2,6-Divinyltetrahydropyran

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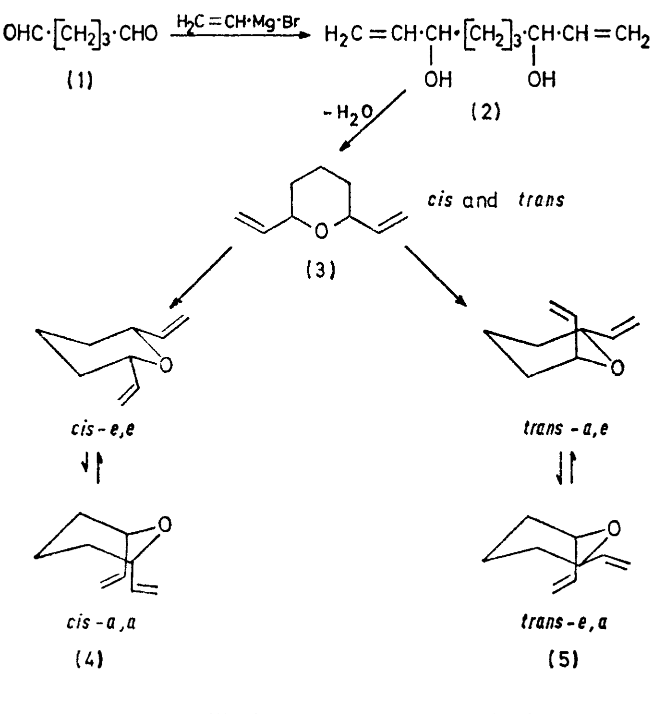
Synthesis of the *cis*- and *trans*-isomers of 2,6-divinyltetrahydropyran is described. Conformational analysis by n.m.r. spectroscopy has given the activation free energy of ring inversion, $\Delta G^{\ddagger}$ = 8·7 kcal mol^{-1} (36·4 kJ mol^{-1}) for the *trans*-isomer.

A MIXTURE of the *cis*- and *trans*-isomers of 2,6-divinyltetrahydropyran (3) was prepared by cyclisation of nona-1,8-diene-3,7-diol (2) obtained from glutaraldehyde (1) *via* a Grignard reaction with vinylmagnesium bromide. Complete separation of the isomers was not achieved by distillation, even at atmospheric pressure using a spinning band column. However, the isomers were separated by preparative g.l.c. and were identified by their n.m.r. spectra. The *cis*-isomer (4) was distinguished from the *trans*-isomer (5) † using the normal criteria that the chemical shift of an axial proton is at higher field than that of an equatorial proton and that the signal due to ring methylene protons is considerably broader in biased systems than in rapidly inverting mobile systems.



Conformational Analysis.—The n.m.r. spectrum of (4) shows regions of absorption at δ 6·2—4·8, 4·0—3·6, and 1·9—0·9 having integrated intensities of 3 : 1 : 3, respectively. On the basis of the value of the chemical shift and peak intensity, the absorptions are assigned to the six protons of the vinyl groups, the two α-protons (at positions 2 and 6) and the six β- and γ-protons (at positions 3, 4, and 5), respectively. Similarly, the spectrum of (5) shows three regions of absorption, a multiplet in the range δ 6·2—4·9 (vinyl protons), a broad singlet at 4·26 (α-protons) and a sharp singlet at 1·56 (β- and γ-protons).

The spectrum of (4) did not change on lowering the temperature to −110 °C which confirms that the only detectable conformer is that in which the vinyl groups are in equatorial positions, *cis-e,e*-(4). However, the spectrum of (5) shows marked changes on decreasing the temperature. The α-protons signal broadens and finally splits into two peaks of equal intensity with ($\nu_A - \nu_B$) = 29·0 Hz. This result demonstrates the temperature dependent equilibrium between the two chair conformations *trans-a,e*- and *trans-e,a*-(5).

