POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES. 8.* SYNTHESIS OF BENZOFURO[2,3-h]-1-OXAAZULENIUM SALTS. MOLECULAR AND CRYSTAL STRUCTURES OF 2,4-DIMETHYLBENZO[b]FURO[2,3-h]-1-OXAAZULENIUM PERCHLORATE

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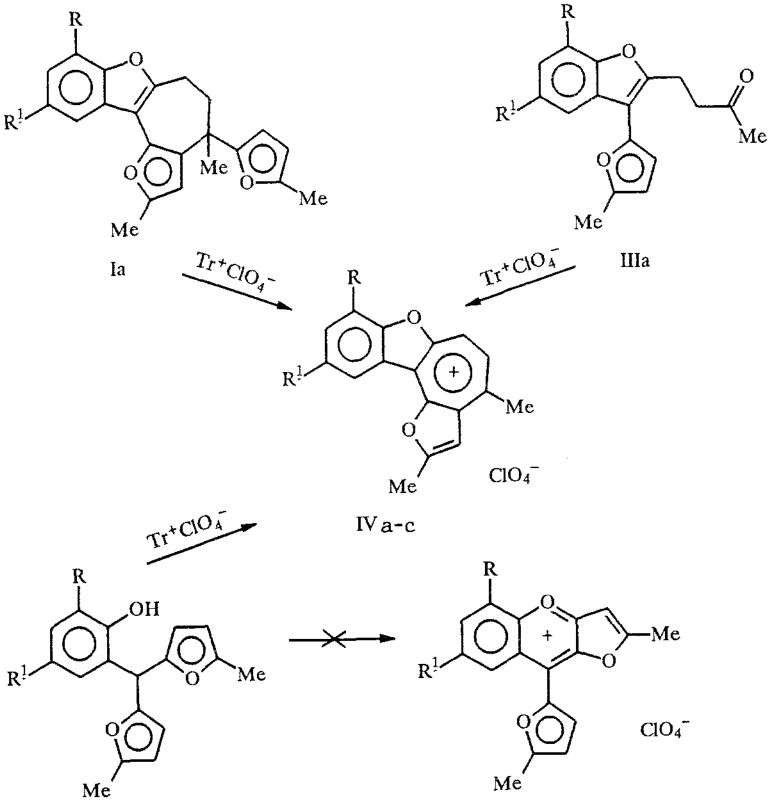
The first representatives of a new heterocyclic system — benzofuro[2,3-h]-1-oxaazulenium salts — were synthesized. Diverse variations of the synthesis of these compounds are proposed. The molecular and crystal structures of 2,4-dimethylbenzo[b]furo[2,3-h]-1-oxaazulenium perchlorate were studied.

In our preceding communication [1] we found that the fragmentation of 5,6-dihydro-2,4-dimethyl-4-(5-methyl-2-furyl)-10-nitro-4H-benzo[b]furo[2,3-h]cyclohepta[b]furan (Ia) under the influence of electron impact leads to the formation of a stable derivative of the benzofuro[2,3-h]-1-oxaazulenium cation. The aim of the present research was to search for preparative methods for the synthesis of compounds with a similar structure.

Scheme 1



I—IV a R = H, $R^1 = NO_2$, b $R = R^1 = Br$; c $R = R^1 = H$

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*See [1] for our preceding communication.

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TABLE 1. Physicochemical Characteristics of Salts IVa-c

Compound	Empirical formula	mp, °C	UV spectrum, λ_{max}, nm (log ε)	Yield, %
IVa	$C_{17}H_{12}ClNO_8$	232...233	223 (4,14); 244 (4,40); 307 (4,63); 373 (4,26)	47
IVb	$C_{17}H_{11}Br_2ClO_6$	260...261	225 (4,43); 266 (4,31); 317 (4,45); 386 (4,22)	38
IVc	$C_{17}H_{13}ClO_6$	239...240	216 (4,39); 245 (4,15); 257 (4,11); 312 (4,47); 388 (4,25)	45

