pK_a Determinations.—The apparent pK_a's of formic acid and 2-(hydroxymethyl)benzoic acid were measured at 60 ± 1° and 0.3 M sodium chloride using a Model E 300B Metrohm pH meter, equipped with scale expander and temperature calibration. The electrode used was the Metrohm EA-120X combination electrode and the meter was calibrated at 60° using commercial standard buffers.

Standard (0.01 M) solutions of the sodium salts of the acids were prepared [the sodium salt of 2-(hydroxymethyl)benzoic acid was prepared by heating phthalide with a slight excess of sodium hydroxide[4]], made up to μ 0.30 with sodium chloride, and titrated with standard 0.1 N HCl solution (Titrisol). The pH's of the solutions were measured after every 5% neutralization from 10 to 90% neutralization, and the pK_a for each point was calculated using the equation

$$pK_a = pH + \log\{([HA]_{st} - [H^+])/([A^-]_{st} + [H^+])\}$$

where pH is the value read from the pH meter and $[H^+]$ is calculated therefrom. Values of pK_a in the region of 30–70% neutralization agreed very well and were averaged to determine the final pK_a value. Owing to instrument drift and instability at the temperature used, the absolute values of the pK_a's are probably less reliable than the relative values, which were determined consecutively as rapidly as possible. The effect of a small error in the absolute value of the pK_a of I on the value of k_{H+} is not appreciable.

The pK_a value of 1 was 3.79 ± 0.01, while that of formic acid was 3.66 ± 0.01.

Kinetic Procedures.—The rates of lactonization of 1 were determined under pseudo-first-order conditions by measuring absorbance due to the hydroxy acid reactant and the lactone product of aliquots of the reaction solution kept in sealed ampoules immersed in an oil bath at 60.00 ± 0.05°. The absorbances at 254 and 276 nm, respectively, were calculated from transmittance values measured on a Hitachi Perkin-Elmer Model 139 spectrophotometer.

A standard solution of the sodium salt of 1 (5×10^{-3} M) was prepared by saponification of the phthalide. In a typical experiment, 10 ml of the standard was combined with appropriate amounts of standard formic acid, sodium hydroxide, and sodium chloride solutions and diluted to the mark in a 100-ml volumetric flask. Aliquots (10 ml) of this solution were then transferred to 10-ml glass ampoules (Kimble Neutraglas), and the ampoules were sealed and immersed in the constant-temperature bath. At appropriate intervals samples were removed from the bath and quenched in ice; the sample was then transferred to a quartz cuvette and the transmittance was recorded. Six to eight points were obtained over a period of *ca.* 2 half-lives; infinity values were recorded at 10 or more half-lives.

The observed pseudo-first-order rate coefficients (k_ψ) were reckoned by a least-squares plot of log ($A_\infty - A$) *vs.* time on an Olivetti-Underwood Programma 101 programmable calculator. Correlation coefficients (r) were 0.999 or better and were typically 0.9999. Agreement between the two rate constants as determined by reactant decrease and product increase was excellent, although the latter generally gave better r values. The k_ψ values reported in Table I are those of product increase. The slopes and intercepts of Figure 1 and of the plot of k_ψ' *vs.* [HA] according to eq 3 (plot 2) were also evaluated by least-squares analysis and the results are summarized in Table III.

TABLE III
EVALUATION OF KINETIC PARAMETERS

Plot	Runs	Slope, M^{-1} sec^{-1}	Intercept, sec^{-1}	r
1	1–8	2.30×10^{-4}	3.05×10^{-5}	0.998
2	8, 12–15	1.42×10^{-4}	6.06×10^{-5}	0.995

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Acknowledgments.—This research was supported in part by the National Science Foundation. N. Tomoto expresses his thanks for a fellowship from the Japanese Ministry of Education.

Solution Photochemistry. X. A Study of the Effects of Double-Bond Geometry and of Increasing Double-Bond Separation on the Photochemical Reactions of Acyclic Nonconjugated Dienes[1,2]

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The triplet-sensitized photochemical reactions of the geometric isomers of the homologous dienes **2a–c**, **3a–c**, **5a–c**, and **6a–c** have been investigated. In the case of the 1,5 dienes **2a–c**, irradiation using acetone as the triplet energy sensitizer leads to cis,trans isomerization and, at a similar rate, to internal "crossed" [2 + 2] cycloaddition to give adducts **7** and **8** in a ratio of 65:35. Similar excitation of the 1,6 dienes **3a–c** causes concurrent geometric isomerism and "straight" [2 + 2] cyclization yielding adducts **9** and **10** (ratio of 3:1). Based on the stereochemistries of the adducts and on the triplet nature of these processes, these cyclizations are interpreted as occurring *via* two-step mechanisms involving the intermediacy of 1,4 diradicals. The specificity observed in the direction of initial bond formation (straight *vs.* crossed) is discussed in terms of excited states **15** and **16** which bond in accordance with strain and entropy effects. Final 1,4-diradical closure is shown to be kinetically controlled and possible explanations for the product ratios are advanced. Triplet excitation of the 1,8 and 1,9 dienes **5a–c** and **6a–c** leads only to geometric isomerism. Since previous work showed that the corresponding 1,7 dienes in this series undergo straight cyclization, the limit of double-bond separation for cyclization has been reached. Direct irradiation studies on trans,trans dienes **2a** and **3a** reveal that α,β to β,γ double-bond migration is an important process; geometric isomerism and internal cyclization are also observed in these cases.

The photochemistry of acyclic nonconjugated dienes has been a subject of continuing interest.[4] Apart from 1,4 dienes, which commonly undergo the di-π-methane rearrangement,[5] the major pathways by which these molecules react upon absorption of a photon of light are cis,trans isomerization and intramolecular [2 + 2] cycloaddition.[6] This latter process can lead to two

(1) Solution Photochemistry. IX: J. R. Scheffer and R. A. Wostradowski, *Tetrahedron Lett.*, 677 (1972).

(2) Portions of this work have appeared as preliminary communications: J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 144 (1971); J. R. Scheffer, R. A. Wostradowski, and K. C. Dooley, *ibid.*, 1217 (1971).

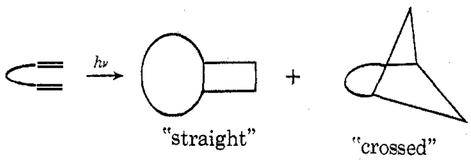
(3) National Research Council Predoctoral Fellow, 1968–1971.

(4) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966). For two key references not included in this review, see R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967); R. S. H. Liu and G. S. Hammond, *ibid.*, **89**, 4936 (1967).

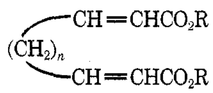
(5) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

(6) In addition, substituted 1,5 dienes are occasionally observed to undergo 1,3-allyl shifts from their singlet excited states. For examples, see R. C. Cookson and J. E. Kemp, *Chem. Commun.*, 385 (1971), and references therein.

basic classes of photoproducts, namely, those formed as a result of "straight" cycloaddition and those derived from "crossed" cyclization.



We have been engaged in a systematic study of this class of reactions to identify those structural features in the starting dienes that are important in determining which mode of cycloaddition will predominate under a standard set of photolysis conditions. For our initial efforts in this area we have chosen to investigate the photochemistry of the homologous series **1** in which *n*, the number of methylene groups separating the two double bonds, has been varied from 2 to 6.

