mum extinction was reached after 36 hr., and after 96 hr. the extinction began to decrease, probably owing to air leaking into the sample; λ_{max}^{THF} 251 (log ϵ 5.0), 319 (3.7), 322 mμ (3.7).

(ii) **Preparared from Potassium Cyclononatetraenide.**—The anion was prepared from 9-methoxybicyclo[6.1.0]nonatriene (2 μl. 0.0204 g., 0.000146 mole) and potassium (0.63 g., 0.016 g.-atom) in 15 ml. of THF in the apparatus described in the preceding paragraph. Early spectra had a peak at 272 mμ (log ϵ 4.3) that later disappeared as the 249 mμ absorption increased in intensity. The maximum extinction of the 249 mμ absorption was reached after 62 hr.; λ_{max}^{THF} 249 (log ϵ 5.0), 314 (ϵ 4.0), 320 mμ (4.0).

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Thermal and Photosensitized Dimerizations of Cyclohexadiene

BY DONALD VALENTINE,[1a] NICHOLAS J. TURRO, JR.,[1b] AND GEORGE S. HAMMOND

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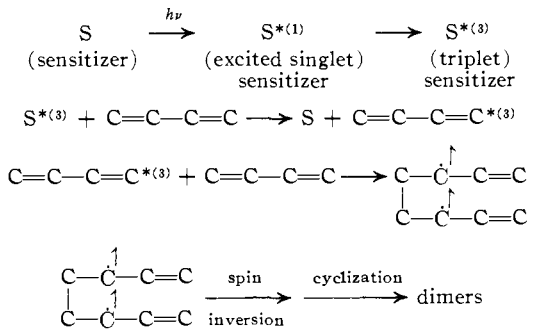
Photosensitized dimerization of 1,3-cyclohexadiene gives 90% yields of *trans-cis-trans*-tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene (**3**), the corresponding *cis-cis-cis*-isomer (**4**), and *exo*-dicyclohexadiene (**2**) in 3:1:1 ratios. Traces of *endo*-dicyclohexadiene (**1**) are also formed. Thermal dimerization of cyclohexadiene gives only **1** and **2** in 4:1 ratio. Novel interconversions of the dimers have been studied. At high temperature **3** and **4** both rearrange to yield, respectively, **1** and **2**. At and below room temperature, however, **1** and **2** revert slowly to **3** and **4** by what is believed to be a surface-catalyzed path.

Introduction

Photosensitized dimerizations have been reported for butadiene, isoprene, cyclopentadiene, and several related systems.[2-5] The mechanism of these reactions is believed to involve four steps

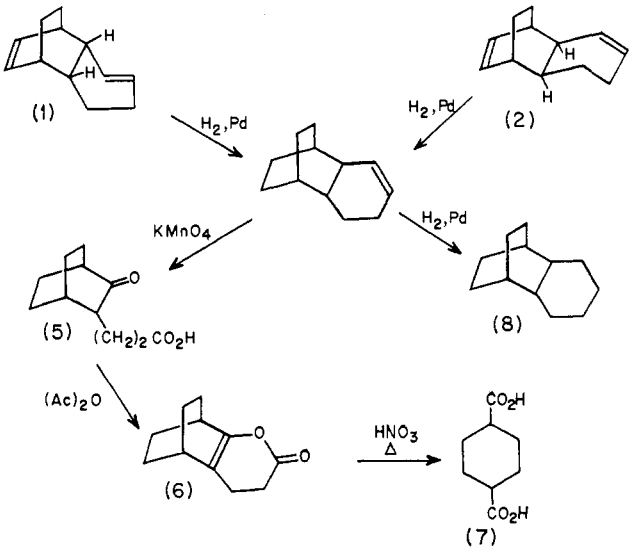


Generally the products of photosensitized and thermal dimerizations of conjugated dienes are different and, at least in the case of cyclopentadiene,[3] the processes appear to proceed through different intermediates. This has been adduced as evidence[3] against a recent formulation of Diels-Alder intermediates as biradicals.[6]

We present here a study of the thermal and photosensitized dimerizations of 1,3-cyclohexadiene. Novel low temperature rearrangements of the dimers are described.

Results and Discussion

Alder and Stein reported isolation of a single product from the thermal dimerization of 1,3-cyclohexadiene at 200°.[7] The structure of the dimer was shown to be either **1** or **2** by the following chemical evidence



The dimerization was repeated and analysis of the products by vapor phase chromatography using Apiezon J columns showed two dimers in a 4:1 ratio. Since the analytical procedure of Alder and Stein could not have shown that **1** and **2** were different compounds because of the initial hydrogenation step, it was suspected that the two dimers observed were **1** and **2**. Hydrogenation of the dimers separately lead to the same saturated hydrocarbon, tricyclo[6.2.2.0^{2,7}]dodecane (**8**), confirming that the dimers are the *endo-exo* isomer pair **1** and **2**.

The major thermal dimer has b.p. 226° (746 mm.), n^{20}D 1.5250. Its n.m.r. spectrum in carbon tetrachloride consists of a quintet centered at τ 4.04, a broad region with maximum at τ 4.58, and broad partially resolved bands from τ 7.61 to 9.00. The relative areas of the three groups are 2:2:12. The

(1) (a) National Science Foundation Predoctoral Fellow, 1963-1965; (b) National Science Foundation Predoctoral Fellow, 1960-1963.

(2) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

(3) N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962).

(4) G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

(5) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

(6) C. Walling and J. Peisch, *J. Am. Chem. Soc.*, **80**, 5819 (1958); C. Walling and H. J. Shugar, *ibid.*, **85**, 607 (1963).

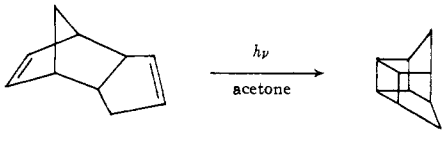
(7) K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

infrared spectrum in chloroform shows principal maxima at: 3020 (s), 2920 (s), 1645 (w), 1440 (m), 1250 (m), 1160 (m), 1070 (m), 940 (m), and 865 (m) cm.$^{-1}$.

