

PHOTOCHEMICAL SYNTHESIS OF A 2,5-DIOXABICYCLO[2.2.0]HEXANE

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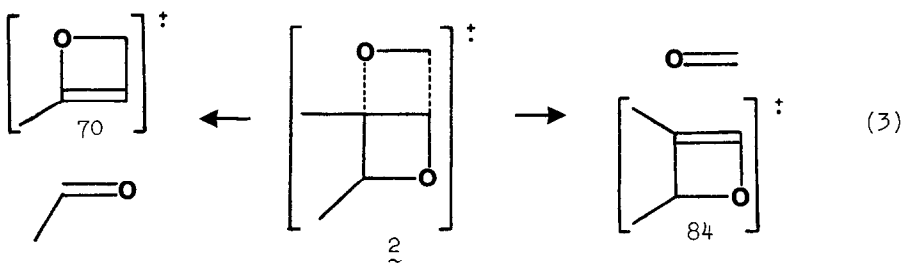
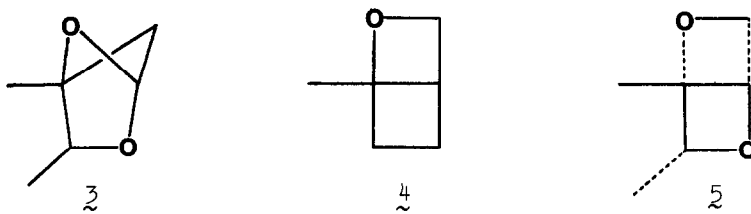
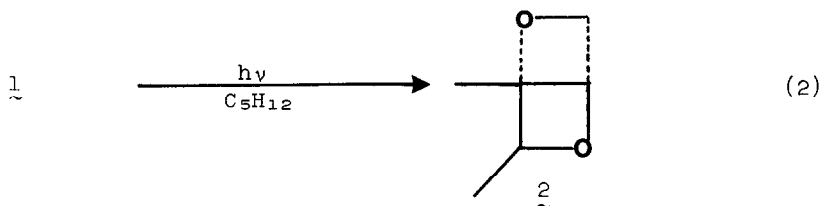
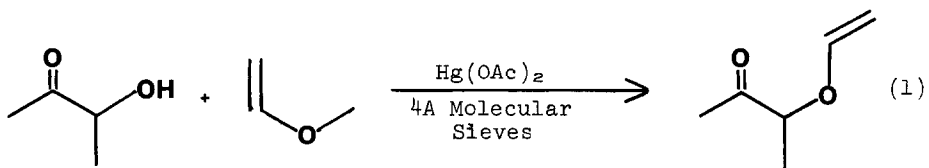
(Received in USA 2 July 1973; received in UK for publication 3 September 1973)

We report that irradiation of 3-methyl-4-oxa-5-hexen-2-one, 1, yields cis-1,6-dimethyl-2,5-dioxabicyclo[2.2.0]hexane, 2, the first 2,5-dioxabicyclo[2.2.0]-hexane to be reported.¹

1 was prepared in 39% yield² by a transesterification reaction³ between 3-hydroxy-2-butanone and methyl vinyl ether (eqn. 1). The structure of 1 is based on the following data: nmr (60 MHz, CCl₄, δ) 1.3 (3 H, d, J = 7 Hz), 2.1 (3 H, s), 4.03 (3 H, m), 6.3 (1 H, m); ir (CCl₄) 1709 and 1626 cm⁻¹; m/e (rel intensity) 114 (M⁺, 34), 71 (49), 45 (94), 43 (100); calcd for C₆H₁₀O₂: C 63.14%, H 8.83%, found: C 63.11%, H 8.92%.

Irradiation of a 0.09 M solution of 1 in pentane through Pyrex using a 450 watt medium pressure mercury lamp for 6 hr results in 70% loss of starting enone and a 40% yield² of product 2 in addition to polymer (eqn. 2). The structural assignment of 2 is based on the following data: nmr (100 MHz, CCl₄, δ) 1.26 (3 H, d, J = 7 Hz), 1.30 (3 H, s), 4.7 - 5.28 (4 H, m); ir (CCl₄) 960 cm⁻¹; m/e (rel intensity, empirical formula), 84 (6.1, C₅H₈O), 83 (5.1, C₅H₇O), 71 (30, C₄H₇O), 70 (28, C₄H₆O), 55 (100), 45 (30), 43 (80); calcd for C₆H₁₀O₂: C 63.14%, H 8.83%, found: C 63.12%, H 8.88%.

