

## THE REACTION OF LEAD TETRA-ACETATE WITH SOME UNBRANCHED $\alpha,\omega$ -DIOLS

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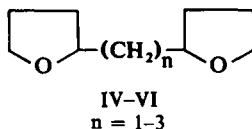
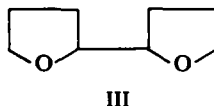
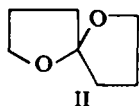
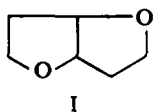
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**Abstract**—Unbranched  $\alpha,\omega$ -diols are mainly converted by means of lead tetra-acetate in refluxing benzene to the corresponding ethers of di- $\alpha$ -tetrahydrofuryl, di- $\alpha$ -tetrahydropyryl and/or  $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyryl type. Thus, 1,6-hexanediol affords *cis*-1,4-dioxaperhydropentalene (Ia) in 15.2% yield; 1,7-heptanediol affords 1,6-dioxaspiro[4.4]nonane (II) in 29.2% yield; 1,8-octanediol cyclizes to 1,6-dioxaspiro[4.5]decane (IIIa) in 39.3% yield; 1,9-nonanediol affords a mixture of di- $\alpha$ -tetrahydrofuryl-methane (IV, 33.2%), 2-( $\alpha$ -tetrahydrofuryl) $\alpha'$ -tetrahydropyran (IVa, 3.7%) and 1,7-di-oxaspiro[5.5]undecane (IVb, 3.3%); 1,10-decanediol is oxidized to a mixture of 1,2-di- $\alpha$ -tetrahydrofurylethane (V, 27.2%), and *threo*- and *erythro*- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethanes (Va, 4.3%); and 1,11-undecanediol affords, as main product, 1,3-di- $\alpha$ -tetrahydrofurylpropane (VI) in 40.1% yield, together with small amounts of four other ethers which were not identified.

LEAD tetra-acetate oxidation of different organic compounds is a free-radical process proceeding in the liquid phase and as such it has been studied extensively.<sup>1-3</sup> Various reaction paths, including cyclization, fragmentation, oxidation and acetoxylation, were found to take place, depending mainly upon the substrate employed and reaction conditions.<sup>4, 5</sup>

In continuation of our interest in this field,<sup>2, 6</sup> we wish to present results on lead tetra-acetate oxidations of a number of polymethylene  $\alpha,\omega$ -glycols in aprotic solvents. As shown previously,<sup>6</sup> lead tetra-acetate oxidations of these glycols in non-polar solvents (e.g. refluxing benzene) afforded, in addition to carbonyl and acetate fractions, bicyclic ether derivatives, which were assigned the following ditetrahydrofuran structures I-VI:



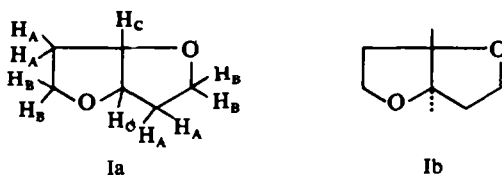
Further study revealed that some of the ether structures proposed<sup>6</sup> were not correct, and therefore, reexamination of all the structures was necessary. The present paper gives a full account of these reinvestigations.

Polymethylene  $\alpha,\omega$ -glycols containing from six to eleven C atoms were oxidized with lead tetra-acetate in refluxing benzene in the presence of calcium carbonate, using a 1:2.05:2 molar ratio of reactants, respectively. The oxidation products were isolated (Experimental) as three main fractions: an aldehyde fraction,\* an ether fraction and an acetate fraction.† The ether fractions were further purified either by removal of the carbonyl compounds with 2,4-dinitrophenylhydrazine or by fractional distillation, followed by distillation over LAH and finally the analytically pure ether fractions obtained subjected to GLC analysis.

The GLC pure ether compounds were identified by interpreting their IR and NMR spectra, and, in a few cases, by comparison of their physical and spectral properties with those of authentic compounds obtained by independent routes.

