Photochemistry of 1,6-Cyclodecadienes. I. 1-Methyl-(*E*,*E*)-1,6-cyclodecadiene[1]

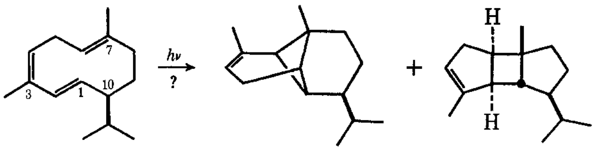
CLAYTON H. HEATHCOCK,*[2] RODNEY A. BADGER,[3] AND RONALD A. STARKEY

Department of Chemistry, University of California, Berkeley, California 94720

Received May 19, 1971

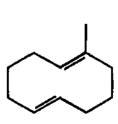
The photochemical behavior of 1-methyl-(*E*,*E*)-1,6-cyclodecadiene (4) has been examined. Diene 4 is converted, by direct irradiation in hexane, benzene, or methanol with Vycor- or Corex-filtered light, to a 9:1 mixture of tricyclo[5.3.0.0^{2,6}]decanes 6 and 7. None of the isomeric tricyclo[4.4.0.0^{2,7}]decane 5 is produced. The same conversion is observed, although in low yield, when 4 is irradiated with Pyrex-filtered light in the presence of benzophenone, naphthalene, or 2-acetonaphthone but not with fluorenone. The *E*,*Z* and *Z*,*Z* isomers of 4 are not observed as intermediates in the photoreaction. A mechanistic scheme is proposed, based on conformational arguments, for the photochemistry of such 1,6-cyclodecadienes.

The isomeric, tricyclic sesquiterpenes, α-copaene (2)[4] and α-bourbonene (3),[5] could conceivably be derived from the alternate modes of photocycloaddition of a cyclodecatriene such as 1. Several years ago, we undertook an investigation of the photochemistry of 1,6-cyclodecadienes for two reasons. Firstly, such an intramolecular 2 + 2 cycloaddition seemed attractive as a possible synthetic route to the sesquiterpenes 2 and 3. Secondly, the suggestion has been made that the *in vivo* formation of 2 and 3 might involve such a photochemical step.[6,7] Although the problems of chemical synthesis of copaene[8] and bourbonene[7,9] have subsequently been solved in other ways, the possible photochemical conversion of a 1,6-cyclodecadiene to compounds of these two types continued to intrigue us.

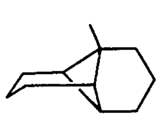


1 2 3

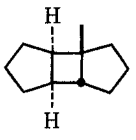
As a logical first step in our investigation of this problem, we decided to examine the photochemical behavior of the known[10] 1-methyl-(*E*,*E*)-1,6-cyclodecadiene (4). Diene 4 seemed to be a good model for triene 1 in that the two double bonds postulated to react are similarly substituted. It lacks the isopropyl group and the third double bond of 1. Although the isopropyl group is probably of no electronic consequence in 1, it may be of conformational importance. The absence of the Δ^3 double bond is a severe structural change. This linkage will obviously have a profound effect, both conformationally and electronically, in compound 1. The two alternate modes of 2 + 2 cycloaddition of diene 4 would yield the tricyclic hydrocarbons 5 and 6, the former related to copaene and the latter to bourbonene.



4



5



6

Experimental Section

1-Methyl-(*E*,*E*)-1,6-cyclodecadiene (4).—Diene 4 was prepared by the method of Marshall and Bundy.[10] The crude diene was separated from isomeric hydrocarbon impurities by extraction into 10% aqueous silver nitrate solution. The diene was regenerated by the addition of aqueous ammonia. Final purification was accomplished by preparative glpc (6 ft × 0.25 in. SE-30 on Chromosorb W at 145°, retention time of 4, 4 min). The diene so prepared and purified was a water-clear liquid which showed absolutely no impurities by glpc (200 ft × 0.01 in. SF-96 at 90°, 500 ft × 0.03 in. SF-96-50 at 120°, both flame ionization detectors). The uv spectrum of 4, measured in spectroquality hexane, had λ_{max} 180 nm (ε 24,700).[11] The absorption, attributable to the $\pi \rightarrow \pi^*$ transitions of the two isolated double bonds, tails strongly toward the red, with measured extinction coefficients as follows: 220 nm (ε 1100), 240 (430), and 260 (30).