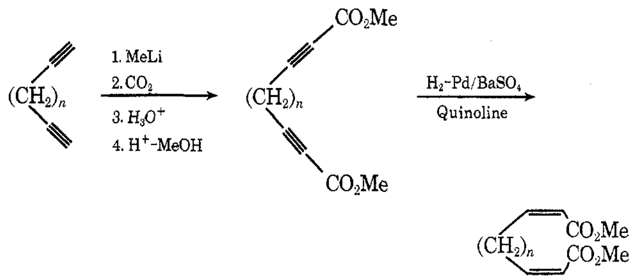


1, $n = 2, 3, 4, 5, 6$

In addition to allowing a study of the effect of double-bond separation on cycloaddition, the system **1** has the added advantages of (a) the existence of cis,cis, cis,-trans, and trans,trans geometric isomers thereby permitting a study of the effect of double-bond geometry on the cyclizations, (b) identical double-bond substituents in every case, a factor which eliminates possible ambiguities which might arise from differing intermediate biradical stabilization energies, (c) a readily accessible uv absorption region for direct irradiations and a triplet energy which is sufficiently low to permit the use of common triplet energy sensitizers, and (d) ease of synthesis and product characterization. This paper reports on the photochemistry of the diene diesters **2**, **3**, **5**, and **6** (n = 2, 3, 5, and 6, respectively); the n = 4 case has been the subject of a previous report.[7]

Synthesis of Starting Materials and General Procedures.—The trans,trans diene–diesters **2a**, **3a**, **5a**, and **6a** were synthesized by the general procedures of Luttringhaus and Merz[8] and Anderson, Baizer, and Petrovitch[9] as shown in Scheme I. This procedure also gave small amounts (<20%) of the corresponding cis,trans isomers **2b**, **3b**, **5b**, and **6b** which could be isolated using preparative vapor phase chromatography. They could also be obtained by the triplet-sensitized photoisomerization (see later) of the corresponding trans,trans isomers followed by preparative vpc. This photoequilibration method, while useful for the preparation of the cis,trans isomers, gave smaller amounts of the cis,cis species. The cis,cis compounds **5c** and **6c** (n = 5 and 6) *could* be isolated in useful amounts through vpc, but, in the cases of the cis,cis isomers **2c** and **3c**, it was necessary, owing to overlapping vpc peaks, to resort to an independent stereoselective synthesis. This was accomplished as shown in Scheme II.

SCHEME II
SYNTHESIS OF CIS,CIS DIENE–DIESTERS **2c** AND **3c**

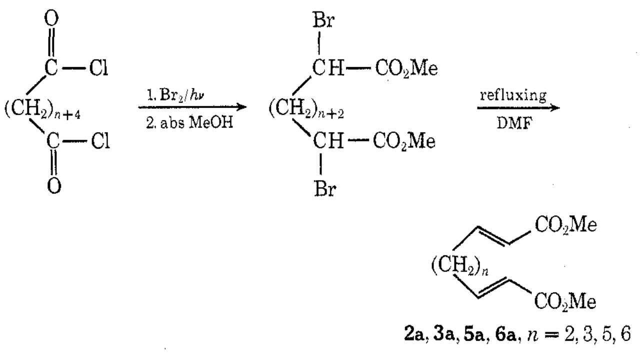


2c, **3c**, $n = 2, 3$

All new compounds described gave satisfactory elemental analyses and exhibited spectral characteristics completely in accord with their proposed structures.

The general procedures followed in the photolysis of the diene diester systems **2**, **3**, **5**, and **6** were the following. Direct irradiations were conducted in methanol or hexane at a concentration of 0.1–0.2% using a 450-W Hanovia lamp and a Vycor filter (transmitting λ >220 nm). Sensitized photolyses were performed in the same concentration range in acetone as the solvent and triplet-energy sensitizer using the same lamp equipped with a Corex filter (transmitting λ >260 nm); >98% of the light was absorbed by the acetone under these conditions. For each of the diene systems **2**, **3**, **5**, and **6**, all three geometric isomers were irradiated. Each photolysis was monitored at suitable intervals by quantitative vpc and plots of the various photoproduct percentages as a function of time constructed.

SCHEME I
SYNTHESES OF TRANS,TRANS DIENE–DIESTERS **2a**, **3a**, **5a** AND **6a**



2a, **3a**, **5a**, **6a**, $n = 2, 3, 5, 6$

Results

Photolyses in Acetone. Irradiation of 2a–2c.—The results of the photolysis of dimethyl *trans,trans*-octa-2,6-diene-1,8-dioate (**2a**) in acetone are shown in Scheme III. Thus, as indicated by vpc, the reaction was one of the disappearance of **2a**, the formation and decay of the cis,trans and cis,cis isomers **2b** and **2c**, and, at a similar rate, the buildup of the internally cyclized products **7** and **8**. After 16–20 hr, depending on the starting diene, none of the diene–diesters **2a–c** remained, and the photostable cycloadducts **7** and **8** were present in the ratio 65:35 **7**:**8** in ~65% yield. A typical plot of the photoisomer percentages as a function of time is shown in Figure 1A.

Photolysis of the cis,trans and cis,cis dienes **2b** and **2c** gave results essentially identical with the results described above. Both **2b** and **2c** gave **7**:**8** ratios of 65:35. The photoproduct time dependence plots for

(7) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971).
(8) A. Luttringhaus and H. Merz, *Arch. Pharm.*, **293**, 881 (1960).
(9) J. D. Anderson, M. M. Baizer, and J. P. Petrovich, *J. Org. Chem.*, **31**, 3890 (1966).

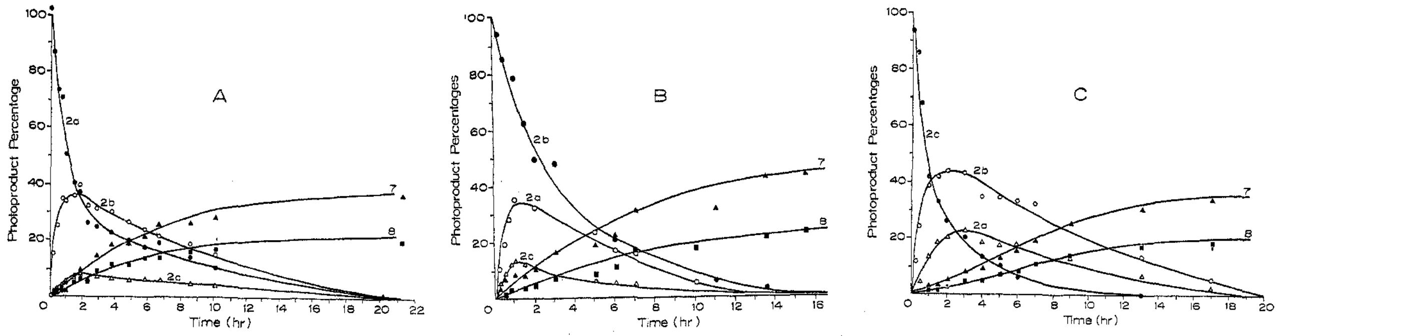


Figure 1.—Photoproduct percentages *vs.* time plots for the photolysis of (A) trans, trans diene–diester **2a**, (B) cis,trans diene–diester **2b**, and (C) cis,cis diene–diester **2c**.

