1,4-Oxymercuration

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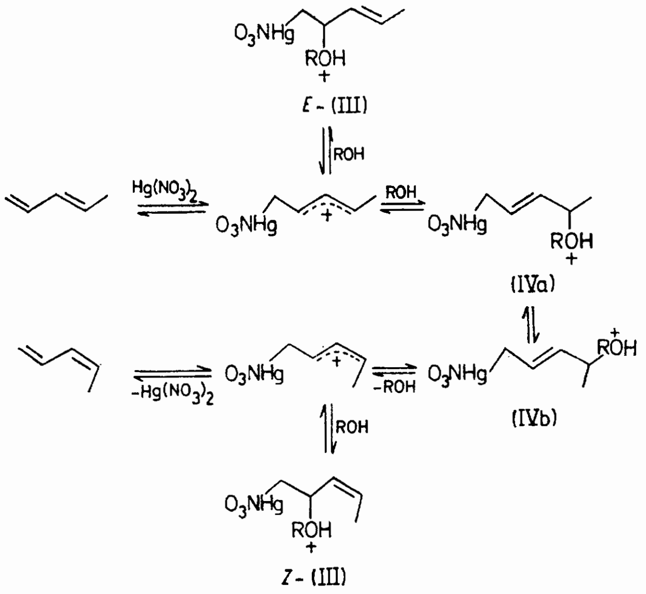
Summary 1,4-Oxymercuration is unambiguously demonstrated by formation of the compound $ClHgCH_2CH{:}CHCH(OMe)Me$ from penta-1,3-diene and mercury(II) nitrate in methanol and shown to be reversible by *Z–E*-isomerisation of the diene.

There is no direct evidence that oxymercuration of conjugated dienes can proceed by 1,4-addition. Such a process has been suggested to account for certain products obtained after subsequent demercuration,[1] but in each case alternative interpretations are possible. Where oxymercurials have been isolated and their structures determined they are, without exception, products of 1,2-addition.[2] We now report the identification by ^1H n.m.r. spectroscopy of the first 1,4-adduct, and present stereochemical evidence which establishes that the 1,4-oxymercuration is reversible.

Penta-1,3-diene (20 mmol) in CH_2Cl_2 (5 cm^3) was added to $Hg(NO_3)_2{\cdot}H_2O$ (10 mmol) in MeOH (20 cm^3) and the mixture was shaken. After 5 min the clear solution gave a negative test (NaOH) for Hg^{2+} and was poured into aqueous

KCl (10 mmol in 50 cm^3). Extraction with CH_2Cl_2 afforded in 89% yield a mixture of the 1,4-adduct (I) and the 1,2-adduct (II) in the ratio 2 : 1 (equation 1); the same ratio was obtained after a reaction time of 1 h. The products were separated by chromatography on silica gel.



SCHEME

$$\mathrm{CH_2{:}CHCH{:}CHMe} \xrightarrow[\mathrm{MeOH}]{\mathrm{Hg(NO_3)_2}} \xrightarrow{\mathrm{Cl^-}} \underset{\text{(I)}}{\mathrm{ClHgCH_2CH{:}CHCH(OMe)Me}} + \underset{\text{(II)}}{\mathrm{ClHgCH_2CH(OMe)CH{:}CHMe}} \qquad (1)$$

The structures of the adducts were established by comparing their ^1H n.m.r. spectra with those of model compounds.† In particular, the CH_2 and Me protons of the 1,4-adduct appear at τ 7·25 br (d, ^3J 8 Hz) and 8·78 (d, ^3J 6 Hz) respectively, while the corresponding groups in the 1,2-adduct are at τ 7·80 (AB part of the ABX system, J_{AB} 11·8 Hz) and 8·28 (dd, ^3J 6·2 and ^4J −1·4 Hz). In compounds of the type $XHgCH_2CH{:}CHR$[3] the CH_2 protons resonate in the range τ 7·04—7·44 (^3J *ca.* 9 Hz) while in simple methoxymercurials such as $ClHgCH_2CH(OMe)Me$,[4] they appear as the AB part of an ABX pattern at τ 7·74. The Me^a and Me^b protons in the compounds $Me^aCH(OMe)CX{:}CHMe^b$ provide good models for the corresponding nuclei in the 1,4- or 1,2-adduct and appear at τ 8·78—8·87 (d, ^3J *ca.* 6·3 Hz) and 8·03—8·34 (d, ^3J *ca.* 6·0 Hz) respectively;[5] in several compounds containing the group $-CH{:}CH{-}Me$, ^4J = *ca.* −1·5 Hz.[6]

The chemical shifts and spin-spin coupling patterns of the remaining resonances are consistent with the proposed structures and an *E*-stereochemistry is indicated for each adduct by values of *ca.* 15 Hz for $J_{CH:CH}$. Structural assignments are strongly supported by the values of ^{13}C chemical shifts and ^{199}Hg–^{13}C coupling constants; ^{13}C n.m.r. spectroscopy also reveals that the *Z*-1,2-adduct is a minor component of the product mixture.

If mercury(II) acetate is used the product is exclusively the 1,2-adduct, but addition of 4 mol % of HNO_3 brings about conversion into the same mixture of isomers as that formed in the reaction with mercury(II) nitrate. Thus the 1,2-adduct must be formed faster than the 1,4-adduct, the latter being produced only under conditions of thermodynamic control. The rate of deoxymercuration by HOAc is slow, but with HNO_3 it is sufficiently rapid to permit the equilibration to take place.

Thus we envisage the series of equilibria shown in the Scheme, the 1,2- and 1,4-adducts arising by deprotonation of (III) and (IV) (R = Me) respectively. The *Z*-1,4-adduct can only arise from energetically less favourable *Z*,*E*- and *Z*,*Z*-cations [formed from *cisoid* conformations of the dienes or alternative conformations about the C(2)–C(3) bonds of the protonated 1,2-adducts].

A consequence of this Scheme is that rotation about the C(3)–C(4) bond of the 1,4-adduct (IVa ⇌ IVb) should provide a pathway for ready isomerisation of the diene, and isomerisation was confirmed by g.l.c. analysis of the reaction mixture. In an independent experiment, a mixture of *Z*- and *E*-penta-1,3-diene in the ratio 17 : 83 was produced rapidly (<25 min) when the *E*-isomer in dichloromethane was shaken with 1 equiv. of $Hg(NO_3)_2{\cdot}H_2O$ (R = H in the Scheme); the same mixture could be obtained after 5 days using only 4 mol % of $Hg(NO_3)_2{\cdot}H_2O$. This is the thermal equilibrium mixture under these conditions since an identical mixture was obtained from the *Z*-isomer.

These data provide support for the proposed Scheme since it is well established that oxymercuration–deoxymercuration does not lead to isomerisation of simple medial alkenes,[7] and isomerisation *via* direct conversion of the *E*,*E*- into the *E*,Z-cation would have a higher activation energy.[8]

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† Compounds (I) and (II) are oils at room temperature and their characterisation by n.m.r. spectroscopy is by far the most diagnostic.

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