POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.
5.* CATIONS AND RADICALS IN THE POLYFURYL(ARYL)METHANE SERIES

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The perchlorates of trifuryl- and difuryl(aryl)carbene have been prepared by the oxidation of polyfuryl(aryl)-methanes with trityl perchlorate and have been characterized. The temperature dependence of the PMR and ^{13}C *NMR spectra of the cations suggests that they exist in solution in the form of various rotamers. X-ray diffraction has been used to establish that the tris(5-methyl-2-furyl)carbene perchlorate molecule is a symmetrical propeller in which each furan ring is twisted from the plane by 10.4°. Reduction of the corresponding perchlorates on a zinc mirror in tetrahydrofuran gives stable polyfuryl(aryl)-methane radicals which were recorded by ESR spectroscopy.*

As a result of the marked ability of furan to stabilize a carbene center [2], furylcarbene cations play an important part in furan chemistry and it is assumed that they are formed in many reactions taking place in acid media [3, 4]. Stable polyfuryl(aryl)carbene ions can serve as convenient models for the study of the interactions of furylcarbene ions with nucleophiles together with recyclization reactions in which the furan ring participates. However, there are few communications describing the isolation of such salts as individual compounds [5, 6].

The object of the present work was the development of a convenient method for the synthesis of polyfuryl(aryl)-carbene salts and the study of their physicochemical characteristics.

It was shown in a previous communication [5] that polyfuryl(aryl)-methanes were convenient precursors of these cations and their preparation does not now present a problem [7, 8].

Using the example of tris(5-methyl-2-furyl)methane (Ic) we have studied the different methods of generating carbene ions by known oxidative dehydrogenation reagents: trityl perchlorate [9, 10], *o*-chloroanil [11], antimony pentachloride [12], and a mixture of bromine and acid [13]. It can be seen from the results in Table 1 trityl perchlorate is the most effective of these reagents and the remaining salts were prepared by this method (see Scheme 1 on the following page).

The physicochemical characteristics of the salts II are set out in Table 2. The IR spectra of the salts show a band at 1070 cm^{-1}, characteristic for the perchlorate anion.

The electronic absorption spectra of the salts II are characterized by the presence of two maxima in the UV region: $\lambda_{max}{}^1$ = 242-255 nm, $\lambda_{max}{}^2$ = 278-285 nm. These correspond to $\pi-\pi^*$ transitions in the isolated aromatic systems of the furan and benzene rings associated with the electron-deficient carbon atom. In the visible region of the spectra of these salts (Table 2) there are two intense bands (compounds IIf, j have a second maximum on the short-wave slope of the more intense band in the form of a shoulder), which characterize the presence of two interacting chromophores [14]. The difuryl cations IIa, b have a single absorption maximum in the visible region (λ_{max} 487 nm) and they are models for one of the chromophores entering into the conjugation system of difurylaryl-methyl salts in which this maximum undergoes a bathochromic, and

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*For Communication 4, see [1].

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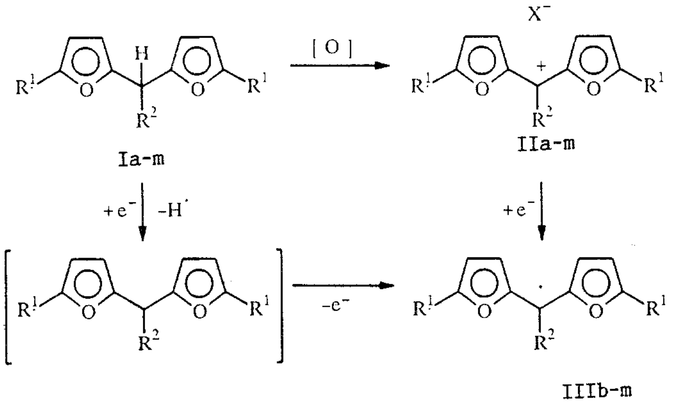
0009-3122/93/2903-0274$12.50

TABLE 1. Methods for the Preparation of Salt IIc

Method	[O]	Solvent	X^-	Yield, %
1	$Tr^+ClO_4^-$	Acetonitrile	ClO_4^-	87
2	$Br_2 + HClO_4$	Acetic acid	ClO_4^-	62
3	o-chloroanil + $HClO_4$	Ethyl ether + acetonitrile	ClO_4^-	78
4	$SbCl_5$	Acetonitrile	$SbCl_6^-$	49

