POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES
9.* POLYFURYL(ARYL)METHANES IN THE DIELS–ALDER REACTION

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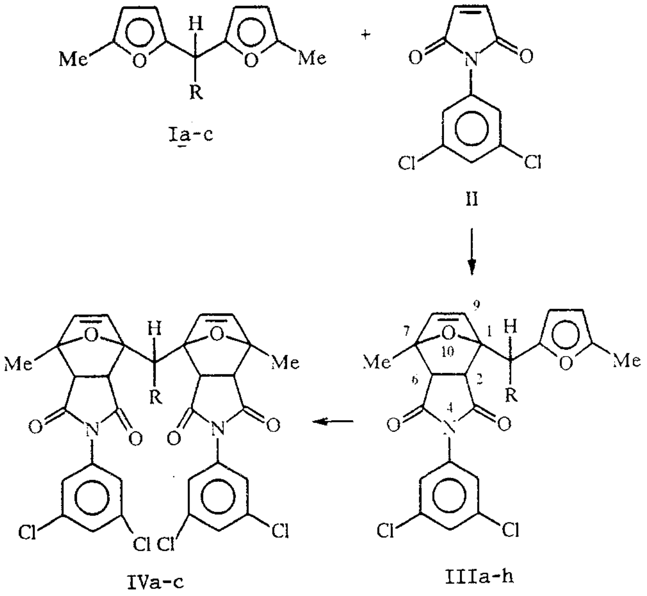
The reaction of polyfuryl(aryl)methanes with N-(3,5-dichlorophenyl)maleimide has been studied. It was found that tetrasubstituted methanes do not react. Difurylmethane, gem-difurylethane, gem-difurylethane, and trifurylmethane form mono- and diadducts, and difurylarylmethanes form only monoadducts. The molecular and crystal structure of the diadduct of gem-difurylethane – gem-bis{4-aza-7-methyl-10-oxa-4-(3,5-dichlorophenyl)tricyclo-[5,2,1,$0^{2,6}$]deca-8-en-3,5-dion-1-yl}ethane has been studied.

It is well known that alkylfurans readily undergo the diene synthesis reaction [2]. To our knowledge, there are no publications devoted to the Diels–Alder reaction in the series of polyfuryl(aryl)methanes. At the same time, the presence of one, two, or three furane rings in the molecules of these compounds may introduce certain characteristics into the course of the indicated reaction, primarily for steric reasons. To study these characteristics, we carried out reactions of polyfuryl(aryl)methanes (I) with N-(3,5-dichlorophenyl)maleimide (II) and obtained monoadducts (III) and diadducts (IV) (schemes 1, 2).



We note that in selecting dienophile II, we took into account the fungicidal activity of the adduct of furane and N-(3,5-dichlorophenyl)maleimide [3].

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*For Communication 8, see [1].

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TABLE 1. Physicochemical Properties of Compounds IIIa-i, IVa-c

Compound	R	Empirical formula	T_m, °C*	IR spectrum, ν, cm^{-1}	Yield, %
				$N(C=O)_2$	
III a	H	$C_{21}H_{17}Cl_2NO_4$	165...168	1690	12
III b	Me	$C_{22}H_{19}Cl_2NO_4$	127...128	1700	7
III c	5-methyl-2-furyl	$C_{26}H_{21}Cl_2NO_5$	153...155	1680	63
III d	4-BrC$_6$H$_4$	$C_{27}H_{20}BrCl_2NO_4$	114...116	1700	58
III e	4-ClC$_6$H$_4$	$C_{27}H_{20}Cl_3NO_4$	110...111	1700	55
III f	Ph	$C_{27}H_{21}Cl_2NO_4$	155...156	1680	45
III g	4-MeC$_6$H$_4$	$C_{28}H_{23}Cl_2NO_4$	105...106	1705	53
III h	2-MeOC$_6$H$_4$	$C_{26}H_{23}Cl_2NO_5$	117...120	1695	74
III i	—	$C_{28}H_{21}Cl_2NO_3$	143...144	1680	72
IV a	H	$C_{31}H_{22}Cl_4N_2O_6$	> 200	1690	63
IV b	Me	$C_{32}H_{24}Cl_4N_2O_6$	175...176	1680, 1690	85
IV c	5-methyl-2-furyl	$C_{36}H_{26}Cl_4N_2O_7$	217...218	1700	54