The minor thermal dimer has b.p. 229° (746 mm.), $n^{20}D$ 1.5265. The n.m.r. spectrum in carbon tetrachloride consists of a quintet centered at τ 3.72, a broad band from τ 3.72 to 4.65, and a broad, partially resolved band from τ 7.70 to 9.25 in the saturated region with relative areas of 2:2:12. The infrared spectrum in chloroform shows maxima at: 3020 (s), 2920 (s), 1610 (w), 1440 (m), 1365 (m), 1250 (m), 1173 (m), 1075 (m), and 880 (m) cm.$^{-1}$.

The major thermal dimer was assigned *endo* stereochemistry on the basis of the Alder rule.[8] Because the minor product constitutes 20% of the product mixture, application of the Alder rule to this system might be thought of questionable validity. Addition of vinyl acetate to cyclohexadiene, however, has recently been reported to give 86% *endo*- and 14% *exo*-5-acetoxybicyclo[2.2.2]octene-2, providing at least one example of an abnormal Diels–Alder reaction in which the Alder rule predicts the principal product in a mixture.[9] Experiments were carried out to confirm that the observed product ratio actually represents relative rates of formation of the dimers in the primary dimerization process. Both dimers were shown to be stable to isomerization under the dimerization conditions and even for very low conversion of diene to dimer (<0.5%), the ratio of dimers was 4:1. Clearly, the observed product ratio is kinetically controlled in the original dimerization process.

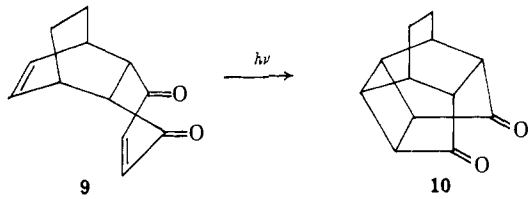
Efforts to provide chemical evidence regarding the stereochemistry of the dimers have failed. Unlike *endo*-dicyclopentadiene, which closes readily upon irradiation in acetone to yield a cage isomer,[10] neither of the dicyclohexadienes forms a cage isomer upon irradiation either in acetone, or in benzene solution



with sensitizers such as benzophenone, β-acetonaphthone, benz[*a*]anthracene, eosin, or 9,10-dibromoanthracene.

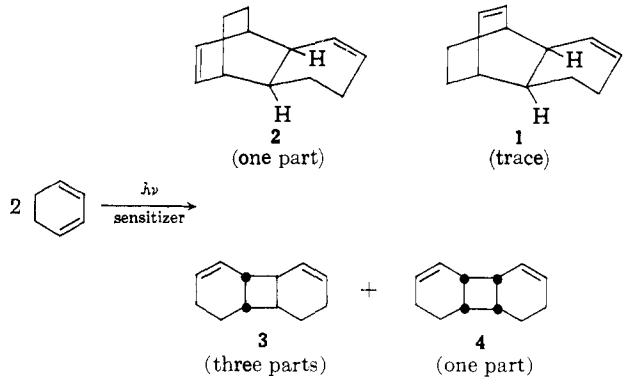
An attempt to synthesize *endo*-dicyclohexadiene from the known adduct of benzoquinone and cyclohexadiene (**9**)[11] was unsuccessful, but led to discovery of a very facile light-induced closure reaction. Upon irradiation either in solution or in the solid state, **9** is converted to **10** with high quantum efficiency.

The structure **10** is assigned to the closure adduct on the basis of its infrared spectrum, which shows a saturated carbonyl (1757 cm.$^{-1}$), the absence of carbon–carbon double bonds, and the presence of cyclobutane ring vibrations (935, 917, 800 cm.$^{-1}$). Because of problems of solubility and thermal instability, it has not been possible to measure the molecular weight of **10** and dimeric structures cannot be rigorously excluded. Structure **10**, however, is analogous to that assigned by Cookson, *et al.*, to the product obtained by photoisomerization of the adduct of cyclopentadiene and benzoquinone.[12]



9 **10**

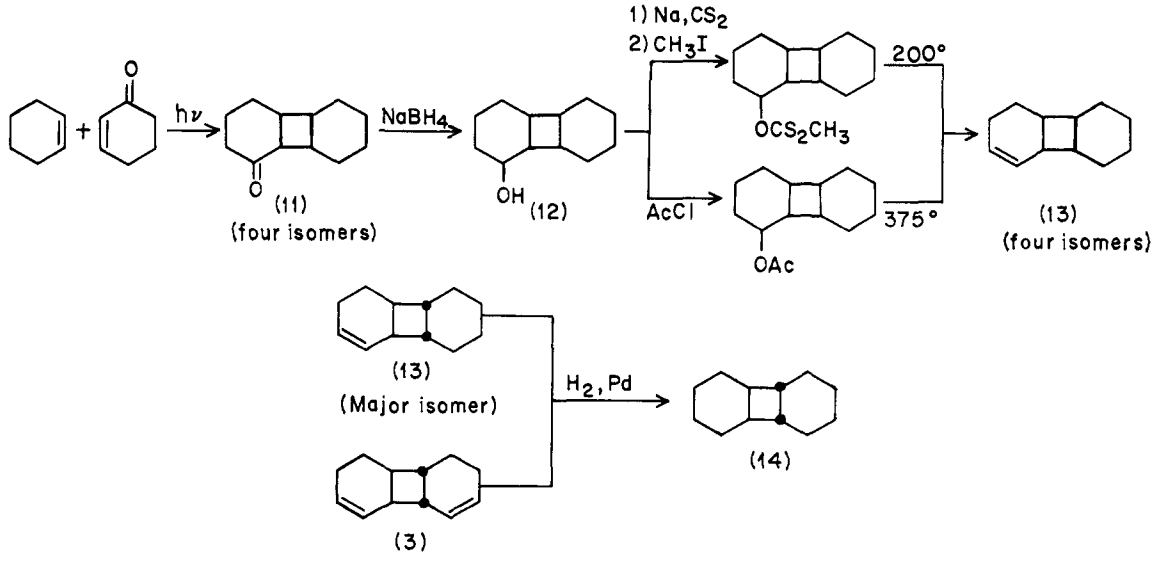
Photosensitized Dimerization of 1,3-Cyclohexadiene.—Irradiation of oxygen-free solutions of cyclohexadiene and various sensitizers in isopentane solutions results in 90% conversion to three dimers which are produced in approximately 3:1:1 ratio. A fourth dimer is produced in trace amounts. The relative amounts of dimers formed are independent of sensitizer employed over a wide range of sensitizer triplet state energies, in contrast to results with open chain dienes.[4] In some cases, notably with α-nitronaphthalene and duroquinone, addition of sensitizer to cyclohexadiene is also observed. Structural evidence presented below indicates that the photosensitized reaction should be represented as



One of the minor photodimers was shown to be *exo*-dicyclohexadiene (**2**) by comparison with the thermal dimer. Comparison of v.p.c. retention times indicates the trace product is probably *endo*-dicyclohexadiene (**1**).