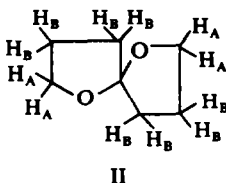
#### RESULTS AND DISCUSSION

It was anticipated that the lead tetra-acetate oxidation of 1,6-hexanediol could give rise to two isomeric 1,4-dioxaperhydropentalenes (Ia and Ib), in which two ring-



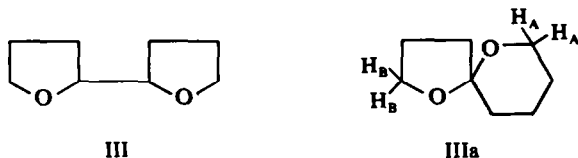
junction hydrogens are either on the same side of the molecule (*cis*-isomer, Ia) or on opposite sides (*trans*-isomer, Ib). Inspection of models revealed that steric requirements in the *trans*-isomer are extremely unfavourable; hence, its formation in the oxidation of 1,6-hexanediol with lead tetra-acetate should not, if at all, take place. Actually, only one ether compound was isolated in 15.2% yield, which was assigned the *cis*-configuration on the basis of model inspection. Its structure was confirmed by its NMR spectrum which shows the following groups of signals: a multiplet at  $\theta$  1.91 for four  $H_A$  protons, a triplet (two overlapped doublets) at  $\theta$  3.8 for four  $H_B$  protons, and a multiplet at  $\theta$  4.42 for two  $H_C$  protons (ring-junction hydrogens).

The oxidation of 1,7-heptanediol with lead tetra-acetate afforded, in 29.2% yield, a GLC pure ether compound with the following spectral characteristics: (a) the most intensive band in its IR spectrum in the region below  $1450\text{ cm}^{-1}$  is positioned at  $1024\text{ cm}^{-1}$  and can be assigned to the stretching vibrations of the 5-membered ring; and (b) the integral ratio of  $H_A$  to  $H_B$  protons in its NMR spectrum is 1:2 (Experimental). These data, taken together, as well as and the correct elemental analysis, strongly suggested the spiro structure II for the compound:



\* The results obtained by analysis and identification of aldehyde and acetate fractions will be published as a separate communication at a later date.

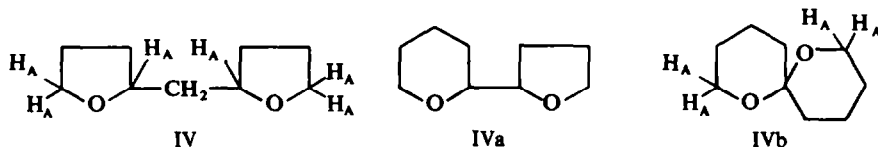
For purposes of identification, this compound was prepared by reacting  $\gamma$ -butyrolactone with sodium ethoxide.<sup>7</sup> The IR and NMR spectra of the resulting 1,6-dioxaspiro[4.4]nonane ("oxetone") are identical with the IR and NMR spectra of the compound obtained in the reaction of 1,7-heptanediol with lead tetra-acetate.



Lead tetra-acetate oxidation of 1,8-octanediol could afford two different ether compounds (III and IIIa) but GLC analysis of the ether fraction obtained in the usual manner, indicated the presence of only one ether compound in 39.3% yield. The IR spectrum of this compound is characterized by relatively sharp and intensive bands in the  $1300\text{--}800\text{ cm}^{-1}$  region, with the bands at  $1010$ ,  $1037$  and  $1075\text{ cm}^{-1}$  being the most intensive ones. The sharpness of bands is apparently due to the presence of a tetrahydropyran nucleus,<sup>8</sup> hence, the structure of 1,6-dioxaspiro[4.5]decane (IIIa) was assigned to the ether isolated. The NMR spectrum of this ether is consistent with the proposed spiro structure IIIa. It shows two multiplets at  $\theta$  3.5 and  $\theta$  3.8 attributed to the  $H_A$  protons of the 6-membered ring and  $H_B$  protons of the 5-membered ring, respectively. Moreover, the integral ratio of the  $H_A$  and  $H_B$  protons (i.e. the protons attached to C atoms linked with O atoms) to all the other protons was 4:10, which is in good accordance with the proposed structure.\*

Final proof of the suggested structure was obtained by an independent synthesis of 1,6-dioxaspiro[4.5]decane.<sup>9</sup> The IR and NMR spectra of the spiro-ether is identical in all respects with the IR and NMR spectra of the reaction product.

