

Photochemistry of Some Carbonyl-Conjugated 1,5-Hexadienes^{1a}J. K. CRANDALL^{1b} AND CHARLES F. MAYER

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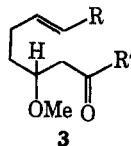
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The photochemical reactions of methyl *trans*-hepta-2,6-dienoate (**1a**), methyl *trans,trans*-octa-2,6-dienoate (**1b**), and *trans*-octa-3,7-dien-2-one (**1c**) have been examined. Each of these compounds undergoes geometrical isomerism and deconjugation to their β,γ -unsaturated isomers upon direct irradiation. Sensitization and quenching experiments implicate a singlet excited state for the latter reaction in the case of **1c**. Attempts to sensitize the deconjugation reaction of **1a,b** were unsuccessful, but prolonged irradiation of **1a** in acetone as solvent and sensitizer gave cyclization to the epimeric 5-carbomethoxybicyclo[2.1.1]hexanes. The details of these reactions are discussed in the context of related photochemical processes.

The photochemical reactions of a series of three compounds, methyl *trans*-hepta-2,6-dienoate (**1a**), methyl *trans,trans*-octa-2,6-dienoate (**1b**), and *trans*-octa-3,7-dien-2-one (**1c**), have been examined. Each of these compounds contains a 1,5-hexadiene unit in which one of the double bonds is conjugated with a pendant carbonyl function. At the outset of this work, the photochemical equivalent of the Cope rearrangement was sought. The conjugating carbonyl function of the present series brings the ultraviolet absorption of the diene into a more easily accessible part of the spectrum for excitation. Since the products (**2a-c**) would be nonconjugated systems, this functionalization might also allow photochemical "pumping" to the thermodynamically less stable 1,5-diene, a process of obvious synthetic interest.

Results

Dienones **1a-c** were prepared by the Emmons-Wadsworth modification² of the Wittig reaction using methoxide in methanol as the base. Thus, **1a** was obtained from 4-pentenal and carbomethoxymethyl diethyl phosphonate, **1b** from this phosphonate and *trans*-4-hexenal, and **1c** from 4-pentenal and acetyl diethyl phosphonate. 4-Pentenal and *trans*-4-hexenal were obtained by thermolysis of allyl vinyl ether and 3-but-1-enyl vinyl ether, respectively, which were obtained by transesterification³ of 1,4-bis(vinylloxy)butane with allyl alcohol and 3-buten-2-ol. The only significant products of the condensation reactions were the desired compounds **1a-c** and the β -methoxy derivatives (**3a-c**) resulting from nucleophilic addition of methanol. Addition product **3c** was the predominant product in the preparation of **1c**. However, the crude mixture of **1c** and **3c** could be transformed to **1c** by acid treatment. Detailed analysis of the spectral properties described in the Experimental Section demonstrates the assigned structures.



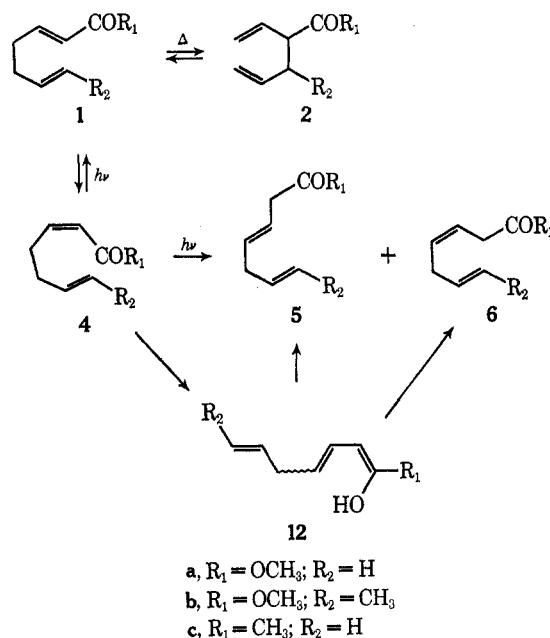
Irradiation of a dilute, degassed solution of **1a** in either methanol or hexane in a Rayonet reactor with 2537-Å lamps gave methyl *cis*-hepta-2,6-dienoate (**4a**)

(1) (a) Supported by a research grant from the Public Health Service; (b) Alfred P. Sloan Research Fellow, 1968-1970.

(2) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Amer. Chem. Soc.*, **83**, 1733 (1961).

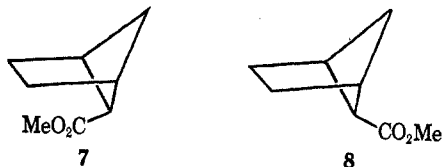
(3) W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

and methyl *cis*- and *trans*-hepta-3,6-dienoate (**5a** and **6a**). Formation of **4a** was rapid at first, reaching about 40% of the total sample after 60% transformation of **1a**. Thereafter, the amounts of both **1a** and **4a** diminished until only **5a** and **6a** remained. Although **5a** and **6a** were not separated, analytical glpc on a capillary column indicated that the glpc-collected sample was a 7:3 mixture of two components and the spectral data were consonant with a mixture of **5a** and **6a**. The intensity of the *trans* olefin peak at 10.3 μ in the ir suggests that the *trans* isomer predominates in this mixture. Under these conditions, photolysis of **1a** is exceptionally clean, giving only traces of other materials. An authentic sample of 2-vinylpent-4-enoate (**2a**) was prepared by pyrolysis of **1a** and shown not to be present in the photolysis mixture.