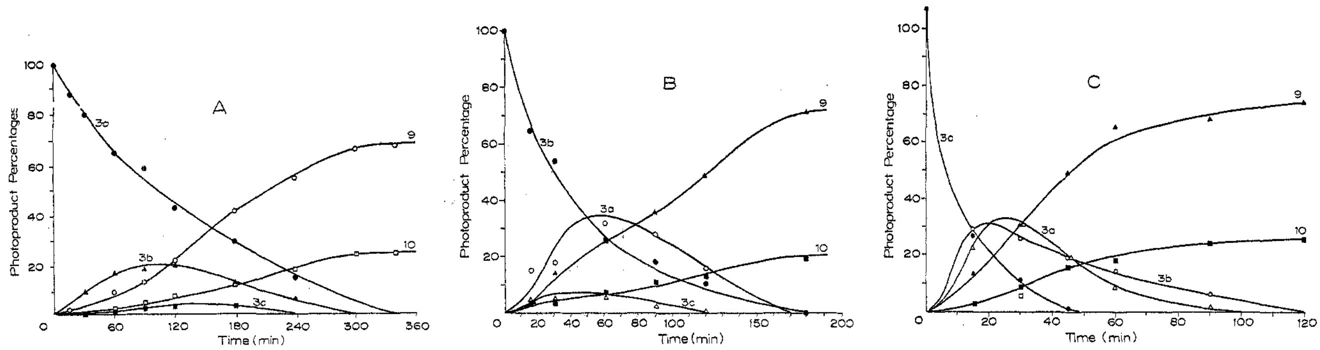
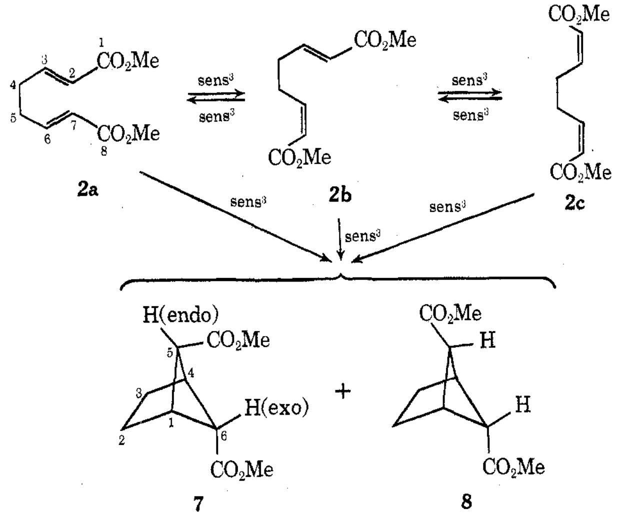


Figure 2.—Photoproduct percentages *vs.* time plots for the photolysis of (A) trans,trans diene–diester **3a**, (B) cis,trans diene–diester **3b**, and (C) cis,cis diene–diester **3c**.

SCHEME III

ACETONE-SENSITIZED PHOTOLYSIS OF DIENE-DIESTERS **2a–2c**



the irradiations of **2b** and **2c** are shown in Figures 1B and 1C, respectively.

Photoisomers **7** and **8** were easily separable by vpc. Each was shown to be isomeric with starting material by elemental analysis and mass spectrometry. A strong indication that photoproducts **7** and **8** were the result of "crossed" [2 + 2] cycloaddition came from the observation that their melting points (65–66 and 83–85°, respectively) differed from the melting points of the three known[10] stereoisomeric dimethyl bicyclo[2.2.0]hexane-2,3-dicarboxylates. The final structure assignments for **7** and **8** were made on the basis of their 100-MHz nmr spectra; neither showed signals attributable to vinyl hydrogens. For **7**, the nmr (CCl_4) showed τ 8.27 (m, 4, C_2 and C_3 CH_2), 7.96 (s, 1, C_5 *endo*-CH), 7.02 (d, 2, J = 3 Hz, C_1 and C_4 CH), 6.75 (m, 1, C_6 *exo*-CH deshielded by C_5 *exo*-CO_2Me), 6.40 (s, 3, C_6 *endo*-CO_2Me), and 6.32 (s, 3, C_5 *exo*-CO_2Me). Photoisomer **8** exhibited the following nmr in CCl_4: τ 8.32 (s, 4, C_2 and C_3 CH_2), 7.76 (t, 2, J = 2.5 Hz, C_5 and C_6 *exo*-CH), 7.11 (t, 2, J = 2.5 Hz, C_1 and C_4 CH), and 6.42 (s, 6, *endo*-CO_2Me). Structure **8** for the symmetrical (C_{2v}) cycloadduct is preferred to the alternative symmetrical structure in which the ester groups are both exo since (a) the experimental coupling $J_{1,6} = J_{4,6} = J_{1,5} = J_{4,5}$ = 2.5 Hz in **8** is typical of exo proton-bridgehead coupling in bicyclo[2.1.1]hexane systems;[11] endo proton–bridgehead proton coupling in bicyclo-[2.1.1]hexane systems is zero[11] as typified in adduct **7** ($J_{1,5} = J_{4,5}$ = 0 Hz, causing the C_5 endo proton to appear as a singlet), and (b) the equivalent C_5 and C_6 protons of the symmetrical photoproduct are likely to be exo since they appear at lower field (τ 7.76) than would be expected if they were endo. For example, the endo proton in **7** appears at τ 7.96.

Attempted epimerization of either **7** or **8** under a variety of conditions was unsuccessful. Similar behavior has been observed for the methyl bicyclo[2.1.1]-hexane-5-carboxylate system.[12]

Photolysis of 3a–3c in Acetone.—The three geometric isomers of dimethyl nona-2,7-diene-1,9-dioate (**3a–3c**) were irradiated in acetone as previously decsribed. In each case the reaction was one of simultaneous cis,trans isomerization and intramolecular [2 + 2] cyclization. Eventually (2–6 hr depending on the geometry of the starting diene; see Figure 2), the acyclic dienes were

(10) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970).

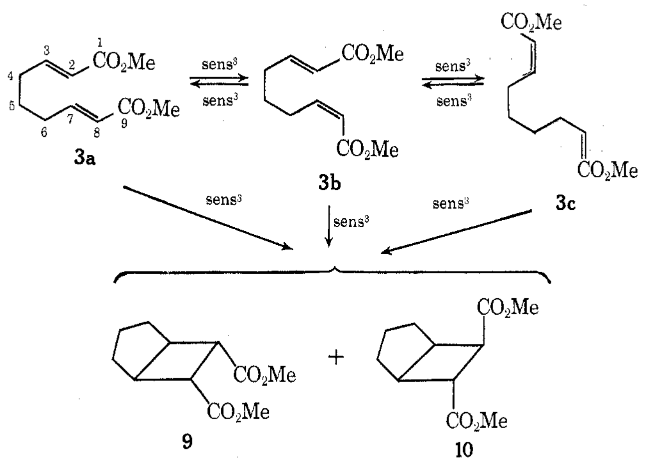
(11) (a) J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961); (b) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *ibid.*, **84**, 1594 (1962).

(12) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3993 (1961).

totally consumed. In each photolysis the final product mixture consisted of the two internally cyclized adducts **9** and **10** in a ratio of 3:1 in an overall yield of ~90%. These results are shown schematically in Scheme IV and quantitatively in Figure 2.

SCHEME IV

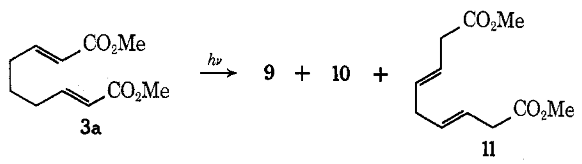
ACETONE-SENSITIZED PHOTOLYSIS OF DIENE-DIESTERS **3a–3c**



Photoproducts **9** and **10** were separated by means of preparative glc and identified by hydrolysis to the known[13] dicarboxylic acids as well as by direct comparison with authentic samples independently prepared by the photochemical addition of dimethyl maleate to cyclopentene.[13]

Photolysis of 5a–c and 6a–c in Acetone.—The trans,trans, cis,trans, and cis,cis 1,8 diene–diesters **5a**, **5b**, and **5c**, respectively, failed to undergo cyclization upon irradiation in acetone. Not surprisingly, similar behavior was observed for the corresponding 1,9 diene–diesters **6a**, **6b**, and **6c**. In all six cases, the sole reaction observed was cis,trans isomerization resulting in each instance in a photostationary trans,trans:cis,trans:cis,cis ratio of 1.5:2.5:1. Interestingly, this ratio differs from the ratio found for the corresponding 1,7 diene–diesters.[7] In this case, photolysis in acetone resulted in a trans,trans:cis,trans:cis,cis ratio of 3.8:3.5:1 which was formed prior to (and maintained during) straight [2 + 2] cycloaddition. As can be seen from inspection of Figures 1 and 2, a constant ratio of geometric isomers is not formed in the acetone-sensitized photolysis of the 1,5- and 1,6-diene–diester systems **2** and **3**. Finally, these results indicate that the limit of double-bond separation which will lead to internal cyclization has been reached at $n = 4$, at least for the homologous series **1**.

