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DOUBLE RING OPENING OF BRIDGED DICYCLOPROPYL KETONES UPON REDUCTION BY LITHIUM IN LIQUID AMMONIA

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Several years ago LeBel and Liesemer reported that lithium ammonia reduction of the bridged dicyclopropyl ketone I led to cleavage of both cyclopropane rings with concomitant formation of a new double bond.[1] Extending a well-established concept in the field of lithium ammonia reduction of simple cyclopropyl ketones - the transition states leading to ring-opened products bear carbanion character - Staley for this special case proposed the intermediacy of a species having bishomocyclopentadienyl anion character.[2] In order to gain more evidence on the occurrence of two-electron double ring opening of bridged dicyclopropyl ketones - and on the potential of this reaction for the generation of transient homoaromatic anions - we have reinvestigated the lithium ammonia reduction of I and have carried out similar reductions of ketones II, III, and IV.[3]

Results (see Table 1):

The products obtained from I-III support the notion that pericyclic processes lead to double ring opening by two electron reduction whenever two cyclopropane rings and a carbonyl group are conjugated in a pericyclic mode. (On prolonged exposure to the conditions of reduction in liquid ammonia the initial ketonic products may be further reduced to alcohols. In the case of III the conjugated diene XII, formed initially, undergoes rapid further reduction to XIII and XIV. XV is formed by intramolecular scavenging of the ketyl derived from XIV). If pericyclic interaction is impeded by insertion of a methylene group as in IV, the bridged dicyclopropyl ketone behaves "normally", only one cyclopropane bond (the one conjugating most effectively with C=O) being opened.[4]

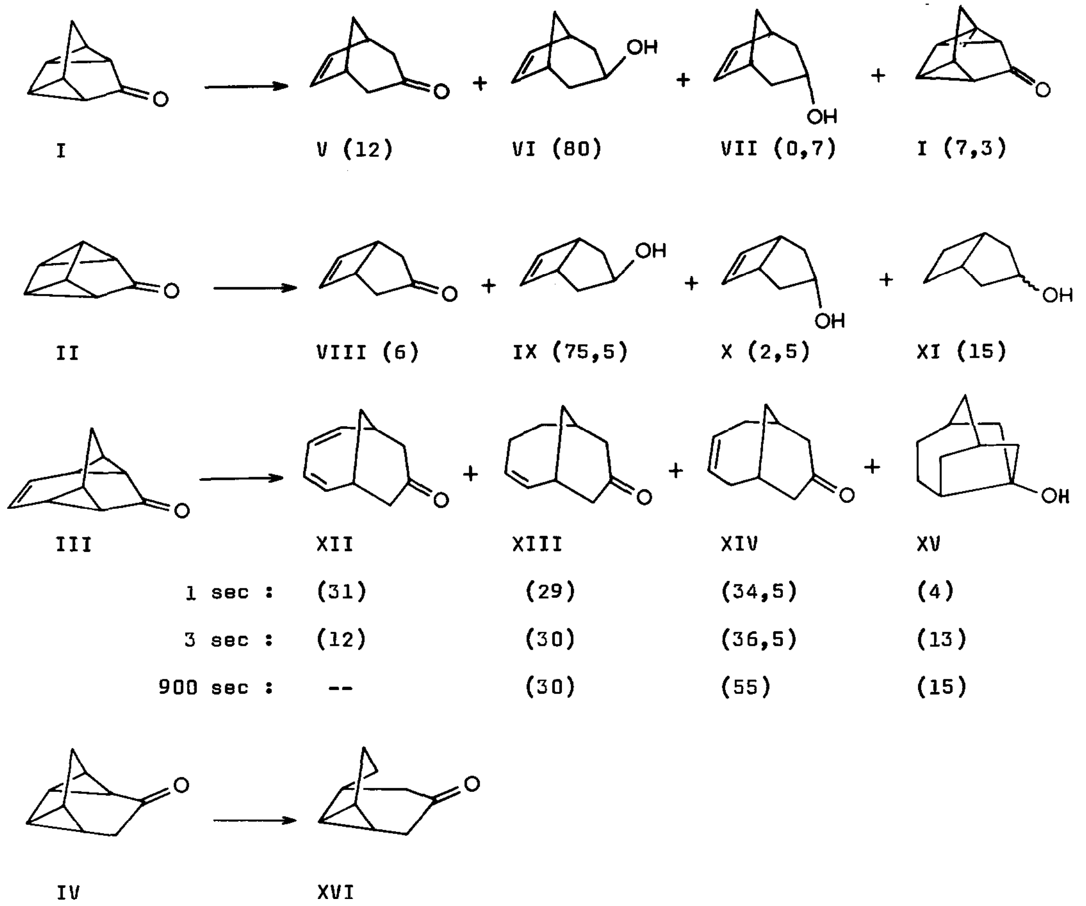

Table 1. Products of the lithium ammonia reduction of dicyclopropyl ketones I-IV. Excess lithium with I, II, IV about twentyfold, with III threefold; reaction time I and II: 4 hours, IV: 30 min; total yield in all cases ca. 65%; relative yields in parentheses.

References and footnotes

1) N.A. LeBel and R.N. Liesemer, J. Amer. Chem. Soc., 87, 4301 (1965).
2) S.W. Staley in "Selective organic transformations", B.S. Thyagarajan, Ed., Vol. II, p. 309, Wiley-Interscience, New York, London, Sydney, Toronto, 1972.
3) New cyclopropyl ketones (III, IV, XVI) were prepared by Cu-catalyzed decomposition of the appropriate unsaturated diazoketones. A preparation of IV duplicating our own synthesis has recently been reported: R.D. Miller and D.L. Dolce, Tetrahedron Letters, 1977, 3329. These authors also confirm our observation that IV, upon glpc at 85°C, rearranges quantitatively into bicyclo[4.2.1]nona-2,7-dien-4-one.
4) We thank Profs. D.I. Schuster (New York) and M. Hartmann (Jena) for providing spectra.