Solution Photochemistry. V. Differences in Singlet and Triplet State Reactivities of Some Acyclic 1,7-Dienes[1,2]

John R. Scheffer* and Brian A. Boire[3]

Contribution from the Department of Chemistry, University of British Columbia, Vancouver 8, British Columbia, Canada. *Received March 12, 1971*

Abstract: The direct and triplet-sensitized photochemistry of the three geometric isomers of diethyl deca-2,8-diene-1,10-dioate has been studied. The triplet reaction is one of rapid cis,trans isomerization accompanied by slower 2 + 2 internal cyclization in a "straight" manner to give four of the six possible stereoisomeric diethyl bicyclo-[4.2.0]octane-7,8-dicarboxylates. The stereochemistry of these products as well as the triplet nature of the reaction are indicative of a two-step mechanism involving 1,4-diradical intermediates. The direct (singlet) reaction of the deca-2,8-diene-1,10-dioates is one of trans to cis isomerization followed by α,β to β,γ double bond migration from the cis isomer; the sole deconjugated product is diethyl *trans,trans*-deca-3,7-diene-1,10-dioate. A possible explanation for this stereoselectivity is advanced.

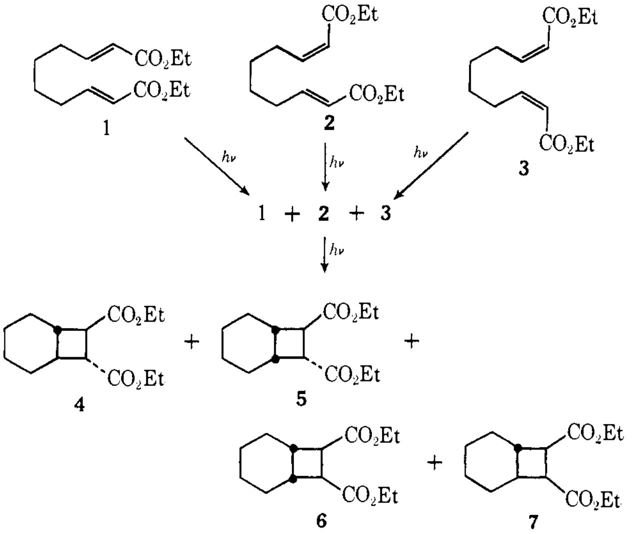
The photochemical cyclobutane-forming reaction between two remote double bonds in the same molecule may in principle give two different products. For an acyclic diene the two possible products of 2 + 2 cycloaddition are members of the bicyclo[n.2.0] and bicyclo[n.1.1] series where n is the number of atoms separating the two double bonds. In actuality, one or the other of these products predominates depending primarily on the value of n.[4] Thus in general, 1,6-dienes ($n = 3$) preferentially form bicyclo[3.2.0] compounds upon ultraviolet irradiation while 1,5-dienes ($n = 2$) give predominantly products of the bicyclo-[2.1.1] series.[4] Acyclic 1,4-dienes ($n = 1$), while most often giving products of the di-π-methane rearrangement,[5] are occasionally observed to undergo 2 + 2 cycloaddition, and in so doing preferentially form addends of the bicyclo[2.1.0] series.[4,6] Bicyclo[n.2.0] ring formation has been termed straight cycloaddition while the term crossed cycloaddition has been coined for bicyclo[n.1.1] ring formation.[7a]

Substituents attached to the double bonds of nonconjugated dienes appear to play little or no role in determining the direction (*i.e.*, straight *vs.* crossed) of their photochemical cycloaddition, at least in the relatively few cases where such effects have been tested.[2b,8] In addition, the generalizations made for acyclic dienes appear to apply equally well to the photochemistry of nonconjugated *cyclic* dienes[7,9] except in cases in which the expected product would be severely strained.[10]

To date no study of the photochemistry of an $n = 4$ acyclic diene (*i.e.*, an acyclic 1,7-diene) has been reported. We felt such a study would be of interest for several reasons: (a) it might possibily, by determining the crossed *vs.* straight nature of such a process, shed light on the reasons for the selectivities observed in the $n = 1$, 2, and 3 systems, (b) to possibly provide a convenient synthesis for unusual and otherwise difficulty obtainable bicyclic ring systems, and (c) to determine the value of n beyond which no 2 + 2 cycloaddition occurs.

Our choice for this study was the diethyl deca-2,8-diene-1,10-dioate system (**1–3**, Scheme I). This choice was dictated by the following considerations. (a) The trans,trans geometric isomer **1** was readily available by literature procedures.[11] (b) The presence of the conjugated carboethoxy groups would shift the absorption maximum of the system to a more readily accessible region of the ultraviolet spectrum compared

Scheme I. Triplet-Sensitized Photolysis Results



---

[1] Financial support from the National Research Council, the Research Corporation, and the University of British Columbia is gratefully acknowledged.

[2] (a) Portions of this work have appeared in communication form; J. R. Scheffer and B. A. Boire, *Tetrahedron Lett.*, 4741 (1970). (b) For Part IV in this series, see J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, 141 (1971).

[3] National Research Council 1967 Science Scholarship Fellow, 1967–present.

[4] R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).

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

[6] J. Meinwald and G. W. Smith, *ibid.*, **89**, 4923 (1967).

[7] (a) J. R. Scheffer and M. L. Lungle, *Tetrahedron Lett.*, 845 (1969); (b) J. W. Stankorb and K. Conrow, *ibid.*, 2395 (1969).

[8] (a) M. Brown, *J. Org. Chem.*, **33**, 162 (1968); (b) J. K. Crandall and C. F. Mayer, *ibid.*, **35**, 3049 (1970); (c) R. C. Cookson, *Quart. Rev., Chem. Soc.*, **22**, 423 (1968).