The infrared and n.m.r. spectra of the major photodimer are consistent with, but not definitive for, structure **3**. A partial structure proof was carried out by comparison with hydrocarbons obtained by chemical modification of the photoadducts formed from 2-cyclohexen-1-one and cyclohexene. Irradiation of degassed mixtures of the latter two compounds in Pyrex vessels results in 70% conversion to a mixture of four isomeric adducts, all having the composition $C_{12}H_{16}O$. The infrared spectrum of the mixture shows characteristic carbonyl absorption bands and bands between 850 and 1000 cm.$^{-1}$ such as are usually associated with vibrations of cyclobutane rings. We presume that the products are stereoisomers having structure **11**. The mixture of ketones reacted with 2,4-dinitrophenylhydrazine to give four dinitrophenylhydrazones which were separated by chromatography on silica gel. Treatment of the mixed ketones with sodium borohydride gives a mixture of isomeric alcohols,

(8) K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1933).
(9) N. A. Le Bel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).
(10) G. O. Schenck and R. Steinmetz, *Ber.*, **96**, 520 (1963).
(11) O. Diels and K. Alder, *ibid.*, **62**, 2337 (1929).
(12) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind.* (London), 1003 (1958).



12. Conversion of the alcohols to the alkenes, **13**, could be accomplished either by acetate pyrolysis at 375° or by xanthate pyrolysis at 200°. From the xanthate pyrolysis, four isomers of **13** were obtained in 2:1:10:2 ratios.[13] The alkenes were separated by preparative v.p.c. with Apiezon J columns. Hydrogenation of the major isomer of the alkenes gave a saturated hydrocarbon **14**, whose n.m.r. and infrared spectra were identical with those for the product of total hydrogenation of the major photodimer of cyclohexadiene.

The above reactions would seem to establish rigorously the presence of a cyclobutane ring in the major photoproduct. The unsymmetrical disposition of the double bonds may be inferred from analogy to other photosensitized dimerizations of conjugated dienes[5] and must be assumed to account for the thermal rearrangement of the compound (*vide infra*).

The third photodimer was assigned the stereoisomeric cyclobutane structure, **4**. The n.m.r. spectrum of the compound is shown in Fig. 1. The sample used was known, by v.p.c. analysis, to contain small amounts of **2**. The strong signal centered at τ 7.12 corresponds to the chemical shift characteristic of protons attached to cyclobutane rings. The broad bands lying between τ 7.8 and 8.4 are assigned to the methylene groups, two allylic and two nonallylic, in **4**. The spectrum is rather similar to that of **3**, which is also shown in Fig. 1. However, the latter shows a larger separation of the methylene resonances. The spectrum of **3** also contains a very closely grouped multiplet at τ 7.65. This is now assigned to protons attached to the four-membered ring, although the high-field position led us, at one time, to question the assignment of the structure of **3** and prompted initiation of the partial chemical proof of structure described above. The infrared spectrum of **4** shows, *inter alia*, maxima at 1015, 975, and 850 cm.$^{-1}$ such as are normally found in the spectra of cyclobutane derivatives. Similar bands are found in the infrared spectrum of **3** at 1006, 930, and 865 cm.$^{-1}$.

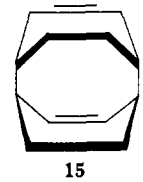
At temperatures above 160°, **3** and **4** rearrange to **1** and **2**, respectively. The reactions have been shown to go essentially to completion at 190° and the rates of rearrangement have been studied at various temperatures. The rate data are summarized in Table I.

TABLE I

KINETICS OF REARRANGEMENTS OF TRICYCLO[6.4.0.0.^{2,7}]DODECA-3,4-DIENES AT ELEVATED TEMPERATURES

Temp., °C.	$k \times 10^6$, sec.$^{-1}$	
	3 → 1	
179.2	6.53 ± 0.12	
189.1	22.2 ± 2.1	ΔH^* = 36.8 kcal./mole
205.1	52.1 ± 3.1	ΔS^* = −3.2 e.u.
218.7	231 ± 1.5	
	4 → 2	
164.0	51.5 ± 1.5	ΔH^* = 33.0 kcal./mole
179.3	196 ± 3	ΔS^* = +4.6 e.u.
188.7	574 ± 5	
205.1	2360 ± 250	

The results may be compared with those recently reported for the rearrangement of the 1,2-divinylcyclobutanes.[14] The *cis* isomer rearranges to 1,5-cyclooctadiene with ΔH^* = 23.7 kcal. per mole and ΔS^* = −11.7 e.u. The *trans* isomer rearranges to a mixture of products with ΔH^* = 34.0 kcal./mole and ΔS^* = −1.2 e.u. Obviously the rearrangements of **3** and **4** fall into the class, exemplified by *trans*-divinylcyclobutane, which is believed to involve formation of biradical intermediates. Even though **4** is believed to be a *cis* compound, the result is not surprising since **4** cannot readily assume the conformation required to convert *cis*-divinylcyclobutane to cyclooctadiene in a concerted process; such a reaction of **4** would produce **15** rather than a dicyclohexadiene.



