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Photorearrangement of 10-Methyloctalone in Concentrated Acid Solution[1]

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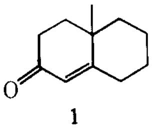
When dissolved in concentrated sulfuric acid, 10-methyloctalone undergoes only complete protonation. It can be recovered unchanged after long periods of storage in the dark and subsequent hydrolysis of the acid solution. Irradiation of the hydroxycarbocation generated by the octalone in acid with ultraviolet light of 300 nm caused an efficient rearrangement to 1-hydroxy-3-(1-methylcyclopentyl)cyclopenten-2-yl cation. Time-lapse spectrometry experiments showed this first transformation to be virtually free of any side reactions. Further photolysis of the resulting solutions with light of 254 nm, where the first photoproduct exhibited strong absorption, caused a second rearrangement to a tricyclic hydroxycarbocation. The identity of the photoproducts was established from the spectral data of their neutral derivatives and their deuterated analogues. A reaction mechanism is proposed.

The photochemistry of unsaturated cyclic ketones has received much attention because these structures offer interesting interactions between the carbonyl and alkene π systems within the steric constraints of the cyclic configuration. Numerous photorearrangements of cyclohexenone incorporated in polycyclic configurations have been reported.[3] Several interesting rearrangements have been uncovered on photolysis of 10-methyloctalone in organic solvents.[4-6]

This paper describes our results obtained by irradiating $\Delta^{1,9}$-10-methyl-2-octalone 1 in concentrated sulfuric acid. The methyl group is not only a useful analytical "label" in the complex problem of elucidating the structure of rearranged photoproducts, but also the natural angular substituent at the 10 position of many steroid hormones. In fact, methyloctalone 1 represents the common "half-molecule" of androgens testosterone 2 and androstenedione 3, without the C and D rings.



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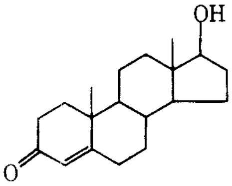

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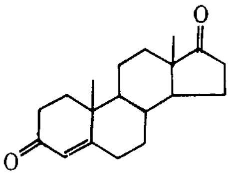

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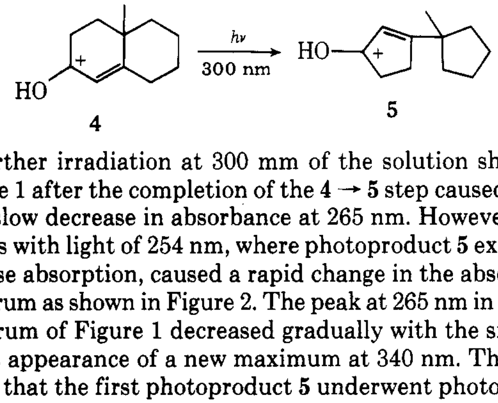
Since the classical method of assay of these hormones in biological fluids involves measurement of fluorescence excited by ultraviolet light in concentrated sulfuric acid, the results outlined in this study are also relevant to the complicated and poorly-understood behavior of natural steroids in strongly acidic solutions.[7]

Results and Discussion

When dissolved in concentrated sulfuric acid, methyloctalone 1 formed stable solutions of hydroxycarbocation 4. The UV spectrum of these solutions remained unchanged for many months. The absence of any dark reaction was also demonstrated by recovery of only the starting octalone 1 from acid solutions stored for a long time.

Time-Lapse Spectrometry (TLS).[8] Figure 1 shows the consecutive changes in the UV spectrum of a dilute solution of 1 in concentrated acid on successive short irradiations at 300 nm. The absorption band centered at 290 nm, characteristic of protonated 1, decreased progressively during the photolysis. The formation of photoproduct 5 was demonstrated by the appearance and corresponding increase in a new absorption band with λ_{max} 265 nm. The UV spectra of 4 and 5 are consistent with α,β-unsaturated alicyclic ketones in sulfuric acid.[9] After a total irradiation time of 6 min there was no residual reactant, as shown by scan 8. The absorption curves in Figure 1 pass through three well-defined isosbestic points at 210, 277, and 318 nm. This isosbestic behavior testifies that the phototransformation is free of significant side or consecutive reactions.[8] The existence of only two components, reactant ion 4 and photoproduct 5, was confirmed by the gas chromatographic analysis of extracted hydrolysates form preparative-scale photoreactions.



Further irradiation at 300 mm of the solution shown in Figure 1 after the completion of the 4 → 5 step caused only a very slow decrease in absorbance at 265 nm. However, photolysis with light of 254 nm, where photoproduct 5 exhibited intense absorption, caused a rapid change in the absorption spectrum as shown in Figure 2. The peak at 265 nm in the last spectrum of Figure 1 decreased gradually with the simultaneous appearance of a new maximum at 340 nm. This indicated that the first photoproduct 5 underwent photolysis to a second product. The isosbestic point formed at about 285 nm by the first seven scans in Figure 2 is less well defined than the isosbestic points in the TLS diagram of Figure 1, with some intersections occurring in the 284–288-nm spectral region. This suggests either the occurrence of minor consecutive or side reactions, or the presence of some residual protonated octalone. Since curves 15 and 16, corresponding to 10 and 12 min total irradiation, did not pass through the isosbestic point, and the scans in 230–240-nm region did not cross at a clearly defined point, some further breakdown of the second photoproduct seems likely.

