Acta Chemica Scandinavica B 31 (1977) 694—700

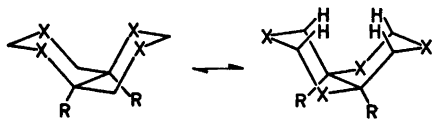
Reactions between Formaldehyde and Polyhydric Alcohols. IV.* Cyclic Acetals from *meso*- and D,L-2,3-Dimethylbutane-1,2,3,4-tetrol and Paraformaldehyde

N. FREDERIKSEN, R. B. JENSEN, S. E. JØRGENSEN, J. U. R. NIELSEN, L. NØRSKOV and GUSTAV SCHROLL

Department of General and Organic Chemistry, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark

Dedicated to Professor K. A. Jensen on his 70th birthday

The acid catalyzed condensations of *meso*- and D,L-2,3-dimethylbutane-1,2,3,4-tetrol with paraformaldehyde have been studied. Possible reaction pathways are discussed and the results obtained by conformational analysis of two bicyclic acetals formed by these reactions are presented.



ΔG°_{300} (*1a*) = 0.0 kJmol^{-1}

ΔG°_{300} (*2a*) > +5.5 kJmol^{-1}

ΔG°_{300} (*2b*) > -11.2 kJmol^{-1}

Scheme 1. Chair-chair interconversions of *1a* (X = CH_2), *2a* (X = O) and *2b* (X = O). (*a*: R = H; *b*: R = CH_3).

Whereas only one chair-chair conformation is possible for *cis*-decalin (*1a*), the compound 2,4,7,9-tetraoxa-*cis*-decalin (*2a*) can adopt two different chair-chair conformations(*O*-inside and *H*-inside, Scheme 1), as pointed out by Mills.[2] On the basis of calculated and measured dipole moments and ^{1}H NMR measurements, Lemieux and Howard [3] have concluded that compound *2a* in benzene solution at 25 °C exists in the *O*-inside conformation to an extent of at least 90 %, corresponding to $\Delta G^\circ_{300} > 5.5$ kJ mol^{-1} for the conformational equilibrium.

The energetic and conformational consequences of the introduction of substituents in the 4- and 5-positions of 1,3-dioxane have been studied in detail by Eliel *et al.*[4,5] and from their results it can be calculated that the introduction of methyl groups at C-1 and C-6 in *cis*-tetraoxadecalin * should destabilize the *O*-inside conformation of *2b* by *ca.* 17 kJ mol^{-1} relative to the *O*-inside conformation of *2a* (Scheme 1).

In the course of studies of the reactions between formaldehyde and polyhydric alcohols we have therefore synthesized compound *2b* in order to test whether this destabilization of the *O*-inside conformation is sufficient to enforce the *H*-inside conformation of *2b*.

A second aim of our investigations has been to determine pathways for the reaction of formaldehyde with polyhydric alcohols so as to establish the mechanism whereby sugar alcohols undergo acetal formation. Rules for the prediction of the products, derived from a study of the structures of the glycitols,[2,6–8] have been known for decades but the mech-

* Part III, see Ref. 1.

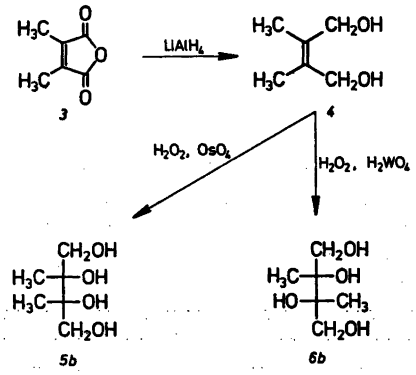
* The positional numerals are omitted for the sake of brevity.

anistic interpretation of these rules remains as a topic for future research.

The reactions between formaldehyde and the tetrols *meso*-erythritol (*5a*) [9,10] and L-threitol (*6a*) [8,11] have been studied previously.

RESULTS AND DISCUSSION

In order to synthesize *meso*- and D,L-2,3-dimethylbutanetetrol (*5b* and *6b*) with unambiguous stereochemistry the sequence shown in Scheme 2 was chosen.