1-Methyltricyclo[4.4.0.0^{2,7}]decane (5).[12]—A solution of 2.5 g of 1-methyltricyclo[4.4.0.0^{2,7}]decan-8-one[8] and 20 ml of 85% hydrazine hydrate in 100 ml of freshly distilled ethylene glycol was heated under dry nitrogen for 2.5 hr at 120°. After cooling, 10 g of potassium hydroxide was added and the condenser was replaced by a distilling head. The bath was slowly raised to 210° and kept at this temperature for 2.5 hr. The water which distilled over during this period was retained. The reaction mixture was cooled and diluted with 150 ml of water. The aforementioned water distillate was added and the whole was extracted first with 150 ml of ether, then with 150 ml of hexane. The combined organic extracts were washed with water and dried over magnesium sulfate. Evaporation of the solvent yielded 1.97 g (86%) of hydrocarbon 5 as a clear liquid. The pmr spectrum (in CCl_4) contained complex methylene and methine absorption and had a sharp methyl singlet at τ 9.20.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.04; H, 12.16.

***cis*,*anti*,*cis*-2-Methyltricyclo[5.3.0.0^{2,6}]decan-5-one.**—A solution of 21.8 g of 3-methyl-2-cyclopentenone in 165 g (174 ml) of cyclopentene was degassed for 30 min with a stream of helium and then irradiated with a 440-W Hanovia lamp through Pyrex for 21 hr. The disappearance of the 227-nm band in the uv was used as a measure of the reaction's progress. The reaction appeared to proceed very cleanly; only one major reaction product was seen on glpc analysis. A minor amount of the isomeric cis,syn,cis isomer (approximately 10%) was the sole contaminant. The solvent was removed by distillation at atmospheric pressure through an 18-in. Vigreux column and the residue (27.0 g) was then distilled at reduced pressure through a 6-in. Vigreux column. After collecting a small forerun [1 ml, bp 25–68° (0.25 Torr)], the product (23.2 g, 63%) was collected at 68–70° (0.25 Torr).

The ir spectrum was typical of that expected for a saturated cyclopentanone: 1730 and 1150 cm^{-1}. The pmr spectrum showed only a complex methylene and methine absorption, with a sharp angular methyl singlet emerging at τ 8.99. Glpc analysis (150 ft × 0.01 in. SF-96 at 125°) indicated that the product was

---

[1] Presented in preliminary form at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8, 1968.

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] National Institutes of Health Predoctoral Fellow, 1965–1968.

[4] P. de Mayo, R. E. Williams, G. Büchi, and S. H. Feairheller, *Tetrahedron*, **21**, 619 (1965).

[5] J. Krepinsky, Z. Samek, F. Sorm, D. Lamparsky, P. Ochsner, and Y. R. Naves, *ibid.*, **58**, 53 (1966).

[6] R. A. Barnes, *An. Acad. Brasil. Cienc.*, **36**, 238 (1964).

[7] M. Brown, *J. Org. Chem.*, **33**, 162 (1968).

[8] C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

[9] J. D. White and D. N. Gupta, *ibid.*, **90**, 6171 (1968).

[10] J. A. Marshall and G. L. Bundy, *ibid.*, **88**, 4291 (1966).

[11] Measured on a Beckman DK-2A "Ratio-Recording" Spectrophotometer.

[12] This preparation was performed by Mr. Bruce E. Ratcliffe.

