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Direct Observation of Dienol Intermediates in Photochemical Deconjugation of an α,β-Uusaturated Ketone. Photoisomerization of 1-Acetylcyclooctene[1]

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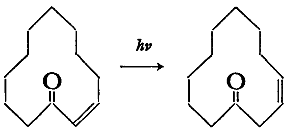
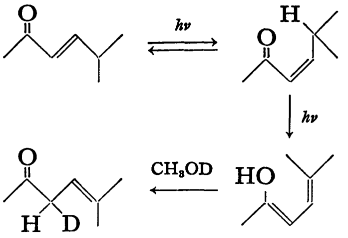
The photolysis of 1-acetylcyclooctene in acetonitrile solution leads to 3-(α-hydroxyethylidene)cyclooctene (two stereoisomers). Structures of the stable 1,3-dienols have been elucidated on the basis of their spectral data and chemical behavior. The dienols are highly air-sensitive. Upon heating, or by the action of an acid or base, they are converted to 3-acetylcyclooctene. In methanol-*O*-*d*, 3-acetylcyclooctene-3-*d* is formed. These findings provide the first, unambiguous evidence for the intervention of 1,3-dienol intermediates in photochemical deconjugation of an α,β-unsaturated ketone into the β,γ isomer.

Photo-irradiation of open-chain α,β-unsaturated ketones which bear hydrogen atom(s) at the position γ to the carbonyl function causes facile double bond migration to give the corresponding β,γ-unsaturated ketones.[2] Large-membered cyclic enones also undergo photoisomerization.[3] The deconjugation reaction is of

$$\mathrm{RCOCH{=}CHCH_2R'} \xrightarrow{h\nu} \mathrm{RCOCH_2CH{=}CHR'}$$



great synthetic value, because (1) the reaction proceeds under neutral and thermally moderate conditions and (2) the nonconjugated enone products are usually less stable compared with the starting conjugated enones. The reaction is considered to proceed *via* the mechanism outlined in Scheme 1, where the reaction of 5-methyl-3-hexen-2-one is exemplified. First, exposure of the α,β-unsaturated ketone leads to a photo-equilibrated mixture of the *trans* and *cis* isomers. The *cis* enone in an n, π* excited state[2] can abstract a γ-hydrogen atom to produce a 1,3-dienol, which upon ketonization results in the formation of the β,γ-isomer. The existence of the unstable dienol species has been suggested by the fact that photolysis in methanol-*O*-*d* affords 3-deuterio-5-methyl-4-hexen-2-one.[2b] However, none of these intermediates has been definitely characterized yet.[4] This paper describes direct observation of such a dienol intermediate in the photochemical deconjugation of enones, which provides unambiguous evidence for the mechanism involving dienol species.[5]



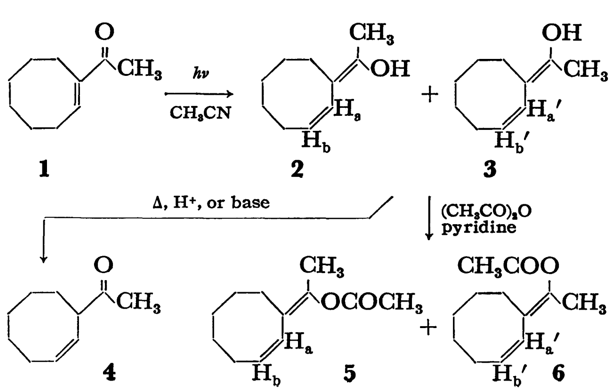
Scheme 1.

Results and Discussion

1-Acetylcyclooctene (**1**), taken as the enone substrate, was prepared by the titanium tetrachloride-catalyzed reaction of cyclooctene and acetyl chloride. The α,β-unsaturated ketone has characteristic IR bands (neat film) at 1668 (C=O) and 1638 cm^{-1} (C=C). The UV absorption maxima in acetonitrile solution occur at 233 (log ε 4.00) (π-π* band) and 319 nm (log ε 0.89) (n-π* band). All photolyses were effected in a well-deoxygenated solution placed in a Pyrex tube. A 200-W high-pressure mercury lamp was used as a light source and a 10% aq copper sulfate solution (1-cm depth) was employed as filter (<350-nm cut-off). Progress of the reaction was monitored spectroscopically.