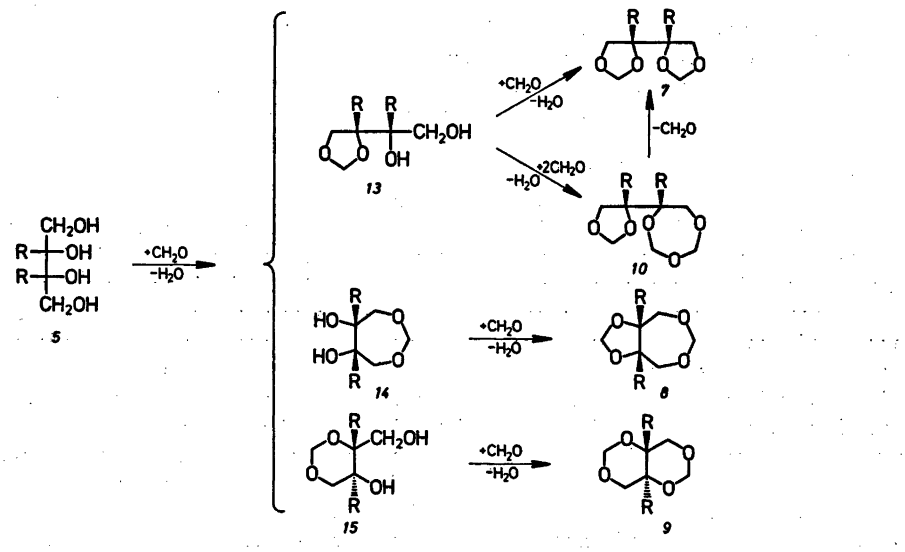


Scheme 2. Synthesis of *meso*- and D,L-2,3-dimethylbutanetetrol.

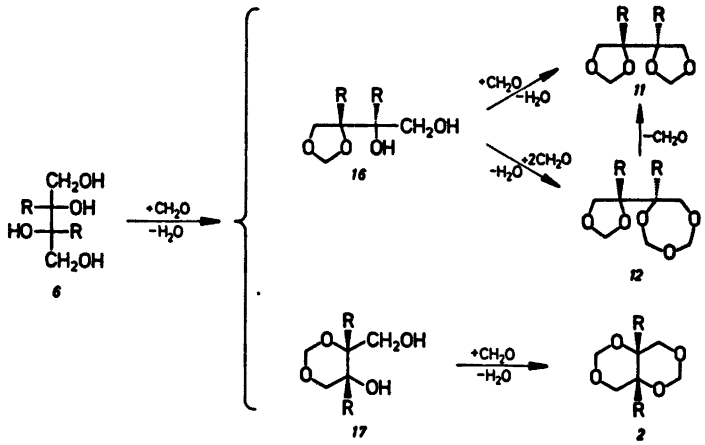
Reactions between 2,3-dimethylbutanetetrols and paraformaldehyde. The condensations of the tetrols (*5b* and *6b*) with paraformaldehyde were carried out in benzene. The workup procedure entailed filtration of the crude reaction mixture through alkaline alumnia and the isolation of monoacetals containing free hydroxy groups was therefore not possible.

meso-*2,3-Dimethylbutanetetrol* (5b). The condensation of *meso*-erythritol (*5a*) with two equivalents of methanal has previously been found to lead to the formation of the three possible diformals *7a*–*9a* (Scheme 3).[10] However, the reaction between *5b* and paraformaldehyde leads to only two isolable products, *7b* and *8b*. Gas chromatographic analysis of the latter product mixture revealed the existence of a third stable product (*9b*?) which could not be isolated; the latter compound constituted about 2 % of the yield as determined by GLC. When the reaction was carried out with a smaller amount of catalyst and stopped at an earlier stage, it was possible to isolate an unstable product with structure *10b*.

D,L-*2,3-Dimethylbutanetetrol* (6b). Lemieux and Howard [8] obtained the tetraoxadecalin, *2a*, from the reaction between L-threitol (*6a*) and dimethoxymethane, whereas the reaction with paraformaldehyde leads also to the bidioxolane,



Scheme 3. Reactions between *meso*-butanetetrols and paraformaldehyde (*a*: R=H; *b*: R=CH_3).



Scheme 4. Reactions between D,L-butanetetrols and paraformaldehyde (*a*: R=H; *b*: R=CH_3).

11a (Scheme 4).[11] The *trans* isomer of *8a* (Scheme 3) has not been obtained (*cf.* Ref. 9).

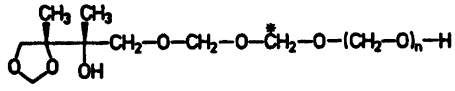
Compounds *2b* and *11b* are both formed by the reaction between *6b* and paraformaldehyde. It was possible to isolate a third product with structure *12b* when the reaction was performed using a smaller amount of catalyst.

