POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

7.* NEW RECYCLIZATION AND CYCLIZATION REACTIONS IN THE 2-HYDROXYARYLDIFURYLMETHANE SERIES

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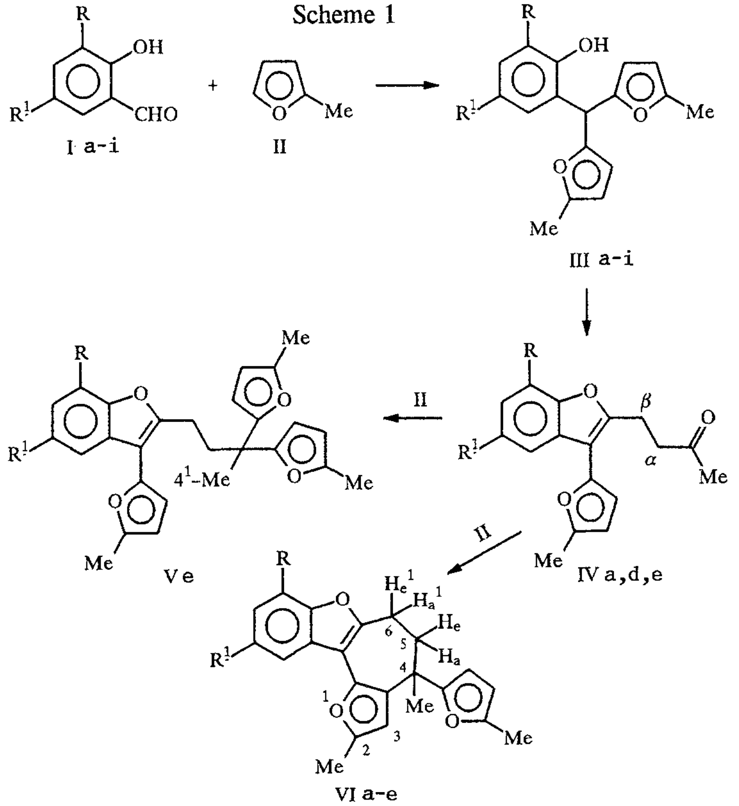
Reaction of 2-hydroxybenzaldehydes with α-methylfuran (sylvan) under acid-catalysis conditions was investigated. It is shown that the reaction does not stop at the step involving formation of 2-hydroxyarylfuryl-methanes but proceeds further with opening of one of furan rings and recyclization to 3-furylbenzo-furan derivatives. The latter in turn undergo transformations that lead to new heterocyclic systems — 5,6-dihydro-2,4-dimethyl-4-(5-methyl-2-furyl)-4H-benzo[b]furo[2,3-h]cyclopenta[b]furans. Data from the IR, PMR, and mass spectra, alternative synthesis, and x-ray diffraction analysis were used to confirm structures of the synthesized compounds.

In a preliminary communication [2] it was shown that, under the usual conditions for the synthesis of polyfuryl(aryl)-methanes [3, 4], the condensation of 5-nitrosalicylaldehyde and α-methylfuran (sylvan) leads to a mixture of substances. To ascertain the sequence of the transformations and the effect of substituents in the starting aldehyde on the compositions and yields of the final products we studied the reaction of a number of substituted salicylaldehydes Ia-i with α-methylfuran (II) in refluxing benzene in the presence of catalytic amounts of perchloric acid. Compounds IIIa-i and, in a number of cases, products of the IV, V, and VI type (Scheme 1) were isolated and identified by column chromatography.

Scheme 1



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*For Communication 6 see [1].

Krasnodar Polytechnical Institute, Krasnodar 350072. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 616-626, May, 1993. Original article submitted December 16, 1992.

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TABLE 1. Yields of Products of the Condensation of Salicylaldehydes Ia-i with α-Methylfuran in the Presence of Perchloric Acid

Aldehyde	R	R^1	Yield,* %				Aldehyde	R	R^1	Yield, %*			
			III	IV	V	VI				III	IV	V	VI
Ia	H	H	21	12		14	If	NO_2	CH_3	79	—	—	—
Ib	H	CH_3	20			18	Ig	NO_2	OCH3	85	—	—	—
Ic	H	OCH_3	34			13	Ih	NO_2	Br	89	—	—	—
Id	Br	Br	24	18		4	Ii	NO_2	NO2	92	—	—	—
Ie	H	NO_2	12	26	10	5							

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*The yields of the compounds are the values obtained after column chromatography with respect to the amount of converted starting aldehyde.

TABLE 2. Characteristics of IIIa-i

Compound	Empirical formula	mp,[1*], °C	PMR spectrum, δ, ppm (SSCC, J, Hz)						
			phenyl or substituted phenyl[2*]				5-methylfuryl		CH (1H, s)
			4-H (1H)	6-H (1H)	J_{46}	OH (1H, s)	3-H and 4-H (4H)	CH_3 (6H, s)	
IIIa	$C_{17}H_{16}O_3$	64...65	6,40...7,53 m		—	5,03	5,70 s	2,13	5,40
IIIb	$C_{18}H_{18}O_3$		6,50...6,95 m		—	5,35	5,83 s	2,15	5,45
IIIc	$C_{18}H_{18}O_4$		6,48 s		—	5,12	5,75 s	2,17	5,38
IIId	$C_{17}H_{14}Br_2O_3$	94...95	7,43 d	7,05 d	2,2	5,52	5,78 s	2,20	5,62
IIIe	$C_{17}H_{15}NO_5$	142...143	8,00 dd	7,92 d	2,5	10,87	5,87 s	2,15	5,77
IIIf	$C_{18}H_{17}NO_5$	92...93	7,86 d	7,12 d	2,2	10,87	5,77 s	2,18	5,77
IIIg	$C_{18}H_{17}NO_6$	103...104	7,38 d	7,07 d	2,8	10,66	5,85 s	2,17	5,78
IIh	$C_{17}H_{14}BrNO_5$	111...112	8,13 d	7,37 d	2,4	10,59	5,72...5,88 m	2,18	—[3*]
IIIi	$C_{17}H_{14}N_2O_7$	111...112	8,60 d	8,17 d	2,8	10,03	5,73...5,97 m	2,10	—[3*]

[1*] After recrystallization from hexane—benzene.