Photolysis of the Enone **1** *in Acetonitrile.* A 5% solution of **1** in acetonitrile was placed in a Pyrex NMR tube and irradiated at room temperature under nitrogen atmosphere. The reaction was monitored by NMR. When the irradiation was continued for 10 h, the starting enone **1** was consumed completely and new alcoholic products (*vide infra*) were produced in *ca.* 80% yield. The products consisted of a 5: 1 mixture of two stereoisomers. The same ratio was obtained by GLPC analysis after conversion to the trimethylsilyl ethers by treating the reaction aliquot with *N*,*O*-bis(trimethylsilyl)acetamide. The photoreaction with more diluted solution (2.7×10^{-3} M) of **1** in acetonitrile proceeded in quantitative yield, as was indicated by monitoring the photolysis by UV spectroscopy. The absorption maximum of the enone at 233 nm was cleanly replaced by a new absorption band, $\lambda_{\max}$ 255 nm (log ε ≈4.0). The new products were identified as the dienols **2** and **3** on the basis of the following spectral and chemical evidence.

Infrared Spectrum of the Dienols **2** *and* **3**. Proof of the dienol structure was gained by the IR spectra shown



in Fig. 1. The photolysate exhibited a strong O–H strech at 3450 cm^{-1}, olefinic absorption at 1656 cm^{-1}, and C–O band at 1191 cm^{-1}, in accord with the assigned structures **2** and **3**. A carbonyl group is not present in the new products. A small absorption band was observed at ≈1700 cm^{-1}, but there were considerable variations in relative intensity of the band depending on the individual photolysis conditions. Therefore, apparently this is due to the presence of some impurities in the reaction mixture.

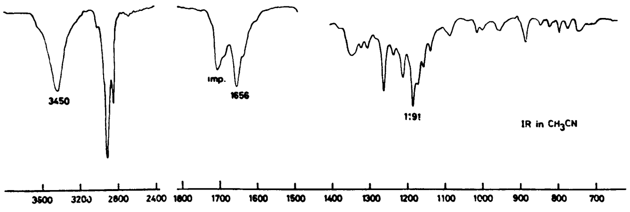


Fig. 1. Infrared spectrum of the photolysate of **1** (5% CH$_3$CN solution).

NMR Spectrum of the Dienols 2 and 3. Figure 2 shows the NMR signals arising from the olefinic protons of the photoproducts. The spectrum can be explained only in terms of a 5: 1 mixture of the dienols **2** and **3**. The observed coupling constants were: $J_{Ha-Hb}=J_{Ha'-Hb'}=12$ Hz and $J_{Hb-CH_3}=8$ Hz. The splitting patterns bear a close resemblance to those of 3-methylenecyclooctene; the endocyclic vinylic protons (δ 5.50 (C-2) and 6.20 (C-1)) are coupled to each other with $J=12$ Hz. Occurrence of the Ha signal at a lower field, δ 6.48, than that of Ha′, δ 6.14, should be ascribed to the anisotropic effect of the enol oxygen. The spectrum at the higher field, even when taken in CD$_3$CN, is rather complicated by overlapping with signals of high molecular weight by-products (<20%) and CHD$_2$CN. However, the spectrum exhibited distinct singlets at δ 1.88 and 1.82 arising from the vinylic methyl groups of **2** and **3**, respectively. The signal assignments were further confirmed by double resonance techniques; when Hb and Hb′ were irradiated, Ha and Ha′ appeared as singlets, while irradiation of Ha changed the signal pattern of Hb into a triplet with $J=8$ Hz.

