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TRIPLET PHOTOCHEMISTRY OF MEDIUM RING TRIENES[1]

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Abstract—The photochemistry of the triplets of 10- and 11-membered ring 1,3,5-trienes has been studied. At −70°, *cis,trans,cis*-cyclodeca-1,3,5-triene goes only to the *cis,cis,cis*-isomer. At 25°, this latter compound is converted into *cis*-bicyclo[4.4.0]deca-2,4-diene via the thermally labile *trans,cis,trans*-cyclodeca-1,3,5-triene. At −70°, *cis,trans,cis*-cycloundeca-1,3,5-triene is converted to the *cis,cis,cis*-isomer. At 25°, this primary photochemical product undergoes a thermal 1,7-sigmatropic hydrogen migration to yield the *trans,cis,cis*-isomer. This latter triene upon sensitized irradiation yields *cis*-bicyclo[5.4.0]undeca-8,10-diene and *trans*-bicyclo[7.2.0]undeca-2,10-diene. The ratio of these latter two products changes with the temperature of the sensitized reaction. The possible mechanisms of these transformations are discussed.

The singlet state photochemistry of *trans,cis,cis*- and the *trans,cis,trans*-cyclic trienes has been extensively studied;[2] such is not the case for their triplet state photochemistry. The probability of intersystem crossing from the singlet to the triplet manifold is intrinsically low[3] for polyolefin compounds and, in the absence of heavy atoms, is not competitive with reactions emanating from the S_1 excited state. Population of the triplet manifold of conjugated trienes can be accomplished, however, by energy transfer from a photosensitizer of appropriate energy (>47 kcal/mol).

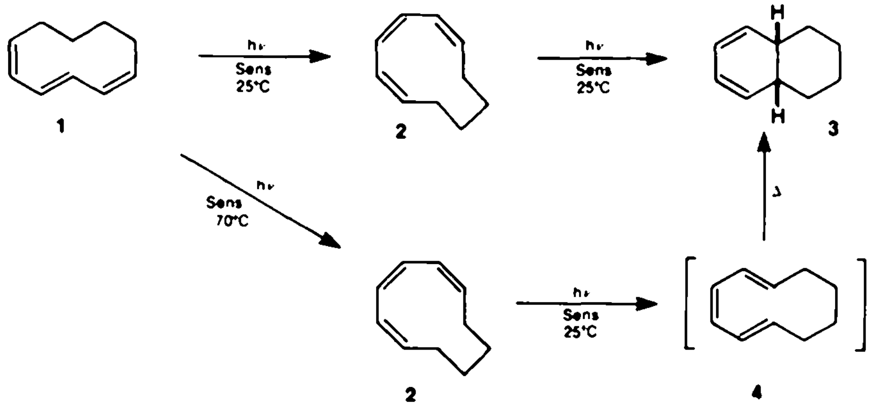
With conjugated trienes which have no geometrical constraints upon the ground state of any possible isomer, it is known that general sensitized irradiation of any isomer results in the rapid *cis,trans* isomerization about the three double bonds to yield the same photoequilibrium of possible trienes.[4] Interestingly, no electrocyclic or sigmatropic rearrangements common to the direct irradiation of trienes are found under sensitized (triplet) conditions; double bond isomerization and dimerization are the normal reactions of diene triplets.[5] The photochemical equilibrium of acyclic conjugated trienes which have a geometrical restriction to a planar configuration of some of its isomers has been shown to be dependent upon the triplet energy of the sensitizer employed, the nonplanar isomers not being activated by low energy sensitizers.[6]

Recently, a new class of cyclic 1,3,5-trienes which possess the *cis,trans,cis* configuration has been prepared.[7] The triplet photochemistry of these new materials has now been investigated in order to further evaluate the role of the ground state conformation upon triplet energy transfer and to study the ground state chemistry of new triene isomers in cyclic systems.

RESULTS

In an initial exploratory experiment, a dilute pentane solution of *cis,trans,cis*-cyclodeca-1,3,5-triene (1) containing an equimolar amount of *m*-methoxyacetophenone (E_T = 74 kcal/mol) was irradiated at 350 nm through Pyrex at room temperature. A single product was rapidly formed and upon continued irradiation this primary photoproduct was slowly transformed into a secondary photoproduct. In a preparative run under the same conditions, the products were isolated by vpc and the primary photoproduct was identified as *cis,cis,cis*-cyclodeca-1,3,5-triene (2) and the secondary photoproduct as the known *cis*-bicyclo[4.4.0]deca-2,4-diene (3).[8] The finding of a product from an electrocyclic reaction was of interest since it was shown that the all *cis*-triene 2, a possible precursor of 3 via a thermal reaction, was stable at this temperature.

