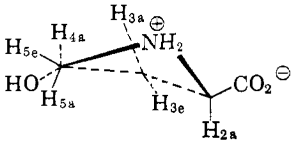
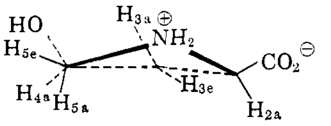
in fact may be a more accurate indicator of the conformation of cyclic compounds than just relying on coupling constants.[34,35] The data on the thymidines and substituted 1,3-dioxolanes are consistent with this general trend.

As pointed out earlier in this article the nmr data of the assigned conformations for the *cis*- and *trans*-3-hydroxy-L-prolines do not conform to this general trend. Conformation **4a** would seem more appropriate for *trans*-3-hydroxy-L-proline in which the orientation of the C_5 hydrogens is reversed compared to that of the same hydrogens in **4** and now conforms to the observed trend of pseudo-axial hydrogens appearing at higher field than pseudo-equatorial hydrogens. The assigned coupling constants are compatible with conformation **4a** with the possible exception of the long-range J_{35} coupling constant. In **4a** both the hydroxyl and carboxylate groups are pseudo-equatorial.



4a



5a

Conformation **5a** would appear to satisfy both the chemical shift and coupling constant data. Conformation **5a** is nearly an "envelope" conformation in which both hydroxyl and carboxylate are pseudo-equatorial. This conformation is more in keeping with the proposed conformation of *cis*-1,3-dimethylcyclopentane.[36]

Acknowledgment. The authors wish to thank Professors Ernest L. Eliel and Gerhard Binsch of our department and Dr. G. Edwin Wilson of the Polytechnic Institute of Brooklyn for helpful discussions, and the Computing Center of the University of Notre Dame for providing the computing time.

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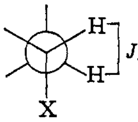
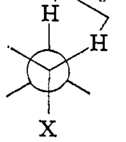
[34] It has been shown recently that the axial hydrogens in *cis*-3-isopropylcyclobutyl amine and alcohol appear at higher field than do the equatorial hydrogens in *trans*-3-isopropylcyclobutylamine and alcohol [I. Lillian and R. A. Doughty, *J. Am. Chem. Soc.*, **89**, 155 (1967)].

[35] The use of the Karplus relationship to determine HCCH dihedral angles should be used in only a qualitative manner [M. Karplus, *ibid.*, **85**, 2870 (1963)], particularly in complex systems. The vicinal coupling constants vary widely as a function of the substituents on the two carbon atoms and the HCC bond angles as well as the HCCH dihedral angle [for a recent review of coupling constants see A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 201 (1965)]. One would also expect the vicinal coupling constants to be a function of the XCCH dihedral angle [G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Am. Chem. Soc.*, **89**, 1135 (1967)], *e.g.*, the vicinal coupling constant $J_g{}^t$ in fragment i may not be equal to $J_g{}^g$ in fragment ii even though the HCCH dihedral angles may be the same. The conversion of one conformation of a substituted five-membered ring to an alternate conformation may well transform $J_g{}^g \rightarrow J_g{}^t$, or *vice versa*, as actually happens in **4** → **4a**, thus inducing changes in coupling constants that will not be indicated by the Karplus relationship. $J_g{}^g$ and $J_g{}^t$ may vary by as much as a factor of 3 (Whitesides, *et al.*).



i



ii

[36] Reference 2a, p 250.

Benzene-Photosensitized Transformations of the Four Geometrical Isomers of 1,5,9-Cyclododecatriene

J. K. Crandall and Charles F. Mayer

Contribution No. 1486 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401. Received March 16, 1967

Abstract: The sensitized photochemical reactions of the four isomeric 1,5,9-cyclododecatrienes in benzene solution have been examined. The predominant process is simple *cis–trans* isomerization of the olefinic bonds which transforms each of the isomers into the same photostationary mixture of all four trienes. In addition, there is an irreversible isomerization to a material identified as *endo,endo*-2,6-divinyl-*cis*-bicyclo[3.3.0]octane. The details of these photochemical reactions are discussed.

This paper is concerned with the photochemical reactions of the isomeric 1,5,9-cyclododecatrienes (I–IV), a set of medium-ring compounds with three formally isolated double bonds.[1] Among the numerous possibilities for phototransformation of this interesting system, we considered the following as most likely: (1) photo-Cope rearrangement of the 1,5-hexadiene units present in the starting material,[2] (2) cycloaddition of two of the olefinic groups to produce a tricyclic cyclobutane species, (3) some more extensive type of "cycloaddition" involving all three of the double bonds.

A recent review article[4] concerned with intramolecular photocycloadditions of nonconjugated olefins reveals very little work on medium-ring compounds with the exception of 1,5-cyclooctadiene. This material can be converted to tricyclo[$3.3.0.0^{2,6}$]octane by mercury

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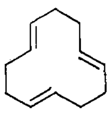
[1] H. Breil, P. Heimbach, M. Kroner, H. Muller, and G. Wilke, *Makromol. Chem.*, **69**, 18 (1963).

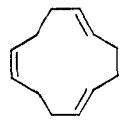
[2] For example, see R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Letters*, 3955 (1965). Such photorearrangements are not common however, and, in fact, are predicted not to be favorable as concerted reactions by Woodward–Hoffmann considerations.[3]

[3] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4389 (1965).

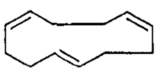
[4] W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966). See also J. Dale and C. Moussebois, *J. Chem. Soc.* (*C*), 264 (1966).



