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THE STEREOCHEMICAL COURSE OF METAL CATALYZED CYCLOADDITION REACTIONS OF NORBORNADIENE

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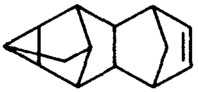
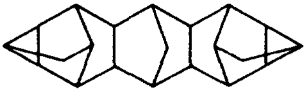
When norbornadiene is refluxed with 5% rhodium on carbon it yields quantitatively a mixture of dimers consisting almost entirely of two stereoisomers of structure I and a trimer of structure II.[1] The remainder of the dimer mixture is the substance assigned structure III. Other dimers as well as these are formed when norbornadiene is reacted with a variety of group VIII metal complexes. The following are all the dimers that have been described: dimers of structure I,[1-5] presumably always the same two stereoisomers described above;[2] III and two of its stereoisomers, IV and V;[1-7] a bis-nortricyclene assigned structure VI;[2] and a caged saturated dimer, either VII or VIII.[3,8]

Reported below is a reaction implying that the stereochemistries of the dimers of structure I are X (the major dimer in the rhodium catalyzed reaction) and XI (the minor dimer), and that the caged saturated dimer is VII, not VIII. The structures of these products suggest a simple formal relationship, described below, that links all the dimers but one. Only if the structure of the one unrelated dimer were possibly misassigned, and its structure were IX, not VI, would it be related to the others. The relationship between the other dimers is pointed out because it suggests that in the metal catalyzed cycloaddition an intermediate is produced in which only one carbon-carbon bond unites the two norbornadiene moieties, about which rotation may occur before the second bond closes. This contrasts with the hypothesis that all new carbon-carbon bonds are formed while the reactants are fixed on the catalyst in a conformation resembling the



I



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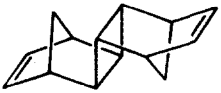

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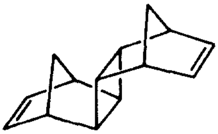

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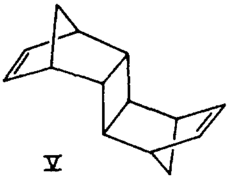
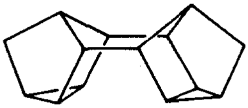
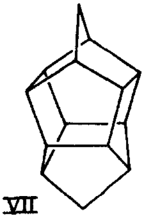


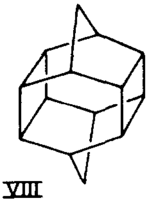
V



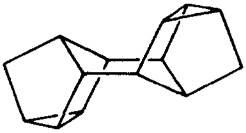
VI



VII



VIII



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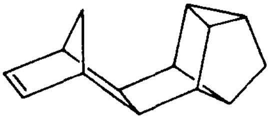
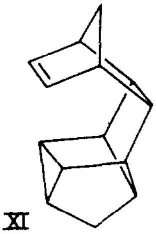


X

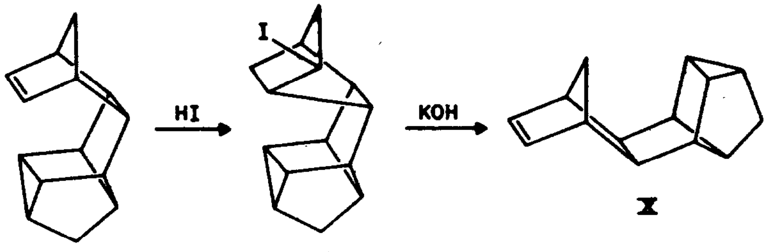


XI

product.[2,9] If the substance assigned structure VI were actually IX, the hypothesis[2] that it is formed by the union of two norbornadiene rings fixed to adjacent metal atoms would be untenable.

The structure VI was assigned to the bis-nortricyclene only on the basis of the observation of a greater number of bands in the infrared spectrum than the number of infrared active fundamental modes allowed structure IX.[2] The reasons for questioning the assignment are that not all the bands observed were necessarily fundamentals, some of the bands reported could not be found in the spectrum (e.g. 2984 and 2940 cm^{-1}), and some bands that are observed in the infrared spectrum are not in the raman spectrum (e.g. 2914, 1045.5, 840.2, 798.8 cm^{-1}), implying, although not definitively, by reasoning similar to that which had been used to assign the structure VI, that this structure should be excluded because for VI, unlike IX, all fundamental vibrations are allowed in the raman spectrum.

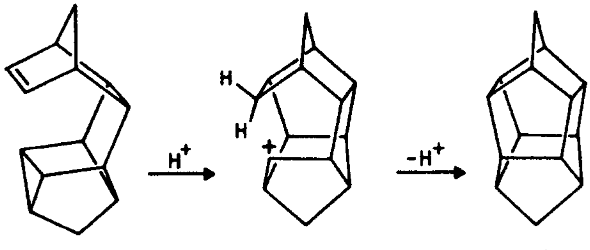
SCHEME I



XI XII X

The reaction that implies the stereochemistries of the dimers of structure I and the structure of the caged saturated dimer is the reaction of the minor dimer of structure I, formed in the rhodium catalyzed reaction and previously suggested to have the stereochemistry XI,[1,10] with hydriodic acid.[11] When this hydrocarbon is shaken for ten hours with 47-50% hydriodic acid at 65-70°, it gives a mixture of substances from which one can isolate by chromatography on alumina the hydrogen iodide adduct presumed to be XII in scheme I, a liquid identified by its analysis and by its spectroscopic properties.* When this iodide is warmed at 80° for 25 hr. with alcoholic potassium hydroxide,[11,12] it gives in high yield the major dimer I from the rhodium catalyzed dimerization.[1] This substance is therefore assigned the structure X.

