

Conformations and Eliminations in 1,4-Benzodioxans and the Preparation of a 1,4-Benzodioxin

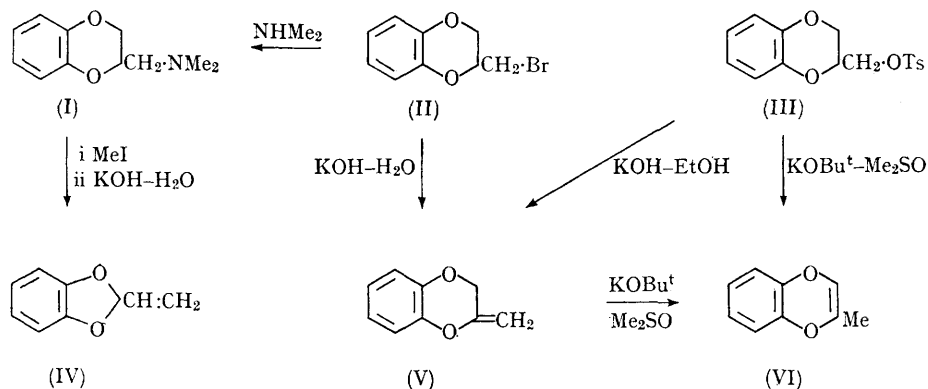
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SUBSTITUENTS normally prefer an equatorial position in saturated six-membered rings, and it

is often assumed that substituents in six-membered rings containing one double bond will prefer a

pseudo-equatorial position.¹ We now show that in 2-methoxy- and 2-ethoxy-carbonyl-1,4-benzodioxan, the substituent is *ca.* 70% axial at equilibrium. The ¹³C satellite proton magnetic resonance spectra of benzodioxan enable calculation² of the coupling constant for this compound as 2.3 c./sec. for *eq/ax* and *eq/eq* coupling (assuming that these are equal), and 11.0 c./sec. for *ax/ax* coupling, in good agreement with the Karplus equation. The benzodioxan esters have been analysed as ABC spectra; $\tau_B \approx \tau_C$, the results show that $\frac{1}{2}(J_{AB} + J_{AC}) = 3.6 \pm 0.2$ c./sec., leading to the result quoted.

infrared spectroscopy, and by hydrogenation experiments. The reaction sequences (I → IV) and (II → V) have been previously described,³ but the Italian workers erroneously assigned to the products the structures (V) and (VI), respectively. Realisation of the significance of the axial conformation of substituents in the 1,4-benzodioxan system, indicates that conformational factors may be responsible for the different courses of these elimination reactions. Our preparation of 2-methyl-1,4-benzodioxin (VI) represents the first well-authenticated compound of this class.⁴ The double-bond migration (V → VI) is of great



In addition, we have carried out the transformations in the chart. The structures of the products (IV), (V), and (VI) were elucidated by a combination of proton magnetic resonance, ultraviolet, and

interest, and the properties of 1,4-benzodioxins are under investigation.⁵

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¹ *E.g.*, H. Booth, *J.*, 1964, 1841. Cf., however, G. P. Kugatova-Shemyakina and Y. A. Ovchinnikov, *Tetrahedron*, 1962, 18, 697.

² Cf. N. Sheppard and J. J. Turner, *Proc. Roy. Soc.*, 1959, A, 252, 506.

³ G. B. Marini-Bettolo, R. Landi Vittory, and L. Paoloni, *Gazzetta*, 1956, 86, 1336.

⁴ 1,4-Benzodioxin has been reported by C. Moureu, *Bull. Soc. chim. France*, 1889, 21, 294; *Compt. rend. Acad. Sci.*, 1889, 128, 559; *Ann. Chem. Phys.*, 1899, 18, 76; and its 2-phenyl derivative by I. Lazennec, *Bull. Soc. chim. France*, 1909, 5, 509.

⁵ Satisfactory analyses have been obtained for all new compounds.