The major ether product in the oxidation of 1,9-nonanediol with lead tetra-acetate is, as reported earlier,<sup>6</sup> di- $\alpha$ -tetrahydrofurylmethane, IV. The structure of this ether was deduced from its IR spectrum which shows a maximum at  $1060\text{--}1065\text{ cm}^{-1}$  with shoulders on both sides of the maximum. The position and shape of this maximum are typical for all 2-alkylsubstituted tetrahydrofuran derivatives.<sup>10</sup> The main feature of its NMR spectrum is a multiplet at  $\theta$  3.65 for  $H_A$  protons (integrating for 6H), which is consistent with the structure assigned to this compound.



In addition to this ether, we found in the ether fraction two other ether compounds in minor quantities, which were assigned the structures of 2-( $\alpha$ -tetrahydrofuryl) $\alpha'$ -tetrahydropyran (IVa) and 1,7-dioxaspiro[5.5]undecane (IVb), respectively. The

\* In a preliminary communication<sup>6</sup> this compound was assigned the structure of octahydro- $\alpha,\alpha'$ -difuryl (III). However, the experiment reported herein was repeated several times and in no case were we able to isolate the compound with such a structure.



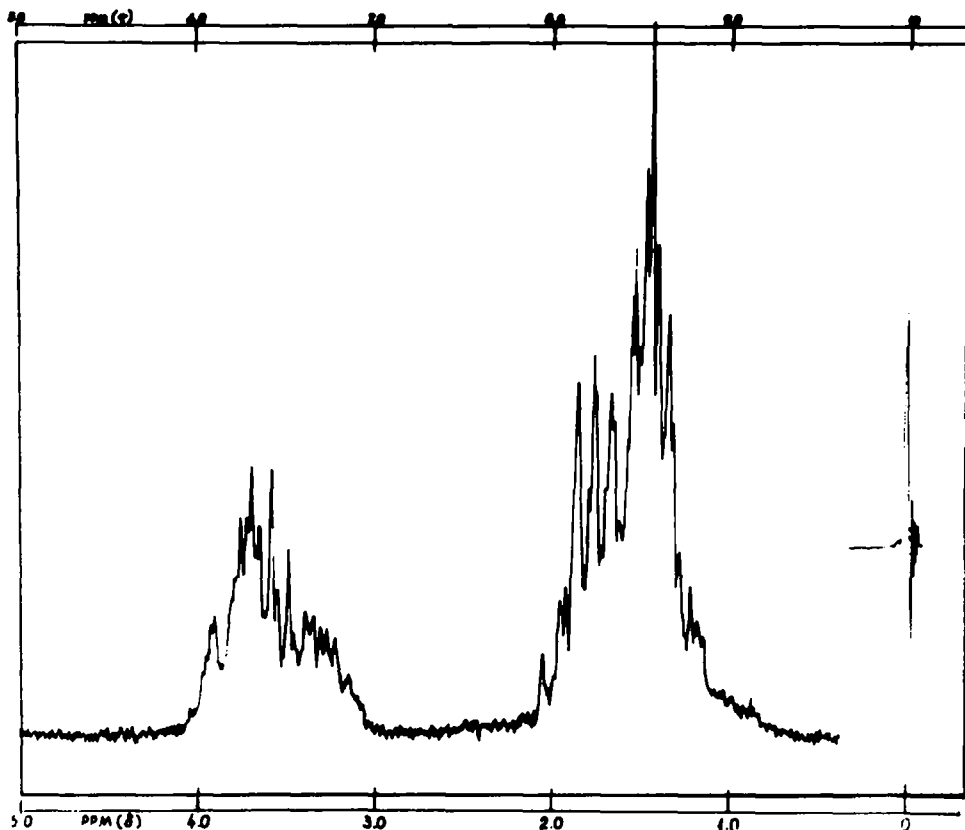


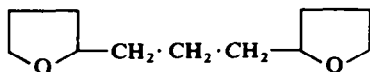
FIG. 1 NMR spectrum of *threo*- or *erythro*- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethane (Va).

