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POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES. 17.* SYNTHESIS OF COMPOUNDS OF THE OXAZULENE SERIES

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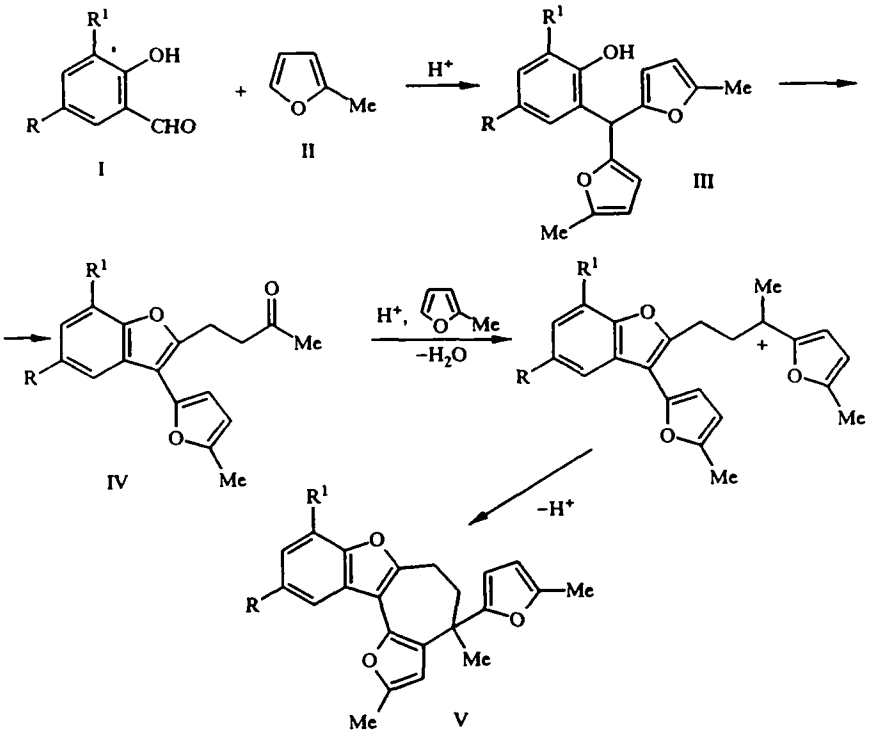
Preparative methods were developed for the synthesis of various compounds of the benzofurooxazulene series. It was established that the formation of an oxazulenium salt and a dihydrooxazulene derivative during the treatment of 3-(5-methyl-2-furyl)-2-(3-oxobutyl)benzofurans with perchloric acid results from disproportionation of the intermediate compound — an oxazulene derivative.

The present paper concludes our series of publications on the reaction of salicylaldehydes (I) and sylvane (II). As we established [2], in the presence of catalytic amounts of perchloric acid in boiling benzene the reaction does not stop at the formation of 2-hydroxyaryldifurylmethanes (III) but is accompanied in a number of cases by side transformations, leading to a mixture of products containing derivatives of benzofuran (IV) and/or the polycyclic system (V) (Scheme 1).

Scheme 1



*For Communication 16, see [1].

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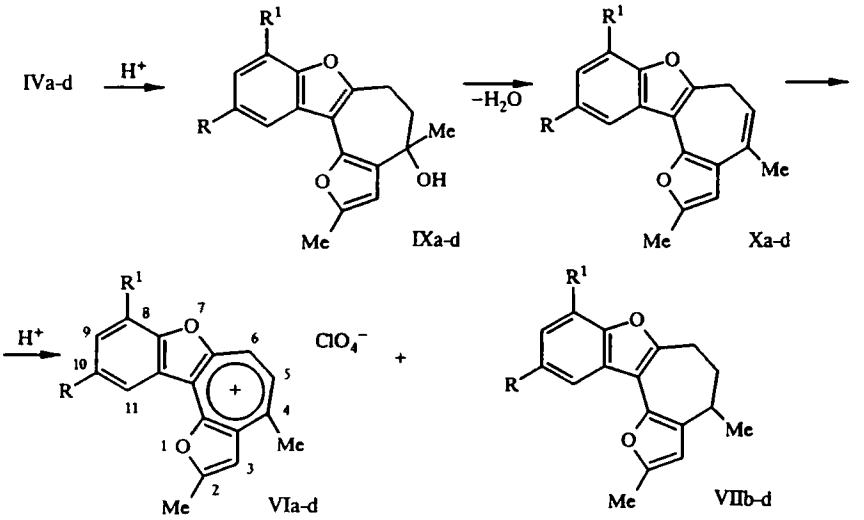
In view of the practical significance of benzofuran derivatives [3, 4] a task was set up to determine the conditions for the specific synthesis of each of the above-mentioned products. Methods for the production of 2-hydroxyaryldifurylmethanes (III) and benzofuran ketones (IV) with high yields were described in Communications 16 and 10 [1, 5].

