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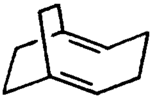
DOUBLE BRIDGEHEAD OLEFINS VIA PYROLYSIS[1]

Philip Warner*[2] and William Boulanger

Iowa State University, Department of Chemistry, Ames, IA 50011

Abstract: Pyrolysis of diacetate 5 produced 3 major products, 6-8. The most reasonable pathway to these products, supported by deuterium labelling studies, is via double bridgehead olefins 11, 13 and 15.

As our understanding of bridgehead olefins has enlarged in recent years,[3] attention has begun to focus on bicyclic molecules containing two bridgehead double bonds. Recently, compounds 1[4] and 2[5] have been isolated, while 3 has been proposed as an intermediate;[6] 4[7] represents a special type of bridgehead olefin in which the π bonds are not twisted. Whereas 1 is thermally labile (Cope rearrangement), 2 is quite stable due to the endo-fused epoxide ring.



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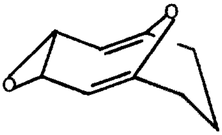

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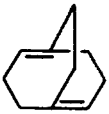

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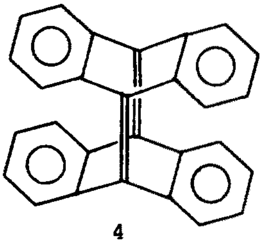

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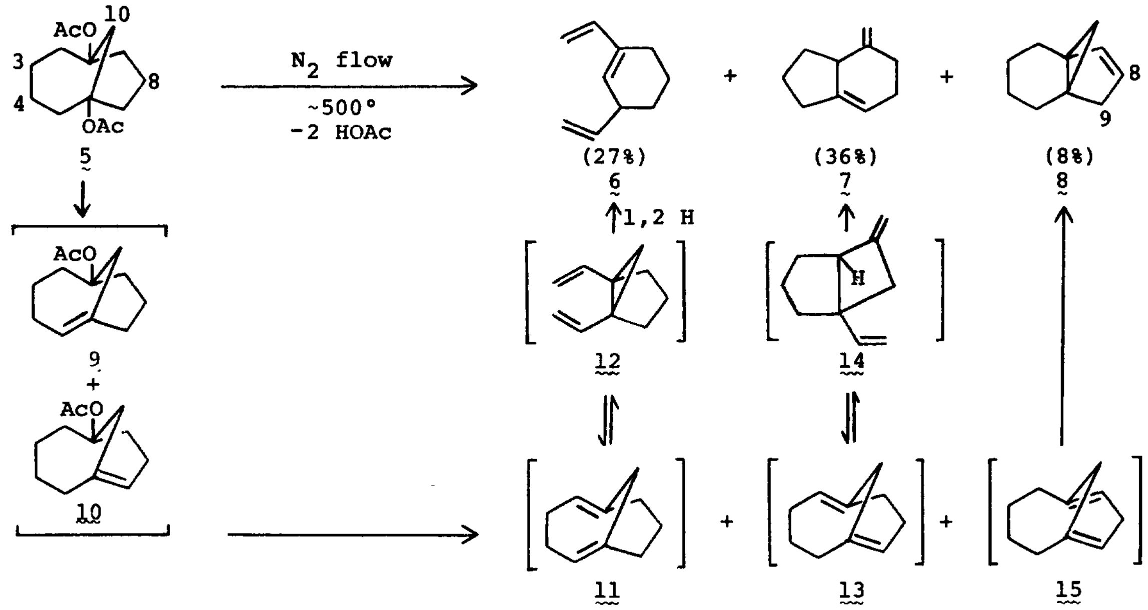
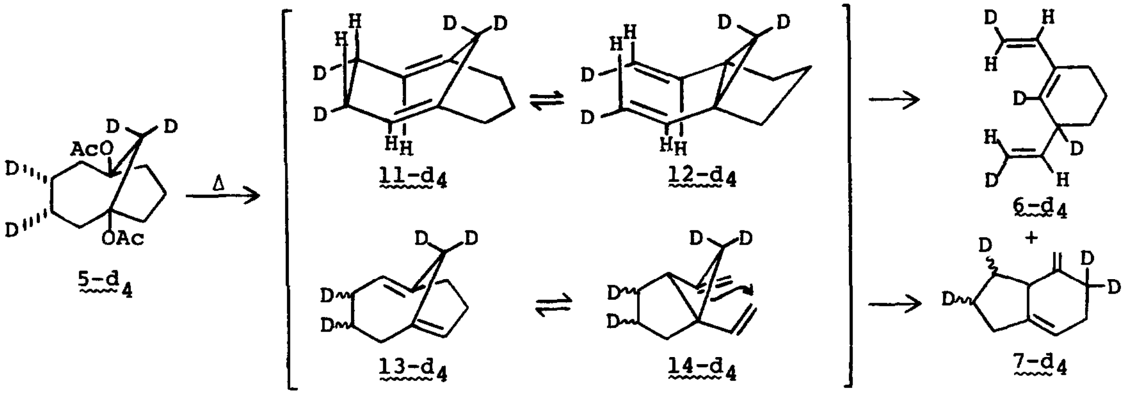
We now wish to report our results on the pyrolysis of diacetate 5.[8a,16] When 5 was transported through a vertical oven chamber[10] by a N$_2$ flow, the products collected in the cold trap were 6,[8b,16] 7,[8c,16] and 8,[8d,16] in the yields indicated. Some other minor products of as yet unknown structure, but isomeric with 6-8 (gc-ms analysis), were formed in 25% yield.[11] Importantly, neither 9[8e,16] nor 10[8f,16] were components of the product mixture, although they were the sole isolable products (in a 4:3 ratio) of the pyrolysis of 5 (horizontal oven, 10^{-6} Torr) at 360°. Further pyrolysis of 9 and 10 did afford 6-8.