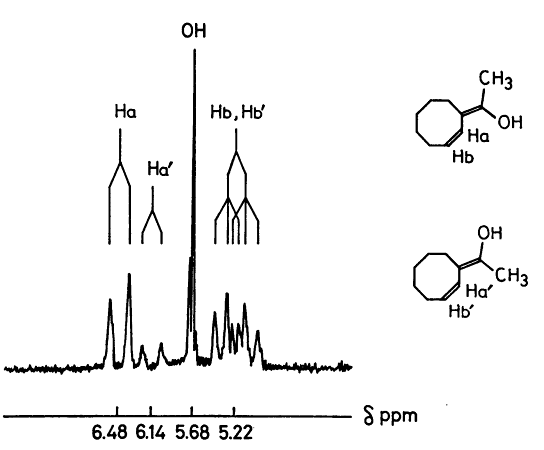


Fig. 2. NMR spectrum of the photolysate of **1** (5% CH$_3$CN solution, 60 MHz, tetramethylsilane as internal standard).

Intermolecular exchange of the hydroxylic protons is not rapid and hence the NMR absorption for each stereoisomer occurred separately. The chemical shift values, δ 5.68 and 5.71, are intermediate between that of ordinaryl alcoholic protons and that of phenolic protons;[6] methyl alcohol and phenol (4% acetonitrile solution, room temperature) give the OH signals at δ 2.45 (quartet) and 6.96, respectively. The low exchangeability of the OH protons should be ascribed to the moderate acidity and the intermolecular hydrogen-bonding with solvent acetonitrile. The hydroxy signals disappeared upon addition of an excess of methanol-*O-d*.

Stability of the Dienols 2 and 3. The dienols produced by photolysis of **1** were highly air-sensitive. When air was introduced to the acetonitrile solution, the dienols disappeared immediately and dimeric and polymeric substances were formed. When the acetonitrile solution was concentrated *in vacuo* at room temperature, polymerization of the products took place. The dienols, however, were quite stable in dilute acetonitrile solution covered by inert gas and remained virtually unchanged for 3 days at ambient temperature. Under forcing conditions, or with added acids or bases, the dienols were converted irreversibly to β,γ-(and α,β-)unsaturated ketones. The product ratio is dependent on the reaction conditions (Table 1). Heating at 100 °C gave an 83: 17 mixture of the β,γ-unsaturated ketone **4** and the starting enone **1**. Addition of a trace amount of sulfuric acid led to a similar mixture of the enones. On the other hand, treatment with potassium *tert*-butoxide produced the β,γ isomer exclusively. When pyridine was added to the acetonitrile solution, the NMR signal due to the OH proton disappeared spontaneously but the isomerization proceeded very slowly. When the mixture stood for 4 days at 25 °C, **4** was formed as a sole product.

Table 1. Ketonization of the dienols **2** and **3**[a)]

Additive	Solvent	Reaction conditions	Yield %[b)]	**4:1** ratio[b)]
None	CH$_3$CN	25 °C, 3 days	0	—
None	CH$_3$CN	100 °C, 2 h	80	83:17
None	CH$_3$OH	25 °C, 4 days	100	100:0
H$_2$SO$_4$[c)]	CH$_3$CN	25 °C, <30 s	100	75:25
t-C$_4$H$_9$OK[c)]/ t-C$_4$H$_9$OH	CH$_3$CN	25 °C, <30 s	80	100:0
(C$_2$H$_5$)$_3$N[d)]	CH$_3$CN	25 °C, <30 s	52	100:0
Pyridine[d)]	CH$_3$CN	0 °C, 4 days	~100	100:0

a) A 5:1 mixture of **2** and **3** in acetonitrile was used as starting material. b) Determined by NMR analysis using benzene as internal standard. c) A trace amount was used. d) Excess reagent was used.

The structure of the enone **4** was fully substantiated by the analytical and spectral data. The nonconjugated enone **4** gave an IR carbonyl band at 1710 cm^{-1}. The presence of an acetyl group and a disubstituted double bond was confirmed by the three-proton NMR singlet at δ 2.10 and two-proton multiplet at δ 5.66, respectively.