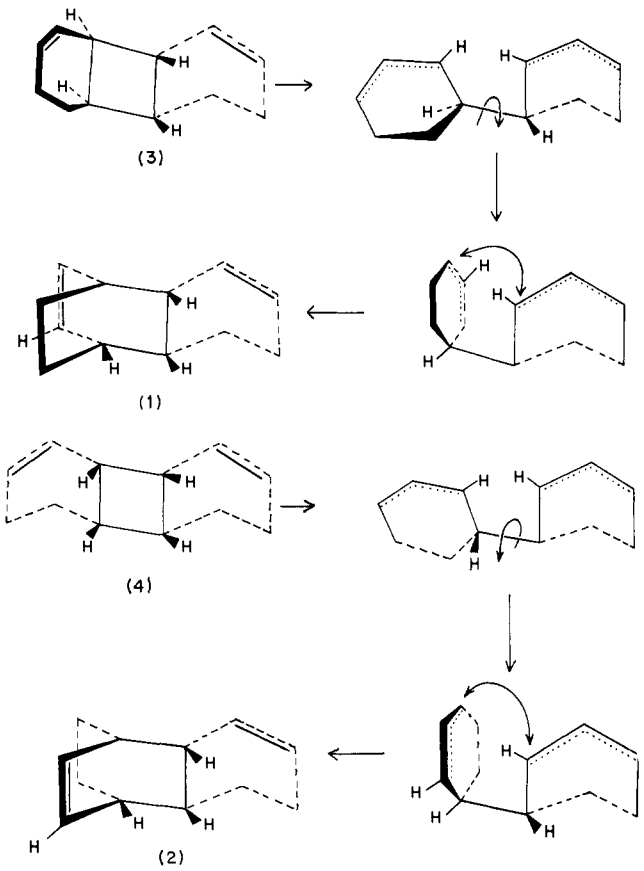
15

Rearrangements of **3** and **4** by the biradical mechanism would be expected to follow the observed courses. Since the biradical intermediates would have different stereochemistry, the paths of the reactions should not

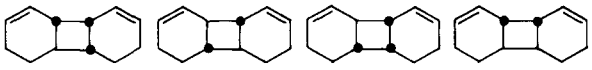
(13) Acetate pyrolysis gave the same products in slightly different ratios.

(14) G. S. Hammond and C. D. DeBoer, *J. Am. Chem. Soc.*, **86**, 899 (1964).

cross. The following equations show the postulated mechanism.

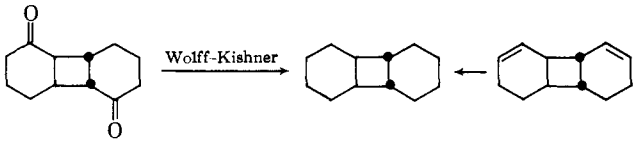


It will be noted that the rearrangement data cannot alone distinguish between structures **3**, **16**, and **17** for the major photodimer or between structures **4**, **18**, and **19** for the minor photodimer. For the major photodimer the *trans*-fused systems can be eliminated



16 **17** **18** **19**

because Wolff–Kishner reduction of the cyclohexenone dimer **20**, which is known to have the *trans-cis-trans* configuration,[15] gives **14**. This requires that the major photodimer have structure **3**.



No information is available about the ring fusions in the minor photodimer, but in view of its unexpectedly high stability (*vide infra*) and the low stability of previously reported 6,4-ring systems,[16] we prefer the all-*cis* structure **4**.

Reversion to Cyclobutanes.—Some samples of **1** and **2** slowly reverted to **3** and **4**, respectively, at room temperature and below. These astonishing transformations were observed in samples collected from vapor chromatography on Apiezon J unless the chromatographed material was redistilled. Redistilled samples were indefinitely stable when stored in clean glass vials but underwent rearrangement when stored in contact with glass wool. At 25° the equilibrium ratio (**3**/**1**) is approximately 9. At temperatures up to 100° measurable conversion of **1** to **3** is observed. Measurement of equilibrium constants is not an easy matter because side reactions tend slowly to consume the photodimers.

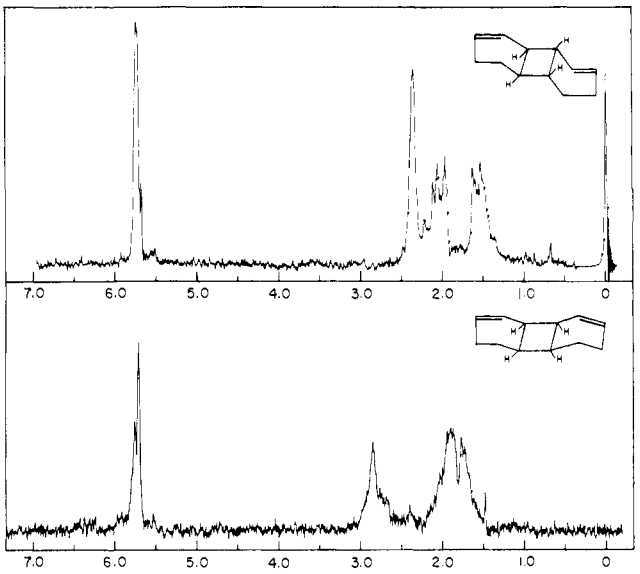


Fig. 1.—N.m.r. spectra of (a) *trans-cis-trans*-tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene and (b) *cis-cis-cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene in carbon tetrachloride. The first spectrum gives parts per million relative to TMS internal standard, the second relative to TMS external. Both spectra recorded on Varian A-60 nuclear magnetic resonance spectrometer.

The behavior of the two pairs of hydrocarbons is puzzling. Even the preliminary observations can be accommodated only if we presume that the Diels–Alder dimers have both substantially higher enthalpy and entropy contents than the isomeric cyclobutanes. This conclusion is very difficult to accept since the enthalpy contents of **3** and **4** should include about 20 kcal./mole strain energy attributed to the cyclobutane rings. Such strain is directly indicated by the heats of combustion of cycloalkanes[17] and is reflected in the kinetics of pyrolysis of cyclobutanes by what is presumed to be a biradical mechanism.[14,18] What few pertinent thermodynamic data are now available are of little help in locating the sources of the driving forces for the rearrangement reactions. The heats of combustion of **8** and what we believe to be a mixture of **1** and **2** have been measured and indicate a heat of hydrogenation of about −57 kcal./mole for hydrogenation of two double bonds in **1** and **2**.[19] Since this value is a "normal" increment for two double bonds, we infer that special strains in **1** and **2** must be associated with the ring systems.

For bicyclo[2.2.2]octene-2, Turner found the heat of hydrogenation to be −28.3 kcal./mole.[20] Compari-

(15) P. A. Eaton, *et al.*, unpublished results.