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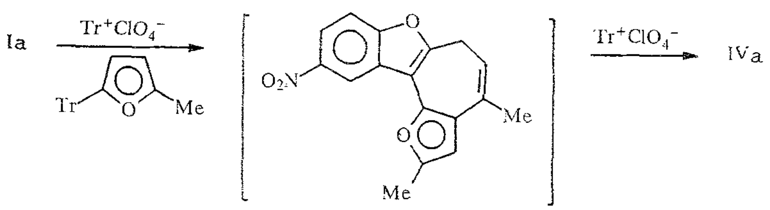
*The yields starting from II.

We ascertained that treatment of the above-mentioned Ia, as well as 2-hydroxy-3-R-4-R^1-phenylbis(5-methyl-2-furyl)methanes IIa-c and 5-nitro-2-(3-oxobutyl)-3-(5-methyl-2-furyl)benzo[b]furan (IIIa), with trityl perchlorate ($Tr^+ClO_4^-$) leads to the corresponding benzofuro[2,3-h]-1-oxaazulenium salts IVa-c (Scheme 1).

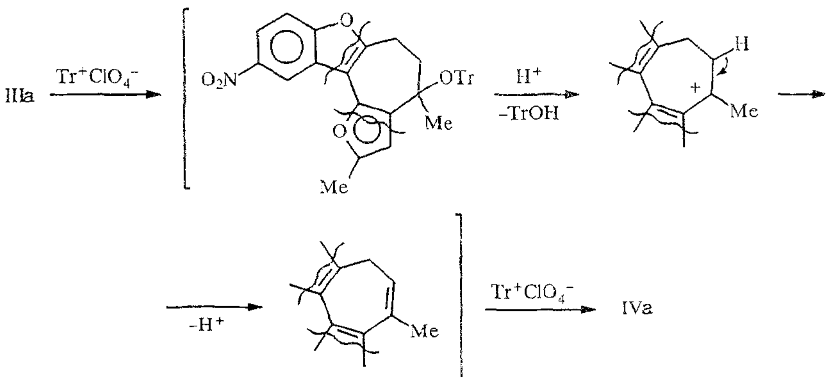
The transformation of tetracyclic Ia to the IVa cation can probably be explained by splitting out of α-methylfuran [3, 4] to give a condensed analog of cycloheptatriene, the aromatization of which by means of cleavage of a hydride ion by trityl perchlorate leads to the final product (Scheme 2); the fact that 5-methyl-2-furyltriphenylmethane was isolated from the reaction mixture serves as a confirmation of this.