Preparative-Scale Irradiation of 1 in Sulfuric Acid. For small scale preparative purposes, a 3 × 10^{-3} M solution of 1 in sulfuric acid was photolyzed at 300 nm in a Vycor preparatory cell. The progress of the photoreaction was evaluated by monitoring the UV spectra of diluted aliquots. At the end of the first 2 h of irradiation, the 4 → 5 conversion was essentially complete with little, if any, other product being formed. Quenching of the photolyzed solution on ice and ether extraction of the hydrolysate followed by solvent evaporation yielded an oil with a faint yellow tint. No degradation products could be identified in the aqueous phase. GLC analysis of the extract indicated the presence of only one volatile component. The UV spectrum of this component, isolated by GLC and redissolved in sulfuric acid, was identical with that of photoproduct 5 shown in scan 8 of Figures 1 and 2. This shows that product 6 was recuperated from concentrated acid solutions without irreversible change.

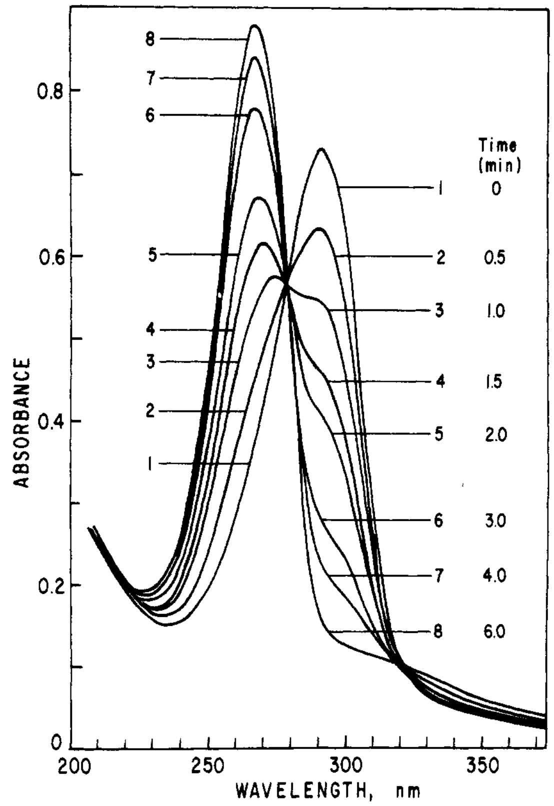


Figure 1. Changes in the UV spectrum of a 6 × 10^{-5} M solution of 10-methyloctalone in sulfuric acid, when irradiated at 300 nm. Total photolysis time indicated in the diagram to the right of the corresponding scan.

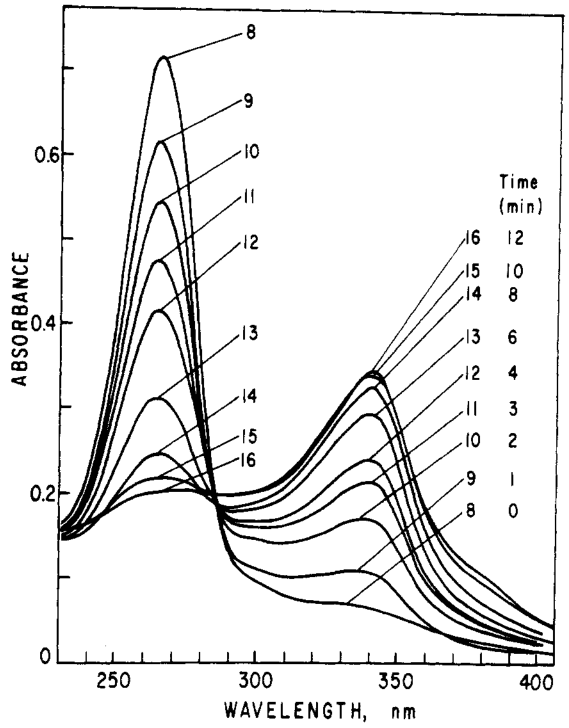


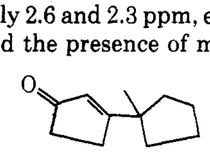
Figure 2. Further changes in the UV spectrum of the same solution shown in Figure 1 on photolysis at 254 nm.

Identification of First Photoproduct. Analytically pure photoproduct by GLC of ether extracted hydrolysate was a clear light-yellow liquid. Its mass spectrum, like that of **1**, showed a prominent molecular ion peak at *m/e* 164. There is little doubt that the overall **1** → **6** reaction represents an isomerization.