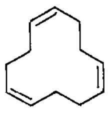
I



II

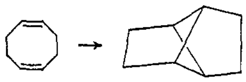


III



IV

sensitization in the gas phase or by cuprous chloride promoted photolysis in ether solution.[5]



Subsequent to the initiation of our work, a brief communication appeared which describes the photolytic behavior of *cis,trans,trans*-cyclododecatriene (II) in the presence of a variety of photosensitizers.[6] Such treatment was reported to give varying mixtures of II, the all-*trans* isomer I, and the *cis,cis,trans* compound III. The work described below elaborates on the photochemistry of the cyclododecatrienes utilizing the high-energy sensitizer benzene and differs in some important respects from the earlier work.

Photolyses were carried out on dilute solutions (0.2%) in purified, degassed benzene under a nitrogen atmosphere. The usual immersion cell was employed with a medium-pressure mercury arc in a quartz probe as the light source. The progress of the reaction was monitored by the periodic removal of aliquots and analysis by gas chromatography (glpc).

Irradiation of a benzene solution of pure, crystalline I for 21 hr resulted in an apparent photostationary mixture of four gas chromatographically separable materials, since further irradiation did not produce appreciable change. The components were present in the ratio of 18:8:31:42 in the order of their elution from the gas chromatograph. The first peak was a new material whose structure is considered below. The remaining components were identified as I, II, and III by retention time comparison and by the similarity of the infrared spectra of the collected peaks to the published curves.[1] (Compound III was subsequently shown to contain small amounts of the remaining isomer IV; see below.) Resubmission of each of the last two peaks to the same photolysis conditions gave rise to essentially the same product mixture as obtained from I. The apparent constancy of the new photoproduct percentage in the product mixtures is fortuitous, however, since this material is not part of the photoequilibrium as evidenced by its inertness to the photolysis conditions.

At this point in our work the last isomeric cyclododecatriene became available when Untch and Martin[7] reported the synthesis of the all-*cis* compound IV. Preparation of a sample of this material revealed an interesting complication when it was found that III and IV were not separable in our gas-chromatographic analysis procedure. Thin layer chromatography on silver nitrate–silica gel did resolve III and IV, however, and in this fashion it could be demonstrated that IV was, in fact, a component of the above photoequilibrium mixtures that had been overlooked previously. The presence of IV in the photolysate seems only reasonable, and we suspect that the previous workers may have also missed this product in their work with lower energy sensitizers.[6] Although quantitative data on the relative proportions of III and IV under the last gas chromatography peak have not been secured, the thin layer chromatography spot intensities and spectral comparisons clearly indicate that III predominates by a fair margin.

As expected, photolysis of pure IV also produced the same photomixture of trienes, but in this instance the unknown compound constituted a substantially larger proportion of the total product than had been found with the other isomers. This is consonant with the irreversible formation of this compound as shown above. Furthermore, the new material was quite evidently formed at an enhanced rate from IV over the other isomers. In fact, one observes a qualitative increase in the rate of formation of this species as the starting material is changed systematically from I through IV. Since equilibration among the triene isomers appears to precede formation of the other product, this suggests that it is formed exclusively, or at least much more rapidly, from IV. If only the triene isomers are considered, the same photostationary state of all four isomers is derived from each individual isomer in which the ratio of I:II:(III + IV) is 10:38:52 within experimental error.[7a]

While the benzene photolyses of the *dilute* solutions described above were well behaved, several attempts to use the readily available commercial mixture of I and II in preparative-scale reactions met with little success. Not only was the equilibration tediously slow, but photochemical change invariably ceased well before the photostationary mixture of trienes was attained and, more importantly, before significant amounts of the unknown photoproduct were present. This frustrating turn of events is attributed to the inadvertent production of sufficient quantities of quenchers in the large-scale reaction that inhibition of the reaction occurred.[8] Some support for this proposal is found in the fact that purification by distillation regenerated photochemical reactivity in the triene mixture. In another instance inhibition was observed in a 0.2% solution photolysis when ordinary nitrogen was used as the "inert atmosphere" in place of the prepurified grade. This appears to be due to oxygen quenching effects

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[5] R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[6] H. Nozaki, Y. Nisikawa, Y. Kamatani, and R. Noyori, *Tetrahedron Letters*, 2161 (1965).

[7] K. G. Untch and D. J. Martin, *J. Am. Chem. Soc.*, **87**, 3518 (1965).

[7a] NOTE ADDED IN PROOF. A detailed account of the Japanese work has now appeared: H. Nozaki, Y. Nisikawa, M. Kawanisi, and R. Noyori, *Tetrahedron*, **23**, 2173 (1967). Complete photoequilibration of the cyclododecatrienes was not achieved in this work, apparently because of inhibition effects. The above workers claim the absence of IV in their photolysis mixtures. However, we have recently been able to affect partial resolution of III an IV by glpc using an 8-ft 20% Carbowax 20M–3% silver nitrate column and definitely find that IV is present *at photoequilibrium* as roughly one-third of the amount of III. Identical results are observed with either I or IV as the starting isomer.