[2*] Unindicated signals: the 3-H (IIIa-c) and 5-H (IIIa) signals are located in the region of the 4-H and 6-H signals (IIIe): 7.02 d, J_{34} = 9.0 Hz; CH_3 (IIIb, f) 2.15 s and 2.23 s, respectively; OCH_3 (IIIc, g) 3.75 s and 3.70 s, respectively.

[3*] The signal is overlapped by the multiplet of furyl protons.

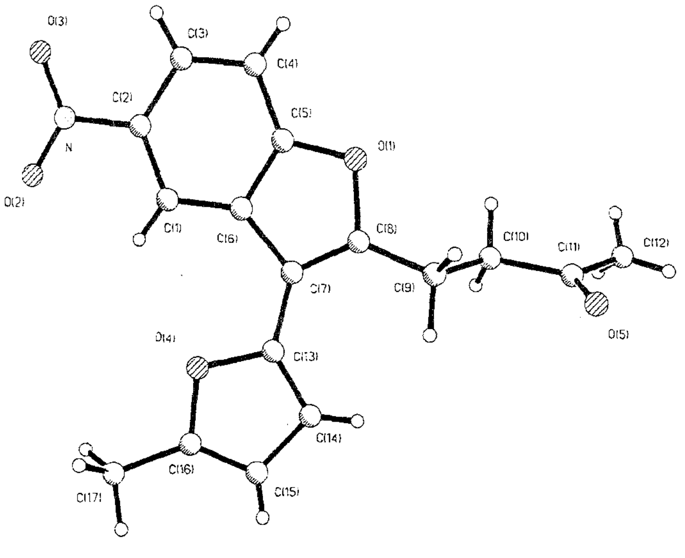


Fig. 1. Projection of a three-dimensional model of the 3-(5-methyl-2-furyl)-5-nitro-2-(3-oxobutyl)benzo[b]furan (IVe) molecule.

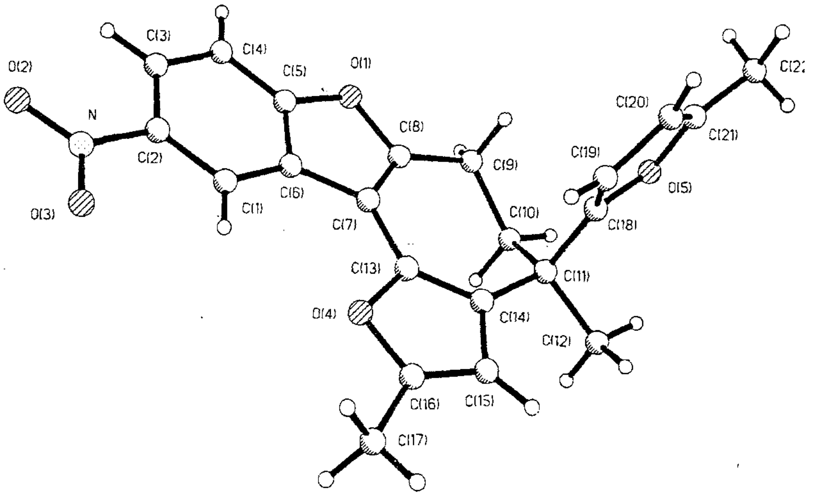
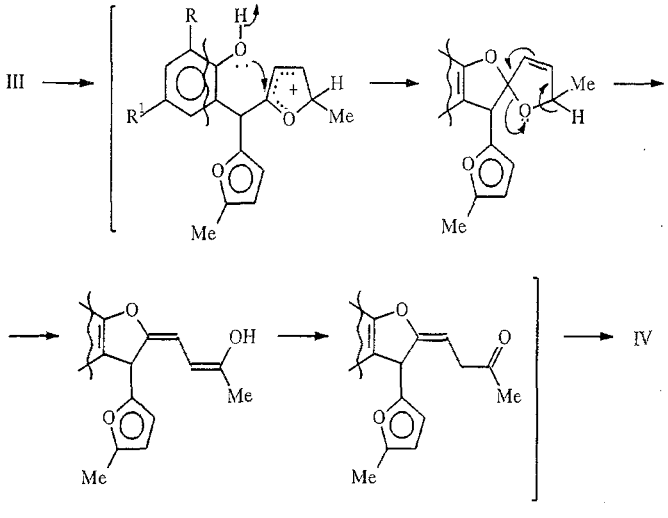


Fig. 2. Projection of a three-dimensional model of 5,6-dihydro-2,4-dimethyl-4-(5-methyl-2-furyl)-10-nitro-4H-benzo[b]furo[2,3-h]cyclohepta[b]furan (VIe) molecule.

Compounds III are the expected products of this reaction. The formation of benzofuran ketones IVa, d, e, which have the same molecular masses and elementary compositions as the corresponding 2-hydroxyphenyldifurylmethanes IIIa, d, e, can be explained by recyclization of the latter, which resembles the conversion of furan to thiophene or selenophene [5]. It probably commences with protonation of the furan ring in the 5 position (see [6]) with subsequent intramolecular nucleophilic attack of the oxygen atom by the hydroxy group at the α position of the furanium ion (Scheme 2). Despite the favorable (for this attack) orientation of the OH group, a mechanism with the participation of a molecule of water and the formation of an intermediate 1,4-dicarbonyl compound is also not excluded, since selective protonation of the furan ring is not required in this case.