Thus, the most characteristic bands in the IR spectrum of both compounds are at 1090, 1063 and 1050  $\text{cm}^{-1}$ , while the NMR spectra of these ethers (Fig. 1) display two multiplets at  $\theta$  3.3 and  $\theta$  3.6, that is, the only difference is the position of a multiplet assigned to two axial protons of the 6-membered ring which is shifted downfield by 0.4  $\theta$  units.

Taking into consideration the above spectral data, both ether compounds had to be assigned the structure of  $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethane, Va. Since this compound contains two unlike asymmetric C atoms (marked in the formula Va with asterisks) it can conceivably exist as two racemic modifications. Therefore, the two ethers isolated may be the diastereoisomers of compound Va, namely, *threo*- and *erythro*- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethanes.\*

\* At this place it should be emphasised that compounds IV, IVa, V and VI (the oxidation product of 1,11-undecanediol, see below) have a similar type of geometry as compound Va; therefore, each one of these compounds can also exist as two diastereoisomeric forms (*meso* and  $(\pm)$ -diastereoisomeric forms when there is an axis of symmetry as in compounds IV, V and VI). However, all attempts to get these forms separated, for the reason which can not be explicitly accounted for, completely failed.

Finally, the lead tetra-acetate oxidation of 1,11-undecanediol afforded, after the usual treatment, the pure ether fraction in 40.1% yield. The IR spectrum of this fraction shows a characteristic band at  $1070\text{ cm}^{-1}$  with two shoulders on both sides of the peak; therefore, it was concluded that the structure for this ether is 1,3-di- $\alpha$ -tetrahydrofurylpropane (VI).



VI

The GLC runs showed, however, that this ether fraction was not homogeneous, having at least four other ether products (in a total yield of not more than 5–8%). These minor ethers were not further investigated, and, therefore, nothing can be said as to their structures.\*

On the basis of all the results presented in this paper, a few general remarks should be pointed out. The yields of the ether products vary from 15.2% (1,6-hexanediol) to 40.1% (1,11-undecanediol); therefore, the lead tetra-acetate oxidation of polymethylene  $\alpha,\omega$ -glycols can provide, in some cases, a convenient method for the preparation of bicyclic ether compounds. As for the mechanism of the reaction, although it has not been the main subject of this study, our results are consistent with the mechanism which has been extensively discussed by earlier authors.<sup>12</sup>

## EXPERIMENTAL

B.ps and m.ps are uncorrected. GLC was run on a Perkin–Elmer instrument, Model 116-E, equipped with a thermistor detector; the columns (2m  $\times$  4mm, 4m  $\times$  6mm, 6m  $\times$  8mm) consisted of Apiezon L adsorbed on Celite (30–40%) except in case of 1,10-decanediol when 1,2,3-tris(2-cyanoethoxy)propane (TCEP) adsorbed on Chromosorb P 60/80 (40%) was used; the temp of the columns, the sensitivity of the detector and the press and flow rate of the carrier gas (dry  $\text{H}_2$ ) were adjusted according to the fractions analysed. The IR spectra were recorded on a Perkin–Elmer Infracord, Model 137. The NMR spectra were registered on a Varian A-60 spectrometer in 10%  $\text{CCl}_4$  solns. For distillations a micro Vigreux column was used.

*Starting materials.* Lead tetra-acetate<sup>13</sup> was dried *in vacuo* at 20 mm over  $\text{P}_2\text{O}_5$  and KOH, and its purity was determined iodometrically.<sup>14</sup>  $\text{CaCO}_3$  was dried *in vacuo* over  $\text{P}_2\text{O}_5$ . Thiophene-free benzene, dried over Na, was used as solvent.

Diols, with the exception of 1,11-undecanediol, were prepared by LAH reduction of the esters of the corresponding dicarboxylic acids,<sup>15</sup> which were made by the standard esterification procedure.<sup>16</sup> B.ps and/or m.ps of the diols obtained were checked with those reported in the literature.

