Tetrahedron Letters No. 34, pp 3555 - 3557, 1972. Pergamon Press. Printed in Great Britain.

THE TRICYCLO[5.3.0.0.^{3,4}]DEC-1-ENE SYSTEM[1]

R. L. Cargill* and A. B. Sears

Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

(Received in USA 3 July 1972; received in UK for publication 19 July 1972)

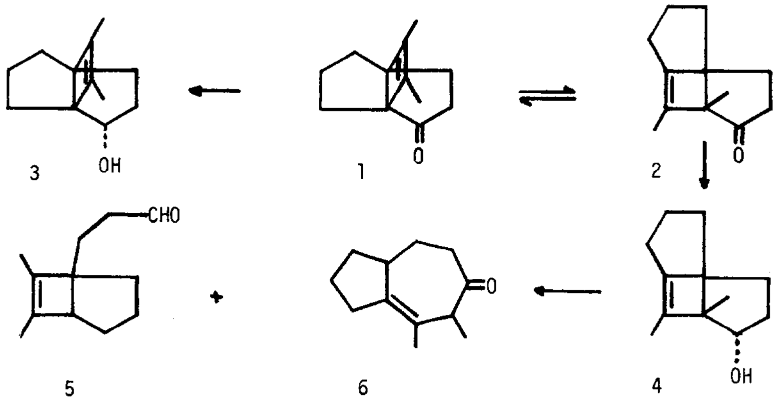
Bicyclo[3.2.0]hept-1(7)-ene and compounds containing this highly strained system have remained fugutive,[2] although related compounds have been prepared.[2-5] The apparent instability of this system presumably arises from the twist imposed upon the double bond by the trimethylene bridge. When both bridgehead carbons are trigonal, however, the entire molecule may assume planarity with consequent relief of this torsional strain.[5] Here we describe the synthesis of compounds which contain the bicyclo[3.2.0]hept-1(7)-ene moiety.

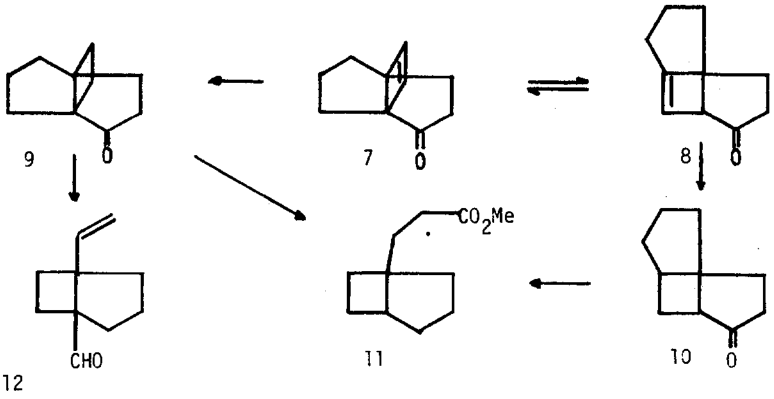
Irradiation of **1**, λ_{max}^{EtOH} 307 nm (ε 210), in pentane (Corex) led to no significant change in the gas chromatogram of the irradiation mixture.[6] Analysis by nmr spectroscopy, however, indicated ca. 70% disappearance of **1**. Solvent removal and distillation gave a clear liquid, bp 60-62° (0.3 Torr), in 53% yield. The nmr spectrum of the distillate showed in addition to the broadened singlets at δ 1.53 and 1.62 due to **1**,[6] a sharp singlet at δ 0.95 and a broad singlet at δ 1.50. The latter pair arise from the methyl resonances of the new ketone **2**.[7] The ratio of **2** to **1** was 2:1 (nmr).

All attempts to isolate **2** by gas chromatography or by column chromatography failed. In every case **2** was converted back into **1**, presumably by the well-known acid-catalyzed 1,3-acyl shift.[8] Reduction of the enone mixture with lithium aluminum hydride provided a 2:1 mixture of the corresponding alcohols, bp 73-76° (0.45 Torr), in 55% yield. The alcohols did survive gas chromatographic purification (DEGS, 130°); thus, **3** and **4** were obtained as pure liquids.[9] The nmr spectrum of **4** contains a singlet at δ 0.97 (3H), a singlet at 1.53 (3H) and an apparent triplet (overlapping doublets) at 2.40 ($J_{AX} = J_{AX'} = 8$ Hz). Pyrolysis of **4** at 460° in a flow system (residence time 2 min) gave a mixture of twelve difficultly separable products.[3,10] Sufficient quantities of the two major products were obtained for spectroscopic analysis. The first, assigned structure **5**, has $\tilde{\nu}_{max}$ 2710 and 1740 cm^{-1}, and in the nmr spectrum a broad singlet at δ 1.43 (6 H) and a triplet (J = 1 H) at δ 9.58 (1 Hz). The second, assigned structure **6**, has

ν_{max} 1715 cm^{-1} and in the nmr spectrum a doublet (J = 7 Hz) at δ 1.08 (3 H) and a singlet at δ 1.72 (3 H).

The above results required our reinvestigation of the photochemistry of the parent tricyclic ketone 7.[11] Irradiation of 7, λ_{max}^{EtOH} 307 (ε 100),[11] as above gave a distillate (bath 60°, 0.5 Torr) containing <u>inter alia</u> two saturated ketones (ratio 1:1) in 35% yield. Preparative glpc provided samples of the known ketone 9,[11] and a new ketone assigned structure 10.[9] The structure of 10 was secured when irradiation of both 9 and 10 (separately) in methanol yielded the same ester 11.[9] In addition, aldehyde 12[9] was obtained from the irradiation of 9. The formation of 10, albeit in small amount, establishes the intermediate formation of the undetected ketone 8.





REFERENCES

1. Grateful acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.
2. I. Flemming and J. Harley-Mason, J. Chem. Soc., 2165 (1964).
3. (a) R. A. Moss and J. R. Whittle, Chem. Commun., 341 (1969); (b) R. A. Moss, U. H. Dolling, and J. R. Whittle, Tetrahedron Lett., 931 (1971).
4. R. Breslow and W. Washburn, J. Amer. Chem. Soc., **92**, 427 (1970).
5. W. Kirmse and K. H. Pook, Angew. Chem. Internat. Ed. Engl., **5**, 594 (1966).
6. R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, J. Org. Chem., **30**, 3647 (1965).
7. These nmr data correspond very closely to those of the next higher homologs.[6]
8. G. Büchi and E. M. Burgess, J. Amer. Chem. Soc., **82**, 4333 (1960).
9. Satisfactory nmr and ir spectra and combustion analyses were obtained.
10. R. L. Cargill and D. M. Pond, J. Org. Chem., **31**, 2414 (1966).
11. R. L. Cargill, M. M. Cooper, and J. R. Damewood, J. Amer. Chem. Soc., **88**, 1330 (1966).