Scheme 2



The formation of benzofurans IV from 2-hydroxyphenyldifurylmethanes III was confirmed by alternative synthesis of ketone IVa directly from IIIa by refluxing the latter in benzene in the presence of $HClO_4$.

The character of substituents R and R^1 of the starting aldehyde and the acidic properties of the OH group associated with it play a rather important role in the transformations involved. Thus an analysis of the data presented in Table 1 shows that recyclization products IV, as well as V and VI formed from them, are present in the reaction mixtures in all cases when R = H (Ia-c, e) or R = Br (Id), regardless of the type of R^1 substituent; it is characteristic that the overall yield of all of the products does not exceed 53%. The latter is reached when $R^1 = NO_2$ (Ie), and this figure also includes IVe-VIe. On the other

TABLE 3. Characteristics of the Synthesized IVa, d, e, Ve, and VIa-e

Com-pound	Empirical formula	mp,^{1*} °C	PMR spectrum, δ, (SSCC, J, Hz)										
			aryl^{2*}			5-methylfuryl^{3*}			α-CH$_2$, m or		β-CH$_2$, m or		other signals^{5*}
			3-H	4-H	6-H	3-H, d	4-H, dq	CH$_3$, d	5-H$_e$^{4*}	5-H$_a$^{4*}	6-H$_e$^{4*}	6-H$_a$^{4*}	
IVa	$C_{17}H_{16}O_3$	Oil	6,92...7,27 m^{6*}		7,57 m^{7*}	6,27	5,90	2,30	3,00...3,32		2,60...2,92		2,03 s
IVd	$C_{17}H_{14}Br_2O_3$	104...105	—	7,50 d	7,81 d	6,42	6,10	2,37	3,23...3,35		2,90...3,02		2,22 s
IVe	$C_{17}H_{15}NO_5$	121...122	7,47d,	8,20 dd	8,70d	6,55	6,16	2,42	3,28...3,40		2,92...3,04		2,33 s
Ve	$C_{27}H_{25}NO_6$	118...119	7,49d	8,21 dd	8,73d	6,39; 5,98^{8*}	6,12; 5,86^{8*}	2,42; 2,24^{8*}	2,40...2,52		2,91...3,03		1,70 s
VIa	$C_{22}H_{20}O_3$	104...105	7,41d	7,26 m^{6*,7*}	8,18d	5,73	5,83	2,42	2,50	2,13	3,10	2,84	2,29d; 1,69s; 6,01q
VIb	$C_{23}H_{22}O_3$	112...113	7,36d	7,14dd	8,02d	5,77	5,87	2,47	2,53	2,16	3,13	2,76	2,34d; 1,72s; 6,06q
VIc	$C_{23}H_{22}O_4$	108...109	7,16d	6,24dd	7,53d	5,58	5,67	2,26	2,34	1,98	2,92	2,66	2,13d; 1,52s; 5,85q
VId	$C_{22}H_{18}Br_2O_3$	141...142	—	7,53d	8,19d	5,68	5,80	2,41	2,46	2,08	3,14	2,84	2,27d; 1,65s; 5,99q
VIe	$C_{22}H_{19}NO_5$	172...173	7,41d	8,17dd	8,97d	5,67	5,79	2,42	2,48	2,08	3,07	2,80	2,27d; 1,66s; 5,99q

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^{1*}After recrystallization from hexane—ethyl acetate (IVd), ethanol (IVe, Ve), hexane (VIa-d), and hexane—chloroform (VIe).

^{2*}Signals: Me (VIb) 2.58, OMe (VIc), 3.79. For VIb, J_{34} = 8.2, J_{46} = 1.5; for VIc, J_{34} = 8.9, J_{46} = 2.6; the other SSCC are similar to those presented in Table 2.

^{3*}J_{34} = 3.2; $J_{4,Me}$ = 1.0.

^{4*}ABXY system: J_{ae} = 14.0; $J_{a'e'}$ = 18.0; $J_{ee'}$ = 7.5; $J_{aa'}$ = 10.5; $J_{ae'}$ = 3.0; $J_{a'e}$ = 3.2.

^{5*}The signals of the MeCO (IVa, d, e), 4'-Me (Ve), 2-Me, 4-Me, and 4-H (VIa-e) protons are presented; $J_{4-H,2-Me}$ = 1.0.

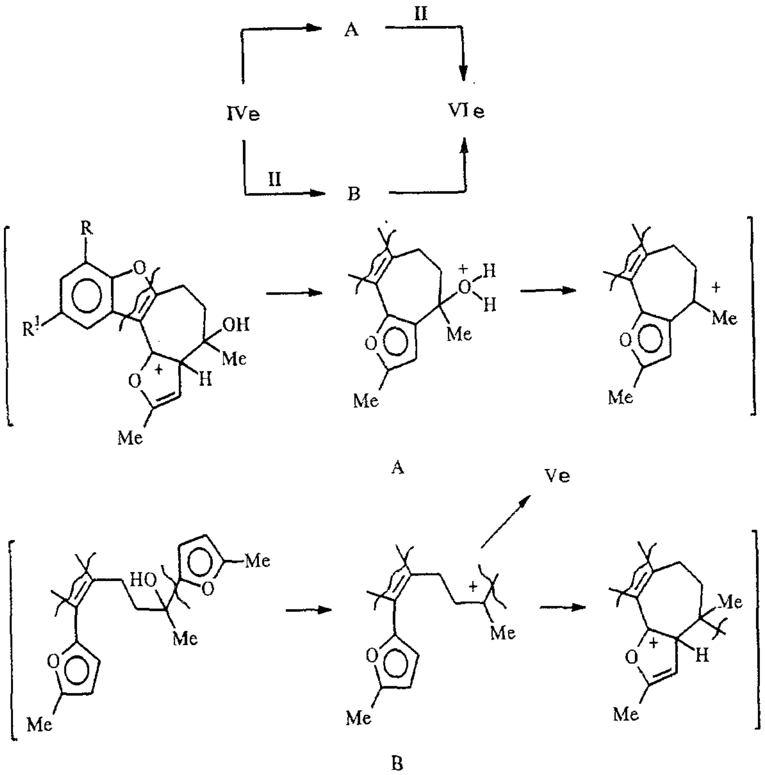
^{6*}The 5-H signal is overlapped by the indicated multiplet.