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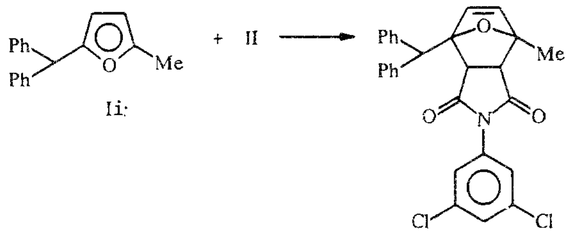
*Compounds IIIa, b were recrystallized from hexane, and the remaining ones, from acetone.

The reaction of trifurylmethane Ic and aryldifurylmethanes Id-h with compound II in acetone at room temperature and a 1:1 ratio of the reactants readily forms monoadducts IIIc-h (Table 1).

The reaction of diphenyl(5-methyl-2-furyl)methane Ii with maleimide II also forms monoadduct IIIi (scheme 2).



Ii

IIIi

We note that in the case of bis-(5-methyl-2-furyl)methane Ia and gem-bis(5-methyl-2-furyl)ethane Ib, the reaction carried out under the above conditions mainly forms diadducts IVa, b, and their yield is 50-55% of theoretical, whereas monoadducts IIIa, b were isolated with a yield of only 7-12% (see Table 1). These results can be accounted for by the fact that monoadducts IIIa, b, owing to their high solubility, accumulate in the reaction medium, competing with the initial difurylalkanes, whereas diadducts IVa, b, which have a very low solubility, are steadily removed from the reaction zone.

The synthesis of diadduct IIIc from trifurylmethane Ic requires prolonged boiling in acetone (for 10-12 h) at a 1:2 molar ratio of the reactants. In turn, the analogous reaction for difuryl alkanes Ia, b is complete in 1-2 h. Aryl difurylmethanes Id-h do not form diadducts even if the boiling lasts for days. From trisubstituted to tetrasubstituted methanes, the steric hindrances increase significantly, considerably impeding the formation of Diels–Alder adducts. Thus, 2,2-bis(5-methyl-2-furyl)propane and triphenyl(5-methyl-2-furyl)methane do not react with maleimide II.

The IR spectra of the synthesized adducts show an intense absorption band of the imide carbonyl group in the 1680-1700 cm^{-1} region (see Table 1). A characteristic feature of the PMR spectra of the compounds obtained is the presence of signals of 2-H and 6-H bridge protons at 2.83-3.95 ppm and 8-H and 9-H ethylene protons around 6.18-6.87 ppm, and the furan protons in the spectra are present in the form of an AB system with a coupling constant of 3.2 Hz (Table 2). The coupling constant of the 2-H and 6-H protons amounts to 6.5-7.7 Hz, indicating their cis position. The PMR spectrum of compound IVc could not be recorded because of its poor solubility.

Of the three compounds (IIIc, f and IVc) for which the mass spectra were recorded (Table 3), the low-intensity peak of a molecular ion ($M^{+\cdot}$) is observed only in the case of compound IIIf. Under the mass spectrometry conditions employed, the