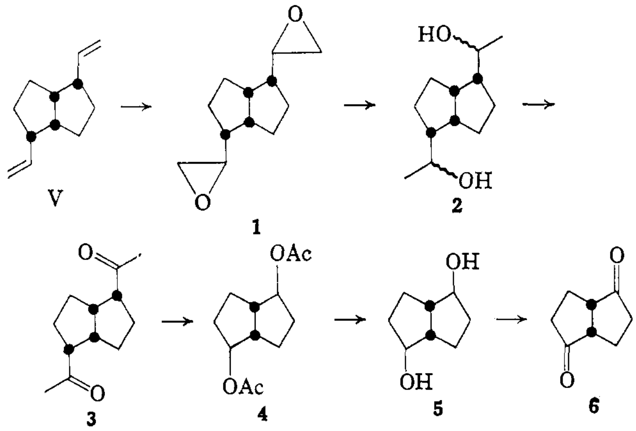
[8] Recent work on the photochemical reactions of benzene has demonstrated that the contention that benzene is an ideal solvent for photochemical reactions because of its inertness to photolysis is no longer entirely tenable. See, for example, L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **88**, 2881 (1966); K. E. Wilzbach and L. Kaplan, *ibid.*, **88**, 2066 (1966); H. R. Ward, J. S. Wishnok, and P. D. Sherman, Jr., *ibid.*, **89**, 162 (1967).

since inhibition was reversed by the simple expediency of degassing with prepurified nitrogen and continuing the photolysis under prepurified nitrogen.

A variety of other conditions for preparative photolysis were examined and some of these are described briefly in the Experimental Section. The use of acetone as both solvent and sensitizer initially appeared useful, but the photolysis components rapidly underwent further reaction, apparently with the solvent.[9] Finally, a system was devised which allowed sufficient amounts of the unknown product to be obtained for characterization purposes. This consisted of irradiating a solution of 100 g of a mixture of I and II in 500 ml of benzene which contained 10 ml of acetone as an additive. Additional acetone was added periodically during the course of about 2 days of irradiation. At the end of this time a good recovery of material was obtained which contained about 3% of the desired compound. Spinning-band distillation and subsequent preparative gas-chromatographic separation provided sufficient pure sample of the unknown material for structural studies. The function of the acetone in this experiment is not entirely clear; perhaps it is acting as the actual sensitizer,[10] or, possibly, it is preventing the formation of quenchers or removing them by chemical reaction. In this connection, it was observed that the tendency of the photolysis mixture to turn yellow is appreciably retarded in the presence of acetone.

At this point it was possible to elucidate the structure of the remaining unknown photoproduct. The mass spectrum displayed a molecular ion peak at m/e 162 and thus confirmed that this material was isomeric with the cyclododecatrienes. The infrared spectrum showed the characteristic bands for a vinyl group and little else.[11] The nuclear magnetic resonance spectrum confirmed this feature of the molecule and, furthermore, indicated that *two* vinyl groups were present as the *only* olefinic protons in the molecule. This information aided by mechanistic interpretation led to the hypothesis that the new compound was *endo,endo*-2,6-divinyl-*cis*-bicyclo[3.3.0]octane (V).

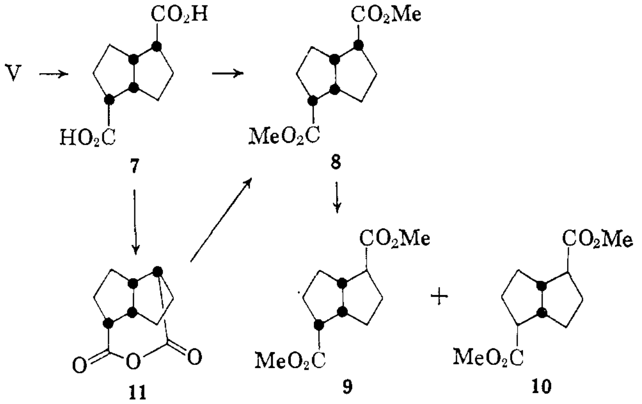
Chart I



The gross structure was, in fact, shown to be that of V by the pedestrian, but effective, dual degradation scheme shown in Chart I. The divinyl compound V was converted to the diepoxide **1** by peracid oxidation. This was reduced with lithium aluminum hydride to a diasteriomeric mixture of secondary diols **2**. Chromic acid oxidation of **2** to diketone **3** was followed by Baeyer–Villiger oxidation to produce diacetate **4**. Lithium aluminum hydride cleavage of **4** gave diol **5**, which upon chromic acid oxidation generated *cis*-bicyclo[3.3.0]octane-2,6-dione (**6**). The identity of the final product was established by comparison with an authentic sample.[12]

While the degradation establishes the over-all structure of V, it does not probe the important question regarding the stereochemistry of the pendant vinyl substituents. Evidence in support of the *endo,endo* assignment suggested above is summarized in Chart II. Ozonolysis of V followed by oxidative work-up produced a crystalline dicarboxylic acid **7** which was readily converted to its dimethyl ester **8**. Equilibration of this material with sodium methoxide in methanol gave a mixture of diesters which contained relatively minor amounts of **8** and approximately equal quantities of two new major diesters. This observation is in accord with the assigned *endo,endo* stereochemistry of **8**, since this diester should be somewhat less stable than either the *endo,exo* isomer **9** or the *exo,exo* compound **10**, due to the additional nonbonded interactions experienced by an *endo*-carbomethoxy group over those of an *exo* function. The major esters formed in the equilibration are thus assigned structures **9** and **10**. Ancillary evidence on the stereostructure of V was provided by its cyclization to anhydride **11** under the influence of dicyclohexylcarbodiimide. The tendency of **11** to polymerize precluded its purification and rigorous characterization.[13] Nonetheless, a crude sample obtained by molecular distillation (to remove polymeric material) had carbonyl absorption in its infrared spectrum at 5.58 and 5.72 μ as expected for a cyclic anhydride of six or more ring members. Furthermore, the relative intensities of these two bands ensure the cyclic nature of the anhydride, since such

Chart II



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[9] J. S. Bradshaw, *J. Org. Chem.*, 31, 237 (1966).