[9] (a) S. Moon and C. R. Ganz, *Tetrahedron Lett.*, 6275 (1968); (b) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Amer. Chem. Soc.*, **91**, 2608 (1969); (c) J. R. Scheffer and B. A. Boire, *Tetrahedron Lett.*, 4005 (1969); (d) C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968); (e) K. Yoshihara, Y. Ohta, T. Sakai, and Y. Hirose, *Tetrahedron Lett.*, 2263 (1969).

[10] H. Yoshioka, T. J. Mabry, and A. Higo, *J. Amer. Chem. Soc.*, **92**, 923 (1970).

[11] (a) J. D. Anderson, M. M. Baizer, and J. P. Petrovich, *J. Org. Chem.*, **31**, 3890 (1966); (b) A. Lutteringhaus and H. Merz, *Arch. Pharm.*, **293**, 881 (1960).

to 1,7-octadiene itself. Indeed, 1,7-octadiene was found to be photochemically inert under both triplet-sensitized and direct irradiation conditions. (c) The presence of geometric isomerism in the starting 1,7-dienes would allow us to compare and contrast any differences in the photochemical reactivities found for the three geometric isomers and thus enable us to make inferences concerning mechanism.

Results

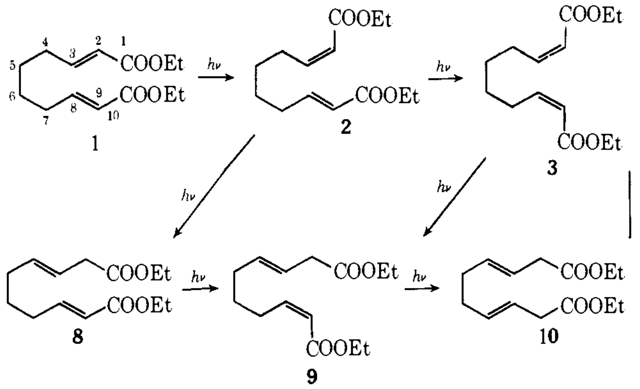
Irradiation in the Presence of Triplet-Energy Sensitizers. Diethyl *trans,trans*-deca-2,8-diene-1,10-dioate (**1**) was irradiated (Corex filter) using acetone as a triplet-energy sensitizer and solvent. The course of the irradiation was followed by vapor-phase chromatography. The initial reaction of **1** was one of isomerization to an equilibrium mixture of geometric isomers **1**, **2**, and **3** in a ratio of approximately 3.8:3.5:1.0. As irradiation was continued, the vpc peaks due to **1–3** slowly diminished (while, however, remaining in the same relative ratio) and were replaced by new peaks due to photoproducts **4–7** (Scheme I). Eventually (8.5 hr starting with 0.5 g of **1**), compounds **1–3** were totally consumed with the concomitant formation of a photostationary state mixture consisting of **4** (42%), **5** (15%), **6** (36%), and **7** (7%). Exactly the same results were obtained within experimental error when the irradiation of **1** was carried out using acetophenone (benzene solvent, Pyrex filter) as the triplet energy sensitizer.

The cis,trans and cis,cis photoproducts **2** and **3**, respectively, could easily be isolated by preparative vapor-phase chromatography of the initial photolysis mixture. A discussion of their characterization is deferred to the section on the direct photolysis results. Each of these compounds was then photolyzed in acetone; in both cases the reaction was one of cis,trans isomerization followed by slower cyclization. Photolysis of **2** gave an initial **1–3** mixture which was identical with that obtained from the photolysis of **1**. Similarly, further photolysis proceeded to give a **4**:**5**:**6**:**7** ratio indistinguishable from that of **1**. Irradiation of the *cis,cis*-diene **3** in acetone solution, however, gave cyclization which was more competitive with isomerization. As a result, an equilibrium mixture of geometric isomers was never established although all three were present. Furthermore, cyclization resulted in a slightly different **4–7** photostationary state mixture consisting of **4** (26%), **5** (17%), **6** (49%), and **7** (8%).

The bicyclo[4.2.0]octane adducts **4–7** were separated and isolated by preparative vapor-phase chromatography. Compounds **4**, **5**, and **6** were identified by direct comparison with authentic samples prepared by the photoaddition of diethyl maleate to cyclohexene[12a] and by hydrolysis to the corresponding known[12] dicarboxylic acids. Samples of photoproduct **7** could not be obtained analytically pure and were invariably contaminated with photoisomer **5**. Consequently, the structure of **7** was proved by subjecting samples of **7** (contaminated with **5**) to base-catalyzed epimerization conditions since it was known[12b] that *dimethyl*-**7** epimerizes to *dimethyl*-**4**, the more stable isomer, upon treatment with sodium methoxide. Treatment of impure **7** with sodium ethoxide afforded a 9:1 equilibrium mixture of **4** and **7**. Treatment of pure **4** under identical conditions gave the same 9:1 product ratio. These experiments permitted the structure assignment for **7** as shown in Scheme I. Further base-catalyzed and thermal isomerization studies revealed an approximately 5:1 preference for epimer **5** over epimer **6** in accord with previous findings for the methyl esters.[12b]

Direct Irradiation Studies. In contrast to the photosensitized results, direct irradiation of 1–2% methanol or hexane solutions of the *trans,trans*-diene diester **1** through a Vycor or Corex filter[13] gave a complex mixture of five products **2, 3, 8, 9,** and **10** (Scheme II) plus starting material. The relative amounts of these products again depended on the length of irradiation. Thus, vapor-phase chromatography peaks attributable to **2**, **3**, **8**, and **9** at first increased and then diminished with time as the peak due to **10** steadily increased and the peak due to **1** steadily decreased. After 2.5 hr (starting with 1.0 g of **1**), vpc peaks corresponding to **1–3** and **8–9** had completely disappeared while that due to **10** had increased accordingly.[14]

