

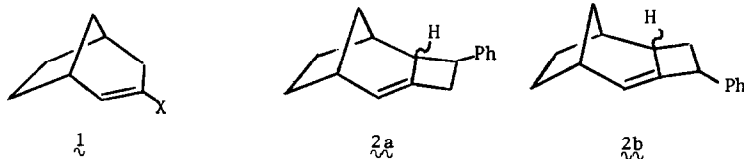
ON YNE AND ALLENE INTERMEDIATES IN THE BICYCLO[3.2.1]OCTANE RING SYSTEM¹

Peter K. Freeman and Thomas A. Hardy

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

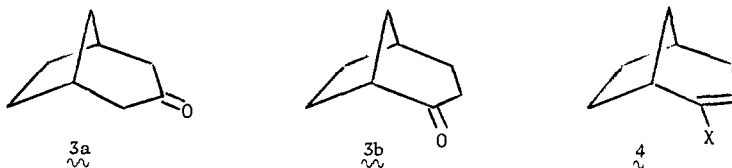
(Received in USA 14 May 1973; received in UK for publication 17 July 1973)

Strained allenic and acetylenic intermediates generated by treatment of 1-halocycloalkenes with strong base have been studied in some detail in recent years.²⁻⁶ Whether an allene or alkyne intermediate is formed depends upon the particular ring system involved, the leaving group, and the base-solvent system employed. Bottini and his co-workers have demonstrated that treatment of 1-bromocyclohexene with potassium *t*-butoxide in dimethylsulfoxide yields 1-*t*-butoxycyclohexene through a mixture of allenic (major pathway) and acetylenic (minor pathway) intermediates.^{5b,c} It has been recently reported⁶ that treatment of 3-bromobicyclo[3.2.1]oct-2-ene (1-Br) with potassium *t*-butoxide in dimethylsulfoxide yields exclusively 3-*t*-butoxybicyclo[3.2.1]oct-2-ene (1-OtBu). An allene was suggested as the sole product determining intermediate, with the supporting evidence that the reaction of 1-Br in the presence of styrene affords styrene:C₈H₁₀ adducts 2a and 2b. These results prompt us to report our observations in this and similar systems.

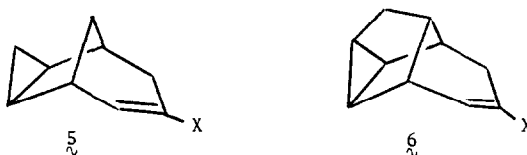


Treatment of 1-Br with potassium *t*-butoxide in dimethylsulfoxide for 24-48 hr afforded an enol-ether in 64% yield, which seemed to be pure by vpc analysis. When subjected to high (*ca.* 250°) injection port temperatures, the product underwent a retro-ene reaction to yield a

ketone fraction. Vpc analysis of the retro-ene product revealed two isomeric ketones, which were identified as $\overset{\sim}{3}a$ and $\overset{\sim}{3}b$, in a ratio of 93:7.⁷ This suggests that the observed enol-ether product is in fact a mixture of $\overset{\sim}{1}$ -OtBu and $\overset{\sim}{4}$ -OtBu.

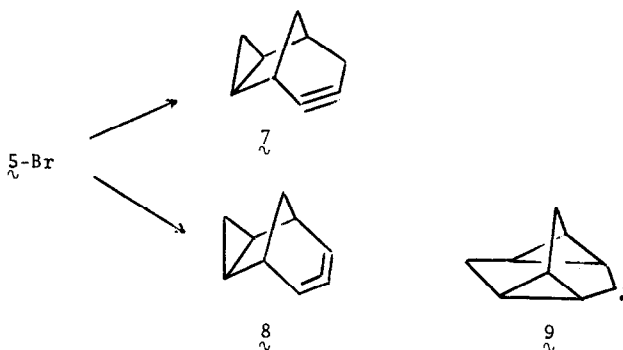


As a check on these results, and as part of our studies on possible remote cyclopropyl interactions during the reactions of allylic systems with strong base,⁸ 7-bromotricyclo-[3.3.1.0^{2,4}]non-6-ene⁸ ($\overset{\sim}{5}$ -Br) and 9-bromotetracyclo[4.4.0.0^{2,4}.0^{3,7}]dec-8-ene⁸ ($\overset{\sim}{6}$ -Br) were treated with potassium *t*-butoxide in dimethylsulfoxide. Stirring for 24-48 hr yielded enol-ethers in yields of 51% and 53% respectively. The enol ether produced from $\overset{\sim}{5}$ -Br was found to consist of > 97% $\overset{\sim}{5}$ -OtBu, while the enol ether from $\overset{\sim}{6}$ -Br was found to consist of > 95% $\overset{\sim}{6}$ -OtBu.