TABLE 2. PMR Spectra of Compounds IIIa-i and IVa, b in $CDCl_3$

Compound	Chemical shifts, δ, ppm									
	Tricyclic fragment[1*]			N-3,5-Dichlorophenyl[2*]		CH,	Furyl			Other signals and couplings constants, J, Hz[3*]
	7-CH_3, s	2-H and 6-H,	8-H and 9-H,	2-H, 6-H, d	4-H, t		3-H, d	4-H, d	CH_3, s	
IIIa	1,67	2,87, 3,03	6,23, 6,45	7,17	7,30		6,23	5,80	2,18	3,23 (1H, d, CH_2); 3,33 (1H, d, CH_2); J – 3,0
IIIb	1,63	2,83, 3,07	6,27, 6,45	7,17	7,30	3,55 q	6,22	5,82	2,18	1,23 (3H, d, CH_3); $J_{CH,CH3}$ – 7,0
IIIc	1,87	3,29, 3,74	6,30, 6,58	7,10	7,36	4,94	6,15, 6,23	5,80, 5,95	2,27, 2,31	
IIId	1,85	3,14, 3,30	6,32, 6,50	7,07	7,38	4,82	6,20	5,87	2,22	7,38 (2H, d, 8,5); 7,50 (2H, d, 8,5)
IIIe	1,85	3,14, 3,30	6,33, 6,50	7,09	7,37	4,82	6,20	5,89	2,22	7,34 (2H, d, 8,5); 7,44 (2H, d, 8,5)
IIIf	1,89	3,34, 3,95	6,23 (s)	7,10	7,37	4,90	6,24	5,93	2,28	7,24...7,36 (3H, m); 7,44...7,55 (2H, m)
IIIg	1,87	3,13, 3,38	6,32, 6,53	7,10	7,38	4,82	6,20	5,87	2,21	2,38 (3H, s, CH_3); 7,18 (2H, d, 8,0); 7,36 (2H, d, 8,0)
IIIh	1,84	3,32, 3,93	6,18, 6,30	7,10	7,36	5,62	6,24	5,90	2,26	3,87 (3H, s, OCH_3); 6,58...6,97 (2H, m); 7,23 (1H, d.d.d, 1H); 7,50 (1H, d.d)
IIIi	1,92	3,18, 3,51	6,30 (s)	7,13	7,37	4,88	—	—	—	7,19...7,40 (6H, m); 7,53...7,64 (4H, m)
IVa[4*]	1,69	3,10, 3,21	6,40, 6,61	7,48	7,53	—	—	—	—	2,95 (2H, s, CH_2)
IVb[5*]	1,63	2,97, 3,13, 3,21, 3,29	6,42, 6,49, 6,51, 6,87	7,33, 7,60	7,65, 7,72	cl.	—	—	—	1,21 (3H, d, CH_3)

[1*] For compounds IIIa, b and IVa, b $J_{2,6}$ = 6.5; for the remaining ones, 7.7; for all compounds except IIIf, i, $J_{8,9}$ = 5.5 Hz.

[2*] $J_{2,4(4,6)}$ = 2.0 Hz.

[3*] Signals for which no assignment is indicated pertain to aromatic protons; the coupling constants for them are given in parentheses.

[4*] Spectrum recorded in D_6-acetone.

[5*] Spectrum recorded in D_6-DMSO.

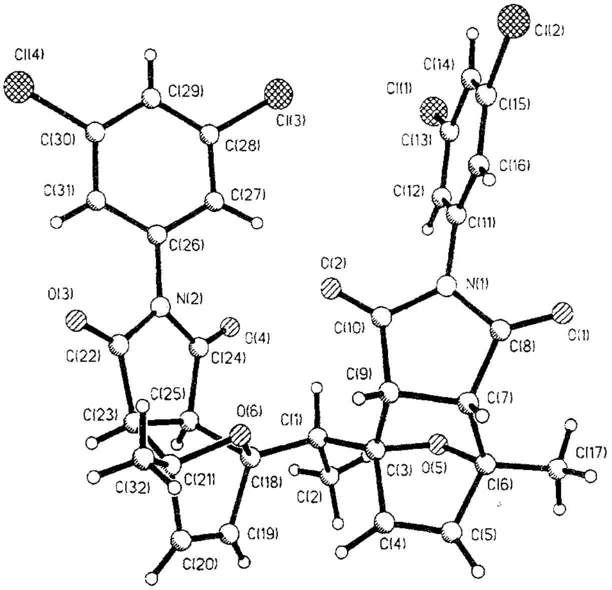


Fig. 1. Projection of the 3-D molecule of gem-bis{4-aza-7-methyl-10-oxa-4-(3,5-dichlorophenyl)tricyclo[5,2,1,0]deca-8-ene-3,5-dion-1-yl}ethane IVb.

