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OXYDATION OF POLYMETHYLENE α,ω - GLYCOLS BY MEANS OF LEAD TETRAACETATE. PREPARATION OF DITETRAHYDROFURAN DERIVATIVES

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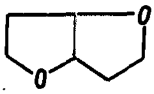
In recent years intensive investigations of the oxidation of monohydroxylic alcohols by means of lead tetraacetate have been performed. When these alcohols contained a methylene or a methine group in the δ-position, they were oxidized to tetrahydrofuran and tetrahydropyran derivatives, and when a tertiary or a quaternary C-atom was present in the α-position, fragmentation reactions occurred (1, 2).

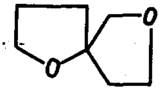
Continuing our investigations in this field, we have oxidized polymethylene α,ω-glycols containing from six to eleven carbon atoms with lead tetraacetate in boiling benzene in the presence of calcium carbonate (molar ration of reactants, glycol: LTA: $CaCO_3$ = 1: 2.05: 2). Oxidation products were isolated in the usual way and three main fractions were obtained: (1) aldehyde fraction[a], (2) ether fraction and (3) acetate fraction[a].

The ether fraction was purified by precipitating the carbonyl compounds with 2,4-dinitrophenylhydrazine, followed by distillation in the presence of lithium aluminium hydride[b]. The structures of the following isolated ditetrahydrofuran derivatives were deduced from their elementary analyses and infrared spectra:



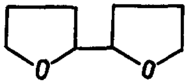
I

1,4-dioxoperhydro-pentalene



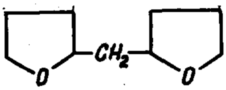
II

oxetone



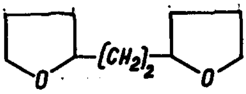
III

octahydro-α,α′-difuryl



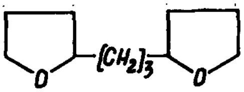
IV

di-α-tetrahydrofurylmethane



V

1,2(di α-tetrahydrofuryl)-ethane



VI

1,3-(di-α-tetrahydrofuryl)-propane

The ethers I, IV, V and VI were not known so far, whereas oxetone (II) and octahydro-α,α′-difuryl (III) are reported in the literature. There are several methods for the pre-

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[a] Experimental details will be published later.

[b] In some cases separations and purifications were effected by means of gas chromatography.

paration of oxetone (3, 4, 5, 6, 7, 8), but the ether III can be obtained only in two ways (9, 10). However, the methods described so far for the preparation of these ethers (II and III) either involve several-stage processes (7, 8) or start from rather difficultly available compounds (3, 4, 5, 6, 9). The lead tetraacetate oxidation of α,ω-polymethylene glycols represent a convenient route to the corresponding ditetrahydrofuran derivatives of this type.

Yields of oxidation products are shown in Table 1. Constants of identified compounds are given in Table 2.

TABLE 1.

Glycol	Aldehyde fraction (%)	Ether fraction		Acetate fraction	Residue %
		Product	Yield (%)		
C_6	34.2	I	25.6	33.4	6.0
C_7	32.4	II	28.3	36.8	2.4
C_8	28.8	III	36.6	28.2	5.4
C_9	28.4	IV	39.4	25.6	5.0
C_{10}	24.4	V	40.1	22.2	11.4
C_{11}	24.8	VI	39.6	21.9	12.2

Oxidations of α,ω-polymethylene glycols containing less than six and more than twelve C-atoms with lead tetraacetate are the subject of our further study.

TABLE 2.

Ether[c]	B.p. °C	n_D^{20}	n_D^{20}(lit.)	IR spectrum[d] cm^{-1}
I	156	1.4571	-	1095 and 1050
II	52-53/14 mm	1.4483	1.4485 (8)	1100[e]
III	78-80/14 mm	1.4561	1.4594 (10)	1075
IV	122/58 mm	1.4616	-	1080
V	116/11 mm	1.4635	-	1100
VI	128/14 mm	1.4640	-	1080

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[c] Satisfactory analytical data were obtained for all cyclic ethers.

[d] Only maxima characteristic for five-membered cyclic ethers are given.

[e] Structure of this spiro-compound was proved by its NMR spectrum. This spectrum was taken at 60 mc in carbon tetrachloride, using tetramethylsilane as internal standard. Multiplet at 3.75 ppm $(-OCH_2)$ corresponds to 4 protons and that at 1.87 ppm $(-O-CH_2-CH_2)$ to 8 protons.

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