[10] Acetone has been found to be an efficient, high-energy (~80 kcal/mole) sensitizer for the *cis–trans* isomerization of simple olefins: R. F. Borkman and D. R. Kearns, *J. Am. Chem. Soc.*, **88**, 3467 (1966). Triplet–triplet transfer from benzene to acetone should proceed at diffusion-controlled rates since the process is exothermic by several kilocalories.

[11] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966, pp 95–102.

[12] We wish to thank Professor H. J. Dauben, Jr., and Dr. M. I. Simpson for kindly providing a comparison sample of **6** (H. J. Dauben, Jr., V. R. Ben, and S. H-K. Chiang, Abstracts, 123rd National Meeting of the American Chemical Society, Los Angeles, Calif., March 15–19, 1953, p 9M.)

[13] J. W. Hill, *J. Am. Chem. Soc.*, **52**, 4110 (1930), describes the similar properties of adipic anhydride.

cyclic species invariably have the stronger of the two carbonyl absorptions at longer wavelengths as seen for **11**, whereas the opposite is found for acyclic anhydrides.[14] The possibility of epimerization during anhydride formation was excluded by conversion of the crude anhydride substantially to **8**, the *least stable* of the dimethyl esters, by methanolysis and diazomethane esterification.

Discussion

In the following discussion we adopt the viewpoint that each of the cyclododecatrienes is an assembly of isolated chromophores in which there is little interaction among the double bonds in either the ground or electronically excited states. This assumption ignores the possibility that the excited states which give rise to the observed photochemical transformations may be of a delocalized nature. A more detailed knowledge of these important species is desirable, but for the present there is no compelling experimental evidence which supports the notion of delocalized triplets, and consequently a noninteracting model appears to be both warranted and preferred.

A number of reports of simple olefin isomerization by benzene photosensitization have appeared in the literature recently.[15] Benzene is especially useful in the sensitization of olefins since its high triplet energy (84 kcal/mole) and relatively efficient intersystem crossing allows for the facile generation of olefin triplets by the usual collisional triplet–triplet transfer.[16] Thus, energy transfer is viewed as indiscriminately promoting to its spectroscopic triplet the olefinic bond of the triene nearest the collisional path of approach of the sensitizer molecule. Relaxation of this species probably occurs much faster than other possible events and thereby results in a lower energy triplet which has torsionally distorted from the planar geometry of the ground-state olefin.[17,18] As with simple olefins, intersystem crossing back to the ground state generates both geometrical isomers of the double bond under consideration. If energy transfer from the sensitizer is indiscriminate, then the photostationary equilibrium ratio for a simple *cis–trans* olefin mixture is given by the rate ratio for the collapse of triplet to *cis* olefin and *trans* olefin, respectively.[18] For a number of examples in which these preconditions are apparently met, the photostationary state consists of approximately equal amounts of *cis* and *trans* isomers.[15] If statistical energy transfer and equivalence of the rates of collapse to *cis* and *trans* olefin are *assumed* for a noninteracting cyclododecatriene, a photostationary state is predicted in which the ratio of I:II:III:IV is 12.5:37.5:37.5:12.5. The experimental value of 10:38:52 for I:II:(III + IV) (with III in fair preponderance over IV) is probably in better accord with this crude prediction than warranted by the nature of the assumptions. Nonetheless, we believe that the experimental data are at least consistent with the isolated triene model insofar as geometrical isomer equilibration is concerned.

The final product compositions obtained in the earlier work[6] by *nonvertical* excitation[18] of II using a range of lower energy sensitizers were variable and, with the exception of acetone, they were not equivalent to the benzene photostationary state observed in this work. This is to be expected since nonvertical excitation does not proceed in the indiscriminate fashion characteristic for exothermic energy transfer.

Competitive with the behavior of the cyclododecatrienes as simple olefins are processes which involve interaction of the olefin triplet with one of the other double bonds in the molecule. This can conceivably take place in at least two different ways. The first of these involves bond formation and is discussed below in connection with the genesis of V. The second possibility is that of physical excitation transfer among the olefinic positions. This can occur prior or subsequent to torsional relaxation of the initially produced spectroscopic triplet. The former will result only in triplet migration since the torsionally relaxed triplet is presumably a required intermediate for geometrical isomerization. Energy transfer from a relaxed triplet to generate the spectroscopic triplet of a second double bond is expected to be appreciably endothermic (~20 kcal/mole), if it is assumed that a measure of of the energy level of the relaxed triplet is given by the fact that nonvertical excitation of simple olefins can occur with sensitizers having triplet energies as low as 50 kcal.[19] Consequently, such a transformation is not likely. However, a nonvertical transfer of triplet energy would be approximately isoenergetic and the intramolecular nature of the transfer could result in an enhanced probability over that of the inefficient intermolecular counterpart. Such an energy migration would have the interesting result of causing olefin isomerization without triplet destruction. However, there is no evidence for this sort of transformation, and intersystem crossing to the ground state and bond formation are viewed as more likely events.

