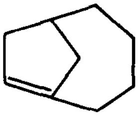
Tetrahedron Letters No. 26, pp 2207 - 2210, 1975. Pergamon Press. Printed in Great Britain.

THE SYNTHESIS OF STRAINED BRIDGEHEAD OLEFINS BY THE INTRAMOLECULAR WITTIG REACTION

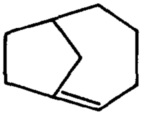
Konrad B. Becker
Institut für Organische Chemie der Universität Basel
4056 Basel, Switzerland

(Received in UK 26 March 1975; accepted for publication 15 May 1975)

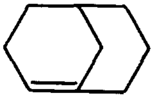
The synthesis of strained bridgehead olefins ("Bredt-olefins") has received much attention in the past few years [1]. An efficient method has now been developed that allows ring closure and formation of the double bond in a single reaction step by the intramolecular Wittig reaction [2]. A preparation of the strained but stable bicyclo[4.2.1]non-1(8)-ene 1 in high yield is described here.



1

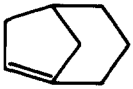


2

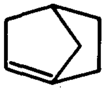


3

Bicyclo[4.2.1]non-1(8)-ene 1 has been synthesized previously in low yield together with its 1(2)-isomer 2 from the corresponding bridgehead ammonium hydroxide by pyrolysis and preparative vapor phase chromatography [3]. The synthesis by the intramolecular Wittig reaction, however, is straightforward and gives the pure olefin 1 in 57 % yield. The use of a keto phosphonium salt as a precursor was developed in our laboratory [4] and successfully applied to the synthesis of bicyclo[3.3.1]non-1-ene 3 [2]. Recently the preparation of the unstable bicyclo[3.2.1]oct-1(7)-ene 4 and the attempted formation of bicyclo[2.2.1]hept-1-ene 5 by the same method was reported by Dauben and Robbins [5].

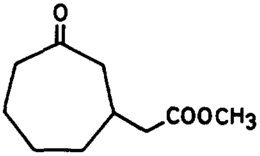


4

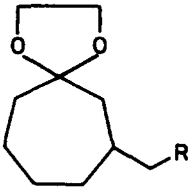


5

Addition of the magnesium enolate of malonic acid monomethyl ester [6] to 2-cycloheptenone gave methyl 3-cycloheptanoneacetate 6. This keto ester was transformed into the ethylene ketal ester 7, which was reduced to the ketal alcohol 8 with lithium aluminum hydride. Reaction with p-toluenesulfonyl chloride in pyridine gave tosylate 9. Treatment with excess lithium bromide in refluxing acetone lead to substitution by bromide and to cleavage of the ketal protecting group [7].



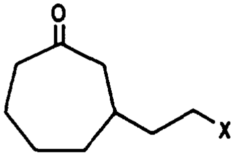
6



7 $R = COOCH_3$

8 $R = CH_2OH$

9 $R = CH_2OSO_2C_6H_4CH_3$



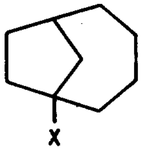
10 $X = Br$

11 $X = P^+(C_6H_5)_3Br^-$

The keto phosphonium salt 11 was obtained as a non-crystalline solid by heating the keto bromide 10 with one equivalent of triphenylphosphine in anhydrous ether at 100°. A suspension of 11 and of 2.2 equivalents of sodium hydride in dry tetraethyleneglycol dimethyl ether (tetraglyme) containing one equivalent of 2-methyl-2-butanol was heated to 70° for 20 min. The reaction temperature was raised to 120° and the olefin distilled at 12 Torr as it was formed. The crude oxygen-sensitive product was dissolved in pentane, washed with water, dried over sodium sulfate, and redistilled to give 57 % of pure bicyclo[4.2.1]non-1(8)-ene 1, mp. 28-30°.

The olefin was characterized by elemental analysis (found: C 88.62 %, H 11.40 %, calc.: C 88.45 %, H 11.55 %) and by its spectral properties (ir: $\lambda_{max}^{CCl_4}$ 3047, 1615, 951 cm^{-1}; ^{1}H-nmr: $\delta_{TMS}^{CCl_4}$ 5.37 ppm (broad singlett); ^{13}C-nmr: $\delta_{TMS}^{C_6D_6}$ 147.2 (bridgehead), 127.4 (=CH-), 45.4, 38.6 (2 C), 34.8, 32.3, 27.1, 23.9 ppm; m/e 122). The uv-spectrum (in cyclohexane) shows a maximum at 186 nm (log ε 3.81) and a shoulder at 200 nm (log ε 3.70). From this it might be concluded that the double bond is less strained than in the case of the isomeric bicyclo[3.3.1]non-1-ene 3, which shows uv-absorption at 206 nm (log ε 3.87) [8].

The addition of water to bicyclo[4.2.1]non-1(8)-ene 1 is observed in aqueous acetone in the presence of catalytic amounts of perchloric acid. The bridgehead alcohol bicyclo[4.2.1]nonan-1-ol 12 [9] is formed regiospecifically. Treatment with acetic acid gives the corresponding bridgehead acetate 13. 1-Bromobicyclo[4.2.1]nonane 14 is formed in the reaction of olefin 1 with hydrogen bromide in ether. Addition of bromine in carbon tetrachloride yields a mixture of mono-, di- and tribromides.



12 X = OH

13 X = $OCOCH_3$

14 X = Br

Electrophilic additions to bicyclo[4.2.1]non-1(8)-ene 1 proceed more slowly than to bicyclo[3.3.1]non-1-ene 3 [2]. This again leads to the conclusion that the double bond in olefin 1 is less strained than in the isomeric olefin 3 [10].

References and Notes

1) G. Köbrich, Angew. Chem. 85, 494 (1973), Angew. Chem. Internat. Ed. Engl. 12, 464 (1973); G.L. Buchanan, Chem. Soc. Rev. 3, 41 (1974).

2) K.B. Becker, Chimia 28, 726 (1974).

3) J.R. Wiseman, Hak-Foon Chan and C.J. Ahola, J. Amer. Chem. Soc. 91, 2812 (1969).

4) K.B. Becker, A.F. Boschung and C.A. Grob, Helv. Chim. Acta 56, 2733 (1973).

5) W.G. Dauben and J.D. Robbins, Tetrahedron Lett. 1975, 151.

6) G. Bram and M. Vilkas, Bull. Soc. Chim. France 1964, 945.

7) All new compounds gave correct elemental analyses, and had spectra in accord with the proposed structure.

8) J.R. Wiseman and W.A. Pletcher, J. Amer. Chem. Soc. 92, 956 (1970).

9) W.G. Dauben and J.L. Chitwood, J. Amer. Chem. Soc. 92, 1624 (1970).

10) The author thanks Professor C.A. Grob for helpful discussions, and the CIBA-GEIGY AG for financial support.