43. T. Konakahara, H. Nishigaki, A. Watanabe, and K. Sato, Heterocycles, 22, 2765 (1984).
44. I. Haiduc and H. Gilman, Rev. Roum. Chim., 16, 597 (1971).
45. W. K. Musker and R. L. Scholl, J. Organomet. Chem., 27, 37 (1971).
46. I. Katz, British Patent No. 757,855; Chem. Abstr., 51, 15,600 (1957).
47. L. H. Sommer, US Patent No. 2,838,515; Ref. Zh. Khim., 83,215 (1959).
48. G. P. Gisby, S. E. Royall, and P. G. Sammes, J. Chem. Soc., Perkin Trans. I, No. 1, 169 (1982).
49. R. I. Papasergio, C. L. Taston, and A. H. White, Chem. Commun., No. 23, 1419 (1983).
50. N. V. Bac and Y. Langlois, J. Am. Chem. Soc., 104, 7666 (1982).
51. J. Verbeek, Y. V. E. George, L. P. de Jong, and L. Brandsma, Chem. Commun., No. 4, 257 (1984).
52. J. Verbeek and L. Brandsma, J. Org. Chem., 49, 3857 (1984).
53. D. Wittenberg and H. Gilman, Chem. Ind., 390 (1958).
54. F. Marsais and G. Queginer, Tetrahedron, 39, 2009 (1983).
55. F. Marsais, B. Laperdrix, T. Güngör, M. Mallet, and G. Queiginer, J. Chem. Res., M, No. 10, 2863 (1982).
56. F. Effenberger and D. Häbich, Lieb. Ann. Chem., No. 6, 842 (1979).
57. British Thomson-Houston Co. Ltd., British Patent No. 685,186; Chem. Abstr., 28, 2783 (1954).
58. É. Ya. Lukevits and I. D. Segal, Pyridine and Quinoline Derivatives of Group IVB Elements. Preprint [in Russian], Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga, Part 1 (1986).

ROTATIONAL ISOMERS OF THE RADICAL-ANIONS OF 2-CARBONYL-CONTAINING DERIVATIVES OF 5-NITROFURAN

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The radical-anions of 2-carbonyl-containing derivatives of 5-nitrofuran were obtained by electrochemical generation. Their ESR spectra indicate the existence of a mixture of O,O-cis and O,O-trans rotational isomers. The parameters of the isomers were identified by INDO calculations. The more polar form (the cis isomer) is more stable in polar media.

Published data on the ESR spectra of the radical-anions of 2-carbonyl-containing derivatives of 5-nitrofuran do not give any information on the stereochemical orientation of the carbonyl-containing substituent in relation to the furan ring. As a rule, an ESR spectrum with a hyperfine structure (hfs) characterizing only one type of structure in the corresponding radical-anion is obtained for each investigated compound [1-4]. This can evidently be explained by the low stability of these radicals [5].

At the same time such radical-anions with a planar structure can be represented in the form of two rotational isomers:

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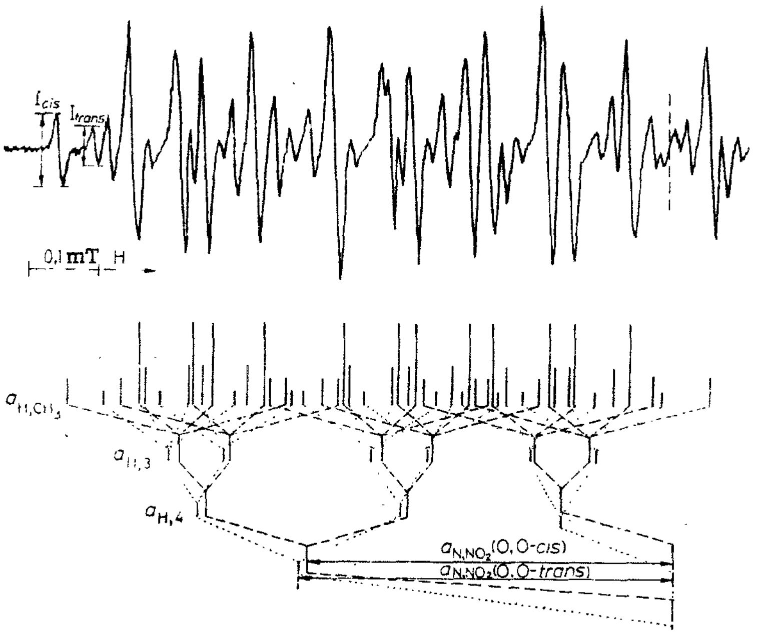