### Lead tetra-acetate oxidations

*General procedure.* In a 1 l. round-bottomed flask, equipped with a sealed stirrer and water separator,<sup>17</sup> containing anhyd  $\text{K}_2\text{CO}_3$  and connected to a reflux condenser, were placed ca. 300 ml benzene, 0.1 mole starting diol, 0.2 mole (+ 5% excess) lead tetra-acetate, and 0.2 mole  $\text{CaCO}_3$  (+ 10% excess). The reaction mixture was stirred and heated to boiling; if the reaction became uncontrollable, heating was intercepted as long as the mixture continued to boil and was resumed after the exothermic reaction had ceased. The consumption of tetravalent lead was checked by starch-iodide test, and, when such a test was negative, heating was stopped and the flask cooled to room temp.

\* Based on the results of the lead tetra-acetate oxidation of 1,10-decanediol, we can presume that 1,2- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylethane and di- $\alpha$ -tetrahydropyrylmethane are present in the ether fraction. However, the experiments which would back this assumption were not carried out, owing to the small amounts of material we had at our disposal.

The reaction mixture was treated with 200 ml dry ether and allowed to stand for 3 hr. The soln was decanted, 50 ml ether was added to the solid residue, and the mixture was heated under reflux for 10 min. After cooling, the mixture was filtered and the combined organic filtrates were successively washed with 5%  $\text{NaHCO}_3$  aq and sat  $\text{NaCl}$  solns. After drying ( $\text{K}_2\text{CO}_3$ ), the solvents were removed by distillation and the products were fractionated through a small Vigreux column. The ether fraction was finally freed from the incorporated aldehyde and  $-\text{OH}$  containing compounds by the treatment with 2,4-dinitrophenylhydrazine, followed by redistillation over LAH.

#### Oxidation of 1,6-hexanediol

1,6-Hexanediol (11.8 g; 0.1 mole), b.p.  $156^\circ/18$  mm (lit.  $152^\circ/17$  mm<sup>18</sup>) and lead tetra-acetate (93 g; 0.2 mole + 5% excess) in 300 ml benzene were stirred and heated under reflux until the reaction was complete (5 hr). After the usual work-up, 1.73 g (15.2%) *cis*-1,4-dioxaperhydropentalene (Ia) was obtained as a colourless, extremely volatile liquid, b.p.  $156^\circ$ ,  $n_D^{20}$  1.4571. (Found: C, 62.8; H, 9.0.  $\text{C}_6\text{H}_{10}\text{O}_2$  requires: C, 63.1; H, 8.8%); IR (neat): 2890, 2790, 1460, 1280, 1195, 1095, 1050, 895 and 815  $\text{cm}^{-1}$ ; NMR:  $\theta$  1.91 (4H, m), 3.80 (4H, t) and 4.42 (2H, m).

#### Oxidation of 1,7-heptanediol

1,7-Heptanediol (13.2 g; 0.1 mole), b.p.  $149\text{--}150^\circ/10$  mm (lit.  $148\text{--}149^\circ/10$  mm,<sup>19</sup> m.p.  $20^\circ$ )<sup>20</sup> reacted with lead tetra-acetate (93 g; 0.2 mole + 5% excess) in 300 ml benzene as reported above for 5 hr. After the work-up, 3.73 g (29.2%) of II was obtained, b.p.  $48\text{--}52^\circ/12$  mm,  $n_D^{20}$  1.4483 (lit. b.p.  $159^\circ$ ,<sup>7</sup>  $52\text{--}53^\circ/14$  mm,<sup>9</sup>  $n_D^{20}$  1.4485). (Found: C, 65.2; H, 9.4. Calc. for  $\text{C}_7\text{H}_{12}\text{O}_2$ : C, 65.6; H, 9.4%); IR (neat): 2950, 2890, 1450, 1340, 1148, 1110, 1040, 1024, 947, 918 and 843  $\text{cm}^{-1}$ ; NMR:  $\theta$  3.78 (4H, m) and 1.9 (8H, m).

The same compound was prepared by reacting butyrolactone<sup>21</sup> with sodium ethoxide,<sup>7</sup> b.p.  $49\text{--}52^\circ/12$  mm,  $n_D^{20}$  1.4483. The IR and NMR spectra of the synthetic spiro-ether ("oxetone") were identical with the spectra of the reaction product.