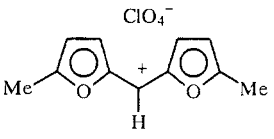
Scheme 1

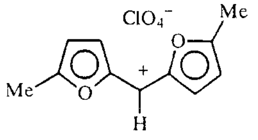


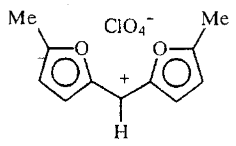
I, II, III a-c R^1 = Me; a R^2 = H; b R^2 = Me; c R^2 = 5-methyl-2-furyl; d R^1 = Et, R^2 = 5-ethyl-2-furyl; e-m R^1 = Me; e R^2 = Ph; f R^2 = $4\text{-}MeC_6H_4$; g R^2 = $4\text{-}BrC_6H_4$; h R^2 = $4\text{-}ClC_6H_4$; i R^2 = $4\text{-}HOC_6H_4$; j R^2 = $3,5\text{-}(t\text{-}Bu)_2\text{-}4\text{-}HOC_6H_2$; k R^2 = $4\text{-}MeOC_6H_4$; *l* R^2 = $3\text{-}MeOC_6H_4$; m R^2 = $3,4\text{-}(MeO)_2C_6H_3$

the band of the second chromophore a hypsochromic shift. These combinations are more significant in the case of trifurylmethyl salts IIc, d where two identical chromophores interact [15].

In the PMR and ^{13}C NMR spectra of cation IIa, run at room temperature (Tables 2, 3), three sets of signals are observed, and for the cation IIb, two sets. Increase in temperature leads to coalescence and the formation of a single set of signals corresponding to the given structure (Fig. 1). This observation can probably be explained by the presence of rotamers in solution at room temperature analogous to those which were observed in a study of ^{13}C NMR spectra of carbonyl compounds of furan [16]. For example, for the cation IIa one can assume the existence of three rotamers A, B, and C.


A


B


C

The smaller barrier to rotation of the aromatic and furan rings around the geminal bonds in the difurylarylmethyl salts IIe-m gives rise only to a broadening of the 3-H proton signal of the furan ring and a doubling or broadening only of certain signals in the ^{13}C NMR spectra. A detailed study of the thermodynamics of rotation of the ring around the geminal bond will be published as one of our subsequent communications.

Transition from polyfurylmethanes to cations is accompanied by a downfield shift of most of the signals of the resonating nuclei as a result of their deshielding. The greatest shift is observed for the central carbon atom C^+ (100 ± 10 ppm). Signals of the carbon nuclei of the furan ring $C_{(3)}$, $C_{(4)}$, and $C_{(5)}$ are shifted downfield by 35-39, ~13, and 21-29 ppm, respectively whereas the position of the $C_{(2)}$ signal is practically unchanged. In the PMR spectra, the signals of the 3-H and 4-H protons of the furan ring are shifted downfield by 1.6-2.0 and 0.6-0.9 ppm, respectively in comparison with the analogous signals in the spectrum of methane [7].