In the present work we attempted the selective synthesis of compounds (V) — the last substances in the chain of transformations that occur. Under the conditions indicated above, which were described in the original source [2], the yields of these products amounted to 0-18% (depending on the nature of the substituents R and R^1).

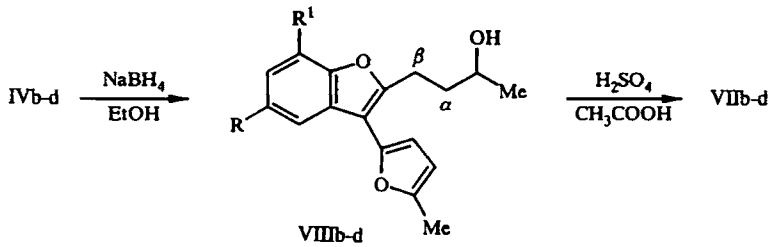
Having the available benzofuran ketones (IVa-d) at our disposal [1], we studied their reaction with sylvane with boiling in benzene in the presence of 70% perchloric acid as catalyst. However, the yields of compounds (V) did not exceed those indicated in [2]. During a search for conditions that would make it possible to increase the yields of the products (V) it was found that when the ketones (IVa-d) were boiled with perchloric acid in dioxane a different cyclization reaction occurred, and high yields of benzofuro[2,3-*h*]-1-oxazulenium salts (VIa-d) were obtained (Scheme 2, Tables 1 and 2). It should be mentioned that we synthesized the salts (VIa, d) earlier by a different method [6].

Scheme 2



IV, VI, VII, VIII a R = R^1 = H; b R = Me, R^1 = H;
c R = Cl, R^1 = H; d R = R^1 = Br

A more detailed investigation showed that in addition to compounds (VI) the products (VIIb-d) accumulated in the reaction mixture (Tables 1 and 3). Their structures were proved by an alternative synthesis, i.e., by reduction of the respective ketones (IVb-d) to the secondary carbinols (VIIIb-d), followed by cyclization of the latter (see the Experimental section).



The transformation (IV) → (VI) + (VII) probably takes place according to Scheme 2. In a strongly acidic medium the benzofuran ketone (IV) undergoes intramolecular cyclization to compound (IX), which is dehydrated. The obtained product (X) disproportionates with the formation of the corresponding oxazulenium salt (VI) and the dihydro derivative (VII).

In order to confirm the proposed scheme of transformations it was necessary to obtain the intermediate product (X). By analogy with the familiar reduction of pyrylium and pyridinium salts to the corresponding dihydropyrans and dihydropyridines [7, 8] we carried out the reduction of the salts (VIa-c), which led to compounds (Xa-c) (Tables 1 and 2). As

