

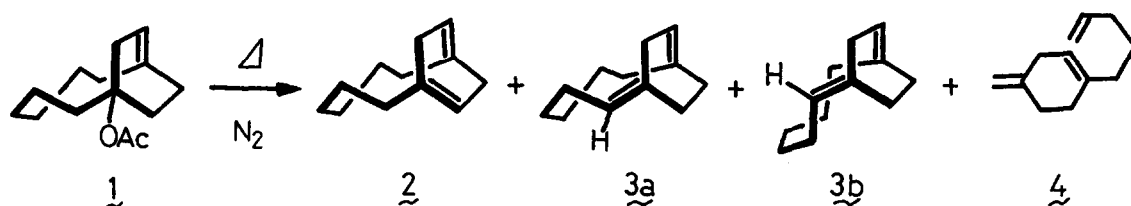
## SYNTHESIS OF BICYCLO[6.2.2] BRIDGEHEAD DIENES

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Summary: Bicyclo[6.2.2]dodecadienes (2), (3a), and (3b) having two bridgehead double bonds were synthesized by the pyrolysis of the acetate (1).

Although syntheses of many bridgehead olefins of various ring systems have been actively done owing to the recent development of new efficient methods for introduction of bridgehead double bond,<sup>1</sup> there has been far less example of highly strained bridgehead dienes.<sup>1d</sup> We wish to report here the synthesis of bicyclo[6.2.2] bridgehead dienes (2), (3a), and (3b) by the pyrolysis of bicyclo[6.2.2]dodec-1(10)-enyl acetate (1).<sup>2</sup>



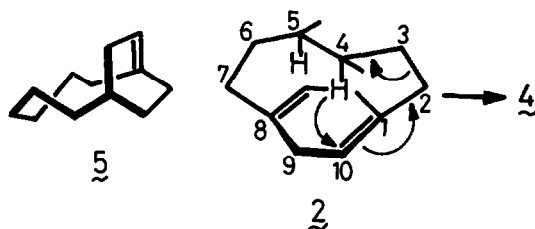
When a solution of 1 in hexane was passed through a Pyrex tube heated at 320-400 °C (contact time ~20 sec) by a nitrogen flow, three major products 2, 3, and 4 were obtained whose distribution was dependent on the reaction temperature (Table 1): with increasing the reaction temperature, the ratio of 2 apparently decreased while that of 4 increased.<sup>3</sup> The structure of the symmetric diene 2 was established on the basis of <sup>13</sup>C NMR spectrum which comprised six signals and <sup>1</sup>H NMR spectrum.<sup>4</sup> Although 3 is homogeneous in glc, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra indicate that 3 is an about 1:1 mixture of unsymmetric dienes 3a and 3b.<sup>4</sup> This was confirmed from the fact that catalytic hydrogenation of 3 (3a+3b) over Pd/C gave the olefin (5)<sup>2b</sup> as a sole product. The structure of the triene 4 was elucidated on the basis of <sup>1</sup>H NMR spectrum<sup>4</sup> and was further confirmed by the identity with the authentic sample prepared independently.<sup>5</sup> Thus, bicyclo[6.2.2] bridgehead dienes 2 and 3 were synthesized successfully from 1 by the simple pyrolytic method.

It is noteworthy that the diene 2, being 2,5-dihydro derivative of [6]paracyclophane<sup>6</sup> which is the smallest [n]paracyclophane, shows attractive

Table 1. Pyrolysis of 1.

Temp (°C)	Conv (%)	Products (%)		
		<u>2</u>	<u>3</u>	<u>4</u>
320	20	25	58	9
350	82	19	57	15
400 <sup>a</sup>	95	3	30	33

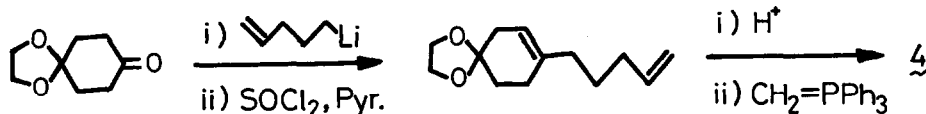
<sup>a</sup> Considerable amounts of unidentified products were formed.



properties: a shoulder at 232 nm ( $\epsilon$  830) in UV spectrum indicates the interaction of nonconjugated bridgehead double bonds<sup>7</sup> and the multiplet absorption appeared at  $\delta$  0.2-0.5 in <sup>1</sup>H NMR spectrum, which is assigned to H-4 and H-5 shielded by the bridgehead double bonds, suggests the proximity of these protons to the double bonds. Moreover, the facility of 2 to undergo the retro ene reaction affording the triene 4 also reflects the above proximity effect.

#### References and Notes

- (1) For recent reviews; (a) G.Köbrich, *Angew.Chem., Int.Ed.Engl.*, **12**, 464(1973). (b) G.L.Buchanan, *Chem.Soc.Rev.*, **3**, 41(1974). (c) R.Keese, *Angew.Chem., Int.Ed.Engl.*, **14**, 528(1975). (d) K.J.Shea, *Tetrahedron*, **36**, 1683(1980).
- (2) (a) Y.Sakai, S.Toyotani, Y.Tobe, and Y.Odaira, *Tetrahedron Lett.*, 3855 (1979). (b) Y.Sakai, S.Toyotani, M.Ohtani, M.Matsumoto, Y.Tobe, and Y.Odaira, *Bull.Chem.Soc.Jpn.*, **54**, 1474(1981).
- (3) From the fact that the independent pyrolysis of 2 under similar conditions at 380 °C gave 4 cleanly, it is deduced that 4 is the secondary product derived by the retro ene reaction of 2. For the retro ene reaction of a bridgehead olefin; K.B.Becker and R.W.Pfluger, *Tetrahedron Lett.*, 3713 (1979).
- (4) The products 2-4, separated by quick chromatography on silica gel followed by preparative glc, are colorless liquids and gave satisfactory analytical data. The dienes 2 and 3 are stable under nitrogen in a refrigerator at least for one month.  
2: IR (cm<sup>-1</sup>) 3030, 1620, 870, 760; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.20-0.52 (m, 2H), 0.68-2.80 (m, 14H), 5.73 (d, J=5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  145.3(s), 126.6(d), 38.1(t), 33.0(t), 29.9(t), 26.6(t).  
3: IR (cm<sup>-1</sup>) 3010, 1650, 1620, 875; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.65-2.90 (m, 16H), 4.75-5.08 (m, 1H), 5.79 (d, J=8 Hz, 0.5H), 5.98-6.20 (m, 0.5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  147.2(s), 145.1(s), 139.3(s), 138.6(s), 133.8(d), 129.9(d), 121.4(d), 121.1(d), 37.8, 36.1, 34.0, 31.4, 30.8, 29.6, 29.3, 26.4, 25.0, 24.8, 24.4, 23.2, 20.6.  
4: IR (cm<sup>-1</sup>) 3060, 1640, 985, 905, 880; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.50 (tt, 2H), 1.87-2.42 (m, 8H), 2.62-2.84 (m, 2H), 4.72 (br s, 2H), 4.94, 4.97 (ABX, 2H), 5.25-5.44 (m, 1H), 5.58-6.06 (m, 1H).
- (5) The authentic sample of 4 was prepared in the following manner.



- (6) V.V.Kane, A.D.Wolf, and M.Jones, Jr., *J.Am.Chem.Soc.*, **96**, 2643(1974).
- (7) For a similar interaction between two bridgehead double bonds; J.L.Marshall and L.Hall, *Tetrahedron*, **37**, 1271(1981), and references therein.