

OXYMERCURATION AND OXYTHALLATION OF
NORBORNADIENE AND RELATED OLEFINS (1)

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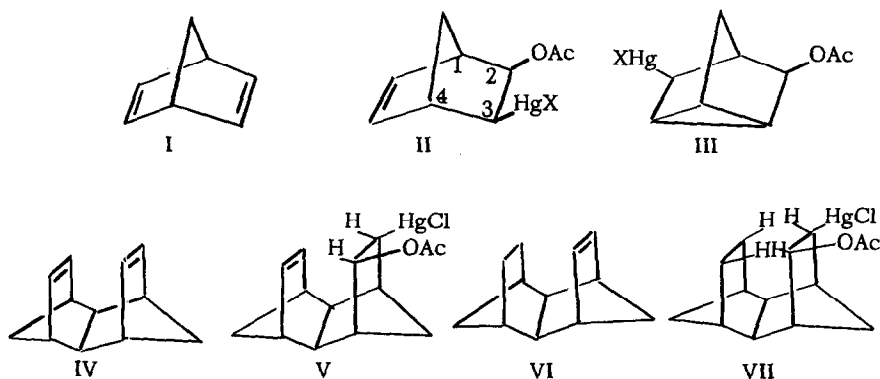
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While oxymercuration is trans (2) with typical olefins, it is cis (2) with norbornene. In the case of the related norbornadiene, oxymercuration has been reported to lead to a nortricyclic oxymercuration in methanol (3a) and ethanol (3b) solvents. Thallic acetate oxidation of olefins is most plausibly explained by way of oxythallation adducts (4). However, such adducts have only recently been isolated from styrene and *o*-allylphenol (4b). We now report some pertinent recent results of our study of oxymercuration and oxythallation of norbornadiene and related olefins.

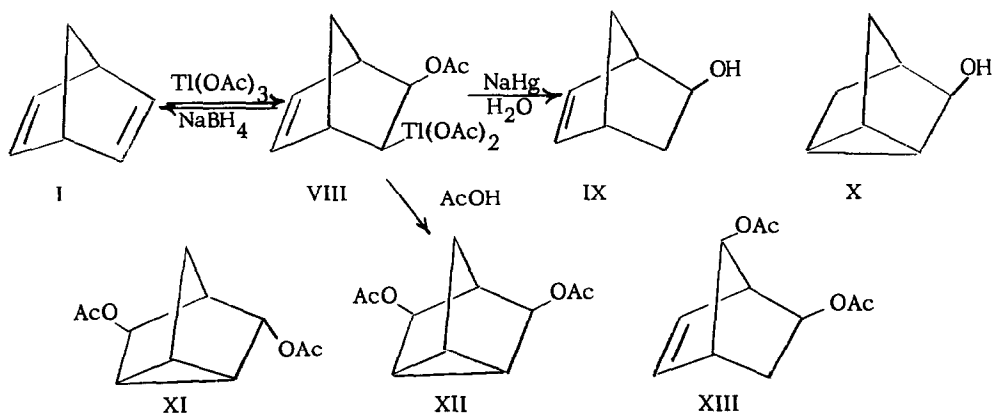
Examination of the oxymercuration of norbornadiene (I) in a variety of solvents shows that kinetic control leads to cis-2,3-exo-oxymercuration (2). Thus, the chloromercurial (5) II-Cl, m.p. 152-153° (dec.), is isolated from the relatively rapid reaction of the diene with mercuric acetate in acetic acid and other solvents when aqueous sodium chloride is used in the work-up. This material is clearly unsaturated from its n. m. r. and infrared spectra and chemical behavior. Its n. m. r. spectrum in DCCl₃ shows

the C_2 -proton as a fairly clean doublet at τ 5.15 with $J_{2,3}$ 7 cps and the C_3 -proton as a doublet of doublets at τ 7.42 with $J_{3,4}$ 2.3 cps. When the oxymercuration reaction is worked up after several days in acetic acid or alcohol solvents, the isolated mercurial is completely nortricyclic (3). From acetic acid, the products (5) III-OAc, m. p. 119-121°, or III-Cl, m. p. 147-148°, may be isolated in good yield. The conversion of II-Cl to III-Cl, observed in an n. m. r. tube in $(CD_3)_2SO$, is quite slow without a catalyst, but appears to be complete in less than 1 minute when a small crystal of $HgCl_2$ is added.