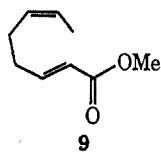
Photolysis of **1a** with 3500-Å lamps in benzene with added benzophenone produced a photostationary mixture of **1a** and **4a** in a 3:1 ratio with less than 1% of any other materials present. Irradiation of a 1% solution of **1a** in acetone at 2537 Å rapidly produced a photostationary mixture of **1a** and *cis* isomer **4a** in a 3:2 ratio. Extended photolysis under these conditions, however, led to formation of additional products. Preparative irradiation of a 1% solution of **1a** in acetone using a 450-W Hanovia source with a Vycor filter gave similar results at a more convenient rate. After 4 hr, a mixture was obtained which glpc indicated to be about

25% **1a** plus **4a** and 75% of a 4:6:2:1 ratio of four new products. The nmr of this product shows that **1a** and **4a** are the only olefinic components according to the integral of the olefinic region relative to that of the methyl ester region. Glpc provided samples of the two major products which were identified as *endo*- and *exo*-5-carbomethoxybicyclo[2.1.1]hexane (**7** and **8**, respec-



tively). The low return from the glpc collection indicates that substantial transformation to higher molecular weight products also occurred during the photolysis. Unfortunately, this prevented isolation of the two lesser products.

The results for photolysis of **1b** are fragmentary owing to the complexity of the product mixtures which prevent glpc separation and complete characterization. The starting samples of **1b** were contaminated with about 5% of a component with a slightly longer glpc elution time. An nmr of a sample consisting largely of this impurity did not differ significantly from that of **1b**, suggesting that the impurity is the *cis* isomer of the isolated double bond, methyl *trans,cis*-octa-2,6-dienoate (**9**). Minor amounts of this isomer are to be expected



from the synthetic sequence utilized. Irradiation of **1b** in methanol or hydrocarbon solvents again showed rapid isomerization to a material identified as the *cis* isomer **4b**, followed by decline of both **1b** and **4b** leading primarily to **5b** and **6b**. However, about 10% of the glpc-detectable product was composed of unidentified materials. The major side-product is tentatively assigned as methyl *cis,cis*-octa-2,6-dienoate. The remaining unidentified components are also thought to be *cis* isomers at the isolated double bond.

Irradiation of **1b** at 3500 Å in benzene with added benzophenone gave a photostationary mixture of **1b** and **4b** in a 3:1 ratio. Small amounts of other products were also formed. Photolysis in acetone at 2537 Å led to a 3:2 mixture of **1b** and **4b** followed by the formation of other products. Prolonged irradiation led to substantial conversion to two new products in a 2:1 ratio. The nmr of this product showed doublets at δ 0.68 and 1.14 which are suggestive of *endo* and *exo* methyls in bicyclo[2.1.1]hexanes.⁴

Photolysis of **1c** in methanol and hydrocarbon solvents at 3500 Å followed the same pattern described for **1a** and **1b** at 2537 Å, but proceeded more slowly. In cyclohexane, a 3:2 ratio of **1c** and **4c** was reached before 5% deconjugation had occurred. No additional products were observed. Neither naphthalene nor perylene affected the course of the reaction. How-

ever, in the presence of large amounts of benzophenone or acetophenone so that these aromatic ketones absorbed most of the incident light, there was essentially no deconjugation observed. Direct irradiation of **4c** gave **1c** and deconjugated ketone; the deconjugated ketone was inert to the photolysis conditions. Glpc comparison of photoproducts with a sample of 3-vinyl-5-hexen-2-one (**2c**), the thermal Cope rearrangement product, demonstrated that this material was not present.

Reaction of **1c** in methanol-*O-d* as solvent gave deconjugated ketone which was a minimum of 88% monodeuterated at C₃ by nmr analysis.

In contrast to the irradiations at 3500 Å, the use of 2537-Å lamps in the photolysis of a cyclohexane solution of **1a** led only to **4c** and did not result in deconjugation even after prolonged reaction times.

Although the spectral data do not specifically demonstrate the *cis* nature of the conjugated double bond of **4c**, analogy with the photolyses of **1a,b** coupled with the spectral data leaves little doubt of the structural assignment. Even capillary glpc would not separate the *cis* and *trans* isomers of deconjugated ketone product (**5c** and **6c**), if indeed both were present. The glpc-collected material gave ir and nmr data comparable to that reported by Conia.⁵ A broad band at 14.2 μ in the ir may indicate the presence of some *cis* isomer **5c**, while the *trans* isomer **6c** is readily apparent at 10.3 μ .

