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THE STEREOCHEMISTRY OF CONJUGATE ADDITION OF LITHIUM ALUMINIUM HYDRIDE TO SOME NORBORNADIENE ESTERS. AN UNUSUAL CASE OF PREFERRED ENDO ATTACK.

W. Roy Jackson, John W. Norman, and Ian D. Rae
Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia.

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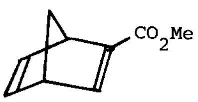
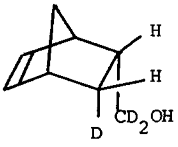
The reduction of α, β-unsaturated carbonyl compounds with lithium aluminium hydride normally does not lead to reduction of the double bond but to the formation of allylic alcohols[1]. Where double bond saturation does occur this may involve further reduction of the allylic alcohol via a reaction involving a cyclic alane[2]. The extensive double bond reduction which occurs when some cycloalkenones, particularly cyclopentenones, are reduced with lithium aluminium hydride has been shown not to involve cyclic alane intermediates but more probably a conjugate addition of hydride[1,3,4]. We wish to report that reduction of both the mono-ester (1) and the di-ester (3) involve similar, conjugate addition of hydride, that the reactions are highly stereoselective, and that this stereoselectively surprisingly involves a preferred endo-attack on the norbornadiene molecule.

Reduction of the monoester (1) with lithium aluminium hydride gave 2-endo-hydroxymethylnorborn-5-ene (2; D=H) as the major product. Reduction with lithium aluminium tetradeuteride and treatment with H_2O gave (2a) as the major product and reduction with lithium aluminium hydride followed by treatment with D_2O gave (2b) as the major product. The ^{13}C n.m.r. spectrum of (2a) showed that the absorption at δ 29.8 ppm, previously assigned to C-3[5] was of diminished intensity and thus deuterium was present at C-3 as well as in the hydroxymethyl group. The 3-endo-D stereochemistry was assigned on the basis of the diminution in intensity of the peak at δ 0.50 ppm in the ^1H n.m.r. spectrum[6].

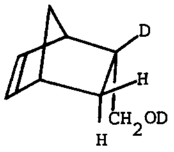


(1)



From $LiAlD_4/H_2O$

(2a)

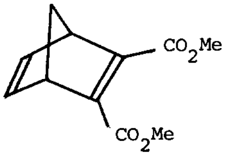


From $LiAlH_4/D_2O$

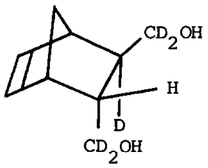
(2b)

The structure of (2b) arising from $LiAlH_4/D_2O$ reaction was similarly assigned on the basis of a diminution of intensity of the peak at δ 43.1 ppm due to C-2 in the ^{13}C n.m.r. spectrum and of the peak at 2.3 ppm assigned to the 2-exo-proton in the ^1H n.m.r. spectrum. In each of the above spectra, integration suggested that the endo-isomers depicted predominated over the exostereoisomers by ratios of ca 2.5-3.0:1.

Reduction of the diester (3) gave the trans-diol (4; D=H)[7] as the only product (80%). Reduction with $LiAlD_4/H_2O$ led to replacement of the endo-proton by deuterium (4a) and reduction with $LiAlH_4/D_2O$ led to (4b).

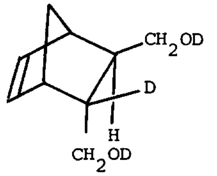


(3)



From $LiAlD_4/H_2O$

(4a)



From $LiAlH_4/D_2O$

(4b)

These results rule out the possibility of a cyclic alane intermediate and support the previously proposed mechanism involving 1,4-addition of hydride. Although the detailed sequence of ester reduction is not evident, both sets of results are compatible with a highly stereoselective initial endo-attack of hydride followed by a final exo-protonation. Preferred endo-attack on a norbornadiene is most unusual. Michael additions to (1) give the products of di-exo-addition[8] and a wide range of both ionic, radical and electrocyclic additions behave similarly e.g. acetoxymercuration[9], iron carbonyl catalysed photochemical acetylene reaction[10], addition of diethyl diazodicarboxylate[11], and the BF_3 catalysed addition of acetic acid[12]. Only when large substituents are present at C-7 does endo-substitution become predominant[13].

REFERENCES

1. H.O. House, 'Modern Synthetic Reactions' W.A. Benjamin, Inc., London, 1972, p. 89.
2. W.T. Borden, J.Amer.Chem.Soc., 1970, 92, 4898 and references therein.
3. H.C. Brown and H.M. Hess, J.Org.Chem., 1969, 34, 2206.
4. W.L. Dilling and R.A. Plepys, J.Org.Chem., 1970, 35, 2971.
5. E. Lippmaa, T. Pehk, J. Passivirta, N. Belikova and A. Plate., Org.Mang.Reson., 1970, 2, 581-604.
6. E. Pretsch, H. Immer, C. Pascual, K. Schaffner and W. Simon, Helv.Chim.Acta., 1967, 50, 105-114; R.G. Foster and M.C. McIvor, J.C.S. Chem.Comm., 1967, 280-81.
7. Characterised by mixed m.p. of a bis-phenylurethane derivative with an authentic sample.
8. K. Alder, H. Wirtz and H. Koppelberg, Annalen, 1956, 601, 138.
9. K.C. Pande and S. Winstein, Tetrahedron Letters, 1964, 46, 3393.
10. K. Hayakawa and H. Schmid, Helv.Chim.Acta., 1977, 60, 2160.
11. J. Tufariello, T. Mich, and P. Miller, Tetrahedron Letters, 1966, 2293.
12. J. Meinwald, J. Crandall, and W.E. Hymans, Organic Syntheses, 1965, 45, 74.
13. D.I. Davies, P. Mason, and M.J. Parrott, J.Chem.Soc., 1971, 3428 and references therein.