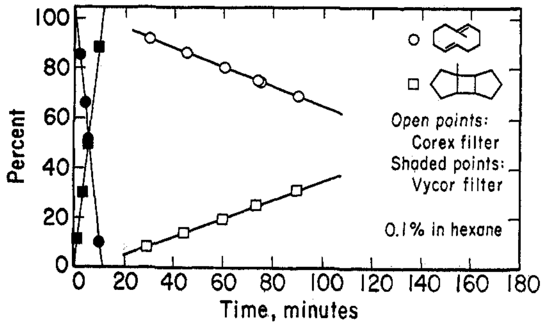


Figure 1.—Irradiation of diene **4**.

a mixture of the cis,anti,cis isomer (90.5%) and the cis,syn,cis isomer (9.5%), as expected.[13]

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.11; H, 9.72.

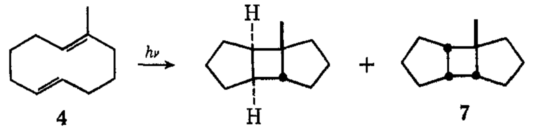
cis,anti,cis-**1-Methyltricyclo[5.3.0.0^{2,6}]decane** (**6**).—Into a 100-ml, three-necked flask were placed 3.25 g of *cis,anti,cis*-1-methyltricyclo[5.3.0.0^{2,6}]decan-5-one (*vide supra*), 50 ml of freshly distilled ethylene glycol, and 20 ml of hydrazine hydrate. The mixture was stirred under nitrogen for 5 hr at 125°. Potassium hydroxide (13.0 g) was introduced and water was removed by distillation through a short Vigreux column until the head temperature reached 208°. The distillation column was then replaced by a reflux condenser and the mixture was heated at reflux for 3.25 hr. The cooled, pale-yellow mixture was diluted with 50 ml of ether and extracted with saturated brine (three 20-ml portions). Drying and evaporation of solvent gave only 206 mg of oil. The initial steam distillate, when worked up in the same manner, yielded a further 2.10 g of oily product. The total yield of crude hydrocarbon was thus 2.306 g (81%). Quantitative glpc analysis showed it to be a mixture of the cis,anti,cis isomer **6** (91.3%) and the cis,syn,cis isomer (8.7%). The analytical specimen was obtained by preparative glpc. The ir showed only hydrocarbon absorption; the pmr spectrum (in CCl_4) contained complex methylene and methine absorption and had a sharp angular methyl singlet at τ 9.08.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.04, 88.31; H, 12.16, 12.02.

Photochemistry of Diene 4.—Solutions of diene **4** were prepared in various spectroquality solvents as follows: 10 mg of **4** (11 μl) in 10 ml of solvent. *n*-Undecane (5 μl) was added to each run as an internal standard for glpc analysis. The solutions were irradiated through the appropriate filter, in a 15-ml capacity quartz apparatus, under helium, with water cooling. Small samples (100 μl) were periodically withdrawn by syringe and analyzed. Analysis was done on an Aerograph 204B instrument with flame ionization detection on the following capillary columns: 150 ft × 0.01 in. SF-96, 500 ft × 0.03 in. SF-96. Quantitative analysis was accomplished by disc integrator or by normalized peak height comparison; peak height normalization factors were determined independently to be *n*-$C_{11}H_{24}$, 1; tricyclic hydrocarbon **6**, 1.86; diene **4**, 0.69.

Results

Irradiation of diene **4** in hexane solution (0.1%, 6.5 × 10^{-2} *M*) through a Vycor filter led to the rapid production of a 9:1 mixture of tricyclic hydrocarbon **6** and its cis,syn,cis isomer **7** in quantitative yield. The course of the reactions is depicted graphically in Figure 1. No trace of the alternate tricyclic hydrocarbon **5** could be detected. When a similar experiment was done, substituting a Corex D filter (17% transmission at 260 nm, 7% transmission at 250 nm), the same result was obtained, albeit at a much slower rate. The time required for one-half conversion in the Vycor experiment was 6 min; in the Corex D experiment it was 278 min. When a Pyrex filter was used, no reaction was observed.



