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NOTE

OXYMERCURATION OF *exo*-TRICYCLO[3.2.1.$0^{2,4}$]OCTANE: A NEW REARRANGEMENT*

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The well known analogy between cyclopropanes and olefins due to the orbital hybridization in the three-membered cycle is demonstrated by a variety of physical and chemical properties. In particular, the reaction of cyclopropanes with mercury salts in hydroxylic solvents first discovered by Levina and Gladstein[3] is an analog of olefin oxymercuration. This reaction was dealt with in later papers (e.g. refs. 4–6). Recently, we have found that, as in the case of olefins, there is a set of analogous reactions of conjugate mercuration with cyclopropanes, where, for example, nitriles[1,2] or hydrogen peroxide[7] can behave as nucleophiles. The conjugate mercuration of a cyclopropane such as norcarane involves inversion at the carbon attacked by the nucleophile[2].

Since the steric course of oxymercuration of the double bond appears to depend on its strain[8,9] (as yet no proper explanation), investigation of the behaviour of the more strained cyclopropanes might be of considerable interest.

For this purpose *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (I) has been chosen as a model; this is a cyclopropane analog of norbornene; the latter is known to be oxymercurated exclusively in the *exo–cis*-manner.

Reaction of (I) with one equivalent of mercuric acetate in water produced 84 % of alcohol (hydroxy-mercurial), isolated in the form of the chloride which according to thin-layer chromatography on silica gel consisted of two compounds (IIa + IIIa). Reduction of the mixture with sodium amalgam in aqueous methanol led to two methylnorbornanols (IIb + IIIb) (9 : 1, GLC analysis). Step-wise crystallization of the mixture of two hydrogen phthalates (IIc + IIIc) afforded one pure phthalate, m.p. 163.5° (IIc) which was hydrolyzed into alcohol, m.p. 84–85° (IIb)** identical with an authentic 7-*syn*-methyl-*exo*-norbornanol-2 prepared by an independent procedure[10]. Oxidation of (IIb) by chromic acid gave 7-*syn*-methylnorbornanone-2 (IV). Its DNPH derivative was identical with an authentic sample.

Hydrolysis and oxidation of the phthalate enriched with (IIIc) resulted in (IV) mixed with ketone, (V). The latter was identified as 3-*exo*-methylnorbornanone-2 *via*

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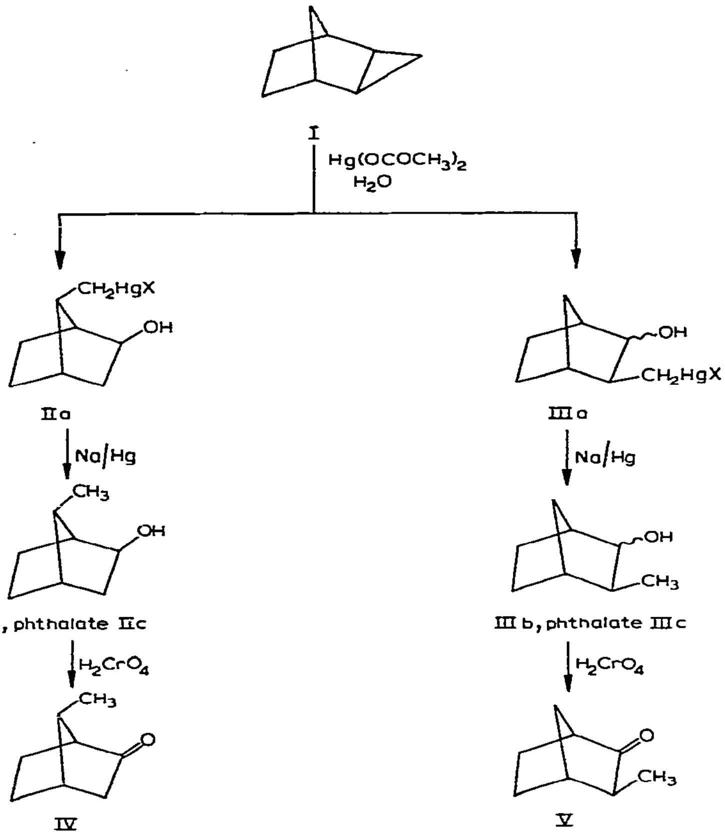
* This paper is the third of a series dealing with the stereochemistry of cleavage of the cyclopropane ring. For previous communications see refs. 1 and 2.