TABLE 2. Characteristics of Compounds IIa-m

Compound	Empirical formula	mp, °C	UV spectrum. λ_{max} (lg ε)	PMR spectrum, δ, ppm (J, Hz)				Yield, %
				CH_3	4-H	3-H		
IIa	$C_{11}H_{11}ClO_6$	152...153	487 (4,89)	2,35, 2,37	6,57, 6,53, 6,68	7,70, 7,75, 8,22	7,33 (s CH); 7,48 (s CH^1)	78
IIb	$C_{12}H_{13}ClO_6$	154...155	487 (4,94)	2,32	6,45, 6,60	7,80, 8,26	2,50 (3H, s CH3)	73
IIc	$C_{16}H_{15}ClO_7$	234...235	457 (4,53), 524 (4,72)	2,23	6,33	7,75		87
IId	$C_{19}H_{21}ClO_7$	187...188	460 (4,41), 526 (4,62)	1,03	6,43	7,80	2,62 (6H, q CH2); $J_{CH2, CH3}$= 7,2	86
IIe	$C_{17}H_{15}ClO_6$	176...177	403 (4,04), 490 (4,79)	2,33	6,53	7,23	7,23 (5H, s, arom	68
IIf	$C_{18}H_{17}ClO_6$	194...195	489 (4,90)	2,35	6,53	7,55	6,93...7,12 (4H, m, arom); 2,10 (3H, s CH3)	79
IIg	$C_{17}H_{14}BrClO_6$	189...190	412 (4,12), 493 (4,75)	2,35	6,57.	7,78	7,12 (2H, d, м-H); 7,37 (2H, d, o-H); $J_{oм}$ = 8	67
IIh	$C_{17}H_{14}Cl_2O_6$	185...186	413 (4,09), 493 (4,69)	2,33	6,57	7,77	7,18 (4H, s, arom)	53
IIi	$C_{17}H_{15}ClO_7$	227...228	422 (4,18), 498 (4,91)	2,31	6,53	7,55	6,81 (2H, d, м-H); 7,25 (2H, d, o-H); $J_{oм}$ = 9	85
IIj	$C_{25}H_{31}ClO_7$	198...200	497 (4,89)	2,32	6,52	7,48	1,10 (18H, s, t-Bu); 7,27 (2H, s, arom))	76
IIk	$C_{18}H_{17}ClO_7$	187...188	428 (4,18), 498 (4,82)	2,30	6,53	7,53	3,61 (3H, s OCH3); 6,81 (2H, d, м-H); 7,27 (2H, d, o-H); $J_{oм}$ = 9	82
IIl	$C_{18}H_{17}ClO_7$	168...169	503 (4,86)	2,33	6,53	7,30	3,55 (3H, s OCH3); 6,67...7,18 (4H, m, arom)	80
IIm	$C_{19}H_{19}ClO_8$	190...191	493 (4,85)	2,33	6,53	7,56	3,58 (3H, s, OCH3); 3,67 (3H, s, OCH_3); 6,75...7,08 (3H, m, arom)	83

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*J_{34} = 4 Hz.

TABLE 3. ^{13}C NMR Spectra of Compounds Ia-c, c-h, k-m and IIa-c, e-i, k-m

Compound	Chemical shift, δ, ppm													
	furyl				aryl						CH	C^+	CH_3	substituent on arom.
	$C_{(2)}$	$C_{(5)}$	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)				
Ia	150,37	151,13	106,49	107,30							27,00		12,77	
Ib	150,86	155,25	105,80	106,35							32,97		12,77	17,69*
Ic	150,66	151,50	106,41	107,95							38,73		12,66	
Ie	151,61	153,03	106,49	108,34	140,46	128,75	128,50	127,27	128,50	128,75	44,95		12,89	
If	151,44	153,13	106,28	108,01	137,33	129,21	128,23	136,85	128,23	129,21	44,37		12,64	20,17
Ig	151,80	152,57	106,45	108,47	139,67	130,37	131,78	120,60	131,78	130,37	44,17		12,77	
Ih	151,77	152,32	106,38	108,40	139,19	130,02	128,63	132,80	128,63	130,02	44,00		12,67	
Ik	151,45	153,31	106,32	107,98	132,32	129,41	113,94	158,87	113,94	129,41	43,96		12,70	54,96
Iℓ	151,58	152,85	106,43	108,30	141,97	114,39	160,03	112,32	120,70	129,74	44,71		12,92	54,93
Im	151,42	153,22	106,27	107,98	132,71	112,12	149,21	148,41	120,47	111,70	44,25		12,63	55,32
														55,39
IIa	150,79	180,32	143,24	120,06								126,23	15,65	
	151,79	180,58	146,34	120,24								128,28	15,80	
		181,64	147,01	122,28										
IIb	152,91	177,90	141,85	119,10								147,58	15,34	16,41**
	153,56	179,68	144,28	121,76										
IIc	147,26	171,84	139,15	116,55								129,69	13,52	
IIe	152,85br	180,79br	145,09	120,00 br	132,07	134,64	129,69	133,56	129,69	134,64		147,60 br	15,37	
			146,27											
IIf	151,64br	177,83	143,64	118,69 br	128,71	133,61	129,99	147,56	129,99	133,61			14,23	20,32
		179,26	145,07			133,20				133,20				
IIg	152,81br	181,64br	145,17	120,38 br	130,54	134,82 br	133,49br	131,64 br	133,49 br	134,82 br		147,12br	15,48	
			146,26											
IIh	151,52 br	180,24br	143,73	118,89 br	130,08	133,44	129,11	141,24 br	129,11	133,44			14,15	
			144,87			133,11	128,85		128,85	133,11				
IIi	151,33	176,98br	142,93br	120,44	125,01	136,60 br	116,68	162,22	116,68	136,60 br		147,23 br	14,03	
IIk	151,21	176,82br	142,73br	118,31	124,87	136,64 br	115,18	166,02	115,18	136,64 br		147,11 br	14,02	55,40
IIℓ	152,05	180,43br	144,34	119,38	133,10	119,38 br	159,32	118,52	125,78	130,25			14,28	55,48
			145,54				158,99		126,16	130,58				
IIm	151,46	177,32br	144,32br	118,92	125,42	116,85br	149,24	155,61	130,80br	111,98		146,18 br	14,53	56,01

