Figure 3. A superposition of the VCD spectra for α- and β-methyl D-glucoside which were shown in Figures 1 and 2, respectively.

resolution of ~10 cm^{-1}, and the sugars were run at 1.0 M concentrations using D$_2$O as the solvent. $|\Delta A/A| \approx 4 \times 10^{-5}$ at the maxima of the major VCD bands shown in Figures 1 and 2.

In Figure 3 we show an overlay of Figures 1 and 2. At least three of the CD bands appear to have changed sign and there has been a 7-cm^{-1} shift in the frequency of all of the band maxima of one spectrum relative to the other. Note, however, that α- and β-methyl glucoside are not enantiomers, but differ in absolute configuration only at the anomeric carbon atom. The other four asymmetric centers have the same absolute configuration in both the α and β forms.

At present the individual CH-stretching bands in pyranose sugars have not been positively assigned. The low frequency stretch, which occurs at 2850 cm^{-1} in the α-methyl D-glucoside, is usually assigned as the symmetric methyl stretch.[6] The asymmetric methyl stretches probably occur at ~2950 cm^{-1} with the single CH stretches and the methylene stretches providing the broad background of bands between 2980 and 2880 cm^{-1}.[7] The CD bands that change sign are most likely due to the methyl stretching modes and the anomeric CH stretch. This is supported by VCD measurements on D-glucose, which exists as a thermodynamic mixture of α and β forms in D$_2$O, and β-methyl-d_3 glucoside-d, where only the methyl group is deuterated. Both of these sugars show substantially smaller VCD signals in the CH-stretching region, indicating that the O-CH$_3$ group is making the dominant contribution to the CH-stretch VCD.

Further studies on the sugars, including normal coordinate analyses and VCD intensity calculations, are in progress.

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Curtis Marcott, Henry A. Havel
John Overend,* Albert Moscowitz*
Department of Chemistry, University of Minnesota
*Minneapolis, Minnesota 55455*
Received June 13, 1978

Organic Photochemistry with 6.7-eV Photons: Bicyclo[n.1.0]alkanes and Tricyclo[3.2.1.0^{2,4}]octane[†]

Sir:

The ultraviolet absorption spectrum of cyclopropane extends to longer wavelengths than those of other cyclic alkanes[1,2] in keeping with the special nature of the bonding in this strained molecule. Cyclopropane absorbs weakly at 185 nm and alkyl cyclopropanes such as bicyclo[3.1.0]hexane (1) and bicyclo[4.1.0]heptane (2) absorb moderately at this wavelength (ε 510 and 610 L/mol·cm, respectively). The identity of the


excited state that is reached with 185-nm radiation seems to be controversial.[3] At least in solution, the absorption is probably a valence shell excitation.[3] Photochemical studies of cyclopropane derivatives in solution have been limited to molecules in which a chromophore that is capable of absorbing at wavelengths >200 nm is attached to the ring.[4] The principal reaction is the cleavage of one bond to give a diradical. Cyclopropane and alkyl cyclopropanes have been studied[5] in the gas phase at wavelengths of 147 nm or less. The principal reactions under these conditions are fragmentations of various kinds the most important of which is a split to give a carbene and an olefin (eq 1). This represents the inverse of the usual
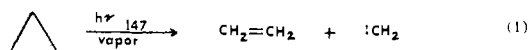
method of synthesis of a cyclopropane and requires the simultaneous or successive break of two of the C–C bonds in the cyclopropane ring. We show here that four hydrocarbons which incorporate a cyclopropane ring, on irradiation with 185-nm light in solution, undergo a parallel reaction with fewer side products.

Results on the photolysis of compounds 1–4 are listed in Table I. These experiments were carried out in pentane solution (~10^{-2} M) in a Suprasil tube with the unfiltered light from a mercury resonance lamp, the useful radiation being the line at 185 nm. Since the olefinic products absorb at this wavelength much more intensely than the reactants, the rates and yields are based on data obtained at low conversions (<10%) from gas chromatograms and extrapolated to zero time.