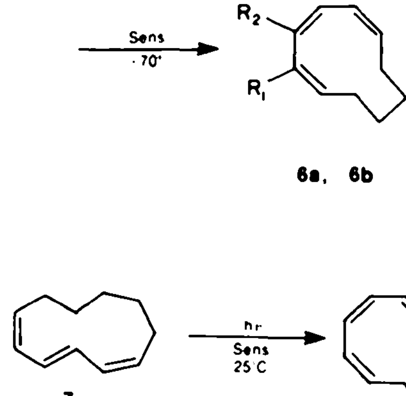
To obtain more detail as to the reaction process, the photoreaction was repeated at −70° and it was found that the *cis,cis,cis*-triene 2 was extremely stable to the photoreaction conditions, less than 2% of the hexalin 3 being found after prolonged irradiation. When the solution of



the *cis,cis,cis*-isomer was allowed to warm to room temperature, the hexalin 3 was formed very rapidly under the irradiation conditions. These results indicate that the *cis,cis,cis*-isomer 2 is converted to the *trans,cis,trans*-isomer 4 which above −40° is known to cyclize to the *cis*-hexalin 3.[9] At −70°, the trienes 2 and 4 must be in a photoequilibrium state which strongly favors 2 since when the cold solution is allowed to warm to room temperature in the dark, 2 is the only product. It was found that the course of the reactions was independent of the energy of the sensitizer (51–74 kcal/mol). That, indeed, the reactions were occurring in the triplet manifold was shown by determination of the rate of reaction as a function of sensitizer concentration. It was found that the rate greatly increased (k from 0.007 to 0.053 sec^{-1}) as concentration of acetophenone increased from 0 to 0.04*M*.

It is to be noted that no *trans,cis,cis*-triene was detected even though it would have been expected to be stable under the reaction conditions.[7,8] This finding of the isomerization of two double bonds in a triplet reaction is a common phenomenon[6,10] due to the lifetime of the triplets which permits the various methylene-pnetadienyl species to equilibrate.

This study shows by temperature variation it is possible in these cyclic systems to guide triplet reactions to specific products. The procedure is carefully balanced with regard to the potential role of the thermally unstable isomer vs the normal triplet dimeric reaction. The two monomethylated *cis,trans,cis*-cyclodeca-1,3,5-trienes (**5a**, **5b**) illustrate this balance in that sensitized activation at −70° clearly yielded the *cis,cis,cis*-trienes **6a** and **6b**. When the reaction was conducted at room temperature, **6a** and **6b** only yielded dimeric materials upon prolonged irradiation, no simple electrocyclization product was formed.