^{7*}Center of a multiplet.

^{8*}A signal of doubled intensity.

hand, when $R^1 = OCH_3$ (Ic), the degree of recyclization is the lowest. It should also be noted that the formation of Ve is the result of the usual reaction of the carbonyl group of ketone IVe with α-methylfuran, while its intramolecular cyclization, which leads to tetracyclic VIe, is a rarely observed process involving electrophilic substitution in the β position of the furan ring (Scheme 3). Donor substituents in the benzene ring of ketones IV promote their conversion to VI; this is probably associated with transmission of the electron density from the benzofuran ring to the furan ring. As compared with the examples examined above, a completely different picture is observed in the case of 3-nitro-substituted aldehydes If-i: regardless of the character of substituent R^1, only products IIIf-i are formed in high yields. This is possibly associated with a decrease in the degree of dissociation of the phenolic OH group due to the presence of an intramolecular hydrogen bond of the latter with an oxygen atom of the nitro group [7].

Scheme 3



The structures of the synthesized compounds were confirmed by data from their IR, PMR, and mass spectra and the results of elementary analysis.

In the IR spectra of 2-hydroxyphenyldifurylmethanes IIIa-e, i the stretching vibrations of the hydroxy group are represented by a narrow band at 3350-3470 cm^{-1}, which indicates that the OH group participates in the formation of only one type of intra- or intermolecular hydrogen bond, for example, with the furan ring.

The ν_{OH} band in the IR spectra of 3-nitro-2-hydroxyphenyldifurylmethanes IIIf-i is broad and is shifted to the lower-frequency side (3160-3200 cm^{-1}); this is possibly associated with the formation of different types of hydrogen bonds [8], including bonds with the o-nitro group.

The PMR spectra of 2-hydroxyphenyldifurylmethanes IIIa-i contain signals of methylidyne, furan, and aromatic protons (see Table 2).

The intense band at 1700-1710 cm^{-1} in the IR spectra of benzofurans IVa, d, e confirms the presence of a carbonyl group in these molecules. Characteristic features of the PMR spectra of IVa, d, e (Table 3) are two multiplets of α- and β-methylene groups and an AB system of protons of the furan ring. As compared with the analogous signals of the protons in the PMR spectra of IIIa, d, e, the signals of the aromatic protons in the spectra of ketones IVa, d, e are shifted to weak field. Although they were not isolated in pure form, ketones IVb, c were, however, detected in one of the fractions obtained during liquid chromatography of the products of the reaction of aldehydes Ib, c by PMR spectroscopy from the reference signals of the protons of the methylene groups.

A $\nu_{C=O}$ band is absent in the IR spectrum of Ve, while a new AB system of protons of two equivalent furan rings (see Table 3), which confirms that ketone IVe reacted with two molecules of α-methylfuran, appears in the PMR spectrum. The disappearance of the deshielding carbonyl group on passing from IVe to difurylalkane Ve is accompanied by a shift of the signals of the protons of the α-methylene group to strong field, while the location of the signals of the protons of the β-methylene link remains virtually unchanged.

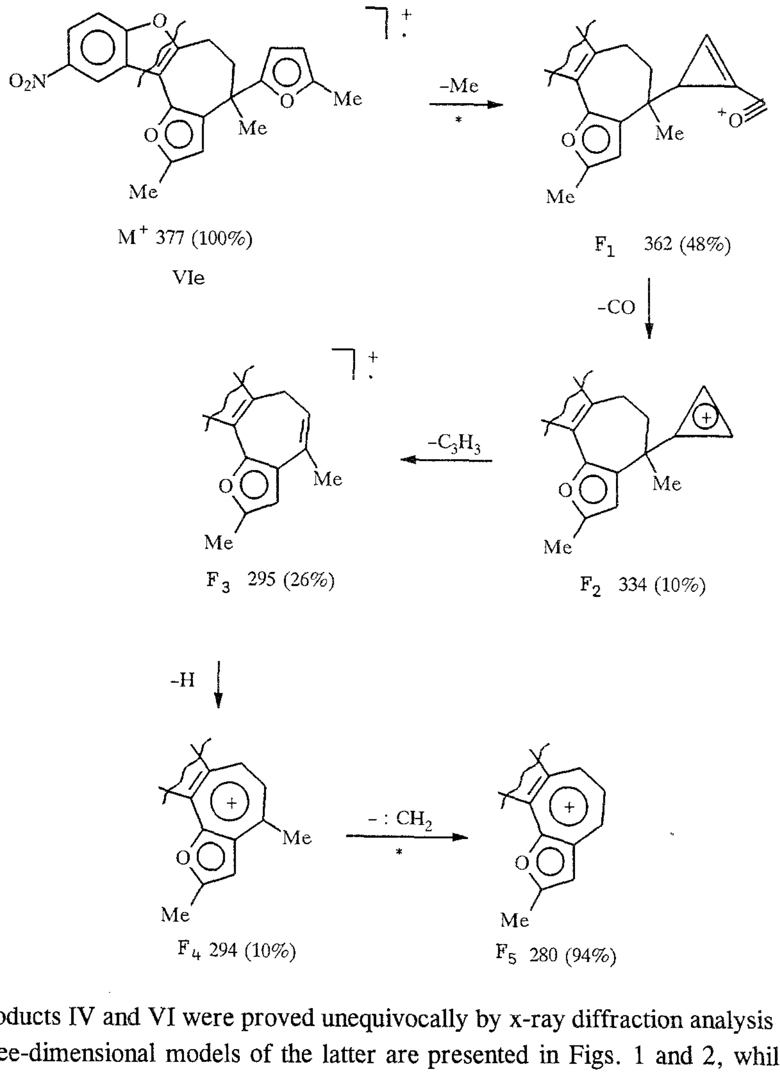
The four-spin ABXY system of protons of the two methylene links of VIa-e is characterized by six spin-spin coupling constants (SSCC) and corresponds to a rigidly bonded ethane fragment (see Table 3). In analogy with the data in [9, 10], the axial protons are more shielded than the corresponding equatorial protons.