TABLE 1. Physicochemical Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %			mp, °C*	Yield, %†
		C	H	Hal		
VIa	$C_{17}H_{13}ClO_6$	58.43 58,55	3.85 3,76	10.12 10,17	239...240	93(46)
VIb	$C_{18}H_{15}ClO_6$	59.73 59,60	4.09 4,17	9.65 9,77	284...285	97(49)
VIc	$C_{17}H_{12}Cl_2O_6$	53.35 53,29	3.28 3,16	18.21 18,50	288...289	85(45)
VId	$C_{17}H_{11}Br_2ClO_6$	40.15 40,31	2.30 2,19	38.44 38,55	260...261	98(41)
VIIb	$C_{18}H_{18}O_2$	81.02 81,17	6.87 6,81		oil	85(55)
VIIc	$C_{17}H_{15}ClO_2$	71.24 71,20	5.19 5,27	12.43 12,36	92...93	74(52)
VIId	$C_{17}H_{14}Br_2O_2$	49.85 49,79	3.32 3,44	38.75 38,97	118...119	83(49)
Xa	$C_{17}H_{14}O_2$	81.52 81,58	5.61 5,64		oil	81
Xb	$C_{18}H_{16}O_2$	81.91 81,79	6.01 6,10		oil	90
Xc	$C_{17}H_{13}ClO_2$	71.63 71,71	4.52 4,60	12.61 12,45	oil	85
XIa	$C_{23}H_{22}O_3$	79.67 79,74	6.55 6,40		65...66	87
XIb	$C_{24}H_{24}O_3$	79.91 79,97	6.62 6,71		86...87	80
XIc	$C_{23}H_{21}ClO_3$	72.61 72,53	5.49 5,56	9.50 9,31	oil	85
XIIa	$C_{23}H_{20}O_2$	84.18 84,12	6.08 6,14		136...137	77
XIIb	$C_{24}H_{22}O_2$	84.23 84,18	6.39 6,48		121...122	68
XIIc	$C_{23}H_{19}ClO_2$	76.08 76,13	5.23 5,28	9.81 9,77	129...130	70
XIId	$C_{24}H_{22}O_3$	80.48 80,42	6.27 6,19		148...149	68
XIIe	$C_{25}H_{24}O_3$	80.55 80,62	6.42 6,49		170...171	63
XIIf	$C_{24}H_{21}ClO_3$	73.30 73,37	5.27 5,39	8.89 9,02	141...142	69
XIIg	$C_{24}H_{20}Br_2O_3$	55.75 55,84	3.98 3,90	31.04 30,96	158...159	60
XIIh	$C_{24}H_{22}O_3$	80.31 80,42	6.30 6,19		159...160	73
XIIi	$C_{25}H_{24}O_3$	80.49 80,62	6.55 6,49		182...183	64
XIIj	$C_{24}H_{21}ClO_3$	73.46 73,37	5.25 5,39	9.12 9,02	204...206	71
XIIk	$C_{24}H_{20}Br_2O_3$	55.79 55,84	4.01 3,90	30.87 30,96	198...200	70

*Compounds (VIa-d) were crystallized from acetonitrile, and the others from hexane.

†The yields of the compounds obtained by the alternative method are given in parentheses.

supposed, they proved extremely sensitive to atmospheric oxygen and were oxidized quite quickly at room temperature. Under the influence of trityl perchlorate they were easily transformed into the corresponding salts (VIa-c). Direct evidence that the compounds (X) are in fact key intermediates in the synthesis of the products (VI, VII) is provided by the transformation of compound (Xc) into a mixture of products (VIc, VIIc) during reaction with an excess of perchloric acid in dioxane.

On the whole the described reaction has analogy with the well studied acid-catalyzed disproportionation of many 4H-dihydropyrans to pyrylium cations and the corresponding tetra- and hexahydropyrans [9]. Similar effects are observed in the case of the tropylium cation. Thus, it is known that cycloheptatriene disproportionates under the influence of Lewis acids such as boron trifluoride or tin tetrachloride to the tropylium cation and cycloheptadiene [10].

TABLE 2. PMR Spectra of Compounds (VIa-d) (deuterotrifluoroacetic acid) and (Xa-c) (deuterochloroform)