4 **6** **7**

Similar results were obtained when diene **4** was irradiated in benzene through a Corex filter (time for one-half conversion, 35 min) or in methanol through Vycor (time for one-half conversion, 4 min). In the benzene experiment, hydrocarbons **6** and **7** were again produced, in a 9:1 ratio, in quantitative yield. In the methanol experiment, although all the starting diene was consumed, hydrocarbons **6** and **7** were obtained (9:1 ratio) in a total yield of only 83%. The remaining diene was apparently converted to nonvolatile products.

Although diene **4** failed to react when irradiated with Pyrex-filtered light, reaction was observed in the presence of various sensitizers (Table I). In these sensitized experiments, most of the diene was converted to nonvolatile material, although tricyclic hydrocarbons **6** and **7** were produced in measurable quantities with all sensitizers except fluorenone.

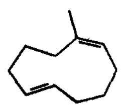
TABLE I

SENSITIZED IRRADIATIONS OF DIENE 4[a]

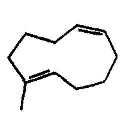
Sensitizer	E_T, kcal/mol[b]	Yield of **6** + **7**, %	Nonvolatile products, %
Benzophenone	68.5	17	81[c]
Naphthalene	60.9	36	64
2-Acetonaphthone	59.3	~10	~90
Fluorenone	53.3	No reaction	

[a] *All irradiations were carried out in hexane solution,* 0.065 *M* in diene **4** and 0.1% in sensitizer, with Pyrex-filtered light. [b] Data of W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964). [c] In this experiment, four additional volatile products, representing a total yield of 2% (based on diene **4**), were produced. None of these products was hydrocarbon **5**.

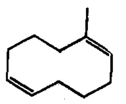
In none of the experiments was there any evidence for the build-up of any detectable amount of an intermediate isomer possessing some other double bond geometry (*i.e.*, dienes **8–10**). In one experiment, designed to rule out the possibility that isomers such as **8–10** might be produced, but have the same glpc retention time as **4**, and thus escape notice, an irradiation of **4** was interrupted after 15% reaction. The glpc peak corresponding in retention time to **4** was then isolated and examined spectroscopically. It was found to be identical with the starting material.



8



9



10

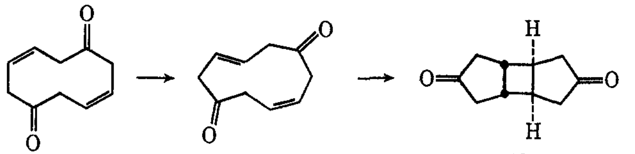
Discussion

The results clearly show that tricyclo[5.3.0.0^{2,6}]decanes **6** and **7** are primary photoproducts of diene **4**. In this system, at least, none of the alternate modes of photocyclization, leading to a tricyclo[4.4.0.0^{2,7}]decane (**5**), occurs. Similar results have been reported by Scheffer and Lungle in the irradation of the unconju-

---

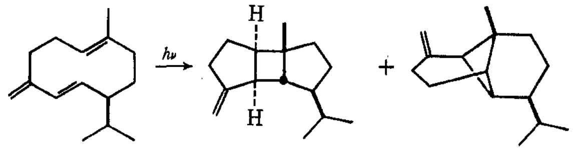
[13] P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

gated diene–dione **11**.[14,15] These workers found that **11** reacts *via* the intermediate *E,Z* isomer to give the cis,anti,cis product **13**.



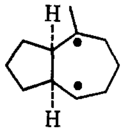
11 **12** **13**

Hirose has reported that germacrene D (**14**), isolated from a natural source, gives mainly β-bourbonene (**15**) on irradiation, accompanied by a small amount of β-copaene (**16**).[17] No mention is made of any cis,syn,cis isomer analogous to compound **7**.