Scheme II. Direct Photolysis Results



Unsaturated esters **2**, **3**, **8**, **9**, and **10** were separated and isolated by preparative vapor-phase chromatography and shown to have the structures outlined in Scheme II on the basis of their elemental analyses, mass spectra, 60- and 100-MHz nmr spectra, and infrared spectra. The structure of photoproduct **2** was further proved by its identity with an independently prepared sample,[15] while the structure of **10** was verified by hydrolysis to the known[16] *trans,trans*-deca-3,7-diene-1,10-dioic acid, mp 118–120° (lit.[17] mp 118–120°) which was identical with an authentic sample.[17]

The pertinent spectral data for compounds **2**, **3**, and **8–10** as well as for **1** are shown in Table I. As summarized in the table, characteristic infrared peaks which indicated the geometries of the various double bonds were found at 10.04–10.27 μ (trans double bond

---

(12) (a) P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964); (b) R. Robson, P. W. Grubb, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

(13) Photolysis through Corex (transmitting light of $\lambda > 260$ nm), while giving exactly the same products as were observed using a Vycor filter ($\lambda > 220$ nm), was much slower due to the fact that only the tail of the n,π^* band (uv of **1** in hexane, sh 241 nm (ϵ 410)) was being irradiated.

(14) Three other peaks were also observed by vpc in addition to **10** but were present in amounts too small to be isolated (sum <15%).

(15) Diethyl *cis,trans*-deca-2,8-diene-1,10-dioate (**2**) is obtained in small yield from the dehydrobromination of diethyl 2,9-dibromodecane-1,10-dioate.[11]

(16) E. Martuscelli, *Acta Crystallogr.*, **23**, 1086 (1967).

(17) G. P. Chiusoli, personal communication. We thank Dr. Chiusoli for an authentic sample of *trans,trans*-deca-3,7-diene-1,10-dioic acid.

Table I. Spectroscopic Properties of the Unsaturated Diesters

Compd	Double bond position and geometry	*C*H=*C*H coupling constants, Hz	Ir double bond C–H rock, μ	Ir C=O, μ
1	Trans α,β	15.5	10.15	5.81
	Trans α,β	15.5	10.15	5.81
2	Trans α,β	15.5	10.04	5.81
	Cis α,β	11.5	11.97	5.81
3	Cis α,β	11.6	12.04	5.82
	Cis α,β	11.6	12.04	5.82
8	Trans α,β	15.4	10.18	5.82
	Trans β,γ	Mult	10.18	5.79
9	Cis α,β	11.5	11.93	5.83
	Trans β,γ	Mult	10.14	5.79
10	Trans β,γ	Mult	10.27	5.74
	Trans β,γ	Mult	10.27	5.74

C–H out-of-plane deformation) and 11.93–12.04 μ (cis double bond C–H out-of-plane deformation), while the positions of the double bonds could be determined from the values of the infrared carbonyl stretching frequencies, 5.74–5.79 μ for the β,γ-unsaturated esters and 5.81–5.83 μ for the α,β-unsaturated systems. In addition, the geometries of the double bonds in the α,β positions could be derived from the nmr spectra. Thus β-vinyl hydrogens invariably appeared as doublets of triplets with the spacing between the two triplets indicating either a trans (J = 15.5 Hz) or cis (J = 11.5 Hz) arrangement. The same couplings could be obtained by inspection of the signals due to the α-vinyl hydrogens which appeared as doublets with small (1.5 Hz) allylic couplings. The vinyl hydrogens of the β,γ-double bonds appeared as complex multiplets.

The multiplets due to the β,γ-vinyl hydrogens could be modified to approximately first order by the use of tris(dipivalmethanato)europium.[18] For example, addition of 30 mg of Eu(DPM)$_3$ to a carbon tetrachloride solution of 70 mg of diethyl *trans,trans*-deca-3,7-diene-1,10-dioate (**10**) caused the equivalent C$_3$ and C$_8$ vinyl hydrogens of **10** to appear as two distinct triplets and permitted the measurement of a typical trans vinyl coupling constant of 15.7 Hz. Similarly the C$_4$ and C$_7$ vinyl hydrogens appeared as a broad doublet, J = 15.7 Hz. These assignments were verified by spin decoupling experiments (see Experimental Section).

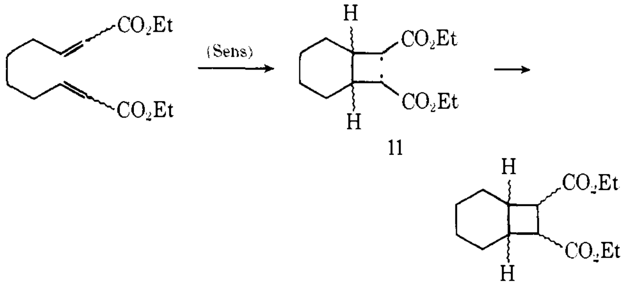
A quantitative plot of the appearance and disappearance of the various photoisomers *vs.* time from the photolysis of **1**, while in accord with Scheme II, was not particularly informative due to the complex nature of the photoproduct interconversions. However, support for Scheme II came from the finding that photolysis of **2** under the same conditions as before led to **3** and **8–10** with the eventual nearly exclusive formation of **10**.[14] In addition, photolysis of **8** gave only **9** and **10**, the latter being the ultimate sole (>95%) product. An induction period for the formation of **10** was noted in this photolysis. Significantly, no **1** was observed during the photolysis of **2**, and compounds **1–3** were not formed in the photolysis of **8** indicating that deconjugation from the cis α,β-unsaturated ester system is faster than cis to trans isomerization.

Discussion

The photosensitized reactions of the diethyl deca-2,8-dienoates **1–3** were those of cis,trans isomerization accompanied exclusively by 2 + 2 cycloaddition. On the other hand, direct irradiation, while also giving cis,trans isomerization, led eventually to nearly exclusive[14] α,β to β,γ double bond migration. Such clear-cut differences in behavior between sensitized and unsensitized photochemical reactions are relatively rare[19] and are almost certainly due to triplet (sensitized)–singlet (unsensitized) reactivity differences. Each of these processes will be discussed in detail below.