Discussion

The results of the present study are in good agreement with developing trends in the literature for related systems. Photo-Cope rearrangements are still not documented, probably because of the unfavorable geometry required for a concerted reaction to follow the orbital symmetry-permitted pathway.⁶ Nor does this study provide evidence for 1,3-sigmatropic migration of one of the allyl moieties relative to the second, although such isomerizations are known for other 1,5-diene systems.⁷ There are two possible ways by which such a transformation can take place depending upon which allyl fragment is the migrating group. In the case of **1a** and **1c**, one of the possible modes is not an observable process because of the absence of an appropriate label in the unconjugated allyl moiety. However, the alternate possibility would lead to **2a** or **2c**, in contrast to experimental fact. (Either mode of 1,3-sigmatropic rearrangement is potentially observable for **1b** but analytical problems prevented exploration of this point.)

A nonconcerted cyclization mechanism involving the formation of biradical **10** and subsequent cleavage of the 1,4-biradical system in the opposite manner could also lead to formal Cope rearrangement. However, isomerization of triplet **1** to **10** is probably not competitive with the formation of five-ring biradical **11**.⁸ This latter species is most likely the precursor of the bicyclo-

(5) J. -M. Conia and P. le Perchee, *Bull. Soc. Chim. Fr.*, 287 (1966).

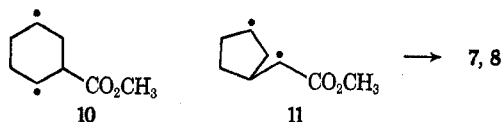
(6) The photochemically allowed process would be a rearrangement of order [3a, 3s]: R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(7) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Tetrahedron*, **24**, 3955 (1968); R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Lett.*, 3955 (1965); R. C. Cookson, *Quart. Rev. (London)*, **22**, 423 (1968).

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

(4) J. Meinwald and R. A. Schneider, *J. Amer. Chem. Soc.*, **87**, 5218 (1965); R. S. H. Liu and G. S. Hammond, *ibid.*, **89**, 4936 (1967).

[2.1.1]hexanes produced in the acetone photosensitized reactions of 1a. This type of reaction finds ample precedent.^{7,9}



The most significant reactions of system 1 are geometrical isomerism and deconjugation to the β,γ -unsaturated derivatives. Sensitization experiments demonstrated that the first process can occur through the triplet state, but the excited singlet probably also undergoes a similar equilibration. Deconjugation appears to be an excited singlet reaction as judged by its insensitivity to triplet quenchers and the inability of triplet sensitizers to promote this transformation. These conclusions are also consistent with recent literature developments.¹⁰ The reactive isomer (necessarily the *cis* compound for geometrical reasons) transfers a hydrogen atom from the γ position to the carbonyl oxygen through a favorable six-center transition state. This process leads to dienol 12 which subsequently tautomerizes to the ultimate product in a normal ground-state process. This mechanistic description is supported by the uptake of one deuterium atom in the deconjugated product when 1c is irradiated in methanol-*O-d* as solvent.

Finally, the interesting behavior of 1c with respect to its photochemical reactivity as a function of excitation energy should be noted. Selective irradiation into the $n-\pi^*$ absorption band leads to deconjugation in accordance with generally accepted views about the characteristic reactivity of $n-\pi^*$ excited carbonyl species. However, irradiation into the higher energy $\pi-\pi^*$ band does not yield deconjugation; only *cis-trans* isomerization is observed. This is not necessarily unexpected for a $\pi-\pi^*$ excited state, but it does indicate that internal conversion to the lowest excited singlet (the $n-\pi^*$ state) is apparently not competitive with other processes which consume the $\pi-\pi^*$ singlet. If this explanation is correct, it violates the usual assumption that internal conversion of higher excited states to the lowest energy excited state is fast relative to other modes of energy degradation. The efficient competitive process for depletion of the $\pi-\pi^*$ excited singlet may be intersystem crossing which for some reason has a large rate constant in this particular instance. A slightly different interpretation would be that internal conversion to the lowest singlet occurs, but that the highly vibrationally excited species initially formed decompose by other modes than the very rapid vibrational relaxation expected in solution. In any event this unusual phenomenon requires exploration by physical methods for a satisfactory explanation.

Experimental Section

General.—Infrared spectra were obtained with Perkin-Elmer Infracord Model 137 and 137-G spectrophotometers as neat films unless otherwise noted. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer in carbon

tetrachloride with tetramethylsilane as internal standard unless otherwise noted. Mass spectra were determined using an AEI MS-9 mass spectrometer at 70 eV. Gas-liquid partition chromatography (glpc) was carried out on a Varian-Aerograph Series 1200 chromatograph (analytical, flame ionization detector) using an 8 ft \times 1/8 in. 15% Carbowax 20 M on 60-80 Chromosorb W column and on an Aerograph A-700 chromatograph (preparative) using a 10 ft \times 3/8 in. column containing a 30% concentration of either Carbowax 20 M, FFAP, LAC-2R-446, or XF-1150 on 60-80 Chromosorb W. Difficult separations were managed analytically by use of a 250-ft Ucon Polar 2000 capillary column. Percentage composition data were estimated by integrated peak areas (Disc Model 224 integrator) and are uncorrected for compound response. Analyses were performed by Midwest Microlab, Inc.

Fisher reagent grade solvents were used for all experiments without further purification.