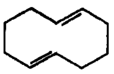
14 **15** **16**

Several interesting features can be noted in the photochemical behavior of diene **4**. Firstly, the only mode of cyclization is that leading to the tricyclo[5.3.0.0^{2,6}]-decane skeleton. Thus, the empirical "Rule of Five," discussed by Brown[7] and Srinivasan,[18] is followed. Secondly, both the cis,anti,cis and cis,syn,cis isomers are produced. These observations suggest that the reaction occurs by an nonconcerted path, probably *via* a 1,4-diradical such as **17**.

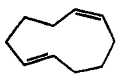


17

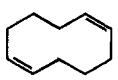
A third interesting feature of the reaction is the apparent absence of *E,Z*, or *Z,Z* intermediates. Moussebois and Dale report that, for 1,6-cyclodecadiene itself, the various double bond isomers are present at equilibrium in the ratio 18:19:20 = 0:4:96.[19] Several attempts to equilibrate diene **4** by the diphenyl disulfide method[20] failed; only nonvolatile products were produced.



18



19

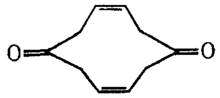


20

As stated above, Scheffer and Lungle established that diene **11** is converted to product **13** *via* its *E,Z* isomer **12**. Isomer **12** was shown to give product **13** without the build-up of the *Z,Z* isomer **11**. The behavior of these systems can be explained by the following hypothesis.

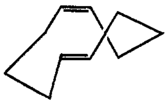
$$\begin{tikzcd}
Z,Z \arrow[r, shift left, "h\nu"] & A^* \arrow[l, shift left] \arrow[r, shift left] & E,Z \arrow[l, shift left, "h\nu"] \arrow[r, shift left, "h\nu"] & B^* \arrow[l, shift left, "k_1"] \arrow[r, shift left, "k_2"'] \arrow[d, "k_3"] & E,E \arrow[l, shift left, "h\nu"'] \\
 & & & \text{1,4-diradical} \arrow[d] & \\
 & & & \text{tricyclic product} &
\end{tikzcd}$$

If excited state A*, reached by excitation of the *Z,Z* or *E,Z* isomer, has a conformation which precludes transannular cyclization, then only double bond isomerization can result. This postulate seems not unlikely in light of established solid-state conformation (21) of diene–dione **11**.[21]

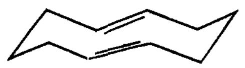


21

On the other hand, either this *E,Z* or the *E,E* isomer can be excited to a state (B*) which is in a conformation amenable to transannular reaction. A study of models suggests that these isomers must exist in conformations having the two double bonds in rather close proximity, as, for example, **22** and **23**. If the rate constant for such a cyclization (k_3) is greater than the rate constant for return to a ground state (k_1 or k_2), then cyclization will be observed to the exclusion of double bond isomerization.



22



23

The last noteworthy feature of the reaction is the behavior of diene **4** in the sensitization experiments. When irradiated in benzene through Corex D, the diene is converted into a 9:1 mixture of tricyclic hydrocarbons **6** and **7** in quantitative yield. This result probably represents energy transfer from benzene to the diene. Although no reaction occurs when **4** is irradiated with Pyrex-filtered light, the conversion of **4** to **6** and **7** does occur in the presence of various sensitizers. As shown in Table I, conversion to product occurs when the sensitizer has a triplet energy of >59.3 kcal/mol, but not with fluorenone, which has a triplet energy of 53.3 kcal/mol. If one assumes triplet sensitization, then diene **4** must have an accessible triplet with an energy of less than 59.3 kcal/mol, an extremely low value for isolated double bonds. However, although the absorption maximum for compound **4** occurs at 180 nm, the band tails strongly toward the red; the extinction coefficient at 260 nm is still 30. Thus, **4** may well have a relatively low-lying $\pi \rightarrow \pi^*$ triplet state available. Bischof and Heilbronner have found, by photoelectron spectroscopy, additional evidence for strong interaction between the two double bonds in *trans,trans*-1,6-cyclodecadiene.[22]

On the other hand, the observed reactions of **4** may

---

(14) J. R. Scheffer and M. L. Lungle, *Tetrahedron Lett.*, 845 (1969).