The Triplet Excited State Reaction. The more rapid reaction of the triplet excited states of compounds **1–3** is cis,trans isomerization, a process which has ample precedent.[20] Accompanying this is the slower triplet process of 2 + 2 cyclization which, as can be seen from Scheme I, leads *exclusively* to products of straight cycloaddition. It was of particular interest for us to observe this specificity in a 1,7-diene system since the "rule of five,"[4] a mnemonic which correctly predicts the major cycloaddition paths taken by 1,5- and 1,6-dienes, is inapplicable in this case, *i.e.*, initial 1,5 bonding is impossible for dienes **1–3**.

The present results with the deca-2,8-diene-1,10-dioates may classically be rationalized on the grounds that formation of the most stable diradical intermediate **11** through a cyclic six-membered transition state determines the crossed *vs.* straight nature of the cycloadditions. Recently, however, the idea that radicals are significantly stabilized by interaction with neighboring carbonyl groups has been questioned.[21] This plus the observation that the internal photochemical cycloaddition reactions of 1,5-dienes do *not* follow the course expected on the basis of radical stability[2b] cast some doubt on the validity of the above rationalization.



In this regard, it is interesting to note that if one allows the two double bonds of compounds **1–3** to interact through space in a conformation favorable for cycloaddition the direction of bond formation found in the present work (straight) is neatly compatible

---

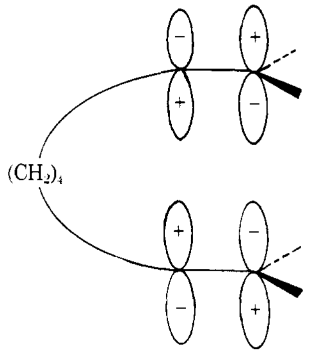
[18] J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970). We thank Mr. I. Armitage for a sample of Eu(DPM)$_3$.

[19] One other chromophore which exhibits equally striking photochemical singlet–triplet reactivity differences is the β,γ-unsaturated ketone system. See, for example, J. Ipaktschi, *Tetrahedron Lett.*, 3179 (1970).

[20] (a) M. J. Jorgenson, *Chem. Commun.*, 137 (1965); (b) P. J. Kropp and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967); (c) R. R. Rando and W. von E. Doering, *ibid.*, **33**, 1671 (1968); (d) J. A. Barltrop and J. Wills, *Tetrahedron Lett.*, 4987 (1968); (e) M. J. Jorgenson and L. Gundel, *ibid.*, 4991 (1968); (f) M. J. Jorgensen, *J. Amer. Chem. Soc.*, **91**, 198 (1969); (g) G. Büchi and S. H. Feairheller, *J. Org. Chem.*, **34**, 609 (1969); (h) M. J. Jorgenson and S. Patumtevapibal, *Tetrahedron Lett.*, 489 (1970); (i) J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, **35**, 3049 (1970).

[21] K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **92**, 5541 (1970).

with the symmetry of the excited state highest occupied molecular orbital **12**[22] and is in accord with molecular



12

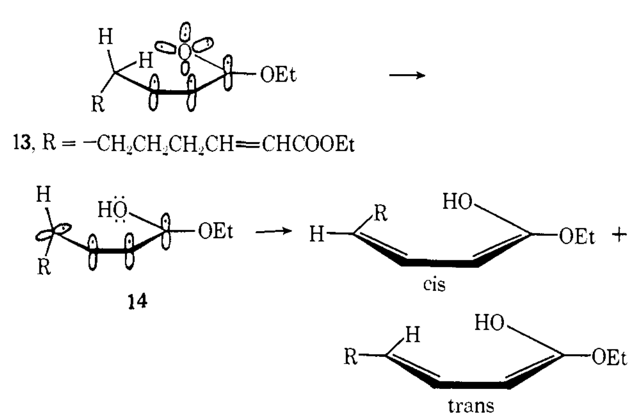
orbital correlation diagrams which may be constructed for the diene → diradical step. Similar relationships apply to the photochemistry of 1,6-dienes which also undergo predominant straight cycloaddition. However, the situation in the case of 1,5-dienes is more complex.[2b]

While the observed photoproducts **4**–**7** can in theory arise from concerted ($_{\pi}2_s + {}_{\pi}2_s$) cycloaddition[23] of **1** and **2** (*i.e.*, **1** → **4** + **6** and **2** → **5** + **7**) it appears more likely that these cycloadditions are proceeding *via* diradical intermediates such as **11** since (a) the cyclizations are exclusively triplet in nature, and (b) the two possible products arising from concerted ($_{\pi}2_s + {}_{\pi}2_s$) internal cyclization of the cis,cis diene **3** are not observed even when pure **3** is used as the starting material and despite the fact that cycloaddition is more competitive with isomerization in the case of **3** than in the cases of **1** and **2**.

Thus, of the six possible stereoisomeric bicyclo[4.2.0]octane-7,8-dicarboxylates which could be formed by straight cycloaddition of dienes **1**–**3**, only four are observed; not observed are the cis,syn,cis and trans,syn,trans isomers which are expected to be the most strained members of the cis-fused and trans-fused ring systems, respectively. Interestingly, the four observed products are partitioned equally (statistically?) between cis and trans fusion in the case of photolysis of dienes **1** and **2**. On the other hand, photolysis of the cis,cis diene **3** leads to an approximately 65:35 preference for formation of the cis-fused ring system, possibly indicating a greater amount of double bond interaction prior to cyclization in this case. Of the two trans-fused epimers which *are* observed, photoproduct **4** is invariably formed in preference to **7** which is in the same direction as their relative thermodynamic stabilities. However, of the two isolated cis-fused photoproducts, stereoisomer **6** is always formed in greater amounts than **5** even though **5** has been shown to be thermodynamically more stable than **6**. Apparently then, factors other than product stability govern the closures of the diradical intermediates at least in the case of the formation of **5** and **6**. These factors may include the question of the conformation of the six-membered ring in the diradical **11** which is initially produced, the relative rates of closure of the cis and trans diradical intermediates, and the degree of interaction between the radical centers before and during closure.