#### Oxidation of 1,8-octanediol

1,8-Octanediol (14.6 g; 0.1 mole), b.p.  $166\text{--}167^\circ/10$  mm, m.p.  $62\text{--}63^\circ$  (lit. b.p.  $167\text{--}168^\circ/10$  mm, m.p.  $63^\circ$ )<sup>22</sup> and lead tetra-acetate (93 g; 0.2 mole + 5% excess) reacted in 300 ml boiling benzene for 2 hr. After the usual work-up, 5.58 g (39.3%) of IIIa was obtained, b.p.  $61^\circ/15$  mm,  $n_D^{20}$  1.4542 (lit. b.p.  $61^\circ/15$  mm,  $n_D^{20}$  1.4552).<sup>9</sup> (Found: C, 67.8; H, 10.1. Calc. for  $\text{C}_8\text{H}_{14}\text{O}_2$ : C, 67.6; H, 9.9%); IR (neat): 2898, 2840, 1430, 1355, 1298, 1260, 1205, 1150, 1105, 1075, 1037, 1010, 970, 938, 910, 890, 858 and 805  $\text{cm}^{-1}$ ; NMR:  $\theta$  3.5 (2H, m), 3.8 (2H, m) and 1.3–2.1 (10H, m).

The synthetic spiro-ether prepared<sup>9</sup> was identical (IR and NMR data) with the oxidation product.

#### Oxidation of 1,9-nonanediol

1,9-Nonanediol (16.0 g; 0.1 mole), b.p.  $168\text{--}169^\circ/15$  mm, m.p.  $45^\circ$  (lit. b.p.  $169^\circ/14$  mm, m.p.  $46^\circ$ )<sup>23</sup> and lead tetraacetate (93 g; 0.2 mole + 5% excess) reacted in 300 ml refluxing benzene for 2 hr. Working-up in the usual manner afforded 6.1 g (40.2%) of the ether fraction, b.p.  $90\text{--}93^\circ/12$  mm. (Found: C, 69.0; H, 10.3.  $\text{C}_9\text{H}_{16}\text{O}_2$  requires: C, 69.2; H, 10.3%). Preparative GLC of this fraction yielded three different ethers:

(a) *Di- $\alpha$ -tetrahydrofurylmethane* (IV) in 33.2% yield,  $n_D^{20}$  1.4609. (Found: C, 69.3; H, 10.5.  $\text{C}_9\text{H}_{16}\text{O}_2$  requires: C, 69.2; H, 10.3%); IR (neat): 3000, 2990, 1475, 1452, 1400, 1290, 1190, 1130, 1065, 1025, 988, 928, 880 and 810  $\text{cm}^{-1}$ ; NMR:  $\theta$  3.65 (6H, m) and 1.2–2.1 (10H, m).

(b) 2-( $\alpha$ -Tetrahydrofuryl)- $\alpha'$ -tetrahydropyran (IVa) in 3.7% yield,  $n_D^{20}$  1.4645. (Found: C, 68.9; H, 10.5.  $\text{C}_9\text{H}_{16}\text{O}_2$  requires: C, 69.2; H, 10.3%); IR (neat): 2950, 2850, 1448, 1375, 1350, 1260, 1220, 1185, 1090, 1063, 1050, 1025, 985, 952, 922, 892, 847, 820 and 802  $\text{cm}^{-1}$ ; NMR:  $\theta$  3.6 (4H, m), 2.9 (2H, m) and 1.2–2 (10H, m).

(c) 1,7-Dioxaspiro[5.5]undecane (IVb) in 3.3% yield,  $n_D^{20}$  1.4639. (Found: C, 69.1; H, 10.4. Calc. for  $\text{C}_9\text{H}_{16}\text{O}_2$ : C, 69.2; H, 10.3%); IR (neat): 2895, 2835, 1448, 1430, 1380, 1360, 1340, 1275, 1250, 1225, 1205, 1178, 1094, 1067, 1038, 989, 935, 915, 875 and 798  $\text{cm}^{-1}$ ; NMR:  $\theta$  3.51 (4H, m) and 1.2–1.5 (12H, m).