Structure determination. The structures assigned to the six isolated compounds are consistent with the spectral data listed in the experimental section below.

Product distribution. The product distribution from the reaction between *5b* and paraformaldehyde was determined by GLC-analysis of the product mixture prior to separation. Workup after 70 h yielded a mixture containing 54 % of *7b*, 44 % of *8b* and 2 % of an unidentified compound. The ^{1}H NMR spectrum indicated a 56:44 ratio of *7b* and *8b*. Workup after *ca.* 45 h resulted in a mixture containing 40 % of *7b*, 43 % of *8b*, 15 % of *10b* and 2 % of the unidentified product. This clearly indicates that *10b* decomposes to give *7b*.

The reaction between *meso*-erythritol (*5a*) and paraformaldehyde under similar conditions has previously been shown to give a mixture of *7a*, *8a* and *9a* in the ratio 50:17:33.[10] It was therefore surprising that *9b* was not formed from *5b* and paraformaldehyde. It is not clear whether the *absence* of *9b* is a consequence of the conformation of the precursor *15b* (for which the more stable conformation is probably that with the two methyl groups equatorial [4,5]) or of kinetic control of the competitive formation of the precursors *14b* (acetal formation by two primary hydroxy groups) and *15b* (acetal formation by a primary and a tertiary hydroxy group).

The formation of *10b* is indicative of reaction between the precursor *13b* and formaldehyde oligomers. The preferred conformation of the $-C-O-C-O-C-$ grouping is all-*gauche* (all-g^+ *or* all-g^-),[12] and paraformaldehyde is thus helical. From inspection of molecular models it is evident that the least hindered position for attack of the free hydroxy group in *18* is at $-{}^*CH_2-$.



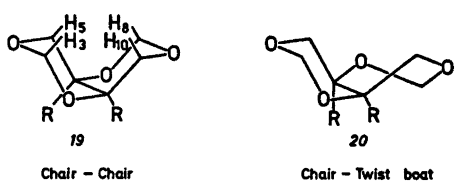
18

The reaction mixture from D,L-*6b* and paraformaldehyde contained after 24 h compounds *2b*, *11b* and *12b* in the ratio 45:53:2. The use of a smaller amount of catalyst led to a mixture of the same compounds but in the ratio 44:44:12. The dioxolanyltrioxepane (*12b*) is thus formed at the expence of the bidioxolane (*11b*).

Conformational analysis. The main purpose of the present investigation was to ascertain whether the theoretically predicted destabilization of the *O*-inside conformation of *cis*-tetraoxadecalin (*2a*) by *ca.* 17 kJ mol^{-1} by the introduction of methyl groups at C-1 and C-6

would force compound *2b* to adopt predominantly the *H*-inside conformation (Scheme 1). The ^1H and ^{13}C NMR spectra recorded between 293 K and 183 K showed no temperature-dependent changes and the geminal coupling constant for the $O-CH_2-O$ protons of *2b* was found to be ± 6.6 Hz, consistent with a normal chair conformation.[13-15] The IR spectra of *2b* in tetrachloromethane solution and in potassium bromide were identical, indicating the same conformation in solution and in the solid state.