Chart III

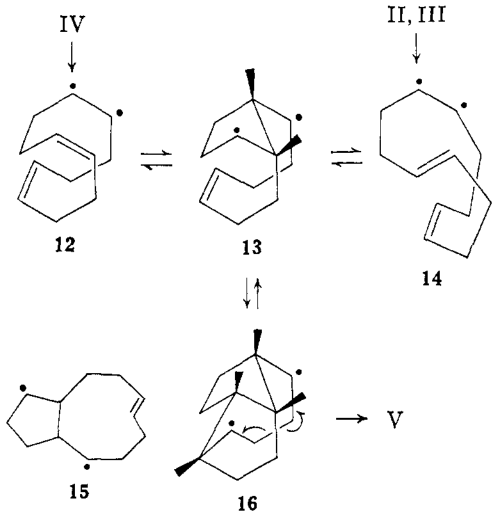

Chart III depicts a chemical sequence that can compete with deactivation of olefin triplets and which ra-

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[14] Reference 11, p 153.

[15] A documented summary of this work appears in M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

[16] F. Wilkinson, *Quart. Rev.* (London), 20, 403 (1966).

[17] J. Saltiel, "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp 254–264.

[18] 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).

[19] M. A. Golub and C. L. Stephens, *J. Phys. Chem.*, **70**, 3576 (1966).

tionalizes the formation of V, including its stereochemistry. The all-*cis*-triene IV is used to illustrate the process in accord with the observation that V is formed most rapidly from this material. Trienes II and III are also potential precursors of V as discussed below.

The olefin triplet **12** can be considered as essentially a diradical species and as such it is not surprising to find that typical radical reactions ensue. Bond formation to give intermediate **13** has good precedent in radical chemistry[20] and is, in fact, analogous with the proposed first step of the mercury-sensitized, gas-phase photocyclization of 1,5-hexadiene to bicyclo[2.1.1]-hexane[21] and the related reaction of 1,5-cyclooctadiene which was mentioned earlier. It is likely that bond formation is reversible and triplet triene **12** can be regenerated from **13**. Reversible bond formation provides an alternate mechanism for geometrical isomerism since inversion at one or both of the radical centers of **13** can intercede between bond formation and bond cleavage. In this fashion **13** can be interconverted with triplet **14** derived from II or III. It is additionally of interest that triplet site migration can also occur in this reversible chemical reaction.

Examination of molecular models of **13** and its *trans* isomer **15** provides an explanation for the preferential formation of V from the all-*cis*-triene IV. Whereas **13** is reasonably strain free both before and during its transformation to **16**, the same is not true for **15** which is strained to begin with and must become appreciably more so in the transition state for bonding between the radical center on the cyclopentane ring and the remaining double bond. As a consequence one *cis* double bond is very probably a requirement for triene triplet to lead to V *via* **16**. On a statistical basis alone, the formation of **16** is expected to proceed from IV more readily than from III, which in turn should be a more effective precursor than II, since the number of *cis* double bonds decreases in this order. There may also be a difference in the ease of cyclization of **12** and **14**, although this is not readily apparent from their models. This rationalization suggests that I cannot give V without prior isomerization to one of the other triene isomers, a condition which is not in disagreement with the qualitative data on the rates of formation of V. The question of the relative effectiveness of II, III, and IV as precursors of V cannot be adequately assessed except to note that the last of these appears to be distinguishably better. In fact, since interconversion among the trienes appears to precede the appearance of V, the available data do not exclude the possibility that IV is the sole immediate precursor of this material.

The uncoupling of the 1,4-diradical system of **16** which generates the two olefinic functions of V is expected to be a facile and irreversible process. This transformation necessarily fixes the stereochemistry of V in the least stable epimeric form as found experimentally. The stage in the sequence of Chart III at which spin inversion takes place is not certain, but the observation that V formation is apparently quenched more effectively than olefin isomerization by oxygen and impurities (without major material loss) would appear to suggest that spin inversion is occurring at the terminal stages.

There are a myriad of other radical addition sequences which might *a priori* appear reasonable for the cyclododecatrienes. These apparently suffer either from the intervention of highly strained intermediates or from the lack of a suitable low-energy termination process (such as the **16** to V conversion) which can effectively compete with reversal of the bond formation reaction. Therefore we conclude that the photochemical isomerization of related nonconjugated cyclic polyenes will depend markedly on the exact structures and conformational features of the specific molecules, but that product prediction should be possible by analysis of the potential reactions with special emphasis on the termination step.

Experimental Section

General. Infrared spectra were obtained with Perkin-Elmer Infracord Model 137 and 137-G spectrophotometers. Unless specified otherwise, these were taken on neat samples between sodium chloride plates. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer and, unless otherwise noted, were taken in carbon tetrachloride solution. Data are given in parts per million (ppm) relative to tetramethylsilane as an internal standard. Mass spectra were obtained with an AEI MS 9 mass spectrometer. Gas chromatography (glpc) was carried out on Aerograph Model 600 (analytical, flame ionization detector) and Model A700 (preparative) chromatographs. The analytical column was 5 ft × $^1/_8$ in. of 15% Carbowax 20M on 60–80 Chromosorb W; the preparative column was 10 ft × $^3/_8$ in. of 15% Carbowax 20M on 60–80 Chromosorb W. Percentage composition data were estimated by peak areas and are uncorrected. Analyses were performed by Midwest Microlab, Inc.