The IR spectrum of **6** exhibited peaks at 1713 and 1683 cm^{-1} characteristic of a carbonyl group which is either unconjugated, out-of-plane with respect to an adjacent alkene group, or part of a cyclopentenone ring.[10] The relatively intense IR peak at 1605 cm^{-1} is usually associated with a conjugated alkene group.

The UV spectrum of **6** in methanol showed a moderately intense band centered at 228 nm with $\epsilon = 1.1 \times 10^4$ L mol^{-1} cm^{-1} consistent with the absorption of a conjugated carbonyl group.

The NMR spectrum showed the presence of a vinyl proton (triplet centered at 5.87 ppm vs. Me_4Si $J = 1.8$ Hz) coupled to two equivalent protons. Multiplets centered at approximately 2.6 and 2.3 ppm, each equivalent to two protons, suggested the presence of methylene groups adjacent to C=O and/or C=C.[11] The rest of the spectrum displayed a broad unresolved band from about 1.3 to 1.9 ppm, with integration equivalent to 8 saturated protons, and a 3 hydrogen singlet at 1.20 ppm.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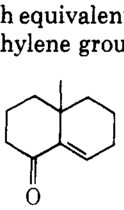
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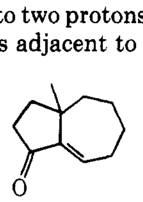
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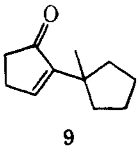
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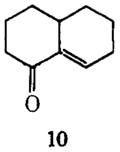
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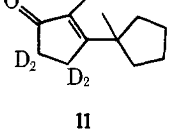
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Structures **6, 7, 8,** and **9** at first sight seemed to satisfy the above analytical data. They all have one vinyl proton, a tertiary methyl group, 8 "high-field" methylene protons, C=O and C=C chromophores, and an appropriate number of methylene groups α to each of the two unsaturated groups. However, only **6** is consistent with a 1.8-Hz coupling constant observed for the vinyl proton of our photoproduct. All other structures contain methylene groups adjacent to the vinyl hydrogen which would be expected to give coupling constants of 6–7 Hz.[14,15] Also the chemical shifts for the vinyl protons of **8** and **9** would be expected to be close to the 6.57 ppm reported by House and Thompson[13] for **10.** We observed an absorption signal attributed to a vinyl hydrogen at 5.87 ppm in the NMR spectrum of **6** in agreement with the resonance observed at 5.81 ppm for 3-*tert*-butylcyclopentenone.[16] Furthermore, the UV and IR data of Djerassi and Marshall[12] for an authentic sample of **7** are incompatible with the data for our photoproduct.

Effects of Deuteration. Following deuterium exchange, **6** had an average of 2.5 deuterium atoms per molecule as determined by mass spectrometry and confirmed by its NMR spectrum. The corresponding methylene and vinyl hydrogen signals were reduced in intensity and showed quadrupole broadening without splitting. Complete exchange of the hydrogens α to the carbonyl and the allyl hydrogens would generate molecule **11** with five deuterium atoms per molecule. Hence, only about 50% exchange was effected. The vinyl hydrogen was replaced by deuterium in 80% of the molecules while only 30% exchange occurred at the high-field methylene group adjacent to the carbonyl group and 60% at the allylic low-field methylene protons. The exchange of the vinyl hydrogen, which appears to be nonreplaceable, has been reported by other investigators.[17] This seemingly unusual isotopic exchange pattern was determined by the stereoelectronic control of the relative rates of exchange. The orienting influence depends on the degree of delocalization of electrons in perturbed axial and equatorial bonds α to the exocyclic π orbital.[18]

Since the transition state for enolization–ketonization type processes is stabilized by bonding between the α carbon and the carbonyl carbon involving δ–π delocalization, an axial δ substituent is lost or gained preferentially over an equatorial δ substituent. In flexible systems such as cyclohexanone, all α hydrogens eventually assume an axial orientation and are subject to facile exchange. In more rigid ring systems such as cyclopentanone and especially cyclopentenone, however, the hydrogens are fixed in an intermediate position midway between the axial and equatorial orientations. Furthermore, the transition state for the allylic hydrogen exchange is stabilized by bond delocalization over the 5 atoms of the enone system. It is reasonable, therefore, that in photoproduct **6** the exchange of hydrogens α to the carbonyl group is less favorable than that of the allylic hydrogens.

Base-catalyzed exchange of **6** over two days in deuteriomethanol yielded a product with an average of 3.6 deuterium atoms per molecule or about 70% replacement of exchangeable hydrogens. The distribution was d_1 3%, d_2 11%, d_3 26%, d_4 44%, and d_5 16%. The main peaks in the mass spectrum of the deuterated **6** were found at m/e 153, 136, and 124 corresponding to loss of CH_3, C_2D_4, and CD_2CO, respectively. The analogous peaks in nondeuterated **6** were at m/e 149 ($M^+ - CH_3$), m/e 136 ($M^+ - C_2H_4$), and m/e 122 ($M^+ - CH_2CO$, base peak).