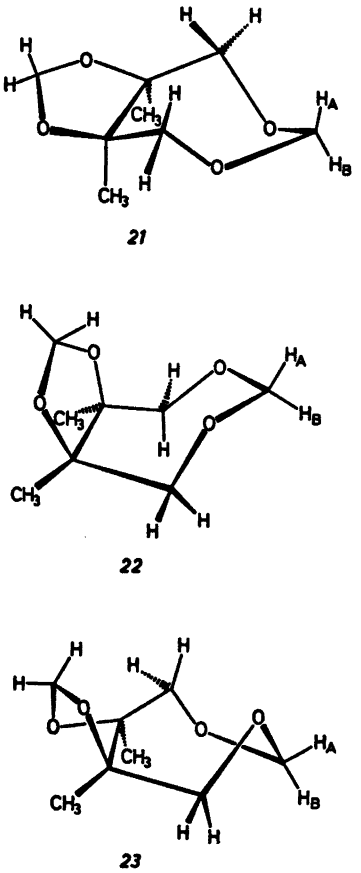
The dipole moments for *2b* in the *O*-inside and *H*-inside conformations were calculated by vector analysis [16] using bond lengths and valence angles from the known structure of 2-(*p*-chlorophenyl)-1,3-dioxane [17] and the reported dipole moment of 1,3-dioxane (2.13 D in benzene at 25 °C).[18] The calculated dipole moments were 4.25 D for the *O*-inside and 1.96 D for the *H*-inside conformation. The dipole moment of *2b* was measured at 25 °C and found to be 4.0 ± 0.1 in benzene and 3.9 ± 0.1 D in tetrachloromethane, *i.e.* in excellent agreement with the value calculated for the *O*-inside conformation. Destabilization of the *O*-inside conformation by *ca.* 17 kJ mol^{-1} is thus not sufficient to enforce the *H*-inside conformation. The H_3-H_{10} and H_5-H_{10} distances (*19*, Scheme 5) were calculated by the vector analysis to be 1.68 and 1.75 Å, respectively, and since these distances are less than twice the van der Waals' radius of hydrogen it is doubtful whether any destabilization of the *O*-inside conformation of *cis*-tetraoxadecalin will lead to the adoption of an undistorted *H*-inside conformation. Formation of a chair-twist boat conformer (*20*) might be expected to result from further destabilization of the *O*-inside conformation, although twist-boat 1,3-dioxane is estimated to be *ca.* 35 kJ mol^{-1} less stable than the chair conformer.[19]



Scheme 5. Chair-chair (*19*) and chair-twist boat (*20*) *H*-inside conformations of 1,6-dialkyl-*cis*-tetraoxadecalin.

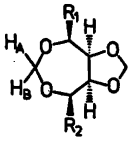
Burden and Stoddart have investigated 2,6-disubstituted *cis*-fused 3,5,8,10-tetraoxabicyclo-[5.3.0]decanes [9] and they claim that compounds of this type occur as an equilibrium mixture of two or more conformers. Three conformations are plausible for compound *8b* (Scheme 6) but an inspection of the Dreiding models of the three conformers (*21*–*23*) indicates conformation *23* to be the most favourable since it minimizes the methyl-methyl interactions.

The observed geminal coupling constant for the $O-CH_2-O$ protons in the dioxepane ring of *8b* was found to be ± 0.9 Hz. This value is numerically very small compared with the coupling constants reported for similar compounds (Scheme 7).[9,17,20] The geminal coupling constants, J_{AB}, will be about -6 Hz for con-



Scheme 6. Plausible conformations (*21*–*23*) of *Z*-1,7-dimethyl-3,5,8,10-tetraoxabicyclo[5.3.0]-decane (*8b*).

formations *21* and *22*, since the orientation of the $O-CH_2-O$ protons in the dioxepane rings of *21* and *22* is nearly the same as that of the $O-CH_2-O$ protons in the chair form of 1,3-dioxane, which displays $J_{gem} = -6.2$ Hz.[14] The orientation of the $O-CH_2-O$ group in conformation *23* corresponds to that in the twisted conformation of 1,3-dioxane, for which $J_{gem} = -2.8$ Hz.[20] The observed coupling constant thus indicates that compound *8b* adopts mainly conformation *23*.



R_1	R_2	J_{AB} Hz
$COOCH_3$	$COOCH_3$	-7.5
CH_2OCH_3	CH_2OCH_3	-7.5
H	$COOCH_3$	-6.7
H	CH_2OCH_3	-6.5
H	H	-6.1

Scheme 7. Reported geminal coupling constants (J_{AB}) of substituted *Z*-3,5,8,10-tetraoxabicyclo-[5.3.0]decanes.

