

SILVER(I) PROMOTED REARRANGEMENT OF BISHOMOCUBANE DERIVATIVES

Tien-Yau Luh

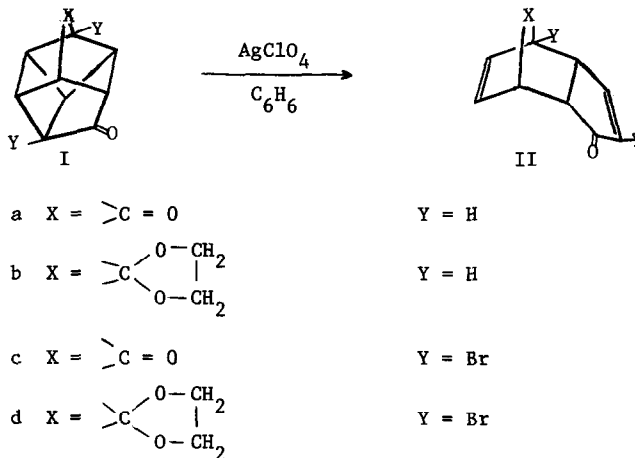
Department of Chemistry, The Chinese University of Hong Kong, Hong Kong

SUMMARY: Silver(I) ion catalyzes the conversion of bishomocubane derivatives into dicyclopentadiene derivatives in quantitative yield.

(Received in Japan 6 June 1977; received in UK for publication 5 July 1977)

Metal-catalyzed rearrangement of small ring compounds is well-documented<sup>1</sup>. Cubane and related compounds rearrange to dienes or cuneane derivatives depending on conditions and catalyst.<sup>2</sup> Surprisingly, no report has been made on such reaction with bishomocubane derivatives I. We now wish to describe the silver(I) ion-catalyzed rearrangement of these compounds. This study was particularly interesting to illustrate whether caged compounds less strained than those previously studied<sup>2</sup> would be subjected to skeletal reorganization.

Compounds Ia-Id were prepared according to literature methods<sup>3,4</sup>. Treatment of Ia with a solution of silver perchlorate in dry benzene afforded dicyclopentadienone, IIa in quantitative yield. In similar manner, exposure of related compounds Ib-Id to benzene solutions of silver perchlorate led quantitatively to the corresponding dienes, IIb-IId. These results suggest that silver(I) ion was very effective in the conversion of bicyclo[2.2.0]hexyl moiety in the

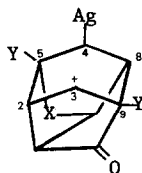


bishomocubane derivatives into non-conjugated diene systems.

Silver(I) ion is generally considered to function as Lewis acid in these catalyzed rearrangement reactions<sup>5</sup>. A stepwise mechanism has been proposed<sup>5</sup>. In general, the fundamental process of the rearrangement in the cubyl or related systems with this catalyst is the facile rearrangement of the cyclopropyl carbinyl carbonium ion<sup>5</sup>. However, in this study, no product with the skeleton III, as predicted from the above mechanism, was isolated. This implies that



III



IV

the reaction may proceed via an alternative intermediate. Our results suggest that silver(I) ion would rather rupture the most strained  $\sigma$ -bond ( $C_3-C_4$  bond) to afford the metallo-carbonium ion, IV. To lead to diene from IV, the migration of  $C_8-C_9$  bond should be either kinetically ( $X = >C=O$ ) or thermodynamically ( $X = \begin{array}{c} O-CH_2 \\ | \\ >C \\ | \\ O-CH_2 \end{array}$ ) favored over the migration of  $C_2-C_5$  bond.

Consequently, only one kind of diene can be obtained. In addition, relief of strain is generally considered as an important factor in these reactions<sup>2a,6</sup>. No product related to III is thus not surprising<sup>8</sup>.

## REFERENCES AND NOTES

- For a recent review see: K.C. Bishop, III, Chem. Rev., **76**, 461 (1976).
- (a) L. Cassar, P.E. Eaton, and J. Halpern, J. Amer. Chem. Soc., **92**, 3515, 6366 (1970).  
(b) W.G. Dauben and A.J. Kielbania, Jr., ibid. **93**, 7345 (1971). (c) L.A. Paquette, R.S. Beckley, and T. McCreadie, Tetrahedron Lett., 775 (1971). (d) R. Askani, ibid., 3349 (1970)  
(e) E.W. Turnblum and T.J. Katz, J. Amer. Chem. Soc., **95**, 4292 (1973). (f) L.A. Paquette, R.A. Boggs, W.B. Farnham and R.S. Beckley, ibid., **97**, 1112 (1975).
- (a) N.B. Chapman, J. M. Key, and K.J. Toyne, J. Org. Chem., **35**, 3860 (1970).  
(b) T.-Y. Luh, Ph.D. Thesis, University of Chicago, 1974.
- Satisfactory spectroscopic properties were obtained for all compounds.
- J.E. Byrd, L. Cassar, P.E. Eaton, and J. Halpern, J. Chem. Soc. Chem. Commun., 40 (1971).
- The strain energies of II and III are unknown. The difference, however, can be estimated<sup>7</sup> to be at least 20 Kcal. III should be as strained as I.
- E.M. Engler, J.D. Andose, and P.v.R. Schleyer, J. Amer. Chem. Soc., **95**, 8005 (1973).
- Dedicated to the memory of the late C. Luh.