Scheme 2



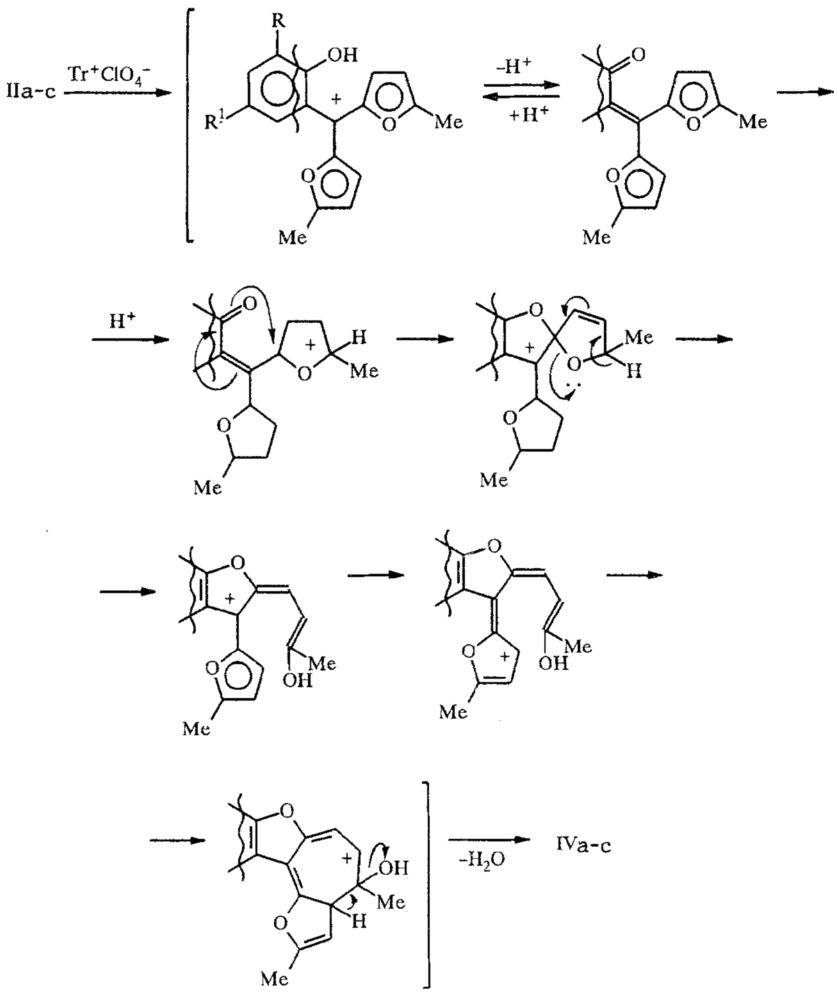
The formation of salt IVa from benzofuran IIIa most likely proceeds through successive steps involving the intramolecular cyclization of the carbonyl group at the β position of the furan ring, acid-catalyzed splitting out of triphenylmethanol, which leads to the cycloheptatriene, and aromatization of the latter to the corresponding tropylium ion (Scheme 3).

Scheme 3



The conversion of 2-hydroxyphenyldifurylmethanes IIa-c under the influence of trityl perchlorate to the corresponding benzofurooxaazulenium salts IVa-c is unexpected, since treatment of 2-hydroxytriphenylmethanol with trityl perchlorate leads to 9-phenylxanthylium perchlorate [5, 6], the formation of which is due to nucleophilic attack of the oxygen atom of the hydroxy group on the ortho position of the unsubstituted benzene ring. In the case of 2-hydroxyphenyldifurylmethanes II, however, the rearrangement of the initially formed 2-hydroxyphenyldifuryl carbonium ions indicated in Scheme 4 evidently occurs.

Scheme 4



The IR spectra of salts IVa-c contain an intense band at 1070 cm^{-1}, which corresponds to the perchlorate anion. The electronic absorption spectra of IVa-c have a complex structure with four intense bands at 216-386 nm (Table 1), while their PMR spectra (Table 2) contain signals of 5-H and 6-H protons with a characteristic spin-spin coupling constant (SSCC) of 11 Hz.

To establish the peculiarities of the structure of the new heterocyclic system IV we carried out an x-ray diffraction study of a single crystal of salt IVc. The coordinates of the atoms and the bond lengths and bond angles are presented in Tables 3-5. A projection of a three-dimensional model of IVc is presented in Fig. 1. We found that all of the atoms of the benzofuro[2,3-h]-1-oxaazulenium cation except for the hydrogen atoms of the methyl groups lie in a plane, while the lengths of most of the bonds are equalized and range from 1.39 to 1.40 Å; this constitutes evidence for significant delocalization of the charge in the aromatic system obtained.

EXPERIMENTAL

The PMR spectra were recorded with a Tesla BS-467 spectrometer (60 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The IR spectra of suspensions in mineral oil were recorded with a Specord M-80 spectrometer.