EXPERIMENTAL

^1H NMR spectra were obtained using Varian T-60 A (60 MHz), Bruker HX-90 E (90 MHz) or Bruker HX-270 S (270 MHz) spectrometers (at *ca.* 30 °C unless otherwise stated). Proton-decoupled ^{13}C NMR spectra were obtained at 22.63 MHz using a Bruker WH-90 instrument. The Bruker WH-90 and HX-270 S systems were used in the Fourier transform mode. IR spectra were recorded on a Perkin-Elmer 337 Grating Infrared Spectrometer. Mass spectra were recorded on an AEI MS-902 mass spectrometer at 70 eV. The samples were introduced through a direct inlet system. Analytical GLC was performed using a Pye Unicam 104 gas chromatograph. (Columns: SE30 [10 % on Chromosorb W, 100/120 mesh] 4 mm × 1.64 m and Carbowax 1500 [10 % on Chromosorb W NAV, 60/80 mesh] 4 mm × 2.0 m. Flow: N_2, 30 ml min^{-1}). GLC separations were performed using a Perkin-Elmer F 21 "Preparative Gas Chromatograph". (Columns: Apiezon L [10 % on Chromosorb W NAV, 60/80 mesh] 6 mm × 1.8 m and SE30 [20 % on Chromosorb W NAV, 60/80 mesh] 6 mm × 1.8 m. Flow: N_2, 250 ml min^{-1}). Preparative layer chromatography (PLC) was carried out with 20 × 100 cm glass plates coated with 150 g of silica gel. (Eluent, ethyl acetate). The dipole moment of *2b* was determined from measurements of the dielectric constants (on a DM 01 instrument from Wissenschaftlich Technische Werkstätten, Weilheim, Germany) and densities of five solutions in benzene and two solutions in tetrachloromethane.

Z-2,3-Dimethyl-2-butene-1,4-diol (4) was prepared by the reduction of dimethylmaleic anhydride (*3*) with lithium aluminium hydride. To a stirred suspension of lithium aluminium hydride (30 g, 0.79 mol) in 1000 ml of ether was added a solution of *3* (76 g, 0.60 mol) in 1800 ml of ether at such a rate as to maintain reflux. The reaction mixture was then stirred and heated under reflux for 1 h. The excess of lithium aluminium hydride was destroyed by the addition of ethyl acetate (27 ml, 0.28 mol), and water (50 ml), sodium hydroxide (20 %, 23 ml) and water (105 ml) were then added successively. The mixture was filtered and the solid material extracted with ether for 24 h in a Soxhlet apparatus. The combined ether fractions were then dried with sodium sulfate and the ether removed by evaporation. The residue was distilled and the fraction boiling at 90 – 95 °C/7 Pa collected, yield of *4*: 52 g (76 %). On cooling the product in ice crystallization occurred. Recrystallization from anhydrous ether led to white hygroscopic needles, m.p. 37 – 38 °C. Anal. $C_6H_{12}O_2$: C, H. ^1H NMR (60 MHz, D_2O): δ 4.14 (4 H, s), 1.78 (6 H, s).

meso-*2,3-Dimethylbutanetetrol (5b)* was prepared by *cis*-hydroxylation[21] of *4*. To a stirred solution of *4* (29 g, 0.25 mol) and osmium tetroxide (0.25 g) in 100 ml of water was added a solution of hydrogen peroxide (0.25 mol) in 125 ml of water at such a rate as to maintain a reaction temperature of *ca.* 30 °C. The reaction mixture was then stirred for 2 h. After the addition of zinc dust (4 g) stirring was continued for a further 12 h. Filtration followed by evaporation under reduced pressure led to 29 g of crude product. The latter was dried by mixing with dry benzene followed by azeotropic evaporation. This procedure was performed twice after which the residue was cooled to −78 °C and 200 ml of pentane was added. After keeping the mixture in a refrigerator for 3 d small crystals could be observed, and when the mixture was allowed to warm up to room temperature the entire product crystallized. Recrystallization from ether/methanol (2:1) led to white hygroscopic crystals. Yield: 20.2 g (54 %), m.p. 84.5 – 85.5 °C. Anal. $C_6H_{14}O_4$: C, H. ^1H NMR (60 MHz, D_2O): δ 3.60 (4 H, s), 1.18 (6 H, s).

D,L-*2,3-Dimethylbutanetetrol (6b)* was prepared by *trans*-hydroxylation[22] of *4*. To a stirred solution of *4* (29 g, 0.25 mol) in 50 ml of water heated to 60 °C was added a solution of hydrogen peroxide (0.25 mol) and white, freshly prepared tungstic acid (0.3 g) in 50 ml of water at such a rate as to maintain a reaction temperature of 55 – 60 °C. The subsequent procedure was analogous to that used in the synthesis of *5b*. Yield: 14.6 g (39 %), m.p. 74 – 75.5 °C. Anal. $C_6H_{14}O_4$: C, H. ^1H NMR (60 MHz, D_2O): δ 3.62 *and* 3.60 (4 H, d), 1.18 (6 H, s).

