2 equiv of benzophenone effectively halted the rearrangement. In the wavelength region employed for these experiments benzophenone absorbed essentially all of the incident radiation while acetophenone absorbed approximately 75% of the incident light (ϵ_{366} 0.55 for triene **2**; ϵ_{366} 0.78 for acetophenone; ϵ_{366} 46 for benzophenone). Degassed solutions of benzophenone and triene **1** showed the same results.

Irradiation of 3,7,7-Trimethylcycloheptatriene (2) in Cyclohexane and in Benzene in the Absence of Oxygen. To each of three test tubes was added 65 mg of triene **2** in 3 ml of solvent (benzene in two tubes, cyclohexane in the remaining tube). One benzene sample was degassed. The samples were irradiated for 70 min. Analysis[20] of the benzene solution containing oxygen showed 40% of bicyclic product, 24% of unreacted **2**, and 36% of new trienes. Analysis of the degassed benzene solution showed 37% of bicyclic products, 23% of unreacted **2**, and 40% of new trienes. Analysis of the cyclohexane solution showed 33% of bicyclic products, 31% of unreacted **2**, and 37% of new trienes.

Irradiation of 2,7,7-Trimethylcycloheptatriene (1) in Cyclohexane and in Benzene in the Absence of Oxygen. To each of three test tubes was added 15 mg of triene **1** containing 10% of **2** in 1 ml of solvent (benzene in two tubes, cyclohexane in the remaining tube). One benzene sample was degassed. The samples were irradiated for 1 hr. Analysis[20] of the benzene solution containing oxygen showed 32% of bicyclic products, 18% of unreacted **1**, and 50% of new trienes. Analysis of the degassed benzene solution showed 28% of bicyclic products, 20% of unreacted **1**, and 52% of new trienes. Analysis of the cyclohexane solution showed 30% of bicyclic products, 15% of unreacted **1**, and 55% of new trienes.

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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[23] The filter system used was similar to that described by Hammond, *et al.*[24] The 450-W Hanovia medium-pressure mercury arc lamp was housed in a quartz Vycor jacket through which cold water was circulated during the period of irradiation. The jacket and lamp were immersed in a filter solution which was 0.50–0.75 *F* in cupric nitrate trihydrate.[25] Samples to be irradiated were placed in Pyrex tubes and immersed in the filter solution at a distance of 20–40 cm from the light source. During some of the irradiations, 0.5 cm of plate glass was placed between the sample and the light source.

[24] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[25] Hammond, *et al.*,[24] report that the only important line transmitted by this solution is the 3660-Å line as well as lines of longer wavelengths.