4-Pentalen.—Allyl vinyl ether was prepared by the method of Watanabe and Conlon.³ Thus, a mixture of 298 g of allyl alcohol and 366 g of 1,4-bis(vinyloxy)butane was heated with 5 g of mercuric acetate in a flask set up for distillation through a 22-in. glass-helices packed, vacuum-jacketed column until 315 g of crude allyl vinyl ether had distilled at 66-68° and no further distillation would occur in this range. The crude material was redistilled to give 244 g (57%) of allyl vinyl ether: bp 66-68°; *ir* 6.10, 6.20, 10.1, and 10.8 μ ; nmr (neat) δ 6.4 (m, 1, OCH=C), 5.9 (m, 1, CH=C), 5.2 (m, 2, CH=CH₂), and 4.1 (m, 4, OCH=CH₂ and OCH₂C=C).

Pyrolysis of allyl vinyl ether was performed by the method of Hurd and Pollack¹¹ using a 300° Pyrex-helices packed Pyrex tube with a nitrogen flow. In this manner, 68 g of ether gave 51 g (75%) of distilled 4-pentalen: bp 103-104°; *ir* 3.6, 3.7, 5.80, 6.10, 10.0, and 10.9 μ ; nmr (neat) δ 9.50 (t, 1, *J* = 1 Hz, CHO), 5.8 (m, 1, CH=CH₂), 5.0 (m, 2, CH=CH₂), and 2.4 (m, 4).

Carbomethoxymethyl Diethyl Phosphonate.—This ester was prepared by the Michaelis-Arbuzov reaction.¹² The temperature of a mixture of 31 g of triethyl phosphite and 20 g of methyl chloroacetate in a flask equipped with a reflux condenser was slowly raised to 225°. At 130° the mixture began to reflux, and by 200° reflux had almost completely subsided indicating that reaction had ceased. The yield of crude product was 40 g. A portion of this was distilled to obtain a pure sample: bp 153-155° (20 mm); *ir* 5.75, 7.9, and 9.8 μ ; nmr (neat) δ 4.09 (octet, 4, *J*_{HCC} = 7 Hz, *J*_{POCH} = 8 Hz, CH₃CH₂O), 3.67 (s, 3, OCH₃), 3.00 (d, 2, *J*_{PCH} = 22 Hz, PCH₂), and 1.27 (t, 6, *J* = 7 Hz, CH₃CH₂O).

Methyl *trans*-Hepta-2,6-dienoate (1a).—This compound was prepared using the Emmons-Wadsworth modification² of the Wittig reaction with sodium methoxide as the base. Sodium metal (3.55 g) was dissolved in 125 ml of dry methanol, and 33 g of crude phosphonate was added. The mixture was stirred for 15 min before 12.0 g of 4-pentalen was added with cooling at a rate to keep the temperature below 50°. After an additional 90 min the solution was diluted with water and extracted with ether. The ether solution was dried (MgSO₄), the ether was removed at reduced pressure, and the residue was distilled to give 15 ml of colorless liquid, bp 82-90° (20 mm), of which 76% was 1a by glpc. Glpc collection gave pure 1a: *ir* 5.80, 6.03, 6.09, 10.1, and 10.9 μ ; nmr (neat) δ 6.91 (d of t, 1, *J* = 16, 7 Hz, CH=CCO), 5.80 (d of t, 1, *J* = 16, 1 Hz, C=CHCO), 5.8 (m, 1, CH=CH₂), 5.0 (m, 2, CH=CH₂), 3.64 (s, 3, OCH₃), and 2.2 (m, 4).

Anal. Calcd for C₈H₁₂O₂: C, 68.55; H, 8.63. Found: C, 68.80; H, 8.68.

From the same collection was obtained a sample of the major by-product (15-20%), methyl 3-methoxy-6-heptenoate (3a): *ir* 5.74, 6.10, 10.0, and 10.9 μ ; nmr (neat) δ 5.8 (m, 1, CH=C), 5.0 (m, 2, CH₂=C), 3.60 (s, 3, CO₂CH₃), 3.25 (s, 3, OCH₃), 2.38 and 2.40 (2d, 2, *J* = 6 Hz, CH₂CO₂), 2.1 (m, 2), and 1.6 (m, 2).

Methyl *trans,trans*-Octa-2,6-dienoate (1b).—*trans*-4-Hexenal was prepared by the method of Watanabe and Conlon.³ A stirred mixture of 25 g of 3-buten-2-ol, 52 g of 1,4-bis(vinyloxy)butane, and 2.0 g of mercuric acetate was heated to 101° for 24 hr. The solution was cooled, diluted with saturated salt solu-

(9) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963).

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

(11) C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, **60**, 1905 (1938).

(12) G. M. Kosolapoff, "Organophosphorus Compounds," 1st ed, Wiley, New York, N. Y., 1950, Chapter 7.

tion, and extracted with 50 ml of ether. The extract was washed with saturated salt solution and dried (MgSO_4). The ether was removed to give 78 g of crude product estimated by glpc to be half *trans*-4-hexenal. Glpc separation gave *trans*-4-hexenal: ir 3.53, 3.66, 5.79, and 10.3 μ ; nmr δ 9.55 (t, 1, $J = 1$ Hz, CHO), 5.4 (m, 2, CH=CH), 2.3 (m, 4), and 1.6 (m, 3).