TABLE 3. Mass Spectra of Compounds IIIc, f, and IVc

Compound	m/z (I, %)*
IIIc	256 (87), 255 (17), 245 (13), 244 (13), 243 (69), 242 (13), 241 (100), 214 (44), 213 (65), 206 (13), 199 (22), 198 (13), 197 (22), 187 (13), 185 (13), 175 (44), 172 (13), 171 (65), 143 (22), 124 (13), 105 (17)
IIIf	493 (2)**, 253 (57), 252 (89), 251 (33), 245 (31), 244 (22), 243 (62), 242 (31), 241 (100), 237 (26), 211 (13), 210 (40), 209 (53), 208 (15), 206 (29), 197 (20), 197 (18), 195 (22), 194 (20), 192 (11), 191 (15), 187 (27), 185 (27), 181 (18), 178 (13), 176 (31), 175 (49), 174 (11), 173 (16), 171 (27), 168 (18), 166 (27), 165 (37), 152 (18), 150 (13), 128 (24), 127 (18), 126 (13), 124 (27), 115 (18), 105 (13), 77 (11)
IVc	256 (17), 255 (22), 245 (13), 244 (11), 243 (64), 242 (11), 241 (100), 214 (17), 213 (22), 206 (14), 199 (14), 197 (17), 187 (14), 185 (14), 175 (14), 171 (25), 124 (17)

*Peaks with I > 10% are shown.

**$M^{+\cdot}$ of low intensity.

adducts probably undergo retrodiene decomposition and are subsequently recorded as a mixture of the initial reactants. This is indicated by the presence in the mass spectra of $M^{+\cdot}$ peaks of maleimide (m/z 241 with 100% intensity in all three mass spectra), phenyldifurylmethane (m/z 252) and trifurylmethane (m/z 256) for compounds IIIf and IIIc, IVc, respectively. The fragmentation of polyfurylarylmethanes is consistent with the data of [4].

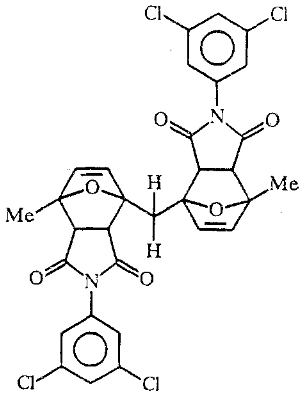
Of particular interest was the structure of diadduct IVb, since in both the PMR spectrum (see Table 2) and the IR spectrum (see Table 1), we observed a double set of signals characterizing the adducts. On the basis of the data cited, it was postulated that in this product, one of the 4,7-endoxotetrahydrophthalimide fragments has an exo configuration, and the other, an endo configuration. To establish the 3-D structure of compound IVb, a single crystal of the latter was subjected to x-ray diffraction analysis. The atomic coordinates and the values of the bond lengths and valence angles are given in Tables 4-6. A projection of a 3-D model of diadduct IVb is shown in Fig. 1. As follows from the data obtained, both indicated fragments of molecule IVb have a thermodynamically more stable exo configuration and differ only in the angle of development of the planes of the aromatic rings relative to the planes of the imide fragments, which form a 36° angle between the planes $C_{(26)}C_{(27)}C_{(28)}$-$C_{(29)}C_{(30)}C_{(31)}$ and $C_{(22)}C_{(23)}C_{(24)}C_{(25)}N_{(2)}$ and a 65° angle between the planes $C_{(11)}C_{(12)}C_{(13)}C_{(14)}C_{(15)}C_{(16)}$ and $C_{(10)}C_{(9)}C_{(7)}C_{(8)}N_{(1)}$.