Fig. 1. The downfield half of the ESR spectrum of the radical-anion of (II) in DMFA at 20°C and its line reconstruction.

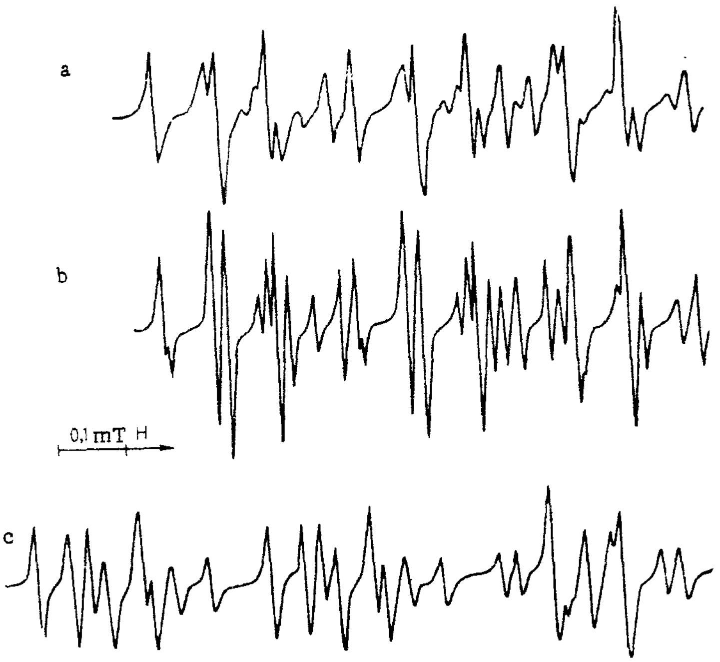

Fig. 2. The downfield halves of the ESR spectra of the radical-anion of (IV) in various solvents: a) propylene carbonate; b) DMFA; c) 2-methoxyethanol.

In fact, such rotational isomers have been detected (although not always identified) in 2-carbonyl-containing furan molecules during numerous investigations over the last 15 years by ^{13}C and ^{1}H NMR, microwave, and IR spectrometric methods, and also by dipole moment measurements [6]. In particular, the O,O-cis form was detected for 5-nitro-2-furfural in DMSO by NMR [7].

In the present work we give the results from an investigation into the radical-anions of 2-carbonyl-containing derivatives of 5-nitrofuran, aimed at the detection of the stereoisomers and their study by the ESR method. The radical-anions of the respective compounds were obtained by electrochemical generation (ECG) [8] during the one-electron electrochemical reduction of the initial compounds (I-IX):

TABLE 1. The Parameters of the ESR Spectra of the Radical-Anions of (I-IX) [a is the hfs constants, I_{cis}/I_{trans} is the ratio of the 0,0-cis and 0,0-trans isomers of the radical-anions (I-IX) in DMFA (0.1 N tetrabutylammonium perchlorate) at 20°C]