Acetylation of the Dienols. Owing to high air-sensitivity, the dienols **2** and **3** could not be isolated from the acetonitrile solution. However, the corresponding acetates were stable enough to isolated and their characterization provided further chemical evidence for the dienol structure. Thus treatment of a mixture of **2** and **3** in acetonitrile with acetic anhydride–pyridine at −20 °C furnished an 83: 17 mixture of the acetates **5** and **6** in 60% yield together with the enone **4** (40%). The acetoxy derivatives **5** and **6** separated by preparative GLPC were identical with samples which were prepared independently by the reaction of the enone **1** and acetic anhydride in the presence of *p*-toluenesulfonic acid (**5**: **6** ratio in the latter case was 24: 76). UV absorption maximum of both acetates occurred at ≈240 nm (log ε 4.0—4.1). The IR spectra exhibited characteristic bands at 1755—1753 and 1206 cm^{-1} due to the acetate moieties. The NMR spectra exhibited singlets at δ 1.87 (broad) and 2.07 (sharp), indicating the presence of vinylic and acetyl methyl groups, respectively. The signal patterns in the olefinic region are given in Figs. 3 and 4. The vinylic proton Ha (or Ha′) is coupled to Hb (or Hb′) with J=12 Hz and appeared as a doublet. The Hb (or Hb′) signal is further split by coupling with the adjacent methylene protons (J=7 Hz). The stereochemistry of these isomers could be distinguished by examining the intermolecular nuclear Overhauser effect (NOE).[7] When the vinylic methyl protons of **6** were saturated by double irradiation, the Ha′ signal showed a 19±1% increase in integrated intensity. By contrast, irradiation of the methyl group in **5** resulted in no change in the signal intensity of Ha (0±1%). These results indicate that the methyl protons and Ha′ proton in **6** are in close proximity but the methyl group and Ha proton in **5** are not.

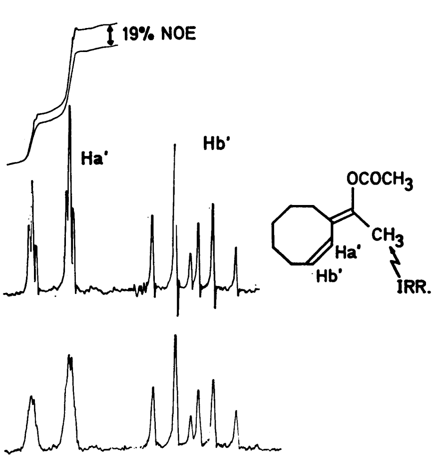


Fig. 3. Measurement of NOE in **6** (10% $CDCl_3$ solution, 100 MHz, tetramethylsilane as internal standard). Upper: spectrum taken with irradiation at the methyl group. Lower: normal spectrum.

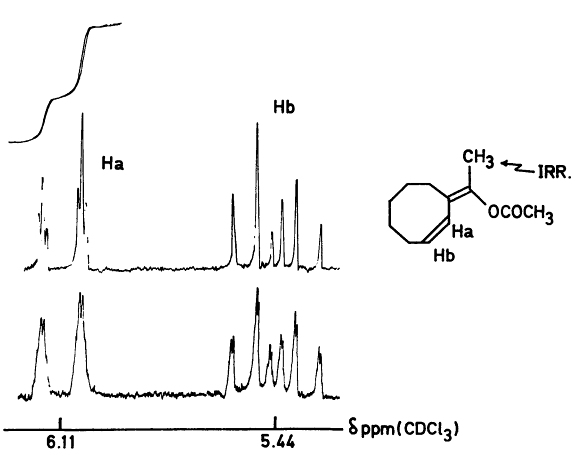
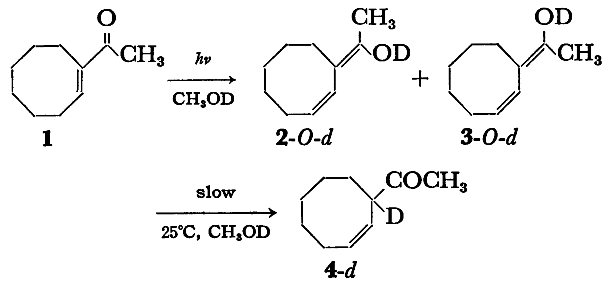