5a: $R_1 = CH_3$; $R_2 = H$
5b: $R_1 = H$, $R_2 = CH_3$

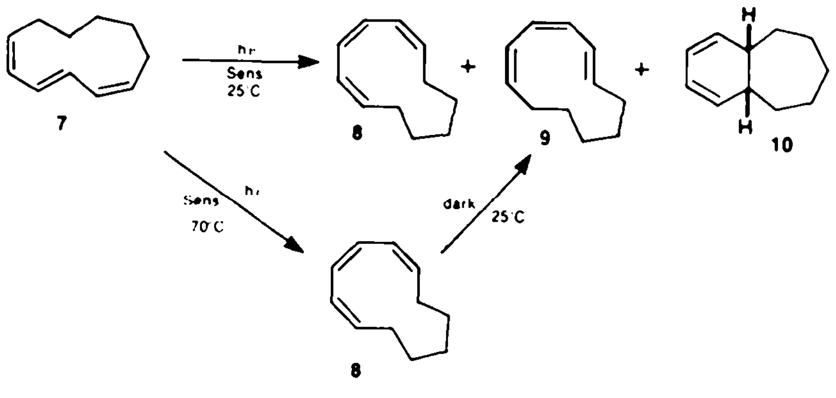
6a, **6b**

The sensitized irradiation of the next higher homolog, *cis,trans,cis* - cycloundeca - 1,3,5 - diene (7) proved to be more complex due to the extreme thermal instability of various of the photoproducts obtained. In an exploratory experiment similar to that described for the sensitized irradiation of 1, vpc analysis during the course of the irradiation at 25° indicated a sequential production of two products, the secondary product appearing more rapidly than in the other series. Analyses of the course of the reaction using silver nitrate impregnated silica gel TLC showed that the primary photoproduct was, indeed, a mixture of two compounds. The secondary photoproduct, which was the major reaction product upon prolonged irradiation, was the known *cis*-bicyclo[5.4.0]undeca-diene (**10**).[8]

When the irradiation was performed at −70°, only the primary products were formed, a result quite similar to that obtained in the other series except there appeared to be two primary products. The sensitized irradiation was repeated on a preparative scale at −70° and analysis of the reaction product by NMR spectroscopy, after removal of the sensitizer by silver nitrate impregnated silica gel tlc, indicated the reaction product was a 1 : 1 mixture of two compounds. When the mixture was chromatographed on silver nitrate impregnated silica gel, only the material of the lower R_f was isolated and it in a yield much higher than indicated by the analysis of the reaction mixture. The product was identified as the known *trans,cis,cis* - cycloundeca - 1,3,5 - triene (**9**).[8]

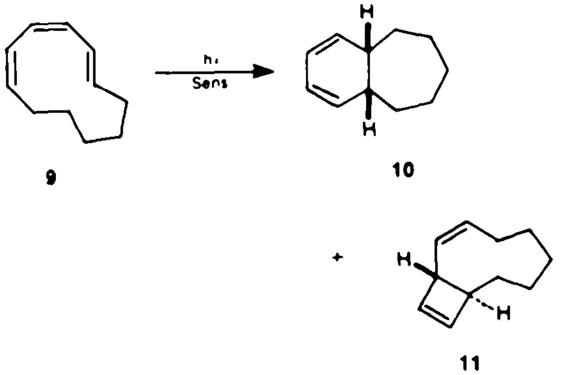
With the knowledge of the structure of one of the components, the material from another −70° sensitized irradiation was examined by ^{13}C NMR spectroscopy. It was found that in addition to the absorption lines for **9**, there were six major lines which were similar to those displayed by the *cis,cis,cis*-triene 2. All these results indicated either a thermal or a silver promoted rearrangement of the second product was occurring. Repetition of the experiment, this time doing all manipulations at as low a temperature as possible and as rapidly as possible, gave a hydrocarbon fraction which was 90% pure *cis,cis,cis* - undeca - 1,3,5 - triene (**8**). This material while in an NMR tube at 25° underwent a thermal rearrangement to the *trans,cis,cis*-triene **9**.

At −70°, the all *cis*-triene 8 failed to undergo further photosensitized rearrangement, within the limits of the



analytical procedures; no *cis,trans,cis*-triene **7** was found. These results are similar to those found in the ten-membered ring system. The formation of the *trans,cis,cis*-triene **9** must proceed via a 1,7-hydrogen shift, a sigmatropic rearrangement allowed in this larger ring by its greater flexibility which permits an orientation for an allowed antarafacial shift.

The triplet photochemistry of the *trans, cis,cis*-triene **9** was also studied. The triene was irradiated at −70° using acetophenone, *m*-methoxyacetophenone, or fluorenone until no change in the composition of the mixture occurred. The reaction mixture was processed and analyzed at as low a temperature as possible and it was found very little reaction had taken place, the composition of the mixture being 80% of starting triene **9**, 5% of bicyclic diene **10**, and 15% of a new compound identified as *trans* bicyclo[7.2.0]undeca - 2,10 - diene (**11**); no *cis,cis,cis*-triene **8** was found. However, when the reaction was run at 25°, the results were quite different, there being obtained only 30% of the starting triene **9** and 70% of the bicyclic diene **10**, less than 1% of the bicyclo[7.2.0]undecadiene **11** was present. Again, none of the all *cis*-triene **8** was formed, showing the high specificity of the reaction.



