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STUDY OF FURAN COMPOUNDS. XXIX[*]. STEREODIRECTION OF A REACTION YIELDING 1,6,8-TRIOXADISPIRO[4.1.4.2]TRIDECENE-12

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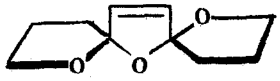
Dielectric constants of solutions of 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12 and 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecane are determined, and the dipole moments calculated.

Comparison of experimental and calculated dipole moments shows that electrolysis of a solution of 2, 5-furandipropanol-3 in methanol yields trans-1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12, thus indicating that the reaction of electrolytic alkoxylation of α, α'-furandialkanol-3s clearly differs from the stated stereodirection.

This note gives new improved data regarding the stereodirection of the reaction of electrolytic alkoxylation of α, α'-furandialkanol-3s, leading to the formation of tricyclic spiranes [2].

Consideration of the model of the molecule of 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12 (I) makes it possible to predict that it exists in two stereoisomeric forms differing in the relative positions of the oxygen atoms in the outer, coplanar, rings [2].

Cis-



Trans-

Both of the forms shown above should be preserved on reduction of the double bond in the molecule.

It was of interest to ascertain which of the two possible forms is obtained on alkoxylation of α, α'-furandialkanol-3, i. e., whether the known stereodirectionality of this process is observed.

To answer this question we determined the dipole moment of the substance obtained by electrolysis, since the forms differ in respect of molecular symmetry. Calculations and measurements were made of the dipole moments of the dispiran I and the 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecane II made by hydrogenating I [2].

Theoretical calculation of dipole moments was by vector addition. The following bond moments were used C→O 1.12 D; H→C 0.4 D[3]; and the angle between the vectors for the C–O bond was taken as 110° [4].

EXPERIMENTAL

1, 6, 8-Trioxadispiro[4. 1. 4. 2]tridecene-12 is made by electrolysis of a solution of 2, 5-furandipropanol-3 in methanol, b.p. 108-108.5° (6 mm), d_4^{25} 1.1385, n_D^{25} 1.4871.

1, 6, 8-Trioxadispiro[4. 1. 4. 2]tridecane is prepared by catalytic hydrogenation of the dispiran I, b.p. 74-75° (3 mm), d_4^{25} 1.0965, n_D^{25} 1.4982,

The solvent used was cryoscopic-grade benzene, dried and twice distilled over sodium metal, b. p. 80-80.2°, d_4^{25} 0.8734, n_D^{25} 1.4982, ε_4^{25} 2.273 [5, 6].

Measurement. Solution dielectric constants were measured by the beat method at 5×10^5 cps, using a hermetically sealed liquid condenser with cylindrical electrodes*. Solution densities were found pycnometrically. All measurements were made at 25°.

The dipole moments are calculated from the formula

$$\mu = 0.01281 \cdot 10^{-18}\sqrt{(P_\infty - P_e)T}$$

P_e, the electron polarization, is assumed equal to the molecular refraction. The atomic polarization was neglected.

P_∞, the polarization at infinite dilution, is calculated by Hedestrand's equation [7].

Table 1 gives the results found by measurement and calculation.

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[*] Part XXVIII, see [1].

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TABLE 1

Results of dipole moment determination

Compound	C, Mole Fraction	$\varepsilon_{1.2}^{25}$	$d_{1.2}^{25}$	α	β	P_∞, cm^3	P_e, cm^3	μ, D
1, 6, 8-Trioxadispiro-[4. 1. 4. 2] tridecane	0.00530	2.290	0.8755	1.328	0.454	95.52	46.61	1.54
	0.00609	2.292	0.8758	1.372	0.452			
	0.00682	2.294	0.8761	1.354	0.453			
	0.00803	2.298	0.8766	1.369	0.456			
	0.01125	2.307	0.8778	1.252	0.418			
				$\alpha_{cp}=1.335$	$\beta_{cp}=0.447$			
1, 6, 8-Trioxadispiro-[4. 1. 4. 2] tridecene-12	0.00453	2.295	0.8752	2.137	0.455	120.31	45.87	1.92
	0.00591	2.301	0.8758	2.085	0.465			
	0.00796	2.311	0.8765	2.101	0.446			
	0.00987	2.320	0.8773	2.095	0.453			
				$\alpha_{cp}=2.104$	$\beta_{cp}=0.455$			

Table 2 contrasts the dipole moments of 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12 and 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecane calculated for the cis and trans configurations and those found experimentally.

From the data given it follows that electrolysis of a solution of 2, 5-furandipropanol-3 gives trans-1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12, so that this reaction differs distinctly from the stated stereodirection.

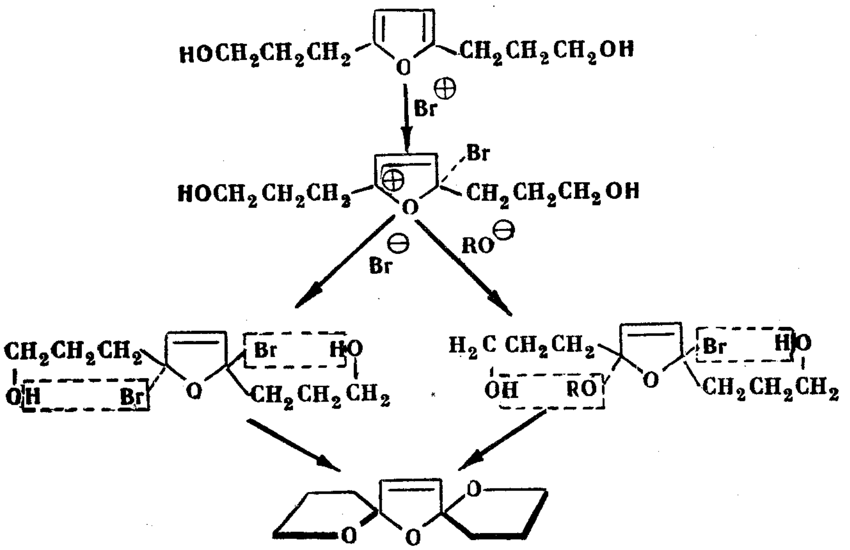
Theoretical reasons for the cause of this phenomenon can be given. It is known that furan differs from a number of heterocyclic systems in possessing an enhanced electron density at the α position due to a +E effect. Electrophilic addition of halogens to unsaturated systems takes place stepwise, and is almost always a trans addition.

TABLE 2

Comparison of calculated and experimental dipole moments

Compound	Dipole moment D		
	Calculated		Found by expt.
	Cis- form	Trans- form	
1, 6, 8-Trioxadispiro[4. 1. 4. 2] tridecene-12	3.78	1.97	1.92
1, 6, 8-Trioxadispiro[4. 1. 4. 2] tridecane	3.64	1.71	1.54

It is known [8] that the reaction mechanism for the methoxylation of furan with bromine and alcohol is based on a two-stage electrophilic addition of bromine to the furan system occurring in the alkoxylation of furan. Taking this mechanism into account, and assuming that addition of Br^- and CH_3O^- takes place simultaneously, the mechanism of alkoxylation of 2, 5-furandipropanol-3 can evidently be represented by:



Intramolecular cyclization, occurring through the hydroxyl and bromine atoms or alkoxyl group, gives the trans form of 1, 6, 8-trioxadispiro[4. 1. 4. 2]tridecene-12, and this configuration is retained on hydrogenation.

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