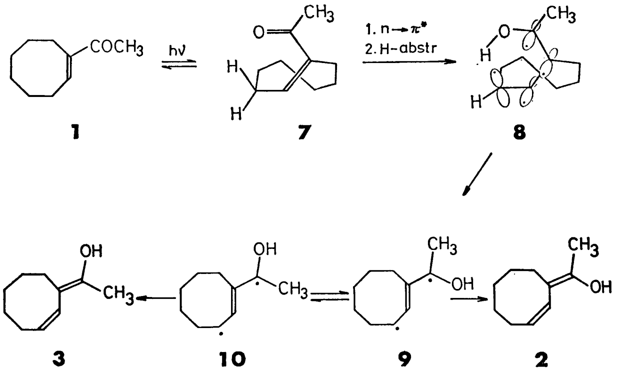
Fig. 4. Measurement of NOE in **5** (10% $CDCl_3$ solution, 100 MHz, tetramethylsilane as internal standard). Upper: spectrum taken with irradiation at the methyl group. Lower: normal spectrum.

Photolysis of the Enone 1 in Methanol. The enone **1** in methanol has in UV region a π-π^* and n-π^* band at 234 (log ε 4.00) and 306 nm (log ε 0.89), respectively. When the enone **1** in methanol-*O*-*d* placed in an NMR tube was exposed to light of wavelength >350 nm for 10 h, the dienols **2**-*O*-*d* and **3**-*O*-*d* were produced. These dienols are remarkably stable even in the alcoholic solvent. The NMR spectrum of the photolysate was practically the same as that obtained in the acetonitrile (Fig. 2) except for the lack of the OH signal. When stood at room temperature, the dienols were isomerized slowly. After 4 days, the deuterated β,γ enone **4**-*d* was formed as a sole product. NMR analysis of the isolated product indicated the isotopic purity of *ca.* 95%; in going from **4** to the deuterated product **4**-*d*, a multiplet at δ 3.4 srising from the $C\underline{H}COCH_3$ proton vanished almost completely.



Photolysis of the Enone 1 under Other Conditions. Neither the dienols **2** and **3** nor the enone **4** was produced by the photolysis of **1** in nonpolar solvents such as benzene, cyclohexane, carbon tetrachloride, chloroform, or carbon disulfide. Irradiation of **1** in pyridine or dimethyl sulfoxide gave the deconjugation product **4**. Attempted sensitization of the photoreaction (benzophenone in acetonitrile, acetophenone in acetonitrile, or acetone as solvent) has not been successful.

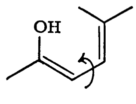
Mechanism of the Dienol Formation from 1. The photochemical formation of the dienols **2** and **3** from the enone **1** is best explained by a mechanism outlined in Scheme 2. The conjugated enone **1** is known to undergo photochemical *cis-trans* isomerization, establishing an equilibrium between **1** and **7**.[8] The *trans* isomer **7** contains a torsionally strained double bond and is much less stable than the starting *cis* enone **1**. Therefore, this isomer with a short lifetime, reverting thermally to **1**, is contained in rather low concentration in the equilibrium mixture. Fortunately, however, the labile isomer **7**, owing to a reduction in the symmetry-forbiddenness of the n-π^* transition, has the enhanced extinction coefficient in the >300-nm region and can absorb incident light



Scheme 2

more efficiently than the major *cis* isomer **1**.[8] Inspection of models indicates that the γ-hydrogen abstraction by the n, π^* carbonyl oxygen through a cyclic transition state is feasible only with such *trans* enone **7**. Although the spin multiplicity of the n, π^* state that causes this hydrogen abstraction is uncertain as yet, the observation can be simply accounted for by assuming the involvement of the triplet species.[2] Thus the twisted triplet biradical **8** initially formed from **7** is stabilized by changing the geometry to give the sterically less constrained, interconvertible biradicals **9** and **10**. Subsequent decay to the ground state affords the dienols **2** and **3**. The production of these two isomers even at an early stage of the reaction as well as the lack of noticeable time-dependency of the isomeric ratio (5: 1 by NMR analysis) is in accord with this consideration. However, the stereoisomeric biradicals **9** and **10** could also be formed *via* the possible long-lived, singlet biradical **8** arising from the excited singlet enone **7**. Finally, thermal or catalyzed ketonization of the dienol intermediates concludes the overall photo-induced deconjugation reaction of the α,β-unsaturated ketone.

