

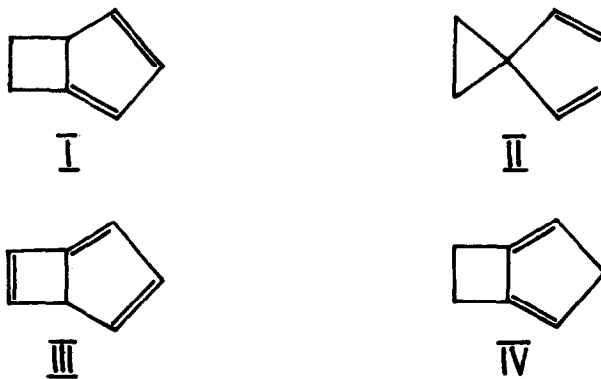
FORMATION OF SPIRO[2.4]HEPTA-4,6-DIENE IN BASE CATALYSED ELIMINATION
OF 4-BROMOBICYCLO[3.2.0]-HEPT-2-ENE

N.K. Hamer and Michael E. Stubbs

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

(Received in UK 13 July 1972; accepted for publication 19 July 1972)

Bicyclo[3.2.0]-hepta-1,3-diene (I) has not been reported but has been proposed as an intermediate in the pyrolysis of both spiro[2.4]hepta-4,6-diene¹ (II) and the lithium salt of norbornenone p-toluenesulphonyl hydrazone.² Our interest in this system arose from the fact that we postulated derivatives of I as intermediates in the photoisomerisation of 4-methylenebicyclo[3.1.0]hex-2-enes (homofulvenes) to spiro[2.4]hepta-4,6-dienes.³ These proposals required that derivatives of I undergo rapid thermal rearrangement via a 1,5-alkyl shift to the more stable II. Considerations of the relative degree of angle strain in

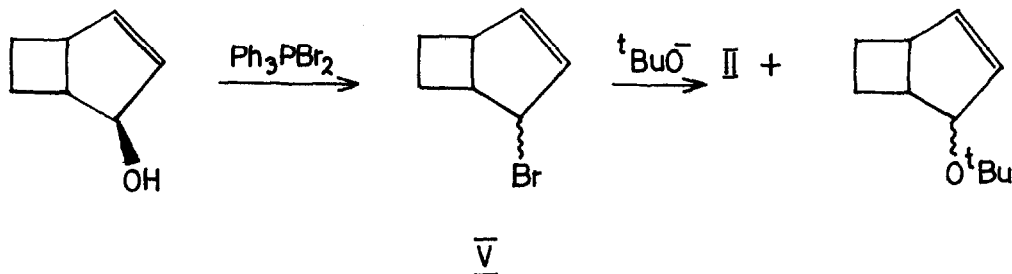


I and II suggest that this is reasonable although it should be noted that the related triene (III) does not appear to undergo such a ring contraction.⁴ A more serious objection arises from the observations that 1,5-alkyl shifts in

cyclopentadienes are very much less facile than 1,5-hydrogen shifts⁵ and that these latter processes could lead to IV which is expected to be relatively stable.⁶

Reaction of *exo*-bicyclo[3.2.0]hept-3-en-2-ol^{7,8} with one equivalent of triphenyl phosphine dibromide in acetonitrile gave 4-bromobicyclo[3.2.0]hept-2-ene (V) as an oil b.p. 33-35°/1.5 mm Hg (64%) (Found: C, 48.6; H, 5.1; Br, 45.9. C_7H_9Br requires C, 48.6; H, 5.2; Br, 46.2%). τ (100 MHz, CCl_4) 4.0 (2H, m), 5.24 (1H, m), 6.54 (1H, m), 6.82 (1H, m), 7.5-8.0 (2H, m), 8.2-8.7 (2H, m). Only one isomer of V was formed and in view of the unfavourable disposition of the system for S_N2 attack it seems likely that it is the *exo*-isomer.

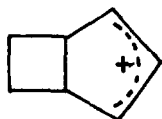
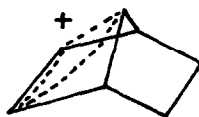
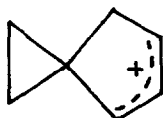
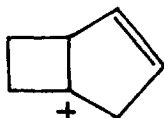
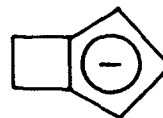
When the above bromide was treated with one equivalent of potassium *t*-butoxide in benzene at 35-40° potassium bromide separated out during the course of 30 min. 1H n.m.r. of the crude reaction mixture showed the characteristic resonances attributable to II which after isolation (12%) was identical with an



authentic sample. Several other products were also produced, of which the major (40-50%) appeared on the basis of its n.m.r. spectrum to be 2-*t*-butoxybicyclo[3.2.0]hept-3-ene but, significantly, no other hydrocarbon of the formula C_7H_8 could be isolated.

Irrespective of the actual isomer of V base elimination of one or other of the bridgehead protons should give rise to (I) and there can be little doubt that it is indeed the precursor of the spiroheptadiene (II). The preponderance of substitution - even by the hindered *t*-butoxide - over elimination is not surprising in view of the large strain developing during the formation of (I). It is most unlikely that the rearrangement occurs in a

carbonium ion prior to elimination since the conditions employed are not conducive to carbonium ion formation. Moreover the only two bicyclic ions of comparable stability to VI are the non classical norbornenyl ion (VII)⁹ and, probably, the spiroheptenyl ion (VIII). There is no evidence to suggest that VI can transform to VII⁸ not is it clear how this could eliminate to give II.

VIVIIVIIIIXX

While elimination from VIII would certainly give II its formation from VI requires two sigmatropic shifts of which the first leads to IX which has lost the allylic stabilisation without release of the ring strain and is therefore most improbable.

Carbanion mechanisms can also be ruled out since the most stable bicyclic anion is undoubtedly X.

- 1 J.M.E. Krekels, J.W. de Haan and H. Kloosterziel, Tetrahedron Letters, 1970, 2751.
- 2 R.A. Moss, U.-H. Dolling and J.R. Whittle, Tetrahedron Letters, 1971, 931.
- 3 N.K. Hamer and M.E. Stubbs, Chem. Comm., 1970, 1013.
- 4 R. Breslow, W. Washburn and R.G. Bergman, J. Amer. Chem. Soc., 1969, 91, 196.
- 5 S. McLean and P. Haynes, Tetrahedron, 1965, 21, 2329.
- 6 M.B. D'Amore and R.G. Bergman, J. Amer. Chem. Soc., 1969, 91, 5694.
- 7 L.A. Paquette and O. Cox, J. Amer. Chem. Soc., 1967, 89, 5633.
- 8 S. Winstein and E.T. Stafford, J. Amer. Chem. Soc., 1957, 79, 505.
- 9 W.G. Woods, R.A. Carboni and J.D. Roberts, J. Amer. Chem. Soc., 1956, 78, 5653.