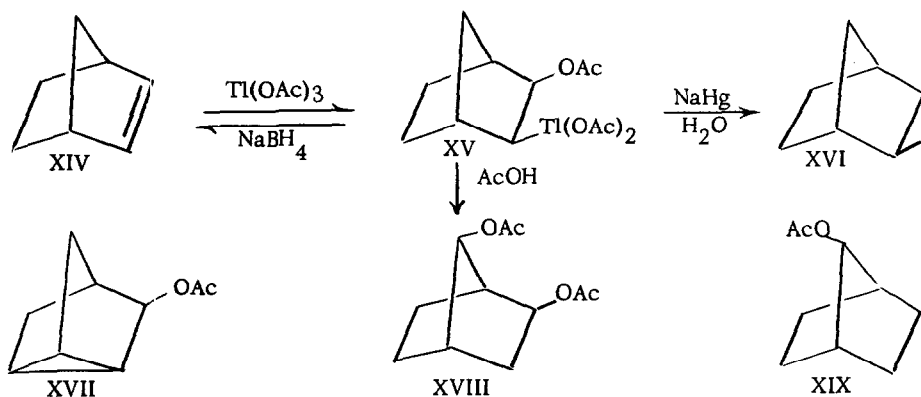
The preference of norbornene for a cis-oxymercuration mechanism (2), which dominates so strongly over a trans-addition mechanism, or one involving carbon participation (3a) with formation of rearrangement product, is clearly shown also by norbornadiene. Two other olefins, which represent systems extremely prone to carbonium ion rearrangements and which are interesting in connection with oxymercuration, are the endo-endo diene (6) IV, m. p. 90-92°, and the endo-endo monoene (6) VI, m. p. 78°. The diene IV leads to the unsaturated cis-exo oxymercuration product (5) V, m. p.

106-108°, when oxymercured with mercuric acetate in chloroform (7), but it leads to saturated oxymercureals when the reaction is carried out in acetic acid or acetic anhydride solvent. The monoene VI gives cis-exo oxymercureal (5) VII, m. p. 108-109° (dec.), even when the reaction is carried out in acetic anhydride.



It has now been shown that oxythallation of norbornadiene and norbornene is analogous to oxymercuration. Thus, shaking a dry chloroform solution of norbornadiene with 1 mole of thallic acetate gives a solution of an adduct. Precipitation of the adduct by addition of dry pentane gives a high yield of mono-adduct, m. p. 116-119° (dec.). This adduct is clearly unsaturated from its infrared spectrum and its behavior towards neutral permanganate. From norbornene there is obtained analogously an adduct,⁵ m. p. 150-151° (dec.). In their infrared spectra both adducts show ester and carboxylate carbonyl bands at ca. 1720 and 1550 cm^{-1} . Soluble in chloroform, acetone and benzene, they can be crystallized from chloroform-pentane.

On treatment with sodium borohydride in ether-methanol, both the norbornadiene and norbornene oxythallation adducts undergo reductive deoxythallation essentially quantitatively to regenerate the parent olefin. On the other hand, reduction with sodium amalgam in aqueous suspension gives a high yield of pure *exo*-norborneol (XVI) from the norbornene adduct. Similar treatment of the norbornadiene adduct and reacylation of the product leads to a high yield of acetate mixture containing mostly (ca. 95%) the acetates of *exo*-5-norbornenol (IX) (ca. 85%) and nortricyclanol (X) (ca. 15%).



The chemical evidence and mechanistic analogy with oxymercuration suggest structures VIII and XV for the oxythallation adducts. However, these structures are not easily confirmed on the basis of their n. m. r. spectra because the latter are complicated by large proton-thallium coupling constants and superposition of some of the bands. In an accompanying Communication, Anet reports an elegant application of the nuclear Over-

hauser effect to these spectra which enable him to pair all the thallium satellites and obtain chemical shifts for the different protons and the various coupling constants. On the basis of this evidence, structures VIII and XV, resulting from cis-exo-oxythallation, are convincingly demonstrated.

In acetic acid solvent at room temperature the oxythallation adducts undergo acetolysis quite rapidly, apparently by way of carbon-thallium bond ionization leading to thallos acetate, acetate ion and acetoxy-substituted carbonium ions. This so-called "dethallation" of VIII leads very predominantly to a mixture of the three diacetates XI-XIII. From "dethallation" of the norbornene adduct XV the product is very predominantly a mixture of nortricycyl acetate XVII and the diacetates XVIII and XIX. The same products are obtained by direct treatment of norbornadiene or norbornene with thallic acetate in acetic acid.

Lead tetraacetate oxidation of norbornadiene and norbornene in acetic acid presumably proceeds also by way of oxymetalation adducts (8). From treatment of norbornadiene with lead tetraacetate in chloroform there was isolated a solid, presumably the oxyplumbation adduct, but this proved to be very unstable. Attempts to characterize it have so far been unsuccessful.

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