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PHOTOISOMERIZATION OF CIS-VERBANONE IN METHANOL

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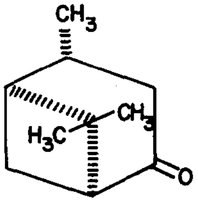
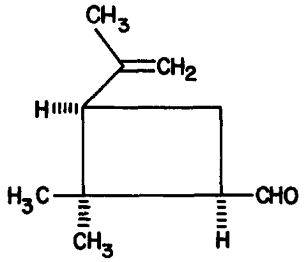
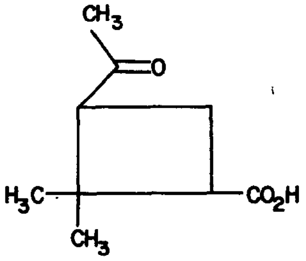
The major product upon photolysis of cycloalkanones in solution generally results from preferential photoinduced cleavage adjacent to the more highly substituted α-carbon(1). Other than for cyclic cyclopropyl ketones, which are known to form a special class and usually cleave on the side of the carbonyl group remote from the three membered ring, only two exceptions to this generalization appear to have been reported (2, 3, 4). Both involve α-ketocyclobutane systems and one such exception cis-verbanone (I) is reported to give the unsaturated aldehyde II as the only significant product upon photolysis(2). We were intrigued by the reason for this 'abnormal' behavior especially since the p.m.r. spectral data reported in support of II assigned the vinyl hydrogens of its semicarbazone derivative to a multiplet at δ 6.65 ppm., more nearly in accord with the range expected for cyclobutene olefinic protons.

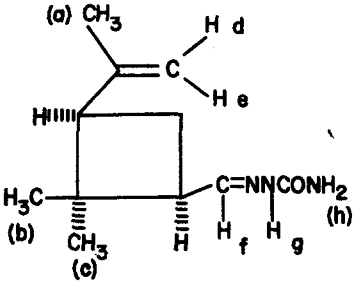

I


II


III

The photolysis of a methanol solution of (±)cis-verbanone in a quartz tube (5) was repeated but gave two unsaturated aldehydes in a ratio of 7:1. The important signals of the p.m.r. spectrum of the semicarbazone (m.p. 176-178°) of the major isomer are listed in the Table and are clearly consistent with the assigned structure although they differ considerably from those reported by Matsui.

The assignment of the cyclobutyl methyl signals has been reversed in accord with previous work on pinene derivatives(6) and the semicarbazone hydrogen resonances verified by D_2O exchange and comparison with other systems. The chemical shifts and multiplicities of the vinyl methyl and vinyl hydrogen signals for both the semicarbazone and the aldehyde (aldehydic hydrogen doublet J=1.7 Hz) provide additional support as does the infrared spectrum of II $\nu_{max}^{CCl_4}$ 2800,2705,1720, 1640cm^{-1}; (Matsui)2618,1701,1639cm^{-1}(recording conditions not reported).



TABLE

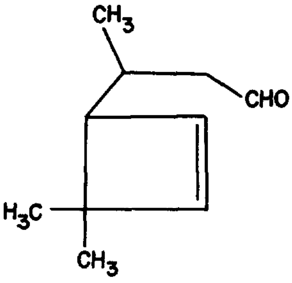
Protons	δ^{CDCl_3}(sparingly soluble)	Matsui δ^{CCl_4}
a	1.68(3H,br s)	1.65(3H,br s)
b	0.84(3H,s)	1.27(3H,s)
c	1.24(3H,s)	0.89(3H,s)
d	4.67(1H,br s,$w_{\frac{1}{2}}$=5Hz)	6.65(2H,br q)
e	4.89(1H,br s,$w_{\frac{1}{2}}$=6Hz)	
f	7.14(1H,d,J=5.7Hz)	4.38(1H,br s)
g	*10.12(1H,br s)	
h	*5.92(2H,br s)	9.02(2H,br s)