Condensation of 2,3-dimethylbutanetetrols with paraformaldehyde. General method. A suspension of the tetrol (1.5 g, 0.01 mol) and paraformaldehyde (1.5 g, 0.05 mol of CH_2O) in 20 ml of benzene was heated under reflux in the presence of *p*-toluenesulfonic acid. The water formed was removed by means of a Dean-Stark trap. The reactions were monitored by GLC and on "completion" of the reaction sodium carbonate (0.5 g) was added so as to neutralize the catalyst. The reaction mixtures were filtered and the solvent removed by evaporation under reduced pressure.

meso-*2,3-Dimethylbutanetetrol and paraformaldehyde.* (Scheme 3, R = CH_3). The reaction was carried out using 0.1 g of *p*-toluenesulfonic acid as catalyst. The GLC-monitoring was carried out using a SE30 column at 150 °C. During the reaction formaldehyde sublimed into the reflux condenser and it was therefore necessary to add more paraformaldehyde (1.5 g after *ca.* 20 h and the same amount again after *ca.* 45 h). The crude reaction mixture was filtered through alkaline alumina using freshly distilled ethyl acetate (200 ml) as eluent, and subsequent evaporation of the solvent under reduced pressure yielded 1.54 g of product. GLC-analysis (Carbowax 1500, 150 °C) indicated the latter to be a mixture of 54 % of *7b*, 44 % of *8b* and 2 % of an unknown product. Cooling of the product mixture to *ca.* −20 °C led to the crystallization of compound *7b* and recrystallization of the latter from ether/ethanol (4:1) gave *ca.* 30 mg of meso-*4-(1-methyl-2,4-dioxolanyl-4-methyl-1,3-dioxolane* (7b), m.p. 54−55 °C. No attempts were made to isolate the remaining *ca.* 800 mg of *7b* in the product mixture. MS [*m/e* (% rel. int.)]: 173 (0.4, [M−H]), 87 (100), 86 (46), 57 (55), 44 (15), 43 (20). ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.08 (2 H, s), 4.96 (2 H, s), 4.01 *and* 3.55 (4 H, AB-system, J ±8.5 Hz), 1.32 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 95.28 (O−CH_2−O), 82.57 (*quat. C*), 72.53 (C−CH_2−O), 20.57 (CH_3−C). The identification of *7b* was based upon the ^{1}H NMR spectrum which displays J 0.0 Hz for the O−CH_2−O protons.[10,20,23]

Z-1,7-Dimethyl-3,5,8,10-tetraoxabicyclo[5.3.0]-decane (8b) was isolated from the product mixture by preparative GLC (Apiezon L, 130 °C). A small portion of the mixture was dissolved in ethanol and injected in 25 µl aliquots. *Ca.* 25 mg of *8b* was isolated, m.p. 41−43 °C.

MS: 174 (1, M), 173 (1), 144 (10), 131 (15), 114 (71), 112 (25), 101 (51), 100 (10), 99 (76), 87 (100), 86 (17), 85 (18), 84 (70), 71 (12), 69 (82), 58 (10), 57 (75), 45 (25), 44 (71), 43 (91), 41 (42).

^{1}H NMR (90 MHz, $CDCl_3$): δ 5.25 and 5.16 (2 H, AB-system, J ±0.9 Hz, O−C(4)H_2−O), 4.87 (2 H, s, O−C(9)H_2−O), 4.04 and 3.60 (4 H, AB-system, J ±12.9 Hz, C−CH_2−O) 1.26 (6 H, s, CH_3−C).

^{13}C NMR ($CDCl_3$): δ 95.96 (O−*C*(9)H_2−O), 92.45 (O−*C*(4)H_2−O), 83.15 (*C*1 and *C*7), 70.32 (C−CH_2−O), 19.27 (CH_3−C). The ^{1}H NMR and ^{13}C NMR spectra of compound *8b* indicate the presence of two different O−CH_2−O groups, one of which displays the zero geminal coupling constant indicative of the dioxolane ring.

meso-*6-(1-Methyl-2,4-dioxolanyl)-6-methyl-1,3,5-trioxepane* (10b) was obtained from the reaction between *5b* and paraformaldehyde using 0.05 g *p*-toluenesulfonic acid. After 20 h 1.5 g of paraformaldehyde was added. The reaction mixture was worked up after *ca.* 45 h, yielding *ca.* 1.5 g of crude product. GLC-analysis (SE30, 110−140 °C, 4° min^{-1}) indicated that the latter contained *ca.* 15 % of *10b*. A small portion of the product mixture was dissolved in ethanol and injected in 100 µl aliquots into the preparative gas chromatograph (SE30, 160 °C), yielding *ca.* 80 mg of *10b*, m.p. 32−34 °C.

