ACTA CHEMICA SCANDINAVICA 27 (1973) 1427–1462

Short Communications

The Mutarotation of D-Glucose and Its Dependence on Solvent

II. The Equilibrium Components in *N,N*-Dimethylformamide

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Investigations of D-glucose in different water-DMF mixtures have shown that at higher concentrations of DMF the mutarotation deviates significantly from the simple logarithmic law.[1] In an earlier report [2] we have described the mutarotation of D-glucose in DMF. By GLC of the HMDS-TMCS treated equilibrium solution it was found a third peak in addition to the two pyranose peaks. Evidence of furanose constituents in mutarotation equilibria of glucose using refluxing pyridine as solvent has been reported earlier.[3,4] The present communication describes the evidence for the presence of substantial quantities of D-glucofuranose in equilibria using DMF as solvent.

The mutarotation of D-glucose in DMF is extremely slow at room temperature. At 20°C several weeks are required to obtain the equilibrium. Increasing the temperature to 70°C, on the other hand, the equilibrium is obtained after a few hours. Furthermore, the third peak is about doubled in area by elevation of the temperature from 20 to 70°C. We therefore preferred to use the latter temperature for the identification of the third peak. GLC gave three distinct peaks A, B, and C with relative retention times of 0.82, 1.00, and 1.33 which accounted for 4.7, 42.5, and 52.8 %, respectively, of the total area. The peaks B and C were assigned to penta-*O*-trimethylsilyl-α- and -β-D-glucopyranose, respectively, by comparisons of their retention times with those of the TMS ethers of pure α- and β-D-glucose. The mixture was analyzed further by combined GLC-mass spectrometry. According to DeJongh *et al.*[4] fully TMS-substituted furanoses will give different mass spectra from the fully substituted pyranoses. A marked distinction between these isomers is the high intensity of *m/e* 204 ion and the low intensity of *m/e* 217 ion in the mass spectra of the pyranoses while the reverse holds true for the mass spectra of the furanoses. Another striking difference is found in the intensity of the fragment at *m/e* 319 which is known to be characteristic of the furanoses. The mass spectrum of A was found to be different from those of B and C which were nearly identical. The most important intensity data for A and C are shown in Table 1.

Table 1. Selected relative intensity data from the mass spectra of A and C.

m/e	525	319	217	205	204	191	147	129	73
A, %	0.3	13	100	7	4	19	23	5	78
C, %	0.3	2	19	21	100	50	27	8	95

A comparison of the data in Table 1 with the data given by DeJongh *et al.*[4] leads to the conclusion that peak A represents penta-*O*-trimethylsilylglucofuranose. Whether the furanose is the α- or the β-anomer or a mixture of both has not yet been established. Such investigation is, however, under progress. Nevertheless, from these experiments it can be concluded that the complex character of the mutarotation of glucose in DMF may be due to the formation of a substantial amount of the furanose isomer(s).

Experimental. The materials and the thermostat equipment were as specified earlier.[1] The equilibrated solution (1 g/100 ml) was silylated with trimethylchlorosilane and hexamethyldisilazane as described by Sweeley *et al.*[3] To secure full silylation the reaction mixture was kept at room temperature for 8 h. The precipitated salts were removed by decantation and the solution was concentrated *in vacuo*, and the TMS-ethers were extracted with hexane.

The gas chromatograph used was a Varian Aerograph, Model 80-P, equipped with a thermal conductivity detector. The chromatography was carried out isothermally (225°C) in an aluminium column (1.7 m × 6 mm) containing 20 % SE-30 on Chromosorb W (60–80 mesh). The combined GLC-mass spectrometric studies were carried out with an Atlas Varian CH7 mass spectrometer using a ionizing energy of 70 eV. Again the GLC was performed with SE-30 as the stationary phase.

Acknowledgement. We are grateful to Dr. E. Jellum at Rikshospitalet for placing the mass spectrometer at our disposal.

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2. Communicated to the 11th National Meeting of the *Norwegian Chemical Society*, June 1970, and briefly reported in *Tidsskr. Kjemi, Bergvesen Met.* **30** No. 6 (1970) 8.
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4. DeJongh, D. C., Radford, T., Hribar, J. D., Hanessian, S., Bieber, M., Dawson, G. and Sweeley, C. C. *J. Am. Chem. Soc.* **91** (1969) 1728.

Received March 16, 1973.

Sterical Orientation in Diels-Alder Dimerisation of *o*-Quinols

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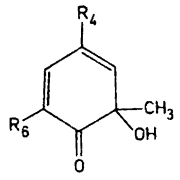
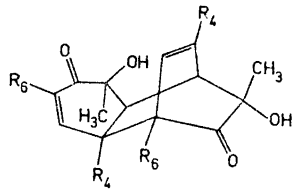
The Diels-Alder dimerisation of *o*-quinols and similar *o*-quinoid compounds gives usually only one of the conceivable stereoisomers. The reaction is considered to be governed by the *endo* rule, by the rule of the lowest dipole moment of the transition state,[1] and by steric requirements.[2,3] From these it follows that the dimer structure should be one of the types *4* – *6* (Fig. 1). For



1-3



4-6

1 $R_4 = R_6 = H$ *4*
2 $R_4 = H$, $R_6 = CH_3$ *5*
3 $R_4 = CH_3$, $R_6 = H$ *6*

a discussion of this subject, see Adler *et al.* A complete structure has, however, been established only for the dimer (Fig. 1, *4*) of 2-methyl-*o*-quinol (Fig. 1, *1*) by a chemical and spectral investigation [4] and an X-ray diffraction analysis.[5]

By X-ray analysis we have now found that the dimers of 2,6-dimethyl-*o*-quinol (Fig. 1, *2*) and 2,4-dimethyl-*o*-quinol (Fig.