The reaction which corresponds to the scission of two of the three bonds in the cyclopropane ring (eq 2) is the most general
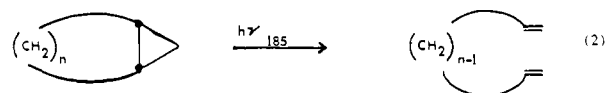
one and yields 33–95% of the products. Cyclic olefin formation which is the usual reaction that is associated with the cleavage of the strained internal bond of the cyclopropane assumes

[†] Dedicated to Professor E. Havinga on his 70th birthday.

Table I. Photolysis of [*n*.1.0]Alkanes at 185 nm

(solvent, pentane; unfiltered light from Hg resonance lamp)

Reactant	Cyclo-ene structure	Cyclo-ene Rate[a] of formation	α,ω-Diene Structure	α,ω-Diene Rate[a] of formation	Rel Rate[a] of Σ Products
[b] structure	structure	0.69	structure	0.90	0.49
[c] structure	none detected		structure	0.44	0.13
[d] structure	structure	2.31	[e] structure	1.08	1.00
[b] structure	[g] structure	0.20	structure	1.51	0.50[h]

[a] All rates in mol/s × 10^11. [b] Rate of disappearance of reactant = rate of Σ products. [c] Relative rate of disappearance = 0.67. [d] Relative rate of disappearance = 1.32. [e] This compound has been described by R. Srinivasan and K. H. Brown, *Tetrahedron Lett.*, submitted for publication. [f] The rate of cis → trans isomerization of *cis*-cyclooctene is set at 1.00 under the same conditions. [g] No *trans*-cyclooctene was observed. [h] <5% cycloheptene also formed.

importance with increasing strain in the molecule. The failure to find cycloheptene in the photolysis of **2** is puzzling and there is no explanation that can be offered at present.[6]

A reasonable mechanism for reaction 2 is an initial break of two bonds to give a carbene and an olefin at the two ends of a carbon chain followed by a rearrangement of the carbene. As mentioned before, this is the intramolecular equivalent of the reaction that has been invoked[5] in the gas-phase photolyses of a number of cyclopropanes at shorter wavelengths. In at
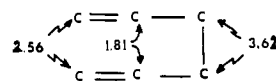
(2a)
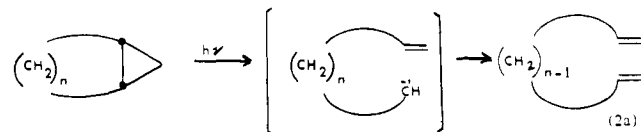
least two instances, it has been reported to occur in solution in certain cyclopropanes substituted with aromatic rings, when the unfiltered light from a mercury arc was used. Thus phenylcyclopropane[7] gave styrene and methylene while 9,10-dihydro-9,10-methanophenanthrene[8] gave phenanthrene and methylene. In contrast, cyclopropane attached to phenyl,[4a] styryl,[9] or carbonyl groups[10] and excited by radiation of wavelength 254 nm or longer underwent only scission at one C–C bond at a time. It is possible that, in the examples in ref 7 and 8, electronic excitation of the cyclopropane group was achieved.

To verify that the carbene mechanism proposed here does prevail, the photolysis of bicyclo[3.1.0]hexane-*6,6-d₂* (**5**) was undertaken. The content and distribution of deuterium in the products were determined by NMR spectroscopy. The cyclo-

hexene that was obtained after 20% decomposition of the reactant corresponded to 1.01 olefinic protons and 2.93 and 3.93 allylic and aliphatic protons respectively.[11] Therefore eq 3 would represent this reaction satisfactorily. The composition

(3)
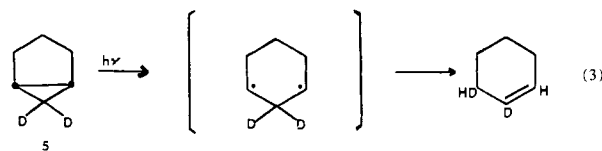
of the 1,5-hexadiene that was isolated corresponded to the proton distribution shown. This indicated that eq 2a represents only one of the possible mechanisms by which 1,5-hexadiene is formed and may account for 44–82% of it depending on the assumptions made with regard to the distribution of the deu-