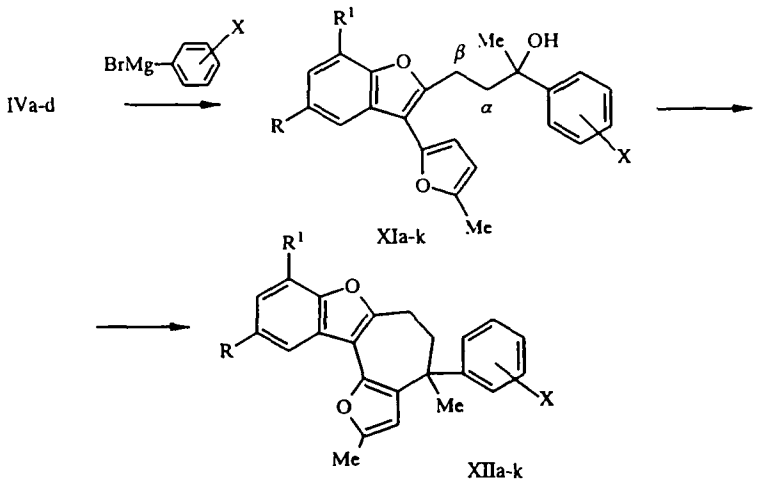
Compound	Chemical Shifts, δ, ppm, SSCC (J), Hz								
	2-Me s	4-Me s	3-H s	5-H	6-H/CH_2* d	8-H	9-H	11-H	Other signals and SSCC
VIa	2,83	2,58	7,05	8,28 d	8,52	7,18...7,80 m†			$J_{5,6}$ = 11,0
VIb	2,81	2,57	7,02	8,21 d	8,49	7,29...7,53 m		8,19 bs	2,26 (3H, s, CH_3), $J_{5,6}$ = 11,0
VIc	2,89	2,61	7,14	8,36 d	8,52	7,54 s		8,39 s	$J_{5,6}$ = 11,0
VId	2,87	2,58	7,07	8,37 d	8,62		7,80 d	8,48 d	$J_{5,6}$ = 11,0; $J_{9,11}$ = 2,0
Xa	2,52	2,11	6,28	5,28 t	3,52	7,29...7,60 m‡		8,01...8,09 m	$J_{5,6}$ = 6,1
Xb	2,40	1,96	6,14	5,12 t	3,32	7,23 d	6,99 dd	7,62 d	2,40 (3H, s, CH_3), $J_{5,6}$ = 5,9; $J_{8,9}$ = 8,3; $J_{9,11}$ = 1,8
Xc	2,35	1,95	6,12	5,08 t	3,34	6,99...7,28 m		7,88...7,97 m	$J_{5,6}$ = 6,2

*For compounds (Xa-c), CH_2.

†The multiplet of the 8-, 9-, 10-, and 11-H protons.

‡The multiplet of the 8-, 9-, and 10-H protons.

We tried to obtain the salts (VI) directly from sylvane (II) and salicylaldehydes (I). Actually, when a mixture of compounds (II) and (Ia, b, c) or (Id) was boiled in dioxane in the presence of an excess of perchloric acid the products (VIa-d) were obtained with yields of 40-50% of the theoretical. On the basis of these results and of previously obtained data [1, 5] it can be concluded that by varying the conditions of the reaction of salicylaldehydes (I) and sylvane (II) it is possible to change the direction of the reaction and to obtain 2-hydroxyaryldifurylmethanes (III) and derivatives of benzofuran (IV) or oxazulene (VI) selectively.



XI, XIIa-c X =H; d-g X = OMe-4; h-k X = OMe-2; a, d, h R = R^1 = H; b, e, i R = Me, R^1 = H; e, f, j R = Cl, R^1 = H; g, k R = R^1 = Br

The synthesis of the benzofurooxazulene derivatives (V) was solved in a different way. We proposed a two-stage synthesis of the analogs of these compounds, involving the reaction of the benzofuran ketones (IV) with arylmagnesium bromides, followed by cyclization of the obtained carbinols (XI) (Tables 1 and 4) to compounds (XII) (Tables 1 and 3). As catalyst for cyclization we used phosphoric acid in acetic acid — a system widely used for the alkylation of phenols by tertiary alcohols and alkenes [11].

The proposed methods for the synthesis of the benzofurooxazulene derivatives are fairly simple and give high yields of the required products.

EXPERIMENTAL

The PMR spectra were recorded on Tesla BS-467 (60 MHz, internal standard HMDS), Bruker AC-200P (200 MHz, internal standard TMS), and Bruker AM-300 (300 MHz, internal standard TMS) instruments. The reaction and the individuality of the final products were monitored by TLC on Silufol UV-254 plates; the eluants were mixtures of hexane, chloroform, and acetone in various ratios, and the salt products were not monitored.

