706. *Ethylidene Acetals of Cyclohexane*-cis- *and* -trans-1,2-*diol.*

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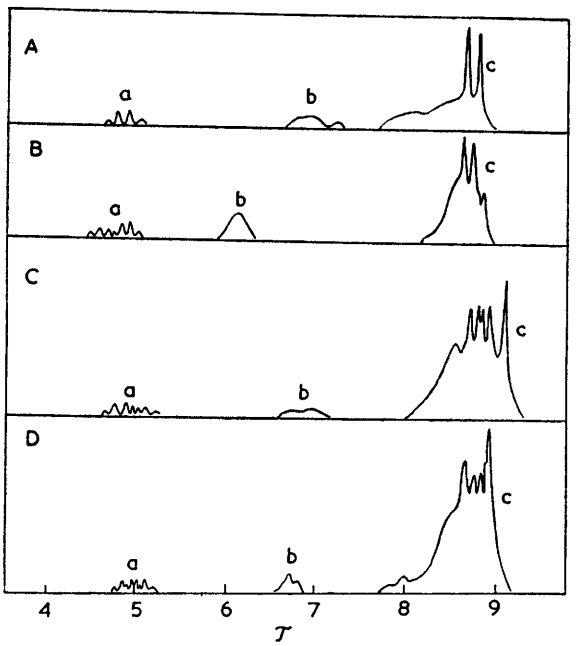
Methods are compared for the preparation of ethylidene acetals of cyclohexane-1,2-diols. The *trans*-acetals are shown to be stable though less readily formed than the *cis*-isomers. The nuclear magnetic resonance spectra are investigated.

It has often been assumed that *trans*-fusion of a dioxolan ring on to a cyclohexane ring is a highly strained, unstable arrangement, because it is not possible to prepare cyclic acetals and ketals of cyclohexane-*trans*-1,2-diols by the normal acid-catalysed reaction with aldehydes and ketones. It was pointed out, however, by Angyal and Macdonald [1] that the distance apart of the oxygen atoms in the chair forms of cyclohexane-*cis*- and -*trans*-1,2-diol (diequatorial conformation) are the same, and that the difference in the ease of acetal and ketal formation is due to the greater number of non-bonded interactions



Nuclear magnetic resonance spectra at 40 *mc./sec. of*: (A) trans-*hexahydro*-2-*methyl*-1,3-*benzodioxolan*; (B) cis-*hexahydro*-2-*methyl*-1,3-*benzodioxolan*; (C) trans-*hexahydro*-2,4-*dimethyl*-1,3-*benzodioxolan*; *and* (D) cis-*hexahydro*-2,4-*dimethyl*-1,3-*benzodioxolan*.

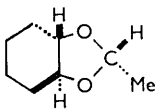
produced when the ring is deformed to bring the oxygen atoms still closer together in the *trans*- than in the *cis*-case. In 1956 Fenton, Franz, and Salcedo [2] described, without experimental detail, the preparation of a number of isopropylidene dervatives of cyclic *cis*- and *trans*-1,2-diols by ketal exchange, benzoyl chloride being used as catalyst; and a further case of a cyclic acetal of the *trans*-diol has since been reported.[3]

A series of methods for the preparation of the ethylidene acetal of cyclohexane-*cis*-1,2-diol has now been tried and compared, and their applicability to the preparation of the *trans*-isomer investigated. The best results for both isomers were obtained by acetal exchange with acetaldehyde diethyl acetal, with benzoyl chloride as catalyst. The benzoyl chloride evidently had some more specific effect than acting as a source of protons,

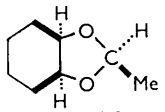
[1] Angyal and Macdonald, *J.*, 1952, 686.
[2] Fenton, Franz, and Salcedo, Abs. 130th Meeting Amer. Chem. Soc., 1956, p. 70.
[3] Roberts, Corse, Boschan, Seymour, and Winstein, *J. Amer. Chem. Soc.*, 1958, **80**, 1247.

because it was much more effective in the preparation of the *trans*-acetal than is toluene-*p*-sulphonic acid, which was equally effective in the *cis*-case. Both isomers were also prepared by Hesse's method,[4] which consists in treating the diol with diazomethane and sulphur dioxide and warming the product with acetaldehyde and an acid catalyst. The *cis*-acetal was also obtained by two other methods, neither of which yielded any *trans*-acetal: treatment of the diol with vinyl acetate in the presence of mercuric acetate and mercuric sulphate,[5] both of which were essential; and, in poor yield, by warming the diol with acetaldehyde and phosphoric acid.[6] Ethylidene-1-methylcyclohexane-*cis*- and *trans*-1,2-diol were also prepared by the benzoyl chloride method. The *trans*-acetals were formed more slowly than the *cis*-isomers, but they were stable and distilled unchanged.