terium.[12] A second labeling reaction was carried out using bicyclo[4.1.0]heptane-*7,7-d₂* (**6**).[11] It gave the following
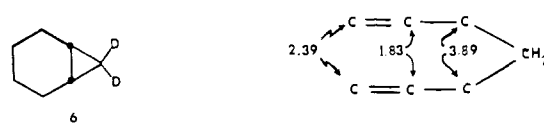
proton distribution in the 1,6-heptadiene that was isolated. This once again indicated that eq 2a was not the exclusive path by which this diene was formed. Additional labeling experiments on these compounds are necessary to establish the alternative mechanisms that are operative in these photolyses.

An interesting speculation that merits further analysis is whether the chronology of events is exactly as in eq 2a. Since carbenes add to olefins to generate cyclopropanes, the first step in this mechanism can be expected to be reversible. A stable product can be formed only when the carbene rearranges by a hydrogen migration. It is possible that the reaction is initiated by such hydrogen migration from C_2 to C_1, i.e., eq 4. It may explain why an alternative cleavage of the bicyclic compounds (eq 5) amounts to <5% of the decomposition.[13,14]
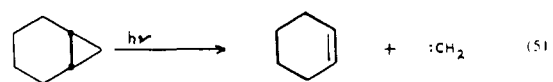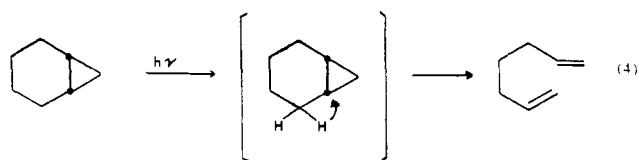
(4)

(5)

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(11) There was no evidence for scrambling of deuterium in the starting material after a portion had been photolyzed.

(12) The uncertainty arises from the fact that it is not possible to tell from the NMR spectrum what proportion of the following compounds make up the product: CD_2=$CHCH_2CH_2CH$=CH_2; CDH=$CDCH_2CH_2CH$=CH_2; CH_2=$CDCHDCH_2CH$=CH_2.

(13) Note that in ref 8 detachment of a CH_2 was achieved in solution phase photolysis, but irradiation was carried out in a medium which served as an effective trap.

(14) Products which would correspond to such a cleavage reaction (e.g., eq 5) were in no case positively identified. A limit to the extent of their formation was estimated from the limits of the analytical method.

R. Srinivasan,* Jose A. Ors

IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

Ketone Photoreactivity as a Probe of the Microenvironment: Photochemistry of the Surfactant Ketone 16-Oxo-16-*p*-tolylhexadecanoic Acid in Monolayers, Micelles, and Solution[1]

Sir:

There has been considerable recent interest in the structure and properties of organized media such as micelles, lipid vesicles, bilayers, and monolayers which are formed by the self-organization of amphipathic molecules.[2-5] A number of techniques have been used as structural probes including fluorescence and other photophysical phenomena.[6-10] Our own work in this area has focused on several photochemical reactions occurring in monolayer films, deposited monolayer assembles, and micelles.[11-13] Most of our previous studies have involved relatively polar chromophores which occupy hydrophilic sites. Recently we have investigated a number of surfactant molecules having a potentially reactive chromophore in a more hydrophobic region. In the present paper we report an investigation of the photoreactivity of the surfactant ketone 16-oxo-16-*p*-tolylhexadecanoic acid (**1**) in monolayer assemblies, anionic micelles, and solution. The results indicate that the microenvironment can produce striking changes in reactivity. Thus we find the characteristic solution process—the type II photoelimination—is effectively eliminated in the highly condensed monolayer assemblies but enhanced compared with hydrocarbon solution in the more fluid micelles.