Direct Photolyses.—Photolysis of either dimethyl *trans,trans*-octa-2,6-diene-1,8-dioate (**2a**) or dimethyl *trans,trans*-nona-2,7-diene-1,9-dioate (**3a**) in methanol or petroleum ether led to geometrical isomerism, to internal cyclization, and to a process not observed in the sensitized irradiations, namely α,β to β,γ double-bond migration. For example, the photolysis mixture from the direct irradiation of **3a** in methanol consisted of ~60% adducts **9** and **10** (ratio of 3:1) and 40% dimethyl *trans,trans*-nona-3,6-diene-1,9-dioate (**11**), the double deconjugation product. Photolysis of **3a** in



hexane led to similar results. In this case the photoisomer mixture consisted of compounds **9**, **10**, and **11** in the ratio of 2:1:3.2. The structure of **11** was proved by spectral data, in particular by nmr using the shift reagent $Eu(DPM)_3$ (see Experimental Section). The preference, in the case of **3a**, for formation of trans-disubstituted β,γ double bonds has been observed in one other similar instance and an explanation advanced.[7] The photochemical conversion of α,β-unsaturated esters possessing γ hydrogen atoms to their β,γ congeners is a well-documented process.[14]

Direct irradiation of dimethyl *trans,trans*-octa-2,6-diene-1,8-dioate (**2a**) in methanol led to a mixture of at least six new transient or photostable products. Four of these were identified as the geometric isomers **2b** and **2c** (transient) and the cycloadducts **7** and **8** (photostable). These latter were formed in ~20% yield in the ratio 73:27, a ratio similar to that observed in the sensitized photolyses of **2a–c**. Examination of the spectra of the remaining two photoproducts (separated by glc) revealed that they were most likely geometric isomers of the 1,3 dienes resulting from double deconjugation.

The use of piperylene as a triplet-energy quencher in the direct irradiation of trans,trans 1,6 diene **3a** in hexane led, in addition to cis,trans isomerization and α,β to β,γ double-bond deconjugation, to a final 2:1 **9**:**10** ratio. This is identical with the ratio obtained in hexane in the absence of piperylene and close to the 3:1 ratio observed in acetone and methanol. It thus appears that internal cyclization can occur in the case of diene–diester **3a** from both the singlet and triplet manifolds depending on the reaction conditions and that the ratio of the cycloaddition products, but not their stereochemistry or the direction (*i.e.*, straight or crossed) of bonding, may differ slightly in each case. Finally, it should be pointed out that unsaturated ester deconjugation is characteristically a singlet-state reaction.[7,14,15]

Discussion

The acetone-sensitized internal cyclizations described in this paper undoubtedly occur in a stepwise fashion involving the formation of one or more reactive intermediates most easily pictured as being 1,4 diradical like in nature. This conclusion is based on two observations: (1) the exclusively triplet nature of the cycloadditions, and (2) the product stereochemistries. In regard to this latter point, if the cyclizations were completely concerted one would expect,[16] for example, that photolysis of the trans,trans 1,5 diene **2a** would lead to the exo,exo cycloadduct **14**. The fact that this product was *not* observed even though cyclization and geometric isomerism are taking place concurrently

(13) P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964).

(14) (a) J. A. Barltrop and J. Wills, *Tetrahedron Lett.*, 4987 (1968); (b) M. J. Jorgenson and L. Gundel, *ibid.*, 4991 (1968).

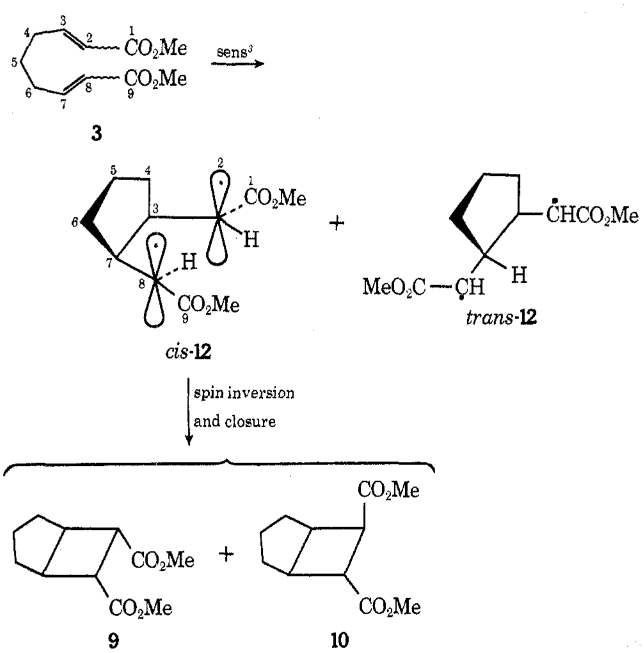
(15) See, however, P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967).

(16) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **91**, 2608 (1969).

(*cf.* Figure 1A) rules out complete concertedness. Similar arguments and conclusions can be made for the other cyclizations described in this work. In fact, nonconcertedness appears to be a general feature of internal [2 + 2] cycloadditions.[4,7]

Leaving aside for the moment the question of the *direction* of cyclization (*i.e.*, straight *vs.* crossed), it is next pertinent to address ourselves to the question of what factors govern the closure stereochemistries of the intermediate 1,4 diradicals involved. In the 1,6-diene case, if we make the reasonable assumption that initial 3,7-bond formation is favored over initial 2,8-bond formation,[17] two 1,4-diradical intermediates may be produced, *i.e.*, *cis*-**12** and *trans*-**12**. While the intermediate *trans*-**12** does not lead to any new photoproducts detectable by glc, the intermediate *cis*-**12** can give three stereoisomeric cis-fused bicyclo[3.2.0]heptanedicarboxylates, only two of which, **9** and **10**, are observed in a ratio of 3:1 (Scheme V). These products must be

SCHEME V



the result of kinetic control in the closure of singlet *cis*-**12** since they are formed in amounts which are in inverse order to their relative thermodynamic stabilities. Thus sealed-tube thermolysis (250°, 24 hr) of either **9** or **10** leads to an equilibrium **9**:**10** ratio of ~1:7 with no other isomeric products being formed. The source of this kinetic control is likely the avoidance of syn nonbonded C_1–C_4 and C_6–C_9 interactions in the transition state for closure of *cis*-**12**. No interactions of this type are involved in the formation of the major photoproduct **9**, one is necessary for the closure to give minor isomer **10**, and two interactions would be present in the closure leading to the third possible (but not observed) cis,syn,cis adduct. The difference in thermodynamic stability between **9** and **10** is thus seen to arise from the presence in **9** (less stable) or absence in **10** (more stable) of vicinal cis ester group interactions. The cis,-syn,cis adduct, combining both unfavorable steric effects, was not observed in the equilibration studies.

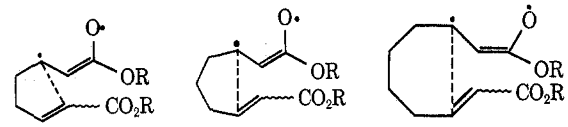
(17) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

These arguments are supported by the observation[13] that **10**, not **9**, is the major cycloaddition product formed in the dimethyl maleate–cyclopentene photolysis. In this case, the bond joining the ester substituents is present *prior* to closure of the probable diradical intermediate, and the stereochemistry of the closure is governed by the avoidance of vicinal syn ester group interactions thus leading to **10** in preference to **9**.

Unlike the 1,6-diene case described above, initial 2,6- (or 3,7-) bond formation in the 1,5-diene series **2** can lead to isomeric 1,4-diradical intermediates (*cis*- or *trans*-**13**, Scheme VI) *both* of which can close to give stable adducts.