NMR Spectroscopy in Sulfuric Acid. The species responsible for light absorption and subsequent rearrangement is undoubtedly hydroxycarbocation **4** formed by protonation of **1** in concentrated sulfuric acid solution. Its NMR spectrum in D_2SO_4 correlates well with that of unprotonated **1** in CD_2Cl_2. The signal for the vinyl proton found at 5.64 ppm in CD_2Cl_2 was shifted to lower field by 0.8 ppm in D_2SO_4. The multiplet between 2.2 and 2.5 ppm in CD_2Cl_2 due to the methylene protons adjacent to C=O and C=C was separated into two broad unresolved bands at 2.6 and 2.9 ppm in D_2SO_4. Except for some loss of resolution, the saturated methylene groups appeared in the same spectral range from 1 to 2 ppm in both solvents. Similarly, the chemical shift of the methyl group remained unchanged. The downfield shift exhibited by protons adjacent to the α,β-unsaturated carbonyl group in sulfuric acid is undoubtedly due to the electron withdrawing or deshielding effect of protonation on the carbonyl group. It is thus apparent that **1** undergoes complete protonation but maintains its structural integrity when dissolved in sulfuric acid solution.

In separate experiments, 10-methyloctalone **1** was photolyzed in D_2SO_4 at 300 nm directly in the NMR tube. The extent of photoconversion was monitored by recording ultraviolet absorption spectra of aliquots diluted with sulfuric acid. After 4 h of total irradiation the **4** → **5** photoreaction was complete. The NMR spectrum of the irradiated solution was remarkably clean and consistent with photonated photoproduct structure **5**.

The Second Photochemical Rearrangement. Solutions (3×10^{-3} M) of 10-methyloctalone in sulfuric acid were first photolyzed at 300 nm until the first step was complete, as determined by recording the UV absorption of diluted aliquots. The photolysis was then continued with a UV source of 254 nm. This second irradiation was terminated before all the first product **5** was reacted in order to minimize the complicating side or consecutive reactions which tended to give more complex reaction mixtures. Usually the first **4** → **5** step required about 4 h for completion. The subsequent photolysis at 254 nm was stopped after another 4 h.

The final solution was hydrolyzed over ice and extracted with methylene chloride. GLC analysis of the extract revealed the presence of one major product representing about 50% of all components, eight other minor products, and unreacted cyclopentenone **6**. When the residue of the evaporated methylene chloride was redissolved in acid, it gave the same UV–visible absorption as the acid solution before hydrolysis, and the same as that prepared from dissolving the GLC-trapped components in acid. These findings show that no essential change occurred during hydrolysis, that virtually all the products are volatile, and that they do not exhibit sensitivity to atmospheric oxygen during processing.

Characterization of Second Photoproduct. Analytical samples of the major product from the photolysis of **5** were obtained by repeated collection of GLC fractions from the mixture of hydrolyzed and extracted products. The mass spectrum exhibited a relatively weak molecular ion peak at m/e 164, the same as that of **1** and its first photoproduct **6**. Therefore, it seems that the second photochemical reaction represents another isomerization. Base-catalyzed deuterium exchange of the second product gave a species with molecular ion at m/e 168, a gain of four mass units, suggestive of four exchangeable hydrogen atoms.

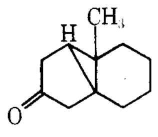
The UV absorption spectrum of an ethanolic solution showed only a low intensity peak (ϵ = 24 L mol^{-1} cm^{-1}) around 280 nm with no other absorption band above 220 nm. The UV spectrum of an alcohol solution of the unresolved reaction mixture showed a broad relatively strong absorption band around 260–280 nm suggesting conjugated chromophores in the minor photoproducts. This could be the source of the 340-nm peak in the TLS diagram of the second photochemical conversion in sulfuric acid. The IR spectrum of the major product showed a peak at 1742 cm^{-1}, consistent with an unconjugated carbonyl group in a five-membered ring.[10]

The ^1H NMR spectrum showed the presence of a methyl singlet at 1.02 ppm, eight methylene protons between 1.4 and 1.8 ppm, a partially resolved multiplet equivalent to three protons between 2.0 and 2.3 ppm, and a singlet equivalent to two protons at 2.4 ppm. There was no signal attributable to vinyl protons.