Compound	X	Conformer	Nature of hfs	$a \cdot 10$, mT				I_{cis}/I_{trans}
				a_{N, NO_2}	$a_{H, 4}$	$a_{H, 3}$	$a_{H, X}$	
I*	H	cis	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	5,16	3,04	0,75 (1,95)	1,95 (0,75)	8—10
		trans	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	5,36	2,96	0,79 (1,43)	1,43 (0,79)	
II	CH_3	cis	$3_N \cdot 2_H \cdot 4_H \cdot 2_H$	6,05	3,57	0,97	1,30	1,9
		trans	$3_N \cdot 2_H \cdot 4_H \cdot 2_H$	6,20	3,57	1,05	0,74	
III	C_2H_5	cis	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,23	3,58	0,96	1,27	1,3
		trans	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,42	3,58	1,05	0,82	
IV	n-C_3H_7	cis	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,35	3,66	0,97	1,19	2,0
		trans	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,51	3,66	1,01	0,87	
V	n-C_4H_9	cis	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,14	3,58	0,93	1,19	1,8
		trans	$3_N \cdot 2_H \cdot 3_H \cdot 2_H$	6,39	3,58	0,97	0,87	
VI*	i-C_3H_7	cis	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	6,28	3,66	1,09 (0,45)	0,45 (1,09)	~1
		trans	$3_N \cdot 2_H \cdot 2_H \cdot 2_H$	6,46	3,66	0,82 (0,45)	0,45 (0,82)	
VII**	i-C_4H_9	cis	$3_N \cdot 2_H \cdot 2_H \cdot 3_H$	7,04	4,18	0,97	0,34	
		trans	$3_N \cdot 2_H \cdot 2_H \cdot 3_H$	7,10	4,18	1,08	0,34	
VIII**	t-C_4H_9	cis	$3_N \cdot 2_H \cdot 2_H$	6,42	3,77	1,06	—	
IX**	NH_2	trans	$3_N \cdot 2_H \cdot 2_H \times$ $\times 3_N \cdot 3_H$	7,76	4,55	1,12	0,32 (N) 0,18 (2H)	

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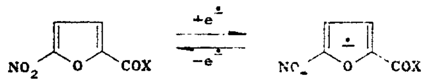
*The $a_{H, 3}$ and $a_{H,X}$ values were not determined unambiguously.

**The I_{cis}/I_{trans} values and also the $a_{H,X}$ values for (VII-IX) could not be determined. The a values averaged among the isomers are given for (VIII) and (IX).



I X=H, II X=CH_3, III X=C_2H_5, IV X=C_3H_7, V X=C_4H_9, VI X=$CH(CH_3)_2$, VII X=$CH_2CH(CH_3)_2$, VIII X=$C(CH_3)_3$, IX X=NH_2

By optimization of the electrochemical generation process and the ESR spectra we were able to achieve conditions under which it was possible by means of the ESR spectra not only to detect free radicals of dual type but also in some cases to determine the individual parameters of each of them. For example, in the ESR spectrum obtained during ECG of the radical-anions of 5-nitro-2-acetylfuran (II) in DMFA (Fig. 1) at the potentials corresponding to the limiting current area of the first polarographic wave the observed number of hfs lines exceeded the expected value (with regard to the free rotation of the acetyl substituent) for the given radical ($3_N \cdot 2_H \cdot 2_H \cdot 4_H$). This spectrum is the superimposition of the ESR spectra of the radical-anions of two forms having the same hfs characteristics typical of the radical-cation of compound (II) but having somewhat different values for the hfs constants. Such characteristics of the obtained free radicals and also the small difference in the values of the g factor, due to change in the spin density at the atoms and not to the atomic composition, indicate that these two types of radicals are stereoisomers (evidently the 0,0-cis and 0,0-trans conformers) of the radical-anion of (II). On the ESR time scale these two rotational isomers are stable states of the radical-anions. From the intensity ratio of the signals in the ESR spectra of these two types of radicals it can be found that the content of the free radicals of the isomer having the smallest a_N constant is almost twice the content of the radicals of the second isomer.