Ketone **1** was synthesized by Friedel-Crafts reaction of toluene with the acid chloride of methyl hydrogenhexadecanedioate, followed by saponification of the methyl ester to a white solid, mp 95–96 °C. Surface pressure–area isotherms of ketone **1** were obtained by spreading 10 μL of a 5×10^{-3} M chloroform solution of the ketone on a clean water surface ($CdCl_2$·$NaHCO_3$) in a circular trough,[14] and then reducing the area of the film by means of a mobile barrier while recording the pressure and area of the film. Films composed of pure **1** were characterized by gradual increases in surface pressure on compression, followed by collapse at relatively low pressure ($\sim$10–15 dyn/cm). In contrast, an equimolar mixture of **1** and arachidic acid ($CH_3(CH_2)_{18}CO_2H$) provided a film
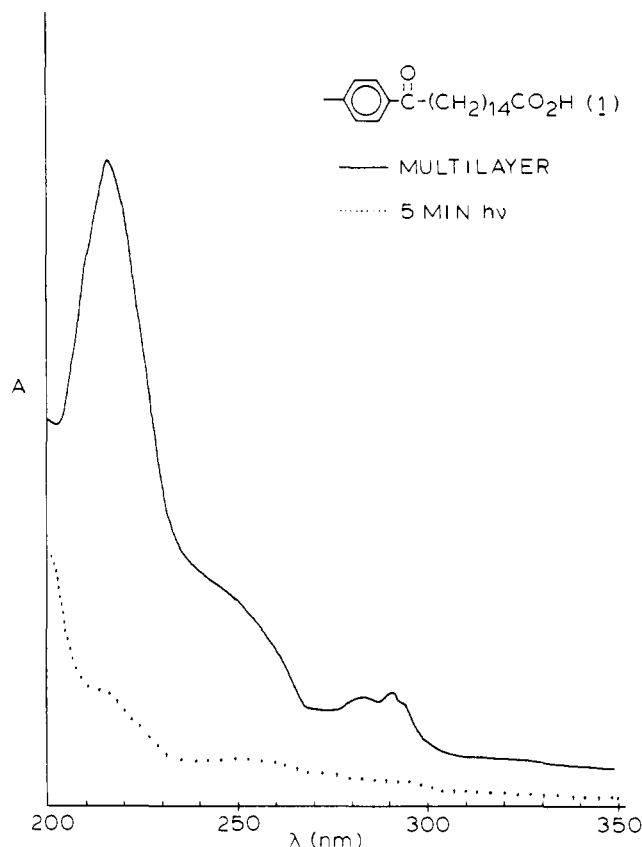

Figure 1. Absorption spectrum of surfactant ketone **1** in an assembly consisting of 12 layers of 1:1 ketone **1**-arachidic acid: solid line, ketone before irradiation; dotted line, spectrum after 5-min irradiation at 290 nm.

which gave a rapid increase in surface pressure at a molecular area of $\sim$20 Å^2/molecule and no collapse at less than 30 dyn/cm. This behavior is typical of a "condensed" fatty acid monolayer.

Monolayer assemblies were easily constructed from the mixture of **1** and arachidic acid by the usual techniques.[6,13] Quartz slides were employed as a support for the assemblies in order that the subsequent reactions of the ketone could be followed by UV spectroscopy.

Generally multilayer assemblies consisting of 12–16 total layers were used in this study. These assemblies gave good UV spectra from which the photoreaction could be easily monitored. Irradiation of the assemblies at 254 or 290 nm resulted in rapid bleaching of the long wavelength absorption (Figure 1). That the observed reaction involves destruction of the carbonyl chromophore was verified by IR spectroscopy. The surface of an aluminum slide was rendered hydrophobic with a thin coating of paraffin and coated with 100 layers of a 1:1 ketone–arachidic acid mixture. A reflectance attachment was used to measure and record the IR spectrum from the slide. The aromatic carbonyl peak (1680 cm^{-1}) and carboxylate carbonyl peak (1540 cm^{-1}) were easily detected and upon irradiation of the assembly the aromatic carbonyl peak was observed to diminish in intensity relative to the carboxylate peak until it could no longer be resolved from the baseline.

Gas chromatographic analysis was employed to determine if volatile products such as *p*-methylacetophenone (from type II cleavage), tolualdehyde (from α cleavage), or toluene (from α cleavage followed by decarbonylation) were formed during the reaction. Irradiation was carried out at 254 nm in a closed quartz cell containing a monolayer assembly and a small amount of hexane to dissolve any volatile materials released from the assembly upon photolysis. Several assemblies were