

COMPARATIVE PHOTO- AND THERMAL CHEMISTRY
OF BICYCLO[3.2.0]HEPT-2-EN-6-ONE

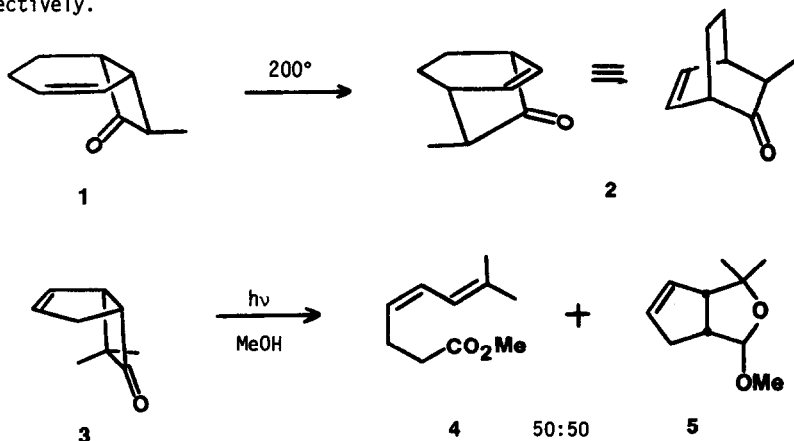
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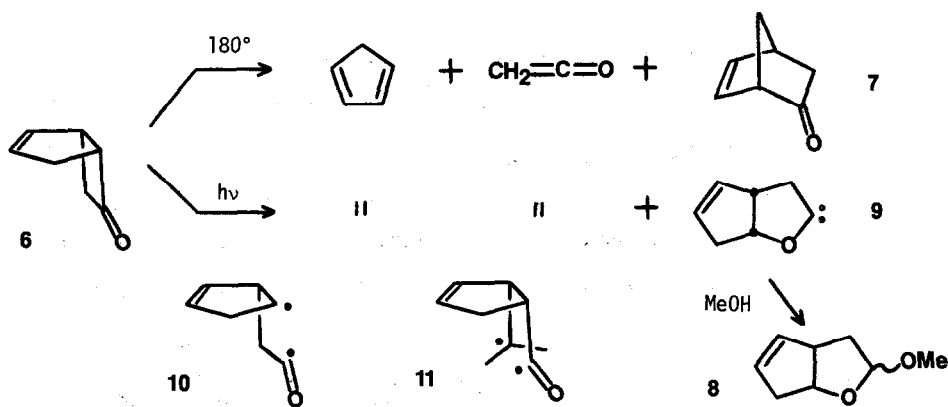
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Considering the recent interest in the thermal rearrangement of 8-methyl bicyclo-[4.2.0]-oct-2-en-7-one ($\underline{1} \rightarrow \underline{2}$) and similar compounds¹ and in the photocleavage and ring expansion of cyclobutanones (e.g., $\underline{3} \rightarrow \underline{4}$ and $\underline{5}$),^{2,3} we would like to report for comparison our findings concerning the pyrolysis and photolysis of the "parent" ketone $\underline{6}$, for which, aside from ketene retrogression, thermal and photochemical patterns are sharply divergent, leading to 1,3 sigmatropic shift and regiospecific cyclobutanone ring expansion, respectively.



Solutions of **6** (20%) were pyrolyzed in medium-walled pyrex nmr tubes in basewashed o-dichlorobenzene at 180°. Cracking to give cyclopentadiene was indicated by nmr analysis, and glc comparison of pyrolysates with authentic olefin confirmed its appearance. Methyl acetate resulting from the trapping of ketene was identified as a major product of pyrolysis in the presence of methanol. The rate of disappearance of starting ketone in o-dichlorobenzene was first order through one half-life and $k = 9.7 \pm 0.7 \times 10^{-5}$ sec (178°). The cycloreversion to give ketene and cyclopentadiene accounted for about 90% of decomposition. A minor product (5% based on unrecovered starting material) displayed glc retention properties identical to independently synthesized⁴ ketone **7**.