** IR- and NMR-spectra of the alcohols and their phthalates are identical; the mixed m.p.'s of the derivatives give no depression.



chromatography of its DNPH derivative (authentic sample was prepared according to ref. 11). Hence, compound (IIIa) is 3-*exo*-methylnorbornanol-2 with the hydroxyl configuration as yet uncertain. The reactions are summarized in Fig. 1.

Thus, the major reaction product is a result of the Wagner–Meerwein rearrangement which is undoubtedly facilitated by the norbornane structure with its exceptional tendency to a skeletal rearrangement when the cationic centre in position 2 is generated. Steric inhibition of the *endo*-attack by an external nucleophile is also well-known for this system. However, oxymercuration of norbornenes usually involves no rearrangement* since no marked positive charge develops on the carbon atom. This rearrangement is probably caused by the structure of an intermediate in the reaction between the cyclopropane moiety and the HgX^+ ions. It seems plausible that here a positive charge is more localized on carbon than in the case of olefins. The unsymmetrically substituted three-membered cycle in (I) may also play a certain role.

Modern concepts of the structure of protonated cyclopropane favour the generation of the edge- rather than the face-protonated cyclopropane[13,14] and are strongly supported by SCF MO calculations[15]. There is no other data on configura-

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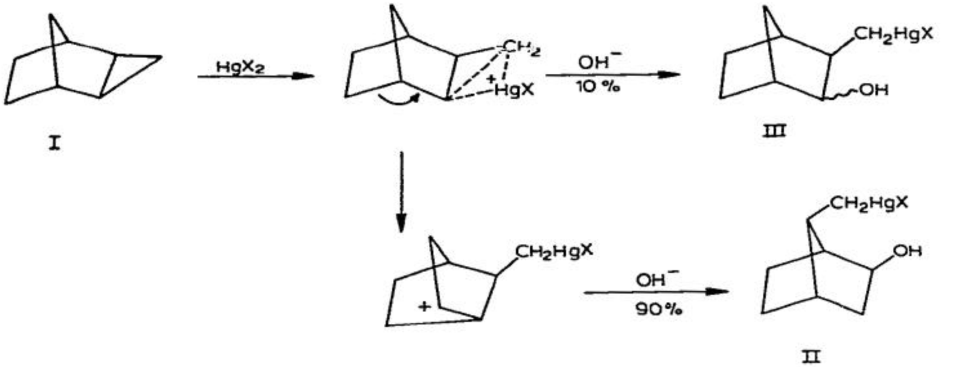
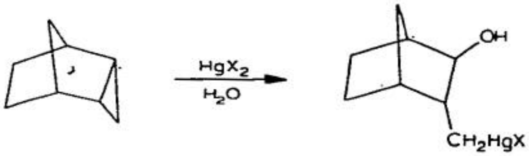
* The only known exception is the tricyclic hydrocarbon described by Corey and Glass[12]. Here, perhaps, a rearrangement is due to an attempt to reduce the extremely high strain in the molecule.



tions of the analogous intermediates containing other electrophilic particles, but mercury is probably located in the plane of the cyclopropane cycle and then the mechanism according to that shown in Fig. 2 is realized.

If the above interpretation of the reaction mechanism is correct, then the oxymercuration of isomeric *endo*-tricyclo[3.2.1.$0^{2,4}$]octane with its geometry restricting anchimeric interaction between the homoallyl C–C bond and the cationic centre developing, would provide as main (if not sole) product, *endo*-3-mercurimethyl-*exo*-norbornanol-2, as a result of the *exo*-attack by the hydroxyl favoured both by steric factors and mechanism, with an inversion at C–2.



