N 18.0%. $C_{10}H_9N_3O_4$. Calculated: C 51.0; H 3.8; N 17.8%.

2-(4-Nitrophenyl)-5-ethoxy-1,3,4-oxadiazole (XXIX). This compound, with mp 246-247° (acetone), was obtained in 60% yield as white crystals by the method used to prepare XXVIII. Found: C 51.2; H 3.7; N 17.9%. $C_{10}H_2N_3O_5$. Calculated: C 51.0; H 3.8; N 17.8%. IR spectrum: 1540 and 1350 (NO_2); 1610 (phenyl ring); 1250, 1120, and 1140 cm^{-1} (C-O-C).

LITERATURE CITED

1. E. Müller, in: Methoden der Organischen Chemie (Houben-Weyl), Georg Thieme Verlag, Stuttgart (1967), 10/2, 123.
2. A. P. Grekov, The Organic Chemistry of Hydrazine [in Russian], Tekhnika, Kiev (1966).
3. M. S. Skorobogatova, Master's Dissertation, S. M. Kirov Institute of Chemical Technology (1969).

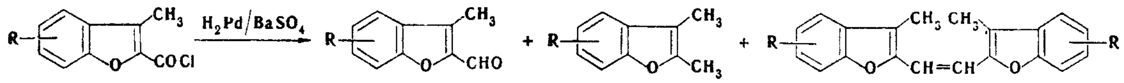
SIDE PRODUCTS IN THE ROSENMUND REDUCTION OF BENZOFURAN-2-CARBOXYLIC ACID CHLORIDES

E. Vojtanis, B. Sila, and T. Lesyak

UDC 542.942:547.728:543.422.25.4

The corresponding 1,2-bis(2-benzofuryl)ethylenes and 2-methylbenzofurans were isolated as side products, along with the principal reaction products (2-formylbenzofurans), in the Rosenmund reduction of 3-, 5-, and 7-alkylbenzofuran-2-carboxylic acid chlorides. The bis(2-benzofuryl)ethylene structure was confirmed by the IR and PMR spectra data and alternative synthesis by reduction of the corresponding benzofuroins, obtained by benzoin condensation of 2-formylbenzofurans, with zinc amalgam in acidic media. The side formation of desoxybenzofuroin derivatives was noted in some cases in the benzoin condensation.

We have previously established (for example, see [1]) that, in addition to the chief reduction products (aldehydes II), small amounts of 2-methylbenzofurans (III) and crystalline side-unsaturated compounds are always formed in the Rosenmund reduction [2] of alkylbenzofuran-2-carboxylic acid chlorides (I). The IR spectra of the crystalline side-unsaturated compounds contain absorption bands at 1615-1620 cm^{-1}, and the PMR spectra contain a two-proton singlet at 7.03-7.06 ppm and a number of other features typical for the CH=CH increment. These data, together with the results of elementary analysis, make it possible to assign to them the structure of 1,2-dibenzofuryl derivatives of ethylene of the general formula IV.



Ia-e IIa-e IIIa-e IVa-e

I–IV a[*] R=H; b R=5-CH_3; c R=7-CH_3; d R=5-C_2H_5; e R=7-C_2H_5

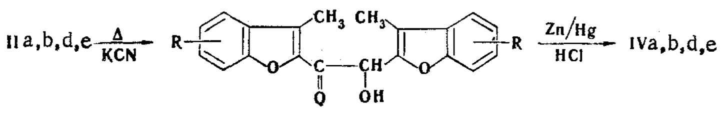
For the alternative synthesis of IV we selected the method proposed by Ballard and Dehn [3] — preparation of 1,2-disubstituted ethylenes with aromatic groups by reduction of the corresponding benzoins. From 2-formylalkylbenzofurans II we obtained the corresponding benzofuroins V, which gave the expected ethylenes IV by reduction with zinc amalgam in

---

[*] In what follows, the R values for V-VII for the letters are corresponding to those presented here.

Institute of Chemistry, N. Copernicus University, Torun, Poland. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 744-748, June, 1977. Original article submitted December 25, 1975; revision submitted June 30, 1976.

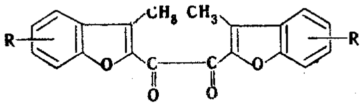
acidic media via the scheme



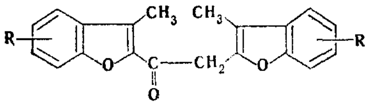
Va,b,d,e

In some cases, in addition to benzofuroins V, the corresponding bis(2,2'-benzofuroyl) derivatives (VI) were also formed in the benzoin condensation of aldehydes II, whereas the corresponding desoxybenzofuroin derivatives (VII) were found in addition to 1,2-disubstituted ethylenes IV in the reduction of furoins V.

