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A FACILE SYNTHESIS OF STRAINED BRIDGEHEAD OLEFINS BY A GAS-PHASE ELIMINATION REACTION

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Summary: A synthesis of bicyclo[3.3.1]non-1-ene 1 and of a 10:1 mixture of bicyclo[4.2.1]non-1(8)-ene 2 and bicyclo[4.2.1]non-1(2)-ene 3 by gas-phase pyrolysis of the corresponding bridgehead acetates and chlorides is reported.

A number of different syntheses are available for the preparation of the methylene-bridged trans-cyclooctene bicyclo[3.3.1]non-1-ene 1 [1], however, most of them are lengthy and not useful for the preparation of larger quantities of this strained bridgehead olefin. Gas-phase pyrolysis of esters is generally used to introduce a double bond without isomerization [2]. We reasoned therefore that a simple gas-phase elimination reaction of bridgehead acetate 4a or chloride 4b might lead to bridgehead olefin 1, if the acid formed could be trapped efficiently. For instance, there is good evidence that the products obtained on pyrolysis of 3-homoadamantyl acetate 6 are formed by rearrangement of two highly strained intermediate bridgehead homoadamantenes [3]. However, pyrolysis of the O-toluyl thiocarbonate 4d of 1-bicyclo[3.3.1]nonanol is reported to give only bicyclo[3.3.1]non-2-ene 7, although the reaction conditions should allow the isolation of the expected bridgehead olefin 1 [4].

1-Bicyclo[3.3.1]nonyl acetate 4a [5,6] was distilled at 135°/12 Torr through a quartz tube heated to 375-400° and the volatile products trapped at -78°. The content of the cold trap was dissolved in pentane and the acetic acid immediately neutralized with potassium carbonate. Vapor phase chromatography revealed that all the starting material had been consumed and that a 2:1 mixture of bicyclo[3.3.1]non-1-ene 1 and 3-methylidene-1,7-octadiene 8 [7] besides several minor unidentified compounds had been formed. No trace of bicyclo[3.3.1]non-2-ene 7 was found. Triene 8, which arises from a retro-Diels-Alder reaction of 1 [8], is the main product at higher temperatures.

Pyrolysis of 1-chlorobicyclo[3.3.1]nonane 4b [9] with subsequent trapping of the acid formed gave erratic results due to the high tendency of bridgehead olefin 1 to recombine with hydrogen chloride. An attempted elimination in solution with sodium amide in toluene [10] or in di-o-xylylethane was also unsuccessful. However, chloride 4b underwent clean elimination when sublimed (70°/12 Torr) through a Pyrex tube containing potassium carbonate heated to 250°. At that temperature, retro-Diels-Alder reaction was only a minor pathway, but considerable amounts of 1-bicyclo[3.3.1]nonanol 4c were formed, although the potassium carbonate was rigorously dried before use. Many other solid bases were tested as to their effectiveness in this gas-phase elimination, but proved to be inferior to potassium carbonate. Bicyclo[3.3.1]non-1-ene 1 could be separated from alcohol 4c, triene 8 and other impurities by extraction with aqueous silver nitrate. The silver complex was immediately decomposed with concentrated aqueous ammonia, and the olefin extracted with pentane, dried, and isolated by flash distillation at reduced pressure in >98% purity and 30-40% yield [11,12]. This simple method combined with the ready synthesis of chloride 4b [6,9] constitutes a new and easy access to the prototype Bredt olefin 1.

Bicyclo[4.2.1]non-1(8)-ene 2 and bicyclo[4.2.1]non-1(2)-ene 3 [13] may be formed by a similar elimination reaction. 1-Bicyclo[4.2.1]nonyl acetate 5a [5,14] underwent elimination at 450-500° to a 8:1 mixture of bridgehead olefins 2 and 3 containing 3-allyl-1-methylenecyclopentane 9 [15] and several minor products. Additional pyrolysis experiments proved that diene 9 is formed from bicyclo-[4.2.1]non-1(8)-ene 2 in a formal retro-ene reaction [16]. Distillation of 1-chlorobicyclo[4.2.1]nonane 5b [17] at 100°/12 Torr through a Pyrex tube containing potassium carbonate heated to 350° gave a 10:1 mixture of bridgehead olefins 2 and 3 in over 95% yield [11], and none of the bridgehead alcohol 5c was observed as in the analogous reaction of chloride 4b. Olefins 2 and 3 may be separated by preparative vapor phase chromatography [13a].

