Entry to the Bicyclo[4,2,1]nonane System

By C. W. JEFFORD, S. N. MAHAJAN, R. T. MEDARY, W. WOJNAROWSKI, and B. WAEGELL
(Chemistry Department, Temple University, Philadelphia, Pa. 19122)

and K. C. RAMEY
(Atlantic Refining Co., Glenolden, Pennsylvania)

THE addition of halogenocarbenes to bridged bicyclic olefins affords a ready means of obtaining conformationally constrained common and medium rings.[1] Although certain selection rules govern the stereochemistry of the rearrangement of the initial cyclopropane adduct,[2] the direction of rearrangement of the cyclopropane adduct formed from an unsymmetrical bridged bicyclic olefin remains unpredictable.

We describe some preliminary findings obtained from the addition of dichloro- and dibromocarbene to bicyclo[3,2,1]oct-2-ene and the reaction of the adducts thus obtained. In both cases a single adduct was obtained in yields of 17 and 39%, namely, 3,3-dichloro- and 3,3-dibromotricyclo[4,2,1,0^{2,4}]nonane (I) and (II) formulated as the *exo*-structures.* Compounds (I) and (II) were thermally stable to a remarkable degree. However, opening of the cyclopropane ring was found to occur under certain conditions. Heating the dichloro-adduct (I) alone at 202° for 24 hr., or in quinoline at reflux for 24 hr., afforded 3-chlorobicyclo[4,2,1]nona-2,4-diene (III) in 14% yield. Similarly, heating the dibromo-adduct (II) in chlorobenzene or pyridine gave better yields (23 and 26%) of 3-bromobicyclo[4,2,1]nona-2,4-diene (IV).

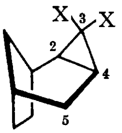
It seemed reasonable that the dienes (III) and

---

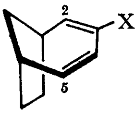
* All compounds reported gave acceptable elemental analyses.

(IV) arose by ring-enlargement of the cyclopropane portions followed by elimination of hydrogen halide. When the dibromo-adduct (II) was heated alone at 150° for 24 hr., or in boiling mesitylene for 30 hr., *exo*-2,3-dibromobicyclo[4,2,1]non-3-ene (V) could be obtained in yields of 79 and 70% respectively.†

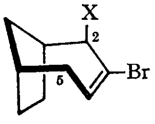
More simply, treatment of the dibromo-adduct (II) with aqueous silver ion at room temperature caused rearrangement to the bicyclo[4,2,1]nonene skeleton without elimination. The major product (75%) was *exo*-3-bromo-2-hydroxybicyclo[4,2,1]non-3-ene (VI), the n.m.r. spectrum of which was similar to that of (V). The minor component (25%) was 3-bromo-4-hydroxybicyclo[4,2,1]non-2-ene. Jones oxidation of (VI) furnished the related 2-ketone (VII).‡



(I; X=Cl)
(II; X=Br)



(III; X=Cl)
(IV; X=Br)



(V; X=Br)
(VI; X=OH)

Some of the driving force for the ready elimination of hydrogen halide from compound (V) (and its chloro-analogue) undoubtedly comes from relief of the diaxial interaction at C-2 and C-5 which is known to be quite severe in the chair or boat conformations of cycloheptene.[3]

The present results indicate that the electrocyclic rearrangement of the *exo*-tricyclo[4,2,1,$0^{2,4}$]nonane skeleton under thermal and ionic conditions occurs with preferential formation of the bicyclo[4,2,1]non-3-ene skeleton rather than its 2-isomer. The complete account of conformational and stereochemical aspects will be reported later.

(*Received, February* 20*th*, 1967; *Com.* 163.)

---

† The vinylic and allylic proton resonances of compound (V) showed as a triplet (^3J ~ 5·2 c./sec.) at 6·19 p.p.m. and as a doublet (^3J ~ 4·8 c./sec.) at 4·84 p.p.m.

‡ The vinylic proton of compound (VII) showed as a triplet (^3J ~ 5 c./sec.) at 6·98 p.p.m.

[1] C. W. Jefford, S. Mahajan, J. Waslyn, and B. Waegell, *J. Amer. Chem. Soc.*, 1965, **87**, 2183.

[2] C. W. Jefford, E. Huang Yen, and R. T. Medary, *Tetrahedron Letters*, 1966, 6317; C. W. Jefford and R. T. Medary, *Tetrahedron*, in the press.

[3] G. L. Buchanan and J. M. McCrae, *Tetrahedron*, 1967, **23**, 279.