(15) An earlier report that compound **11** gives a cis,syn,cis tricyclic diketone[16] has been refuted.[14]

(16) A. Shani, *Tetrahedron Lett.*, 5175 (1968).

(17) K. Yoshihara, Y. Ohta, T. Sakai, and Y. Hirose, *ibid.*, 2263 (1969).

(18) R. Srinivasan, Abstracts, 156th National Meeting of the American Chemical Society, San Francisco, Calif., Apr 1968, p 86P.

(19) E. Moussebois and J. Dale, *J. Chem. Soc. C*, 264 (1966).

(20) C. Moussebois and J. Dale, *ibid.*, 260 (1966).

(21) H. L. Carrell, B. W. Roberts, J. Donohue, and J. J. Vollmer, *J. Amer. Chem. Soc.*, **90**, 5263 (1968).

(22) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).

result from singlet–singlet sensitization, or sensitization by upper triplet states. At the present time, the multiplicity of the excited state responsible for cyclization should be regarded as uncertain.

The reasons for the low yields in the reactions sensitized by benzophenone, 2-acetonaphthone, and naphthalene are unknown. With the carbonyl sensitizers, some 2 + 2 cycloaddition of the sensitizer to the diene may occur. In the case of naphthalene, we have no hypothesis to explain the diminished yield. This question cannot be answered until the nonvolatile reaction products are investigated.

Registry No.—**4**, 13304-33-1; **5**, 32722-85-3; **6**, 32659-16-8; **7**, 32659-17-9; *cis,anti,cis*-2-methyltricyclo[5.3.0.0^{2,6}]decan-5-one, 32659-18-0; cis,syn,cis isomer, 32659-19-1.

Acknowledgments.—We gratefully acknowledge financial support by the National Science Foundation and the Public Health Service. The senior author (C. H. H.) acknowledges several stimulating discussions on this subject with Professor Kurt Schaffner of the ETH, Zürich, Switzerland. We also thank one of the referees for numerous helpful comments.

Photochemistry of 1,6-Cyclodecadienes. II. Synthesis and Photochemistry of 6-Methyl-1,6-cyclodecadien-3-one[1]

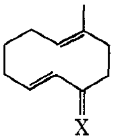
CLAYTON H. HEATHCOCK*[2] AND RODNEY A. BADGER[3]

Department of Chemistry, University of California, Berkeley, California 94720

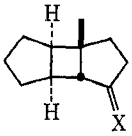
Received May 19, 1971

6-Methyl-1,6-cyclodecadien-3-one (5) has been synthesized by a multistage route and its photochemical behavior has been examined. Irradiation of dienone 5, with Pyrex-filtered light in either ether or hexane, gives tricyclic ketones 6, 7, and 8. The interesting tricyclo[4.4.0.0^{2,7}]decanone 8 arises from a triplet intermediate.

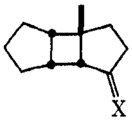
In the previous paper in this series, we reported on the photochemical behavior of 1-methyl-(*E,E*)-1,6-cyclodecadiene (**1**).[4] Diene **1** was found to undergo photochemical 2 + 2 cycloaddition, probably in a stepwise fashion, yielding only the tricyclo[5.3.0.0^{2,6}]decanes **2** and **3**. No tricyclo[4.4.0.0^{2,7}]decane (*e.g.*, **4**) was produced. In the present work, we have prepared and photolyzed the analogous ketone, **5**.