TABLE 4. Coordinates of Nonhydrogen Atoms (Å × 10^4) and Temperature Factors ($Å^2$ × 10^3) in the Molecule of Compound IVb

Atom	*x*	*y*	*z*	*u*	Atom	*x*	*y*	*z*	*u*
$Cl_{(1)}$	5216(1)	458(1)	1261(1)	55(1)	$C_{(11)}$	2231(3)	2967(2)	1265(2)	31(1)
$Cl_{(2)}$	8(1)	639(1)	1658(1)	73(1)	$C_{(12)}$	3487(3)	2380(2)	1231(2)	35(1)
$Cl_{(3)}$	3860(1)	845(1)	4179(1)	78(1)	$C_{(13)}$	3649(3)	1237(2)	1311(2)	38(1)
$Cl_{(4)}$	1998(1)	1697(1)	8604(1)	59(1)	$C_{(14)}$	2598(3)	695(2)	1424(2)	41(1)
$O_{(1)}$	1538(2)	4487(1)	-461(1)	42(1)	$C_{(15)}$	1358(3)	1317(2)	1468(2)	40(1)
$O_{(2)}$	2334(2)	4309(1)	2889(1)	46(1)	$C_{(16)}$	1154(3)	2452(2)	1387(2)	35(1)
$O_{(3)}$	923(2)	5530(1)	6880(1)	51(1)	$C_{(17)}$	3011(3)	6576(2)	-1390(2)	51(1)
$O_{(4)}$	4826(2)	4599(1)	3882(1)	43(1)	$C_{(18)}$	3010(2)	6590(2)	3384(2)	31(1)
$O_{(5)}$	3548(2)	6320(1)	368(1)	34(1)	$C_{(19)}$	2931(3)	8182(2)	3453(2)	42(1)
$O_{(6)}$	1600(2)	6838(1)	3892(1)	31(1)	$C_{(20)}$	1881(3)	8474(2)	4357(2)	49(1)
$N_{(1)}$	2016(2)	4150(1)	1210(2)	31(1)	$C_{(21)}$	1259(3)	7452(2)	4888(2)	38(1)
$N_{(2)}$	2798(2)	4792(2)	5405(2)	32(1)	$C_{(22)}$	1869(3)	5656(2)	6025(2)	37(1)
$C_{(1)}$	3690(2)	6418(2)	2247(2)	31(1)	$C_{(23)}$	2288(3)	6739(2)	5443(2)	37(1)
$C_{(2)}$	5053(3)	6810(3)	1598(2)	50(1)	$C_{(24)}$	3837(2)	5183(2)	4478(2)	34(1)
$C_{(3)}$	2775(2)	6638(2)	1521(2)	28(1)	$C_{(25)}$	3546(2)	6420(2)	4396(2)	36(1)
$C_{(4)}$	2112(3)	7813(2)	1306(2)	37(1)	$C_{(26)}$	2795(2)	3644(2)	5744(2)	33(1)
$C_{(5)}$	1946(3)	7851(2)	316(2)	43(1)	$C_{(27)}$	3223(3)	2897(2)	4904(2)	42(1)
$C_{(6)}$	2482(3)	6702(2)	-123(2)	35(1)	$C_{(28)}$	3301(3)	1782(2)	5233(2)	46(1)
$C_{(7)}$	1371(2)	6009(2)	666(2)	29(1)	$C_{(29)}$	2928(3)	1394(2)	6360(2)	47(1)
$C_{(8)}$	1631(2)	4824(2)	362(2)	31(1)	$C_{(30)}$	2474(3)	2166(2)	7174(2)	40(1)
$C_{(9)}$	1598(2)	5948(2)	1817(2)	28(1)	$C_{(31)}$	4212(2)	3286(2)	6891(2)	35(1)
$C_{(10)}$	2024(2)	4739(2)	2084(2)	31(1)	$C_{(32)}$	-234(3)	7602(2)	5538(2)	54(1)

Thus, the doubling of the signals in the spectra of compound IVb can probably be explained by steric hindrances caused by the presence in the molecule of a methyl group and a central carbon atom, which apparently are preserved in the solution as well.