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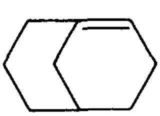

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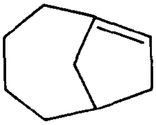

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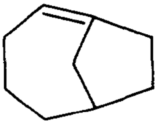

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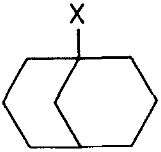

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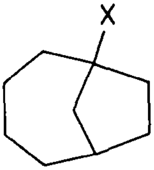

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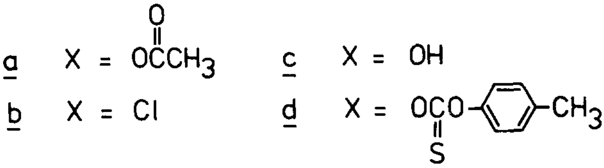
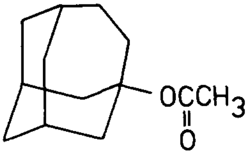


a $X = \mathrm{O\overset{\overset{O}{\|}}{C}CH_3}$

b $X = \mathrm{Cl}$

c $X = \mathrm{OH}$

d $X = \mathrm{O\underset{\underset{S}{\|}}{C}O{-}C_6H_4{-}CH_3}$



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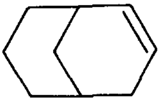

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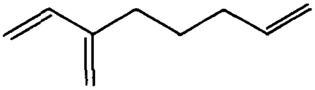

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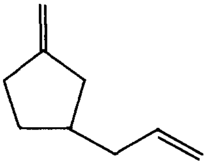

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References and Notes:

1) a) J.A. Marshall & H. Faubl, J. Amer. Chem. Soc. 89, 5965 (1967); 92, 948 (1970).

b) J.R. Wiseman, J. Amer. Chem. Soc. 89, 5966 (1967); J.R. Wiseman & W.A. Pletcher, J. Amer. Chem. Soc. 92, 956 (1970).

c) K.B. Becker, Chimia 28, 726 (1974); Helv. Chim. Acta 60, 81 (1977).

d) Moon-geu Kim & J.D. White, J. Amer. Chem. Soc. 97, 451 (1975); 99, 1172 (1977).

e) K.J. Shea & S. Wise, J. Amer. Chem. Soc. 100, 6519 (1978).

2) G.G. Smith & F.W. Kelly, Progr. Phys. Org. Chem. 8, 75 (1971).

3) B.L. Adams & P. Kovacic, J. Amer. Chem. Soc. 97, 2829 (1975).

4) H. Gerlach, T.T. Huong & W. Müller, Chem. Commun. 1972, 1215.

5) K.B. Becker, Helv. Chim. Acta 60, 94 (1977).

6) Acetate 4a was best prepared by solvolysis of 1-bicyclo[3.3.0]octylmethyl methanesulfonate in acetic acid, see W.G. Dauben & C.D. Poulter, J. Org. Chem. 33, 1237 (1968). This methanesulfonate is formed from 1-bicyclo-[3.3.0]octylcarboxylic acid (available from 1,5-cyclooctadiene in a Koch-Haaf reaction according to D.R. Kell & F.J. McQuillin, J. Chem. Soc. Perkin I 1972, 2096) by reduction followed by treatment with methanesulfonyl chloride and triethylamine in methylene chloride.

7) Identical with triene 8 prepared from vinyl acetylene and 4-pentenylmagnesium cuprate following a general method of H. Westmijze, H. Kleijn, J. Meijer & P. Vermeer, Tetrahedron Letters 1977, 869.

8) This retro-Diels-Alder reaction and the corresponding Diels-Alder synthesis of olefin 1 from triene 8 have recently been reported by Shea and Wise (ref. 1e). For other examples of retro-Diels-Alder reactions of strained bridgehead olefins see A.D. Wolf & M. Jones jr., J. Amer. Chem. Soc. 95, 8209 (1973); R. Bloch, F. Boivin & M. Bortolussi, Chem. Commun. 1976, 371.

9) Prepared from 1-bicyclo[3.3.1]nonanol 4c and thionyl chloride, m.p.87-88°[6].

10) Y. Fujikura, Y. Inamoto, N. Takaishi, H. Ikeda & K. Aigami, J. Chem. Soc. Perkin I 1976, 2133.

11) Due to the high reactivity of olefins 1, 2 and 3 towards oxygen, these compounds should be handled under an inert atmosphere.

12) Alcohol 4c may be readily isolated and recycled[9]. This raises the effective yield based on consumed 4c to 60-70%.

13) a) J.R. Wiseman, Hak-Foon Chan & C.J. Ahola, J. Amer. Chem. Soc. 91, 2812 (1969).

b) K.B. Becker, Tetrahedron Letters 1975, 2207 and ref. 1c.

14) Prepared by solvolysis of 1-bicyclo[4.2.0]octylmethyl p-toluenesulfonate in acetic acid, see W.G. Dauben & J.L. Chitwood, J. Amer. Chem. Soc. 92, 1624 (1970).

15) Identical with the compound obtained from methylenetriphenylphosphorane and 3-allylcyclopentanone, which was prepared from cyclopent-2-en-1-one and allyltrimethylsilane with titanium tetrachloride in methylene chloride following a general procedure of A. Hosomi & H. Sakurai, J. Amer. Chem. Soc. 99, 1673 (1977).

16) For similar retro-ene reactions compare e.g. A.T. Blomquist & P.R. Taussig, J. Amer. Chem. Soc. 79, 3505 (1957); A.C. Cope & M.J. Youngquist, J. Amer. Chem. Soc. 84, 2411 (1962).

17) Prepared from 1-bicyclo[4.2.1]nonanol 5c[14] and thionyl chloride in 90% yield after short path distillation, m.p. 22-23°.

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