1,7-Dioxaspiro[5.5]undecane was synthesized,<sup>11</sup> and found to be identical (IR and NMR data) with the oxidation product IVb.

#### Oxidation of 1,10-decanediol

1,10-Decanediol (17.4 g; 0.1 mole), b.p.  $179^\circ/15$  mm, m.p.  $71.5^\circ$  (lit. b.p.  $175\text{--}176^\circ/14$  mm, m.p.  $72\text{--}74^\circ$ )<sup>24</sup> and lead tetra-acetate (93 g; 0.2 mole + 5% excess) reacted in 300 ml boiling benzene for 1 hr. After the

work-up, 5.4 g (31.5%) of the ether fraction, b.p. 116°/11 mm was obtained. (Found: C, 70.6; H, 10.7.  $C_{10}H_{18}O_2$  requires: C, 70.5; H, 10.7%). Preparative GLC of this fraction yielded three different ethers:

(a) 1,2-Di- $\alpha$ -tetrahydrofurylethane (V) in 27.2% yield,  $n_D^{20}$  1.4602. (Found: C, 69.9; H, 10.9.  $C_{10}H_{18}O_2$  requires: C, 70.5; H, 10.7%); IR (neat): 2900, 2825, 1452, 1445, 1370, 1350, 1240, 1180, 1065, 1048, 1015, 922 and 870  $cm^{-1}$ ; NMR:  $\theta$  3.65 (6H, m) and 1.1–2.1 (12H, m).

(b) Threo-(or erythro)- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethane (Va) in 2.2% yield,  $n_D^{20}$  1.4621. (Found: C, 70.3; H, 10.8.  $C_{10}H_{18}O_2$  requires: C, 70.5; H, 10.7%); IR (neat): 2900, 2810, 1455, 1430, 1370, 1350, 1280, 1255, 1205, 1175, 1090, 1063, 1050, 1030, 958, 922, 870, 812 and 788  $cm^{-1}$ ; NMR:  $\theta$  3.6 (4H, m), 3.3 (2H, m) and 1.1–2.1 (12H, m).

(c) Erythro-(or threo)- $\alpha$ -tetrahydrofuryl- $\alpha'$ -tetrahydropyrylmethane (Vb) in 2.1% yield,  $n_D^{20}$  1.4627. (Found: C, 70.0; H, 10.9.  $C_{10}H_{18}O_2$  requires: C, 70.5; H, 10.7%). IR (neat): 2955, 2855, 1440, 1375, 1280, 1260, 1205, 1175, 1095, 1063, 1050, 1030, 952, 922, 899, 870, 820 and 790  $cm^{-1}$ ; NMR:  $\theta$  3.6 (4H, m), 3.3 (2H, m) and 1.1–2.1 (12H, m).

#### Preparation of 1,11-undecanediol

1,11-Undecanediol, b.p. 176°/12 mm, m.p. 63° (lit. b.p. 178/12 mm, m.p. 62–62.5°<sup>25</sup>) was prepared by the reduction of  $\omega$ -acetoxyundecanoic acid with LAH.<sup>26</sup> The  $\omega$ -acetoxyundecanoic acid was synthesized from castor oil, via undecilenic acid,<sup>27</sup> and 11-bromoundecanoic acid.<sup>28</sup>

#### Oxidation of 1,11-undecanediol

1,11-Undecanediol (18.8 g; 0.1 mole) and lead tetraacetate (93 g; 0.2 mole + 5% excess) reacted in 200 ml boiling benzene for 40 min. After the work-up, 7.5 g (40.1%) of 1,3-di- $\alpha$ -tetrahydrofurylpropane (VI) was obtained, b.p. 128°/14 mm,  $n_D^{20}$  1.4640. (Found: C, 71.8; H, 11.0.  $C_{11}H_{20}O_2$ : requires: C, 71.7; H, 10.9%); IR (neat): 2950, 2790, 1445, 1390, 1330, 1305, 1272, 1205, 1115, 1070, 1020, 985, 935 and 888  $cm^{-1}$ . This ether is not pure and contains four other ethers in minute quantities.

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