The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

X-Ray Diffraction Analysis of IVc. Prismatic crystals of 2,4-dimethylbenzo[b]furo[2,3-h]-1-oxaazulenium perchlorate (IVc) were grown from acetonitrile and had the following unit cell parameters: a = 6.693(2), b = 12.863(4), c = 20.680(6) Å, V = 1780.4(1.6) $Å^3$, space group P mcn, and Z = 4. The unit cell parameters and the intensities of 1174 independent

TABLE 2. PMR Spectra of Salts IVa-c in CF_3COOD

Compound	Chemical shifts, δ, ppm								
	2-CH_3, s	4-CH_3, s	3-H, s	5-H, d	6-H, d	8-H	9-H	11-H	SSCC, J, Hz
IVa	2,88	2,63	7,13	8,45	8,67	7,70d	8,50d	9,33d	$J_{5,6}$ = 11,5; $J_{8,9}$ = 9,5; $J_{9,11}$ = 2,0
IVb	2,87	2,58	7,07	8,37	8,62		7,80dd	8,48d	$J_{5,6}$ = 11,0; $J_{9,11}$ = 2,0
IVc	2,83	2,58	7,05	8,28	8,52	7,18...7,80m*			$J_{5,6}$ = 11,0

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*A multiplet formed by three protons including 10-H.

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

Atom	x	y	z	u	Atom	x	y	z	u
Cl	2500	4207(1)	2435(1)	28(1)	$C_{(7)}$	2500	5889(3)	5182(2)	19(1)
$O_{(1)}$	2500	4923(2)	6109(1)	26(1)	$C_{(8)}$	2500	4800(3)	5007(2)	21(1)
$O_{(2)}$	2500	6622(2)	4148(1)	23(1)	$C_{(9)}$	2500	4259(3)	5589(2)	24(1)
$O_{(3)}$	2500	5296(2)	2287(1)	54(1)	$C_{(10)}$	2500	3182(3)	5629(2)	29(1)
$O_{(4)}$	4225(3)	3965(2)	2805(1)	62(1)	$C_{(11)}$	2500	2659(3)	5043(2)	28(1)
$O_{(5)}$	2500	3623(2)	1848(1)	50(1)	$C_{(12)}$	2500	3189(3)	4452(2)	29(1)
N	2500	795(3)	3822(2)	46(1)	$C_{(13)}$	2500	4251(3)	4415(2)	24(1)
$C_{(1)}$	2500	5917(3)	5864(2)	22(1)	$C_{(14)}$	2500	8338(3)	4324(2)	27(1)
$C_{(2)}$	2500	6741(3)	6293(2)	26(1)	$C_{(15)}$	2500	7598(3)	3869(2)	25(1)
$C_{(3)}$	2500	7792(3)	6148(2)	25(1)	$C_{(16)}$	2500	9489(3)	5577(2)	35(1)
$C_{(4)}$	2500	8313(3)	5554(2)	25(1)	$C_{(17)}$	2500	7614(3)	3153(2)	36(1)
$C_{(5)}$	2500	7834(3)	4941(2)	22(1)	$C_{(18)}$	2500	915(3)	3276(2)	33(1)
$C_{(6)}$	2500	6764(3)	4799(2)	21(1)	$C_{(19)}$	2500	1057(3)	2580(2)	42(1)