In order to probe the mechanism of enol ether formation, after determining that $\overset{\sim}{5}$ -OtBu undergoes no exchange with the solvent under the reaction conditions, $\overset{\sim}{1}$ -Br and $\overset{\sim}{5}$ -Br were treated with potassium *t*-butoxide in perdeuteriodimethylsulfoxide. Nmr analysis of the product enol ethers showed that in each case, the olefinic absorption was reduced to 0.15 ± 0.1 of that of the undeuteriated product. Nmr analysis of the corresponding ketones obtained from retro-ene reaction of deuteriated enol ethers indicated that each ketone had incorporated 0.9 ± 0.2 deuterium atoms α to the carbonyl. These results strongly support the suggestion that acetylenic intermediates (for example $\overset{\sim}{7}$) are the major product determining intermediates leading to *t*-butyl enol ether and consequently allenic intermediates (for example $\overset{\sim}{8}$) can only play a minor role. Furthermore, the additional variation structurally available to substrates $\overset{\sim}{5}$ and $\overset{\sim}{6}$, that of generation of a dicyclopropylcarbene species (for example $\overset{\sim}{9}$) *via* a trishomocyclopentadienyl anion,⁹ is not revealed. No cyclopropylcarbene fragmentation products^{9,10} were uncovered and formation of *t*-butyl enol ether *via* a dicyclopropylcarbene intermediate

(for example $\overset{\sim}{9} \rightarrow \overset{\sim}{5}\text{-OtBu}$) would be expected to provide the same distribution of deuterium label as the allene. The fact that the homoaromatic anion to carbene route is not observed, in contrast to the 3-bromobicyclo[3.2.1]octa-2,6-diene case⁹ is consistent with the lack of enhanced acidity found for hydrocarbons $\overset{\sim}{5}\text{-H}$ and $\overset{\sim}{6}\text{-H}$.⁸



The regioselectivity of attack by *t*-butoxide upon the unsymmetrical acetylenic intermediates is not surprising, as steric effects appear to be quite important in reactions of this type.^{11,50} The styrene addition products $\overset{\sim}{2a}$ and $\overset{\sim}{2b}$ isolated in the trapping experiment of Mohanakrishnan *et al.* suggest that an allene intermediate is present, but do not rule out a cycloalkyne cycloaddition¹² followed by rearrangement under the reaction conditions. In addition, since several competing pathways are possible for allene and for alkyne, we focus our attention on the product determining intermediates for *t*-butyl enol ether formation.

Acknowledgement. The authors acknowledge the generous support of the National Science Foundation and thank Professor A. T. Bottini for stimulating discussions.

REFERENCES

1. Presented in part at the 26th Annual Northwest Regional Meeting of the American Chemical Society, Bozeman, Montana, Paper 152, June, 1971.
2. a) L. K. Montgomery and L. E. Applegate, *J. Amer. Chem. Soc.*, 89, 2952 (1967) and references cited therein; b) L. K. Montgomery, A. O. Clouse, A. M. Crelier and L. E. Applegate, *ibid.*, 89, 3453 (1967).
3. a) G. Wittig and P. Fritze, *Angew. Chem. Int. Ed.*, 5, 846 (1966); b) G. Wittig and P. Fritze, *Justus Liebigs Ann. Chem.*, 711, 76, 82 (1968).

4. a) W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); b) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).
5. a) A. T. Bottini and W. Schear, *J. Amer. Chem. Soc.*, 87, 5802 (1965); b) A. T. Bottini, F. P. Corson, R. Fitzgerald and K. A. Frost, Jr., *Tetrahedron Lett.*, 4753, 4757 (1970); c) A. T. Bottini, F. P. Corson, R. Fitzgerald and K. A. Frost, Jr., *Tetrahedron*, 4883 (1972).
6. P. Mohanakrishnan, S. R. Trayal, R. Viadyanathaswamy and D. Devaprabhakara, *Tetrahedron Lett.*, 2871 (1972).
7. A. T. Bottini and F. P. Corson have found that retro-ene conversions of 1-*t*-butoxy-4- and 5-*t*-butylcyclohexene to the corresponding cyclohexanones can be used to determine per cent composition, F. P. Corson, Ph. D. Thesis, University of California, Davis (1967).
8. P. K. Freeman and T. A. Hardy, *Tetrahedron Lett.*, 3939 (1971).
9. R. G. Bergman and V. J. Rajadhyadsha, *J. Amer. Chem. Soc.*, 92, 2163 (1970).
10. P. K. Freeman and D. M. Balls, *J. Org. Chem.*, 32, 2354 (1967); P. K. Freeman and D. G. Kuper, *ibid.*, 30, 1047 (1965).
11. a) J. Wolinsky, *J. Org. Chem.*, 26, 704 (1961); b) P. Caubere and J. J. Brunet, *Tetrahedron*, 27, 3515 (1971).
12. a) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, 1967, pp 200-205, 352-355; b) A. Krebs in "Chemistry of Acetylenes," ed. by H. G. Viehe, Marcel Dekker, New York, 1969, pp 1024-1027.