Tetrahedron Letters No. 28, pp 2871 - 2872, 1972. Pergamon Press. Printed in Great Britain.

A HIGHLY STRAINED BICYCLIC ALLENE-BICYCLO(3.2.1)OCTA-2,3-DIENE INTERMEDIATE

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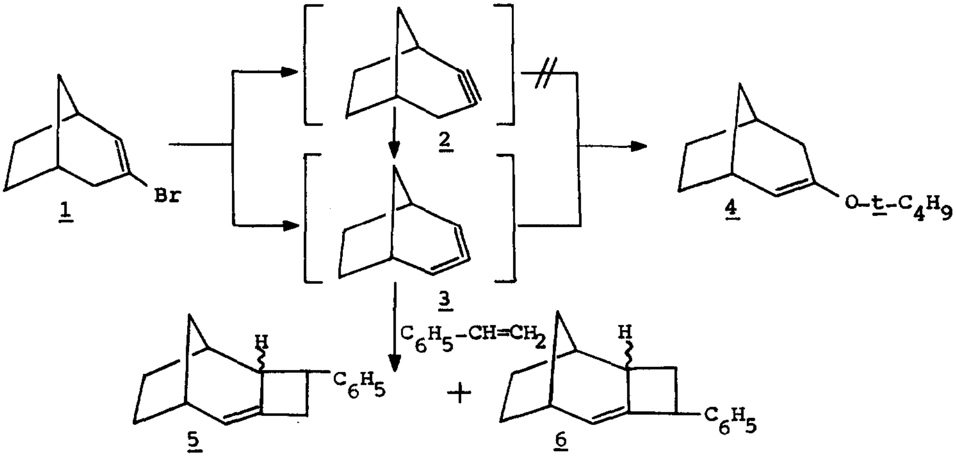
(Received in UK 23 May 1972; accepted for publication 7 June 1972)

In our continuing investigations on the chemistry of cyclic allenes, we have shown that the lowest isolable cyclic allene (1,2-cyclononadiene) shows certain properties which are different from its higher homologues due to the strain in the ring.[1,2] An interesting problem associated with the chemistry of reactive strained cyclic allenes is the study of the reactivity as a function of the ring system and the possible isomerization of cyclic acetylenic intermediate to cyclic allenic intermediates Compelling evidence [3-5] have been obtained in recent years to show that cyclic allenes (1,2-cyclohexadiene,[3,4] 1,2-cycloheptadiene[5] and 1,2-cyclooctadiene[6]) containing less than nine carbon atoms have transitory existence in the reaction of 1-bromo cyclic olefin with potassium t-butoxide in DMSO. These observations prompted a study of the similar reaction of 3-bromobicyclo(3.2.1)oct-2-ene (1), a system which would appear capable of giving the highly strained and as yet unknown bicyclic allene, bicyclo(3.2.1)oct-2,3-diene (3) for inclusion in this study.

The reaction of bromoform with potassium t-butoxide in the presence of bicyclo(2.2.1)heptene in dry pentane at -15° gave exo-3,4-dibromobicyclo(3.2.1)-oct-2-ene. Reduction of dibromide with lithium aluminium hydride gave 1 whose properties were in complete agreement with those reported in the lit.[7] Treatment of 1 with freshly sublimed potassium t-butoxide in dry DMSO with stirring for 24 hr at room temperature gave 3-t-butoxybicyclo(2.2.1)heptene (4) in 62% yield. Careful glc analysis indicated it to be pure. The structure 4 was confirmed by spectral and analytical data.[8] Furthermore, the reaction of 1 with potassium t-butoxide in DMSO in presence of styrene gave, after distillation, a 50% yield of a mixture of 1:1 styrene:C_8H_{10} adducts (5 and 6) as the major product. Attempts made to separate the positional isomers by glc were not successful. It gave satisfactory analytical results. Its ir and nmr spectra were consistent with the assigned gross structures 5 and 6 for the mixture.



The above results are completely consistent with the formation of 4 by means of two concurrent elimination-addition mechanism involving 3. The other possibility involving the isomeric bicyclic acetylenic intermediate (2) has been rejected as 2 is capable of giving rise to two isomeric t-butyl vinyl ethers. Therefore, we conclude that the bicyclic acetylenic intermediate (2), if formed, rapidly undergoes isomerization to 3. Currently the work is in progress to study other interesting reactions of this highly reactive bicyclic allene.

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8. All Compounds gave acceptable microanalytical data.