The molecular masses of IVa, d, e and VIa, e were confirmed by mass-spectroscopic data.

A study of the behavior of VIe under the influence of electron impact (Scheme 4)* shows high stability ($W_m = 30\%$) of its molecular ion (the $M^{+\cdot}$ ion has the maximum intensity in the mass spectrum). The fragmentation of the $M^{+\cdot}$ ion occurs as a result of the well-known stepwise decomposition of the disubstituted furan ring [11], which is accompanied by splitting out of $^{\cdot}CH_3$, CO, and cyclopropene and leads to the no less stable F_5 cation ($I_{F_5}/I_{M^{+\cdot}} = 0.94$).

The formation under the influence of electron impact of stable cations of the F_5 type compelled us to effect the preparative synthesis of compounds with a similar structure, as we will report in one of our future communications.

Scheme 4



The structures of products IV and VI were proved unequivocally by x-ray diffraction analysis of single crystals of IVe and VIe. Projections of three-dimensional models of the latter are presented in Figs. 1 and 2, while the coordinates of the atoms and the bond lengths and bond angles are presented in Tables 4-6 and 7-9, respectively. The benzofuran fragments in the IVe and VIe molecules are planar (the average deviations from the planes are 0.0085 and 0.0035 Å, respectively). The

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*The peaks with I ≥ 10% of the maximum peak are depicted in Scheme 4.

TABLE 4. Coordinates of the Nonhydrogen Atoms ($\text{Å}\cdot 10^4$) and Temperature Factors ($\text{Å}^2\cdot 10^3$) of the IVe Molecule

Atom	*x*	*y*	*z*	*u*
$O_{(1)}$	1319(2)	4988(2)	2406(3)	56(1)
$O_{(3)}$	2445(2)	2339(2)	-712(4)	73(2)
$O_{(2)}$	2104(3)	3083(2)	-2166(4)	69(2)
$O_{(5)}$	339(3)	7274(3)	3972(5)	92(2)
$O_{(4)}$	1344(2)	5569(2)	-1795(4)	52(1)
N	2175(3)	2916(3)	-1068(5)	51(2)
$C_{(1)}$	1683(3)	4117(3)	-509(6)	40(2)
$C_{(2)}$	1948(3)	3456(3)	-115(6)	41(2)
$C_{(4)}$	1803(4)	3760(4)	2047(7)	53(3)
$C_{(3)}$	2013(3)	3268(4)	1141(6)	51(3)
$C_{(5)}$	1535(3)	4423(3)	1638(6)	44(2)
$C_{(8)}$	1095(3)	5555(3)	1612(6)	51(2)
$C_{(7)}$	1166(3)	5363(3)	397(5)	40(2)
$C_{(6)}$	1462(3)	4623(3)	393(5)	39(2)
$C_{(9)}$	874(4)	6232(3)	2264(7)	59(3)
$C_{(10)}$	76(4)	6097(4)	2972(7)	62(3)
$C_{(11)}$	-118(4)	6700(4)	3861(6)	56(3)
$C_{(12)}$	-878(5)	6568(6)	4606(10)	86(4)
$C_{(13)}$	986(3)	5784(3)	-700(5)	45(2)
$C_{(14)}$	538(4)	6363(4)	-968(8)	68(3)
$C_{(15)}$	631(5)	6507(5)	-2268(8)	75(4)
$C_{(16)}$	1106(4)	6027(3)	-2745(6)	58(3)
$C_{(17)}$	1450(7)	5892(6)	-3993(7)	86(4)

TABLE 5. Bond Lengths in the IVe Molecule

Bond	*l*, Å	Bond	*l*, Å
$O_{(1)}—C_{(5)}$	1,371(7)	$O_{(1)}—C_{(8)}$	1,395(6)
$O_{(3)}—N$	1,220(6)	$O_{(2)}—N$	1,218(7)
$O_{(5)}—C_{(11)}$	1,197(7)	$O_{(4)}—C_{(13)}$	1,380(7)
$O_{(4)}—C_{(16)}$	1,382(7)	$N—C_{(2)}$	1,472(8)
$C_{(1)}—C_{(2)}$	1,361(8)	$C_{(1)}—C_{(6)}$	1,391(8)
$C_{(2)}—C_{(3)}$	1,389(9)	$C_{(4)}—C_{(3)}$	1,371(9)
$C_{(4)}—C_{(5)}$	1,371(8)	$C_{(5)}—C_{(6)}$	1,384(8)
$C_{(8)}—C_{(7)}$	1,349(8)	$C_{(8)}—C_{(9)}$	1,468(8)
$C_{(7)}—C_{(6)}$	1,449(7)	$C_{(7)}—C_{(13)}$	1,437(8)
$C_{(9)}—C_{(10)}$	1,50(1)	$C_{(10)}—C_{(11)}$	1,49(1)
$C_{(11)}—C_{(12)}$	1,47(1)	$C_{(13)}—C_{(14)}$	1,355(9)
$C_{(14)}—C_{(15)}$	1,42(1)	$C_{(15)}—C_{(16)}$	1,32(1)
$C_{(16)}—C_{(17)}$	1,48(1)		