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*Chemical shift of carbon atom of CH_3 group coupled with CH.

**Chemical shift of carbon atom of CH_3 group coupled with C^+.

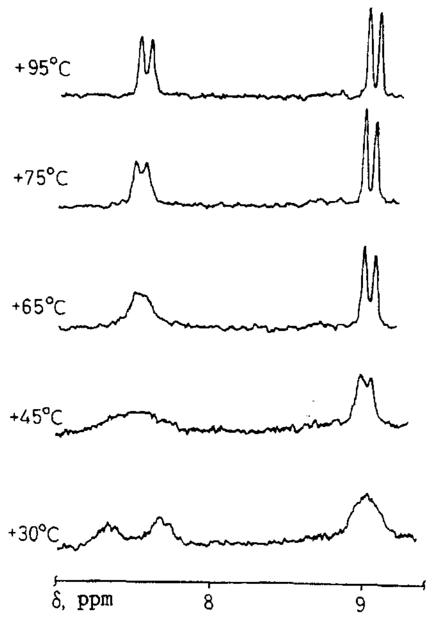

Fig. 1. Temperature variation of PMR spectra of compound IIb run in CH_3NO_2.

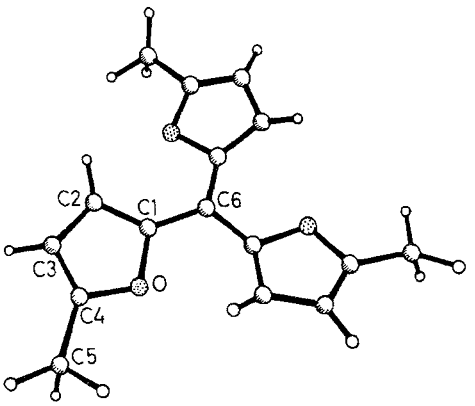

Fig. 2. Projection of three-dimensional model of the cation of IIc.

TABLE 4. Coordinates of Nonhydrogen Atoms ($\times 10^4$ Å) of the IIc Cation*

Atom	x	y	z	Atom	x	y	z
O	1822(4)	-321(5)	2216(7)	$C_{(4)}$	2086(10)	-1291(11)	2366(14)
$C_{(1)}$	474(6)	-879(6)	2450(9)	$C_{(5)}$	3508(10)	-880(12)	2067(19)
$C_{(2)}$	-12(8)	-2161(7)	2790(12)	$C_{(6)}$	0	0	2519(14)
$C_{(3)}$	1037(12)	-2373(10)	2731(17)				

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*Coordinates of hydrogen atoms are not shown; they may be obtained from the authors.

Coupling of the signals of the resonating nuclei of the benzene rings is less marked, possibly because the furan ring makes a less ponderable contribution and the positive charge is delocalized [3, 17].