Several noise-decoupled ^{13}C magnetic resonance spectra were recorded with a different number of scans, different angles of pulsation, and different time intervals between pulses. Analysis of these spectra revealed the presence of two quaternary carbon atoms at 50.2 and 54.1 ppm, a carbonyl carbon part of a cyclopentanone ring at 219.2 ppm,[19] and eight carbons bearing hydrogen atoms between 14.4 and 43.6 ppm. Again, no absorption signals appeared in the spectral range between 120 and 170 ppm, usually associated with alkene carbon atoms. The ^{13}C atoms with chemical shifts of 54.1 and 50.2 ppm and the carbonyl carbon gave resonance signals of lower intensity than the rest of the carbon atoms by a factor of about 2–2.4, as expected for ^{13}C atoms not bonded to hydrogens. The two quaternary carbons and the non-aldehydic carbonyl carbon require longer relaxation times and a slower scan rate than the proton-bearing carbons.[20]

The above analytical data have established that the second photoproduct must have a molecular weight of 164, a cyclopentanone ring, four exchangeable hydrogen atoms, five low-field protons, two of which give rise to an NMR singlet, eight protons in the methylene region between 1 and 2 ppm, a methyl group giving a singlet NMR peak, two quaternary carbon atoms, and no alkene group. There are three structures satisfying these requirements, namely **12**, **13**, and **14**.

Both configurations **12** and **13** contain the bicyclo[3.1.0]-hexan-3-one moiety. Strong support for the existence of such a group in the structure of the second photoproduct was provided by the similarity of its infrared spectrum with that of bicyclo ketone **15** synthesized by Winstein and Sonnensberg.[21] The resemblance is strong enough to exclude possibility **14** from consideration.[22]



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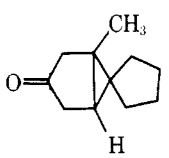

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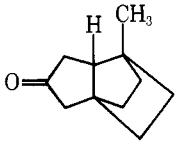

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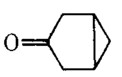

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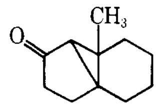

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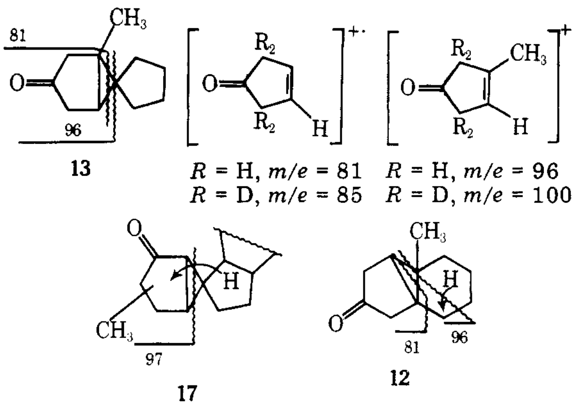
The selection of structure **13** over **12** was more subtle. A singlet corresponding to the angular methyl group was reported[5] at 1.20 ppm in the ^{1}H NMR spectrum of **16** which has marked structural similarity to **12**. In contrast, the methyl signal of our second photoproduct was found at 1.02 ppm. Molecular models showed that the hydrogens of the freely rotating methyl groups of **12** and **16** have very similar orientations with respect to the carbonyl groups. Therefore, one would expect almost identical chemical shifts in their signal. On the other hand, the methyl group in **13** is oriented directly away from the carbonyl group and would be expected to absorb at higher field than in **16**. This also agrees with the reported signals at 1.1 ppm for methyl groups located at the bridgehead carbon in bicyclopropanes.[23]

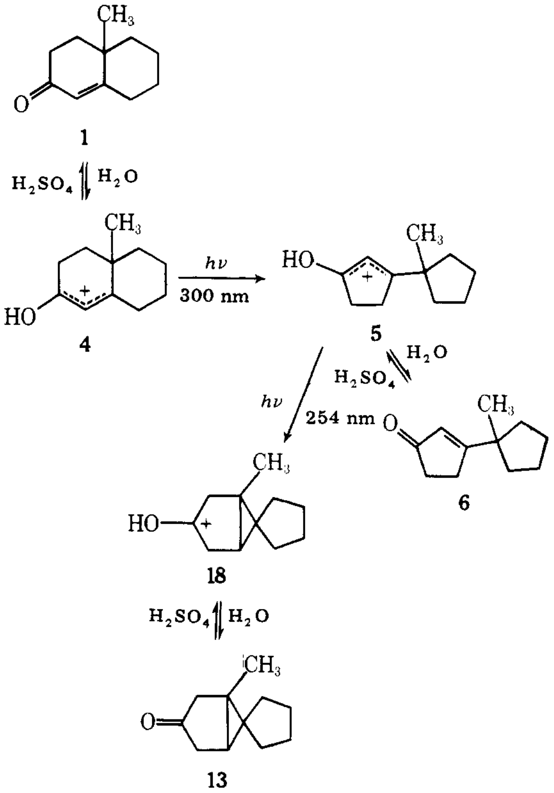
The mass spectra of our last photoproduct and its deuterated analog are also more consistent with configuration **13** than with **12**. The base peak in the second photoproduct was found at *m/e* 81. The analogous peak in its deutero derivative is also at *m/e* 81 but relatively less abundant. This suggests that the peak at *m/e* 81 is caused by different fragments, one of which contains no exchangeable hydrogen atoms. When the fragment containing exchangeable hydrogens is "subtracted out" by deuteration, the base at *m/e* = 81 becomes relatively less abundant. The presence of such a fragment was confirmed by the appearance of a prominent new peak at *m/e* 85 in the deuterated analog. Another significant difference between the two spectra consists of the changing of the prominent peak at *m/e* 96 in the product to *m/e* 100 in the deuterated product. This fragmentation pattern is easier to rationalize with structure **13** than **12** as shown in Scheme I. Loss of exocyclic methyl group is expected to occur readily. The double fission of the three-member ring suggested above is not unique. In fact,[24] cleavage of the two bonds of the cyclopropane ring lead to the base peak at *m/e* 97 in the mass spectrum of **17**. The formation of fragments at *m/e* 81 and 96 in the spectrum of **12** would require cleavage of two cyclopropane bonds (one of which is part of a cyclohexane ring) and cyclohexane bond adjacent to the quaternary C_9 (*m/e* 81) or to C_9 (*m/e* 96) as shown in Scheme I. Such events, requiring a two-ring opening step, seem substantially less probable than the fragmentation shown for **13** in the same scheme.

