Tetrahedron Letters No. 5, pp 441 - 444, 1974. Pergamon Press. Printed in Great Britain.

BICYCLOBUTANES FROM CYCLOPROPYLIDENE INSERTION REACTIONS AND PHOTOLYTIC CLOSURE OF A DIENE

R. B. Reinarz[*] and G. J. Fonken

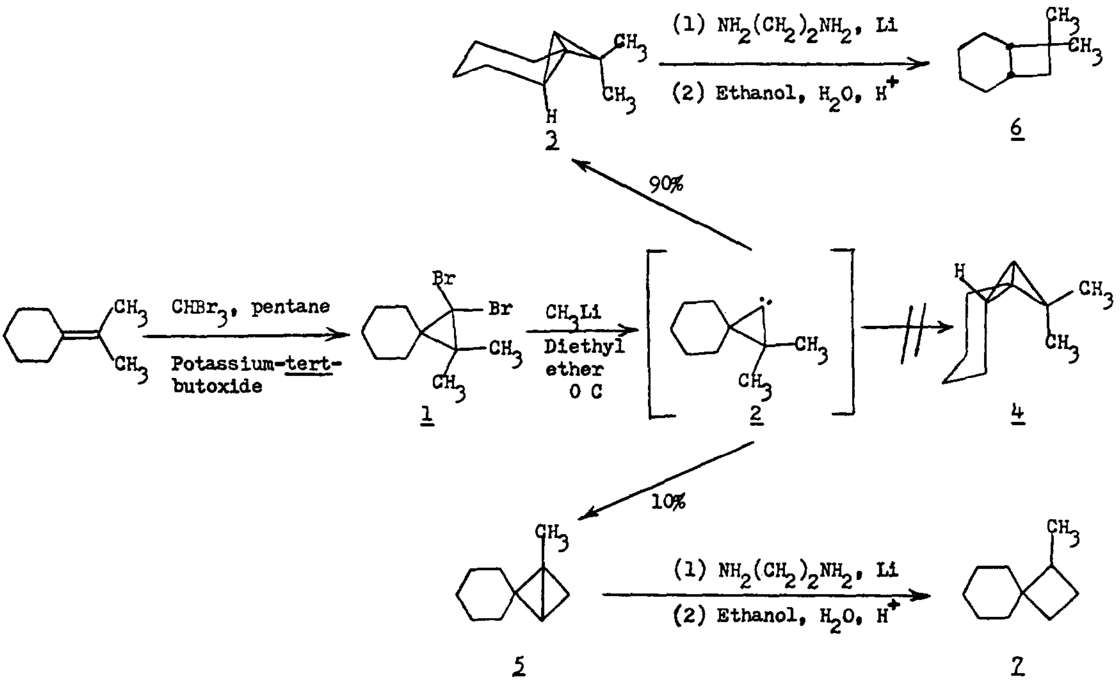
Department of Chemistry, The University of Texas at Austin

Austin, Texas 78712

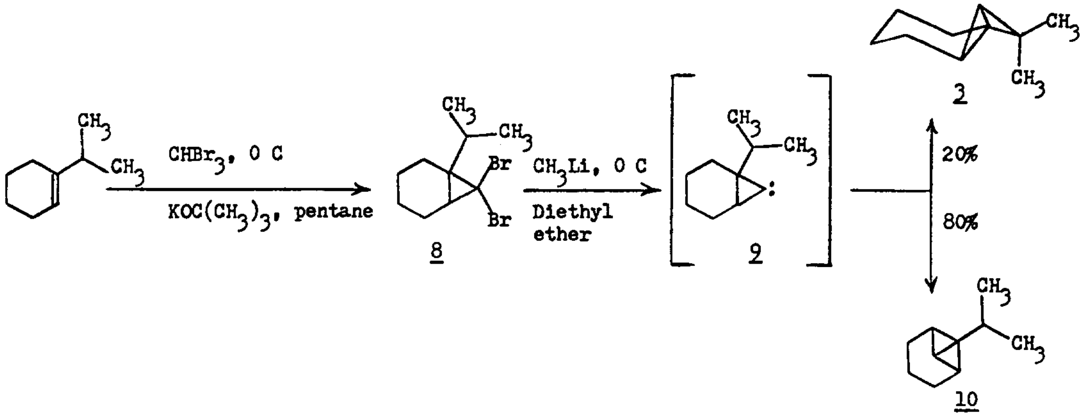
(Received in USA 14 September 1973; received in UK for publication 28 December 1973)