While there is no experimental evidence available on the relative thermodynamic stabilities of adducts **7** and **8** owing to their extreme reluctance to epimerize, there is no reason to expect that the closure step will be reversible, and we are likely dealing with kinetic control of closure in this case as well. Molecular models reveal no marked steric effects which would favor formation of **7** over **8** as is observed experimentally (ratio of 65:35). It may be that this ratio is partially governed by statistical factors, photoproduct **7** being capable of being formed from both diradical intermediates while **8** can be formed from only one. In any case, the failure to observe adduct **14** is not surprising since models reveal that its formation would involve severe nonbonded ester group interactions.

Straight *vs.* Crossed Bonding.—The remarkably general finding that both cyclic and acyclic 1,5 dienes undergo preferential "crossed" photochemical cyclization while 1,6 dienes cycloadd in a predominantly "straight" manner has been noted previously.[4,7] The results described in this paper are seen to be no exception. However, it still remains to explain these results in a satisfactory manner. A rationalization which has ground-state analogy involves the reasonable assumption that initial bond formation originates from triplet excited states (intramolecular exciplexes?) which can be represented in valence bond terms as **15**, **16**, and **17**

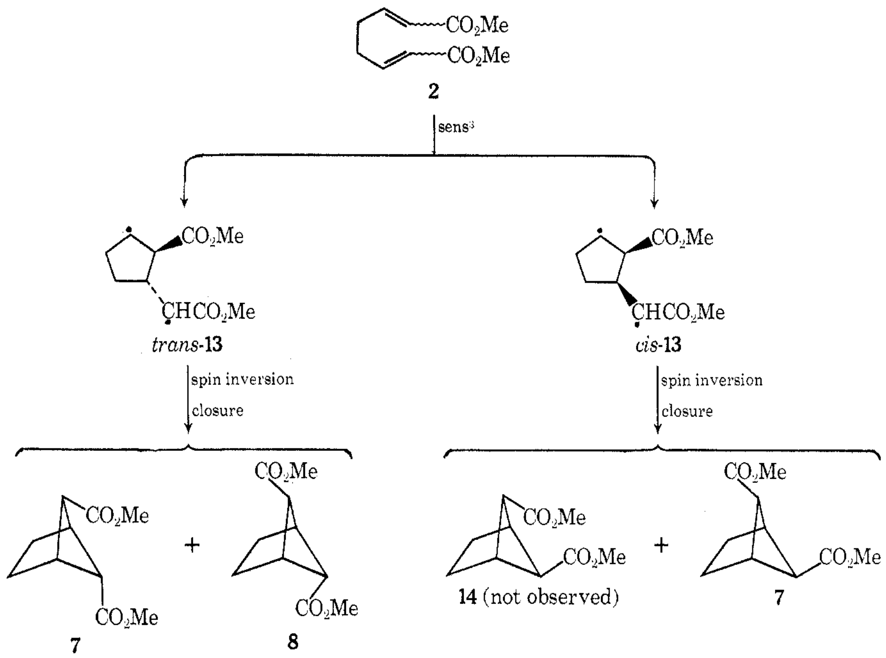


(n = 2, 3, and 4, respectively).[18] The direction of initial bond formation then becomes a question of which end of the ground-state double bond the radical center on the β carbon atom prefers to bond to in each case.[19] The experimentally observed directions are shown by the dotted lines in structures **15**–**17**. Thus five-membered formation is preferred to both four-membered- and six-membered-ring formation (*cf.* **15** and **16**), and six-membered-ring formation predominates over seven (*cf.* **17**).[7] This is exactly the pattern which has been found for the ground-state cyclizations of the 1-penten-5-yl, 1-hexen-6-yl, and 1-hepten-7-yl

(18) These excited states are presumably n → π^* in nature and are represented as having diradical character in analogy to α,β-unsaturated ketone n → π^* triplets. See H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

(19) Initial bonding from the β carbon of an excited α,β-unsaturated carbonyl compound to a ground-state olefin has recently been demonstrated. See W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *ibid.*, **92**, 1399 (1970).

SCHEME VI



free radicals, respectively.[20] These cyclizations have been interpreted in terms of strain and entropy effects, and, while readily understandable in the 1-penten-5-yl and 1-hepten-7-yl cases, these effects do not clearly predict the preferential formation of the cyclopentylmethyl radical in the closure of the 1-hexen-6-yl radical. To the best of our knowledge, this dilemma has not yet been resolved.

Finally, the possibility that the direction of initial bond formation in the photochemical cyclizations of nonconjugated dienes may be the result of orbital symmetry effects should not be overlooked. A rationalization in these terms of the exclusive straight photocyclization observed in the case of the 1,7-diene system **1** ($n = 4$) has been presented[7] and may be applied without modification to the cyclization of the 1,6-diene system **3**. The situation with regard to the 1,5-diene–diester system **2** is more complex, and a discussion of these complexities will be deferred until our photoelectron spectroscopic studies on these and related systems are complete.

Experimental Section[21]

Synthesis of Trans,trans Diene–Diesters 2a, 3a, 5a, and 6a.— These materials were prepared by bromination of the di(acid chlorides) of the appropriate α,ω-dicarboxylic acids (Eastman) followed by treatment with methanol[8] and dehydrobromination in refluxing dimethylformamide.[9] The following procedure for the preparation of dimethyl *trans,trans*-octa-2,6-diene-1,8-dioate (**2a**) is typical.

A mixture of suberic acid (technical grade, 25 g, 0.14 mol) and thionyl chloride (43 g, 0.33 mol) in a flame-dried 1-l. round-bottom flask equipped with a thermometer, condenser, and dropping funnel was heated at 70–85° for 1.5 hr. Heating was discontinued and bromine (52 g, 0.33 mol) was added dropwise to the now clear yellow solution while irradiating the entire apparatus with a 275-W sun lamp. After addition was complete (45 min), the dark red reaction mixture was heated at 85° for 6 hr and cooled in an ice bath, and 40 ml of absolute methanol was carefully added followed by 50 ml of saturated sodium bicarbonate solution. After stirring overnight, the reaction mixture was extracted with 2 × 50 ml of chloroform. The combined chloroform extracts were washed with water (2 × 50 ml), saturated sodium bicarbonate (2 × 50 ml), saturated sodium chloride (2 × 50 ml), and saturated sodium thiosulfate (2 × 50 ml) and dried ($MgSO_4$). Removal of chloroform *in vacuo* gave 51 g of pale yellow oil which was shown to be dimethyl 2,7-dibromosuberate from the following spectral data: ir (neat) 5.75 (C=O) μ; nmr (CCl_4) τ 5.84 (t, 2, $J = 7$ Hz, $CHBrCO_2Me$), 6.25 (s, 6, CO_2Me), 8.0 (m, 4, CH_2CHBr), 8.5 (m, 4). This material was refluxed in dimethylformamide (100 ml) for 4 hr. The dark reaction mixture was cooled, diluted with 100 ml of water, and extracted with 2 × 75 ml of ether. The combined ether extracts were washed as above and dried over $MgSO_4$. Removal of ether *in vacuo* gave 25 g (90%) of pale yellow oil. Vapor phase chromatographic analysis of this material (5 ft × 0.25 in. stainlesss steel column packed with 20% DEGS on 60–80 Chromosorb W) at 160° and a flow rate of 120 ml/min showed that this mixture was composed of trans,trans diene–diester **2a** (retention time 14 min) and cis,trans isomer **2b** (retention time 8 min) in a ratio of 5:1. Distillation yielded pure **2a**, a colorless liquid, bp 115–120° (0.01 mm), which exhibited the following spectral data:[23] uv max (MeOH) 228 nm; ir (neat) 5.79 (C=O), 6.03, 10.2 μ; nmr (CCl_4) τ 3.10 (d of t, 2, $J_{2,3} = J_{6,7} = 15.5$, $J_{3,4} = J_{5,6} = 7$ Hz, *trans*-$CH{=}CHCO_2Me$), 4.20 (d, 2, $J_{2,3} = J_{6,7} = 15.5$ Hz, *trans*-$CH{=}CHCO_2Me$), 6.30 (s, 6, CO_2Me), 7.60 (m, 4, methylenes).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07. Found: C, 60.60; H, 6.91.