The 1,2-bis(2-benzofuryl)ethylenes obtained in this way are identical to the side products of the reduction of acid chlorides I.



VI



VII

Despite numerous attempts, we were unable to carry out the benzoin condensation of aldehyde IIc and obtain benzofuroin Vc, which even *in statu nascendi* underwent oxidation to 2,2'-bis(3,7-dimethylbenzofuroyl) (VIc). The latter on reduction with zinc amalgam did not give the expected ethylene derivative IVc but only traces of the corresponding benzofuroin Vc and desoxybenzofuroin VIIc. We therefore established the 1,2-bis(3,7-dimethyl-2-benzofuroyl)ethylene structure (IVc) (Table 1) from the results of its elementary analysis and spectroscopic data.

From the side products in the reduction of acid chlorides I we isolated, in addition to unsaturated IV, the known 2-methylbenzofurans III, the physical constants of which are in agreement with the literature data [1, 4]. Unfortunately, we were unable to isolate the expected alkyl derivatives of (2-benzofuryl)carbinol and establish the mechanism of the formation of III and IV from the corresponding acid chlorides. This problem is currently under investigation and will be the subject of a separate publication.

The formation of 1,2-disubstituted ethylenes in the Rosenmund reduction of acid chlorides has not been previously noted in the literature.

TABLE 1. Bis(3-methyl-2-benzofuryl)ethylenes (IV)

No.	Compound	mp, °C	Found, %		Empirical formula	Calc., %		PMR spectrum, δ, ppm	IR spectrum, cm⁻¹	Yield, %
			C	H		C	H			
IVa	1,2-Bis(3-methyl-2-benzofuryl)-ethylene	183—184	83,2	5,6	$C_{20}H_{16}O_2$	83,3	5,6	2,32 (s, 6H, $2CH_3$), 7,03 (s, 2H, CH=CH), 7,19 (m, 8H, arom.)	1615	0,4
IVb	1,2-Bis(3,5-dimethyl-2-benzofuryl)ethylene	241—243	83,6	6,5	$C_{22}H_{20}O_2$	83,5	6,4	2,26 (s, 6H, $2CH_3$), 2,37 (s, 6H, $2CH_3$), 7,07 (s, 2H, CH=CH), 7,12 (m, 6H, arom.)	1618	0,5
IVc	1,2-Bis(3,7-dimethyl-2-benzofuryl)ethylene	227—229	83,3	6,4	$C_{22}H_{20}O_2$	83,5	6,4	2,34 (s, 6H, $2CH_3$), 2,52 (s, 6H, $2CH_3$), 7,05 (s, 2H, CH=CH), 6,79 (m, 6H, arom.)	1620	0,05
IVd	1,2-Bis(3-methyl-5-ethyl-2-benzofuryl)ethylene	230—233	83,7	7,0	$C_{24}H_{24}O_2$	83,7	7,0	1,22 (t, 6H, $2CH_2\mathbf{CH_3}$), 2,30 (s, 6H, $2CH_3$), 2,66 (q, 4H, $2\mathbf{CH_2}CH_3$), 7,00 (s, 2H, CH=CH), 7,06 (m, 6H, arom.)	1620	0,2
IVe	1,2-Bis(3-methyl-7-ethyl-2-benzofuryl)ethylene	162—164			$C_{24}H_{24}O_2$			1,34 (t, 6H, $2CH_2\mathbf{CH_3}$), 2,30 (s, 6H, $2CH_3$), 2,92 (q, 4H, $2\mathbf{CH_2}CH_3$), 7,10 (s, 2H, CH=CH), 7,16 (m, 6H, arom.)	1630	0,01