Origin of the High Stability of the Dienol Species. The existence of the simple dienols **2** and **3** as long-lived species seems highly unusual.[9] Full account for this observation is open to further detailed studies. At present, the following three factors are conceived to be contributing to the stability. First, the dienols **2** and **3** have the fairly rigid *s-trans* diene structure. The restriction of conformational freedom may preserve stability through double bond conjugation. On the other hand, in the ordinary photoisomerization of α,β-unsaturated ketones, the initially formed dienols have an open-chain *s-cis* dienoid structure. The flexible dienols are liable to ketonize through conformational change accompanying loss of the conjugation (*cf.* **11**). Secondly, the dienol-enone isomerization **2**→**4** (or **3**→**4**) is accompanied by decrease in the number of sp^2-hybridized carbons in the eight-membered skeleton (three to two). The favoring of sp^2 configuration in eight-membered rings over sp^3 structure[10] may be one source of the unusual stability. Finally, the presence of strong intermolecular hydrogen bonding between the dienols and the acetonitrile solvent may be an additional stabilization factor.[11]



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Experimental

General. NMR spectra were measured with a JEOL CO JMN-C-60H or C-100H spectrometer. Unless otherwise stated, tetramethylsilane was used as internal standard. IR spectra were recorded with a Japan Spectroscopic Co. DS-402G spectrometer, with a polystyrene film used for calibration. Air-sensitive solutions were transferred to a cell with a syringe which had been previously wet with nitrogen-saturated solvent to preclude air leakage along the barrel. UV spectra were taken with a Perkin-Elmer 202 spectrometer. Mass spectra were taken with a Hitachi RMU-6C spectrometer. Analytical gas-liquid partition chromatography (GLPC) was performed on a Yanagimoto Model G-8 instrument, equipped with a 2 mm × 2 m column of Apiezon grease L (5%) on Chromosorb W and a flame ionization detector using nitrogen as carrier gas. The column temperature was maintained at 160 °C. In quantitative analyses, areas under the peaks in the chromatogram were measured by the cut-and-weigh method. Preparative GLPC was done on a Yanagimoto Model GCG-3D instrument using helium as carrier gas and a 4 mm × 2 m column of Apiezon grease L (10%) on Chromosorb W. All irradiations were effected externally using a 200-W high-pressure mercury arc through 10% aq $CuSO_4$ filter solution (1 cm depth).

Materials. Solvents for photochemical reactions were purified by simple distillations and stored under nitrogen atmosphere. Acetonitrile was dried by distillation from P_2O_5 (four times) and anhydrous K_2CO_3. The solvent was further purified by simple distillation under nitrogen. 1-Acetylcyclooctene (**1**), bp 75—85 °C (3 mmHg), was prepared by the method of Cantrell and Shechter from cyclooctene and acetyl chloride.[12] As the Lewis acid catalyst, titanium tetrachloride was used in place of stannic chloride. Usually, the material was freshly purified by preparative GLPC before each photolytic experiment.

*Photolysis of **1** in Acetonitrile.* A 5% acetonitrile solution of **1** was placed in a Pyrex NMR tube and deoxygenated by bubbling slowly with pure nitrogen for 30 min. The solution covered by nitrogen was irradiated at room temperature. Progress of the reaction was monitored by NMR analysis. After 10-h irradiation, the starting material was consumed completely and a 5: 1 mixture of the dienols **2** and **3** was formed. Its NMR spectrum is given in Fig. 2; δ 5.22 (dt, J=12 and 8 Hz, Hb and Hb′), 5.68 (s, OH of **2**), 5.71 (s, OH of **3**), 6.14 (d, J=12 Hz, Ha′), and 6.48 (d, J=12 Hz, Ha). The OH signals disappeared upon addition of an excess of CH_3OD. Yield determined on the basis of added benzene standard was *ca.* 80%. The photolysate obtained by the reaction in CD_3CN showed NMR signals at δ 1.88 and 1.82 (singlets) due to the olefinic methyl groups of **2** and **3**. Results of the decoupling experiments were in accord with the assignments. The photolysate in an NMR tube was transferred with a syringe into an NaCl IR cell which had been flushed with nitrogen, and subjected to IR measurement (Fig. 1).