Sodium metal (6.03 g-atoms) was added to 200 ml of methanol, and 62 g of crude phosphonate was added. The crude *trans*-4-hexenal (78 g) was added dropwise with cooling. After an additional 15 min the solution was diluted with water and extracted with ether. The solution was dried (MgSO_4), and the ether was removed. The residue was distilled to give 24.6 g of colorless liquid (bp 100–110°, 15 mm), which glpc indicated as 67% **1b**. Glpc separation gave pure **1b**: glpc assay, 95%; ir 5.78, 6.02, and 10.3 μ ; nmr δ 6.89 (d of t, 1, $J = 16$, 7 Hz, CH=CCO), 5.77 (d of t, 1, $J = 16$, 1 Hz, C=CHCO), 5.4 (m, 2, CH=CH), 3.64 (s, 3, OCH₃), 2.2 (m, 4), and 1.6 (m, 3).

Anal. Calcd for C₉H₁₄O₂: C, 70.10; H, 9.15. Found: C, 69.96; H, 9.18.

trans-Octa-3,7-dien-2-one (1c).—Iodoacetone was prepared by treatment of chloroacetone (46 g) with sodium iodide (100 g) in 500 ml of acetone at reflux for 8 hr.¹³ The solid sodium chloride was removed by suction filtration. The solvent was removed at reduced pressure. The residue was distilled to give 56 g of brown liquid (bp 70–73°, 21 mm) whose nmr showed singlets at δ 3.90 and 2.39 for iodoacetone and at 4.20 and 2.11 for chloroacetone, indicating a 4:1 ratio of these compounds.

Acetyl diethyl phosphonate was obtained by slow addition of 56 g of crude iodoacetone to 50 g of ice-cold triethyl phosphite with stirring.¹⁴ (Caution is necessary in this addition to prevent a vigorous exothermic reaction.) The solution was heated to 35–40° for 2 hr. Distillation gave 21.7 g of product: bp 76–78° (0.3 mm); nmr (neat) δ 4.10 (octet, 4, $J_{\text{HCH}} = 7$ Hz, $J_{\text{POCH}} = 8$ Hz, OCH₂), 3.20 (d, 2, $J_{\text{POCH}} = 23$ Hz, PCH₂), 2.26 (s, 3, CH₃CO), and 1.29 (t, 6, $J = 7$ Hz, CH₃CH₂O).

Sodium metal (2.0 g-atoms) was dissolved in 50 ml of methanol; 16.5 g of acetyl diethyl phosphonate was added to the solution. Rapid dropwise addition of 6.50 g of 4-pentenal was begun immediately with ice-bath cooling, and 5 min after the addition was completed, the solution was diluted with water. The resulting mixture was extracted with pentane; the extract was washed with saturated salt solution and dried (MgSO_4). The pentane was removed, and the residue was distilled to give 7.5 g (bp 88–101°, 22 mm) of colorless liquid indicated by glpc analysis to be an *ca.* 2:1 mixture of 4-methoxyoct-7-en-2-one (**3c**) and **1c**. This mixture was added to a stirred mixture of 150 ml of tetrahydrofuran, 30 ml of 6 N sulfuric acid, and 25 ml of concentrated sulfuric acid to give a homogeneous solution. After 1.5 hr the solution was diluted with water and extracted with pentane. The extract was washed with sodium bicarbonate and saturated salt solution. The solvent was removed, pentane was added, and the resulting solution was dried (MgSO_4). Removal of the solvent and distillation of the residue through a 12-in. Nester-Faust stainless steel spinning-band column gave 3.85 g of **1c**: bp 88–90° (22 mm); glpc assay, 90%; uv max (hexane) 326 nm (ϵ 32) [lit.⁵ uv max (isooctane) 324 m μ (ϵ 34)]; ir 5.96, 6.09, 6.14, 10.1, and 11.0 μ ; nmr δ 6.76 (d of t, 1, $J = 16$, 7 Hz, CH=CCO) 5.97 (d of t, 1, $J = 16$, 1 Hz, C=CHCO), 5.7 (m, 1, CH=CH₂), 5.0 (m, 2, CH=CH₂), 2.3 (m, 4), and 2.13 (s, 3, CH₃CO).

Pyrolysis of Methyl *trans*-Hepta-2,6-dienoate (1a).—The apparatus consisted of a horizontal 10-mm i.d. Pyrex tube packed with 0.25-in. o.d. Pyrex helices and inserted through a 170-mm long E. H. Sargent and Co. tube furnace. Samples were placed in a flask at one end of the tube, and the vapors were condensed in a Dry Ice trap at the other end. A pressure of 1 mm was maintained by a vacuum pump attached at the trap.

Pyrolysis at 470° of about 1 g of a sample estimated by glpc analysis to be 75% **1a** gave a product mixture containing about 10% of methyl 2-vinylpent-4-enoate (**2a**). Preparative glpc provided pure **2a**: ir 5.74, 6.08, 10.1, and 10.9 μ ; nmr δ 5.7 (m, 2, CH=C), 5.0 (m, 4, CH₂=C), 3.62 (s, 3, OCH₃), 3.04 (m, 1, CHCO), and 2.4 (m, 2).

