Stereospecificity of Oxidative Cycloaddition Reactions of 1,5-Dienes

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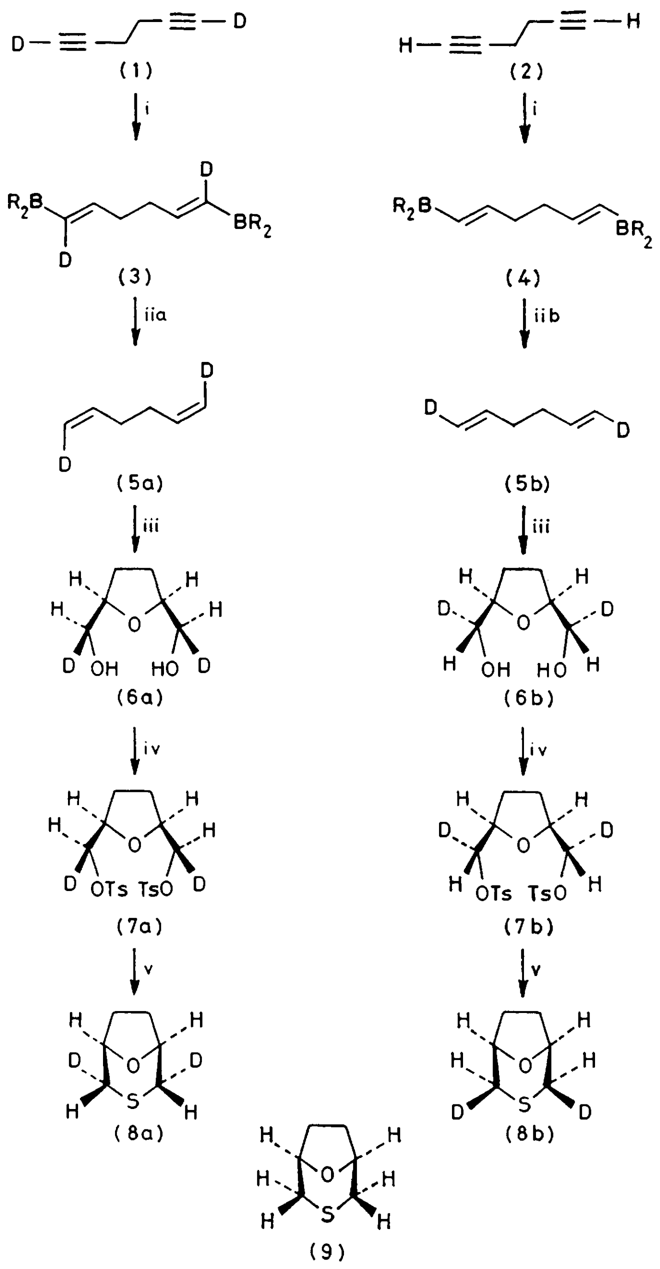
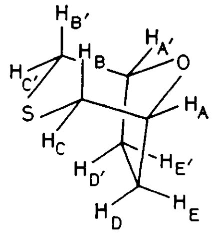
Summary The oxidative cycloaddition of hexa-1,5-dienes to bis(hydroxymethyl)tetrahydrofurans with potassium permanganate proceeds with complete stereospecificity.

THE oxidation of geranyl acetate with potassium permanganate proceeds stereospecifically to yield a tetrahydrofurandiol with three chiral centres.[1] We now report that oxidation of labelled hexa-1,5-dienes with permanganate generates four new chiral centres with complete stereospecificity. Thus, *Z,Z*-[1,6-$^2H_2$]hexa-1,5-diene (**5a**) yields racemic (**6a**) 40% yield), and correspondingly *E,E*-[1,6-$^2H_2$]hexa-1,5-diene (**5b**) yields racemic (**6b**, 30% yield) (Scheme 1). The stereochemistry of these products requires that all new bonds are formed by suprafacial processes.