Trans,trans diene–diesters **3a**,**5a**, and **6a**, all colorless liquids were prepared in an analogous manner and were characterized on the basis of the following information.

(20) M. Julia, *Pure Appl. Chem.*, **15**, 167 (1967), and references cited therein.

(21) Ir spectra were obtained, unless otherwise stated, on neat liquid samples between sodium chloride plates with a Perkin-Elmer 137 spectrophotometer. Nmr spectra were determined in carbon tetrachloride solution with either a Varian T-60, HA-100, or XL-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained on a direct-inlet AEI MS-9 instrument at 70 eV, and uv spectra were recorded on a Unicam SP-820 spectrophotometer. Melting points were taken on either a Thomas-Hoover capillary apparatus or a Fisher-Johns hot stage apparatus and are uncorrected. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. Vpc was carried out on a Varian-Aerograph 90-P3 instrument using helium as the carrier gas. The most useful columns for separating the compounds described in this work were found to be those packed with DEGS on Chromosorb W. All solvents were distilled, the methanol being distilled from a solution of sodium methoxide and dimethyl phthalate,[22] and the tetrahydrofuran being distilled from sodium–potassium alloy. All photolysis solutions were degassed prior to irradiation with Canadian Liquid Air argon containing <5 ppm of oxygen.

(22) E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

(23) This compound has been very briefly described in ref 10.

Dimethyl *trans,trans*-nona-2,7-diene-1,9-dioate (**3a**): uv max (MeOH) 215 nm; ir (neat) 5.79 (C=O), 6.02, 10.1 μ; nmr (CCl_4) τ 3.15 (d of t, 2, $J_{2,3} = J_{7,8} = 16$, $J_{3,4} = J_{6,7} = 7$ Hz, *trans*-CH=$CHCO_2Me$), 4.30 (d, 2, $J_{2,3} = J_{7,8} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 6.35 (s, 6, CO_2Me), 7.77 (m, 4, allylic CH_2), 8.30 (m, 2).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.15; H, 7.75.

Dimethyl *trans,trans*-undeca-2,9-diene-1,11-dioate (**5a**): ir (neat) 5.80 (C=O), 6.01, 10.2 μ; nmr (CCl_4) τ 3.13 (d of t, 2, $J_{2,3} = J_{9,10} = 16$, $J_{3,4} = J_{8,9} = 6.5$ Hz, *trans*-CH=$CHCO_2Me$), 4.25 (d, 2, $J_{2,3} = J_{9,10} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 6.32 (s, 6, CO_2Me), 7.83 (m, 4, allylic CH_2), 8.58 (m, 6).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 64.72; H, 8.27.

Dimethyl *trans,trans*-dodeca-2,10-diene-1,12-dioate (**6a**): ir (neat) 5.80 (C=O), 6.04, 10.2 μ; nmr (CCl_4) τ 3.15 (d of t, 2, $J_{2,3} = J_{10,11} = 16$, $J_{3,4} = J_{9,10} = 6.5$ Hz, *trans*-CH=$CHCO_2Me$), 4.30 (d, 2, $J_{2,3} = J_{10,11} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 6.35 (s, 6, CO_2Me), 7.85 (m, 4, allylic CH_2), 8.58 (m, 8).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 65.89; H, 8.84.

Preparation of Cis,trans Diene–Diesters 2b, 3b, 5b, and 6b.— These compounds were obtained by preparative vpc of the crude reaction mixtures from dehydrohalogenation of the corresponding α-bromo esters and by preparative vpc of the mixtures obtained from brief triplet-sensitized (acetone) irradiation of the corresponding trans,trans compounds. All were colorless liquids; they were characterized on the basis of the following data.

Dimethyl *cis,trans*-octa-2,6-diene-1,8-dioate (**2b**):[23] uv max (MeOH) 233 nm; ir (neat) 5.79 (C=O), 6.03, 10.1, 12.2 μ; nmr (CCl_4) τ 3.10 (d of t, 1, $J_{2,3} = 15.5$, $J_{3,4} = 7$ Hz, *trans*-CH=$CHCO_2Me$), 3.81 (d of t, 1, $J_{6,7} = 11.2$, $J_{5,6} = 7$ Hz, *cis*-CH=$CHCO_2Me$), 4.19 (d, 1, $J_{2,3} = 15.5$ Hz, *trans*-CH=$CHCO_2Me$), 4.23 (d, 1, $J_{6,7} = 11.2$ Hz, *cis*-CH=$CHCO_2Me$), 6.32 (s, 6, CO_2Me), 7.20 (m, 2, cis allylic CH_2), 7.60 (m, 2, trans allylic CH_2).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07. Found: C, 60.60; H, 6.69.

Dimethyl *cis,trans*-nona-2,7-diene-1,9-dioate (**3b**): uv max (MeOH) 216 nm; ir (neat) 5.79 (C=O), 6.02, 10.2, 11.8 μ; nmr (CCl_4) τ 3.15 (d of t, 1, $J_{2,3} = 16$, $J_{3,4} = 7$ Hz, *trans*-CH=$CHCO_2Me$), 3.88 (d of t, 1, $J_{7,8} = 12$, $J_{6,7} = 7$ Hz, *cis*-CH=CH-CO_2Me), 4.26 (d, 1, $J_{2,3} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 4.30 (d, 1, $J_{7,8} = 12$ Hz, *cis*-CH=$CHCO_2Me$), 6.37 (s, 6, CO_2Me), 7.32 (m, 2, cis allylic CH_2), 7.75 (m, 2, trans allylic CH_2), 8.34 (m, 2).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.10; H, 7.70.

Dimethyl *cis,trans*-undeca-2,9-diene-1,11-dioate (**5b**): ir (neat) 5.80 (C=O), 6.03, 10.2, 12.2 μ; nmr (CCl_4) τ 3.13 (d of t, 1, $J_{2,3} = 16$, $J_{3,4} = 6.5$ Hz, *trans*-CH=$CHCO_2Me$), 3.83 (d of t, 1, $J_{9,10} = 11.5$, $J_{8,9} = 6.5$ Hz, *cis*-CH=$CHCO_2Me$), 4.28 (d, 1, $J_{2,3} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 4.30 (d, 1, $J_{9,10} = 11.5$ Hz, *cis*-CH=$CHCO_2Me$), 6.35 (s, 6, CO_2Me), 7.37 (m, 2, cis allylic CH_2), 7.86 (m, 2, trans allylic CH_2), 8.58 (m, 6).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 64.79; H, 8.34.

Dimethyl *cis,trans*-dodeca-2,10-diene-1,12-dioate (**6b**): ir (neat) 5.80 (C=O), 6.06, 10.2, 12.2 μ; nmr (CCl_4) τ 3.15 (d of t, 1, $J_{2,3} = 16$, $J_{3,4} = 6.5$ Hz, *trans*-CH=$CHCO_2Me$), 3.90 (d of t, 1, $J_{10,11} = 11.5$, $J_{9,10} = 6.5$ Hz, *cis*-CH=$CHCO_2Me$), 4.28 (d, 1, $J_{2,3} = 16$ Hz, *trans*-CH=$CHCO_2Me$), 4.32 (d, 1, $J_{10,11} = 11.5$ Hz, *cis*-CH=$CHCO_2Me$), 6.37 (s, 6, CO_2Me), 7.36 (m, 2, cis allylic CH_2), 7.79 (m, 2, trans allylic CH_2), 8.59 (m, 8).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 66.00; H, 8.70.