TABLE 5. Interatomic Distances in the IIa Cation

Bond	*l*, Å	Bond	*l*, Å	Bond	*l*, Å
$O—C_{(1)}$	1,401(8)	$C_{(1)}—C_{(6)}$	1,413(8)	$C_{(4)}—C_{(5)}$	1,517(17)
$O—C_{(4)}$	1,341(16)	$C_{(2)}—C_{(3)}$	1,389(19)	$C_{(6)}—C_{(1A)}$	1,413(5)
$C_{(1)}—C_{(2)}$	1,350(10)	$C_{(3)}—C_{(4)}$	1,289(13)	$C_{(6)}—C_{(1B)}$	1,413(5)

TABLE 6. Valence Angles in the IIa Cation

Angle	ω	Angle	ω	Angle	ω
$C_{(1)}—O—C_{(4)}$	106,7(6)	$C_{(1)}—C_{(2)}—C_{(3)}$	106,5(7)	$C_{(3)}—C_{(4)}—C_{(5)}$	135,3(15)
$O—C_{(1)}—C_{(2)}$	107,2(7)	$C_{(2)}—C_{(3)}—C_{(4)}$	109,4(12)	$C_{(1)}—C_{(6)}—C_{(1A)}$	119,9(2)
$O—C_{(1)}—C_{(6)}$	115,9(5)	$O—C_{(4)}—C_{(3)}$	110,2(12)	$C_{(1)}—C_{(6)}—C_{(1B)}$	119,9(1)
$C_{(2)}—C_{(1)}—C_{(6)}$	136,4(6)	$O—C_{(4)}—C_{(5)}$	114,5(9)	$C_{(1A)}—C_{(6)}—C_{(1B)}$	119,9(3)

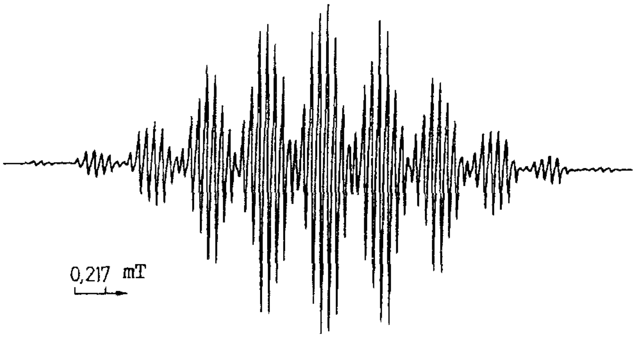

Fig. 3. ESR spectrum of radical IIIc.

To establish the features of the stereostructure of tris(5-methyl-2-furyl)carbene perchlorate we carried out an x-ray diffraction study of its monocrystal. The coordinates of the atoms, bond lengths, and valence angles are shown in Tables 4-6, respectively. A projection of a three-dimensional model of the cation IIc is shown in Fig. 2. The low precision in the determination of bond lengths and valence angles is apparently connected with the small number of reflections which in its turn results from the poor quality of the monocrystal. We have not therefore discussed these geometrical parameters. We note only that the tris(5-methyl-2-furyl)carbenium cation is a symmetrical propeller and all three of the furan rings are twisted from the plane passing through the $C_{(1)}$, $C_{(1A)}$, $C_{(1B)}$, and $C_{(6)}$ carbons at an angle of 10.4° (in the monococrystal of tris(4-aminophenyl)methyl perchlorate these angles are different and amount to 29, 34, and 34° [18]).

ESR spectroscopy was used to study the free radicals III in the polyfuryl(aryl)methane series; these were prepared by reduction of the cation II in THF on a zinc mirror or by reduction of the methanes I to the anions with alkali metal followed by a one-electron oxidation (see scheme 1).

The parameters of the ESR spectra of some of these radicals are shown in Table 7. The absolute values of the hyperfine interaction constants were supported by a theoretical reconstruction of the spectra. Analysis of the hyperfine structure of the spectra of the radicals provided evidence of a significant delocalization of the unpaired electrons on the furyl rings (Fig. 3). Interaction of an unpaired electron with the protons of the furan rings in positions 3 and 4 corresponds to a spin polarization mechanism, and interaction with the methyl group protons is explained by the hyperconjugation model. To assign the hyperfine interaction constants we used straightforward calculation by the MOKh method. The results of the calculation, carried out for radical IIIc enabled us to evaluate, on a qualitative level, the tendency to distribution of the density of the unpaired electron. Figure 4 shows part of the radical IIIc and the squares of the coefficients at the atomic orbitals composing the molecular orbital occupied by the unpaired electron. From these results one can postulate that $a_H^3 > a_H^{CH3} > a_H^4$. A similar relationship for the densities of the unpaired electron is observed in the case of the 2-furylmethyl

