

CIS OXYMERCURATION OF NORBORNENE

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TWO different mechanisms for oxymercuration, one involving cis addition² and another involving trans addition³, have been previously proposed. Recent deoxymercuration studies⁴⁻⁵, have shown that olefins add mercuric salts in a trans fashion just as do simple acetylenes. This communication reports the first case of cis oxymercuration of an olefin (norbornene) and an ionic addition to norbornene which is not accompanied by rearrangement.

The intermediate (I) has been written⁶ to explain the products of ionic additions to the double bond in the 2,2,1-bicycloheptene series.

¹This work was carried out at The Dow Chemical Company, Pittsburg, California.

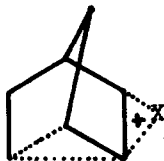
²O. W. Berg, W. P. Lay, A. Rodgman, and G. F. Wright, Can. J. Chem. 36, 358 (1958) and other references found therein.

³H. J. Lucas, F. R. Hepner, and S. Winstein, J. Am. Chem. Soc. 61, 3102 (1939).

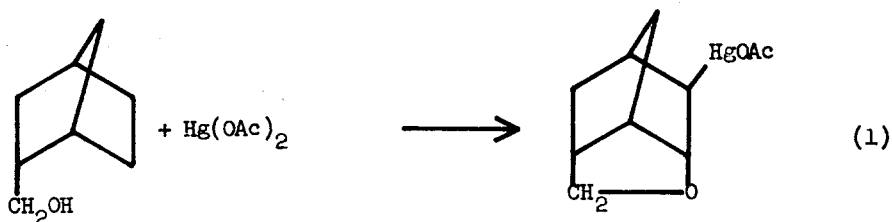
⁴M. M. Kreevoy, Abstracts 135th Meeting of The American Chemical Society, Boston, Massachusetts, April, 1959, page 81-0.

⁵T. G. Traylor and S. Winstein, ibid., page 82-0.

⁶H. Kwart, et al., J. Am. Chem. Soc. 76, 4072, 5400 (1954); 78, 5678 (1956).



Inversion at C₃ or C₄ would lead to the 2,3-trans and 2,7-syn products which are usually obtained⁷⁻⁸. Addition of iodine⁹, acid¹⁰, or mercuric acetate¹⁰ to endo-2-hydroxymethyl-5-norbornene yields cyclic ethers indicating that oxygen competes successfully with C₅ in the opening of the olefin-X⁺ complex (e. g., Equation 1).



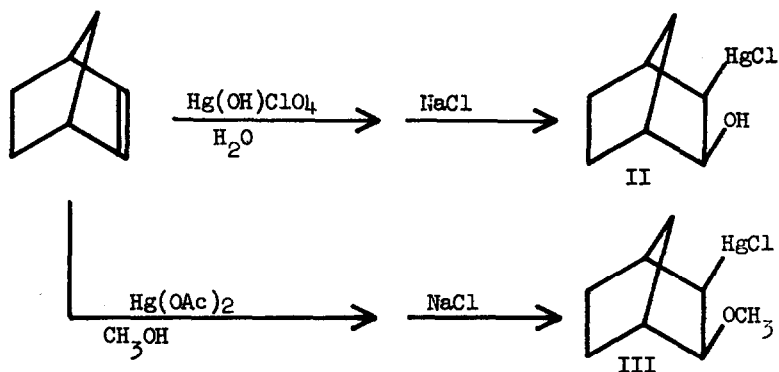
However, in the addition of mercuric salts to unsubstituted norbornene an entirely different situation obtains. Neither trans addition nor rearrangement occurs; the only product being the exo-cis oxymercurial.

⁷W. G. Woods, R. A. Carboni, and J. D. Roberts, ibid., 78, 5653 (1956).

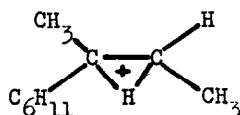
⁸H. M. Walborsky and D. F. Loncrini, ibid., 76, 5397 (1954).