TABLE 2. Products of the Benzoin Condensation of 2-Formylbenzofurans

No.	Compound	mp, °C	Found, %		Empirical formula	Calc., %		IR spectrum, cm-1	PMR spectrum, δ, ppm	Yield, %
			C	H		C	H			
	Benzofuroins (V)									
Va	3,3'-Dimethylbenzofuroin	151—153	75,1	5,1	$C_{20}H_{16}O_4$	75,0	5,0	1680 (C=O), 3455 (OH)	2,29 (s, 3H, CH_3), 2,52 (s, 3H, CH_3), 3,94 (s, 1H, OH), 6,10 (s, 1H, $\mathbf{CH}OH$) 7,35 (m, 8H, arom.)	43
Vb	3,3',5,5'-Tetramethylbenzofuroin	154—156	75,7	5,7	$C_{22}H_{20}O_4$	75,8	5,8	1680 (C=O), 3440 (OH)	2,07 (s, 3H, CH_3), 2,11 (s, 3H, CH_3), 2,57 (s, 3H, CH_3), 3,97 (d, 1H, $CH\mathbf{OH}$), 5,90 (d, 1H, $\mathbf{CH}OH$), 7,02 (m, 6H, arom.)	44
Vc*	3,3',7,7'-Tetramethylbenzofuroin	118—120							2,31 (s, 3H, CH_3), 2,37 (s, 6H, $2CH_3$), 2,55 (s, 3H, CH_3) 4,06 (s, 1H, $CH\mathbf{OH}$), 5,92 (s, 1H, $\mathbf{CH}OH$), 7,06 (m, 6H, arom.)	
Vd	3,3'-Dimethyl-5,5'-diethylbenzofuroin	121—123	76,5	6,4	$C_{24}H_{24}O_4$	76,6	6,4	1670 (C=O), 3465 (OH)	1,15 (t, 6H, $2CH_2\mathbf{CH_3}$), 2,34 (s, 3H, CH_3), 2,51 (s, 3H, CH_3), 2,59 (q, 4H, $2\mathbf{CH_2}CH_3$), 2,80 (d, 1H, $CH\mathbf{OH}$), 5,89 (d, 1H, $\mathbf{CH}OH$), 7,01 (m, arom.)	37
Ve	3,3'-Dimethyl-7,7'-diethylbenzofuroin	98—100	76,5	6,5	$C_{24}H_{24}O_4$	76,6	6,4	1685 (C=O), 3520 (OH)	1,10 (t, 3H, $CH_2\mathbf{CH_3}$), 1,21 (t, 3H, $CH_2\mathbf{CH_3}$), 2,32 (s, 3H, CH_3), 2,51 (s, 3H, CH_3), 2,71 (q, 4H, $2\mathbf{CH_2}CH_3$), 4,09 (d, 1H, $CH\mathbf{OH}$), 5,94 (d, 1H, $\mathbf{CH}OH$), 7,11 (m, 6H, arom.)	14
	2,2'-Dibenzofuroyls (VI)									
VIa	2,2'-Bis(3-methylbenzofuroyl)	203—205	75,3	4,4	$C_{20}H_{14}O_4$	75,5	4,4	1670 (C=O)	2,61 (s, 6H, $2CH_3$), 7,41 (m, 8H, arom.)	2,23
VIb	2,2'-Bis(3,5-dimethylbenzoforoyl)	176,5—178	76,1	5,2	$C_{22}H_{18}O_4$	76,3	5,2	1670 (C=O)	2,38 (s, 6H, $2CH_3$), 2,55 (s, 6H, $2CH_3$), 7,32 (m, 6H, arom.)	0,35
VIc	2,2'-Bis(3,7-dimethylbenzofuroyl)	182—183	76,3	5,2	$C_{22}H_{18}O_4$	76,3	5,2	1670 (C=O)	2,45 (s, 6H, $2CH_3$), 2,64 (s, 6H, $2CH_3$), 7,26 (m, 6H, arom.)	45,5
VId	2,2'-Bis(3-methyl-5-ethylbenzofuroyl)	146—147	77,0	6,0	$C_{24}H_{24}O_4$	77,0	5,9	1670 (C=O)	1,21 (t, 6H, $2CH_2\mathbf{CH_3}$), 2,61 (s, 6H, $2CH_3$), 2,67 (q, 4H, $\mathbf{CH_2}CH_3$), 7,25 (m, 6H, arom.)	7,6

---

*Traces of Vc were obtained by reduction of 2,2'-dibenzofuroyl VIc.

TABLE 3. Desoxybenzofuroins (VII)

