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STRUCTURE OF THE IODO-LACTONE DERIVED FROM NORBORN-5-ENE-2-ENDO-CARBOXYLIC ACID

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In a recent communication, Risinger, Green and Green[1] have suggested that the iodo-lactone obtained[2] from the action of iodine and potassium iodide in alkaline solution on norborn-5-ene-2-endo-carboxylic acid should be formulated as 6-exo-iodo-5-endo-hydroxynorbornane-2-endo-carboxylic acid lactone 1, rather than the hitherto accepted 5-exo-iodo-6-endo-hydroxynorbornane-2-endo-carboxylic acid lactone 2. Beckmann and his co-workers[3,4] have carried out a number of reactions on the iodo-lactone which on the basis of structure 2 yield 2,6-disubstituted norbornanes (Chart 1). Thus hydrogenolysis yielded lactone 3, and saponification and dehydrohalogenation yielded keto-acid 4,

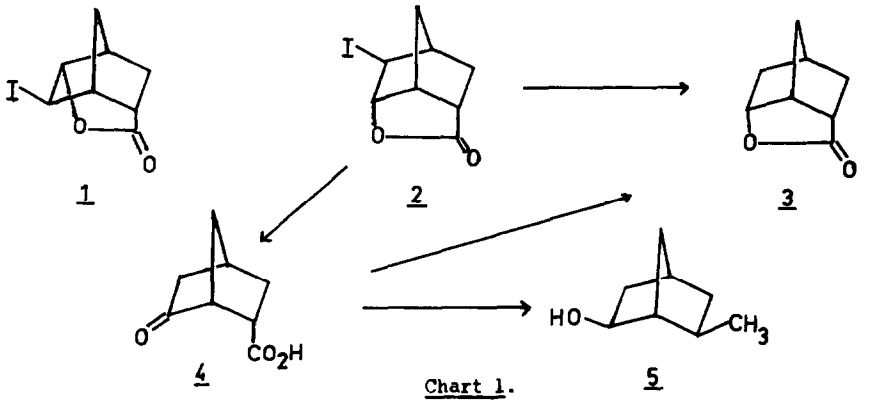


Chart 1.

which on reduction with sodium borohydride gave lactone 3.[3] Keto-acid 4 has also recently been correlated with alcohol 5.[4] Clearly if the iodo-lactone is represented by structure 1, structures 3 - 5 must be replaced by the appropriate 2,5-disubstituted norbornanes. Because of the key position of the iodo-lactone in the assignment of structures to these norbornyl derivatives, we report evidence that firmly establishes the structure as 2.

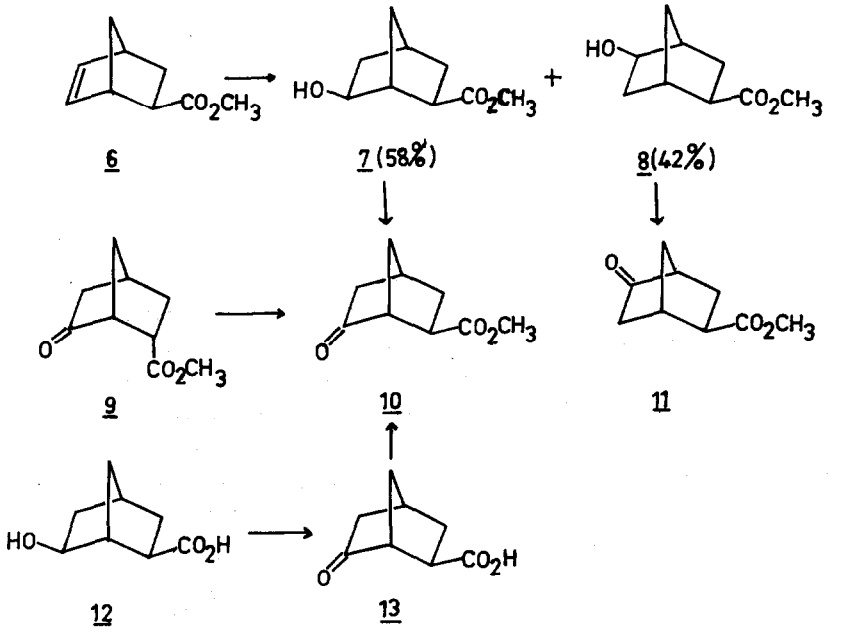


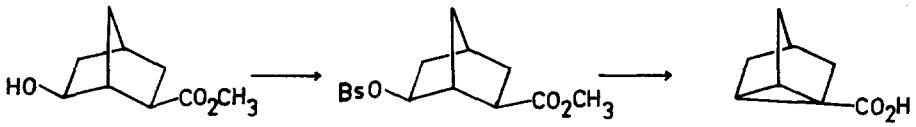
Chart 2.