Reaction Mechanism. The overall photochemical transformation of **1** in sulfuric acid is summarized is Scheme II. The outcome is quite different from the reactions reported for the photolysis of 10-methyloctalone in various neutral organic solvents.[4-6] The absence of dimerization and reduction–dimerization combinations is not surprising, since, in acid, such reactions would require collisional interaction of two cations, an electrostatically unfavorable event. That α,β to β,γ double bond photoisomerization does not occur in acid is understandable since it also involves a collision between two cationic solute molecules and since it seems to originate in an n,Π^* rather than a Π,Π^* excited triplet state. Since in sulfuric acid the nonbonding electrons of the carbonyl oxygen are subject to protonation, a n,Π^* reactive level excitable with light of 300 nm is extremely unlikely.

Scheme I

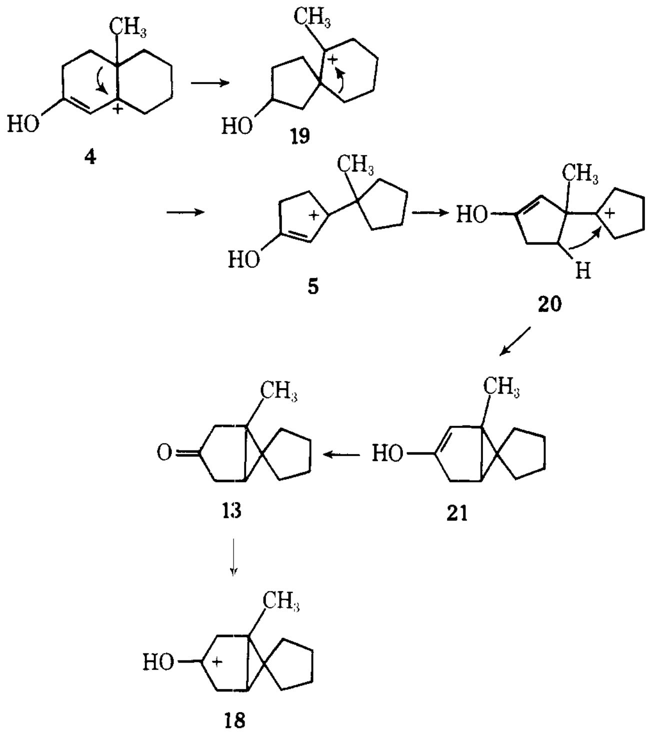


Scheme II



The formation of hydroxycarbocation **5** from protonated bicyclic cyclohexenone **4** is readily visualized in terms of two 1,2 shifts with the intermediate formation of tertiary cation **19**, as shown in Scheme III. Actually only the first 1,2 migration needs to be photochemically induced since the second **19** → **5** step could well take place after demotion to the ground state. The latter involves an energetically favorable transformation to a more stable allylic cation with further delocalization on the hydroxyl oxygen.

The hydrolysis product **6** was isolated in 2–5% during the photolysis of **1** in alcohol.[5] It was shown to be a side product from the photoreaction of tricyclic ketone **16** and not directly from **1**. The photochemical **16** → **6** rearrangement was reversible. To explain retention of chirality at C_1 and inversion at C_{10} on going from **16** to **6**, the authors had to postulate a diradical intermediate formed by initial homolytic cleavage of the C_4–C_{10} bond, an unusual step in both ground and photochemical reactions.[5] We feel that the two 1,2-shifts mechanism from **4** to **5** is reasonable. Furthermore, no hydroxycarbocation corresponding to **16** could be detected during the **4** → **5** reaction. If an intermediate similar to the diradical proposed for **16** → **6** reaction were formed in the acid reaction, Scheme III



some protonated **16** should have been detectable. There is one more basic difference between the photochemical reaction of **1** in alcoholic solution and in concentrated acid. The former gave side-product cyclopentenone **6** in less than 5% whereas the **4** → **5** reaction was essentially quantitative.

