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PHOTOCHEMISTRY OF 2-ACETO-2-METHYLMETHYLENECYCLOHEXANES

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Direct irradiation of β,γ-unsaturated ketones with accessible allylic γ-hydrogens has been reported to yield intramolecular γ-hydrogen abstraction,[1] intramolecular cycloaddition[1e] and 1,3-acyl shift and α-cleavage processes.[1a,b,f] As part of a study of the effect of stereochemistry on the relative photoreactivity of β,γ-unsaturated ketones toward these processes, we describe the solution photochemistry of 2-aceto-2-methylmethylenecyclohexane, 1, in which the acetyl group can be equatorial or axial, and trans-2-aceto-2-methyl-4-t-butylmethylenecyclohexane, 2, in which the acetyl group is held equatorial. In a related study, Lewis and Johnson have recently noted that α-methylcyclohexyl phenyl ketone undergoes predominantly intramolecular transannular hydrogen abstraction when the benzoyl group is axial and α-cleavage when the benzoyl group is equatorial.[2]

Irradiation[3] of a solution of 1 in benzene (0.6M) for seven hours results in greater than 95% loss of starting material and a 55% yield of two products, 3 and 4 in a ratio of 3.2 to 1.0.[4] Products 3 and 4 are purified by preparative glpc[4] and assigned the structures shown in equation 1 based on analogy and the following data: 3, an oil, ir (CCl_4) 3650, 3500, and 1660 cm^{-1}; nmr (CCl_4, 60MHz, δ) 0.8-3.1 (m, 15H, with singlets at 1.13, 1.24 and 1.5, last concentration dependent), 5.28 (m, 1H); mass spectrum (70 eV), m/e (rel intensity) 152 (M^+, 5); 4, a solid, mp 74-5°, ir (CCl_4) 3600, 3450, 1645 and 900 cm^{-1}; nmr (CCl_4, 60 MHz, δ) 0.9 (s, 3H), 1.05 (s, 3H), 1.2 (s, 1H, concentration dependent), 1.4-2.75 (m, 7H), 4.68 (m, 2H); mass spectrum (70 eV), m/e (rel intensity) 152 (M^+, 18).

Both of the products are clearly alcohols isomeric with 1. The nmr and ir olefinic absorptions provide strong evidence for the presence of an endocyclic double bond in 3 and an exocyclic double bond in 4. Stereochemistry has not been determined in 3.[5] Cyclobutanol 4 is assigned the stereochemistry shown because the presence of the methyl group in the shielding cone of the exocyclic double bond rationalizes the methyl being shifted upfield to δ1.05 or above.[6] The absence of methyl singlets downfield from δ1.05 also argues against structure 5 for the exocyclic methylenecyclobutanol. We observe no formation of the 1,3-acyl shift product, 6, whose photochemistry we have investigated previously,[1g,8] or intramolecular cycloaddition products.

Formation of both 3 and 4 can be rationalized by an initial intramolecular transannular allylic γ-hydrogen abstraction generating a long-lived 1,4-biradical intermediate, 7, which can subsequently close at either end of the allylic system. We have recently demonstrated that intramolecular allylic γ-hydrogen abstraction in β,γ-unsaturated ketones can generate a 1,4-biradical intermediate with a lifetime long relative to the rate of rotation about the α,β-bond.[1g] Clearly, the transannular hydrogen abstraction must take place from the chair conformation 1a, in which the acetyl group is axial and thus able to reach the γ-hydrogen. When the acetyl group is equatorial (1b) there are no accessible reactive γ-hydrogens.[9]

In order to determine the effect of constraining the 2-acetyl group equatorial on the methylenecyclohexane, we have also studied the photochemistry of trans-2-aceto-2-methyl-4-t-butylmethylenecyclohexane, 2. Irradiation of a solution of 2 in benzene (0.5M) for 3.5 hours results in $\geq$98% loss of 2 and formation of 8 (13%) in addition to polymer and several minor products. The structural assignment of 8 is based on the following spectral data: ir (CCl_4) 950 cm^{-1}; nmr (CCl_4, 60MHz, δ) 0.5-2.3 (m, 22H, with singlets at 0.82, 1.2 and 1.48), 3.7 (d, J_{ab} = 6 Hz, 1H), 4.1 (d, J_{ab} = 6 Hz, 1H); mass spectrum (70 eV), m/e (relative intensity) 208 (M^+, 2), 193 (20), 165 (22), 109 (74) and 57 (100). Particularly pertinent is the absence of any double bond or hydroxyl stretch in the ir and vinyl C—H absorption in the nmr. The alternative oxetane structure, 9, which would arise from a crossed 2 + 2 addition, would not be expected to have methylene absorption as far downfield as δ3.9, since it has no hydrogens on carbons α to oxygen.[10] The tricyclic oxetane, 8, is found to be quite heat sensitive, undergoing some rearrangement at glpc temperatures greater than 150°C to starting ketone 2.