The Singlet Excited State Reaction. The photochemical conversion of α,β-unsaturated esters possessing γ-hydrogen atoms to β,γ-unsaturated esters has become a well-documented reaction during the past 5 years.[20] Evidence has been presented[20d,e,i] which indicates that this reaction proceeds *via* a singlet excited state of the unsaturated ester in which the carbon bearing the γ-hydrogen is cis to the carboalkoxy group.[24] Our results are in accord with these postulates. For example, in the photolysis of diester **8**, an induction period was noted for the appearance of the deconjugated product **10**, but not for the formation of the geometric isomer **9**, thus strongly suggesting that **9** and not **8** is the immediate precursor of **10**. That both the trans → cis isomerizations and the deconjugation reactions were proceeding from singlet excited states was shown in experiments using piperylene as a triplet-energy quencher. Thus irradiation (Corex) of 0.005 *M* solutions of *trans,trans*-diene **1** in hexane containing up to 1 *M* piperylene led to exactly the same results as observed in the absence of piperylene.

An interesting point in photochemical deconjugation rections of α,β-unsaturated esters concerns the geometry of the new β,γ-double bond which is produced. The marked preference for formation of trans-disubstituted double bonds found in the present work may perhaps be most economically explained as shown below. γ-Hydrogen abstraction by the half-filled n orbital on oxygen in the n,π^* singlet excited state **13** would lead initially to a species **14** which could undergo rotation about the β,γ carbon–carbon bond to give either the cis or trans dienol,[25] the latter being favored on steric grounds. Ketonization would then give as the major product the trans-β,γ-unsaturated ester. The supposition that the n,π^* singlet excited state is responsible for the deconjugation reaction is reasonable on the grounds that the irradiations could be carried out using a Corex filter so as to selectively excite the n,π^* absorption bands of the esters under study.[13]



13, R = $-CH_2CH_2CH_2CH{=}CHCOOEt$

14

---

(22) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971). This argument assumes that the conjugated carboethoxy groups of **1**–**3** do not alter the symmetries of the four ethylenic molecular orbitals. Similar assumptions are implicit in the rationalization of many reactions which occur in accordance with orbital symmetry considerations.[23]

(23) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(24) However, methyl crotonate is reported[20b] to undergo deconjugation upon direct *and* sensitized irradiation.

(25) Evidence that a dienol intermediate is formed in these reactions comes from deuterium exchange studies in methanol-*O-d* in which the β,γ-unsaturated product was found to have incorporated one deuterium at the α-carbon.[20d,e,i] A dienol intermediate has recently been isolated from the photolysis of an α,β-unsaturated ketone; see R. Noyori, H. Inoue, and M. Katô, *J. Amer. Chem. Soc.*, **92**, 6699 (1970).

Other workers have found less marked preference for trans-β,γ double bond formation.[20c]

The present results point out the potential synthetic utility of the photochemical ester deconjugation reaction in preparing small amounts of diene diesters of nearly any chain length with accurately known double bond position and geometry.

Experimental Section[26]

General Procedures. Large scale photolyses were carried out in a water-cooled quartz immersion well apparatus. Small scale photolyses were performed by placing the solution to be photolyzed in a 50-ml quartz tube and strapping this to the outside of the water-cooled immersion well. In either case, a Hanovia 450-W Type L lamp with a Vycor or Corex filter was used. All solvents were distilled, the methanol being distilled from a solution of sodium methoxide and dimethyl phthalate.[27] Photolysis solutions were degassed prior to irradiation with Canadian Liquid Air argon containing less than 5 ppm of oxygen.

Preparation of Diethyl *trans,trans*-Deca-2,8-diene-1,10-dioate (1). This material was prepared by bromination of the acid chloride of 1,10-decanedioic acid (Eastman Organic Chemicals) followed by treatment with ethanol[11b] and dehydrobromination in refluxing dimethylformamide.[11a] Compound **1**, a colorless liquid, bp 104° (0.02 mm) (lit.[11a] bp 127° (0.28 mm)), showed the following spectral data: uv max (hexane) 207 (ϵ 23,000) and sh 241 nm (ϵ 410); ir (neat) 5.81 (C=O), 6.06, and 10.15 μ; nmr (CCl$_4$) τ 3.06 (d of t, 2, $J_{2,3} = J_{8,9} = 15.5$ Hz, $J_{3,4} = J_{7,8} = 6.8$ Hz, *trans*-CH=CH-COOEt), 4.22 (d, 2, $J_{2,3} = J_{8,9} = 15.5$ Hz, *trans*-CH=CHCOOEt), 5.85 (q, 4, COOCH_2CH$_3$), 7.78 (broad d, 4, $J_{3,4} = J_{7,8} = 6.8$ Hz, C$_4$ and C$_7$, CH$_2$), 8.50 (m, 4, C$_5$ and C$_6$, CH$_2$), and 8.73 (t, 6,COOCH$_2$-CH_3); mass spectrum parent (70 eV) *m/e* 254.

Direct Photolysis of Diethyl *trans,trans*-Deca-2,8-diene-1,10-dioate (1). This photolysis could be carried out in either methanol or hexane with no observed differences; the following description is typical. Diene diester **1** (2.54 g, 10 mmol) in 1 l. of methanol was irradiated through Vycor[13] and the course of the reaction followed by analytical vapor-phase chromatography using a 5 ft × $^1/_4$ in. stainless steel column packed with 20% DEGS on 60–80 Chromosorb W at a temperature of 170° and a helium flow rate of 120 ml/min. Five new peaks in addition to starting material were observed corresponding to photoproducts **2**, **3**, **8**, **9**, and **10**, the latter being the ultimate sole product after 2.5 hr of irradiation.[14] The retention times were as follows (retention time, compound): 10.5 min, **3**; 11.7 min, **9**; 12.9 min, **10**; 16.2 min, **2**; 17.5 min, **8**; and 28.2 min, **1**.