Anal. Calcd for C₈H₁₂O₂: C, 68.55; H, 8.63. Found: C, 68.61; H, 8.72.

(13) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Amer. Chem. Soc.*, **72**, 4077 (1950); F. Sondheimer, G. Rosenkranz, O. Mancera, and C. Djerassi, *ibid.*, **75**, 2601 (1953).

(14) H. I. Jacobson, M. J. Griffin, S. Preis, and E. V. Jensen, *ibid.*, **79**, 2608 (1957).

Pyrolysis of *trans*-Octa-3,7-dien-2-one (1c).—Pyrolysis of 2.5 g of 83% pure **1c** at 500° using the apparatus described above gave a product mixture containing 8% 3-vinyl-5-hexen-2-one (**2c**). Preparative glpc provided pure **2c**: ir 5.83, 6.10, 10.1, and 10.9 μ ; nmr δ 5.6 (m, 2, CH=C), 5.1 (m, 4, CH₂=C), 3.15 (q, 1, $J = 7$ Hz, CHCO), 2.3 (m, 2), and 2.06 (s, 3, CH₃CO). Anal. Calcd for C₈H₁₂O: C, 77.38; H, 9.74. Found: C, 77.22; H, 9.94.

Photolysis of Methyl *trans*-Hepta-2,6-dienoate (1a).—Qualitative photolyses were carried out using a Rayonet photochemical reactor with a bank of sixteen 2537-, 3100-, or 3500-Å bulbs as noted below. Samples were contained in quartz test tubes for work at 2537 Å and in Pyrex test tubes at other wavelengths. Each solution was degassed before irradiation by bubbling prepurified nitrogen through it for 1 min. The tubes were then sealed with rubber serum caps through which glpc samples were removed by syringe.

Solutions were prepared containing 55 ± 5 mg of **1a** in 5.0 ml of hexane, methanol, and acetone. Irradiation at 2537 Å gave methyl *cis*-hepta-2,6-dienoate (**4a**) and methyl *cis*- and *trans*-hepta-3,6-dienoate (**5a** and **6a**) as illustrated in Table I which presents the ratio of **1a**:**4a**:(**5a** + **6a**).

TABLE I

Time, hr	Hexane	Methanol	Acetone ^a
1	40:36:24	29:30:41	60:37:0:3
2.5	24:29:47	14:18:68	54:40:0:6
4	7:11:82	4:0:96	49:40:0:11

^a The fourth figure represents 7 plus 8.

Irradiation of a solution of ~50 mg of **1a** and 13 mg of benzophenone in 5 ml of benzene at 3500 Å for 2 hr gave a 3:1 mixture of **1a** and **4a** with no **5a** and **6a** apparent. Further irradiation did not affect the product ratio. Similar irradiation of a sample without benzophenone gave no reaction.

Preparative photolyses were performed using either the Rayonet system or a Hanovia system in which the sample solution was placed in a tubular cell surrounding a water-cooled, quartz immersion well. The source for the latter case was a 450-W Hanovia Type L mercury lamp. Solutions were degassed by bubbling prepurified nitrogen through them vigorously for 1 min, closed by inserting the immersion well, and maintained under a slight nitrogen pressure throughout the photolysis. Aliquots were removed by syringe through a serum cap for glpc examination.

A stirred solution of 1.00 g of methyl *trans*-hepta-2,6-dienoate (**1a**) in 105 ml of methanol was irradiated using the Hanovia source with a Vycor filter. After 115 min glpc analysis revealed that deconjugated esters **5a** and **6a** comprised 93% of the product mixture. The methanol was removed at reduced pressure. Preparative glpc provided a mixture of **5a** and **6a**: ir 5.73, 6.10, 10.0, 10.3, and 10.9 μ ; nmr δ 5.6 (m, 3, CH=C), 5.0 (m, 2, CH₂=C), 3.59 (s, 3, OCH₃), 3.0 (m, 2), and 2.7 (m, 2). Glpc analysis by capillary column revealed a 3:7 ratio of two components.

Anal. Calcd for C₈H₁₂O₂: C, 68.55; H, 8.63. Found: C, 68.50; H, 8.48.

Irradiation of a solution of 0.50 g of **1a** in 50 ml of acetone in the Rayonet reactor at 3100 Å gave in 4.5 hr a 3:2 mixture of **1a** and **4a**. The acetone was removed at reduced pressure. The residue was glpc separated to obtain **4a**: ir (CCl₄) 5.78, 6.07, 10.1, 10.9, and 14.5 μ ; nmr δ 6.13 (d of t, 1, $J = 11$, 7 Hz, CH=CCO), 5.8 (m, 2, CH=CH₂ and C=CHCO), 5.0 (m, 2, CH₂=C), 3.64 (m, 3, OCH₃), 2.7 (m, 2), and 2.1 (m, 2).

Anal. Calcd for C₈H₁₂O₂: C, 68.55; H, 8.63. Found: C, 68.44; H, 8.69.