3-(5-Methyl-2-furyl)-2-(3-oxobutyl)benzo[*b*]furans (IVa-d). The compounds were obtained by the method described in [1].

Reaction of 3-(5-Methyl-2-furyl)-5-chloro-2-(3-oxobutyl)benzo[*b*]furan (IVc) with Perchloric Acid. A solution of 3 g (0.01 mole) of compound (IVc) and 1.6 ml (0.02 mole) of 70% perchloric acid in 10 ml of dioxane was boiled with a reflux condenser with agitation for 15 min. When the mixture had cooled the precipitate was filtered off and washed thoroughly with dioxane and then with diethyl ether. After drying the product was recrystallized from acetonitrile. We obtained 1.63 g (85%) of compound (VIc); mp 288-289°C. The mother solution was diluted with water, the oil that separated was washed by decantation with water, and the product was extracted with boiling hexane (2 × 20 ml). The extract was filtered through aluminum oxide, and the filtrate was evaporated. From the residue by chromatography on aluminum oxide (eluant 3:2 hexane–benzene) we isolated 1.05 g (74%) of compound (VIIc) in the form of colorless crystals; mp 92-93°C (from hexane).

The reactions of the ketones (IVa, b, d) were conducted similarly.

TABLE 3. PMR Spectra of Compounds (VIIb-d) and (XIIa-k) in Deuterochloroform

Compound	Chemical shifts, δ, ppm, SSCC (J), Hz										
	2-Me, s	4-Me, s	3-H, s	5a-H*	5e-H*	6a-H*	6e-H*	8-H	9-H	11-H	Other signals and SSCC
1	2	3	4	5	6	7	8	9	10	11	12
VIIb	2,51 d	1,35	6,06	1,94...2,20 m		3,17...3,29 m		7,40 d	7,17 d	8,06 s	2,63 (3H, s, CH_3); 2,92...3,07 (1H, m, 4-H); $J_{4,4\text{-}CH_3}$ = 7,1; $J_{8,9}$ = 8,3
VIIc	2,41 d	1,27	5,99	1,87...2,15 m		3,07...3,20 m		7,30 d	7,21 dd	8,08 d	2,92...3,07 (1H, m, 4-H); $J_{4,4\text{-}CH_3}$ = 7,2; $J_{8,9}$ = 8,8; $J_{9,11}$ = 2,1
VIId	2,40 d	1,26	5,98	1,88...2,15 m		3,11...3,27 m			7,54 d	8,15 d	2,90...3,09 (1H, m, 4-H); $J_{4,4\text{-}CH_3}$ = 7,1; $J_{9,11}$ = 1,7
XIIa	2,43 s	1,75	5,97	2,22	2,34	2,68	3,00	7,11...7,40† m		8,05...8,13 m	7,24 (5H, s, H_{Ph}); $J_{6a,6e}$ = 18,3; $J_{5a,5e}$ = 14,0; $J_{6a,5a}$ = 11,0; $J_{6e,5e}$ = 6,7; $J_{6a,5e}$ = 3,1; $J_{6e,5a}$ = 2,8
XIIb	2,45 s	1,73	5,93	2,22	2,33	2,67	2,98	7,26 d	7,08 d	7,97 s	2,53 (3H, s, CH_3); 7,22 (5H, s, H_{Ph}); $J_{6a,6e}$ = 18,1; $J_{5a,5e}$ = 14,0; $J_{6a,5a}$ = 11,1; $J_{6e,5e}$ = 6,7; $J_{6a,5e}$ = 3,3; $J_{6e,5a}$ = 2,8; $J_{8,9}$ = 8,3
XIIc	2,44 s	1,72	5,94	2,21	2,33	2,67	2,98	7,27 d	7,20 dd	8,14 d	7,23 (5H, s, H_{Ph}); $J_{6a,6e}$ = 18,3; $J_{5a,5e}$ = 13,9; $J_{6a,5a}$ = 11,2; $J_{6e,5e}$ = 6,5; $J_{6a,5e}$ = 3,2; $J_{6e,5a}$ = 2,8; $J_{8,9}$ = 8,8; $J_{9,11}$ = 2,0
XIId	2,44 s	1,74	5,94	2,22	2,29	2,71	3,00	7,23...7,42† m		8,19...8,23 m	3,79 (3H, s, OCH_3); 6,82 (1H, d, J = 8,8, H_{Ar}); 7,12 (1H, d, J = 8,8, H_{Ar}); $J_{6a,6e}$ = 18,2; $J_{5a,5e}$ = 14,3; $J_{6a,5a}$ = 10,6; $J_{6e,5e}$ = 6,6; $J_{6a,5e}$ = 3,4; $J_{6e,5a}$ = 2,8
XIIe	2,46	1,73	5,95	2,21	2,28	2,68	2,98	7,27 d	7,09 d	7,99 s	2,54 (3H, s, CH_3); 3,78 (3H, s, OCH_3); 6,82 (1H, d, J = 8,8, H_{Ar}); 7,12 (1H, d, J = 8,8, H_{Ar}); $J_{6a,6e}$ = 18,2; $J_{5a,5e}$ = 13,8; $J_{6a,5a}$ = 10,6; $J_{6e,5e}$ = 6,5; $J_{6a,5e}$ = 3,7; $J_{6e,5a}$ = 2,9; $J_{8,9}$ = 8,3
XIIf	2,45	1,73	5,95	2,19	2,29	2,68	2,98	7,29 d	7,22 dd	8,16,d	3,78 (3H, s, OCH_3); 6,82 (1H, d, J = 8,8, H_{Ar}); 7,09 (1H, d, J = 8,8, H_{Ar}); $J_{6a,6e}$ = 18,3; $J_{5a,5e}$ = 14,1; $J_{6a,5a}$ = 11,0; $J_{6e,5e}$ = 6,5; $J_{6a,5e}$ = 3,6; $J_{6e,5a}$ = 2,8; $J_{8,9}$ = 8,8; $J_{9,11}$ = 2,0