Methyl lithium reactions on selectively substituted *gem*-dibromocyclopropanes were studied with the intent of generating bicyclobutanes of known stereochemistry in high yield. Bicyclobutanes produced in this way were to be compared to the monomeric photolysis product(s) of a fixed s-*trans* diene and, therefore, evidence could be obtained on the mode of diene closure. From methyl lithium reaction of 1,1-dibromo-2,2-dimethylspiro[2.5]octane (**1**) was expected three possible bicyclobutanes **3**, **4**, and **5**. It was anticipated that insertion of cyclopropylidene **2** would occur preferentially with the secondary C-H bond at C-4 or C-8 and yield *cis*-fused bicyclobutane **3**. Less likely, secondary insertion might yield *trans*-fused bicyclobutane **4**. Primary site insertion into either methyl group at C-2 would yield **5**. Our observations[1] were in agreement with other examples[2,3,4,5] in which insertions of cyclopropylidenes into substituted C-H bonds occur more readily. From the methyl lithium reaction of **1** was produced a mixture of two bicyclobutanes in greater than 90% yield and indicated from NMR data to occur in a 9:1 ratio. The lack of any allene formation from **1** corresponds with other reports[2,6,7] of similar reactions. To identify the products, the reaction mixture was reduced using lithium and ethylenediamine by the method of Moore *et al.*[8] and yielded two separable hydrocarbons determined to be **6** and **7**, identified by respective spectral data [for **6**: NMR 0.95 δ (singlet, 3H), 1.15 δ (singlet, 3H), 1.30 δ-1.82 δ (multiplet, 12H); IR 1387 cm^{-1}, 1379 cm^{-1}, 1273 cm^{-1}] and [for **7**: NMR 0.92 δ (doublet, J=6hz, 3H), 1.38 δ (singlet, 9H), 1.47 δ -2.18 δ (multiplet, 6H), 1.47 δ -2.18 δ (multiplet, 6H); IR 1375 cm^{-1}, 934 cm^{-1}, 913 cm^{-1}, 844 cm^{-1};[*] mass spectrum with a parent peak at 138 for both **6** and **7**]. Both isomers had suitable elemental analyses. Since this process saturates only the 1,3 bond of bicyclobutanes, it is clear that **6** could arise only from **3** and **7** only from **5**.

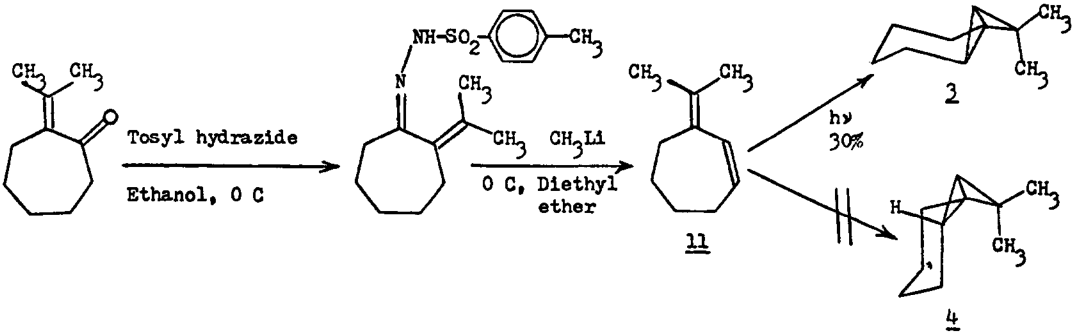
As a consequence, the quanitative preference for cyclopropylidene 2 insertion into a secondary rather than a primary bond is substantiated.