A 2.7×10^{-3} M solution of **1** in acetonitrile was deoxygenated by four freeze(−78 °C)-pump(0.008 mmHg)-thaw cycles, transferred directly to a UV cell (1 cm × 1 cm), and sealed under nitrogen atmosphere. The photolysis was conducted by external irradiation (>350 nm) and the reaction course was monitored by UV analysis. The absorption of **1**, λ_{max} 233 nm, was cleanly replaced by a new band, λ_{max} 252 nm (log $\varepsilon \approx 4.0$). After a 6 h irradiation, the reaction was complete.

*Preparation of the Dienol Acetates **5** and **6**.* An acetic anhydride solution (170 ml) containing **1** (1.2 g, 80 mmol) and *p*-toluenesulfonic acid (1.5 g, 80 mmol) was slowly distilled under atmospheric pressure through a short column. About 4 h were required until the final volume was reduced to 70 ml. Most of the acetic anhydride then was removed under reduced pressure. The residue was dissolved in ether, treated with ice-cooled 5% aq sodium hydroxide and then with water, and dried over $MgSO_4$. Concentration followed by distillation gave an oil (830 mg), bp 95—100 °C (3 mmHg). GLPC analysis gave three peaks at 4.7 (71%, **6**), 5.4 (22%, **5**), and 6.6 min (7%). Each component was collected by preparative GLPC. **5**, UV (95% C_2H_5OH) 241 nm (log ε 4.15); IR (neat) 1755 and 1206 cm^{-1} (acetate); NMR (CCl_4) δ 1.59 (m, 6H, CH_2), 1.87 (broad s, 3H, $=C(OCOCH_3)C\underline{H}_3$), 2.07 (sharp s, 3H, $COCH_3$), 2.2—2.6 (m, 4H, allylic CH_2), 5.44 (dt, 1H, $J=12$ and 7 Hz, Hb), and 6.11 (d, 1H, $J=12$ Hz, Ha); the exact mass spectrum *m/e* 194.1310 (calcd for $C_{12}H_{18}O_2$: 194.1307). **6**, UV (95% C_2H_5OH) 239 nm (log ε 3.98); IR (neat) 1753 and 1206 cm^{-1} (acetate); NMR (CCl_4) δ 1.55 (m, 6H, CH_2), 1.87 (broad s, 3H, $=C(OCOCH_3)C\underline{H}_3$), 2.07 (sharp s, 3H, $COCH_3$), 2.2—2.5 (m, 4H, allylic CH_2), 5.60 (dt, 1H, $J=12$ and 7 Hz, Hb′), and 6.07 (d, 1H, $J=12$ Hz, Ha′); exact mass spectrum *m/e* 194.1300 (calcd for $C_{12}H_{18}O_2$: 194.1307). The nuclear Overhauser effects in the NMR of **5** and **6** were measured in the well-deoxygenated $CDCl_3$ solutions. The results were shown in Figs. 3 and 4. The third component was produced in only a small amount and was not isolated in an analytically pure state. Based on the following spectral data, it was tentatively assigned as 1-(α-acetoxyvinyl)-cyclooctene. IR(neat) 1757 (acetate), 1635 and 1608 (C=C), 1214 and 1184 (acetate), and 871 cm^{-1} ($=CH_2$); NMR (CCl_4) δ 1.49 (m, 8H, CH_2), 2.12 (s, 3H, $COCH_3$), 2.2—2.5 (m, 4H, allylic CH_2), 4.64 and 4.93 (d, 1H each, $J=2$ Hz, $=CH_2$), and 5.78 (t, 1H, $J=8$ Hz, =CH); mass spectrum *m/e* 194 (M^+).

