The Stereospecific Hydrogenation of an Exocyclic Methylene Group

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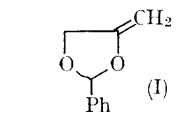
FOSTER and his co-workers[1] have recently reported the stereospecific reduction (with Adams catalyst in methanol) of 4-methylene-2-phenyl-1,3-dioxolan (I) to *cis*-4-methyl-2-phenyl-1,3-dioxolan (II). They explained this stereospecificity as arising from addition of hydrogen from the less hindered *trans*-side to give the *cis*-product.

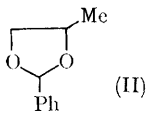
We have recently examined the catalytic hydrogenation of 2-substituted 5-methylene-1,3-dioxans (III, R = methyl, t-butyl, or phenyl) under varying conditions (5% platinum on carbon, in methyl acetate, ethyl acetate, or chloroform; or Adams catalyst in methanol), and have found that in all cases the product is principally (93—95%) the thermodynamically less stable *cis*-isomer (IV), with small amounts (5—7%) of the more stable *trans*-isomer (V). The isomers were distinguished by their nuclear magnetic resonance (n.m.r.) spectra, which are quite different, and have been assigned unambiguously by comparison with spectra of authentic samples of the isomer pair (IV and V, R = t-butyl).[2] The reaction products containing predominantly *cis*-isomers are equilibrated in the presence of trifluoroacetic acid to give an equilibrium mixture containing predominantly the *trans*-isomer.[3] The proportions of isomers were measured by integration of suitable regions of the n.m.r. spectra.

At first glance, the explanation proposed for the stereospecificity of the hydrogenation of (I), by Foster *et al.*,[1] would appear to hold in the present case. However, the results of Siegel and Dunkel,[4] on the hydrogenation (over Adams catalyst in acetic acid) of similar alicyclic compounds (VI—VIII) do not support this for they found that the proportions of *cis*-isomer formed are 65%, 69%,

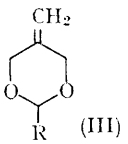
and 54% respectively. It appears that while there is a certain preference for *trans*-addition of hydrogen to give the *cis*-disubstituted product, nonetheless when the substituent is in the 4-position with reference to the exocyclic double bond, addition is almost random. In fact, for (VIII) with other catalysts, a preponderance of *cis*-addition to give the more stable *trans*-disubstituted product is observed.[4] In contrast, for the corresponding dioxan (III, R = methyl) we observe 95% *trans*-addition to give the *cis*-product.



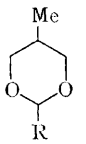
(I)



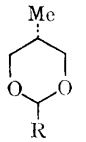
(II)



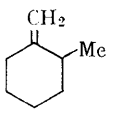
(III)



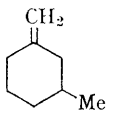
(IV)



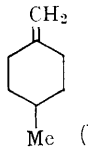
(V)



(VI)



(VII)



(VIII)

For the hydrogenation of 4-t-butylmethylenecyclohexane, Siegel and Dmuchovsky[5] observed rather more stereospecificity (84% *cis*-isomer), but this is still considerably less than we observe for the corresponding dioxan (95%) under the same conditions.

We conclude that in the 5-methylene-1,3-dioxan series at least, the ring-oxygen atoms play a significant role in determining the stereospecificity of catalytic hydrogenation. Our investigations are continuing.

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[1] N. Baggett, J. M. Duxbury, A. B. Foster, and J. M. Webber, *J. Chem. Soc.* (*C*), 1966, 208.
[2] F. G. Riddell and M. J. T. Robinson, unpublished results.
[3] The free-energy difference between (IV) and (V), (R = t-butyl) is 0·9 kcal./mole at 30° c. (Ref. 2).
[4] S. Siegel and M. Dunkel, *Adv. Catalysis*, 1957, **9**, 15.
[5] S. Siegel and B. Dmuchovsky, *J. Amer. Chem. Soc.*, 1962, **84**, 3132.