9 **10** **11**

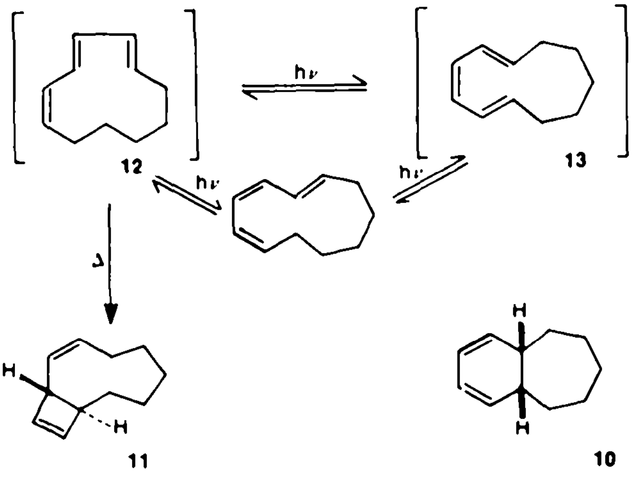
A mechanism for the triplet-induced rearrangements of *trans,cis,cis*-triene **9**, consistent with the temperature dependence found, can be viewed in the following manner. Irradiation of the triene at −70° sets up a facile equilibrium with the *trans,trans,cis* - isomer **12** and the *trans,cis,trans* - isomer **13** and at this low temperature the highly strained *trans,trans,cis* - isomer ring closes to yield **11** while the *trans,cis,trans* - isomer is stable, the photoequilibrium highly favoring the *trans,cis,cis* - triene. The small amount of **10** found in the irradiation products could have been formed by a slow reaction at −70° or be simply the result of the processing of the reaction mixture. Clearly, this is an early pseudophotostationary state since, in time, the major product must be **11** which is photochemically inert under these reaction conditions.

The results obtained at 25° show that the *trans,cis,trans* - triene **13** is removed from the photoequilibrium by a thermal reaction to yield **10**. The almost total disappearance from the reaction mixture of **11** at this temperature shows that the left side of the reaction schemes did not function under these reaction conditions. One possible reason for this change could be that at 25° the lifetime of **12** is too short to permit conformational changes so it could adopt an orientation conducive for the electrocyclization and, thus, only reisomerizes to starting triene.

The stereoselectivity found in these photosensitized reactions warrant further evaluation, i.e. why does the *cis,trans,cis* - isomer go only to the *cis,cis,cis* - isomer which is photochemically stable at −70° and why does the *trans,cis,cis* - isomer readily isomerize to the *trans,cis,trans*- and *trans,cis,cis* - isomer but not to the *cis,cis,cis* - isomer? Some insight into this specificity can be gained by considering the hypothetical energy surfaces of the triplet and ground states.

For the acyclic trienes which upon triplet transfer excitation give rise to the same photostationary state starting with any triene isomer there are two critical features. First, all ground state isomers are thermally stable. Second, the energy barriers between the various triplet states are small enough to permit a long lived triplet to readily pass through all triplet configurations, there being no great preference due to a high energy barrier. Thus, triplet molecules readily lose their identity to any one starting isomer.

In cyclic trienes, however, many ground state configurations are thermally unstable and there are barriers on the T_1 surface which can be quite large due to the constraints places upon various rotational modes by the ring system. It must also be recognized that there are many more energy minima in the triplet state than in the



12 **13** **11** **10**

ground state. There are the spectroscopic triplets and the relaxed triplets and between any two minima are barriers to the isomerization of the triplet. Using the ten-membered ring as an example, it is evident that the *cis,trans,cis* - isomer readily relaxes and intersystem crosses to form both the *cis,trans,cis*- and the *cis,cis,cis* - isomer. However, the *cis,cis,cis* - isomer upon excitation must have a large energy barrier to move from its spectroscopic triplet to the same relaxed triplet arrived at from the *cis,trans,cis* - isomer. Thus, the latter isomer is removed, irreversibly, to give the *cis,cis,cis* moiety. Since the all *cis*-isomer slowly goes over to the *trans,cis,trans* - isomer at 25°, the energy barrier for this rotation must be smaller than that required to go to the *cis,trans,cis* - isomer and so the *trans,cis,trans* - isomer is inefficiently formed. Although this latter isomer is formed inefficiently, it is thermally unstable and ring closes, irreversibly, to the *cis*-hexalin. This last process draws off all the triene and does not permit further equilibrations at 25°. When the excitation of the *cis,cis,cis* - isomer is done at −70°, the spectroscopic triplet does not have sufficient energy to overcome the barrier or is also inhibited by solvent to rotation and, thus, simple intersystem crossing back to its ground state occurs.

