Ring Expansion by a 1,3-Shift of Carbon during Reaction of *cis*-Myrtanylamine with Nitrous Acid

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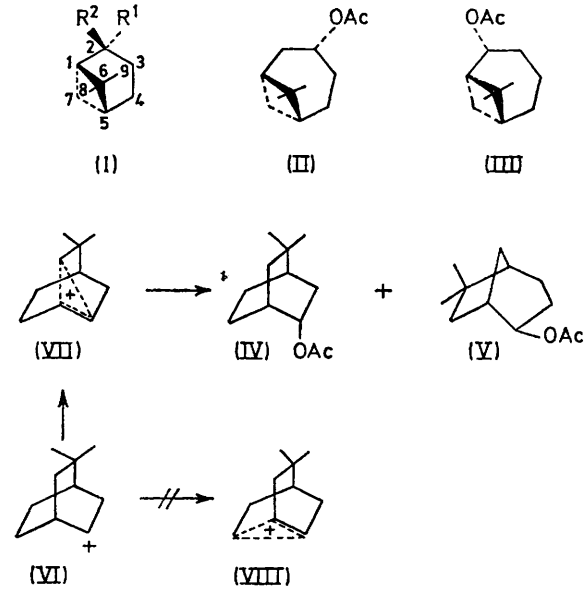
Summary Reaction of *cis*-myrtanylamine with nitrous acid gives 20% of products of ring expansion *via* a 1,3-carbon shift, despite competing 1,2-carbon shift and hydride shift reactions.

SOLVOLYSES of the *cis*- (I; $R^1 = H$, $R^2 = CH_2{\cdot}OSO_2{\cdot}C_6H_4Me$) and *trans*-(I; $R^1 = CH_2{\cdot}OSO_2{\cdot}C_6H_4Me$, $R^2 = H$) myrtanyl toluene-*p*-sulphonates in methanol containing sodium methoxide proceed by simultaneous unimolecular and bimolecular reactions, the unimolecular reaction involving a rate-determining hydride shift to give the 2-pinanyl cation;[1] this ion subsequently decomposes to give pinanyl-, bornyl-, fenchyl-, and terpinyl-derivatives.

Reaction of *cis*-myrtanylamine (I; $R^1 = H$, $R^2 = CH_2NH_2$) with nitrous acid would be expected to be more likely to give ring expanded products than toluene-*p*-sulphonate solvolysis.[2] Shift of either the C-1 to C-2 bond electrons or the C-3 to C-2 bond electrons would be expected to yield bicyclo[4,1,1]octane derivatives (II) and (III) respectively.

The reaction, however, gave 2-acetoxy-5,5-dimethylbicyclo[2,2,2]octane, (IV) (9%), and 2-acetoxy-6,6-dimethylbicyclo[3,2,1]octane (V) (11%). We suggest that these products arise from the ion (VI), which must arise from *cis*-myrtanylamine *via* a 1,3-carbon shift; two successive 1,2 shifts in this system could not give rise to (VI). After formation, we suggest that (VI) forms (VII), from which the observed products are formed; this appears to be an example of expected behaviour of a "hot" carbonium ion, undergoing rearrangement, followed by electron delocalisation. However, (VI) does not form (VIII), suggesting that (VI) is part of an ion pair, ionisation of which is assisted by electron delocalisation.

1,3-Carbon shifts of this type are very uncommon,[3] and are particularly unexpected when a competing 1,2-carbon



shift pathway is available. We suggest that the observed reaction is favoured by the conformation of the amine placing the reaction centre at the correct position for reaction to occur, and by the greater relief of strain obtained by expanding a cyclobutane ring to cyclohexane, compared to expanding a cyclohexane ring to cycloheptane.

The remaining products of the reaction are consistent with the routes observed in solvolytic reactions[1,4] together with two unknown ring expanded acetates, which we believe to arise from a 1,2-carbon shift, and an unknown, ring expanded olefin.

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