Hydroboration of methyl norborn-5-ene-2-exo-carboxylate 6 gave a mixture of two hydroxy-esters, formulated as 7 and 8 on the basis of the known exo-stereopecificity in the addition of diborane to norbornene.[5] The major hydroxy-ester (58%) was assigned structure 7 on the basis of the correlations outlined below (Chart 2).

Oxidation of the hydroboration product gave a mixture of keto-esters, which were separated by preparative vapour phase chromatography (vpc). The major keto-ester 10[6] was identical (IR and NMR spectra, vpc retention time) with a

sample obtained from the equilibration (sodium methoxide in methanol) of the endo-keto-ester 9.[6,7] The ester 9 was prepared from the keto-acid 4, which was obtained from the iodo-lactone by the reported procedure.[3]

Saponification of the hydroboration product 7 + 8 followed by fractional recrystallization gave hydroxy-acid 12[6], m.p. 163.5 - 164.5° (reported[4] m.p. 161 - 163°), which on oxidation gave keto-acid 13[6], m.p. 83 - 4° (reported[4] m.p. 86 - 87°). Methylation of 13 with diazomethane provided keto-ester 10.



7 14 15

Chart 3

The hydroxy-ester 7[6] was converted into the p-bromobenzenesulphonate 14[6], m.p. 82 - 3°, which with potassium t-butoxide in t-butanol underwent 1,3-elimination[8] to give, after saponification, in 90% yield[9] nortricyclene-1-carboxylic acid 15, identical with an authentic sample.[10] This transformation clearly demands a 2,6-relationship of the carbomethoxy and p-bromobenzenesulphonyloxy groups in 14, and hence establishes by the correlations outlined in Charts 1 and 2 the structure of the iodo-lactone as 2.

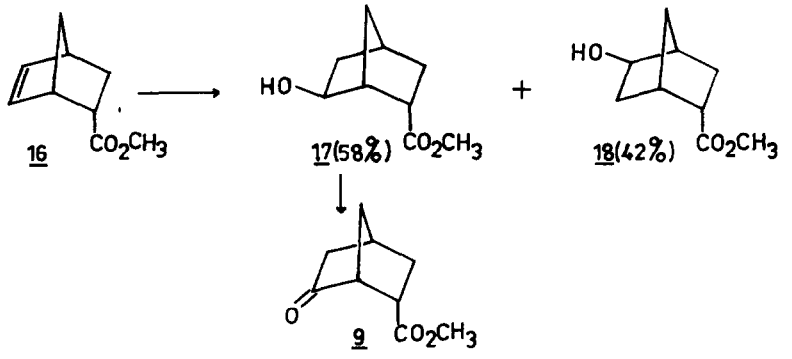


Chart 4.

The hydroboration of methyl norborn-5-ene-2-endo-carboxylate 16 gave a mixture of two hydroxy-esters.[11] The major product (58%) was assigned structure 17, since on oxidation it was converted into keto-ester 9 (Chart 4). Thus in the hydroboration of both unsaturated esters 6 and 16 a small preference for diborane addition to the end of the double bond nearer the ester function is observed. This directing effect of the carbomethoxy group is presumably electronic in nature, and has also been observed in the hydroboration of methyl cyclohex-3-ene-carboxylate.[12]

References and Footnotes

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3. S. Beckmann and H. Geiger, Chem. Ber., 94, 48 (1961).
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6. Satisfactory analytical data and IR and NMR spectra consistent with this structure have been obtained.
7. A similar equilibration has been independently reported by Beckmann and his co-workers.[4]
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9. Yield of isolated acid. Vpc examination of the methylated (diazomethane) reaction product indicated that 99% of it was derived by 1,3-elimination, and 1% was solvolysis product (t-butyl ethers). The product expected from β-elimination, exo-ester 6, could not be detected.
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