It is appreciated that the foregoing concepts are speculative and much more study of a quantitative nature with regard to other parameters is needed.

EXPERIMENTAL

All H NMR and ^{13}C NMR spectra were run in deuterochloroform unless otherwise noted. All vpc analyses used a 10 ft by 1/8 in column containing 10% Carbowax 6000 and 10% KOH on 60/80 Chromosorb W support. A temp program for temp change was used (70°–150° at 4°/min). The $AgNO_3$ impregnated silica gel for column chromatography contained 28 g $AgNO_3$ per 100 g silica gel. Corresponding tlc plates were prepared from an aqueous slurry of 5 g $AgNO_3$ and 16 g silica gel G (with $CaSO_4$ binder).

All irradiations utilized a Rayonet Photochemical Reactor with RPR 3500*A* lamps except where noted. For low temp irradiations, the irradiation vessel was placed in a quartz Dewar flask containing dry-ice and anhyd MeOH. For irradiations, anhyd ether was distilled from LAH and spectroscopic-grade hexane was distilled from P_2O_5.

Sensitized irradiation of cis,trans,cis *- cyclodeca - 1,3,5 - triene* (**1**)

(A) *At* 25°. A soln of 166 mg (1.24 mmol) of **1**[7] and 192 mg (1.28 mmol) *m*-methoxyacetophenone in 50 mL pentane was irradiated through Pyrex at room temp under the general irradiation procedure for a period of 8.5 hr. The mixture was concentrated and the residue chromatographed on 7 g silica gel using benzene as the eluent to yield 80 mg of olefinic material which was further purified by preparative vpc.

The first material collected, accounting for 40% of isolated olefinic material, was identified as *cis* **3** by comparison with authentic material.[8] A ^{13}C NMR spectrum of this material displayed resonance lines at δ 23.42 (t), 27.81 (t), 34.77 (d), 123.52 (d), 131.73 (d) ppm.

The second material collected, comprising the remaining 60% of the olefinic reaction mixture, was identified as *cis,cis,cis* **2**: UV_{max} (hexane) 216 nm (ε 4200); IR 1669, 1648, 817, 727, 695 cm^{-1}; H NMR δ 1.54 (m, 4), 2.17 (m, 4), 5.53 (m, 2), 5.68 (d, 2, $w_{1/2}$ = 2 Hz) ppm; mass spectrum (70 ev) *m/e* 134. This compound upon hydrogenation yielded cyclodecane as the sole product, identified by comparison with authentic sample.

(B) *At* −70°. A soln of 67 mg (0.50 mmol) of **1** and 81 mg (0.54 mmol) *m*-methoxyacetophenone in 25 mL pentane was irradiated at −70° according to the general procedure for 8 hr and the course of the irradiation followed by vpc. The composition of the mixture changed as follows: 2 hr, 11% **1**, 88% **2**, <1% **3**; 5 hr, 8% **1**, 90% **2**, 1% **3**; 8 hr, 6% **1**, 93% **2**, 2% **3**.

The reaction soln was concentrated, dissolved in 25 mL ether and an additional 158 mg *m*-methoxyacetophenone added. The irradiation was continued for 3 hr at −70° and the composition of the mixture was 3% **1**, 94% **2** and 3% **3**. The cooling bath was removed and the irradiation continued to give the following results: 20 min, 3% **1**, 84% **2**, 13% **3**; 90 min, 2% **1**, 77% **2**, 21% **3**; 150 min, 1% **1**, 63% **2**, 3% **3**.

Sensitized irradiation of 2 - methyl - cis,trans,cis *- cyclodeca - 1,3,5 - triene* (**5a**)