Materials. Benzene was distilled from phosphorus pentoxide. Fisher reagent grade acetone was used as a sensitizer without further purification. Tetrahydrofuran was distilled from lithium aluminum hydride immediately prior to use. Anhydrous magnesium sulfate was used for all drying operations.

trans,trans,trans-1,5,9-Cyclododecatriene (I) was obtained by crystallization from a cold mixture of 1,5,9-cyclododecatriene isomers[1] and was recrystallized from pentane, mp 33.5–34.5° (lit.[1] mp 34°). The infrared spectrum (CCl_4) was identical with the published spectrum[1] for I.

cis,trans,trans- and *cis,cis,trans*-1,5,9-cyclododecatriene (II and III) were obtained by glpc separation of the mixture of isomers from the photolysis of I. These samples gave infrared spectra identical with the published curves.[1] The sample of III obtained in this fashion was shown by thin layer chromatography (tlc; 1 × 3 in. microscope slides were dipped in a slurry containing 3 g of silica gel G per 6 ml of absolute ethanol which was saturated with silver nitrate and dried 30 min at 100°; ethyl acetate was used as the developer) to contain some *cis,cis,cis*-1,5,9-cyclododecatriene (IV), but comparison of the nmr with that of pure IV indicated that III was the predominant material.

cis,cis,cis-1,5,9-Cyclododecatriene (IV) was prepared by the general route described by Untch and Martin,[7] and gave infrared and nmr spectral data identical with those reported. Tlc (silica gel-silver nitrate, ethyl acetate) showed that no III was present in this sample. A variety of glpc columns and experimental conditions failed to separate III and IV.

Photolysis of the 1,5,9-Cyclododecatrienes. A stirred solution of 0.20 g of I in 100 ml of dry benzene in a tubular Pyrex cell surrounding a quartz immersion well was degassed by repeated application of an aspirator vacuum and replenishment of the atmosphere with prepurified nitrogen. The solution was irradiated with an unfiltered 450-w Hanovia Type L medium-pressure quartz mercury-vapor light source. Samples were removed by a syringe through a serum cap at intervals and analyzed by glpc. This procedure was repeated with II, III, IV, and *endo,endo*-2,6-divinyl-*cis*-bicyclo[3.3.0]octane (V). The normal photostationary state of trienes, which consisted of 10% I, 38% II, and 52% III + IV (all values ±2%), was reached after about 6 hr when starting with I, II, III, or IV. The amount of V increased at a rate which was proportional to the total content of III plus IV in the sample. The

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Table I. Photoisomerization of the 1,5,9-Cyclododecatrienes

Time, hr	Ratio[b]	Time, hr	Ratio[b]
	I[a]		II[a]
1	1:47:33:19	1.5	1:8:46:45
2	3:30:37:30	5	5:8:37:50
5	5:15:36:43	18	18:9:31:42
21	18:8:31:42		
	III[a,c]		IV[a]
2	9:6:29:57	1	10:4:24:62
5	13:7:32:48	2	16:6:28:51
18	22:8:29:41	6	20:8:29:43
		23	26:7:27:39

[a] Starting isomer. [b] V:I:II:(III + IV); all values ±2%. [c] Contains IV.

data are summarized in Table I. Compound V did not react under these conditions.

***endo,endo*-2,6-Divinyl-*cis*-bicyclo[3.3.0]octane (V).** A solution of 100 g of a mixture of 1,5,9-cyclododecatriene isomers (57% I, 36% II, 7% III) in 500 ml of dry benzene was degassed as described above. To this mixture 10 ml of acetone was added through a serum cap, and the stirred solution was irradiated with the 450-w Hanovia source through a Vycor filter for 33 hr with the addition of 10 ml of acetone each 11 hr. The amount of V rose to about 1%. Removal of the solvent and vacuum distillation of the residue gave 87 g of colorless liquid. A solution of this material in 500 ml of dry benzene was degassed, 10 ml of acetone was added, and the stirred solution was irradiated as before for 27 hr with the addition of 10 ml of acetone after 14 hr. The amount of V in the product mixture thus obtained was 3%. Removal of the solvent, followed by distillation of the residue through a 22 in. Nester/Faust Teflon annular spinning-band column gave 5.2 g of a colorless liquid, bp 72–96° (35 mm), which contained 43% of V. Preparative glpc gave a pure sample of V; infrared analysis showed peaks at 3.24, 6.11, 10.04, and 10.97 μ ($CH{=}CH_2$); nmr analysis showed a complex two-proton multiplet at δ 5.8 ($CH{=}CH_2$), a four-proton pair of multiplets at 5.05 and 4.8 ($CH{=}CH_2$), a four-proton multiplet at 2.5 (CH), and an eight-proton multiplet at 1.5 (CH_2). A second passage through the preparative glpc gave an analytical sample.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.05.

The mass spectrum of V showed a molecular ion at *m/e* 162. The fragment peaks appeared in a series of groups spaced as anticipated for a hydrocarbon with the base peak at *m/e* 67 and peaks greater than 50% of the base peak at *m/e* 41, 54, 79, and 93.

Other Photolyses. An experiment on a 0.2% solution of I as described above with the exception that ordinary dry nitrogen was substituted as the atmosphere gave the usual equilibrium mixture of trienes, but the maximum amount of V obtainable even after prolonged irradiation was only 8%. Simply degassing this solution with prepurified nitrogen allowed the reaction to proceed to the "usual" product composition. With 1 g of IV in 100 ml of benzene, only 10% of the product was V after 7 hr. At the same concentration with added acetone (0.5 ml) and use of a Pyrex filter, 28 hr were required to reach the same concentration of V. In this case 86% of C_{12} products were isolated. In large scale photolyses in benzene alone, no V was formed at starting material concentrations above a few grams per 100 ml, and the triene interconversion stopped short of its normal photostationary state. A similar concentration effect was noted in the reactions with added acetone sensitizer, but conversion to V was possible at substantially higher concentrations. Irradiation of IV in acetone solution initially gave the same products as before plus several new products. Further irradiation, however, gave total conversion to these unidentified products.