⁹Interchemical Corporation, Commercial Development Department Bulletin CD-104.

¹⁰H. B. Henbest and B. Nichols, J. Chem. Soc. 1959, 221.



The cis opening of the intermediate (I) is as novel in general oxymercuration reactions as it is in ionic additions to norbornene and bears a striking resemblance to the cis opening of the substituted ethylene protonium ion IV reported recently by Cram and Tadanier¹¹.



IV

These observations suggest that mercury and hydrogen are much more strongly solvated than are other positive ions in this type of intermediate. However, the cis opening of the ion (I) is quite exceptional in mercuration reactions and recommends the exercise of caution in generalizing cis openings of such cyclic intermediates.

The oxymercurial (II), obtained in 86% yield by treating norbornene

¹¹D. J. Cram and J. Tadanier, J. Am. Chem. Soc. 81; 2745 (1959).

with aqueous mercuric hydroxyperchlorate (followed by precipitation as the chloride), analyzed accurately for $C_7H_{11}HgClO$, and had a single hydroxyl stretching frequency at 3604.0 cm.^{-1} in carbon tetrachloride. It could be oxidized in 73% yield with alkaline permanganate to a ketone C_7H_9HgClO (1724.1 cm.^{-1}) in which the mercury was adjacent to the keto group. This was evidenced by its facile removal with stannite or iodide ions¹² to produce norcamphor.

The oxymercurial (II) was reduced with sodium amalgam to exo-norborneol which was then converted to the acetate. The infrared spectrum of this acetate was identical to that of exo-norbornyl acetate reported by Winstein and Trifan.¹³

The relative configurations of the mercury and methoxy groups in the 3-methoxy-2-norcamphanylmercuric chloride (III) can be established with the data of Wright et al.¹⁴ In general, the dipole moments of oxymercuration products have been found to be higher than those of their diastereomers which are obtained by carbon-mercury epimerization.¹⁴ This is true of cyclopentene and cyclohexene oxymercuration products. However, III was found to have a dipole moment of 4.22 D whereas its diastereomer had a dipole moment of 2.77 D. Because the cyclopentene and cyclohexene oxy-

¹²O. A. Reutov and Lu Tszin Chzhu, Doklady Akad. Nauk. S. S. S. R. 110, 575-7 (1956).

¹³S. Winstein and D. Trifan, J. Am. Chem. Soc. 74, 1148 (1952).

¹⁴M. J. Abercrombie, A. Rodgman, K. R. Bharucha, and G. F Wright, Can. J. Chem. 37, 1328 (1959).

mercuration products have been shown to be trans,⁴ the norbornene adduct must be exo-3-methoxy-exo-2-norcamphanylmercuric chloride (III).¹⁵

The authors wish to thank Dr. M. M. Kreevoy for helpful discussions.

¹⁵After this work was completed, there appeared a publication¹⁴ reporting an identical oxymercuration of norbornene. This paper purports to prove that the adduct (II) is endo-3-hydroxy-exo-2-norcamphanylmercuric chloride by its reduction to "endo-norborneol". We have repeated the reduction procedure outlined, to obtain their "endo-norborneol" which has proven to be di-(exo-3-hydroxy-2-norcamphanyl) mercury (by infrared and C, H, Hg analyses). There was also produced, in 35% yield, exo-norborneol which apparently escaped the observation of these workers. In addition, reduction of 3-methoxy-2-norcamphanylmercuric chloride with sodium stannite yields, not endo-norbornyl methyl ether as reported, but exo-norbornyl methyl ether identified by comparing its infrared spectrum with that of the ether obtained by adding methanol to norbornene in sulfuric acid. Therefore, their configurational assignments and mechanistic interpretations based on these assignments¹⁶ are incorrect.

¹⁶D. D. K. Chiu and G. F. Wright, Can. J. Chem. 37, 1425 (1959).