(16) Examples of *trans*-fused 6,4-ring systems produced photochemically are given by: E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 363 (1963); **86**, 485 (1964); P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963).

(17) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 479.

(18) H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 4884 (1961).

(19) K. Alder and G. Stein, *Ber.*, **67**, 613 (1934).

(20) R. B. Turner, W. R. Meader, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

son of this value with that for cyclohexene (−27 kcal./mole), which gives a staggered hydrogenation product, leads to the conclusion that there is relatively little difference in the strain energies of bicyclooctene and bicyclooctane. This is a surprising result since there are numerous eclipsed interactions present in the latter compound which are not present in the former. To explain this, Turner[20] postulated that bicyclooctane, and perhaps bicyclooctene also, exist largely in a twisted conformation which relieved eclipsed interactions without increasing bond angle strain. If the bicyclooctyl and octenyl systems in **1** and **2** were prevented from twisting by the additional cyclohexyl ring system, a considerable destabilization attributed to strain would be expected and could help explain the observed equilibria. Unfortunately, this explanation is not supported by the data of Alder and Stein[19] who found the heat of combustion of **8** to be 1761 kcal./mole, only slightly less than the 1765 kcal./mole predicted by Klages' rules.[21,22] Since Klages' rules take only minor account of strain, if **8** were appreciably strained the experimental heat of combustion would be much higher than the estimated value. Since the heat of combustion measurements on "dicyclohexadiene" were made on what is now presumed to have been a mixture of **1** and **2**, an extensive reinvestigation of the thermodynamic properties of these compounds is indicated. Such a study is now in progress. One other feature of the problem warrants passing note. It is certain that the above discussion, which is centered entirely on consideration of zero point potential energy differences, will not suffice to account for the driving force for conversion of **3** and **4** to **1** and **2** at elevated temperatures. The large entropy change required to account for the reactions demands that the partition functions of **1** and **2** be much larger than those of their isomers, at least at temperatures above 170°.

Experimental

Photodimers of 1,3-Cyclohexadiene.—Cyclohexadiene (Aldrich Chemical, 100 g.) and β-acetonaphthone (reagent grade, 9 g.) were dissolved in sufficient isopentane to give 500 ml. of solution. Nitrogen was bubbled through the solution for 5 min. and the solution was then irradiated for 24 hr. with a 450-watt medium pressure mercury arc housed in an Hanovia immersion reactor. The reaction mixture was concentrated by rotary evaporation with aspirator suction, then vacuum distilled to give 92 g. (92%) of dimeric products, b.p. 34–39° (1 mm.). About 6 g. of polymeric material was also recovered. *Anal.* (of mixed dimers). Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.66, 89.75; H, 10.19, 10.22.

The isomeric dimers were separated completely on a 150-ft. Apiezon J Golay column. The isomers were separated by preparative vapor phase chromatography with a Beckman Megachrom using eight 6 ft. Apiezon J columns. The dimers were not completely separated but could be obtained pure by taking cuts which eliminate mixed fractions. The first cut consisted of essentially pure **3**. The last cut consisted of **2** and **4** in 2:3 ratio and pure compounds were obtained by further preparative chromatography with a Wilkins Autoprep using a 12 ft. column of 35% Apiezon J on firebrick. During all v.p.c. work the column, injector, and detector temperatures were kept below 160° to prevent thermal rearrangements of the photodimers.

Thermal Dimerization of Cyclohexadiene.—Cyclohexadiene (30.0 g.) was degassed twice by freeze–thaw cycles and sealed under vacuum in a thick-walled tube. The tube was heated to 200° for 24 hr., cooled, and opened, and the contents were distilled under vacuum to give 9.7 g. (32%) of dimeric products, b.p. 31–33° (1 mm.).

Rearrangement of the Photodimers.—Cyclohexadiene photodimers (6.0 g.), distilled but not separated, were degassed twice by freeze–thaw cycles and sealed under vacuum in a thick-walled tube. The tube was heated to 200° for 24 hr., cooled, and opened, and the contents distilled under vacuum to give 5.0 g. (88%) of a 3:2 mixture of *endo*- and *exo*-dicyclohexadiene, identified by comparison with authentic samples. About 0.5 g. of polymeric material and traces of monomer were obtained. Shorter heating times gave no polymer, but left some photodimer unconverted. *Anal.* Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.99; H, 9.88.

Hydrogenation of Thermal Dimers.—Cyclohexadiene thermal dimers (5.0 g.) in 3:2 ratio were dissolved in 25 ml. of 95% ethanol (not denatured) and 0.5 g. of Engelhard platinum dioxide catalyst was added to the solution. The mixture was placed under hydrogen at room temperature and pressure until no more hydrogen was absorbed. The catalyst was then removed by filtration, 50 ml. of water was added, and the mixture extracted with 2 × 25 ml. of pentane. The pentane layer was washed twice with water to remove ethanol, dried over magnesium sulfate, and evaporated to give 4.8 g. of tricyclo[6.2.2.0^{2,7}]dodecane, b.p. 233° (746 mm.), $n^{20}D$ 1.4445; n.m.r. resonances at τ 8.38, 8.72; the infrared spectrum in chloroform showed maxima at 2950, 1465, 1125, 940, and 860 cm.$^{-1}$. *Anal.* Calcd. for $C_{12}H_{20}$: C, 87.81; H, 12.19. Found: C, 87.45; H, 12.44.

Hydrogenation of *trans-cis-trans*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,11-diene.—The diene (400 mg.) was dissolved in 5 ml. of 95% ethanol (not denatured) and hydrogenated in the same way as the thermal dimers. About 370 mg. (92%) of *trans-cis-trans*-tricyclo[6.4.0.0^{2,7}]dodecane was obtained. The hydrogenated material had b.p. 233° (746 mm.); infrared maxima in carbon tetrachloride at 2920, 2856, 2689, 1575, 1462, 1451, 1357, 1318, 1310, 1287, 1269, 1235, 1203, 1138, 1127, 1030, 980, 880, and 850 cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed maximum absorptions at τ 7.88 and 8.50. *Anal.* Calcd. for $C_{12}H_{20}$: C, 87.81; H, 12.19. Found: C, 87.32; H, 12.49.