(A) *At* −70°. A soln of 196 mg (1.32 mmol) of **5a** and 372 mg (2.48 mmol) in 80 mL ether was irradiatied at −70° according to the general procedure. After 80 min, all the starting material had been consumed and a single product had been formed. The soln was concentrated and the residue chromatographed on 30 g silica gel using benzene as the eluting solvent. Fractions of 25 mL were collected and fractions 3 and 4 yielded 164 mg (84%) of **6a**: UV_{max} (hexane) 217 nm (ε 3440); IR 1645, 880, 830, 768, 751, 714 cm^{-1}; H NMR δ 1.47 (m, 4), 1.68 (s, 3, $w_{1/2}$ = 3.5 Hz), 2.10 (m, 4), 5.26 (t, 1, J = 8.0 Hz), 5.40 (td, 1, J = 9.0, 7.0 Hz), 5.67 (d, 1, J = 9.0 Hz), 5.96 (s, 2, $w_{1/2}$ = 2,0 Hz) ppm; ^{13}C NMR 23.55 (q), 24.42 (t), 24.90 (t), 26.02 (t), 26.50 (t), 125.30 (d), 127.00 (d), 127.68 (d), 133.12 (d), 133.46 (d), 133.60 (d) ppm; mass spectrum (70 ev) *m/e* 148.

The same results were obtained using acetophenone as the sensitizer.

(B) *At* 25°. The above experiment was repeated at 25° and initially **5b** was formed but on extended irradiation it disappeared and no new monomeric products were formed.

Sensitized irradiation of 3 - methyl - cis,trans,cis *- cyclodeca- 1,3,5 - triene* (**5b**)

(A) *At* −70°. Following the conditions used for **5a**, a soln of 272 mg (1.84 mmol) of **5b** was irradiated for 65 min and the product chromatographed to yield 232 mg (85%) of **6b**: UV_{max} (hexane) 221 nm (ε 3700); IR 1665, 1645, 830, 735 cm^{-1}; H NMR δ 1.50 (m, 4), 1.80 (s, 3, $w_{1/2}$ = 3.0 Hz), 2.12 (m, 4), 5.08–5.90 (m, 5) ppm, ^{13}C NMR δ 23.84 (t), 23.99 (t), 24.72 (q), 25.74 (t), 26.23 (t), 126.71 (t), 129.63 (d), 131.80 (d), 133.13 (d), 136.91 (s) ppm; mass spectrum (70 ev) *m/e* 148.

The same results were obtained using 9-fluorenone as the sensitizer.

(B) *At* 25°. The above experiment was repeated at 25° and initially **6b** was formed but upon extended irradiation it disappeared and no new monomeric products were formed.

Sensitized irradiation of cis,trans,cis *- cycloundeca - 1,3,5 - triene* (**7**)

Analytical study at 25°. A soln of 11 mg of **7**[7] and 14.7 mg *m*-methoxyacetophenone, containing n-decane as an internal standard, in 4 mL hexane was placed in a Pyrex tube, deareated by a N_2 purge, and sealed with a rubber septum. The soln was irradiated in the standard manner and the course of the reaction followed by vpc. At the end of 40 min, the starting triene had disappeared and the product consisted of 60% of a mixture of **8** and **9** and 40% of **10**. At the end of 120 min, the composition had changed 40% and 55%, respectively. (The composition of these fractions is based on the following detailed study.)

Sensitized irradiation of cis,trans,cis *- cycloundeca - 1,3,5 - triene* (**7**)

Preparative run at −70°. (A) A soln of 100 mg (0.68 mmol) of **7** and 202 mg (1.35 mmol) *m*-methoxyacetophenone in 25 mL ether was irradiated at −70° according to the standard procedure. At the end of 1.6 hr, vpc analysis indicated that greater than 95% of **7** had been consumed to produce a sole, yet broad, peak of shorter retention time. Analysis by $AgNO_3$ impregnated silica gel tlc, in contrast, indicated that two, slightly faster moving spots (R_f = 0.52 and 0.44) were formed at the expense of the starting triene (R_f = 0.40).

The soln was allowed to warm to room temp and concentrated at reduced pressure. The residual oil was chromatographed on 7.0 g silica gel, using benzene as the eluting solvent. Fractions (5-mL) 2–4 contained the olefinic material. These fractions were combined and concentrated at reduced pressure to yield 90 mg (90%) of a clear colorless oil which was examined by H NMR spectroscopy (benzene-d_6). Resonance signals occurring at δ 6.30, 6.11 and 1.44 ppm were ascribed to the known *trans,cis,cis* **9**[7] while those occurring at δ 6.30, 5.84 and 1.49 were characterized as arising from *cis,cis,cis* **8**, based upon the similarity to triene **2**. Integration of the two sets of bands indicated the materials were present in about a 1:1 ratio.