Based on the spectral data for the molecule of diadduct IVa, one should expect a symmetric structure such as the one given below:



IVa

EXPERIMENTAL

The PMR spectra were recorded by means of a Bruker AC-200 instrument with a TMS internal standard. The IR spectra were taken in Vaseline oil with a Specord M-80 instrument. The mass spectra were obtained by means of a Varian MAT-112 mass spectrometer with direct introduction of the sample into the ion source. The energy of the ionizing electrons was 70 eV. The temperature of the ionization chamber was 120-200°C.

TABLE 5. Bond Lengths in the Molecule of Compound IVb

Bond	l, Å	Bond	l, Å
$Cl_{(1)}$—$C_{(13)}$	1,739(3)	$Cl_{(2)}$—$C_{(15)}$	1,741(3)
$Cl_{(3)}$—$C_{(28)}$	1,739(3)	$Cl_{(4)}$—$C_{(30)}$	1,739(2)
$O_{(1)}$—$C_{(8)}$	1,208(3)	$O_{(2)}$—$C_{(10)}$	1,202(3)
$O_{(3)}$—$C_{(22)}$	1,202(3)	$O_{(4)}$—$C_{(24)}$	1,211(2)
$O_{(5)}$—$C_{(3)}$	1,449(2)	$O_{(5)}$—$C_{(6)}$	1,452(3)
$O_{(6)}$—$C_{(18)}$	1,438(3)	$O_{(6)}$—$C_{(21)}$	1,446(3)
$N_{(1)}$—$C_{(8)}$	1,395(3)	$N_{(1)}$—$C_{(10)}$	1,401(3)
$N_{(1)}$—$C_{(11)}$	1,435(3)	$N_{(2)}$—$C_{(22)}$	1,406(3)
$N_{(2)}$—$C_{(24)}$	1,404(3)	$N_{(2)}$—$C_{(26)}$	1,432(3)
$C_{(1)}$—$C_{(2)}$	1,534(4)	$C_{(1)}$—$C_{(3)}$	1,525(4)
$C_{(1)}$—$C_{(18)}$	1,522(3)	$C_{(3)}$—$C_{(4)}$	1,522(3)
$C_{(3)}$—$C_{(9)}$	1,570(4)	$C_{(6)}$—$C_{(5)}$	1,521(3)
$C_{(6)}$—$C_{(7)}$	1,574(3)	$C_{(6)}$—$C_{(17)}$	1,506(3)
$C_{(5)}$—$C_{(4)}$	1,313(4)	$C_{(7)}$—$C_{(8)}$	1,513(3)
$C_{(7)}$—$C_{(9)}$	1,541(4)	$C_{(9)}$—$C_{(10)}$	1,506(3)
$C_{(11)}$—$C_{(12)}$	1,379(3)	$C_{(11)}$—$C_{(16)}$	1,377(4)
$C_{(12)}$—$C_{(13)}$	1,388(3)	$C_{(13)}$—$C_{(14)}$	1,377(4)
$C_{(14)}$—$C_{(15)}$	1,377(4)	$C_{(15)}$—$C_{(16)}$	1,377(3)
$C_{(18)}$—$C_{(19)}$	1,526(3)	$C_{(18)}$—$C_{(25)}$	1,590(4)
$C_{(19)}$—$C_{(20)}$	1,308(3)	$C_{(20)}$—$C_{(21)}$	1,515(4)
$C_{(21)}$—$C_{(23)}$	1,572(4)	$C_{(21)}$—$C_{(32)}$	1,494(4)
$C_{(22)}$—$C_{(23)}$	1,514(3)	$C_{(23)}$—$C_{(25)}$	1,534(3)
$C_{(24)}$—$C_{(25)}$	1,500(3)	$C_{(26)}$—$C_{(27)}$	1,387(3)
$C_{(26)}$—$C_{(31)}$	1,390(3)	$C_{(27)}$—$C_{(28)}$	1,384(3)
$C_{(28)}$—$C_{(29)}$	1,377(4)	$C_{(29)}$—$C_{(30)}$	1,383(4)

The data of the ultimate analysis of the synthesized compounds for C, H, Hal, and N correspond to the calculated data.