It is clear that the photochemistry observed from 2-aceto-2-methylmethylenecyclohexanes is strongly dependent on whether the acetyl group is equatorial or axial. Intramolecular hydrogen abstraction occurs when the acetyl group is axial and intramolecular cycloaddition when it is equatorial. Although the enone is well set-up for the intramolecular hydrogen abstraction when the acetyl group is axial, the complete absence of any 1,3-acyl shift product in this case is surprising. One might anticipate that if the transition state for the 1,3-acyl shift involves partial cleavage of the carbonyl carbon α-carbon bond, 2-acetomethylenecyclohexanes in which the acetyl group is axial would be quite reactive toward the 1,3-acyl shift process. An axial acetyl group allows for maximum delocalization of the developing radical center at the α-carbon as the α-cleavage occurs (see 10). We observe, however, that even when 1 is in the best conformation (1a, acetyl axial) for facilitating α-cleavage through allylic stabilization, the 1,3-acyl shift is still unable to compete with intramolecular transannular γ-hydrogen abstraction. When the 2-acetyl group is equatorial (1b or 2) the β,γ-enone is in the syn, syn configuration which should be required for intramolecular cycloaddition.[11] Clearly in this geometry the reactivity toward intramolecular cycloaddition must be much greater than that toward the

1,3-acyl shift. For 2-aceto-2-methylmethylenecyclohexanes, an equatorial acetyl group provides minimum allylic resonance stabilization of α-cleavage processes.

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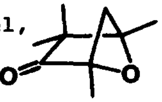
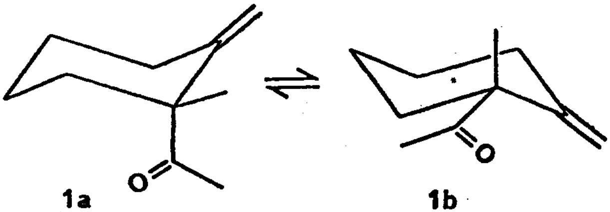
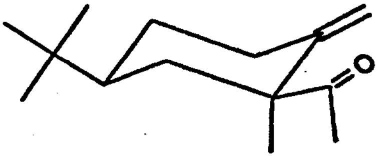
2. F. D. Lewis and R. W. Johnson, *J. Amer. Chem. Soc.*, **94**, 8914 (1972).
3. All irradiations are done in quartz test tubes using a 450 watt medium pressure mercury lamp with a quartz well.
4. All reactions are analyzed and products isolated by glpc using either a 10' x ¼" 5% Carbowax 20M on Chromosorb W 45/60 column or a 9' x ¼" 10% SE30 on Chromosorb W 60/80 column.
5. We have also assigned this structure to a minor photoproduct of 2-methyl- and 6-methyl-1-cyclohexenylacetone which has methyl singlets at δ1.35 and 1.18.[1g] Different stereoisomers must be produced by the different routes to **3**.
6. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, 1969, p. 83-88.
7. Normally absorption for a methyl attached to a carbon containing a hydroxyl appears in the region of δ1.20 (R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc. New York, New York, 1967).
8. The major photoproducts which would result from secondary photolysis of **6** are also absent.
9. There are no reports of intramolecular abstraction of vinyl hydrogens by n,π* excited states of ketones.
10. In a model,  methylene hydrogen absorption occurs in the region of δ2.5 (R. Bishop, N. K. Hammer, *J. Chem. Soc. C*, 1197 (1970)).
11. H. E. Zimmerman, P. Baeckstrom, T. Johnson and D. W. Kurtz, *J. Amer. Chem. Soc.*, **94**, 5504 (1972).



1a 1b



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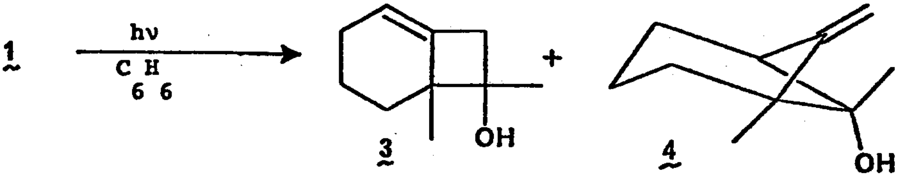
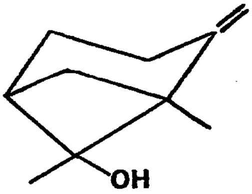
(1)





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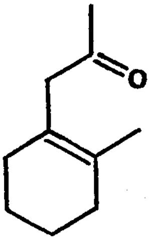

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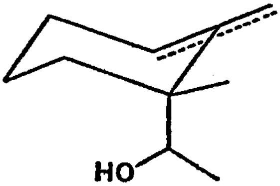

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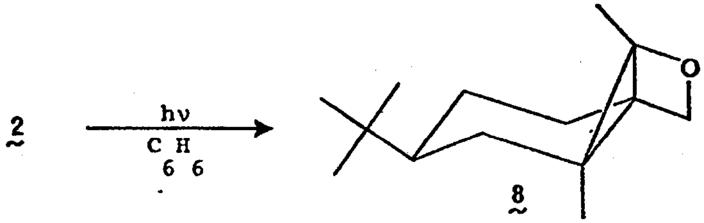
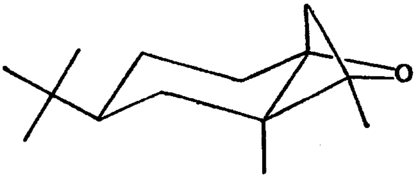
(2)





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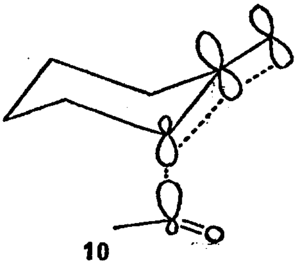

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