The rate constant, k_c, of ring inversion at the coalescence temperature of the two peaks (117 ± 2 K) is calculated to be 64·4 s^{-1} from the equation $k_c = \pi(\nu_A - \nu_B)/\sqrt{2}$. This corresponds to an activation free energy, $\Delta G^{\ddagger}$ = 8·7 kcal mol^{-1} (36·4 kJ mol^{-1}) calculated from absolute rate theory with the transmission coefficient equal to unity.[1] This result, in addition to those on tetrahydropyran,[2,3] seems to indicate that the presence of an oxygen atom in the ring tends to lower the free energy of activation for ring inversion compared to a cyclohexane ring.

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† The *cis*-isomer is a *meso*-form but the *trans*-isomer is a mixture of two enantiomeric chiral configurations, of which only one is shown.

[1] I. O. Sutherland, *Ann. Report N.M.R. Spectroscopy*, 1972, **4**, 71.

[2] R. K. Harris and R. A. Spragg, *J. Chem. Soc.* (*B*), 1968, 684.

[3] G. Gatta, A. L. Segre, and C. Morandi, *J. Chem. Soc.* (*B*), 1967, 1203.

EXPERIMENTAL

2,6-Divinyltetrahydropyran.— Nona-1,8-diene-3,7-diol[4] (10·0 g, 0·064 mol) was dissolved in benzene (25 ml) and toluene-*p*-sulphonic acid monohydrate (0·3 g) was added. The mixture was refluxed for 24 h using a Dean and Stark apparatus. The solution was allowed to cool to room temperature and filtered to remove precipitated toluene-*p*-sulphonic acid. The benzene was removed under reduced pressure and the almost colourless residue was distilled *in vacuo* using hydroquinone as polymerisation inhibitor, to give a mixture of *cis*- and *trans*-2,6-divinyltetrahydropyran (5·7 g, 64·4%), b.p. 59—60° at 10—11 mmHg, 155—160° at 760 mmHg (Found: C, 78·25; H, 10·0. Calc. for $C_9H_{14}O$: C, 78·2; H, 10·2%). Considerable thermal degradation and/or polymerisation occurred during the distillation procedure, despite the presence of inhibitor.

Separation of Isomers.—Complete separation of the isomers was achieved using a Pye 105 chromatograph with a 30 ft × 0·25 in column packed with 10% Apiezon L on Celite. The column temperature was 158°, with a nitrogen carrier gas flow rate of 90 ml min^{-1} and column pressure of 44 lb in^{-2}. The injected volume of sample was 0·2 ml and the instrument was operated manually, cutting the peaks sharply to obtain pure isomers. From 6 ml of distilled mixture of isomers was obtained cis- (1·5 g) (Found: C, 78·15; H, 10·3%) and trans-*2,6-divinyltetrahydropyran* (1·1 g) (Found: C, 78·0; H, 10·4%). The purity of the separated isomers was checked by g.l.c. and by n.m.r. spectroscopy and the lower boiling isomer was shown to be the *trans*-isomer (R_t 1250 s) and the higher boiling isomer to be the *cis*-isomer (R_t 1000 s), as expected. I.r. spectra showed: *cis*-isomer, $CH_2=$ at 3100, 1850 (overtone), 1650, and 925; ν_{CH} 2950 and 2870; δ_{CH} 1460, 1445, 1425; and ν_{C-O} 1200 cm^{-1} and *trans*-isomer, $CH_2=$ at 3090, 1840 (overtone), 1640, and 925; ν_{CH} 2950 and 2880, δ_{CH} 1460—1410; and ν_{C-O} 1200 cm^{-1}.

N.m.r. spectra were recorded on a JEOL C60HL spectrometer in carbon disulphide.

[3/683 *Received, 2nd April*, 1973]

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[4] R. G. Woolford, *J. Org. Chem.*, 1958, **23**, 2042.