Photoaddition of 2-cyclohexen-1-one to Cyclohexene.—A mixture of 30 g. of cyclohexene (reagent grade) and 10 g. of 2-cyclohexen-1-one (Aldrich reagent chemical) was degassed twice by freeze–thaw cycles and sealed under vacuum in 15 × 125 mm. Pyrex tubes. The tubes were irradiated for 72 hr. with a 450-watt medium pressure mercury arc in an Hanovia immersion reactor. Vacuum distillation of the contents gave 14.1 g. (70% based on cyclohexenone) of the adducts, b.p. 77–91° (1 mm.). *Anal.* (of mixed adducts). Calcd. for $C_{12}H_{18}O$: C, 80.84; H, 10.11: Found: C, 80.79; H, 10.22. Further distillation of the reaction mixture gave 2.1 g. (12%) of what appeared to be cyclohexenone dimers, b.p. 130–144° (1 mm.).

The 2,4-dinitrophenylhydrazones of the mixed cyclohexene–cyclohexenone ketones were prepared by the method of Vogel.[23] Separation of the DNP's was accomplished by column chromatography on a 2 × 28 cm. silica gel column eluted with 3:1 benzene–60–70° ligroin. The silica gel used was prepared by mixing Mallinckrodt silicic acid and Celite in 20:3 ratio and then heating over a Meeker burner for 6 hr. Four separate DNP's were obtained (none of which were identical with 2-cyclohexen-1-one DNP), melting at 160–164, 143–145, 172–176, and 161–165°.

Reduction of Mixed Tricyclo[6.4.0.0^{2,7}]dodecan-3-ones.—The ketones (11 g.) were dissolved in 250 ml. of 95% ethanol (denat.) and the solution was cooled to 0° in an ice bath. The solution was stirred rapidly and a solution of 2.5 g. of sodium borohydride in 30 ml. of 0.1 *N* sodium hydroxide was added dropwise. After 3 hr., the reaction mixture was concentrated to 50 ml. by distillation, 150 ml. of water was added, and the mixture extracted with four 50-ml. portions of ether. The ether layer was washed once with water, dried over magnesium sulfate, and evaporated by boiling to give crude alcohols, which upon distillation gave 9.0 g. (88%) of pure material. *Anal.* (of mixed alcohols). Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.79, 79.86; H, 11.23, 11.16.

Acetates of Mixed Tricyclo[6.4.0.0^{2,7}]dodecanols.—The alcohols were mixed with equal volumes of reagent grade acetyl chloride and allowed to stand for 5 min. with occasional shaking. The reaction mixture was then diluted with water and the organic layer which separated was dried over magnesium sulfate to give

(21) G. Klages, *Ber.*, **82**, 358 (1949).

(22) G. W. Wheland, "Resonance In Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 89.

(23) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans Green and Co., London, 1956, p. 344.

93–95% yields of the acetates. The infrared spectrum of the mixture in chloroform showed maximum absorption at 3075, 3043, 2957, 2880, 2420, 1763, 1650, 1535, 1457, 1383, 1265, 1230, 1032, and 934 cm.$^{-1}$.

Pyrolysis of the Mixed Acetates.—A solution of 2.0 g. of the acetates in 15 ml. of cyclohexane was dropped slowly through a pyrolysis tube packed with glass beads and heated to 375°. A small quantity of the desired alkenes was obtained; most of the acetates, however, failed to decompose and 0.85 g. of the acetates was recovered by washing the column repeatedly with cyclohexane.

Tricyclo[6.4.0.0^{2,7}]dodecane-3-xanthates.—The tricyclic alcohols (11 g.) were dissolved in 50 ml. of dry ether. Freshly cut sodium slivers (1.4 g.) were added to the solution and the mixture was then stirred at room temperature for 24 hr., while 6 ml. (9.8 g.) of carbon disulfide was added in small portions at intervals. The sodium was then removed mechanically and stirring was continued for another hour. Methyl iodide (16.8 g.) was then added to the solution and stirring was continued overnight. After 14 hr., 1.0 g. of additional methyl iodide was added and stirring continued for 1 more hr. The inorganic salts were removed by filtration and the ether solution was evaporated at 25° under reduced pressure to yield a red oil which was crystallized by allowing it to stand on a porous clay plate. About 2.0 g. of whitish crystals was obtained. Recrystallization from ethanol gave white crystals, m.p. 35–46° (a mixture of four isomers).

Pyrolysis of Tricyclo[6.4.0.0^{2,7}]dodecane-3-xanthates.—The xanthates (0.95 g.) were placed in a 25-ml. flask equipped with a reflux condenser and gas buret. The flask was heated to 205–210° for 65 min., then allowed to cool, and the contents vacuum distilled to give 0.200 g. (40%) of a mixture of four alkenes in 2:1:10:2 ratios as determined by v.p.c. analysis on Apiezon J. The major isomer was obtained pure by preparative v.p.c. on the Autoprep using an Apiezon J column. The n.m.r. of the mixed alkenes showed most of the vinyl protons as an asymmetric multiplet with maxima at τ 4.18 and 4.23 and the saturated region as a broad band.

Hydrogenation of *trans-cis-trans*-Tricyclo[6.4.0.0^{2,7}]dodec-3-ene. The major component of the alkene mixture was washed from the collection trap of the Autoprep with 4.0 ml. of absolute ethanol; 50 mg. of Engelhard 5% palladium-on-charcoal catalyst was added to the solution, and the mixture stirred under hydrogen at room temperature and atmospheric pressure until no more hydrogen was consumed. The catalyst was removed by filtration and 5.0 ml. of water was added to the reaction mixture, which was then extracted with two 5-ml. portions of pentane. The pentane solution was washed twice with water, dried over magnesium sulfate, then evaporated by boiling to give the crude tricyclo[6.4.0.0.^{2,7}]dodecane. After purification by preparative vapor phase chromatography with the Autoprep v.p.c., the n.m.r. and infrared spectra of the alkane were identical with those of the product obtained by hydrogenation of the major photodimers.