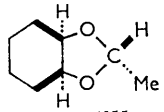
The nuclear magnetic resonance spectrum (Figure) of ethylidenecyclohexane-*trans*-1,2-diol (I) showed the expected features: (*a*) a 1 : 3 : 3 : 1 quartet near τ 4·8 due to the lone hydrogen atom of the ethylidene group adjacent to two oxygen atoms; (*b*) a peak attributed to the hydrogen atoms on the bridgehead; (*c*) a sharp doublet due to the methyl group superimposed on a broad band due to the hydrogen atoms attached to the cyclohexane ring. The other three compounds have more complex spectra, which can be analysed into two overlapping quartets in region (*a*) and two overlapping doublets in region (*c*) with an additional sharp singlet due to the bridgehead-methyl group (when present). These pairs of similar features with a small chemical shift between them were



(I)



(II)



(III)

attributed to the two possible geometrical isomers of these compounds, which have the methyl group and hydrogen atom of the ethylidene group transposed. The unequal intensities of the pairs of quartets showed that the isomers were present in unequal amounts; and the disparity was particularly marked in a sample of ethylidenecyclohexane-*cis*-1,2-diol (II and III) prepared by the vinyl acetate method, the proportion of the minor component, which had the higher chemical shift for the methyl group and the lower one for the adjacent hydrogen atom, being still further reduced. The enhanced stereospecificity in this case is probably due to the large size of the mercury atom in the attacking reagent $AcO\cdot{}^{+}CH\cdot CH_2\cdot Hg\cdot OAc$ postulated by Hirsch, Hoaglin, and Kubler.[5] This effect would be expected to favour the isomer (III), in which the methyl group is less hindered sterically by the methylene groups of the cyclohexane ring. The other isomer (II) would be expected to have the higher chemical shift for the methyl group and the lower shift for the adjacent hydrogen atom, as observed, on account of the diamagnetic anisotropy of the C–C bonds of the cyclohexane rings.[7] The bands due to the methylene groups in the cyclohexane rings were broader in the more rigid *trans*-acetals than in the more flexible *cis*-acetals, in which the chemical shift between the axial and the equatorial protons and the consequent spin–spin splitting would be minimised by rapid conformational inversion, as was pointed out by Musher and Richards [8] for *cis*- and *trans*-decalin.

Experimental

Nuclear magnetic resonance spectra were determined with a Varian V4300B spectrometer at 40 mcycles/sec., for 10% solutions in chloroform. Chemical shifts were measured relative to chloroform (τ = 2·75) by applying side-bands with a Muirhead decade oscillator.

[4] Hesse, *Angew. Chem.*, 1958, **70**, 134.
[5] Hirst, Hoaglin, and Kubler, *J. Org. Chem.*, 1958, **23**, 1083.
[6] Verley, *Bull. Soc. Chim.*, 1899, **21**, 275.
[7] Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.
[8] Musher and Richards, *Proc. Chem. Soc.*, 1958, 230.

cis-*Hexahydro*-2-*methyl*-1,3-*benzodioxolan* (II and III).—(*a*) Cyclohexane-*cis*-1,2-diol (3 g.) was boiled with acetaldehyde diethyl acetal (15 g.) and benzoyl chloride (0·1 g.) for 2 hr. The reaction was completed by allowing ethanol to distil, as it was formed, through a short fractionating column. The mixture was shaken with sodium carbonate solution, then extracted with ether. After removal of the solvents the residue was twice distilled over lithium aluminium hydride under reduced pressure, yielding the cyclic acetal (2·5 g., 68%), b. p. 64°/18 mm., n_D^{20} 1·4510 (Head [9] gives b. p. 77—82°/33 mm., n^{20} 1·4497) (Found: C, 67·3; H, 10·0. Calc. for $C_8H_{14}O_2$: C, 67·6; H, 9·9%), $\nu_{max.}$ (liquid film) 690, 714, 772, 807, 832, 857, 883, 916, 957, 997, 1014, 1042, 1083, 1098, 1113, 1142, 1196, 1250, 1307, 1323, 1343, 1357, 1370, 1411, 1437, 1451, 2795, 2875, and 2940 cm.$^{-1}$.