Irradiation of a solution of 1.00 g of **1a** in 110 ml of acetone with the Hanovia source using a Vycor filter led to rapid *cis*-*trans* equilibration followed by relatively slow conversion to a number of products. Glpc examination after 4 hr indicated a mixture of 14% starting material, 9% **4a**, and four new products in about a 4:6:2:1 ratio. The nmr of this mixture denotes that **1a** and **4a** are the only olefinic components (assuming that all the components are methyl esters). The two major new products were isolated by glpc. The first, *endo*-5-carbomethoxybicyclo[2.1.1]hexane (**7**), was obtained in 86% purity: ir (CCl₄) 5.74 μ ; nmr δ 3.53 (s, 3, OCH₃), 2.7 (m, 2), 2.4 (m, 1, CHCO), 1.6 (m, 4),

1.4 (m, 1, *exo* CH), and 0.79 (d, 1, $J = 7$ Hz, *endo* CH),¹⁵ in addition to impurity absorptions. The second, *exo*-5-carbomethoxybicyclo[2.1.1]hexane (**8**), was obtained in 97% purity: ir (CCl₄) 5.74 μ ; nmr (100 MHz) δ 3.62 (s, 3, OCH₃), 2.7 (m, 2), 2.3 (m, 1, *exo* CH), 2.07 (d, 1, $J = 7.5$ Hz, CHCO), 1.60 (broad s, 4), and 0.95 (t, 1, $J = 7.5$ Hz, *endo* CH).¹⁶ The relatively small return obtained upon glpc collection suggests that polymerization consumed much of the monomeric materials.

Photolysis of Methyl *trans,trans*-Octa-2,6-dienoate (1b).—Accurately measured solutions of 11.5 mg of 96% pure **1b** in 1.5 ml of cyclohexane, methanol, and acetone were prepared and degassed. Irradiation at 2537 Å produced methyl *cis,trans*-octa-2,6-dienoate (**4b**) and methyl *cis,trans*- and *trans,trans*-octa-3,6-dienoate (**5b** and **6b**). The data are presented in Table II as the ratio of **1b**:**4b**:(**5b** + **6b**), ignoring a number of minor

TABLE II

Time, hr	Cyclohexane	Methanol	Acetone
1	43:38:19	38:38:24	68:31:1
2	24:33:43	23:26:51	60:38:2
3	12:20:68	7:16:77	55:41:4
4	4:8:88	2:7:91	53:43:4

components (maximum ~15% of the mixture) believed to be *cis* isomers at the isolated double bond. Irradiation of a solution of 18 mg of **1b** and 9 mg of benzophenone in 1.8 ml of benzene at 3500 Å for 2.5 hr gave an *ca.* 3:1 mixture of **1b** and **4b** with less than 5% of **5b** and **6b** present. Further irradiation did not affect the ratio of the first two components.

A solution of 0.15 g of **1b** in 10 ml of methanol was irradiated in the Rayonet reactor at 2537 Å for 11 hr. Glpc indicated that 80% of the product mixture was **5b** and **6b** in about a 1:7 ratio. The methanol was removed at reduced pressure. Glpc gave **6b**: glpc assay, 90% (+10% **5b**); ir (CCl₄) 5.73 and 10.3 μ ; nmr δ 5.4 (m, 4, CH=C), 3.59 (s, 3, OCH₃), 2.9 (m, 2), 2.6 (m, 2), and 1.6 (m, 3). Compound **5b** was obtained in a 1:1 mixture with **6b**: ir (CCl₄) 5.73 (C=O), 10.3, and 14.5 μ ; nmr δ 5.4 (m, 4, CH=C), 3.59 (s, 3, OCH₃), 3.0 (m, 2), 2.7 (m, 2), and 1.6 (m, 3).

A solution of 0.34 g of **1b** in 34 ml of acetone was irradiated at 2537 Å in the Rayonet reactor for 7 hr. Glpc examination disclosed that 78% of the product was a 3:2 mixture of **1b** and *cis* isomer **4b**. The solvent was removed at reduced pressure. Preparative glpc provided **4b**: ir (CCl₄) 5.79 (C=O), 6.06, and 10.4 μ ; nmr δ 6.18 (d of t, 1, $J = 12, 7$ Hz, CH=CCO), 5.70 (d of t, 1, $J = 12, 1$ Hz, C=CHCO), 5.4 (m, 2, CH=C), 3.61 (s, 3, OCH₃), 2.71 (m, 2), 2.1 (m, 2), and 1.6 (m, 3).

