Tetrahedron Letters No. 33, pp 2917 - 2918, 1975. Pergamon Press. Printed in Great Britain.

STEREOCHEMISTRY AND MECHANISM OF IRON CARBONYL INDUCED OLEFIN ISOMERISATION IN ALLYLIC ALCOHOLS

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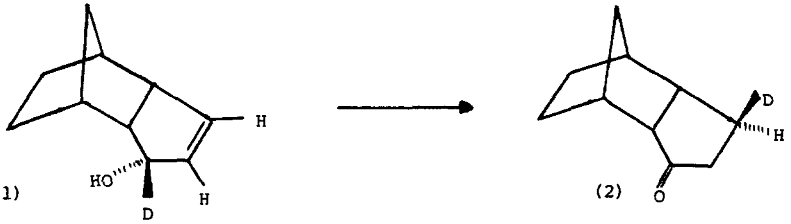
(Received in UK 30 June 1975; accepted for publication 7 July 1975)

As part of an investigation of the iron carbonyl catalysed isomerisation of allylic alcohols[1,2,3], Cowherd and von Rosenberg[2] showed that, whereas the tricyclic alcohol (1, D = H) isomerised to the ketone (2, D = H) on heating in the presence of iron pentacarbonyl, its epimer did not react under similar conditions.



In order to investigate the stereochemistry at the reception site, the stereospecifically deuterio-labelled alcohol (90%, D_1) (1) was heated with iron pentacarbonyl. The ketone (88%, D_1) (2) was obtained in 45% yield and the stereochemistry of deuterium incorporation shown to be exclusively exo (± 10%) (2) by n.m.r. studies using $Eu(FOD)_3$ in $CDCl_3$ and synthesis of an authentic stereospecifically labelled sample of (2) using the method of Bugel [4]

When the deuterio alcohol (1) was heated with iron pentacarbonyl in the presence of cyclohex-2-en-ol, only the deuterio ketone (2) and unlabelled cyclohexanone were obtained showing that crossover had not occurred These results, together with those of von Rosenberg[1,2] demonstrate conclusively that the transformation (1) to (2) occurs with an overall intramolecular [1,3] suprafacial shift of hydrogen on the same side of the molecule as the iron atom

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Values of the primary kinetic isotope effect for the isomerisation of (1) were obtained for reactions at 136° at conversions ranging from 10 to 40%*. The values ranged from 1.12 to 1.46 with an average of 1 23, very similar to that of 1.12 recorded by Day[3] for the rearrangement of allyl alcohol at 100°. In contrast the dodecacarbonyl tris iron catalysed isomerisation of 3-ethyl-1-pentene[5], proceeding through a π allyl metal hydride intermediate, shows no primary kinetic isotope effect. As most [1,3]H shift reactions catalysed by iron carbonyls are believed to involve the same catalytically active unsaturated iron carbonyl species[7], the results show that the introduction of a hydroxyl group[8] has changed the rate determining step of the rearrangement, and perhaps made the preferred route, a concerted suprafacial [1,3]H migration, with the migrating H atom on the same face as the metal atom.[2]

We thank Dr. Q. N. Porter, Melbourne University, for help with gas chromatography, and Professor W. R. Jackson, Monash University, for comments.

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* Deuterium content of the product and starting material was measured using a Perkin-Elmer 900-270B combined g.c./m.s. system fitted with a 2 m by 3 mm free fatty acid polymer column at temperatures from 120-170°.

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