No.	Compound	mp, °C	Found, %		Empirical formula	Calc., %		IR spectrum, cm-1	PMR spectrum, δ, ppm	Yield, %
			C	H		C	H			
VIIa	3,3'-Dimethyl-2,2'-desoxybenzofuroin	82—84	78,9	5,4	$C_{20}H_{16}O_3$	78,9	5,3	1685 (C=O)	2,19 (s, 3H, CH_3), 2,50 (s, 3H, CH_3), 4,25 (s, 2H, CH_2), 7,26 (m, 6H, arom.)	43
VIIc*	3,3',7,7'- Tetramethyl- 2,2'-desoxybenzofuroin	133—136							2,21 (s, 3H, CH_3), 2,42 (s, 3H, CH_3), 2,50 (s, 3H, CH_3), 2,55 (s, 3H, CH_3), 4,30 (s, 2H, CH_2), 7,14 (m, 6H, arom.)	Traces
VIId	3,3'-Dimethyl-5,5'-diethyl-2,2'-desoxybenzofuroin	79—81	79,9	6,8	$C_{24}H_{24}O_3$	80,0	6,7	1685 (C=O)	1,21 (t, 3H, $CH_2\mathbf{CH}_3$), 1,24 (t, 3H, $CH_2\mathbf{CH}_3$), 2,20 (s, 3H, CH_3), 2,52 (s, 3H, CH_3), 2,66 (q, 4H, $2\mathbf{CH}_2CH_3$), 4,25 (s, 2H, CH_2), 7,12 (m, 6H, arom.)	12
VIIe	3,3'-Dimethyl-7,7'-diethyl-2,2'-desoxybenzofuroin	104—106	80,0	6,6	$C_{24}H_{24}O_3$	80,0	6,7	1685 (C=O)	1,24 (t, 3H, $CH_2\mathbf{CH}_3$), 1,31 (t, 3H, $CH_2\mathbf{CH}_3$), 2,20 (s, 3H, CH_3), 2,50 (s, 3H, CH_3), 2,15 (q, 2H, $\mathbf{CH}_2CH_3$), 2,24 (q, 2H, $\mathbf{CH}_2CH_3$), 4,30 (s, 2H, CH_2), 7,14 (m, 6H, arom.)	43

---

*Compound VIIc was obtained in traces by reduction of 2,2'-dibenzofuroyl (VIc).

EXPERIMENTAL

The IR spectra of films (alkylbenzofurans) and Nujol or hexachlorobutadiene suspensions (the remaining compounds) were recorded with a UR-10 spectrometer (with an NaCl prism). The PMR spectra were recorded with a Tesla B-487-C spectrometer (80 MHz) on the δ scale with hexamethyldisiloxane as the internal standard.

Brief Method for the Rosenmund Reduction of Alkylbenzofuran-2-carboxylic Acid Chlorides. A stream of dry hydrogen was passed with vigorous stirring through a solution of 0.5 mole of acid chloride I in 1000 ml of dry xylene containing 15 g of a palladium catalyst [5] and 1 ml of an inhibitor (quinoline–sulfur) [5]). The reaction was carried out at 139-141° for 10-16 h until HCl evolution ceased (negative test with $AgNO_3$).

Isolation of the Side Products in the Rosenmund Reduction of Alkylbenzofuran-2-carboxylic Acid Chlorides. The xylene solution obtained as a result of reduction of acid chlorides I (Table 1) was concentrated at 20-30 mm (mercury column), the residue remaining after complete removal of the solvent by distillation was dissolved in ethanol, and the solution was treated with excess saturated aqueous $NaHSO_3$ solution. The precipitated bisulfite adducts of aldehydes II (Table 1), which also contain nonaldehyde components, were dried at room temperature and then washed thoroughly on the filter with ether. The ether was removed by distillation to give the resinous nonaldehyde reaction product (in 17-26% yield), which was allowed to stand in a closed vessel for several weeks. After this time, the portion of the components that had crystallized out was removed by filtration and treated with hot methanol (~15 ml of methanol per gram of substance). The alkyl derivatives of benzofuran-2-carboxylic acid and its ethyl ester were extracted. The methanol-insoluble portion was dissolved in benzene and crystallized by simultaneous slow evaporation of the solvent. This procedure gave the alkyl derivatives of 1,2-bis(2-benzofuryl)ethylene (IV, Table 1), which were identical to authentic samples with respect to their melting points and spectral data. Compound IV displayed bluish-violet fluorescence in benzene solution.

The remaining uncrystallized portion of the preparation was vacuum distilled to give alkylbenzofurans III in 1-4% yields.

Benzoin Condensation of Alkyl-2-formylbenzofurans (II). Solutions of 0.06 mole of aldehyde II in 40 ml of methanol and 1 g (~0.02 mole) of NaCN in 10 ml of water were mixed, and the mixture was refluxed for 30 min. It was then cooled, and the resulting precipitate was removed by filtration and washed repeatedly with water. The crude preparation was crystallized repeatedly from ethanol–benzene (1:1) until the product had a constant melting point. This procedure gave alkylbenzofuroins V (Table 2). The side-product 2,2'-benzofuryl (VI) (Table 2) were isolated from the mother liquors.

Only the corresponding bisbenzofuroyl was always formed in the benzoin condensation of aldehyde IIc (Table 2).