*Acetylation of the Dienols **2** and **3**.* (*a*) *Analytical Scale*: Under nitrogen atmosphere a 5-μl portion of a 5 : 1 mixture of **2** and **3** in acetonitrile (photolysate of **1**) was added to a mixture of pyridine (10 μl) and acetic anhydride (5 μl) which had been cooled at −20 °C in a semimicro sampling tube. GLPC analysis of the mixture revealed the formation of **4** (42%, 2.8 min), **5** (48%, 6.6 min), and **6** (10%, 4.7 min).

(*b*) *Preparative Scale*: A solution of **1** (500 mg; 3.3 mmol) in acetonitrile (12 ml) was divided in three Pyrex tubes (0.8 cm × 4 cm), deoxygenation by bubbling with purified nitrogen for 10 min, and irradiated under the above described conditions. The photolysate obtained after 18-h irradiation was treated with a mixture of pyridine (0.2 ml) and acetic anhydride (0.3 ml) for 1 h at room temperature. The solutions were combined and concentrated *in vacuo*. The residue was dissolved in ether, washed with water, and dried over $MgSO_4$. Concentration and distillation (90—100 °C (3 mmHg)) gave an oil (256 mg). GLPC analysis of the oil afforded three peaks at 2.8 (80%, **4**), 4.7 (3%, **6**), and 6.6 min (15%, **5**). Each component was isolated by preparative GLPC and identified on the basis of its spectral properties. The dienol acetates **5** and **6** were compared with the authentic samples. Spectral characteristics of 3-acetylcyclooctene (**4**)[13] were: IR (neat) 1710 (C=O) and 1360 cm^{-1} ($COCH_3$); NMR (CCl_4) δ 1.60 (m, 8H, CH_2), 2.10 (s, 3H, $COCH_3$), 2.20 (m, 2H, allylic CH_2), 3.37 (m, 1H, $C\underline{H}COCH_3$), and 5.66 (m, 2H, =CH); mass spectrum *m/e* 152 (M^+).

Found: C, 78.95; H, 10.69%. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.57%.

*Silylation of the Dienols **2** and **3**.* A 5-μl portion of the photolysate of **1** in acetonitrile was mixed with *N,O*-bis(trimethylsilyl)acetamide (10 μl) in a semimicro sampling tube under nitrogen atmosphere at room temperature. GLPC analysis of the mixture revealed eluates at 2.8 (28%), 7.7 (14%), and 8.8 min (60%). The first peak was due to **4**, and the latter two were assigned as the silyl ethers of **2** and **3**.

*Examination of the stability of **2** and **3**.* The stability of the dienols was examined under various conditions. When air was admitted to an acetonitrile solution of **2** and **3**, polymeric substances were formed immediately. A solid dimer was separated from the solution; mass spectrum *m/e* 302 (M^+); IR (KBr) 1656 cm^{-1} (C=O). The exact structure remains to be determined. The dienols, however, were fairly stable under inert gas atmosphere. The dienols were allowed to react in an NMR tube under conditions described in Table 1.

*Photolysis of **1** in Methanol-*O*-*d.* The enone **1** (35 mg, 0.23 mmol) was dissolved in methanol-*O*-*d* (0.5 ml, E. Merck, deuterium content >99%) in an NMR tube, deoxygenated, and irradiated as described above. After a 10 h irradiation, **1** was consumed completely to yield the dienols **2**-*O*-*d* and **3**-*O*-*d*. NMR in the olefinic region was identical with that taken in acetonitrile except the absence of OH signals. After the solution stood at 25 °C for 4 days, the signals due to these dienols vanished completely and the peaks due to the enone **4**-*d* appeared. GLPC analysis of the aliquot exhibited a single peak with retantion time of 2.8 min (identical with that of **4**) except for the solvent peak. Concentration of the photolysate, followed by distillation (bath temp 75—85 °C (3 mmHg)) gave 3-acetylcyclooctene-3-*d* (**4**-*d*) as a colorless oil. NMR analysis (CCl_4) revealed the isotopic purity of *ca.* 95%; δ 1.60 (m, 8H, CH_2), 2.10 (s, 3H, $COCH_3$), 2.20 (m, 2H, allylic CH_2), and 5.66 (m, 2H, =CH). Mass spectrum *m/e* 153 (M^+).

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