TABLE 3 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
XIIg	2,43	1,71	5,95	2,22	2,31	2,72	3,03		7,56 d	8,25 d	3,77 (3H, s, OCH_3); 6,81 (1H, d, J = 8,9, H_{Ar}); 7,08 (1H, d, J = 8,9, H_{Ar}); $J_{6a,6e}$ = 18,4; $J_{5a,5e}$ = 14,3; $J_{6a,5a}$ = 10,8; $J_{6e,5e}$ = 6,5; $J_{6a,5e}$ = 3,9; $J_{6e,5a}$ = 2,9; $J_{9,11}$ = 1,8
XIIh	2,46	1,80	6,01	2,01...2,14 m	2,61...2,74 m	2,98...3,16 m		7,23...7,39 m†		8,18...8,23 m	6,72...7,21 (4H, m, H_{Ar}); 3,85 (3H, s OCH_3)
XIIi	2,48	1,80	6,01	2,02...2,13 m	2,60...2,72 m	2,96...3,14 m		7,24 d	7,06 d	7,98 s	2,53 (3H, s, CH_3); 3,85 (3H, s, OCH_3); 6,72...7,21 (4H, m, H_{Ar}); $J_{8,9}$ = 8,3
XIIj	2,45	1,78	6,00	1,97...2,11 m	2,57...2,72 m	2,95...3,12 m		7,25 d	7,18 dd	8,14 d	3,84 (3H, s, OCH_3); 6,71...7,20 (4H, m, H_{Ar}); $J_{8,9}$ = 8,8; $J_{9,11}$ = 2,0
XIIk	2,46	1,79	6,02	1,98...2,12 m	2,64...2,79 m	3,03...3,15 m			7,53 d	8,24 d	3,85 (3H, s, OCH_3); 6,71...7,22 (4H, m, H_{Ar}); $J_{9,11}$ = 1,8

*In the case of compounds (XIIa-g) the signal has the ddd form.

†The multiplet of the 8-, 9-, and 10-H protons.