(*b*) (Dr. B. S. Joshi). Cyclohexane-*cis*-1,2-diol (2·3 g.), acetaldehyde (2 c.c.), and phosphoric acid (3 c.c.) were boiled under reflux for 2 hr., cooled, neutralised with aqueous sodium hydroxide, and extracted with ether. Removal of the ether and distillation of the residue gave the cyclic acetal (1 g., 36%).

(*c*) Cyclohexane-*cis*-1,2-diol (2 g.), vinyl acetate (16 g.), mercuric acetate (0·5 g.), and mercuric sulphate (0·4 g.) were stirred together at 40° for 2 hr. After filtration, most of the vinyl acetate was removed under reduced pressure. The remainder was destroyed by shaking the residue with 30% aqueous sodium hydroxide for 5 min., and the product (1·3 g., 53%) was isolated by ether-extraction, and was purified as in method (*a*).

(*d*) Sulphur dioxide was passed through a solution of cyclohexane-*cis*-1,2-diol (3 g.) in ether (150 c.c.) containing diazomethane (*ca.* 3·5 g.) at −10° until the yellow colour had disappeared; the whole was set aside overnight, then boiled under reflux for 30 min. After removal of most of the ether, acetaldehyde (20 c.c.) and benzoyl chloride (0·1 g.) were added and boiling was continued for 2 hr. The mixture was evaporated to a small volume, shaken with sodium hydrogen carbonate solution, and extracted with ether. The product (1·5 g., 41%) was isolated as in method (*a*).

trans-*Hexahydro*-2-*methyl*-1,3-*benzodioxolan* (I).—Cyclohexane-*trans*-1,2-diol (11·5 g.) was caused to react with acetaldehyde diethyl acetal (60 g.) by method (*a*) above, but 6 hours' boiling were needed for complete reaction. The cyclic *acetal* (6·8 g., 49%), isolated as above, had b. p. 70°/18 mm., n_D^{20} 1·4418 (Found: C, 67·6; H, 10·2%), $\nu_{max.}$ (liquid film) 695, 713, 823, 837, 851, 877, 905, 927, 941, 964, 1037, 1050, 1115, 1130, 1208, 1237, 1276, 1325, 1338, 1354, 1367, 1383, 1408, 2960, and 2930 cm.$^{-1}$. This compound (1·0 g., 25%) was also obtained from the diol (3·5 g.) by method (*d*).

trans-*Hexahydro*-2,4-*dimethyl*-1,3-*benzodioxolan*.—1-Methylcyclohexane-*trans*-1,2-diol (5 g.) was treated with acetaldehyde diethyl acetal (30 g.) by method (*a*) above with 5 hours' boiling, giving the cyclic *acetal* (3·0 g., 50%), b. p. 75—76°/18 mm., n_D^{20} 1·4635 (Found: C, 69·1; H, 10·5. $C_9H_{18}O_2$ requires C, 69·2; H, 10·2%), $\nu_{max.}$ (liquid film) 685, 713, 743, 805, 836, 848, 873, 925, 948, 970, 1037, 1067, 1080, 1115, 1130, 1147, 1218, 1246, 1276, 1290, 1326, 1390, 1450, 1465, 2885, and 2958 cm.$^{-1}$.

cis-*Hexahydro*-2,4-*dimethyl*-1,3-*benzodioxolan*.—1-Methylcyclohexane-*cis*-1,2-diol (3 g.) was treated with acetaldehyde diethyl acetal (30 g.) by method (*a*), giving the cyclic *acetal* (1·7 g., 47%), b. p. 65°/18 mm., n_D^{20} 1·4472 (Found: C, 69·2; H, 10·1%), $\nu_{max.}$ (liquid film) 685, 698, 735, 794, 836, 847, 871, 886, 917, 953, 970, 997, 1033, 1050, 1077, 1125, 1145, 1207, 1243, 1325, 1339, 1374, 1411, 1453, 2795, 2870, and 2945 cm.$^{-1}$.

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[9] Head, *J.*, 1960, 1778.