Preparation of Cis,cis Diene–Diesters 2c, 3c, 5c, and 6c.— Diene–diesters **5c** and **6c** were obtained by preparative vpc of the photostationary mixtures obtained from acetone-sensitized irradiation of **5a** and **6a**, respectively. Each mixture contained ~12% of the desired cis,cis isomer at the photostationary state. Compounds **5c** and **6c** were both colorless liquids and were characterized on the basis of the following information.

Dimethyl *cis,cis*-undeca-2,9-diene-1,11-dioate (**5c**): ir (neat) 5.80 (C=O), 6.08, and 12.2 μ; nmr (CCl_4) τ 3.80 (d of t, 2, $J_{2,3} = J_{9,10} = 11.5$, $J_{3,4} = J_{8,9} = 6.5$ Hz, *cis*-CH=$CHCO_2Me$), 4.50 (d, 2, $J_{2,3} = J_{9,10} = 11.5$ Hz, *cis*-CH=$CHCO_2Me$), 6.35 (s, 6, CO_2Me), 7.37 (m, 4, allylic CH_2), 8.58 (m, 6).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 65.00; H, 8.33. Found: C, 64.76; H, 8.51.

Dimethyl *cis,cis*-dodeca-2,10-diene-1,12-dioate (**6c**): ir (neat) 5.80 (C=O), 6.09, 12.2 μ; nmr (CCl_4) τ 3.90 (d of t, 2, $J_{2,3} = J_{10,11} = 12$, $J_{3,4} = J_{9,10} = 7$ Hz, *cis*-CH=$CHCO_2Me$), 4.33 (d, 2, $J_{2,3} = J_{10,11} = 12$ Hz, *cis*-CH=$CHCO_2Me$), 6.37 (s, 6, CO_2Me), 7.37 (m, 4, allylic CH_2), 8.58 (m, 8).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.14; H, 8.66. Found: C, 66.08; H, 8.70.

Dimethyl *cis,cis*-octa-2,6-diene-1,8-dioate (**2c**)[23] was prepared by carbonation of the di(lithium salt) of 1,5-hexadiyne followed by esterification and hydrogenation. The following procedure is typical.

A solution of 1,5-hexadiyne (3.9 g, 50 mmol) in 500 ml of dry THF was cooled to 0° in a flame-dried 1-l. flask equipped with a dropping funnel and an overhead stirrer. Methyllithium (60 ml, 2 *M* in ether, 0.12 mol) was added at 0° during 1 hr with rapid stirring followed by stirring for an additional 2 hr at 0°. Next, excess dry CO_2 was bubbled through the reaction mixture for a period of 4 hr at 0°; THF was added periodically to replace that which had evaporated. The resulting heavy white slurry was then diluted with 400 ml of 0.6 *M* HCl and the subsequent clear yellow solution concentrated *in vacuo* to remove most of the THF. The aqueous solution was continuously extracted with 400 ml of ether for 24 hr and the resulting ether layer dried ($MgSO_4$) and concentrated *in vacuo* to yield 10 g of yellow oil. This material was dissolved in 250 ml of methanol containing 4 ml of concentrated sulfuric acid and refluxed for 6 hr. After neutralization, methanol was removed *in vacuo* to give 4.5 g of yellow solid, mp 51–55°. Recrystallization from ether–hexane gave 4.05 g (45%) of colorless crystals, mp 65–65.5°. The following data supports the structure dimethyl octa-2,6-diyne-1,8-dioate:[23] ir ($CHCl_3$) 4.44 (C≡C), 5.81 (C=O), 6.99, 7.79, 9.25 μ; nmr ($CDCl_3$) τ 6.32 (s, 6, CO_2Me), 7.40 (s, 4); mass spectrum parent (70 eV) *m/e* 194.

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.86; H, 5.15. Found: C, 61.83; H, 5.13.

Dimethyl octa-2,6-diyne-1,8-dioate (0.95 g, 4.9 mmol) and a mixture of 40 mg of synthetic quinoline and 40 mg of 5% palladium on barium sulfate in 20 ml of methanol was hydrogenated at atmospheric pressure. The uptake of hydrogen after 15 min was 250 ml (calculated 222 ml). Removal of methanol *in vacuo* followed by silica gel column chromatography to remove quinoline gave 0.90 g (92%) of a 9:1 mixture of **2c**:**2b** as determined by vpc. Pure dimethyl *cis,cis*-octa-2,6-diene-1,8-dioate (**2c**)[23] was obtained from this mixture by preparative vpc and exhibited the following spectra: uv max (MeOH) 223 nm; ir (neat) 5.79 (C=O), 6.05, 12.1 μ; nmr (CCl_4) τ 3.80 (d of t, 2, $J_{2,3} = J_{6,7} = 11.2$, $J_{3,4} = J_{5,6} = 7$ Hz, *cis*-CH=$CHCO_2Me$), 4.30 (d, 2, $J_{2,3} = J_{6,7} = 11.2$ Hz, cis CH=$CHCO_2Me$), 6.32 (s, 6, CO_2Me), 7.2 (m, 4).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07. Found: C, 60.40; H, 7.12.

Dimethyl *cis,cis*-nona-2,7-diene-1,9-dioate (**3c**) was prepared in an analogous manner from hepta-1,6-diyne. The intermediate diyne–diester in this case was a liquid which showed the following spectra: ir (neat) 4.45 (C≡C), 5.80 (C=O), 6.99, 8.0, 9.26 μ; nmr (CCl_4) τ 6.33 (s, 6, CO_2Me), 7.50 (br t, 4, $J = 7$ Hz, C≡CCH_2), 8.12 (m, 2); mass spectrum parent (70 eV) *m/e* 208.

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.48; H, 5.79. Found: C, 63.23; H, 6.00.

Hydrogenation and chromatography as before yielded pure **3c**: uv max (MeOH) 216 nm; ir (neat) 5.78 (C=O), 6.04, 12.2 μ; nmr (CCl_4) τ 3.85 (d of t, 2, $J_{2,3} = J_{7,8} = 12$, $J_{3,4} = J_{6,7} = 7$ Hz, *cis*-CH=$CHCO_2Me$), 4.30 (d, 2, $J_{2,3} = J_{7,8} = 12$ Hz, *cis*-CH=$CHCO_2Me$), 6.35 (s, 6, CO_2Me), 7.33 (m, 4, allylic CH_2), 8.44 (m, 2).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.37; H, 7.46.

Acetone-Sensitized Photolysis of 1,5 Diene–Diesters 2a–2c.— The results of photolysis of the trans,trans,cis,trans, and cis,cis diene–diesters **2a**, **2b**, and **2c**, respectively, were essentially identical. Each photolysis resulted in geometric isomerization and "crossed" internal cyclization to give a final product mixture consisting of adducts **7** and **8** in the ratio 65:35. Preparative runs were conducted at a concentration of $\sim 5 \times 10^{-2}$ *M* in acetone using a water-cooled quartz immersion well apparatus and a Hanovia 450-W type L lamp fitted with a Corex filter; under these conditions complete conversion to **7** and **8** occurred within

2 hr. Small-scale photolyses (photoproduct time dependence studies) were performed in quartz tubes situated externally (~7 cm) to the same lamp, filter, and immersion well apparatus. These analytical runs were carried out at a concentration of ~1 *M* in acetone using either *n*-octadecane or *n*-decanol as vpc internal standards; both internal standards were stable under the reaction conditions. The results of these kinetic runs (two runs per diene) are shown in Figure 1.

The products from each photolysis were isolated by preparative vpc and identified on the basis of their spectra. The structure of photoproduct **7** was deduced to be dimethyl bicyclo[2.1.1]hexane-5-*exo*,6-*endo*-dicarboxylate from the nmr data previously given and from the following information: mp 65–66°; ir (KBr) 5.80 (C=O) μ; mass spectrum parent (70 eV) *m/e* 198.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.07. Found: C, 60.54; H, 7.07.