TABLE 4. PMR Spectra of Compounds (XIa-c) (deuterochloroform)

Compound	Chemical shifts, δ, SSCC, J, Hz								
	Me s	OH bs	α-H$_a$ ddd	α-H$_e$ ddd	β-H$_a$ ddd	β-H$_e$ ddd	5-Methyl-2-furyl*		
							3-H d	4-H d	Me s (3H)
XIa	1,66	1,97	2,25	2,37	2,90	3,10	6,34	6,08	2,37
XIb	1,66	1,89	2,27	2,38	2,90	3,09	6,35	6,08	2,38
XIc	1,67	1,89	2,27	2,38	2,89	3,08	6,36	6,10	2,37

Chemical shifts, δ, SSCC, J, Hz

Benzofuran†			Phenyl, m (5H)	SSCC
4-H	6-H	7-H		
7,40...7,85 m	7,17...7,61‡ m		7,17...7,61	$J\beta a,\beta e$ = 16,0; $J\alpha a,\alpha e$ = 13,3; $J\beta a,\alpha a$ = 9,5; $J\beta e,\alpha e$ = 10,0; $J\beta a,\alpha e$ = 6,6; $J\beta e,\alpha a$ = 6,4
7,53 s	7,12 d	7,32 d	7,23...7,58	$J\beta a,\beta e$ = 16,3; $J\alpha a,\alpha e$ = 13,9; $J\beta a,\alpha a$ = 9,6; $J\beta e,\alpha e$ = 9,8; $J\beta a,\alpha e$ = 6,1; $J\beta e,\alpha a$ = 6,4; $J_{6,7}$ = 8,2
7,77 d	7,27 ddd	7,41 d	7,21...7,58	$J\beta a,\beta e$ = 17,6; $J\alpha a,\alpha e$ = 13,6; $J\beta a,\alpha a$ = 9,7; $J\beta e,\alpha e$ = 9,3; $J\beta a,\alpha e$ = 6,2; $J\beta e,\alpha a$ = 6,9; $J_{4,6}$ = 2,0; $J_{6,7}$ = 8,8

*$J_{3,4}$ = 3.2 Hz.

†In the spectrum of compound (XIb) there is a singlet in the region of 2.48 ppm for the protons of the methyl group at position 5 of the benzofuran fragment.

‡The multiplet of the 5-, 6-, and 7-H protons.

2,4-Dimethylbenzo[*b*]furo[2,3-*h*]-1-oxazulenium Perchlorate (VIa). To 2.44 g (0.02 mole) of compound (Ia) and 4 ml (0.05 mole) of sylvane (II) in 25 ml of dioxane we added 3 ml of 70% perchloric acid. The mixture was boiled for 10 min and cooled, and 5 ml of diethyl ether was added. The precipitate was filtered off, washed with dioxane and ether, and recrystallized from acetonitrile. We obtained 1.6 g (46%) of yellow crystals of compound (VIa); mp 239-240°C.

Compounds (VIb-d) were obtained similarly. The spectral characteristics and melting points of the salts (VIa-d) obtained by the described method were identical with the characteristics of the same compounds obtained from the benzofuran ketones (IVa-d).

5,6-Dihydro-2,4-dimethyl-10-chloro-4H-benzo[*b*]furo[2,3-*h*]-1-oxazulene (VIIc). We dissolved 3 g (0.01 mole) of compound (IVc) in 20 ml of hot alcohol, and with gentle boiling we added 200 mg (0.005 mole) of sodium tetrahydroborate in several portions. The reaction mixture was stirred at 70-75°C for 1 h, cooled, carefully acidified with dilute hydrochloric acid, and added to water. The oil that separated was washed by decantation with water. After drying in air the oil was dissolved in 10 ml of glacial acetic acid, 1 ml of sulfuric acid was added, and the mixture was boiled for 2 h. After cooling the greatly darkened solution was poured into water, and 1.5 g (52%) of compound (VIIc) was obtained from the oil that separated after treatment [see the reaction of the benzofuran (IVa) with perchloric acid].