Irradiation of a solution of 1.02 g of **1b** in 110 ml of acetone with the Hanovia source through a Vycor filter initially led to *cis-trans* isomerization. Upon further irradiation several unidentified products were formed, some of which later declined. The nmr of the crude product after 105 min (glpc analysis shows two important new products in a 2:1 ratio forming 65% of the mixture) revealed that the majority of the product was not unsaturated. A doublet ($J = 7$ Hz) at the unusually high-field positions of δ 0.68 most likely represents an *endo* methyl group in a bicyclo[2.1.1]hexane system, and another doublet at 1.14 ($J = 5$ Hz) is appropriately positioned for an *exo* methyl group in the same type of system.⁴

Photolysis of *trans*-Octa-3,7-dien-2-one (1c).—Samples were prepared containing 10 mg of **1c** in the following: 1.0 ml of methanol, cyclohexane, and benzene; 0.9 ml of benzene with 0.1 g of added benzophenone, acetophenone, or naphthalene; and 0.8 ml of benzene with 0.2 ml of added piperylene. These samples were simultaneously irradiated at 3500 Å in the Rayonet

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reactor using a merry-go-round. The solutions in cyclohexane, methanol, and benzene yielded *cis*-octa-3,7-dien-2-one (**4c**) and *cis*- and *trans*-octa-4,7-dien-2-one (**5c** and **6c**). Table III pre-

TABLE III

Time, hr	Cyclohexane	Methanol	Benzene
1	59:39:2	70:24:6	60:38:2
2	52:42:6	56:30:14	51:40:9
4	44:28:28	26:25:49	36:39:25
8	11:9:80	2:8:88	7:8:84

sents these data in terms of the ratio **1c**:**4c**:(**5c** + **6c**). The data for the samples containing naphthalene and piperylene were essentially identical with those for benzene alone. The samples containing benzophenone and acetophenone reached a 3:1 ratio of **1c** and **4c** after 1 hr and did not change upon further irradiation.

Another series of solutions was prepared consisting of 10 mg of **1c** in 1.0 ml of cyclohexane or benzene and 10 mg of **1c** in 0.9 ml of cyclohexane with 0.1 g of added benzophenone or naphthalene. These were simultaneously irradiated at 2537 Å. After 8 hr no more than 10% of any components other than **1c** and **4c** were present. The ratio of these was 2.5:1 in cyclohexane and in the sample with added benzophenone, and about 1:1 in the other samples.

Simultaneous irradiation at 3100 Å of solutions containing 10 mg of **1c**, **4c** (83%, +**5c** and **6c**), and **5c** + **6c** in 1.0 ml of pentane demonstrated that *cis* isomer **4c** yields **1c** and **5c** + **6c**, and that **5c** and **6c** are essentially inert to these conditions.

A solution of 2.51 g of 87% pure *trans*-octa-3,7-dien-2-one (**1c**) in 410 ml of redistilled 30–60° petroleum ether was irradiated with the Hanovia source through a Pyrex filter for 30 min. Glpc examination indicated that a 46:31:16 mixture of **1c**:**4c**:(**5c** + **6c**) comprised 93% of the sample. The solvent was removed at reduced pressure, and the residue was distilled to give 2.11 g of colorless liquid (bp 66–89°, 10 mm) of the same composition as above. Glpc separation gave a 91% pure sample of **4c** containing **5c** and **6c** as the only impurities: ir 5.90, 6.09, 6.17, 10.1, and 11.0 μ ; nmr (neat) δ 6.1 (m, 2, CH=CHCO), 5.8 (m, 1, CH=C), 5.0 (m, 2, CH₂=C), 2.7 (m, 2), 2.12 (s, 3, CH₃CO), and 2.1 (m, 2); mass spectrum *m/e* (rel intensity) 124 (2), 109 (4), 81 (21), 55 (15), 43 (100).

From the same collection was obtained a sample of **5c** and **6c**: capillary glpc assay, 96% (one peak); ir 5.83, 6.09, 10.1, 10.3, 11.0, and 14.2 μ ; nmr δ 5.6 (m, 3, CH=C), 5.0 (m, 2, CH₂=C), 3.1 (m, 2), 2.7 (m, 2), and 2.05 (s, 3, CH₃CO).

A solution of 0.10 g of **1c** in 10 ml of deuteriomethanol (82%) was irradiated at 3500 Å in the Rayonet reactor for 22 hr. Glpc examination indicated that the product was about a 1:3 ratio of *cis*-enone **4c** to deconjugated isomers **5c** and **6c**. The solvent and most of the *cis* enone were removed at reduced pressure to give 97% pure **5c** and **6c**: nmr (neat) δ 5.6 (m, 3), 5.0 (m, 2), 3.1 (m, 1.12 \pm 0.16, CHD), 2.7 (m, 2.00), and 2.05 (m, 3). Complete monodeuteration of C₃ would be represented by an integrated value of 1.18 for the 3.1 absorption since the methanol was only 82% deuterated. The observed value represents a minimum of 88% of the possible amount of monodeuteration at C₃, not taking into account an isotope effect.

Registry No.—Allyl vinyl ether, 3917-15-5; 4-pentenol, 2100-17-6; carbomethoxymethyl diethyl phosphonate, 1067-74-9; acetyl diethyl phosphonate, 1067-71-6; **1a**, 25172-04-7; **1b**, 25172-05-8; **1c**, 25172-06-9; **2a**, 922-00-9; **2c**, 25183-60-2; **3a**, 25183-61-3; **4a**, 25172-07-0; **4b**, 25184-12-7; **4c**, 25172-08-1; **5a**, 25172-09-2; **5c**, 25172-10-5; **6a**, 25172-11-6; **6b**, 25184-13-8; **6c**, 25172-12-7; **7**, 20441-29-6; **8**, 824-41-9; *trans*-4-hexenal, 25166-87-4.