

CCA-404

541.124:547.599.4

Note

Deuterium Scrambling During Stereochemical Equilibration of *endo*- and *exo*-Norbornanol-3,3- d_2

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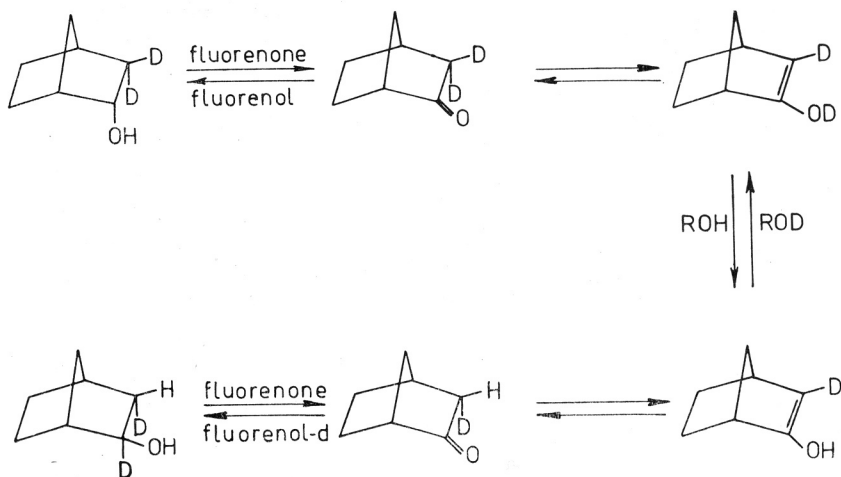
Received December 13, 1965

Herewith we wish report about an interesting case of deuterium scrambling during the attempted preparation of *exo*-norbornanol-3,3- d_2 from the *endo*-isomer through equilibration with the aid of fluorenone.

Norcamphor was deuterated in the 3-position through repeated base catalyzed exchange with heavy water.¹ The mass spectrum of this compound indicated 48.5% of monodeuterated and 46.2% of dideuterated species. From recently published work,^{1,2} it can be assumed that the deuteration was complete at the *exo*-position and only partial at the *endo*-position.

Reduction with lithium aluminum hydride, carried out in the usual manner, yielded *endo*-norbornanol-3,3- d_2 . The NMR spectrum of this compound was recorded and the relative resonance peak areas integrated. To evaluate the accuracy of deuterium analysis by peak integration, the deuterium content was calculated by taking either the α -hydrogen or the bridgehead hydrogens resonance peak³ areas as standard. Thus the values of 1.36 and 1.55 atoms D per molecule respectively were obtained and can be compared with the value of 1.41 atoms D per molecule available from mass spectrometry.

SCHEME I



endo-Norbornanol-3,3- d_2 (2.1 g.) was dissolved in toluene (5.5 ml.), fluorenone (50 mg.) and sodium (25 mg.) added and the mixture refluxed for 60 hours.⁴ Toluene was then removed under reduced pressure and the resulting mixture of stereoisomeric norbornanols⁴ sublimed. NMR spectroscopy revealed (taking bridgehead hydrogens resonance peak area as standard) that the product contained only about 0.9 atoms D per molecule bound to carbon, of which 0.34 atoms D were at the α -position while 0.56 atoms D remained presumably at the 3-position.

The observed deuterium scrambling during equilibration can be rationalized by the mechanism^{1,2,4,5} shown in Scheme 1. A series of reversible steps, *i. e.* an Oppenauer oxidation of the *endo*-norbornanol-3,3- d_2 , enolization of the resulting ketone and exchange of the hydroxyl deuterium of the enol account for all experimental results.

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IZVOD

**Premještanje deuterija kod stereokemijske ekvilibracije *endo*-
i *ekso*-norbornanola-3,3- d_2**

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endo-Norbornanol-3,3- d_2 (sadržaj deuterija 1.41 atoma D po molekuli) podvrgnut je stereokemijskoj ekvilibraciji pomoću fluorenona. Iz NMR spektra nastale smjese epimernih karbinola određen je sadržaj deuterija od 0,9 atoma D po molekuli i to 0,56 atoma D u položaju 3 a 0,34 atoma D u položaju 2.

Gubitak i premještanje deuterija za vrijeme ekvilibracije objašnjen je mehanizmom prikazanim u Shemi.

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ZAGREB

Primljeno 13. prosinca 1965.