*Signals disappear on shaking with D_2O

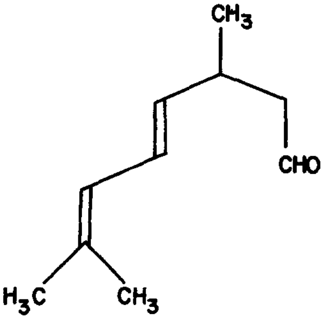
Ozonolysis of II followed by oxidation with Jones' reagent gave cis-pinononic acid(III)(7) which was identical (spectra, mixed m.p.) with an authentic sample prepared from (±)verbenone (4,6,6-trimethylbicyclo[3·1·1]hept-3-en-2-one) and firmly established the structure of the major photolysis product.

The minor isomer is assigned the cyclobutene structure IV. This assignment is supported by the spectral data $\nu_{max}^{CCl_4}$ 2810sh, 2710, 1730, 1640 cm^{-1}; δ^{CCl_4} 6.09 (2 vinyl H,m), 9.78(aldehydic H,t,J=2Hz) and was further established by thermally induced conrotatory ring opening to give the octadienal V, δ^{CCl_4} 1.11(3H,d,J=6.5Hz), 1.73(6H,s), 2.78(1H, quintet, J=6.5Hz), 2.35 (2H, m), 5.40 (1H, d of d, J=6.5, 15Hz), 5.70(1H, d of br s, J=10.5Hz), 6.21 (1H, d of d, J=10.5, 15Hz), 9.73 (1H,t,J=2Hz).

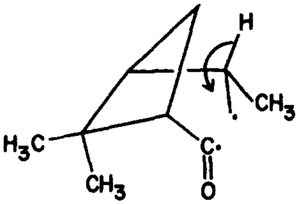
The preferential photolytic formation of II was previously rationalized on the basis of orbital overlap and the suggestion that β-hydrogen atom migration was probably concerted with ring cleavage to give the cyclobutane product directly(2). However, in the light of evidence that diradicals are discrete intermediates for Norrish Type I cleavage reactions(8), this may be an oversimplification.



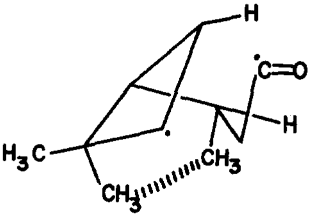
IV



V



VI



VII

Examination of molecular models (Dreiding, Prentice-Hall) suggests that steric interactions may be partially responsible for the preferential formation of II. Cleavage of _cis_-verbanone on the side of the carbonyl group remote from the four membered ring requires only a slight rotation to permit product formation (_cf_.VI) while the opposite cleavage gives an intermediate VII which must adopt a conformation possessing nearly a 1,3-diaxial methyl-methyl interaction in order for hydrogen abstraction to proceed to give the cyclobutene aldehyde IV. This is probably sufficient to permit reclosure to I to compete efficiently and to minimize the formation of III. Thus photolysis of suitable bicyclic ketones with this non-bonded interaction removed should afford increased amounts of cyclobutene aldehydes. This is the case for nopinone[4] although the product from cleavage of the least substituted α-bond still predominates.

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3. P.J. Nelson, D. Ostrem, J.D. Lassila, and O.L. Chapman, J. Org. Chem., 34, 811 (1969).
4. Nopinone also belongs in this category, A.G. Fallis, unpublished results; we thank Professor N.J. Turro, Columbia University, for informing us of his parallel studies on nopinone and recently another report has appeared; G.W. Schaffer, A.B. Doerr, and K.L. Parzyck, J. Org. Chem., 37, 25 (1972).
5. Irradiations were conducted with a Hanovia 450W medium-pressure mercury arc lamp on solutions (ca. 0.1M) which contained ca. 1 mg. anhydrous $NaHCO_3$ per ml. of solution to prevent ketal and acetal formation.
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