TABLE 4. Bond Lengths in the IVc Molecule

Bond	l, Å	Bond	l, Å	Bond	l, Å	Bond	l, Å
Cl—$O_{(3)}$	1,433(3)	$C_{(4)}$—$C_{(16)}$	1,513(5)	Cl—$O_{(4)}$	1,420(2)	$C_{(5)}$—$C_{(6)}$	1,406(5)
Cl—$O_{(5)}$	1,428(3)	$C_{(5)}$—$C_{(14)}$	1,430(5)	Cl—$O_{(4A)}$	1,420(2)	$C_{(6)}$—$C_{(7)}$	1,377(5)
$O_{(1)}$—$C_{(1)}$	1,375(4)	$C_{(7)}$—$C_{(8)}$	1,446(5)	$O_{(1)}$—$C_{(9)}$	1,374(4)	$C_{(8)}$—$C_{(9)}$	1,391(5)
$O_{(2)}$—$C_{(6)}$	1,358(4)	$C_{(8)}$—$C_{(13)}$	1,412(5)	$O_{(2)}$—$C_{(15)}$	1,382(4)	$C_{(9)}$—$C_{(10)}$	1,387(5)
N—$C_{(18)}$	1,139(6)	$C_{(10)}$—$C_{(11)}$	1,387(5)	$C_{(1)}$—$C_{(2)}$	1,382(5)	$C_{(11)}$—$C_{(12)}$	1,400(5)
$C_{(1)}$—$C_{(17)}$	1,411(5)	$C_{(12)}$—$C_{(13)}$	1,368(5)	$C_{(2)}$—$C_{(3)}$	1,385(5)	$C_{(14)}$—$C_{(15)}$	1,339(5)
$C_{(3)}$—$C_{(4)}$	1,399(5)	$C_{(15)}$—$C_{(17)}$	1,481(5)	$C_{(4)}$—$C_{(5)}$	1,411(5)	$C_{(18)}$—$C_{(19)}$	1,451(6)

reflections with $I > 3\sigma(I)$ were obtained at 150 K with an Enraf—Nonius CAD4 automatic diffractometer without a monochromator (Mo K_α emission, $\theta/2\theta$ scanning up to $2\theta_{max} = 50°$). The structure was decoded by the direct method by means of the set of SHELXTL programs [7] and was refined within the anisotropic (isotropic for the hydrogen atoms) approximation up to divergence factors $R = 0.036$ and $R_w = 0.040$.*

The starting compounds were obtained by the methods described in [1, 8].

2,4-Dimethylbenzo[b]furo[2,3-h]-1-oxaazulenium Perchlorate (IVc). A mixture of 0.54 g (0.002 mole) of 2-hydroxyphenylbis(5-methyl-2-furyl)methane (IIc) and 0.68 g (0.002 mole) of trityl perchlorate in 5 ml of methylene chloride was maintained at room temperature for 3 h, after which the mixture was diluted with 15 ml of ethyl acetate, and the resulting mixture was cooled in a refrigerator. The precipitated IVc was removed by filtration, washed with ether, and recrystallized from acetonitrile. The yield was 3.12 g.

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*The coordinates of the hydrogen atoms can be obtained from the authors.

TABLE 5. Bond Angles in the IVc Molecule

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O_{(3)}ClO_{(4)}$	109,2(1)	$O_{(1)}C_{(9)}C_{(8)}$	111,5(3)	$C_{(4)}C_{(5)}C_{(14)}$	127,1(3)
$O_{(4)}ClO_{(5)}$	110,1(1)	$C_{(8)}C_{(9)}C_{(10)}$	123,5(3)	$O_{(2)}C_{(6)}C_{(5)}$	109,7(3)
$O_{(4)}ClO_{(4A)}$	108,8(2)	$C_{(10)}C_{(11)}C_{(12)}$	121,8(3)	$C_{(5)}C_{(6)}C_{(7)}$	132,8(3)
$C_{(1)}O_{(1)}C_{(9)}$	106,9(3)	$C_{(8)}C_{(13)}C_{(12)}$	116,9(3)	$C_{(1)}C_{(7)}C_{(8)}$	106,0(3)
$O_{(1)}C_{(1)}C_{(2)}$	118,5(3)	$O_{(2)}C_{(15)}C_{(14)}$	110,6(3)	$C_{(7)}C_{(8)}C_{(9)}$	105,6(3)
$C_{(2)}C_{(1)}C_{(7)}$	131,4(3)	$C_{(14)}C_{(15)}C_{(17)}$	133,9(3)	$C_{(9)}C_{(8)}C_{(13)}$	119,9(3)
$C_{(2)}C_{(3)}C_{(4)}$	131,2(3)	$O_{(3)}ClO_{(5)}$	109,4(2)	$O_{(1)}C_{(9)}C_{(10)}$	125,0(3)
$C_{(3)}C_{(4)}C_{(16)}$	116,8(3)	$O_{(3)}ClO_{(4A)}$	109,2(1)	$C_{(9)}C_{(10)}C_{(11)}$	115,6(3)
$C_{(4)}C_{(5)}C_{(6)}$	127,9(3)	$O_{(5)}ClO_{(4A)}$	110,1(1)	$C_{(11)}C_{(12)}C_{(13)}$	122,3(3)
$C_{(6)}C_{(5)}C_{(14)}$	105,0(3)	$C_{(6)}O_{(2)}C_{(15)}$	107,0(3)	$C_{(5)}C_{(14)}C_{(15)}$	107,7(3)
$O_{(2)}C_{(6)}C_{(7)}$	117,4(3)	$O_{(1)}C_{(1)}C_{(7)}$	110,1(3)	$O_{(2)}C_{(15)}C_{(17)}$	115,5(3)
$C_{(1)}C_{(7)}C_{(6)}$	123,7(3)	$C_{(1)}C_{(2)}C_{(3)}$	127,5(3)	$NC_{(18)}C_{(19)}$	179,4(4)
$C_{(6)}C_{(7)}C_{(8)}$	130,3(3)	$C_{(3)}C_{(4)}C_{(5)}$	125,4(3)		
$C_{(7)}C_{(8)}C_{(13)}$	134,5(3)	$C_{(5)}C_{(4)}C_{(16)}$	117,7(3)		