TABLE 7. Parameters of the ESR Spectrum of Radicals III

Compound	Hyperfine coupling constant, mT			
	a_H^3	a_H^{CH3}	a_H^4	other constants
IIIc	0,48 (6)	0,37 (2)	0,06	
IIId	0,49		0,06	a_H^{CH2}=0,35(6)
IIIi	0,58 (3)	0,45 (3)	0,06 (5)	a_H^o = 0,13; a_H^m = 0,06 (5)
IIIj	0,56	0,42	0,07	a_H^o = 0,14 (6); a_H^{OH} = 0,04 (8)
IIIℓ	0,52	0,46	0,06	a_H^o = 0,12; a_H^p = 0,05 (6)

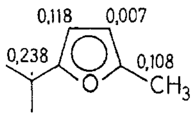

Fig. 4. Part of radical IIIc and squares of coefficients of atomic orbitals composing the molecular orbital occupied by the unpaired electron.

radical [19]. The parameters, allowing for the effect of the heteroatom and the CH_3 group (induction model), were taken from [20].

Replacing the methyl group by ethyl in position 5 of the furyl ring does not result in any significant redistribution of the unpaired electron density (radicals IIIc, d) [21].

In the oxidation of the methane Ij by lead dioxide a phenoxyl radical is recorded with a hyperfine coupling constant $a_H^{CH} = 0.586$ mT, $a_H^{arom} = 0.178$ mT.

EXPERIMENTAL

PMR spectra were run on a Tesla BS-467 spectrophotometer in trifluoroacetic acid with HMDS as internal standard. ^{13}C NMR spectra were run on a Bruker AM-300 instrument in trifluoroacetic acid for salts II and in acetonitrile-D_3 for the methanes I with TMS internal standard. Electronic absorption spectra were recorded on a Specord M-40 and IR spectra on a Specord M-80. ESR spectra were run on an SE/X-2543 spectrometer in tetrahydrofuran. Ampuls containing the solutions were subjected to preliminary evacuation up to 10^{-3} mm.

The results of elemental analysis for C, H, Hal were in agreement with those calculated.

Monoclinic crystals of compound IIa were grown in 1:1 acetone–acetonitrile; unit cell dimensions were: $a = b = 11.872$ Å, $c = 6.705$ Å, $V = 818.4$ Å^3, $\gamma = 120°$, space group $P\bar{3}$, $Z = 2$. The unit cell dimensions and intensity of 475 independent reflections with $J > 3\sigma(J)$ were obtained on a PT Syntex automatic diffractometer with Mo-K_α radiation and a β-filter. The structure was interpreted by a direct method using the SHELTX set of programs [22] and refined in an anisotropic approximation (isotropic for hydrogen atoms) to a divergence of $R = 0.085$ and $R_w = 0.097$.

The method for the synthesis and physicochemical characterization of compounds Ia-c, e-i, k-m was as given in [7, 8]. Compounds Id and Ij were prepared similarly.

Tris(5-ethyl-2-furyl)methane (Id, $C_{19}H_{22}O_3$), bp 192-195°C/5 mm, $n_D^{20} = 1.5130$. PMR spectrum (CCl_4, δ ppm): 1.15 (9H, t, CH_3), 2.52 (6H, q, CH_2) $J_{CH_2CH_3} = 7.2$ Hz, 5.17 (1H, s, CH), 5.72 (6H, s, fur.).

4-Hydroxy-di-3,5-tert-butylphenyl-bis)5-methyl-2-furyl)methane (Ij, $C_{25}H_{32}O_3$). mp 122-123°C (from ethanol). PMR spectrum (CCl_4, δ ppm): 1.32 (18H, s, t-Bu), 2.15 (6H, s, CH_3), 4.88 (1H, s, OH), 5.02 (1H, s, CH), 5.67 (4H, s, fur.), 6.87 (2H, s, arom.).

General Method for the Preparation of Compounds IIa-*l*. A mixture of 4 mmole methane I in 8 ml acetonitrile (in the case of difurylaryl-methanes, methylene chloride was used, and in the case of difurylmethane, dichloroethane) and 4 mmole trityl perchlorate was prepared at room temperature and then diluted with ether or ethyl acetate. The precipitate which formed was filtered off and washed with ether.

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