The mechanism of the second photorearrangement in acid solution from **5** to **18** is also reasonably explained by a sequence of a 1,2-shift, γ-proton elimination, tautomerization, and reprotonation, as shown in Scheme III. In terms of ground-state reactions, the 1,2 shift of a methyl group in the **5** → **20** initial step is apparently endothermic, as it converts an allylic cation with further stabilization from delocalization over the hydroxylic oxygen, to a simple tertiary carbocation. This undoubtedly is an excited-state reaction. Elimination of a proton with cyclopropane ring formation, as shown for the **20** → **21** step, is a well established pathway for carbocation stabilization.[25] The remaining enol → ketone tautomerization from **21** to **13** and reprotonation to homoaromatic[26] carbocation **18** are readily acceptable steps. Again, only the initial 1,2 shift requires an electronically excited state, while all the subsequent steps of the **5** → **18** rearrangement are well understood in terms of ground-state reactions.

Experimental Section

General. Ultraviolet spectra were recorded with a Cary 14 spectrophotometer.[27] Infrared spectra (IR) were obtained on a Perkin-Elmer 467 grating spectrophotometer with CCl_4 as solvent. Nuclear magnetic resonance (NMR) spectra were recorded with a Brucker WH-90 Fourier-transform spectrometer in CD_2Cl_2 or $CDCl_3$, and chemical shifts are reported in parts per million (δ) from tetramethylsilane. Gas–liquid chromatographic (GLC) analyses were performed with a Hewlett-Packard 5750B gas chromatograph with flame ionization detector and helium carrier gas. Columns were: column A, 6 ft × 0.125 in., 5% Triton X-305 on Chromasorb W; column B, 10 ft × 0.125 in., 3% JXR on Gas Chrom Q; column C, 4 ft × 0.125 in., 3% JXR on Gas Chrom Q; column D, 17 × 0.25 in., 5% Triton X-305 on Chromasorb W. Mass spectra were obtained with an LKB-9000 combined gas chromatograph–mass spectrometer at an ionization potential of 70 eV employing either columns A or C.

The photolysis apparatus consisted of five low-pressure lamps, either 1.3-W type RPR-3000A or 1.8-W type RPR-2537A (The Southern New England Ultraviolet Co., Middletown, Conn.) arranged in a circle with a 30-mm core. Photolysis of dilute solutions was carried out in a 1-cm ground glass stoppered quartz cuvette polished on four sides, with magnetic stirring and cooling by forced air draft. Preparatory reactions on more concentrated solutions were carried out in a Vycor cylindrical cell (22-mm i.d. × 33-cm length) cooled with a 16-mm o.d. cold-finger condenser with nitrogen bubbling for agitation.

Synthesis of $\Delta^{1,9}$-10-Methyl-2-octalone. The procedure of Hussey[28] was followed except that the mole ratio of methiodide to ketone was 2:1, essentially as recommended by Dauben.[29] A solution of 9 g each of 2-methylcyclohexanone and potassium *tert*-butoxide in 100 mL of anhydrous *tert*-butyl alcohol was refluxed for 1 h. A solution of 46 g of 4-diethylamino-2-butanone methiodide (from 23 g each of 4-diethylamino-2-butanone and methyl iodide mixed slowly in 100 mL of anhydrous *tert*-butyl alcohol) was added slowly with good cooling. After 16 h at room temperature, the mixture was heated to reflux for 1 h, and then acidified with ice cold hydrochloric acid. Solvent was removed under vacuum and the residue extracted with ether. Removal of the ether solvent and vacuum distillation of the remaining liquid gave 2.2 g of the crude octalone, bp 114–127 °C (4 mm), which proved to be 75% 10-methyloctalone by GLC analysis (13% yield). Further purification was by GLC fractionation using column D.

Preparation of Deuterated Species. Exchange deuteration was carried out on milligram amounts of photoproduct dissolved in a few tenths of a milliliter of deuteriomethanol to which a catalytic amount of sodium methoxide was added. The temperature of the solution was maintained at 50 °C for several hours after which the solvent was removed under a stream of nitrogen. The residue was dissolved in methylene chloride for injection into the gas chromatograph–mass spectrometer.

Time-Lapse Spectrometry. Changes in the UV spectrum of a 6×10^{-5} M solution of 10-methyloctalone in concentrated sulfuric acid were recorded upon successive short intervals of irradiation with light of 300-nm wavelength (RPR-3000A source). Upon disappearance of the last traces of the starting octalone, 254-nm wavelength source lamps (RPR-2537A) were installed in the photochemical reactor and further changes in the UV spectrum were recorded upon continued photolysis.

