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OXIDATIVE HYDROBORONATION OF (+)-CAR-3-ENE

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A previous report[1] of the hydroboronation of (+)-car-3-ene (I) states that at 20° the only product is (−)-*trans*-caran-*trans*-4-ol (II). Formation of this alcohol however requires either *trans*- addition of diborane to the double bond of car-3-ene, or *cis*- addition to the sterically hindered β- face of this molecule and subsequent epimerisation of the 4- carbon atom. Both these processes are unlikely.

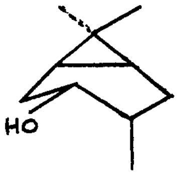
The evidence for the configuration of the alcohol (II) and its epimer (+)-neocaranol[3] ((+)-*trans*-caran-*cis*-4-ol, III) was based on (a) the assumption of a *trans*- arrangement of groups in (−)-caran-4-one,[2] and (b) the relative rates of hydrolysis of the acid phthalates of (II) and (III) which indicated[3] equatorial and axial hydroxyl groups respectively.

We have carried out the oxidative hydroboronation of (+)-car-3-ene (I) under a variety of conditions. At 20°, with external generation of diborane, the product, which is formed nearly quantitatively, is (−)-*cis*-caran-*trans*-4-ol (IV), $[\alpha]_D^{20}$ − 73°, n_D^{20} 1.4810, with properties very similar to those reported for the alcohol (II).[1] The 4- epimer of (IV) (+)-*cis*-caran-*cis*-4-ol, has structure (V).

The evidence for structure (IV) is as follows: (a) It is to be expected from the accepted mechanism of hydroboronation,[4] (b) Reduction of the tosylate of (IV) with lithium aluminium hydride gives (−)-*cis*-carane (VI) identical to the product of careful hydrogenation of (+)-car-3-ene,[5] and readily distinguishable from (+)-*trans*-carane (VII), $[\alpha]^{20}_{D}$+ 63.5°, n^{20}_{D} 1.4565, obtained by Wolff-Kishner reduction of (−)-*trans*-caran-2-one (VIII),[6] (c) Structures(IV) and (V) are more sati factorily consistent with the assignment of equatorial and axial OH groups (from the phthalate hydrolysis rates)[3] than (II) and (III), for steric considerations suggest that forms (IIIa) and possibly (IIa) would be the preferred ones, (d) The n.m.r. spectrum of (IV) shows two axial/axial ($J \sim$ 9 c.p and 1 axial/equatorial ($J \sim$ 6 c.p.s.) couplings for the axia C_4 hydrogen atom.

Oxidation of (IV) with chromic acid gives (−)-*cis*-caran-4-one (IX), $[\alpha]^{20}_{D}$- 135°, n^{20}_{D} 1.4700, which is virtually unchanged (optical activity, infrared, g.l.c. and n.m.r.) on equilibration with sodium ethoxide. This is consistent with the formation of a stable *cis* ketone.

Hydroboronation of (+)-car-2-ene (X) at 50° gave about 95% of (−)-*cis*-caran-*trans*-2-ol (XI), $[\alpha]^{20}_{D}$- 34°, n^{20}_{D} 1.4767, which on chromic acid oxidation gave (−)-*cis*-caran-2-one (XII), $[\alpha]^{20}_{D}$- 81°, n^{20}_{D} 1.4717. Equilibration of this with sodium ethoxide gave (−)-*trans*-caran-2-one (VIII), $[\alpha]^{20}_{D}$- 153 n^{20}_{D} 1.4750, identical with a sample prepared by Baeyer's



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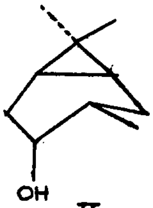

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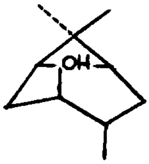

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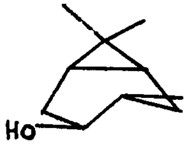

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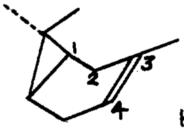

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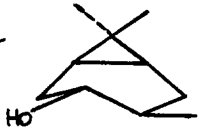

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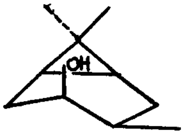

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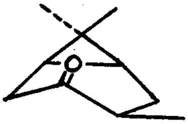

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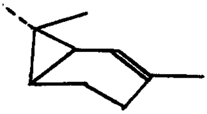

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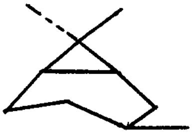

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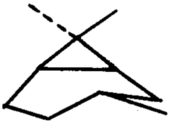

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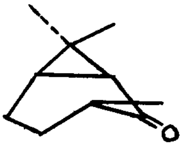

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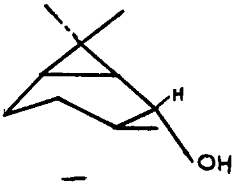

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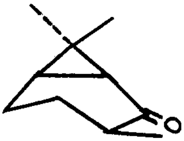

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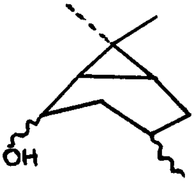

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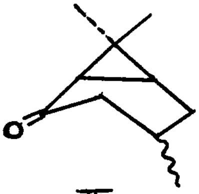

XIV

method[7] from (–)-carvone.

With external generation of diborane, hydroboronation of (+)-car-3-ene (I) followed by heating the borane at 50° for 1 hour gave about 93% of (–)-cis-caran-trans-4-ol (IV) and 7% of a new compound, caran-5-ol (XIII), presumed to be cis-caran-trans-5-ol. The latter was only revealed on oxidation of the mixture of alcohols to the corresponding ketones, (–)-cis-caran-4-one (IX), described above, and caran-5-one (XIV), $[\alpha]_D^{20} + 190°$, n_D^{20} 1.4741, which are separable by g.l.c. On heating to 100° for 1 hour compounds (IV) and (XIII) were obtained in proportions of about 25% and 50% respectively, and in addition, 25% of (–)-cis-caran-trans-2-ol (XI) (identified by g.l.c.) was present.

The formation of the alcohols, (IV), (XIII), and (XI) is in accord with the migration of the boron in two directions around the cyclohexane ring. Migration to the 5-position (from 4-) appears to be more facile than to the 2-position. This is particularly evident when the reaction is carried out with in situ generation of diborane; at 50° the proportions of (IV) and (XIII) were then about 70% and 30% respectively with less than 2% of the caranol (XI).

Further work on this reaction is in progress.

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