***endo,endo*-2,6-Diacetyl-*cis*-bicyclo[3.3.0]octane (3).** To an ice-cold, stirred solution of 0.82 g of V in 20 ml of methylene chloride was added 2.00 g of 85% *m*-chloroperbenzoic acid (FMC Corp.). The solution was stirred at room temperature for 3 days. The solid *m*-chlorobenzoic acid was removed by suction filtration and washed with additional methylene chloride. The filtrate was washed with dilute sodium hydroxide solution and dried. The solvent was removed to give 1.14 g of **1** as a colorless liquid; infrared: 3.31, 11.6, and 12.4 μ; nmr: a complex eight-proton multiplet at δ 2.5 and a ten-proton multiplet at 1.6. Absorption at 7.3 was indicative of the presence of about 10% *m*-chlorobenzoic acid in the sample.

A solution of 1.14 g of crude *endo,endo*-2,6-dioxiryl-*cis*-bicyclo[3.3.0]octane (**1**) in 10 ml of tetrahydrofuran was added dropwise to an ice-cold, stirred suspension of 0.50 g of lithium aluminum hydride in 10 ml of tetrahydrofuran. After heating to reflux for 12 hr, 20 ml of 2 *N* sulfuric acid was added to the ice-cold mixture. The liquid phase was extracted with three portions of ether, and the combined ether solutions were dried. Removal of the solvent gave 1.12 g of white, semisolid **2**; infrared: 3.00 and 7.31 μ; nmr (deuterioacetone): a symmetrical multiplet at δ 3.6 overlapped by a sharp singlet at 3.47 for a total of four protons ($CHOH$), a broad two-proton multiplet at 2.5 and a broad ten-proton multiplet at 1.5 (CH and CH_2), and a pair of doublets at 1.15 and 1.11 (CH_3, J = 6 cps). Absorption at 7.3 is indicative of the presence of about 10% of an aromatic impurity. Trituration with pentane left 0.75 g of white solid **2**, which gave infrared and nmr spectra identical with those of the semisolid. Glpc analysis showed three overlapping peaks which indicated that a mixture of stereoisomeric diols had been formed.

To a stirred solution of 0.75 g of crude *endo,endo*-2,6-bis(1-hydroxyethyl)-*cis*-bicyclo[3.3.0]octane (**2**) in 15 ml of acetone was added a solution of 0.80 g of chromium trioxide in 6.0 ml of 6 *N* sulfuric acid (a rise in temperature to about 50° was observed). After 3 hr at room temperature, the solution was diluted to 100 ml with water, and the resulting solution was extracted with three portions of ether. The combined ether extracts were dried, and the solvent was removed to give 0.55 g of **3** as a moist, white solid. Trituration with pentane left 0.42 g of solid **3**; infrared: 5.87 μ; nmr: a four-proton multiplet at δ 2.9 (CH), a six-proton singlet at 2.07 ($COCH_3$), and an eight-proton multiplet at 1.6 (CH_2). Two recrystallizations from water gave an analytical sample, mp 61.7–62.2° (Reichert micro heating stage).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.39; H, 9.57.

Glpc analysis showed only one component in the recrystallized sample, while the crude sample was about 80% pure.

***cis*-Bicyclo[3.3.0]octane-2,6-dione (6).** To a solution of 0.23 g of crude **3** in 25 ml of chloroform was added 2.00 g of 85% *m*-chloroperbenzoic acid. The solution was heated to reflux for 34 hr, then allowed to return to room temperature. The solid *m*-chlorobenzoic acid was removed by suction filtration and washed with additional chloroform. The filtrate was washed with three portions of dilute sodium hydroxide solution and dried. Removal of the solvent gave 0.25 g of **4** as a yellow liquid; infrared: 5.77 and 8.05 μ; nmr: a broad two-proton multiplet at δ 4.9 ($CHOAc$), a six-proton singlet at 1.97 (OAc), a broad two-proton multiplet at 2.7 (CH), and a broad eight-proton multiplet at 1.6 (CH_2). Absorption at 7.5 is indicative of about 30% of aromatic impurities in the sample.

A solution of 0.25 g of crude 2,6-diacetoxy-*cis*-bicyclo[3.3.0]octane (**4**) in 10 ml of ether was added dropwise to an ice-cold, stirred suspension of 0.12 g of lithium aluminum hydride in 10 ml of ether. After heating to reflux for 16 hr, 10 ml of 2 *N* sulfuric acid was added to the ice-cold mixture. The layers were separated, and the water layer was extracted with three portions of ether. The combined ether solutions were dried, and the solvent was removed to give 0.06 g of a brown oil. Molecular distillation gave **5** as a light brown oil; infrared: 3.03 μ; nmr: a two-proton multiplet at δ 3.9 ($CHOH$), a two-proton singlet at 3.71 ($CHOH$), a broad two-proton multiplet at 2.5 (CH), and a broad eight-proton multiplet at 1.7 (CH_2). Absorptions at 7.3 and 4.6 in a 2:1 ratio are indicative of the presence of about 30% *m*-chlorobenzyl alcohol in the sample.

To a stirred solution of 0.20 g of crude 2,6-dihydroxy-*cis*-bicyclo[3.3.0]octane (**5**) in 15 ml of acetone was added a solution of 0.40 g of chromium trioxide in 3.0 ml of 6 *N* sulfuric acid. The solution was stirred at room temperature for 21 hr. Methylene chloride (150 ml) was added, and the layers were separated. The methylene chloride layer was washed with saturated sodium bicarbonate solution and water, then dried. Removal of the solvent left a brown oil; infrared: 5.75 μ. Glpc analysis showed 85% of the volatile material to be **6**.