TABLE 6. Bond Angles in the IVe Molecule

Angle	ω, deg	Angle	ω, deg
$C_{(5)}O_{(1)}C_{(8)}$	105,8(4)	$C_{(13)}O_{(4)}C_{(16)}$	107,6(4)
$O_{(3)}NO_{(2)}$	123,9(5)	$O_{(3)}NC_{(2)}$	118,1(5)
$O_{(2)}NC_{(2)}$	118,0(5)	$C_{(2)}C_{(1)}C_{(6)}$	118,2(6)
$NC_{(2)}C_{(1)}$	118,3(5)	$NC_{(2)}C_{(3)}$	118,7(5)
$C_{(1)}C_{(2)}C_{(3)}$	123,0(6)	$C_{(3)}C_{(4)}C_{(5)}$	116,6(6)
$C_{(2)}C_{(3)}C_{(4)}$	119,9(6)	$O_{(1)}C_{(5)}C_{(4)}$	124,7(6)
$O_{(1)}C_{(5)}C_{(6)}$	110,5(4)	$C_{(4)}C_{(5)}C_{(6)}$	124,8(6)
$O_{(1)}C_{(8)}C_{(7)}$	111,5(4)	$O_{(1)}C_{(8)}C_{(9)}$	114,2(5)
$C_{(7)}C_{(8)}C_{(9)}$	134,2(5)	$C_{(6)}C_{(7)}C_{(8)}$	106,1(5)
$C_{(8)}C_{(7)}C_{(13)}$	128,7(5)	$C_{(6)}C_{(7)}C_{(13)}$	125,2(5)
$C_{(1)}C_{(6)}C_{(5)}$	117,6(5)	$C_{(1)}C_{(6)}C_{(7)}$	136,3(5)
$C_{(5)}C_{(6)}C_{(7)}$	106,1(5)	$C_{(8)}C_{(9)}C_{(10)}$	113,3(5)
$C_{(9)}C_{(10)}C_{(11)}$	117,1(5)	$O_{(5)}C_{(11)}C_{(10)}$	120,7(6)
$O_{(5)}C_{(11)}C_{(12)}$	121,0(7)	$C_{(10)}C_{(11)}C_{(12)}$	118,2(6)
$O_{(4)}C_{(13)}C_{(7)}$	115,4(4)	$O_{(4)}C_{(13)}C(14)$	108,2(5)
$C_{(7)}C_{(13)}C_{(14)}$	136,4(6)	$C_{(13)}C_{(14)}C_{(15)}$	106,7(7)
$C_{(14)}C_{(15)}C_{(16)}$	108,8(7)	$O_{(4)}C_{(16)}C_{(15)}$	108,7(6)
$O_{(4)}C_{(16)}C_{(17)}$	115,5(6)	$C_{(15)}C_{(16)}C_{(17)}$	135,8(7)

TABLE 7. Coordinates of the Nonhydrogen Atoms (Å·10^4) and Temperature Factors (Å^2·10^3) of the VIe Molecule

Atom	*x*	*y*	*z*	*u*
$O_{(1)}$	9253(1)	6228(1)	6258(1)	51(1)
$O_{(2)}$	5795(2)	1428(1)	5088(2)	82(1)
$O_{(3)}$	4395(2)	2142(1)	3129(2)	89(1)
$O_{(4)}$	4825(1)	5879(1)	1889(1)	42(1)
$O_{(5)}$	9738(1)	9166(1)	2176(1)	44(1)
N	5502(2)	2205(1)	4327(2)	57(1)
$C_{(1)}$	6130(2)	4157(1)	4050(2)	43(1)
$C_{(2)}$	6516(2)	3268(1)	4677(2)	46(1)
$C_{(3)}$	7828(3)	3320(2)	6210(2)	54(1)
$C_{(4)}$	8813(2)	4297(2)	6744(2)	56(1)
$C_{(5)}$	8425(2)	5189(2)	5918(2)	45(1)
$C_{(6)}$	7109(2)	5150(1)	4593(2)	40(1)
$C_{(7)}$	7161(2)	6250(1)	4096(2)	40(1)
$C_{(8)}$	8448(2)	6856(2)	5120(2)	44(1)
$C_{(9)}$	9143(2)	8028(2)	5249(2)	51(1)
$C_{(10)}$	8039(2)	8813(1)	4448(2)	48(1)
$C_{(11)}$	7306(2)	8577(1)	2566(2)	42(1)
$C_{(12)}$	6563(2)	9631(2)	2056(3)	56(1)
$C_{(13)}$	6095(2)	6625(1)	2735(2)	39(1)
$C_{(14)}$	6101(2)	7566(1)	2023(2)	40(1)
$C_{(15)}$	4746(2)	7379(2)	643(2)	46(1)
$C_{(16)}$	4018(2)	6369(1)	603(2)	42(1)
$C_{(17)}$	2585(2)	5704(2)	-471(2)	52(1)
$C_{(18)}$	8479(2)	8372(1)	1716(2)	40(1)
$C_{(19)}$	8578(2)	7600(1)	504(2)	48(1)
$C_{(20)}$	9959(2)	7921(2)	185(2)	50(1)
$C_{(21)}$	10638(2)	8866(2)	1216(2)	44(1)
$C_{(22)}$	12062(2)	9608(2)	1510(3)	59(1)