Reduction of Alkylbenzofuroins V. Zinc dust (8 g) was added to a solution of 2 g of mercuric chloride in 30 ml of water, and the mixture was stirred vigorously for 20 min. The resulting amalgam was washed three times with water, and a solution of 0.01 mole of benzofuroin V in a mixture of 160 ml of ethanol and 40 ml of benzene was added to it. Concentrated HCl (15 ml) was then added with stirring at 10° in the course of 2 h, after which the mixture was stirred for another 2 h. The resulting suspension was treated with 500 ml of water and extracted with benzene. The benzene extract was washed to pH 7 with water and dried over $MgSO_4$. The solvent was evaporated at room temperature to a volume of ~10 ml, and the resulting precipitate was removed by filtration and washed with ethanol to give IV (Table 3). Evaporation of the filtrate to dryness and recrystallization of the residues from ethanol gave the corresponding alkyldesoxybenzofuroins VII (Table 3).

Traces of the corresponding benzofuroin Vc, as well as traces of the corresponding desoxybenzofuroin VIIc, were obtained by similar reduction of bisbenzofuroyl VIc.

We were unable to obtain benzofurylethylene IVc, which is formed in the Rosenmund reduction of acid chloride Ic. Unreduced substrate VIc was also recovered (58%).

LITERATURE CITED

1. B. Sila. Roczn. Chem., 42, 1773 (1968).
2. K. Rosenmund, Ber., 51, 585 (1918).
3. D. A. Ballard and W. M. Dehn, J. Amer. Chem. Soc., 54, 3969 (1932).

4. E. Bisagni and R. Royer, Bull. Soc. Chim., France, 925 (1962).
5. E. Müller, Methoden der organischen Chemie (Houben-Weyl), Vol. 7/1, Georg Thieme Verlag, Stuttgart (1954), p. 289.

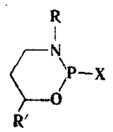
MASS SPECTRA OF A NUMBER OF 1,3,2-OXAZAPHOSPHORINANES

R. Z. Musin, Yu. Ya. Efremov, and M. A. Pudovik

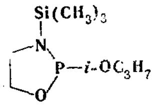
UDC 547.794:543.51

The mass spectra of a number of 1,3,2-oxazaphosphorinanes were obtained. The possibility of the mass spectrometric identification of this class of compounds, including the isomers that differ with respect to both the nature of the alkoxy groups attached to the phosphorus atom and the size of the ring, was demonstrated. The principal pathways of dissociative ionization of the investigated molecules were established by comparison of the mass spectra and the fragmentation reactions of the metastable ions.

In the present research we continued our study of the dissociative ionization, under the influence of electron impact, of cyclic esters of phosphorus acids and their derivatives. The mass spectra of some 1,3,2-oxazaphosphorinanes (I-IV) and 2-isopropoxy-3-trimethylsilyl-1,3,2-oxazaphospholane (V) were obtained:



I–IV



V

I $R=R'=H$, $X=OC_2H_5$; II $R=H$, $R'=CH_3$, $X=OC_2H_5$; IIa $R=D$, $R'=CH_3$, $X=OC_2H_5$;
III $R=R'=H$, $X=i\text{-}OC_3H_7$; IV $R=Si(CH_3)_3$, $R'=H$, $X=i\text{-}OC_3H_7$

The mass spectra of substituted 1,3,2-oxazaphospholanes [1] and 1,3,2-dioxaphospholanes [2] have been previously discussed. A comparative analysis of the mass spectra of six- and five-membered cyclic phosphites in [2, 3] demonstrated the possibility of the application of mass spectrometry for the determination of the size of the rings of these compounds.

The relative intensities of the ion peaks characteristic for the investigated 1,3,2-oxazaphosphorinanes are presented in Table 1, and a portion of the mass spectrum of deutero analog IIa is presented in Fig. 1.

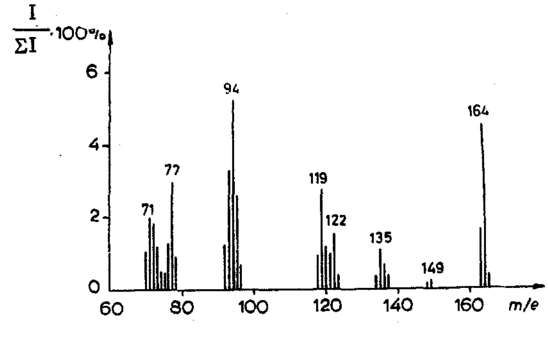


Fig. 1. Mass spectrum of deutero analog IIa.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR, Kazan 420083. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 749-752, June, 1977. Original article submitted November 24, 1975; revision submitted September 13, 1976.