The most attractive mechanistic explanation for our observations is indicated in Scheme 1, where we propose the intermediacy of bridgehead dienes 11, 13 and 15. As 1,5-dienes, both 11 and 13 are subject to (reversible) Cope rearrangement to 12 and 14, respectively. Triene 6 derives from 12 via a cyclopropane-propene rearrangement;[12] diene 7 comes from 14 via a 1,3-sigmatropic carbon shift (vide infra); propellene 8 stems from 15 via a homo-1,5-H shift.

Scheme 1



Some evidence for these pathways comes from deuterium labeling experiments. Thus pyrolysis of 5-d_2, with the deuteria at C_8, results in 8-d_2, with one deuterium at C_8 and one at C_9. Additionally, thermolysis of 5-d_4 affords 6-d_4, where the (E,E) configuration of the vinyl groups indicates that 11 has the (Z,Z) configuration, in which both double bonds are expectedly *trans*-cyclononenoid.[13] As shown, the 7-d_4 produced from 5-d_4 contains no deuteria in the



vinylidene position. This implies that 14-d_4 is converted to 7-d_4 via a 1,3-sigmatropic shift (rather than a Cope rearrangement).[14,15]

Further work aimed at refining the mechanistic picture presented herein is in progress.

References and Notes

1. This work was supported, in part, by the National Science Foundation under Grant No. CHE-7618701.

2. Alfred P. Sloan Foundation Fellow, 1976-80.

3. For reviews see (a) G. L. Buchanan, Chem. Soc. Rev., 3, 41 (1974); (b) G. Köbrich; Angew. Chem. Int. Ed., 12, 464 (1973); (c) J. Liebman and A. Greenberg, Chem. Rev., 76, 311 (1976).

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5. (a) W. H. Rastetter, T. J. Richard, N. D. Jones and M. O. Chaney, Chem. Comm., 377 (1978); (b) W. H. Rastetter, T. J. Richard, J. Bordner and G. L. Hennessee, J. Org. Chem., 44, 999 (1979); (c) W. H. Rastetter and T. J. Richard, J. Am. Chem. Soc., 101, 3893 (1979).