Isolation and Identification of Photoproducts 2, 3, 8, 9, and 10. Irradiation as above for 90 min led to near-maximum amounts of photoproducts **2**, **3**, **8**, and **9**. These products were separated and isolated by preparative vpc using a 20 ft × $^3/_8$ in. aluminum column packed with 30% DEGS on 45–60 Chromosorb W at 175° and a flow rate of 200 ml/min. Photoisomer **10** was isolated by preparative vpc of the final (2.5 hr) photolysis mixture. All the products were colorless liquids.

The structure of **2** was deduced to be diethyl *cis,trans*-deca-2,8-diene-1,10-dioate from the following data: uv max (isooctane) 208 (ϵ 22,000) and sh 241 nm (ϵ 425); ir (neat) 5.81 (C=O), 6.07, 10.04, and 11.97 μ; nmr (CCl$_4$) τ 3.20 (d of t, 1, $J_{8,9} = 15.5$ Hz, $J_{7,8} = 6.8$ Hz, *trans*-CH=CHCOOEt), 3.92 (d of t, 1, $J_{2,3} = 11.5$ Hz, $J_{3,4} = 7.3$ Hz, *cis*-CH=CHCOOEt), 4.32 (d, 1, $J_{8,9} = 15.5$ Hz, *trans*-CH=CHCOOEt), 4.36 (d, 1, $J_{2,3} = 11.5$ Hz, *cis*-CH=CHCOOEt), 5.94 (q, 4, COOCH_2CH$_3$), 7.37 (broad d, 2, $J_{3,4} = 7.3$ Hz, C$_4$, CH$_2$), 7.80 (broad d, 2, $J_{7,8} = 6.8$ Hz, C$_7$, CH$_2$), 8.52 (m, 4, C$_5$ and C$_6$, CH$_2$), and 8.76 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254. Photoproduct **2** was identical with an independently prepared sample of diethyl *cis,trans*-deca-2,8-diene-1,10-dioate.[15]

Photoisomer **3** was shown to be diethyl *cis,cis*-deca-2,8-diene-1,10-dioate from the following: ir (neat) 5.82 (C=O), 6.07, and 12.04 μ; nmr (CCl$_4$) τ 3.91 (d of t, 2, $J_{2,3} = J_{8,9} = 11.6$ Hz, $J_{3,4} = J_{7,8} = 7.3$ Hz, *cis*-CH=CHCOOEt), 4.38 (d, 2, $J_{2,3} = J_{8,9} = 11.6$ Hz, *cis*-CH=CHCOOEt), 5.95 (q, 4, COOCH_2CH$_3$), 7.37 (broad d, 4, $J_{3,4} = J_{7,8} = 7.3$ Hz, C$_4$ and C$_7$, CH$_2$), 8.53 (m, 4, C$_5$ and C$_6$, CH$_2$), and 8.78 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.94; H, 8.59.

Photoisomer **8** was shown to have the structure diethyl *trans,trans*-deca-3,8-diene-1,10-dioate from the following data: ir (neat) 5.79 (C=O), 5.82 (C=O), 6.07, and 10.18 μ; nmr (CCl$_4$) τ 3.18 (d of t, CH=CHCOOEt, 1, $J_{8,9} = 15.4$ Hz, $J_{7,8} = 6.8$ Hz, *trans*-CH=CHCOOEt), 4.32 (d, 1, $J_{8,9} = 15.4$ Hz, *trans*-CH=CHCOOEt), 4.50 (m, 2, CH=CH), 5.90 (q, 2, COOCH_2CH$_3$), 5.92 (q, 2, COOCH_2-CH$_3$), 7.07 (m, 2, C$_2$, CH$_2$), 7.85 (m, 4, C$_5$ and C$_7$, CH$_2$), 8.38 (m, 2, C$_6$, CH$_2$), and 8.70 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.94; H, 8.80.

Photoproduct **9** was proved to be diethyl deca-*trans*-3-*cis*-8-diene-1,10-dioate from the following: ir (neat) 5.79 (C=O), 5.83 (C=O), 6.12, 10.14, and 11.93 μ; nmr (CCl$_4$) τ 3.91 (d of t, 1, $J_{8,9} = 11.5$ Hz, $J_{7,8} = 7.2$ Hz, *cis*-CH=CHCOOEt), 4.37 (d, 1, $J_{8,9} = 11.5$ Hz, *cis*-CH=CHCOOEt), 4.53 (m, 2, CH=CH), 5.95 (q, 2, COOCH_2CH$_3$), 5.97 (q, 2, COOCH_2CH$_3$), 7.09 (m, 2, C$_2$, CH$_2$), 7.38 (broad d, 2, $J_{7,8} = 7.2$ Hz, C$_7$, CH$_2$), 7.93 (m, 2, C$_5$, CH$_2$), 8.43 (m, 2, C$_6$, CH$_2$), 8.75 and 8.78 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.14; H, 8.55.

Compound **10** was identified as diethyl *trans,trans*-deca-3,7-diene,1,10-dioate on the basis of the following information: uv max (hexane) 208 nm (ϵ 1300); ir (neat) 5.74 (C=O) and 10.27 μ; nmr (CCl$_4$) τ 4.45 (m, 4, CH=CH), 5.87 (q, 4, COOCH_2CH$_3$), 6.97 (m, 4, C$_2$ and C$_9$, CH$_2$), 7.87 (broad s, C$_5$ and C$_6$, CH$_2$), and 8.73 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

The nmr spectrum of a CCl$_4$ solution containing 70 mg of **10** plus 30 mg of Eu(DPM)$_3$[18] showed the following signals attributable to the vinyl hydrogens at C$_3$ and C$_8$: τ 3.30 (d of t, 2, $J_{3,4} = J_{7,8} = 15.7$ Hz, $J_{2,3} = J_{8,9} = 6.8$ Hz, *trans*-CH=CHCH$_2$COOEt). The C$_4$ and C$_7$ vinyls appeared as: τ 3.68 (broad d, 2, $J_{3,4} = J_{7,8} = 15.7$ Hz, *trans*-CH=CHCH$_2$COOEt). Irradiation at C$_2$ and C$_9$ caused the C$_3$ and C$_8$ vinyl hydrogens to appear as a doublet, $J = 15.7$ Hz. Irradiation at C$_5$ and C$_6$ caused sharpening of the C$_4$ and C$_7$ doublet.