TABLE 8. Bond Lengths in the VIe Molecule

Bond	*l*, Å	Bond	*l*, Å
$O_{(1)}$—$C_{(5)}$	1,370(2)	$O_{(1)}$—$C_{(8)}$	1,392(2)
$O_{(2)}$—N	1,216(2)	$O_{(3)}$—N	1,212(2)
$O_{(4)}$—$C_{(13)}$	1,376(2)	$O_{(4)}$—$C_{(15)}$	1,374(2)
$O_{(5)}$—$C_{(18)}$	1,378(2)	$O_{(5)}$—$C_{(21)}$	1,380(3)
N—$C_{(2)}$	1,468(2)	$C_{(1)}$—$C_{(2)}$	1,376(3)
$C_{(1)}$—$C_{(6)}$	1,387(2)	$C_{(2)}$—$C_{(3)}$	1,396(2)
$C_{(3)}$—$C_{(4)}$	1,374(3)	$C_{(4)}$—$C_{(5)}$	1,380(3)
$C_{(5)}$—$C_{(6)}$	1,397(2)	$C_{(6)}$—$C_{(7)}$	1,449(2)
$C_{(7)}$—$C_{(8)}$	1,349(2)	$C_{(7)}$—$C_{(13)}$	1,442(2)
$C_{(8)}$—$C_{(9)}$	1,478(3)	$C_{(9)}$—$C_{(10)}$	1,520(3)
$C_{(10)}$—$C_{(11)}$	1,550(2)	$C_{(11)}$—$C_{(12)}$	1,515(2)
$C_{(11)}$—$C_{(12)}$	1,542(3)	$C_{(11)}$—$C_{(18)}$	1,503(3)
$C_{(14)}$—$C_{(13)}$	1,362(2)	$C_{(14)}$—$C_{(15)}$	1,433(2)
$C_{(15)}$—$C_{(16)}$	1,341(3)	$C_{(16)}$—$C_{(17)}$	1,480(2)
$C_{(18)}$—$C_{(19)}$	1,344(2)	$C_{(19)}$—$C_{(20)}$	1,425(3)
$C_{(20)}$—$C_{(21)}$	1,342(2)	$C_{(21)}$—$C_{(22)}$	1,475(3)

angle between the planes of the furan ring $C_{(13)}C_{(14)}C_{(15)}C_{(16)}O_{(4)}$ and the benzofuran ring in the IV molecule is 18.6°. In the case of IVe this angle is significantly smaller (7.6°); this is due to the presence of an additional bridge between these rings.

The geometry of the cycloheptadiene fragment in the VIe molecule is interesting. The $C_{(7)}$, $C_{(8)}$, $C_{(9)}$, $C_{(12)}$, and $C_{(13)}$ atoms of this ring virtually lie in a single plane (the average deviation is 0.028 Å), while the $C_{(10)}$ and $C_{(11)}$ atoms deviate 0.6234 Å and 0.1403 Å, respectively, from this plane on different sides.

The plane of the furan ring $C_{(18)}C_{(19)}C_{(20)}C_{(21)}O_{(5)}$ in the VIe molecule is turned 88.8° relative to the plane of the benzofuran ring and is close to shielding of the $C_{(11)}-C_{(14)}$ bond [torsion angle $C_{(12)}C_{(11)}C_{(18)}C_{(19)}$ is equal to 9.7°], which is characteristic for alkylfurans [12, 13].