Photoproduct 6. Forty milliliters of a 0.003 M solution of 10-methyloctalone in concentrated sulfuric acid was irradiated for 2 h with light of 300-nm wavelength. Monitoring of the photolysis was by UV spectroscopy on diluted aliquots. Upon disappearance of the last trace of starting material, the sulfuric acid solution was quenched in 250 g of ice and extracted with ether. Analysis of the extract showed the presence of a single photoproduct **6**. Isolation of **6** was by GLC employing column B; spectral data: UV_{max} (MeOH) 228 nm, log ε 4.04; IR (CCl_4) 3080, 2875, 1713, 1683, 1605, 1184, 990, 866, and 847 cm^{-1}; ^1H NMR (CD_2Cl_2, 90 MHz) δ 5.87 (*t*, 1 H, *J* = 1.8 Hz vinylic H), 2.6, 2.3 (m, 2H ea, cyclopentenone CH_2), 1.9-1.3 (unresolved m, 8H cyclopentane CH_2), 1.20 (s, 3H, CH_3). Mass spectrum *m/e* (rel. intensity): perhydro species 164 (M^+, 33), 149 (22), 136 (47), 122 (100); deuterated species 168 (M^+, 45), 153 (16), 136 (43), 124 (100).

Photoproduct 13. Forty milliliters of a 0.05 M solution of 10-methyloctalone in concentrated sulfuric acid was irradiated for 24 h with light of 300-nm wavelength. Conversion of the protonated octalone to protonated photoproduct **6** was complete as shown by UV scans of diluted aliquots. The source lamps were changed to 254-nm wavelength (RPR-2537A) and irradiation continued for an additional 48 h. The sulfuric acid solution was quenched in 250 g of ice and extracted with ether. Analysis of the extract and isolation of the principal photoproduct **13** was by GLC using column A.

Spectral data: IR (CCl_4) 3470, 2990 (v w sh) 2952, 2920 (sh), 2887, 2860 (sh), 1742, 1715 (sh), 1480, 1452, 1402, 1380, 1261, 1177, 1160, 1130, 1103, 1062, 1025, 955, 910, and 840 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 M Hz) δ 2.40 (s, 2H); 2.3–2.0 (m, 3H); 1.7–1.4 (unresolved m, 8H cyclopentane CH_2); 1.02 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 22.6 M Hz) δ (rel. intensity) 219.2 (45), 54.1 (47), 50.2 (42), 43.6 (81), 41.9 (70), 40.4 (88), 37.8 (82), 31.5 (83), 25.5 (83), 24.8 (100), 14.4 (74). Mass spectrum m/e (rel. intensity): perhydro species 164 (M^+, 5), 149 (13), 136 (10), 123 (14), 122 (18), 109 (30), 107 (20), 96 (42) 93 (30), 91 (22), 81 (100), 67 (68); deuterated species 168 (M^+, 8), 153 (16), 140 (15), 127 (22), 124 (18), 113 (22), 112 (26), 110 (20), 109 (22), 100 (58), 95 (32), 93 (28), 85 (72), 81 (100), 69 (52).

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Stereoselectivity of the Retro-Ene Reaction of 2-Vinylcyclohexanols[1]

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The retro-ene reaction of a 2-vinylcyclohexanol occurs readily in the vapor phase at 400–450 °C giving an unsaturated carbonyl compound in good yield. For the reactant the terms cis and trans refer to the hydroxyl and vinyl groups, R_1 refers to the other group on C_1, and R_2 to that at C_2. The numbers listed refer to percent E, percent Z, percent unidentified materials, and overall yield of product. Vapor phase reaction of the following examples was carried out: trans, 1 H, 2 H, 96, 0, 4, 95; cis, 1 H, 2 H, 59, 36, 5, 97; trans, 1 Me, 2 H, 92, 0, 8, 98; cis, 1 Me, 2 H, 52, 44, 4, 93; mixture trans (53), cis (47), 1 H, 2 Me, 81, 14, 5, 92; mixture trans (90) cis (10), 1 Me, 2 Me, 92, 0, 8, 96. The results suggest that the reaction is concerted and the products are kinetically determined. The reaction constitutes a useful stereoselective procedure for the synthesis of trisubstituted olefins.

The last decade has seen a great enhancement of interest in the stereoselective syntheses of double bonds of known configuration. Problems associated with the widespread dispersal of persistent insecticides in the environment and the discovery of insect pheremones have focussed attention particularly on the preparation of trisubstituted double bonds.[3] Many concerted thermal rearrangements exhibit a high degree of stereoselectivity, and numerous examples of their use for the synthesis of such alkenes have been reported.[4] Though the retro-ene reaction has not been used for this purpose, Arnold and Smolinsky[5] have established that rearrangement of *trans*-2-(alk-1-enyl)cycloalkanols leads to unsaturated aldehydes in high yield and apparently with high stereoselectivity. They examined cycloalkanols of varying ring size from cyclopentanols to cycloheptanols. In all cases the double bonds formed were disubstituted, and only the trans isomers were found. These results suggested that the retro-ene reaction might be useful for the stereoselective synthesis of more highly substituted alkenes. However, in view of the known sensitivity of the ene reaction to steric effects,[6] the stereoselectivity observed for disubstituted alkenes cannot a priori be extrapolated to more hindered systems. Therefore to ascertain the