A 60% aqueous dioxane solution of **10** (150 mg) containing 0.3 ml of concentrated HCl was refluxed under nitrogen for 22 hr. Removal of solvent *in vacuo* afforded a white solid residue which was recrystallized from water, filtered, and dried over P$_2$O$_5$ *in vacuo* to yield 35 mg of yellow crystals. Norit decolorization followed by a further recrystallization from water afforded 25 mg of pure *trans,trans*-deca-3,7-diene-1,10-dioic acid, mp 118–120° (lit.[17] 118–120°): ir (KBr) 3.56 (OH), 5.91 (C=O), and 10.37 μ; nmr (DMSO-d_6) τ 4.47 (m, 4, CH=CH), 7.03 (m, 4, C$_2$ and C$_9$, CH$_2$), and 7.90 (s, 4, C$_5$ and C$_6$, CH$_2$). This material was identical (mixture melting point, ir, and nmr) to an authentic sample.[17]

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.63; H, 7.21.

Direct Photolysis of Diethyl *cis,trans*-Deca-2,8-diene-1,10-dioate (2). Compound **2** (211 mg) in 200 ml of hexane was irradiated through a Vycor filter and the course of the reaction followed by analytical vpc. Peaks attributable to photoproducts **3**, **8**, and **9** grew and then diminished while the peak due to **2** steadily decreased and that due to **10** steadily increased. After 30 min, **10** was the only product detectable by vpc.[14] A peak corresponding to **1** was not observed at any time during the photolysis. A preparative vpc-collected sample of **10** from this run was identical with previous samples.

Direct Photolysis of Diethyl *trans,trans*-Deca-3,8-diene-1,10-dioate (8). Compound **8** (62 mg) in 45 ml of hexane was photolyzed through Corex and the reaction followed by vpc. For the first hour the disappearance of **8** and the appearance of **9** was observed. At this point a peak corresponding to **10** appeared, until after 2.15 hr there were approximately equal amounts of **8**, **9**, and **10**. After 3.6 hr, **10** was the sole product (>95%) detectable by vpc. At no point during the photolysis were peaks corresponding to isomers **1**,

---

[26] Infrared spectra were obtained, unless otherwise stated, on neat liquid samples between sodium chloride plates with a Perkin-Elmer 137 spectrophotometer. Nuclear magnetic resonance spectra were determined in carbon tetrachloride solution with either a Varian T-60 or HA-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained on a direct inlet AEI MS-9 instrument at 70 eV, and ultraviolet spectra were recorded on a Unicam SP-820 spectrophotometer. Melting points were taken on a Thomas-Hoover capillary apparatus and are corrected. Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda. Vapor phase chromatography was carried out on a Varian-Aerograph 90-P3 instrument using helium as the carrier gas.

[27] E. L. Smith, *J. Chem. Soc.*, 1288 (1927).

2, or **3** observed. A sample of **10** from this run, collected by preparative vpc, was identical with previous samples.

Acetone-Sensitized Photolysis of Diethyl ***trans,trans*****-Deca-2,8-diene-1,10-dioate (1).** Diene diester **1** (1.27 g, 5 mmol) in 400 ml of acetone was irradiated through Corex and the course of the reaction followed by analytical vpc using the 5-ft DEGS column previously described. A photostationary state mixture of products **1**, **2**, and **3** (94%) was formed after 40 min in the ratio of 3.8:3.5:1.0. These products were isolated using the 20-ft DEGS column and identified by ir, nmr, and vpc retention time.

In a separate experiment, 0.51 g (2 mmol) of **1** in 500 ml of acetone was irradiated through Corex until analytical vpc indicated the presence of products **4–7** and the disappearance of geometric isomers **1–3** (8.5 hr). The **1**:**2**:**3** ratio remained constant at 3.8:3.5:1.0 during the transformation into cyclized products **4–7**. Compounds **4–7** had the following retention times on the 5-ft DEGS column at 150° and a flow rate of 200 ml/min: 11.8 min, **4**; 15.1 min, **5**; 16.2 min, **7**; and 19.7 min, **6**. The products were formed in the following relative amounts (average of three runs): **4** (42%), **5** (15%), **6** (36%), and **7** (7%).

Isolation and Identification of Cyclized Products 4–7. The crude photolysate from above (525 mg) was subjected to preparative vpc on the 20-ft DEGS column and the isolated products **4–7** further purified by Kugelrohr distillation; all were colorless liquids.

Photoproduct **4** had the following spectral characteristics: ir (neat) 5.79 μ (C=O); nmr (CCl$_4$) τ 5.90 (q, 4, COOCH_2CH$_3$), 7.15 (m, 2, CHCOOEt), 8.44 (m, 10, cyclohexane ring CH$_2$ and CH), 8.74 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Photoproduct **5** exhibited the following spectral data: ir (neat) 5.79 μ (C=O); nmr (CCl$_4$) τ 5.88 (q, 4, COOCH_2CH$_3$), 6.80 (d, 2, J = 9.5 Hz, CHCOOEt), 7.57 (m, 2, CHCHCOOEt), 8.43 (m, 8, cyclohexane ring CH$_2$), 8.70 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Photoisomer **6** had the following spectral characteristics: ir (neat) 5.78 μ (C=O); nmr (CCl$_4$) τ 5.95 (q, 4, COOCH_2CH$_3$), 7.05 (m, 2, CHCOOEt), 7.34 (m, 2, CHCHCOOEt), 8.52 (m, 8, cyclohexane ring CH$_2$), and 8.80 (t, 6, COOCH$_2$CH_3); mass spectrum parent (70 eV) *m/e* 254.