6. K. J. Shea and S. Wise, Tetrahedron Lett., 2283 (1978).

7. R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, and L. M. Trefonas, J. Am. Chem. Soc., 96, 4342 (1974).

8. (a) **5** was made via nBu$_3$SnH reduction of the known[9] 10-bromo derivative; pmr (CCl$_4$): δ1.87(s) 1.5-2.4(m), 3.05(d, $J_{10\alpha,10\beta}$=12Hz); cmr(CDCl$_3$): δ169.9(20.3), 84.3(28.7), 43.0(22.2), 39.2(40.2), 36.9(38.6), 24.5(32.3), 22.5(23.0), 20.4(15.4); (b) **6**: pmr: δ6.2(dd, 1H, J=10, 17Hz), 5.7(m, 1H), 5.5(s, 1H), 4.7-5.1(m, 4H), 2.8(br. s, 1H), 1.0-2.25(m, 6H); cmr: δ142.1(12.1), 140.0(15.0), 136.5(5.0), 131.7(13.8), 113.7(15.7), 110.6 (16.5), 40.0(10.0), 28.9(8.7), 23.8(9.9), 20.5(8.2); ir: 3087, 3060, 3030, 3000, 1637, 1607 cm^{-1}; (c) **7**: pmr: δ5.42(br. s, 1H), 4.75(t, 1H, J≈1Hz), 4.65(t, 1H, J≈1Hz), 2.7-3.1(m, 1H), 1.2-2.7(m, 10H); cmr: δ149.4 (28.0), 144.0(27.3), 117.0(74.0), 104.6(76.2), 46.1(59.5), 32.0(46.7), 29.8(62.9), 29.7(53.1), 28.2(46.6), 22.8(34.6); ir: 3080, 3040, 1658 cm^{-1}; (d) **8**: pmr: δ5.98(dt, 1H, J=2, 6Hz), 5.40(dt, 1H, J=2, 6Hz), 2.6, 2.3 (ABq, t, 2H, J=2, 16Hz), 1.1-2.2(m, 8H), 0.85, 0.15 (ABq, 2H, J=4Hz); cmr: δ139.7(18.9), 126.5(24.7), 77.3(21.0), 44.6(27.8), 30.6(26.9), 27.7(27.7), 26.4(29.1), 21.8(55.0), 2 quaternary cyclopropyl C's not observed; ir: 3040, 1590 cm^{-1}; **8** was prepared independently via elimination of the corresponding *endo*-8-bromo[4.3.1]propellane; (e) **9**: so far not separated from **10** due to instability upon chromatography; distinguished by acetate peak at δ1.9(pmr); (f) **10**: independently synthesized via nBu$_3$SnH reduction of the known[9] 10-bromo derivative; pmr: δ5.5(t, 1H, J≈2Hz), 3.05, 2.80 (ABq, 2H, J=13Hz), 2.0(s, 3H), 1.4-2.6(m, 12H); ir: 3020, 1740, 1685 cm^{-1}; the mixture of **9** and **10** gave the same acetate, upon hydrogenation, as did **10**.

9. P. Warner, S. Lu, E. Myers, P. De Haven and R. A. Jacobson, *J. Am. Chem. Soc.*, **99**, 5102 (1977).

10. Due to the "chimney" effect in a vertical column, the inside temperature was closer to 500° than the 400° reading given by the oven thermocouple. However, the horizontal vacuum pyrolysis temperatures were accurately reflected by the thermocouple. We have been able to produce **6**-**8** from **5** under vacuum conditions, and the yields and ratios are comparable.

11. While 25% isn't a "minor" amount, it is clear, from other runs, that most of these products are secondary, and include aromatic products such as dihydrotetralin. In some runs, the yield of **6** + **7** + **8** approached 90%. However, there is definitely a fourth product formed which may be **14**.

12. For leading references to this well-known rearrangement, see J. March, "Advanced Organic Chemistry," McGraw-Hill Book Co. (New York, 1977), p 986.

13. J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970).

14. W. R. Dolbier, Jr. and G. J. Mancini, *Tetrahedron Lett.*, 2141 (1975).

15. Inversion of the migrating methylene, predicted by orbital symmetry considerations, is likely involved. For a similar instance, see J. Berson, *Accts. Chem. Res.*, **1**, 152 (1968).

16. Satisfactory elemental analyses or exact masses have been obtained for **5**-**8**, **10**; also, the exact mass of **9** and **10** as a mixture, has been obtained.

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