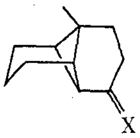
1, X = H_2
5, X = O



2, X = H_2
6, X = O



3, X = H_2
7, X = O



4, X = H_2
8, X = O

Preparation of Dienone 5.—The starting point for the preparation of dienone **5**, outlined in Scheme I, was the readily available Wieland–Miescher diketone (**9**),[5] which was transformed by established procedures[6] into the ketal acetate **10**. Oxidation of **10** with *m*-chloroperbenzoic acid in chloroform gave a 1:1 mixture of epoxides **11** and **12**, which could be separated by fractional crystallization. Stereostructures were assigned to compounds **11** and **12** on the basis of their pmr spectra. Williamson has found[7] that angular methyl groups in trans-fused decalins give broader resonance lines ($W_{1/2}$ = 0.80 ± 0.20 Hz) than the corresponding cis-fused isomers ($W_{1/2}$ = 0.25 ± 0.11 Hz). The higher melting isomer, mp 137–139°, was assigned structure **11** since it gave a sharp angular methyl resonance. The lower melting isomer, mp 65.5–66.5°, was assigned the cis structure **12** on the basis of its broad methyl singlet.

Lithium aluminum hydride reduction of **11** and **12** gave corresponding diols **13** (mp 89–90°) and **14** (mp 106–107°), respectively, which were converted, by selective esterification with methanesulfonyl chloride in pyridine, to monomethanesulfonates **15** (mp 104.5–105.5°) and **16** (mp 109–110°). The line widths of the angular methyl resonances in the pmr spectra of compounds **11–14** corroborated the assigned stereostructures.

Base-catalyzed fragmentation[8] of either **15** or **16** (or a mixture of the two) with potassium *tert*-butoxide in *tert*-butyl alcohol gave excellent yields (>95%) of the cyclodecenedione monoketal **17**, mp 50.5–51.5°. On the basis of good analogy,[8a] the double bond in **17** can be assigned the *E* configuration. Reduction of **17** with lithium aluminum hydride in ether gave the crystalline hydroxy ketal **18**. The overall yield for the eight stages from enedione **9** to intermediate **18** was 37%.

Compound **18** was hydrolyzed by refluxing with an equal weight of oxalic acid in aqueous acetone. The product, β-hydroxy ketone **19**, showed surprising resistance to dehydration. Attempts to dehydrate the ketol with basic alumina or methanolic potassium hydroxide led only to recovered starting material, as did vacuum distillation from oxalic acid. Treatment of **19** with even trace amounts of mineral acid gave intense violet solutions from which no tractable products could be isolated.[9]

The corresponding acetate, **20**, prepared from **19** by acetylation with acetic anhydride in pyridine, eliminated acetic acid smoothly when warmed to 50° in tri-

---

[1] This paper was presented in preliminary form at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8, 1968. See also, C. H. Heathcock and R. A. Badger, *Chem. Commun.*, 1510 (1968).

[2] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

[3] National Institutes of Health Predoctoral Fellow, 1965–1968.

[4] C. H. Heathcock, R. A. Badger, and R. H. Starkey, *J. Org. Chem.*, **37**, 231 (1972).

[5] (a) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **33**, 2215 (1950); (b) S. Ramachandran and M. S. Newman, *Org. Syn.*, **41**, 38 (1961).

[6] C. H. Heathcock and R. Ratcliffe, *J. Amer. Chem. Soc.*, **93**, 1746 (1971).

[7] K. L. Williamson, T. Howell, and T. A. Spencer, *ibid.*, **88**, 325 (1966).

[8] (a) P. S. Wharton and G. A. Hiegel, *J. Org. Chem.*, **30**, 3254 (1965); (b) H. H. Westen, *Helv. Chim. Acta*, **47**, 575 (1964).

[9] Similar behavior was noted with compounds **17**, **18**, **20**, and **5**. The violet color which is produced immediately upon treating a dilute solution of any of these compounds with dilute mineral acid is discharged upon basification.