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PHOTOCYCLIZATIONS OF 5-ACYLNORBORNENES; A SYNTHESIS OF TRICYCLO [3.3.0.0^{3,7}]OCTAN-2-OLS

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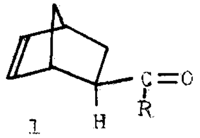
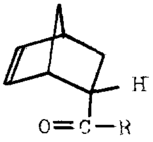
A study of the photochemistry of 5-acylnorbornenes (1 and 2) has been initiated with the hope of providing information of stereochemical and structural relevance to the three major photoprocesses characteristic of γ,δ-unsaturated ketones: intramolecular oxetane formation,[2,3,4] intramolecular energy transfer,[4] and sigmatropic rearrangement.[5] Reported herein are the chemical results of this investigation. Subsequently, some aspects of the photochemical processes will be detailed.



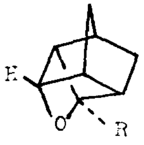
1



2

Irradiation of a 5% solution of 2 (R = CH_3) in de-oxygenated benzene with a medium pressure mercury lamp (Pyrex filter) led to the production of a single new volatile product. Isolation of this material by preparative gas chromatography yielded a colorless oil which did not show significant absorptions in the hydroxyl and carbonyl regions of the infrared spectrum. The appearance of a moderately strong absorption band at 10.2 μ was suggestive of an oxetane system.[6] This conclusion was strengthened by the appearance of a quartet (1 H) at δ4.43

in the nmr spectrum. The spectral data are thus consistent with oxetane 3 or 4. The results of degradative experiments described below can be derived only from structure 3.



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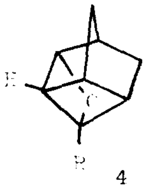
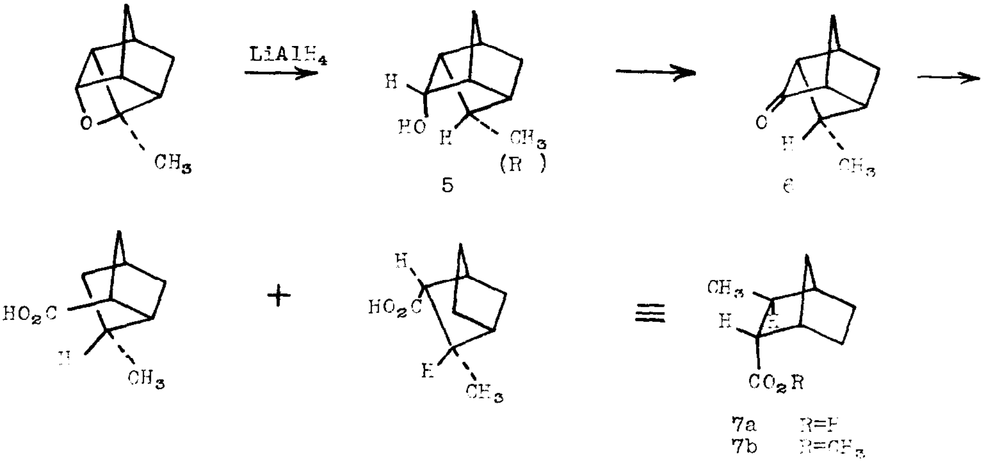


4

Reductive cleavage of the oxetane with lithium aluminum hydride in refluxing N-ethylmorpholine produced a secondary alcohol,[7] m.p. 29.5-30.5°, as shown by the appearance of doublets at δ3.71 (H-C-O proton, J= 3 cps) and δ0.90 (CH_3 protons, J = 7 cps) in the nmr spectrum. Chromic acid oxidation of the alcohol produced a ketone ($\lambda_{CCl_4}^{C=O}$ 1754 cm^{-1}); 2,4-DNPH, m.p. 165.5-166°, which could be cleaved by potassium t-butoxide[8] to an equimolar mixture of two carboxylic acids. Identification of one of these as 3-exo-methylnorbornane-2-endo-carboxylic acid (7a) was accomplished by conversion of the mixture to methyl esters (via CH_2N_2) followed by gas chromatographic separation and direct comparison of the ester 7b with an authentic sample.[9] The structures of the intermediate ketone (6) and alcohol (5) are thus established beyond doubt.



Similarly,[10] the following derivatives of 2 have been prepared[11] and photocyclized: R = H, CH_2CH_3, $CH_2C_6H_5$, C_6H_5, α-$C_{10}H_7$. The close resemblance of the nmr spectra of the oxetanes so produced suggests that they all have the same basic structures as 3 (see Table I). In addition, the oxetanes could be converted to the corresponding tricyclo $[3.3.0.0^{3,7}]$ octanols by lithium aluminum hydride reduction or by Raney nickel-catalyzed hydrogenolysis in the aromatic cases. The carbinol proton in each case appeared as a closely spaced doublet (J = 2-3 cps).

TABLE I

Physical Properties of Oxetanes and Alcohols (3 and 5)

	Oxetanes		Tricyclo$[3.3.0.0^{3,7}]$octanols	
R =	m.p. or b.p.	δ (ppm) O-C-H	m.p. or b.p.	δ (ppm) O-C-H
CH_3	60°(10 mm)	4.43	29.5-30.5°	3.71
CH_2CH_3	106°(48 mm)	4.48	150-168°(30 mm)	3.77
$CH_2C_6H_5$	89-91°(0.75 mm)	4.44	175-180°(26 mm)	3.62
H	136-137.5°	4.58*	134-135°	3.83
C_6H_5	+	4.53	88-89°	3.82
α-$C_{10}H_7$	+	4.68	174-175°	3.98

*sextet, relative area equal to two protons

+decomposed on attempted purification

It was anticipated that sigmatropic rearrangement would be the major, if not exclusive, photoreaction of the exo-systems. Unfortunately, irradiation of 1 (R=CH_3) under the above conditions led to no new volatile products but instead to a slow consumption of starting material. Apparently, intermolecular processes competitively destroyed the starting ketone.

In summary, a novel series of oxetanes and alcohols has been produced from 5-acylnorbornenes. The facile photocyclization of the α-naphthyl ketone 2 (R = α-$C_{10}H_7$) is of particular interest owing to the known inertness of naphthyl ketones in intermolecular oxetane reactions.[12]

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6. S. Searles, Jr. in "Heterocyclic Compounds with Three- and Four-membered Rings, Part II, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., Chap. IX.
7. This unexpected result attests to the inertness of the oxetane ring toward nucleophilic cleavage; cf S. Searles, E. F. Lutz, and M. Tamres, J. Am. Chem. Soc., **82**, 2932 (1960).
8. P. G. Gassman and F. V. Zalar, ibid., **88**, 2252 (1966).
9. We are indebted to Prof. J. Berson for an infrared spectrum of this material.
10. Preparative scale experiments were carried out on *exo*-*endo*-mixtures. The oxetanes (20-50%) were isolated by distillation or sublimation after removal of unreacted starting material by washing with dilute $KMnO_4$.
11. The benzyl, phenyl, and naphthyl ketones were prepared by addition of the appropriate Grignard reagent to 2 (R=H) followed by chromic acid oxidation.
12. N. C. Yang, Pure Appl. Chem., **9**, 591 (1964).