TABLE 9. Bond Angles in the VIe Molecule

Angle	ω, deg	Angle	ω, deg
$C_{(5)}O_{(1)}C_{(8)}$	106,2(1)	$C_{(13)}O_{(4)}C_{(16)}$	106,7(1)
$C_{(18)}O_{(5)}C_{(21)}$	107,6(1)	$O_{(2)}NO_{(3)}$	122,6(2)
$O_{(2)}NC_{(2)}$	119,1(2)	$O_{(3)}NC_{(2)}$	118,4(2)
$C_{(2)}C_{(1)}C_{(6)}$	117,2(1)	$NC_{(2)}C_{(1)}$	118,4(1)
$NC_{(2)}C_{(3)}$	118,2(2)	$C_{(1)}C_{(2)}C_{(3)}$	123,5(2)
$C_{(2)}C_{(3)}C_{(4)}$	119,7(2)	$C_{(3)}C_{(4)}C_{(5)}$	116,9(2)
$O_{(1)}C_{(5)}C_{(4)}$	125,8(1)	$O_{(1)}C_{(5)}C_{(6)}$	110,3(2)
$C_{(4)}C_{(5)}C_{(6)}$	124,0(2)	$C_{(1)}C_{(6)}C_{(5)}$	118,8(2)
$C_{(1)}C_{(6)}C_{(7)}$	135,6(1)	$C_{(5)}C_{(6)}C_{(7)}$	105,6(1)
$C_{(6)}C_{(7)}C_{(8)}$	106,5(1)	$C_{(6)}C_{(7)}C_{(13)}$	127,4(1)
$C_{(8)}C_{(7)}C_{(13)}$	126,0(2)	$O_{(1)}C_{(8)}C_{(7)}$	111,4(2)
$O_{(1)}C_{(8)}C_{(9)}$	115,9(1)	$C_{(7)}C_{(8)}C_{(9)}$	132,7(2)
$C_{(8)}C_{(9)}C_{(10)}$	114,7(2)	$C_{(9)}C_{(10)}C_{(11)}$	118,3(2)
$C_{(10)}C_{(11)}C_{(14)}$	112,1(2)	$C_{(10)}C_{(11)}C_{(12)}$	107,0(1)
$C_{(14)}C_{(11)}C_{(12)}$	109,2(1)	$C_{(10)}C_{(11)}C_{(18)}$	111,4(1)
$C_{(14)}C_{(11)}C_{(18)}$	108,1(1)	$C_{(12)}C_{(11)}C_{(18)}$	109,0(2)
$C_{(11)}C_{(14)}C_{(13)}$	127,0(1)	$C_{(11)}C_{(14)}C_{(15)}$	128,0(2)
$C_{(13)}C_{(14)}C_{(15)}$	105,1(1)	$O_{(4)}C_{(13)}C_{(7)}$	116,1(1)
$O_{(4)}C_{(13)}C_{(14)}$	110,5(1)	$C_{(7)}C_{(13)}C_{(14)}$	133,3(1)
$C_{(14)}C_{(15)}C_{(16)}$	108,1(2)	$O_{(4)}C_{(16)}C_{(15)}$	109,6(1)
$O_{(4)}C_{(16)}C_{(17)}$	115,6(2)	$C_{(15)}C_{(16)}C_{(17)}$	134,8(2)
$O_{(5)}C_{(18)}C_{(11)}$	116,0(1)	$O_{(5)}C_{(18)}C_{(19)}$	109,0(2)
$C_{(11)}C_{(18)}C_{(19)}$	134,9(2)	$C_{(18)}C_{(19)}C_{(20)}$	107,1(2)
$C_{(19)}C_{(20)}C_{(21)}$	107,6(2)	$O_{(5)}C_{(21)}C_{(20)}$	108,7(2)
$O_{(5)}C_{(21)}C_{(22)}$	116,7(1)	$C_{(20)}C_{(21)}C_{(22)}$	134,5(2)

EXPERIMENTAL

The IR spectra were recorded with a Specord M-80 spectrometer. The mass spectra were obtained with a Varian MAT-112 mass spectrometer with direct introduction of the samples into the ion source; the ionizing-electron energy was 20 eV, and the temperature of the ionization chamber was 80-170°C. The PMR spectra of solutions in $CDCl_3$ and d_6-acetone (in the case of IIIe) were recorded with Tesla BS-467 (60 MHz, hexamethyldisiloxane as the internal standard) and Bruker AC-200P (200 MHz, tetramethylsilane as the internal standard) spectrometers.

The reaction products were separated by liquid chromatography with a column (30 by 2.5 cm) packed with L 40/100 silica gel by elution with hexane—chloroform—acetone (6:1:1) (for the products from Ia-c), (4:1:1) (from Ie), hexane—chloroform (3:1) (from Id), and hexane—acetone (3:1) (from If-i). The progress of the reactions and the individuality of the substances were monitored by TLC on Silufol UV-254 plates in a system of suitable eluents with development by iodine vapors.

The results of elementary analysis of the compounds obtained for C, H, N, and Hal were in agreement with the calculated values.

X-Ray Diffraction Study of IVe and VIe. Monoclinic crystals of 3-(5-methyl-2-furyl)-5-nitro-2-(3-oxobutyl)benzofuran (IVe) were grown from ethanol and had the following unit cell parameters: $a = 16.311(5)$, $b = 17.730(5)$, $c = 10.678(3)$ Å, $\gamma = 96.45(2)°$, $V = 3068.5(2.8)$ Å^3, space group A 2/a, and Z = 8. The unit cell parameters and the intensities of 727 independent reflections with $I > 3\sigma(I)$ were obtained with a Nicolet P3 automatic diffractometer without a monochromator (Mo K_α emission, $\theta/2\theta$ scanning up to $2\theta_{max} = 45°$).

Triclinic crystals of 5,6-dihydro-2,4-dimethyl-4-(5-methyl-2-furyl)-10-nitro-4H-benzo[b]furo[2,3-h]cyclohepta[b]furan (VId) were grown from hexane—chloroform—acetone (4:1:1) and had the following unit cell parameters: $a = 9.256(2)$, $b = 12.071(2)$, $c = 8.683(1)$ Å, $\alpha = 97.25(1)°$, $\beta = 107.39(1)°$, $\gamma = 94.24(1)°$, $V = 912.9(0.5)$ Å^3, space group P-1, and Z = 2. The experimental data were similarly obtained ($\theta/2\theta$ scanning up to $2\theta_{max} = 50°$). A total of 2083 independent reflections with $I > 3\sigma(I)$ were measured.

The structures were decoded by the direct method by means of the set of SHELXT programs [14] and were refined within the anisotropic (isotropic for the hydrogen atoms) approximation up to divergence factors $R = 0.029$ and $R_w = 0.032$ for IVe and $R = 0.032$ and $R_w = 0.036$ for VIe.

Reaction of Aldehydes Ia-i with α-Methylfuran. A 0.1-ml sample of a 1 N solution of perchloric acid in acetic acid was added to a refluxing solution of 0.02 mole of aldehyde I in 40 ml of benzene, after which 0.04 mole of α-methylfuran was added dropwise, and the reaction mixture was refluxed for 2 h with removal of the water by azeotropic distillation. The mixture was then cooled to room temperature, washed with $NaHCO_3$ solution and water, and dried with anhydrous Na_2SO_4. The solvent was removed by distillation, and the residue was subjected to column chromatography to give unchanged aldehyde I and the reaction products. The characteristics of the synthesized compounds are presented in Tables 1-3.

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