The radical-anions were generated electrochemically for the remaining compounds (I-IX) in the same way at the potentials corresponding to the limiting current of the first polarographic wave (between —0.7 and —0.9 V with reference to a saturated calomel electrode). However, the signals of the individual isomers were not resolved on account of the overlap of the signals in the ESR spectra of the radical-anions (VIII) and (IX) due to the more complex hfs. The partial overlap of the ESR signals also did not make it possible to determine the

TABLE 2. The Quantum-Chemical Parameters of the Radical-Anions of the cis and trans Isomers of (I) and (II) (E is the total energy, μ is the dipole moment)

Compound	X	Conformer	E, au	μ, D	$a \cdot 10$, mT			
					a_{N, NO_2}	$a_{H, 4}$	$a_{H, 3}$	$a_{H, X}$
I	H	cis	−117,849	9,0	4,14	−2,85	1,80	0,21
		trans	−117,866	6,9	5,27	−3,54	2,67	1,33
II	CH_3	cis	−126,293	10,0	5,51	−3,62	2,76	−3,3
		trans	−126,296	7,2	5,89	−3,75	2,74	−3,1

ratio of the isomers of the radical-anion of (VII) in DMFA. The parameters of the ESR spectra for the radical-anions of (I-IX) are given in Table 1.

Although the obtained data demonstrate convincingly the presence of two forms of the stereoisomers in the radical-anions, it is not possible to determine whether a given isomer is the cis or trans form of the radical-anion on the basis of these data alone. We sought a solution to this problem in an analysis of investigations into the dependence of the forms of the rotational isomerism on the properties of the medium. Although the conclusions from individual papers on the derivatives of furan with carbonyl-containing substituents are somewhat contradictory, the polarization of the molecule by the medium is nevertheless discussed. Thus, for example, from data in [9] it follows that the O,O-trans form of the furfural molecules is more stable than the O,O-cis form in media with dielectric constant $\varepsilon < 5$ and less stable in media with $\varepsilon > 5$. On the other hand, these molecules have a higher dipole moment in the cis form than in the trans form [10].

In order to obtain a theoretical estimate of the characteristics of the conformers for the investigated compounds we calculated the molecular orbitals by the INDO method for the cis and trans isomers of the radical-anions of (I) and (II) not interacting with the medium. From the data in Table 2 it follows that for the radical-anions of (I) and (II) not interacting with the medium the trans isomer is more stable than the cis isomer. [The difference between the calculated total energies of these isomers amounts to 11 kcal/mole for the radical-anion of (I) and 2 kcal/mole for (II); the calculated barrier for the trans—cis transition amounts to 14 kcal/mole for the radical-anion of (I) and 19 kcal/mole for (II).] However, in view of the fact that the cis isomer of the radical-anion is characterized by a lower value for the a_N constant than the trans isomer (Table 2) it follows from the ESR spectra of the radical-anions of (I-VI) (Table 1) that the cis isomers of these radicals are more stable than the trans isomers in DMFA. The probable reason for such change in the conformation of the radical-anion due to the polarity of the medium may be its polarization by the solvent molecules. In fact, to judge from the calculated dipole moments, the cis isomer of the investigated radical-anions is more polar than the trans isomer. This evidently determines the stabilization of the cis isomer in the polar media.

The cis—trans equilibrium of the radical-anions is also affected by the individual characteristics of the substituent X. This shows up most clearly during comparison of the radical-anions of (I) and (II): Substitution of H by CH_3 displaces the cis—trans equilibrium toward the less polar trans form (Table 1). However, the a_N values increase identically with increase in the electron-donating characteristics both for the cis and for the trans form. This indicates the absence of an effect from changes in the intramolecular interactions on the cis—trans equilibrium due to change in the substituent X. The effect of the characteristics of the substituent X on the cis—trans equilibrium can therefore be explained rather by steric hindrance to polarization of the radical-anion by the molecules of the medium.