MS: 203 (0.2, [M−H]), 117 (21), 87 (100), 86 (30), 57 (31), 44 (31), 43 (22).

^{1}H NMR (90 MHz, $CDCl_3$): δ 5.18 (1 H, s), 5.11 (2 H, s), 5.06 (1 H, s), 4.98 (2 H, s) [three different O−CH_2−O groups], 4.30 *and* 3.58 (2 H, AB-system, J ±9.1 Hz, *dioxolane* C−CH_2−O), 4.12 *and* 3.85 (2 H, AB-system, J ±13.4 Hz, *trioxepane* C−CH_2−O), 1.39 (3 H, s, CH_3−C), 1.31 (3 H, s, CH_3−C).

The structure of *10b* was assigned on the basis of the following observations: (a) The ^{1}H NMR spectrum indicates the presence of three different O−CH_2−O groups, two C−CH_2−O groups and two CH_3−C−O groups. Thus *10b* is formed by the reaction between *5b* and three equivalents of methanal. (b) The mass spectrum of *10b* displays abundant peaks at *m/e* 117 and 87, corresponding to rupture of the bond between the dioxolane and trioxepane rings.

D,L-*2,3-Dimethylbutanetetrol and paraformaldehyde.* (Scheme 4, R = CH_3). The condensation was carried out using 0.1 g of *p*-toluenesulfonic acid. The reaction time was *ca.* 20 h. After removal of solvent by evaporation 1.65 g of product mixture was obtained. GLC-analysis (SE30, 150 °C) indicated the composition: 45 % of *2b*, 53 % of *11b* and 2 % of *12b*. One g of the mixture was subjected to preparative layer chromatography, when two fractions were obtained (fraction 1: R_F = 0.2−0.4, fraction 2: R_F = 0.7). Fraction 1 was recrystallized from ether-ethanol (4:1), yielding *ca.* 330 mg of D,L-*1,6-dimethyl*-cis-*tetraoxadecalin* (2b), m.p. 101.0−101.5 °C. Anal. $C_8H_{14}O_4$: C, H.

MS: 174 (0.8, M), 144 (25), 114 (9), 87 (100), 84 (16), 69 (23), 57 (40), 44 (16), 43 (28), 41 (14).

^{1}H NMR (270 MHz, CD_2Cl_2, *ca.* 15 °C): δ 4.96 *and* 4.92 (4 H, AB-system, J ±6.6 Hz, O−CH_2−O), 3.67 *and* 3.61 (4 H, AB-system, J ±12.3 Hz, C−CH_2−O), 1.14 (6 H, s, CH_3−C). ^{13}C NMR ($CDCl_3$): δ 87.93 (O−CH_2−O), 72.01 (*C*1 and *C*6), 71.04 (C−CH_2−O), 16.40 (CH_3−C). The ^{1}H and ^{13}C NMR spectra are consistent with the presence of equivalent

pairs of $O-CH_2-O$, $C-CH_2-O$ and CH_3-C-O groupings. The geminal coupling constants for the two types of CH_2 protons are in good agreement with the reported values for compound *2a* (J ±6.25 and ±12.3 Hz, resp.).[3]

Fraction 2 from the PLC was purified by preparative GLC (SE30, 160 °C), yielding *ca.* 170 mg of D,L-*4-(1-methyl-2,4-dioxolanyl)-4-methyl-1,3-dioxolane* (11b), m.p. < 20 °C.

MS: 173 (0.4, [M−H]), 87 (100), 86 (45), 57 (49), 44 (17), 43 (19).

^{1}H NMR (90 MHz, $CDCl_3$): δ 5.02 (2 H, s), 4.98 (2 H, s), 4.15 *and* 3.58 (4 H, AB-system, J ±8.3 Hz), 1.30 (6 H, s). ^{13}C NMR ($CDCl_3$): δ 95.44 ($O-CH_2-O$), 83.09 (*quat. C*), 72.37 ($C-CH_2-O$), 21.45 (CH_3-C).

The structural assignment for compound *11b* is based upon the ^{1}H NMR spectrum which displays the zero geminal coupling constant for the $O-CH_2-O$ protons. Furthermore, the mass spectra of compounds *7b* and *11b* are identical.