The hydrocarbon mixture was chromatographed on AgNO$_3$ impregnated silica gel but only the material of the R_f of 0.44 was obtained. This material was identified as *trans,cis,cis* **9**. on the basis of UV, IR and NMR spectra, all of which were identical to those reported for this compound.[8]

(B) A soln of 213 mg (1.44 mmol) of **7** and 261 mg (1.45 mmol) 9-fluorenone in 50 mL ether was irradiated at −70° under the standard conditions and after 45 min, vpc analysis indicated more than 95% of the starting diene had disappeared.

Two 1-mL aliquots were removed and rapidly transferred to two Pyrex tubes which were purged with N$_2$ and sealed with rubber septums. One tube was irradiated at −70° while the other was concurrently irradiated at 25°. After 60 min, the contents of the tube maintained at −70° showed no change in the mixture composition, whereas the room temp tube had undergone ~40% conversion to **10** (coinjection).

Concurrently, the original irradiation mixture was concentrated at −20° and rapidly passed through a pad of silica gel using pentane as the eluting solvent. This entire operation of separating the sensitizer from the hydrocarbon fraction required less than 20 min. The pentane eluate was concentrated under reduced pressure at −20° to yield 186 mg (87%) of *cis,cis,cis* **8**: UV$_{max}$ (cyclohexane) 226 nm (ϵ 4500); IR 1650, 780, 762, 655, 600 cm^{-1}; H NMR δ 1.50 (m, 6), 2.14 (m, 4), 5.08–5.64 (m, 2), 5.89 (d, 2, J = 12.0 Hz), 6.02 (bs, 2, $w_{1/2}$ = 3.5 Hz); ^{13}C NMR 23.35 (t), 27.33 (t), 28.11 (t), 126.66 (d), 129.09 (d), 133.70 (d).

The H NMR sample was stored for 13 hr at 0° and the new spectrum revealed extensive isomerization had occurred. The sample was then heated at 40° for 1 hr and this third spectrum revealed the absence of **8** and the sole presence of *trans,cis,cis* **9**. A detailed study of this thermal isomerization using UV, IR and ^{13}C NMR spectroscopy yielded first order rate constants of 3.15×10^{-3} min^{-1} at 22.3° and 7.62×10^{-3} min^{-1} at 35°; the energy of activation being 12.6 kcal/mol.

Sensitized irradiation of trans,cis,cis - *cycloundeca* - 1,3,5 - *triene* (**9**)

(A) *At* −70°. A soln of 74 mg (0.5 mmol) of **9** and 75 mg (0.5 mmol) *m*-methoxyacetophenone in 20 mL ether was irradiated under the standard conditions at −70° for 6 hr. The mixture was processed rapidly at −20° and examined by vpc and H NMR spectroscopy. From these two methods of analysis, the composition was shown to be 80% of starting **9**, 15% of a new diene **11** (see below), and 5% of the known *cis* **10**.[8]

A similar experiment run at 25° showed the composition to be 30% of **8**, 70% of **10**, and less than 1% of **11**.

Preparation of trans - *bicyclo*[7,2,0]*undeca* - 2,10 - *diene* (**11**)

A soln of 304 mg of **7** in 200 mL pentane was irradiated at 300 nm in a Rayonet reactor at room temp for 6.5 hr. The irradiation mixture was concentrated and chromatographed on 30 g AgNO$_3$ impregnated silica gel using a mixture of 60% hexane, 39% benzene and 1% EtOAc as the eluting solvent. Fractions (10-mL) were collected and fractions 55–80 were combined and concentrated at reduced pressure to yield 128 mg of *trans* **11**: IR 1640, 1565, 1295, 725, 695 cm^{-1}; H NMR δ 1.1–2.3 (m, 10), 2.68 (m, 1), 3.48 (d, 1, J = 8.0 Hz), 5.36 (m, 1), 5.70 (dd, 1, J = 8.0, 11.5 Hz), 6.11 (s, 2, $w_{1/2}$ = 2.0 Hz) ppm; ^{13}C NMR 19.57 (t), 22.63 (t), 22.94 (t), 23.94 (t), 25.73 (t), 29.83 (t), 44.34 (d), 51.07 (d), 127.51 (d), 133.31 (d), 136.73 (d), 140.31 (d) ppm; mass spectrum (70 ev) *m/e* 148.

This material is extremely air sensitive, polymerizing on standing at room temperature.

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