Photoproduct **7** could not be obtained free of isomer **5** due to their similar vpc retention times. Spectra of **7** slightly contaminated with **5** were in accord with the structure proposed. The structure of **7** was proved by sodium ethoxide catalyzed epimerization (*vide infra*) to be the more stable trans-fused isomer **4** in direct analogy to results obtained with the corresponding *dimethyl* esters.[12b]

The structures of photoproducts **4–6** were proved by direct comparison (retention time, ir, and nmr) with authentic samples obtained by the photoaddition of diethyl maleate to cyclohexene[12a] and by hydrolysis to the known[12] dicarboxylic acids. Thus hydrolysis of **4** gave *trans,anti,trans*-bicyclo[4.2.0]octane-7,8-dicarboxylic acid, mp 180–182° (lit.[12a] mp 181–182°). Similarly, **5** afforded *cis,trans*-bicyclo[4.2.0]octane-7,8-dicarboxylic acid, mp 197–198° (lit.[12a] mp 199–200°) and **6** gave *cis,anti,cis*-bicyclo[4.2.0]-octane-7,8-dicarboxylic acid, mp 170–172° (lit.[12a] mp 174–176°).

Acetone-Sensitized Photolysis of Diethyl ***cis,trans*****-Deca-2,8-diene-1,10-dioate (2).** Diene diester **2** (0.16 g, 0.63 mmol) in 200 ml of acetone was irradiated through Corex to give an initial 3.8:3.5:1.0 mixture of products **1**, **2**, and **3**, respectively. Further photolysis (2.8 hr) caused the disappearance of geometric isomers **1–3** with the concomitant formation of cyclized products **4–7** in the following relative amounts: **4** (44%), **5** (18%), **6** (31%), and **7** (7%). These photoproducts were identical in vpc retention times and spectral characteristics with those previously observed.

Acetone-Sensitized Photolysis of Diethyl ***cis,cis*****-Deca-2,8-diene-1,10-dioate (3).** Diene diester **3** (89 mg, 0.35 mmol) in 50 ml of acetone was irradiated externally through Corex until only photoproducts **4–7** were present (5.5 hr). Removal of the acetone yielded 0.144 g of yellow oil. The products were separated by preparative vpc and were identical in all respects with those obtained in the photolysis of **1** and **2**. The initially formed geometric isomers never reached an equilibrium state as in the photolysis of **1** and **2**, and the final **4–7** photostationary state differed as follows: **4** (26%), **5** (17%), **6** (49%), and **7** (8%).

Acetophenone-Sensitized Photolysis of 1. *trans,trans*-Diene diester **1** (0.254 g, 1 mmol) and acetophenone (0.240 g, 2 mmol) in 200 ml of benzene were irradiated through Pyrex and the reaction followed carefully by analytical vpc. Initially the ratios of **1**, **2**, and **3** were identical with those found in the acetone-sensitized photolysis of **1** and **2**. After 24 hr, only products **4–7** remained in the following relative percentages: **4** (45%), **5** (16%), **6** (31%), and **7** (8%). The photoproducts were identified by their vpc retention times and ir spectra which were identical with previously isolated samples. Benzophenone was also found to sensitize the cycloaddition, but because of its retention time, the ratios of **4–7** could not be obtained. Naphthalene failed to sensitize the photocycloaddition.

Base-Catalyzed Epimerization of Cyclized Products 4–7. Diethyl *trans,anti,trans*-bicyclo[4.2.0]octane-7,8-dicarboxylate (**4**) (0.052 g, 0.21 mmol) and sodium (5 mg) in 1.5 ml of absolute ethanol were sealed in a vial and heated for 12 hr at 80°. Standard work-up procedures afforded 0.036 g of oil. Analytical vpc indicated the presence of three products in the ratio 87:10:3. The first of these was identical with starting material (vpc, ir, nmr), and the second was shown to be stereoisomer **7** by vpc retention time and ir. The third product, present in minute quantities, was not isolated.

Cis,anti,cis diester **6** (0.068 g, 0.28 mmol) under identical conditions gave 0.054 g of oil. Analytical vpc showed two products in an 86:14 ratio. Spectral data and vpc retention times proved the major product to be photoproduct **5** and the minor product to be **6**.

A 50:50 mixture of isomers **5** and **7** (0.047 g, 0.19 mmol) gave four products corresponding in retention times to **4**, **5**, **6**, and **7** after being subjected to the basic conditions previously described. The ratios of **4**:**7** and **5**:**6** were 90:10 and 85:15, respectively. Compounds **4** and **6** prepared in this manner had identical spectral properties with those previously observed.

Thermolysis of Diesters 4, 5, and 6. Diester **6** (0.030 g, 0.11 mmol) was heated in a sealed tube at 250° for 88 hr. Analytical vpc indicated that the diester slowly epimerized to diester **5**. After 28 hr, no further change in the **5**:**6** ratio was observed. This ratio consisted of 81% **5** and 19% **6**; the identity of both was authenticated by vpc and ir. With the exception of two low retention time products (diethyl maleate and cyclohexane on the basis of retention times, sum <1%), these were the only two products observed.

Diester **5** (0.030 g, 0.11 mmol) under identical conditions gave a mixture of **5** (82%) and **6** (18%) after 62 hr.

Diester **4** initially appeared to give the same products as in its base-catalyzed isomerization, but upon increased thermolysis times (88 hr), **4** was converted to a mixture of five products in the ratio 1.12:1.00:3.31:1.56:1.19. The first of these is diester **4**. The remaining products were not identified.