D,L-*6-(1-Methyl-2,4-dioxolanyl)-6-methyl-1,3-5-trioxepane* (12b) was obtained from *6b* and paraformaldehyde using 20 mg of *p*-toluenesulfonic acid. GLC-analysis (SE30, 150 °C) indicated the following composition of the product mixture: 44 % of *2b*, 44 % of *11b* and 12 % of *12b*.

The PLC fraction with $R_F = 0.7$ was separated into *11b* and *12b* by preparative GLC (SE30, 170 °C), when *ca.* 20 mg of *12b* was obtained. MS: 203 (0.1, [M−H]), 117 (22), 87 (100), 86 (25), 57 (32), 44 (30), 43 (25).

^{1}H NMR (270 MHz, $CDCl_3$, *ca.* 15 °C): δ 5.01 (1 H, s), 4.98 (1 H, s), 4.97 (1 H, s), 4.93 (1 H, s), 4.93 *and* 4.78 (2 H, AB-system, J ±5.5 Hz) [three different $O-CH_2-O$ groups], 4.33 *and* 3.49 (2 H, AB-system, J 8.5 Hz, *dioxolane* $C-CH_2-O$), 4.05 *and* 3.82 (2 H, AB-system, J ±13.1 Hz, *trioxepane* $C-CH_2-O$), 1.29 (3 H, s, CH_3-C), 1.28 (3 H, s, CH_3-C). The spectral data for compound *12b* are very similar to those for compound *10b*.

REFERENCES

1. Nielsen, J. U. R., Jørgensen, S. E., Frederiksen, N., Jensen, R. B., Schroll, G. and Williams, D. H. *Acta Chem. Scand. B 31* (1977) 227.
2. Mills, J. A. *Adv. Carbohydr. Chem. 10* (1955) 1.
3. Lemieux, R. U. and Howard, J. *Can. J. Chem. 41* (1963) 393.
4. Eliel, E. L. *Acc. Chem. Res. 3* (1970) 1.
5. Kaloustian, M. K., Dennis, N., Mager, S., Evans, S. A., Alcudia, F. and Eliel, E. L. *J. Am. Chem. Soc. 98* (1976) 956.
6. Hann, R. M. and Hudson, C. S. *J. Am. Chem. Soc. 66* (1944) 1909.
7. Barker, S. A. and Bourne, E. J. *J. Chem. Soc.* (1952) 905.
8. Zissis, E. and Richtmyer, N. K. *J. Am. Chem. Soc. 76* (1954) 5515.
9. Burden, I. J. and Stoddart, J. F. *J. Chem. Soc. Perkin Trans. 1* (1975) 666.
10. Jensen, R. B., Buchardt, O., Jørgensen, S. E., Nielsen, J. U. R., Schroll, G. and Altona, C. *Acta Chem. Scand. B 29* (1975) 373.
11. Jørgensen, S. E., Frederiksen, N., Jensen, R. B., Nielsen, J. U. R., Nørskov, L. and Schroll, G. *Acta Chem. Scand. B. To be published.*
12. Dale, J. *Tetrahedron 30* (1974) 1683.
13. Anteunis, M., Tavernier, D. and Borremans, F. *Bull. Soc. Chim. Belg. 75* (1966) 396.
14. Swaelens, G., Anteunis, M. and Tavernier, D. *Bull. Soc. Chim. Belg. 79* (1970) 441.
15. Anteunis, M. and Swaelens, G. *Org. Magn. Reson. 2* (1970) 389.
16. Corey, E. J. and Sneen, R. A. *J. Am. Chem. Soc. 77* (1955) 2505.
17. De Kok, A. J. and Romers, C. *Recl. Trav. Chim. Pays-Bas 89* (1970) 313.
18. Walker, R. and Davidson, D. W. *Can. J. Chem. 37* (1959) 492.
19. Clay, R. M., Kellie, G. M. and Riddell, F. G. *J. Am. Chem. Soc. 95* (1973) 4632.
20. Burden, I. J. and Stoddart, J. F. *J. Chem. Soc. Perkin Trans. 1* (1975) 675.
21. Reppe, W. *Justus Liebigs Ann. Chem. 596* (1955) 137.
22. Mugdan, M. and Young, D. P. *J. Chem. Soc.* (1949) 2988.
23. Anteunis, M., Anteunis-De Ketelaere, F. and Borremans, F. *Bull. Soc. Chim. Belg. 80* (1971) 701.

Received April 18, 1977.