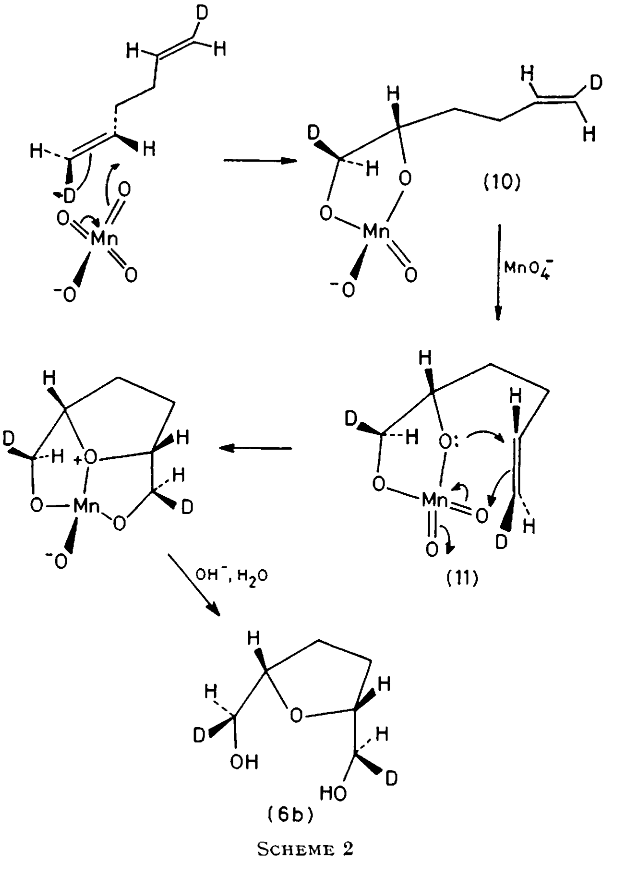
SCHEME 1. i, R_2BH in diglyme, R = $-CHMeCHMe_2$; iia, AcOH; iib, AcOD; iii, $KMnO_4$; iv, *p*-$MeC_6H_4SO_2Cl$ in pyridine; v, $Na_2S.9H_2O$ in Me_2SO.

This stereochemical course was proved by n.m.r. spectral studies on (**8a**) and (**8b**), derived by stereochemically defined processes from (**6a**) and (**6b**), respectively (Scheme 1). Thus, hydroboration of the diyne (**1**) with the sterically hindered disiamylborane yielded the vinylborane (**3**) Similarly, the diyne (**2**) gave (**4**). Stereospecific protonolysis of the vinylborane (**3**) with glacial acetic acid gave the *Z,Z*-[1,6-$^2H_2$]hexa-1,5-diene isomer (**5a**) exclusively [δ-($CDCl_3$, 270 MHz) 5·08 (1-H,6-H), 5·89 (2-H, 5-H), $J_{1,2}$ and $J_{5,6}$ 10·3 Hz, characteristic of *cis*-vinylic protons in these systems[2]]; the vinylborane (**4**) was similarly converted with [$^2H_1$]acetic acid into the *E,E*-isomer (**5b**) [δ ($CDCl_3$, 270 MHz) 5·02 (1-H, 6-H) and 5·89 (2-H, 5-H), $J_{1,2}$ and $J_{5,6}$ 17·1 Hz]. Permanganate oxidation, by the method of Klein and Rojahn,[1] of dienes (**5a**) and **5b**) gave the diols (**6a**) and (**6b**), respectively, which were transformed with toluene-*p*-sulphonyl chloride into ditosylates (**7a**, 29%, m.p. 131·5—132·5 °C) and (**7b**, 38%, m.p. 126·0—127·0 °C). Cyclization of each of these was achieved by reaction with sodium sulphide in dimethylsulphoxide, providing, by double inversion,[3] the cyclic sulphides (**8a**, 58%) and (**8b**, 59%).



(9)

Double resonance experiments were used to confirm the proton assignments[4] in the n.m.r. spectrum of unlabelled 8-oxa-3-thiabicyclo[3.2.1)]octane (**9**, m.p. 77—78 °C, *m/e* 130·04528). The separation of the resonances of H_B, $H_{B'}$ [δ($CDCl_3$) 3·21] and H_C, $H_{C'}$ [δ($CDCl_3$) 2·02] made possible the unambiguous determination of the stereochemistry of labelled compounds (**8a**) and (**8b**). In each case, only a single isomer was detectable by n.m.r. spectroscopy.



SCHEME 2

TABLE. N.m.r. data for 8-oxa-3-thiabicyclo[3.2.1]octane (**9**) in $CDCl_3$

Chemical shifts, δ/p.p.m. from Me_4Si		Coupling constants, J/Hz	
H_A $H_{A'}$	4·52	J_{AB}	2·6
H_B $H_{B'}$	3·21	J_{AC}	2·0
H_C $H_{C'}$	2·02	J_{BC}	−13·5
H_D $H_{D'}$ H_E $H_{E'}$	2·09	$J_{A'C}$	1·5

Intramolecular cycloaddition of an Mn^{VI} ester (**11**), generated from an initially formed Mn^V ester (**10**) by rapid oxidation with permanganate,[5] to the remaining olefinic double bond could account for the stereospecificity of this reaction (Scheme 2). Such a mechanism is also supported by evidence for the intermediacy of a cyclic Mn^V ester in the reactions of alkenes with permanganate,[6] the fact that the Mn^V species, MnO_4^{3-}, does not oxidize alkenes,[5] and our observation that the 1,6-diene, linalyl acetate, does not undergo a similar cyclization.

The oxidative cycloaddition constitutes a method for the formation, stereospecifically, and in a single step, of four chiral centres from an achiral, acyclic reactant. The synthetic potential of this highly stereospecific reaction and its applicability to other substrates are currently under investigation in our laboratories.

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