In view of the dependence of the conformations of the investigated radical-anions on the properties of the medium (Fig. 2) we realized the electrochemical generation of the radical-anions of the investigated compounds in solvents with various polarities. The change in the parameters of the ESR spectra for the radical-anions of (I) and (IV) and the ratios of their conformers can be traced from the data in Tables 3 and 4. The low stability of the radical-anions and the overlap of the ESR signals for the two isomers made it difficult to study the cis—trans equilibrium in various solvents. The widest range of solvents could be tested successfully in the case of (IV) (Table 3). The trans conformer, which is more stable than the cis isomer in the state not interacting with the medium (Table 2), can

TABLE 3. The hfs Constants and the Ratios of the 0,0-cis and 0,0-trans Isomers of the Radical-Anion of (IV) [in various solvents (0.1 N tetrabutylammonium hexafluorophosphate) at 20°C]

No.	Solvent	Conformer	$a \cdot 10$, mT				I_{cis}/I_{trans}
			a_{N, NO_2}	$a_{H, 4}$	$a_{H, 3}$	$a_{H, X}$	
1	Propyl alcohol	cis	7,89	3,83	1,10	0,89	0,6
		trans	8,31	3,83	1,15	0,57	
2	Ethyl alcohol	cis	8,26	4,04	1,10	0,90	1,0
		trans	8,68	4,04	1,24	0,64	
3	Methyl alcohol	cis	8,45	4,02	1,08	0,82	1,4
		trans	8,71	4,04	1,29	0,57	
4	Ethyl acetate	cis	5,72	3,17	0,80	1,05	2,5
		trans	6,19	3,30	1,06	0,64	
5	Water*						0,5
6	Chloroform	cis	6,56	3,51	0,96	0,96	2,1
		trans	7,11	3,53	1,08	0,69	
7	2-Methoxyethane	cis	7,03	3,19	0,90	0,82	1,0
		trans	7,38	3,49	1,07	0,53	
8	Pyridine	cis	5,98	3,37	0,80	1,10	2,8
		trans	6,15	3,40	1,06	0,78	
9	Quinoline	cis	6,10	3,44	0,85	1,15	2,5
		trans	6,74	3,58	0,96	0,78	
10	Acetone	cis	6,20	3,49	0,90	1,06	2,0
		trans	6,50	3,56	1,03	0,71	
11	Nitromethane	cis	6,98	3,72	1,06	1,06	2,3
		trans	7,34	3,76	1,19	0,71	
12	N,N-DMFA	cis	6,13	3,40	0,87	1,10	2,0
		trans	6,29	3,40	0,96	0,80	
13	Acetonitrile	cis	6,22	3,42	0,90	1,15	2,2
		trans	6,49	3,42	1,03	0,76	
14	DMSO	cis	6,10	3,33	0,90	1,10	3,0
		trans	6,24	3,35	0,96	0,76	
15	Propylene carbonate	cis	6,01	3,44	0,90	1,06	4,5
		trans	6,17	3,40	0,99	0,75	

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*The ratio of the isomers was obtained by extrapolation of the values for DMFA–water mixtures. The hfs constants were not determined.

be either more or less stable than the cis isomer in solutions, depending on the polarity of the medium. Such distinctive changes of the difference in the free energies of the conformers, which arise in the transition from nonpolar to polar media, are evidently due to intermolecular interactions between the radical-anion and the molecules of the medium. Parameters of a continuous medium, which the dielectric constant ε is, for example, are unsuitable for the characterization of these features of the medium. A more suitable although also limited characteristic of the medium is the dipole moment of the solvent molecules μ. Since the largest range of solvents was used in the case of (IV), the change in the equilibrium of the cis and trans forms in relation to the polarity of the solvent molecules, expressed in terms of the dipole moment, can be traced best in the case of this radical (Fig. 3). For this case the following linear relationship is obtained:

$$I_{cis}/I_{trans}=0.2+0.7\mu\ [\mathrm{D}]\quad (n=15,\ r=0.72).$$

However, as expected, on account of the uncertainty in the correspondence of the structure of the molecule to a specific value of the dipole moment and on account of the complex nature of the interaction between the solvent molecules and the radical-anion, significant deviations from the obtained relationship are observed. Nevertheless, even with such a small value for the correlation coefficient the fairly large range of solvents (15) leads to the result that the probability of a tendency for the stability of the cis isomer to increase with increase in the polarity of the solvent is fairly high (more than 0.99 according to the Student test).