Glpc separation gave 25 mg of **6** as a white solid. This sample gave an infrared spectrum identical with that of an authentic sample of *cis*-bicyclo[3.3.0]octane-2,6-dione (**6**).[12] The diketone and authentic **6** gave identical R_f values in a comparative tlc on silica gel G using ethyl acetate as the developer. The glpc elution time of the diketone was also found to be identical with that of the authentic **6** on four different columns (10% SE-30, 15% XF-1150, 15% FFAP, and 15% Carbowax 20M). The nmr spectrum of an impure sample of diketone showed all the bands corresponding to the authentic material (as well as some impurity absorptions).

***endo*,*endo*-2,6-Dicarboxy-*cis*-bicyclo[3.3.0]octane (7).** The output of a Welsbach Model T-408 Ozonator was bubbled through an ice-cold solution of 0.78 g of V in 50 ml of 90% acetic acid until the exhaust gases turned a 2% potassium iodide solution dark brown. After addition of 4.5 ml of 40% peracetic acid in acetic acid to the ice-cold, stirred solution, the mixture was heated to reflux for 2 hr. The acetic acid was removed to give a quantitative yield of a moist, white solid which was recrystallized from water to yield 0.36 g (38%) of **7** as a white, crystalline solid, mp 222–225°; infrared (Nujol): 3–4 and 5.9 μ. A second recrystallization from water gave an analytical sample, mp 222–223°.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.48; H, 7.18.

Equilibration of *endo*,*endo*-2,6-Dicarbomethoxy-*cis*-bicyclo[3.3.0]-octane (8). The diacid **7** (0.36 g) was esterified with diazomethane in the usual manner to give 0.43 g of **8** as a yellow oil. Molecular distillation gave a colorless oil; infrared: 5.77 μ; nmr ($CDCl_3$): a sharp six-proton singlet at δ 3.64 (OCH_3), a broad four-proton multiplet at 2.8 (*CH*), and a broad eight-proton multiplet at 1.7 (CH_2). Glpc analysis showed 90% of the major component **8** plus three minor components.

A solution of 50 mg of this diester in 5 ml of methanol containing a catalytic amount of sodium methoxide was heated to reflux for 28 hr. Glpc assay showed that one minor component was gone, the major component (**8**) was reduced to about 5% of the total sample, and the two other minor components were increased to about 95% of the total product in roughly equivalent amounts. No further change in the product composition was effected by an additional 24 hr of heating. The solution was diluted with 40 ml of water and extracted with three portions of ether. The combined ether solutions were dried, and the solvent was removed to leave a yellow oil. Both the infrared and nmr spectra of this material were similar to, but not identical with, those of **8**, and fully in accord with expectation for a mixture of **9** and **10**.

***cis*-Bicyclo[3.3.0]octane-*endo*,*endo*-2,6-dicarboxylic Acid Anhydride (11).** To a stirred solution of 0.20 g of **7** in 150 ml of dry acetonitrile at room temperature was added a solution of 0.19 g of distilled dicyclohexylcarbodiimide in 25 ml of dry acetonitrile and two drops of pyridine. The solution was stirred for 26 hr at room temperature during which time a white solid precipitated. The solid was removed by suction filtration, and the solvent was evaporated from the filtrate to give *ca.* 100 mg of a colorless oil; infrared: 5.58 and 5.72 μ, and 5.88 μ (diacid). Molecular distillation gave crude **11** as a colorless liquid (~50 mg); infrared: 5.58 and 5.72 μ (second band stronger).

This oil was dissolved in methanol and left at room temperature for 3 days. The methanol was removed and the residue was esterified with diazomethane to give a white semisolid which yielded a colorless oil upon molecular distillation. Glpc examination indicated that the major component (~80%) of this material was identical with **8**; infrared comparison confirmed this conclusion.

Acknowledgments. This work was supported by the Public Health Service in the form of a research grant (GM 12860) and by the National Science Foundation which provided an equipment grant (GP 5234) for the purchase of the mass spectrometer used in this work. The gift of a sample of cyclododecatrienes from the Columbian Carbon Company is acknowledged with pleasure.

Emission Spectra and Excited-State Geometry of α-Diketones

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Abstract: Absorption and emission spectra of a series of open-chain and cyclic aliphatic and aromatic α-diketones have been measured. From absorption, fluorescence, and phosphorescence data singlet–triplet splittings have been measured, and scrutiny of absorption and fluorescence curves permits an estimation of conformational differences between ground and emitting excited states.

The geometry of ground states of complex molecules can be qualitatively determined by numerous methods, but few ways exist for determining conformations or geometries of excited states of the same molecules. Often the configuration is assumed to be the same as that for the ground state, or is assumed to be different on the basis of intuition,[1] or is deduced by reasonably elaborate measurements.[2]

Several groups of workers have clearly shown that the n–π* absorption of α-diketones is strongly dependent upon the intercarbonyl dihedral angle of the diketone.[3-9] Leonard and co-workers, in the most extensive study, found that the long wavelength n–π* transition occurred at 420–500 mμ for either cisoid or transoid coplanar dicarbonyl systems, and shifted to substantially higher energies (λ_{max} <400 mμ) whenever the intercarbonyl dihedral angle deviated significantly from 0 or 180°.

Surprisingly the emission spectra of few α-diketones have been reported. Biacetyl has been used in a number of triplet energy-transfer studies because of its property of phosphorescing both in fluid solution at room temperature and in a glass at 77°K.[10-15] The

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