X-ray Analysis of gem-bis{4-aza-7-methyl-10-oxa-4-(3,5-dichlorophenyl)-tricyclo[5,2,1,$0^{2,6}$]deca-8-ene-3,5-dion-1-yl}ethane (IVb). Colorless triclinic crystals of compound IVb of the composition $C_{32}H_{24}Cl_4N_2O_6$ were grown from a 3:2:1 acetonitrile–acetone–methylene chloride mixture; the unit cell parameters were: a = 10.647(2), b = 12.402(2), c = 12.576(2) Å, α = 82.50(1), β = 69.07(1), γ = 78.35(1)°, V = 1519.8(0.6) Å^3. Space group P-1, Z = 2. The unit cell parameters and intensities of 3249 independent reflections with I > 3σ(I) were obtained with a Syntex P1 automatic diffractometer without monochromator (Mo Kα radiation, $\theta/2\theta$ scanning up to $2\theta_{max}$ = 50°). The structure was identified by the direct method by means of the SHELXTL program system [5] and refined in the anisotropic approximation (isotropic for hydrogen atoms) up to divergence factors R = 0.030 and R_W = 0.034. (The coordinates of the hydrogen atoms can be obtained from the authors.)

The initial polyfuryl(aryl)methanes were obtained by the methods described in [6, 7].

4-Aza-7-methyl-10-oxa-4-(3,5-dichlorophenyl)tricyclo[5,2,1,$0^{2,6}$]deca-8-ene-3,5-dion-1-yl-bis(5-methyl-2-furyl)methane (IIIc). A solution of 2.56 g (0.01 mole) of tris(5-methyl-2-furyl)methane Ic and 2.41 g (0.01 mole) of N-(3,5-dichlorophenyl)maleimide IIc in 5 ml of acetone is kept at room temperature for 7 days. The precipitated crystals of product IIIc are filtered off and washed with a small amount of benzene. Yield, 3.14 g.

Compounds IIIa, b, d are similarly obtained. To isolate monoadducts IIIa, b, the corresponding diadducts IVa, b are filtered off first, then the mother liquor is evaporated, and the residue is recrystallized from hexane.

Bis{4-aza-7-methyl-10-oxa-4-(3,5-dichlorophenyl)tricyclo[5,2,1,$0^{2,6}$]deca-8-ene-3,5-dion-1-yl}methane (IVa). A solution of 0.88 g (0.005 mole) of bis(5-methyl-2-furyl)methane and 2.41 g (0.01 mole) of N-(3,5-dichlorophenyl)maleimide in 5 ml of acetone is boiled for 1 h. The crystals of product IVa precipitated on cooling of the reaction mixture are filtered off and washed with acetone. Yield, 2.1 g.

In the synthesis of diadduct IVb, the reaction mixture is boiled for 2 h, and in the case of diadduct IVc, for 12 h.