Photodimerization of 2-Cyclohexen-1-one.—The method used was that of Eaton.[15] Twenty grams of freshly vacuum-distilled cyclohexenone was irradiated for 72 hr. with a 450-watt Hanovia lamp through two layers of Pyrex. At the end of this period the excess cyclohexenone (2.6 g.) was removed under vacuum and the residue distilled to give 15.2 g. (87% based on unrecovered cyclohexenone) of a colorless oil, b.p. 125–128° (0.3 mm.). An attempt to chromatograph the mixture of dimers on Woelm neutral, activity grade 1 alumina led to a violent evolution of heat, but chromatography on Merck acid-washed alumina eluting with methylene chloride gave **20**; the corresponding *syn* isomer was removed by elution with ether containing 10% ethanol. Rechromatography of the major fractions gave the *anti* dimer (eluted by methylene chloride) as stout prisms, m.p. 53–55° (from hexane), and the *syn* isomer as white flakes, m.p. 79–80° (from hexane).

Wolff-Kishner Reduction of 20.—The dione (2.5 g.) was dissolved in 30 ml. of diethylene glycol. Hydrazine hydrate (85%, 30 ml.) was added and the mixture heated to 100° for 30 min. After the reaction mixture had cooled to room temperature, 8 g. of potassium hydroxide pellets was added and the mixture heated to 200° for 30 min. The alkane **14** was steam distilled from the reaction mixture, most of the alkane having been removed before the pot temperature reached 100°. The aqueous distillate (150 ml.) was washed with three 100-ml. portions of pentane and the pentane layer dried over magnesium sulfate and evaporated on the steam bath to yield crude **14**, which after preparative vapor phase chromatography on Apiezon J had n.m.r. and infrared spectra identical with those of the hydrogenation product of the major photodimer.

***syn*-Tricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-3,6-dione.**—Technical grade *p*-benzoquinone was passed through Rosite (1 part Norit, 3 parts Celite by weight) in benzene solution and recrystallized from benzene; m.p. 114–115° (sealed capillary). Thirteen grams of the purified quinone and 40 ml. of cyclohexadiene (Aldrich Chemical) were stirred for 48 hr. in the dark at room temperature. The solution was evaporated on a steam bath to give 17 g. (74%) of product, m.p. 94–95° (reported[12] 94°). The ultraviolet spectrum in methanol gave λ_{max} 2845 Å. (ϵ_{max} 27,500). The infrared spectrum in a potassium bromide pellet gave maxima at 3050 (s), 2960 (s), 2880 (s), 1690 (s), 1615 (w), 1280 (m), 1100 (m), 880 (m), and 760 (m) cm.$^{-1}$. The n.m.r. spectrum in carbon tetrachloride showed a sharp singlet at τ 2.45 (2 protons), a quartet centered at 2.76 (2 protons), a broader band at 6.54–6.85 (2 protons), a triplet centered at 7.06 (2 protons), and a broad quartet centered at 8.54 (4 protons). *Anal.* Calcd. for $C_{12}H_{12}O_2$: C, 76.53; H, 6.38. Found: C, 76.51; H, 6.36.

Photoisomerization of *syn*-Bicyclo[6.2.2.0^{2,7}]dodeca-4,9-dien-3,6-dione.—This substance was prepared in high yield by either of two methods: (a) An ether solution of the unsaturated ketone was allowed to evaporate on a flat glass plate, leaving a film of crystals which was then irradiated for an hour through Pyrex, giving a quantitative yield of adduct. (b) An ether solution of the ketone was irradiated and gave in 1–2 hr. quantitative yields of the adduct (m.p. 165° dec.), which precipitated from solution as it was formed.

The adduct has infrared maximum absorptions (potassium bromide pellet) at: 3050, 2960, 1757, 1302, 1240, 1205, 1145, 1060, 935, 917, 880, 850, and 760 cm.$^{-1}$. The n.m.r. spectrum in dilute deuterioacetone solution showed only a broad band in the saturated region. The ultraviolet spectrum in methanol showed λ_{max} 3000 Å. (ϵ_{max} 5). *Anal.* Calcd. for $C_{12}H_{12}O_2$: C, 76.53; H, 6.38. Found: C, 76.58; H, 6.50.

Attempted Aromatization of *cis-cis-cis*-Tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene.—The diene (25 mg., 0.00014 mole) and sulfur flowers (18 mg., 0.00056 mole) were heated to 150° in an evacuated sealed tube for 25 hr. The foul-smelling reaction mixture was dissolved in benzene and chromatographed on alumina by elution with 2:1 petroleum ether–benzene. Only low melting solids were obtained. Biphenyl may have been one of the products, but could not be positively identified. No evidence for biphenylene formation could be found.

A similar experiment with the *trans-cis-trans* isomer **3** also failed to give biphenylene.

The dimers were hydrogenated and heated with selenium for 72 hr. at 275°. No reaction was observed.

Low Temperature Rearrangement of Thermal Dimers.—Samples of **1** and **2** obtained from vapor chromatography on Apiezon J columns were, especially with older v.p.c. columns, contaminated with varying amounts of high boiling material. Such samples reverted slowly to the photodimers at 25 and 0°, degassed and not degassed, and in various types of glass vessels. Analysis of samples was made using n.m.r., and v.p.c. techniques described in "Kinetic Study of High Temperature Rearrangements."

Samples of the thermal dimers were vacuum distilled and the purified materials were placed in clean glass vessels, both Pyrex and soft glass, degassed and in the presence of oxygen. An unpurified sample, as a 15% solution in carbon tetrachloride, was stored in the presence of oxygen. After more than 12 months no rearrangement was observed in any of these cases.

It was found possible to effect rearrangement even of pure material by placing it in contact with Corning Pyrex brand glass wool (used as received). Degassed and nondegassed systems showed ~20% rearrangement in 41 days at 0°, as determined by n.m.r. analysis. The rate constant for rearrangement at 0° is thus about 10^{-8} sec.$^{-1}$.

A sample of unpurified **1** from the Megachrom was allowed to stand for 9.5 months at 25° (conditions which should have permitted complete rearrangement to **3**) showed 90% rearrangement by n.m.r. analysis. Samples of **3** collected from Apiezon J columns tended *very slowly* to form **1** unless purified. The difference in rates of formation of the two products is probably attributed to unequal contamination occasioned by passage through the Megachrom. The equilibrium value **3**/**1** at 25° is thus calculated to be about 9. Similar studies with **4** and **2** are not possible because of side reactions which appear to consume **4**. Available data seem to indicate, however, that at 25° (**4**/**2**) $K_{eq} \leq 1$.