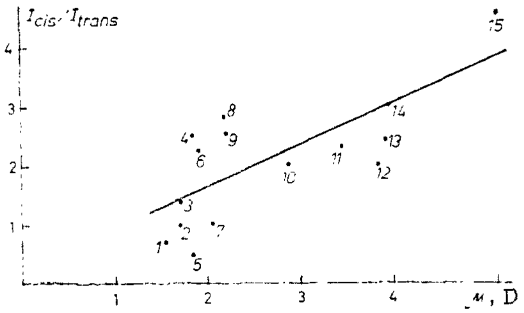

Fig. 3

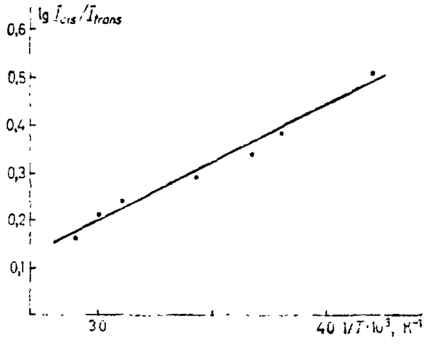

Fig. 4

Fig. 3. The dependence of the intensity ratio of the ESR signals for the cis and trans isomers of the radical-anion of (IV) (I_{cis}/I_{trans}) on the dipole moment (μ) of the solvent molecule. The numbers of the solvents are given in Table 3.

Fig. 4. The dependence of the ratio of the cis and trans isomers of the radical-anion of (IV) in DMFA on the temperature of the medium.

The ability to polarize the radical-anions in the state of the cis form is determined not only by the nature of the solvent but also by the structure of the carbonyl-containing substituent. By comparison of the ratio of the isomers for the radical-anions of (I) (Table 4) and (IV) (Table 3) in various solvents it can be found that substitution of the aldehyde hydrogen by C_3H_7 sterically hinders polarization of the radical-anion to the cis state by one and the same solvent by 2-4 times.

If the suggestion about the polarization of the radical-anions from the trans to the cis form by the molecules of the medium is correct, weakening of the interaction between the radical-anion and the solvent molecules and, thereby, weakening of the ability of the solvent for such polarization of the radical-anions can be expected with increase in temperature. In fact, measurements of the intensities of the ESR signals for the rotational isomers of the radical-anions of (II) and (IV) in DMFA showed that the conformational distribution of the radical-anions is shifted toward the cis isomer with decrease in the temperature of the medium, i.e., toward the isomer with the larger dipole moment. According to the data in Fig. 4, the difference in free energy between the cis and trans isomers of the radical-anion of (IV) amounts to ~1.1 kcal/mole. The same difference in free energy was obtained for the radical-anion of (II).

The unique behavior of water as solvent should be noted. The addition of water to the aprotic solvent (DMFA, DMSO, acetone) leads to a decrease in the amount of the O,O-cis isomer compared with its fraction in the pure solvent. Thus, for the DMFA—water mixture the change in the ratio of the cis and trans isomers of the radical-anion of (II) in relation to the concentration of the water is described by the linear equation:

$$I_{cis}/I_{trans} = 1.98 - 0.02\ c_{H_2O} \quad (n = 7,\ r = 0.996).$$

Extrapolation to pure water (c_{H_2O} = 56 M) gives the ratio I_{cis}/I_{trans} = 0.64, which is significantly lower than could be expected from the dipole moment of water. Consequently, having a high dielectric constant (ε = 78.5) and a comparatively small dipole moment (μ = 1.85 D) compared with the other employed solvents, water polarizes the investigated radical-anions to the cis form most weakly. The low polarizing capacity of the water is evidently due not only to the comparatively small dipole moment of the water molecule but also to the noncorrespondence between the dimensions of the dipoles of the water molecules and the radical-anion and also to the strong interaction between the water molecules.