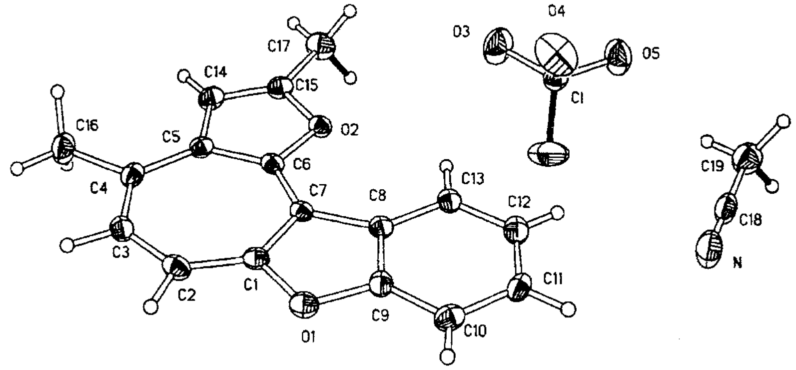

Fig. 1. Projection of a three-dimensional model of 2,4-di-methylbenzo[b]-furo[2,3-h]-1-oxaazulenium perchlorate.

Salts IVa, b, respectively, were similarly obtained from IIa, b, while salt IVa was also obtained from IIIa (in 68% yield) and form Ia (in 14% yield).

REFERENCES

1. A. V. Butin, G. D. Krapivin, V. E. Zavodnik, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 5, 616 (1993).
2. A. V. Butin, V. T. Abaev, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 8, 1142 (1992).
3. A. V. Butin, V. G. Kul'nevich, V. T. Abaev, and O. Yu. Okhlobystin, *Khim. Geterotsikl. Soedin.*, No. 8, 1141 (1992).
4. E. B. Usova, G. D. Krapivin, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 9, 1289 (1992).
5. R. Elderfield (ed.), *Heterocyclic Compounds* [Russian translation], Vol. 2, Izd. Inostr. Lit., Moscow (1954), p. 340.
6. S. M. Luk'yanov, L. N. Étmetchenko, and G. N. Dorofenko, *Zh. Org. Khim.*, **14**, 399 (1978).
7. G. M. Sheldrick, *Computational Crystallography*, Oxford University Press, New York—Oxford (1982), p. 506.
8. A. V. Butin, V. E. Zavodnik, and V. G. Kul'nevich, *Khim. Geterotsikl. Soedin.*, No. 7, 997 (1992).