Compounds (VIIb, d) were obtained similarly. The obtained samples were identical with the products (VIIb-d) of the reaction of the benzofurans (IVb-d) with perchloric acid (the absence of a melting point depression in mixed melting tests, the identity of the spectral characteristics).

2,4-Dimethyl-4H-benzo[*b*]furo[2,3-*h*]-1-oxazulenes (Xa-c). The compounds were obtained by methods analogous with those described in [7, 8], i.e., by treatment of solutions of the salts (VIa-c) with sodium tetrahydroborate in acetonitrile at room temperature. The transformation of compound (Xc) into the products (VIc) and (VIIc) was realized under conditions similar to the reaction of the benzofuran (IVa) with perchloric acid; here the boiling was continued for 2-3 min. The obtained products were identical with compounds (VIc) and (VIIc) obtained by other methods.

3-(5-Methyl-2-furyl)-2-(3-phenyl-3-hydroxybutyl)benzo[*b*]furan (XIa). To a solution of phenylmagnesium bromide, prepared from 1.4 g (0.06 mole) of magnesium, 5.2 ml (0.05 mole) of bromobenzene in 50 ml of absolute ether, with stirring and moderate boiling we added from a dropping funnel 8 g of compound (IVa) in 30 ml of absolute ether. The mixture was stirred for a further minute and carefully decomposed with water by adding it dropwise until the reaction mixture became transparent. The ether layer was removed, dried, and evaporated. The residue was dissolved in hexane. The solution was filtered through a layer of aluminum oxide, the filtrate was evaporated, and the residue was recrystallized from hexane. We obtained 10.3 g (87%) of colorless crystals of compound (IXa); mp 65-66°C.

The alcohols (XIb, c) were obtained similarly.

5,6-Dihydro-2,4-dimethyl-4-phenyl-4H-benzo[*b*]furo[2,3-*h*]-1-oxazulene (XIIa). To a solution of 3.46 g (0.01 mole) of the carbinol (XIa) in 30 ml of glacial acetic acid we added 3 ml of concentrated phosphoric acid. The mixture was boiled for 3 h and was then diluted with 70 ml of water. The warm reaction mixture was extracted with hot hexane (2 × 50 ml), and the extract was quickly dried with potassium carbonate. The product was filtered hot through a layer of aluminum oxide, and the filtrate was evaporated to 50 ml. The crystals that separated after a short time were filtered off and washed with cold hexane. We obtained 2.52 g (77%) of the product (XIIa); mp 134-135°C (light-yellow crystals).

Compounds (XIIb, c) were obtained similarly. Compounds (XIId-k) were synthesized by the method described above but without isolation of the intermediate alcohols (XId-k).

REFERENCES

1. V. T. Abaev, A. V. Gutnov, and A. V. Butin, Khim. Geterotsikl. Soedin., No. 5, 603 (1998).
2. A. V. Butin, G. D. Krapivin, V. E. Zavodnik, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 5, 616 (1993).
3. P. Cagniat and D. Cagniat, Adv. Heterocycl. Chem., **18**, 337 (1975).
4. A. N. Grinev, S. A. Zotova, and T. M. Gololobova, Khim.-Farm. Zh., No. 4, 427 (1985).
5. A. V. Gutnov, V. T. Abaev, A. V. Butin, V. E. Zavodnik, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 2, 162 (1996).
6. A. V. Butin, V. T. Abaev, V. E. Zavodnik, and V. G. Kul'nevich, Khim. Geterotsikl. Soedin., No. 5, 627 (1993).
7. R. V. Acheson and G. Paglietti, J. Chem. Soc. Perkin Trans. I, No. 1, 45 (1962).
8. A. T. Balaban, G. Mihai, and C. D. Nenitzescu, Tetrahedron, **18**, 257 (1962).
9. V. G. Kharchenko and V. I. Kleimenova, Zh. Org. Khim., **7**, 613 (1971).
10. K. M. Harmon, A. B. Harmon, and F. E. Cummings, J. Am. Chem. Soc., **83**, 3912 (1961).
11. R. Kinishi, S. Wakamatsu, and T. Iki, US Patent No. 4950810; Ref. Zh. Khim., No. 18, N86 (1991).