EXPERIMENTAL

1. *Oxymercuration of exo-tricyclo*[3.2.1.$0^{2,4}$]*octane* (*I*)

5.73 g of (I) was stirred at room temperature with 20 g of mercuric acetate in 60 ml of water until (I) was completely dissolved. The reaction mixture was filtered and excess of saturated NaCl solution added. The oil formed was extracted with chloroform (6 × 30 ml) and dried over $MgSO_4$. The chloroform was evaporated and the residue triturated with light petroleum; 15.9 g (83.9 %) of product m.p. 96–104°, was obtained. Chromatography on a thin-fixed layer of silica gel (Woehlm, propanol–triethylamine–water, 2:1:1, as the eluent; 2 % dithizone solution in chloroform as the developing agent) revealed two organomercurials with R_F 0.27 and 0.38, respectively, and traces of a third compound with R_F, 0.58. Multiple recrystallization from methanol and nitromethane gave a product with m.p.101–103° (IIa). (Found: C, 26.52; H, 3.55; Cl, 10.56; Hg, 54.36: $C_8H_{13}ClHgO$ calcd.: C, 26.59; H, 3.64; Cl, 9.81; Hg, 55.51 %.)

IR spectra exhibit an absorption band at 3400 cm^{-1} (hydroxyl) and no bands at 3100–3000 cm^{-1} (cyclopropane) and 1600 cm^{-1} (double bond).

2. *Reduction of the mixture of hydroxymercurials* (*IIa and IIIa*)

16 g of (IIa)+(IIIa) was reduced with stirring in 50 % aqueous methanol with

25 g of 1.5% sodium amalgam. After 1.5 h, the solution was diluted with water and extracted with chloroform. The extract was dried over $MgSO_4$ and distilled at 18 mm Hg at 60° (bath temperature); 5 g (90%) of product was obtained (m.p. 65–88°) consisting of two components (9:1) according to GLC analysis.*

3. *Isolation of 7-syn-methyl-exo-norbornanol-2 (IIa) from the mixture of (IIa)+(IIIb)*

A solution of 3 g of (IIa)+(IIIa) and 3.96 g of phthalic anhydride in 25 ml of absolute pyridine was heated at 100° for 4 h. The mixture was poured into ice-water, acidified with diluted HCl and extracted with benzene; 5.73 g (88.2%) of phthalate was obtained, m.p. 143–149°. Four crystallizations from ethylacetate afforded 2.0 g of the phthalate (IIc), m.p. 162–163.5° with IR and NMR spectra** identical with an authentic sample of 7-*syn*-methyl-*exo*-norbornanol-2 phthalate, prepared by an independent procedure[10].

Phthalate (IIc) and 4 g of KOH were dissolved in 20 ml of water, and the solution was steam-distilled. The distillate was extracted with chloroform and dried over $MgSO_4$. After evaporation of the solvent, the residue was sublimed. 7-*syn*-Methyl-*exo*-norbornanol-2 (IIb) was produced (0.65 g, 67.3%) m.p. 85–87° (lit.[10] 86–88°). GLC shows that (IIa) is the main component of the alcohol mixture.

4. *Oxidation of (IIb) into 7-syn-methyl-norbornanone-2 (IV)*

0.6 g of (IIb) was stirred with 0.5 g of $K_2Cr_2O_7$ and 0.24 ml of concentrated H_2SO_4 in 2.6 ml of water for 1 h. The mixture was extracted with ether, the solvent evaporated and the residue steam-distilled to give 0.42 g of product, (IV), m.p. 70° (11 mm), n_D^{22} 1.4712; semicarbazone; m.p. 175–177.5° (lit.[11] 182°), dinitrophenylhydrazone: m.p. 151–152°.

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* Polymethylphenylsiloxane on firebrick, 2 m, 160°.

** Multiplet from H_2(δ 4.8) is used to estimate $J_1=6.0$ Hz (*cis-endo*-2,3), $J_2=4.4$ Hz (*trans*-2,3) and $J_3=1.1$ (*endo-2-anti*-7), for the long-range coupling[18].