SCHEME II



XI VII

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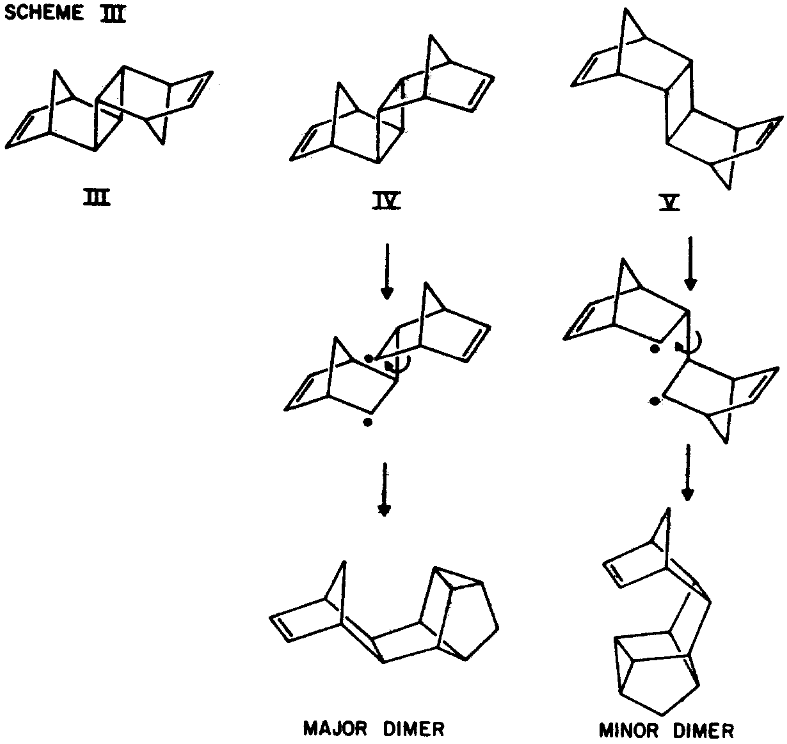
*The absence of olefinic protons is indicated in its n.m.r. spectrum by the absence of absorption below 6τ and in its infrared spectrum by the absence of strong absorption between 700 and 750 cm^{-1}. The presence of a nortricyclene is indicated in the infrared by strong absorption at 800 and 814 cm^{-1}, and in the n.m.r. spectrum by an AB_2 absorption pattern at 8.75 and 9.17τ ($J=4.6$ cps) characteristic of the cyclopropane and by the absorption at 8.67τ characteristic of the methylene bridge of a nortricyclene.

SCHEME III



Besides the iodide XII, the reaction of the minor dimer (XI) with hydriodic acid yields other products including, interestingly, the caged dimer.[3,8] This product is therefore assigned the structure VII because, unlike the alternative VIII, this structure is derived simply from the original hydrocarbon, as shown in scheme II, by protonation of either the olefin or the cyclopropane and reorganization of neighboring bonds.[13] The reaction also supports the assignment of structure XI to the minor dimer.

A relationship between the norbornadiene dimer is, as shown in scheme III, that they are derived from the three possible trans bis-norbornenes, III, IV, and V, by cleavage of one of the carbon-carbon bonds joining the norbornadiene moieties, and re-formation of the bond in the homoconjugate position. The implication may be that in all the metal catalyzed dimerizations one new carbon-carbon bond is formed before the other, and the product only subsequently determined.

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REFERENCES

(1) J.J. Mrowca and T.J. Katz, J. Am. Chem. Soc., 88, 4012, 5941 (1966).

(2) G.N. Schrauzer, B.N. Bastian, and G.A. Fosselius, ibid., 88, 4890 (1966).

(3) C.W. Bird, D.L. Colinese, R.C. Cookson, J. Hudec, and R.O. Williams, Tetrahedron Letters, 373 (1961).

(4) G.N. Schrauzer and S. Eichler, Chem. Ber., 95, 2764 (1962).

(5) P.W. Jolly, F.G.A. Stone, and K. Mackenzie, J. Chem. Soc., 6416 (1965).

(6) R. Pettit, J. Am. Chem. Soc., 81, 1266 (1959).

(7) D.R. Arnold, D.J. Trecker, and E.B. Whipple, J. Am. Chem. Soc., 87, 2596 (1965).

(8) D.M. Lemal and K.S. Shim, Tetrahedron Letters, 368 (1961).

(9) G.N. Schrauzer, P. Glockner, and S. Eichler, Angew. Chem. Intern. Ed. Engl., 3, 185 (1964).

(10) T.J. Katz, J.C. Carnahan, Jr., and R. Boecke, J. Org. Chem., 32, May (1967).

(11) P.D. Bartlett and I.S. Goldstein, J. Am. Chem. Soc., 69, 2553 (1947) and references therein.

(12) G.T. Youngblood and P. Wilder, Jr., J. Org. Chem., 21, 1436 (1956).

(13) cf. S. Winstein, Experientia Supplementum II, 137 (1955); L. de Vries and S. Winstein, J. Am. Chem. Soc., 82, 5363 (1960).