In addition, the methyl lithium treatment of 7,7-dibromo-1-isopropylbicyclo[4.1.0]heptane (8) was examined in the anticipation that insertion into the most substituted C-H bond of the C-1 isopropyl group, a tertiary center, would occur via cyclopropylidene 9 and produce 3. Since the stereochemistry of 8 is cis, derived by a cis addition of dibromocarbene to 1-isopropylcyclohexene, and should be unaltered in forming cyclopropylidene 9, subsequent insertion into the C-H bond of the isopropyl group should produce the cis-fused bicyclobutane 3. The methyl lithium reaction gave two bicyclobutane products in greater than 90% yield. Separation was achieved at 90 C using a 10 ft x 1/4 in aluminum column packed with 60/80 mesh chromosorb G, 20% squalene, and 2% KOH. The 20% fraction resulted from insertion into the isopropyl group and identification showed it to 3 based on spectral data [NMR 0.68 δ (singlet, 1H), 0.77 δ (singlet, 3H), 1.01 δ (singlet, 3H), 1.20 δ -2.30 δ (multiplet, 9H); IR 1378 cm^{-1}, 1325 cm^{-1}, 770 cm^{-1}; mass spectrum with parent peak at 136]; suitable elemental analysis. The stereochemistry of bicyclobutane 3, therefore, has been determined unequivocally as cis. The 80% fraction proved to be compound 10 in which insertion had occurred at C-2 [NMR 0.95 δ (doublet, J=6 hz, 6H), 1.28 δ (singlet, 7H), 2.05 δ (heptet, J=6 hz, 1H), 2.20 δ (multiplet, 2H); IR 1384 cm^{-1}, 1368 cm^{-1}, 1140 cm^{-1}, 937 cm^{-1}, 808 cm^{-1}, 758 cm^{-1} (strong); mass spectrum with parent peak at 136]; suitable elemental analysis.



Since our results had established the stereochemistry of 3, the synthesis of 11 was studied to ascertain if the product from UV photolysis might be identical to compound 3 from the two methyl lithium reactions. If so, a bicyclobutane would have been generated by two independent routes, methyl lithium reactions and one photolysis, and would prove its stereochemistry while providing evidence for the mode of closure of an s-trans diene. The methyl lithium reaction on the tosylhydrazone of 3-isopropylidenecycloheptanone produced 3-isopropylidenecycloheptene (11) [NMR 1.70 δ (singlet, 6H), 1.60 δ (multiplet, 4H), 1.96 δ -2.52 δ (multiplet, 4H), 5.57 δ (doublet of triplets, J=11 hz, J=5 hz, 1H), 6.30 δ (doublet, J=11 hz, 1H); IR 3010 cm^{-1} (strong), 1645 cm^{-1}, 1610 cm^{-1}, 1372 cm^{-1}, 853 cm^{-1}, 744 cm^{-1} (strong); mass spectrum with parent peak at 136; UV λ_{max}=237 nm, ε_{max}=17,000]; suitable elemental analysis. Bicyclobutane 4 is the anticipated photolytic closure product of 11 by Woodward-Hoffmann theory[9]. However, cis-fused bicyclobutane 3 is expected based on reports by Dauben[10] and Short[11].



Photolysis of 11 gave a single product in 30% yield. Spectral data demonstrated that the photoproduct was identical in all respects to 3 produced by methyl lithium reactions on 1 and 8. This observation substantiates the applicability of the mechanism proposed by Dauben[10]. It is significant that a bicyclobutane is produced in common from a photolysis of a fixed s-*trans* diene and cyclopropylidene insertion reactions.

In summary, bicyclobutanes can be produced nearly in quanitative yield with known stereochemistry from reactions of methyl lithium with substituted *gem*-dibromocyclopropanes. Since a bicyclobutane from two methyl lithium reactions was identical to that by a photochemical closure of a fixed s-*trans* diene, the mode of closure and stereochemistry of this photolysis product was established. Also, the utility of bicyclobutanes from these procedures has been explored in a limited manner and provides cyclobutanes via known chemical transformations.

Acknowledgement. The authors are grateful to the Robert A. Welch Foundation for predoctral and research grant support.

References

*Author to whom correspondence should be addressed at the Department of Chemistry, North Texas State University, Denton, Texas 76203.

1. R. B. Reinarz and G. J. Fonken, *Tet. Let.*, 4013 (1973).
2. W. R. Moore and J. B. Hill, *ibid.*, 4343 (1970).
3. W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, *92*, 5469 (1970).
4. W. R. Moore and B. J. King, *J. Org. Chem.*, *36*, 1882 (1970).
5. W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, *83*, 2019 (1961).
6. W. R. Moore and J. B. Hill, *Tet. Let.*, 4553 (1970).
7. L. Skattebol, *ibid.*, 2361 (1970).
8. W. R. Moore, S. S. Hall, and C. Largman, *ibid.*, 4353 (1969).
9. R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Academic Press, New York (1970).
10. W. G. Dauben and J. S. Rita, *J. Amer. Chem. Soc.*, *92*, 2925 (1970).
11. M. R. Short, Dissertation, The University of Texas at Austin, Austin, Texas (1971).