These and other similar data (Fig. 3) indicate that the ability of the solvent molecules to polarize the investigated radical-anions to the cis state is not only determined by the magnitude of the dipole moment of these molecules. The complex nature of the interaction between the radical-anion and the molecules of the medium is also demonstrated by the generally known fact that the ESR spectra of radical-anions characteristic of the individual solvent are not observed in mixed media. However, in spite of this, according to the experimental data contact dipole—dipole interaction, i.e., interaction at distances of the same

TABLE 4. The hfs Constants and the Ratios of the Isomers of the Radical-Anion of (I) [in various solvents (0.1 N tetrabutylammonium hexafluorophosphate) at 20°C]

Solvent	Conformer	$a \cdot 10$, mT				I_{cis}/I_{trans}
		a_{N, NO_2}	$a_{H, 4}$	$a_{H, 3}$	$a_{H, X}$	
Ethyl alcohol*	cis trans	7,26	3,63	1,40	0,96	3
Chloroform	cis trans	6,17 6,77	3,39 3,39	1,83 1,58	0,87 1,04	4
Acetone	cis trans	5,14 5.55	3,01 3,03	1,69 1,38	0,71 0,87	6
N,N-Dimethylformamide	cis trans	5,16 5,35	3,16 2,96	1,95 1,43	0,71 0,79	8

*It was not possible to determine the hfs constants for the trans isomer.

order of magnitude as the dimensions of the dipoles, play a significant role in the polarization of the radical-anions of 2-carbonyl-containing 5-nitrofurans from the less polar trans form to the more polar cis form.

EXPERIMENTAL

The free radicals of the investigated compounds were generated under steady-state conditions by electrochemical reduction at the potentials corresponding to the limiting current of the first one-electron polarographic wave at a platinum electrode in an ECG cell placed in the rectangular resonance cavity (of the H_{102} type) of the ER-9 ESR spectrometer (Carl Zeiss, Jena, GDR) by the method described in [8]. As supporting electrolyte we used 0.1 N solutions of $(C_4H_9)_4NPF_6$ or $(C_4H_9)_4NClO_4$. The measurements at various temperatures were made on an ER-9 spectrometer fitted with a temperature regulator. While the ESR spectra were being recorded, in each case the conditions both for electrochemical generation (the concentrations of the initial molecules and the radical-anions) and for the recording of the spectra (degree of magnetic field modulation, UHF field power, magnetic field sweep rate) were optimized from the decrease in the width of the individual lines of the ESR signals. The magnetic field sweep was calibrated by means of the ESR spectrum of the radical-anions of nitrobenzene [11]. The quantum-chemical calculations of the models of the investigated radical-anions of (I) and (II) were made by the INDO method with standard parametrization [12] using the program listed in [13] in FORTRAN-IV. The initial compounds (I-IX) were described in [14].

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LITERATURE CITED

1. Landolt-Börnstein, Zahlwerte und Funktionen aus Naturwissenschaften und Technik. Neue Serie, Springer-Verlag, Heidelberg—New York (1980), Group 2, Vol. 9, Part dl, p. 576.
2. J. Ćernak, A. Staśko, F. Tomanovic, L. Nemethy, and I. Sroková, Chem. Zvesti, 37, 385 (1983)
3. J. Klima, J. Prousek, J. Ludvík, and J. Volke, Coll., 49, 1627 (1984).
4. R. Gavars, J. Stradins, L. Baumane, and L. Baider, J. Mol. Struct., 102, 183 (1983).
5. J. Klima, L. Baumane, J. Stradins, J. Volke, and R. Gavars, Collect. Czech. Chem. Commun., 50, 1594 (1986).
6. D. J. Chedvik and I. A. Cliff, Khim. Geterotsikl. Soedin., No. 5, 579 (1984).
7. Yu. Yu. Popelis, É. É. Liepin'sh, and Ya. P. Stradyn', Khim. Geterotsikl. Soedin., No. 2, 174 (1980).
8. Ya. P. Stradyn', R. A. Gavar, and L. Kh. Baumane, Izv. Akad. Nauk. Latv. SSR, No. 2, 73 (1986).
9. R. J. Abraham and M. Siverns, Tetrahedron, 28, 3015 (1972).
10. B. N. Sheinker, A. S. Kuzharov, S. V. Bulgarevich, E. G. Derecha, O. A. Osipov, and V. I. Minkin, Zh. Obshch. Khim., 44, 175 (1974).

