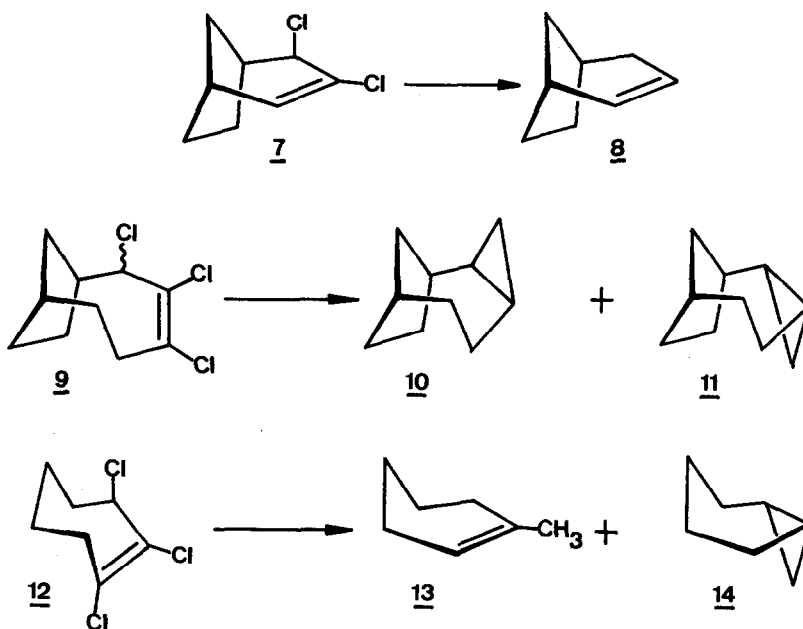


Reduction of the dichloro or tetrachloro olefins 5 and 6 proceeds entirely normally to give 3. Moreover, it is significant that 5 and 6 under the reaction conditions undergo easy elimination of hydrogen chloride to bicyclo[4.2.1]nonadienes, whereas the trichloro derivative remains intact. The dienes undergo reduction to give only 3.

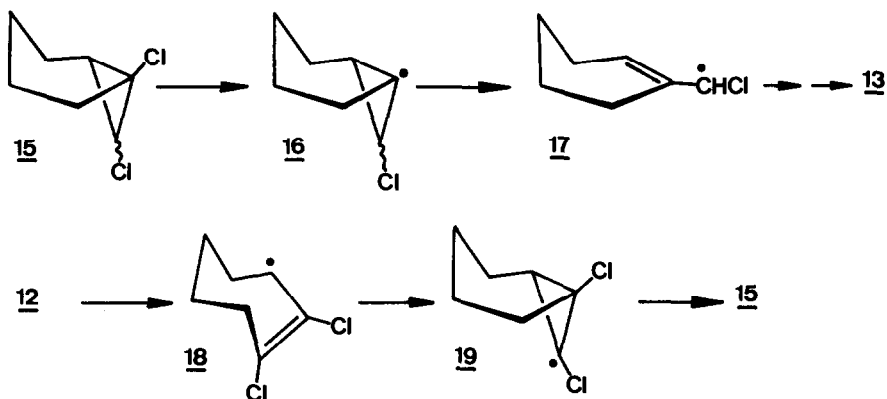
Birch reduction of the bridged trichlorocyclohexenyl compound 7 gives merely bicyclo[3.2.1]oct-2-ene (8)⁵. However, reduction of the cyclo-octenyl derivative, 2,3,4-trichlorobicyclo[5.2.1]dec-3-ene (9) furnishes both the *exo*- and *endo*-bicyclo[5.2.1.0^{2,4}]decanes (10 and 11) in yields of 31 and 4%.

Lastly, for the non-bridged, conformationally free, 1,2,3-trichlorocycloheptene (12), 1-methylcyclohexene (13) and bicyclo[4.1.0]heptane (14) are formed in yields of 14 and 17%⁶.



In summary, 1,2,3-trichlorocycloalkenes having rings larger than cyclohexene undergo reductive dechlorination to afford bicyclo[n.1.0]alkanes. On the basis of the present evidence it is difficult to unequivocally account for this unexpected divergence of reaction course. Clearly two competing reduction pathways

exist. When elimination is possible, or the ring is too small, then the usual reduction obtains. To explain the usual, and in particular the unusual courses, carbanions or radicals of some kind must be invoked. A carbanion mechanism appears unlikely. Internal nucleophilic displacement by a neighbouring carbanion on a chlorine substituted carbon is geometrically impossible as the ring prevents Walden inversion. Similarly, alkyl radical intermediates can be discounted, although closure of a 1,3 diradical is feasible. A better intermediate is an alkenyl radical. A sign to this effect is the production of the ring contracted olefin (13). Evidently, a cyclopropane derivative, but not 14 which is stable under the reaction conditions, must be the precursor to 13. As a working hypothesis we suggest that this precursor is the dichlorocyclopropane 15. Reaction of 15 with an atom of sodium can generate the bridgehead cyclopropyl radical 16 which then opens to the allyl radical 17 and thence to 13. The reverse of this process should explain how the cyclopropanes themselves are formed. Similar action of sodium on 12 would produce the allylic radical 18 which on electrocyclic closure gives the cyclopropyl radical 19 thereby leading to 15.



These remarkable findings indicate that electrocyclic closure of an alkenyl radical with all its stereochemical implications exists as a distinct and intriguing possibility; a possibility which awaits confirmation by a study of the behaviour of radicals related to 17 and 18.

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- 5) Compounds 7, 9 and 12 were prepared by the thermal rearrangement of the adducts formed by the addition of dichlorocarbene to 2-chloronorborn-2-ene, 3-chlorobicyclo[4.2.1]non-2-ene, and 1-chlorocyclohexene (F. Delay, work to be published).
- 6) In addition to the products isolated and expressed in percentage yield, the remainder of the reaction mixture was assayed as high-boiling polymeric material.
- 7) Little experimental evidence exists concerning the opening of cyclopropyl radicals (S. Sustmann, C. Rüchardt, A. Bieberbach & G. Boche, *Tet. Letters*, 4759 (1972); S. Sustmann & C. Rüchardt, *ibid.*, 4765 (1972)). Theoretical considerations favour disrotatory opening (E. Haselbach, *Helv.* 54, 2257 (1971); G. Boche & G. Szeimies, *Angew. Chem.* 83, 978, 979 (1971); M.J.S. Dewar & S. Kirschner, *J. Amer. Chem. Soc.* 93, 4290 (1971)). Cf. H.C. Longuet-Higgins & F.W. Abrahamson, *J. Amer. Chem. Soc.* 87, 2045 (1965); R.B. Woodward & R. Hoffmann, *ibid.* 87, 395 (1965).