Photolysis of 0.05 M solutions of **6** in methanol with a trace of NaHCO₃ using 450 W immersion apparatus and pyrex filter gave cyclopentadiene, methyl acetate, and a pair of acetals **8** (ratio 60:40). The latter were obtained in pure form by preparative glc and identified by elemental analysis, and ir and nmr spectral data,⁵ with strong analogy to photoproducts of other cyclobutanones.^{2,3} The ratio according to glc analysis of photolytic cracking to acetal formation was 4:1. Parallel irradiations (Rayonet Reactor, 313 nm band maximum, pyrex tubes) of **6** in methanol and in the presence of 2,5-dimethyl-2,4-hexadiene (0.25-1.0 M) revealed that neither photoreaction was retarded by a conventional triplet quencher.

The thermally induced ketene retrogression of 6 in the gas phase has been previously reported,^{6a} and the apparent rate acceleration (10X) due to favorable interaction with solvent is consistent with the suggested semipolar concerted mechanism.⁶ Formation of 7 via a concerted pericyclic pathway is probable considering the impressive stereospecificity for the transformation 1 → 2.¹

Photochemical cracking and ring expansion yielding a carbene intermediate (e.g., 9) is well precedented.³ A mechanism involving an n, π^* singlet (or unquenchable triplet) excited species leading directly to product or via an extremely short-lived diradical seems reasonably secure³ and applicable for 6. The point here is the effect of structure on reactivity (comparing cycloreversion and ring expansion modes for 3 and 6) in which it is apparent that regioselectivity may be firmly predicted on the basis of preferred leading α -cleavage at most highly substituted carbon. Although this has been pointed out,³ we provide here an example of a complex (bicyclic) cyclobutanone in which more subtle factors might have supervened.⁷ Interestingly, while ease of α -cleavage appears to control the direction of ketene retrogression and ring enlargement the balance of these (compare product ratios for 3 and 6) may depend on the predilection for cleavage of the remaining bond to give olefin. The nucleophilicity³ of the carbon migrating to e -deficient oxygen to give carbene in diradicals 10 and 11 may be similar; but if these transition states or intermediates approximate starting material geometries, cleavage to olefin and ketene will be favored for 10 due to orbital overlap factors (interaction with olefin portion).⁸

While it is tempting to suggest that S_0 and S_1 potential surfaces merge early to give the cycloreversion products common to pyrolysis and direct photolysis of 6, the pathways not in common reveal that substantially different geometries may be explored before reaching a "funnel" in which ground and excited configurations are mixed.⁹ Our results and data for 3¹⁰ indicate that energy is quite specifically localized for these bicyclic systems in the weak allylic bond on the one hand (thermal activation) and the bond to α carbon on the other (photochemical activation).¹¹

ACKNOWLEDGMENTS

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4. P.K. Freeman, D.M. Balls, and D.J. Brown, J. Org. Chem., **33**, 2211 (1968).
5. For the major acetal the nmr data are: (CCl₄) δ 1.5-2.6 (m, 5H, methylene and methine groups), 3.22 (s, 3H, -OMe), 4.10 (m, 1H, C₅ methine), 4.65 (pseudo doublet, 1H, acetal hydrogen) and 5.55 (m, 2H, olefinic hydrogens). Doping with Eu(Fod)₃ shifts strongly those resonances (5H) assigned to H adjacent to O. The stereochemistry at C₈ has not been assigned.
6. (a) K.W. Egger and A.T. Cocks, J.C.S. Perkin II, 2014 (1972); (b) K.W. Egger, J. Amer. Chem. Soc., **95**, 1745 (1973).
7. R.D. Miller and V.Y. Abraitys, J. Amer. Chem. Soc., **94**, 663 (1972).
8. J.A. Berson and R.S. Wood, ibid., **89**, 1043 (1967).
9. J. Michl, Mol. Photochem., **4**, 243 ff (1972).
10. Thermal cracking of 3 to give dimethylketene and cyclopentadiene has been reported.^{6b}
11. Photochemical 1,3 shift and thermal α cleavage resulting in isomerization via H transfer are formal possibilities but unobserved here for 6. For comparison see R.L. Cargill, et al., J. Amer. Chem. Soc., **92**, 3809 (1970) and P. Schiess and P. Funfschilling, Tetrahedron Lett., 5191 (1972).