Kinetic Study of High Temperature Rearrangements.—Pure samples of the dimers were prepared as described above and distilled immediately prior to use.

Kinetic runs were performed according to the procedures described by Hammond and DeBoer,[14] and will not be described here. Control experiments showed the absence of surface effects and confirmed that no material was lost to polymerization. Occasionally, slight oxidation of the photodimer **4** accompanied rearrangement. This was attributed to the inferior degassing procedure (see ref. 14) necessitated by the small sample size and by the small sample tubes employed.

Analysis of samples was conducted with a Loenco 15 B flame ionization detector using a 150-ft. Apiezon J Golay column. The column temperature was 95–105°; the carrier gas pressure was 30 p.s.i. Samples of 0.01 μl. were delivered with a Hamilton 1-μl. syringe. This technique was the best found for this purpose and gave good separations of **2** and **4**. Compounds **1** and **3** were not entirely separated, however, and the analysis for rearrangement of **3** suffers imprecision for this reason.

All rates and activation parameters were obtained from slopes of least-squares plots of the data.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Photochemistry of Enolic Systems. I. Irradiation of Enol Acetates

BY AMNON YOGEV, MALKA GORODETSKY, AND YEHUDA MAZUR

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Irradiation of enol acetates with a low-pressure mercury lamp was studied. Irradiation of isopropenyl acetate (**1**) and cyclohexenyl acetate (**3**) resulted in an acetyl rearrangement and yielded, respectively, acetylacetone (**2**) and α-acetylcyclohexanone (**4**). Similarly, steroidal enol acetates **9**, **11**, and **13** gave corresponding ketones **10**, **12**, and **14**. In all these irradiations considerable amounts of the starting materials were isolated. Enol acetate with a fully substituted double bond (**5**) gave, in addition to 2-acetyl-2-methylcyclohexanone (**7**), 2-methylcyclohexanone (**6**) and its dimer **8**. An analogous steroidal enol acetate **15** resulted mainly in the dimer **21** and also in the ketones **16**, **17**, and **18**. It was found that acetyl migration occurs by an intramolecular process, suggesting a cage mechanism. The stereochemistry of this photochemical acetyl rearrangement is also discussed.

The reactivity of the enol–acetate system in thermal reactions is well established. One of the main changes observed is the formation of β-diketones by acetyl migration from the oxygen to the vinylic carbon atom.[1]

We have undertaken an investigation of the behavior of these systems on ultraviolet irradiation, analogous acetyl migration being expected to occur. Our previous results of photolysis of enol benzoates[2] and the recently published observations of a photochemical Fries rearrangement[3] support the assumption that the O-acyl bond of the enol-acetate chromophore is most likely to cleave under the influence of the ultraviolet radiation.

The ultraviolet source chosen in the following experiments was a low pressure immersion mercury lamp (Hanau, NT 6/20) which emits almost entirely at 253.7 mμ, and the solvent chosen was cyclohexane. The enol acetates to be irradiated show absorption maxima in this solvent in the region 190–200 mμ (*ca.* ϵ 7000) and possess a finite, although small, absorption at 253.7 mμ (ϵ 30–50).[4] The light quantum absorbed at this higher wave length is sufficient to cause a photochemical change in the absorbing molecule.

When isopropenyl acetate (**1**) was irradiated, the product isolated was the expected acetylacetone (**2**) [λ_{max} 271 mμ (ϵ 9200) in cyclohexane].[5] This β-diketone could be obtained in pure form as the copper chelate after evaporation of the solvent and treatment of the residue with aqueous cupric acetate, and was found to be identical with an authentic sample of the chelate (**2**). The progress of the conversion of **1** to **2** was followed by the absorption intensity of **2** at 271 mμ in the irradiated solution. It was found that on irradiation of a 1% cyclohexane solution of **1**, the yield of **2** approached asymptotically the value of 29%[6] in 45 hr., and remains practically constant upon further irradiation. Working with more concentrated solution of **1**, the limit yield of **2** decreases, although it is reached after similar reaction periods. Thus, starting with a 10% solution of **1**, only a 9% conversion was observed after 45 hr. and further irradiation did not increase this yield appreciably. In all these cases the reaction mixtures were found to contain a considerable amount of the unrearranged starting material **1**. The product **2**, which exists in cyclohexane mainly in the enolic form,[5] does not undergo observable change when irradiated in cyclohexane solution under similar conditions, by itself or in admixture with isopropenyl acetate (**1**).[7]

(1) (a) P. E. Reiminger and P. D. Ritchie, *J. Chem. Soc.*, 2678 (1963); (b) W. M. Muir and P. D. Ritchie, *ibid.*, 2692 (1963); (c) R. J. P. Allan, R. L. Forman, and P. D. Ritchie, *ibid.*, 2717 (1955); (d) F. G. Young, F. C. Frostic, J. J. Sanderson, and C. H. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

(2) M. Feldkimel-Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

(3) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962); J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.*, 217 (1960).

(4) *E.g.*, cholest-2-en-3β-ol acetate was found to have in cyclohexane λ_{max} 190 mμ (ϵ 6800) and ϵ-value of 4800 at 200 mμ. Compared with cholest-2-en [λ_{max} 190 mμ (ϵ 4700) and ϵ-value of 1500 at 200 mμ] it shows a bathochromic shift and an increase of the extinction coefficient. (*Cf.* J. H. Chapman and A. C. Parker, *J. Chem. Soc.*, 2075 (1961), and references cited therein.)

(5) Acetylacetone was found by us to exist in cyclohexane in the enolic form to the extent of 88%, as calculated from the n.m.r. spectrum in this solvent; *cf.* B. Eistert and W. Reiss, *Chem. Ber.*, **87**, 92 (1954).

(6) (a) These yields were calculated spectroscopically. The isolated compounds were obtained in somewhat smaller yields. (b) Similar values were obtained from the n.m.r. spectra of the total irradiated solution; see Experimental.

(7) No addition products between acetylacetone and isopropenyl acetate were observed in this irradiation; *cf.* P. de Mayo H. Takeshita, and A. B. M. A. Satter, *Proc. Chem. Soc.*, 119 (1962).