11. L. H. Piette, P. Ludwig, and R. N. Adams, Anal. Chem., 34, 916 (1965).
12. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, J. Chem. Phys., 47, 2026 (1967).
13. J. A. Pople and D. L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York (1970).
14. M. Černayová, Diz. Kand. Chem. Vied. Vysoká Technická Škola, Bratislava (1976).

HETEROORGANIC FURAN DERIVATIVES.

61.* TRIMETHYL(5-METHYL-2-FURYL)SILANE AND TRIMETHYL(5-METHYL-2-FURYL)GERMANE

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The transformations of trimethyl(5-methyl-2-furyl)silane and trimethyl(5-methyl-2-furyl)germane were studied upon vapor-phase oxidation by atmospheric oxygen on a V-Mo-Ag-O catalyst. Under these conditions, trimethyl(5-formyl-2-furyl)silane and trimethyl(5-formyl-2-furyl)germane are formed albeit in only 5-7% yield. This low yield is a consequence of the thermal instability of the starting compounds and the aldehydes formed. The oxidation of 2-methyl-5-tert-butylfuran was studied under comparable conditions. The corresponding aldehyde was obtained in 30% yield. A scheme was proposed for the catalytic oxidation of 5-substituted 2-methylfurans.

The catalytic oxidation of methyl-substituted heterocyclic compounds by oxygen in the vapor phase on oxide catalysts is a means for the preparation of the corresponding hetarylaldehydes [2]. Vanadium oxide and molybdenum oxide, characterized by variable valence of the metal and labile oxygen, and their mixtures with various additives are used as catalysts.

This method has been used for the preparation of formyl derivatives of pyridine [3-5], pyrazine [6, 7], pyrimidine [6], thiophene [8], and thiazoline [9]. In the case of furan derivatives, the liquid-phase catalytic oxidation of 5-methylfurfural by atmospheric oxygen gives furan-2,5-dialdehyde in addition to the major reaction product, furan-2,5-dicarboxylic acid [10]. This result indicates the possibility of oxidizing the methyl group of 5-methylfurfural to a formyl group.

Various biologically active compounds have recently been prepared form 5-trimethylgermyl- (Ia) and 5-trimethylsilylfurfural (IIa). Aldehydes Ia and IIa were obtained by a six-step synthesis from furfural in 70-80% yield [11-13]. In light of previous results [2-10], we may assume that another method for the preparation of aldehydes Ia and IIa may be used for the catalytic vapor-phase oxidation of the methyl group attached to the ring in trimethyl-(5-methyl-2-furyl)germane (Ib) and trimethyl(5-methyl-2-furyl)silane (IIb).

In the present work, we studied the catalytic vapor-phase oxidation of Ib and IIb and their carbon analog, 2-methyl-5-tert-butylfuran (IIIb), in order to determine the direction of their transformations and elucidate the feasibility of obtaining the corresponding aldehydes by this method.

The catalytic oxidation of Ib-IIIb was carried out by the action of atmospheric oxygen in the presence of a catalyst consisting of V_2O_5, MoO_3, and Ag_2O (V:Mo:Ag = 1:1:0.02) in the vapor phase at 300-450°C and contact time from 0.1 to 0.5 sec. The catalyst composition is optimal for the oxidation of 2,5-dimethylfuran to 5-methylfurfural as shown by preliminary experiments. The pulse macrocatalytic method was used which permits the operative determina-

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*For Communication 60, see [1].

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