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STEREO- AND REGIOSELECTIVE OXYMERCURATION - DEMERCURATION OF BICYCLO[3.2.1]OCT-2-ENE SKELETON

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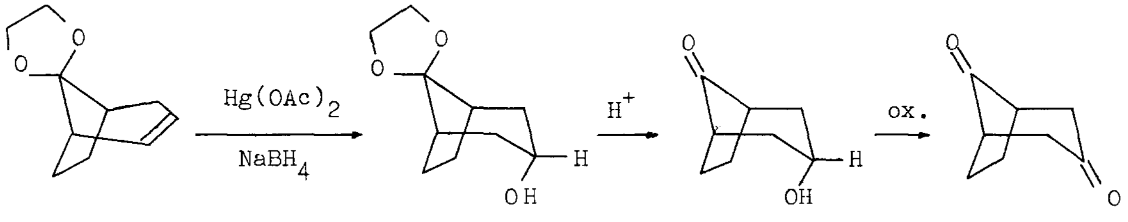
Abstract: The oxymercuration - demercuration of ethylene ketal of bicyclo[3.2.1]oct-2-en-8-one is reported. This reaction proceeds with high regio- and stereoselectivity.

Various types of bicyclic olefins have been reported to undergo hydration by oxymercuration - demercuration procedure[1-3]. Some of them react with considerable stereoselectivity, resulting in mainly exo-hydroxylated products.

We investigated the hydration of the ethylene ketal derivative of the bicyclo[3.2.1]oct-2-en-8-one[6] (1). The hydroboration - oxidation of the bicyclo[3.2.1]oct-2-ene carried out by Sauers *et al.*[4] previously led to isomeric mixture of its 2- and 3-oxo derivatives. In contrast, the oxymercuration - demercuration of 1 has been proved in our experiments highly regio- and stereoselective and produced the 3-endo-hydroxy derivative not known so far.

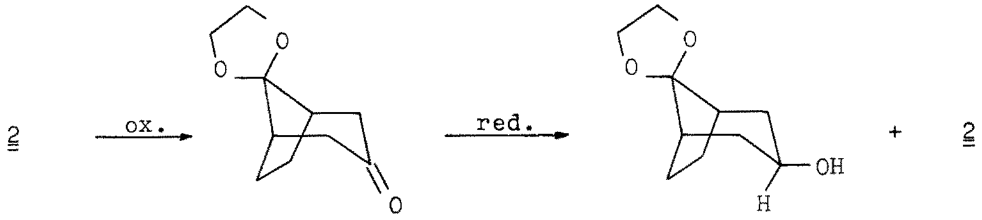
Oxymercuration[5] of 1 (66,4 g) in aqueous tetrahydrofuran (1:1 V/V, 800cm^3) by mercuric acetate (147 g) followed by *in situ* reduction of the organomercurial by alkaline sodium borohydride (800cm^3 3m NaOH, 40 g $NaBH_4$) offered only one product, the ethylene ketal derivative of 3-endo-hydroxy-bicyclo[3.2.1]-octan-8-one (2) in 80% yield, mp. 103°C. ^1H NMR: δ 3,85 ppm, s ($-OCH_2CH_2O-$); δ 3,91 ppm, t (C(3)-H, partially covered)[7]. IR(KBr): 3400-3200 cm^{-1} (ν OH)[8].



1 2 3 4

The ethylene ketal group of 2 was removed by Amberlite IR 120 (H$^+$) ion-exchange resin in methanol - water under reflux. The symmetrical structure of the keto alcohol 3 thus obtained was proved by its ^{13}C NMR spectrum (δ 22,0 ppm, C(6), C(7); 42,2 ppm, C(1), C(5); 44,5 ppm, C(2), C(4); 66,1 ppm, C(3); 223,4 ppm, C(8)). The relatively narrow (20 Hz) band of the C(3)-H proton at δ 4,00 ppm in the ^{1}H NMR spectrum can be interpreted with its exo position[9]. Jones oxidation of 3 (mp. 216-217°C, IR(KBr): 1715 cm^{-1}, C=O) led to bicyclo[3.2.1]octan-3,8-dione (mp. 151°C; IR(KBr): 1765 cm^{-1} and 1720 cm^{-1}, C=O in five- and sixmembered rings, resp.; ^{13}C NMR: δ 23,9 ppm, C(6), C(7); 42,1 ppm, C(2), C(4); 50,7 ppm, C(1), C(5); 207,6 ppm, C(3); 218,2 ppm, C(8)).

The ethylene ketal of the 3-exo-hydroxy-bicyclo[3.2.1]octan-8-one (5) was also prepared from 2 by Jones oxidation followed by sodium - isopropanol reduction yielded a mixture of 3-exo and endo alcohols (7:3, GLC). The pure 6 was separated by preparative TLC, mp. 95,5°C. ^{1}H NMR: δ 3,86 ppm, C(3)-H, partially covered; IR(KBr): 3300 cm^{-1} (ν OH).



5 6

Our results indicate a rather large regioselective effect in the course of the oxymercuration - demercuration reaction. The endo attachment of the 3-hydroxy group can be rationalized in terms of the trans addition mechanism and means a further piece of evidences to the stereochemical course[2] of the oxymercuration.

References and Notes

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7. The ^{1}H and ^{13}C NMR spectra were recorded at 80 MHz and 25,1 MHz, resp., on $CDCl_3$ solutions containing tetramethylsilane.
8. All new compounds described in this paper gave satisfactory C,H analyses.
9. To the determination of endo or exo position of the C(3) substituent in derivatives having bicyclo[3.2.1]octane skeleton cf. P. Scheiber, G. Kraiss, K. Nádor, A. Neszmélyi, J.Chem.Soc.(B), 1971, 2149.

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