Photoproduct **8** was shown to be dimethyl bicyclo[2.1.1]-hexane-5-*endo*,6-*endo*-dicarboxylate from the nmr data previously given and on the basis of the following: mp 83–85°; ir (KBr) 5.80 (C=O) μ; mass spectrum parent (70 eV) *m/e* 198.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.07. Found: C, 60.40; H, 7.12.

Acetone-Sensitized Photolysis of 1,6 Diene–Diesters 3a–3c.—The photolyses of diene–diesters **3a–3c** in acetone were carried out exactly as described for the 1,5 dienes **2a–c**. Again the reactions were those of cis,trans isomerization accompanied by internal [2 + 2] cycloaddition to give, in this case, the "straight" cyclized products **9** and **10**. All three 1,6-diene geometric isomers gave, within experimental error, identical 3:1 **9**:**10** mixtures after 2 hr (preparative runs) with no other products detectable by vpc. Small-scale kinetic runs gave the photoproduct time dependence plots shown in Figure 2.

Compound **9** was shown to be dimethyl *cis,anti,cis*-bicyclo-[3.2.0]heptane-2,3-dicarboxylate by comparison of its spectra with that of an authentic sample independently prepared by the photocycloaddition of dimethyl maleate and cyclopentene.[18] Hydrolysis of both gave the corresponding diacid, mp 178–80° (lit.[18] mp 178–179.5°); the mixture melting point was undepressed.

Analogously, photoproduct **10** was shown to be dimethyl *cis,trans*-bicyclo[3.2.0]heptane-2,3-dicarboxylate. Hydrolysis of **10** gave the corresponding diacid, mp 175–76° (lit.[18] mp 175–177°), whose mixture melting point with an authentic sample was, once again, undepressed.

The relative thermodynamic stabilities of photoproducts **9** and **10** were determined by thermal epimerization studies. Sealed-tube thermolysis of either **9** or **10** at 200° for 48 hr in the presence of a trace of water gave an equilibrium mixture of **9**:**10** of 1:7.4 ± 0.1. The identity of the thermolysis products was authenticated by ir; no other products were detectable by vpc.

Acetone-Sensitized Photolysis of 1,8 Diene–Diesters 5a–c and 1,9 Diene–Diesters 6a–c.—Photolysis of dilute acetone solutions of geometric isomers **5a–c** and their homologs **6a–c** through Corex led only to geometric isomerism. All six compounds were individually irradiated and in each case a photostationary ratio of *trans,trans*:*cis,trans*:*cis,cis* of 32:49:19 (±2%) was attained within 1 hr; prolonged irradiation led to polymer formation.

Direct Irradiation of Dimethyl *trans,trans*-Nona-2,7-diene-1,9-dioate (3a).—Diene-diester **3a** (0.25 g) in 200 ml of anhydrous methanol was irradiated through Vycor and the course of the reaction followed by vpc. Five new peaks in addition to starting material were noted corresponding to photoproducts **3b**, **3c**, **9**, **10**, and **11**. The latter three were the only detectable products left after 1.5 hr; the final ratio was 2.9:1:3.4 **9**:**10**:**11**.

Compounds **3b**, **3c**, **9**, and **10** were isolated by vpc and identified by spectral comparison with samples obtained previously. Photoproduct **11** was obtained by preparative vpc and further purified by Kugelrohr distillation. It was identified as dimethyl *trans,trans*-nona-3,6-diene-1,9-dioate on the basis of the following data: ir (neat) 5.75 (C=O), 10.3 μ; nmr (CCl_4) τ 4.56 (m, 4, vinyls), 6.45 (s, 6, CO_2Me), 7.10 (m, 4), 7.30 (m, 2); mass spectrum parent (70 eV) *m/e* 212. The nmr spectrum of 50 mg of **11** in the presence of 30 mg of tris(dipavalmethanato)europium showed the following signals: τ 3.9 (d of t, 2, $J_{3,4} = J_{6,7} = 15.5$, $J_{2,3} = J_{7,8} = 6.5$ Hz, C_3 and C_7 vinyls), 4.2 (d of t, 2, $J = 15.5$ and 6.5 Hz, C_4 and C_6 vinyls), 5.6 (m, 6, CO_2Me), 6.15 (m, 4, C_2 and C_8 methylenes), 7.07 (m, 2, C_5 methylene). Irradiation at τ 6.15 caused the doublet of triplets at τ 3.9 to collapse to a doublet ($J = 15.5$ Hz). Irradiation at τ 7.07 caused the doublet of triplets at τ 4.2 to collapse to a broad doublet ($J = 15.5$ Hz).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55. Found: C, 62.28; H, 7.75.

Photolysis of **3a** in hexane under similar conditions led to the same five photoproducts. In this case the final (1.5 hr) photoisomer mixture consisted of compounds **9**, **10**, and **11** in the ratio 2:1:3.2.

Photolysis of Dimethyl *trans,trans*-Nona-2,7-diene-1,9-dioate (3a) in the Presence of Piperylene.—A hexane solution 9.4×10^{-3} *M* in dimethyl *trans,trans*-nona-2,7-diene-1,9-dioate (**3a**) and 0.15 *M* in piperylene was irradiated externally through Corex. This led to the formation and disappearance of geometric isomers **3b** and **3c** until, after 13 hr, only photoproducts **9**, **10**, and **11** remained in the ratio 2.2:1:2.3, respectively. These compounds were isolated by glpc and identified by comparison with previously obtained samples.

Direct Irradiation of Dimethyl *trans,trans*-Octa-2,6-diene-1,8-dioate (2a).—Diene–diester **2a** (0.25 g) in 200 ml of methanol was irradiated through Corex and the course of the reaction followed by vpc. This showed the formation and decay of the geometric isomers **2b** and **2c** along with the buildup of four additional products. After 14 hr, no **2b** or **2c** remained, and preparative vpc of the remaining mixture afforded photoproducts **7** and **8** (average ratio of 2.7:1, ~20% yield) along with two unknown compounds, **X** and **Y**, in a ratio of ~1:1. The spectra of **X** and **Y**, while not definitive, are compatible with geometric isomers possessing the basic dimethyl octa-3,5-diene-1,8-dioate structure. Photoisomer **X** showed ir (neat) 5.75 (C=O) μ; nmr (CCl_4) τ 3.8–4.5 (m, 4), 6.40 (s, 6, CO_2Me), 7.00 (d, 4, $J = 6$ Hz).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07. Found: C, 60.45; H, 7.12.

Photoproduct **Y** showed ir (neat) 5.75 (C=O) μ; nmr (CCl_4) τ 3.6–4.6 (m, 4), 6.40 (s, 6, CO_2Me), 6.90 (m, 4).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.61; H, 7.07. Found: C, 60.67; H, 7.30.

Similar results were obtained in the photolysis of **2a** in hexane. After 26 hr, the **7**:**8**:**X**:**Y** ratio was 1.8:1.2:1.9:2.6. A third unknown glpc peak was observed in this photolysis but was not investigated further.

Registry No.—**2a**, 4756-84-7; **2b**, 32347-19-6; **2c**, 32347-20-9; **3a**, 34333-79-4; **3b**, 34333-78-3; **3c**, 34333-77-2; **5a**, 36615-25-5; **5b**, 36615-26-6; **5c**, 36615-27-7; **6a**, 36615-28-8; **6b**, 36615-29-9; **6c**, 36615-30-2; **7**, 32426-60-1; **8**, 32426-61-2; **11**, 36615-33-5; dimethyl octa-2,6-diyne-1,8-dioate, 36612-10-9; dimethyl nona-2,7-diyne-1,9-dioate, 36612-11-0.

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