Particularly pertinent is the lack of any ir absorption in the C=C or C=O region (1600 - 1800 cm⁻¹) and the presence of absorption in the characteristic region for oxetanes around 950 cm⁻¹.⁴ A 100 MHz nmr spectrum in deuterobenzene shows a quartet (J = 7 Hz) integrating for 1 H at δ 5.28 assigned to the C₆ methine hydrogen and a 3 H multiplet between δ 4.55 and 4.85.⁵ The alternative intramolecular cycloaddition product, 3, would be expected to show methylene nmr absorption in the δ 2.5 region⁶ and can thus be eliminated as a possible structure. The absence of a parent peak in the mass spectrum is not uncommon for ox-



etanes.⁷ The empirical formulas given for the fragmentation products were obtained from a high resolution mass spectrum⁵ and suggest that the molecular ion of 2 fragments into inter alia oxetenes and aldehydes (see eqn. 3).⁸ The stereochemistry assigned to 2 is based on a comparison of the nmr spectra of 2 and 5 (vide infra) and should be considered tentative.


Although fluorescence is normally observed for alkyl ketones, 1 does not fluoresce, suggesting that 2 is formed by intramolecular cycloaddition occurring in the excited singlet state. Analogous intramolecular cycloadditions have been observed previously for acyclic γ,δ -unsaturated ketones.⁹ Srinivasan, for example, reported in 1959 that irradiation of 5-hexen-2-one yields 1-methyl-2-oxabicyclo[2.2.0]hexane, 4.^{9a}

Flow pyrolysis of 2 at 360° over Pyrex beads results in formation of 1 as the major product accompanied by small amounts of both 5 and an unidentified aldehyde. A tentative structure assignment for 5 is based on the following spectral data: nmr (100 MHz, CCl₄, δ) 1.40 (3 H, s), 1.44 (3 H, d, $J = 7$ Hz), 4.64 - 5.12 (4 H, m); ir (CCl₄) 960 cm⁻¹; m/e (rel intensity) 96 (13), 95 (11), 84 (4), 83 (3), 81 (11), 71 (33), 70 (53), 55 (100), 45 (36), 43 (72). The nmr and ir of 2 and 5 are very similar suggesting that 5 is an isomer of 2. The stereochemistry of 2 and 5 can then be assigned on the basis of the chemical shifts of the methyl singlets. The C₁ methyl in 2 (δ 1.30) appears at higher field than the C₁ methyl in 5 (δ 1.40) due to shielding by the adjacent cis carbon-methyl bond at C₆.¹⁰ The thermal isomerization from 2 to 5 presumably occurs through initial cleavage of the central C₁-C₄ bond followed by ring flip and closure. A similar mechanism has been recently postulated to explain the competitive isomerization and cleavage which is observed upon pyrolysis of bicyclo[2.2.0]hexanes.¹¹ Further experiments investigating the chemistry of this novel heterocyclic system are in progress.

References

1. A 2,5- or 2,6-dioxabicyclo[2.2.0]hexane structure has been suggested for a product resulting from photoaddition of benzophenone to tetramethyl oxetene (G. B. Schuster, Ph.D. Thesis, 1971, University of Rochester, Rochester, New York). Since completion of our work L. E. Friedrich and J. D. Bower

have isolated 1,4-dimethyl-3,6-diphenyl-2,5-dioxabicyclo[2.2.0]hexane from irradiation of benzaldehyde and 2-butyne (L. E. Friedrich and J. D. Bower, submitted).

2. Product analyses were carried out and yields determined by glpc using a 10' x 1/4" 5% or 15% Carbowax 20M on Chromosorb P column at 120°.
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4. G. M. Barrow and S. Searles, J. Amer. Chem. Soc., 75, 1175 (1953).
5. We would like to thank Professor Thomas Krugh of the University of Rochester for the 100MHz nmr spectrum and Mr. David Maier of the Eastman Kodak Company for the high resolution mass spectrum.
6. In a model compound, , methylene hydrogen absorption occurs in the region of δ 2.5. R. Bishop and N. K. Hammer, J. Chem. Soc., C, 1197 (1970).
7. See for example, N. J. Turro and P. A. Wriede, J. Org. Chem., 34, 3562 (1969).
8. Analogous fragmentations have been observed in the mass spectra of 2-oxabicyclo[2.2.0]hexanes. See, for example, reference 10c, e.
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10. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, 1969, Chapters 3-8. For a specific example see: H. van Bekkum, F. van Rantwijk, G. van Minnen-Pathius, J. D. Remijwse and A. van Veen, Rec. Trav. Chim., 88, 911 (1969).
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