TABLE 6. Valence Angles in the Molecule of Compound IVb

Angle	ω, deg	Angle	ω, deg
$C_{(3)}O_{(5)}C_{(6)}$	97,2(2)	$C_{(18)}O_{(6)}C_{(21)}$	98,5(2)
$C_{(8)}N_{(1)}C_{(10)}$	113,2(2)	$C_{(8)}N_{(1)}C_{(11)}$	124,0(2)
$C_{(10)}N_{(1)}C_{(11)}$	122,4(2)	$C_{(22)}N_{(2)}C_{(24)}$	112,0(2)
$C_{(22)}N_{(2)}C_{(26)}$	124,6(2)	$C_{(24)}N_{(2)}C_{(26)}$	123,0(2)
$C_{(2)}C_{(1)}C_{(3)}$	110,9(2)	$C_{(2)}C_{(1)}C_{(18)}$	110,1(2)
$C_{(34)}C_{(1)}C_{(18)}$	112,2(2)	$O_{(5)}C_{(3)}C_{(1)}$	110,3(2)
$O_{(5)}C_{(3)}C_{(4)}$	101,5(2)	$C_{(1)}C_{(3)}C_{(4)}$	119,7(2)
$O_{(5)}C_{(3)}C_{(9)}$	99,6(2)	$C_{(1)}C_{(3)}C_{(9)}$	118,6(2)
$C_{(4)}C_{(3)}C_{(9)}$	104,0(2)	$O_{(5)}C_{(6)}C_{(5)}$	101,1(2)
$O_{(5)}C_{(6)}C_{(7)}$	100,1(2)	$C_{(5)}C_{(6)}C_{(7)}$	103,4(2)
$O_{(5)}C_{(6)}C_{(17)}$	111,3(2)	$C_{(5)}C_{(6)}C_{(17)}$	119,1(2)
$C_{(7)}C_{(6)}C_{(17)}$	118,8(2)	$C_{(6)}C_{(5)}C_{(4)}$	107,0(2)
$C_{(3)}C_{(4)}C_{(5)}$	106,4(2)	$C_{(6)}C_{(7)}C_{(8)}$	114,1(2)
$C_{(6)}C_{(7)}C_{(9)}$	101,7(2)	$C_{(8)}C_{(7)}C_{(9)}$	105,3(2)
$O_{(1)}C_{(8)}N_{(1)}$	124,2(2)	$O_{(1)}C_{(8)}C_{(7)}$	127,8(2)
$N_{(1)}C_{(8)}C_{(7)}$	108,0(2)	$C_{(3)}C_{(9)}C_{(7)}$	102,1(2)
$C_{(3)}C_{(9)}C_{(10)}$	113,3(2)	$C_{(7)}C_{(9)}C_{(10)}$	105,2(2)
$O_{(2)}C_{(10)}N_{(1)}$	123,3(2)	$O_{(2)}C_{(10)}C_{(9)}$	128,4(2)
$N_{(1)}C_{(10)}C_{(9)}$	108,3(2)	$N_{(1)}C_{(11)}C_{(12)}$	119,4(2)
$N_{(1)}C_{(11)}C_{(16)}$	118,5(2)	$C_{(12)}C_{(11)}C_{(16)}$	122,1(2)
$C_{(11)}C_{(12)}C_{(13)}$	117,8(3)	$Cl_{(1)}C_{(13)}C_{(12)}$	119,6(2)
$Cl_{(1)}C_{(13)}C_{(14)}$	118,6(2)	$C_{(12)}C_{(13)}C_{(14)}$	121,8(2)
$C_{(13)}C_{(14)}C_{(15)}$	118,3(2)	$Cl_{(2)}C_{(15)}C_{(14)}$	118,7(2)
$Cl_{(2)}C_{(15)}C_{(16)}$	119,4(2)	$C_{(14)}C_{(15)}C_{(16)}$	121,9(3)
$C_{(11)}C_{(16)}C_{(15)}$	118,2(2)	$O_{(6)}C_{(18)}C_{(1)}$	112,2(2)
$O_{(6)}C_{(18)}C_{(19)}$	101,3(2)	$C_{(1)}C_{(18)}C_{(19)}$	120,7(2)
$O_{(6)}C_{(18)}C_{(25)}$	100,2(2)	$C_{(1)}C_{(18)}C_{(25)}$	116,8(2)
$C_{(19)}C_{(18)}C_{(25)}$	102,6(2)	$C_{(18)}C_{(19)}C_{(20)}$	106,2(2)
$C_{(19)}C_{(20)}C_{(21)}$	107,3(2)	$O_{(6)}C_{(21)}C_{(20)}$	101,1(2)
$O_{(6)}C_{(21)}C_{(23)}$	99,1(2)	$C_{(20)}C_{(21)}C_{(23)}$	104,6(2)
$O_{(6)}C_{(21)}C_{(32)}$	11,2(2)	$C_{(20)}C_{(21)}C_{(32)}$	117,9(2)
$C_{(23)}C_{(21)}C_{(32)}$	119,9(2)	$O_{(3)}C_{(22)}N_{(2)}$	124,5(2)
$O_{(3)}C_{(22)}C_{(23)}$	127,1(2)	$N_{(2)}C_{(22)}C_{(23)}$	108,4(2)
$C_{(21)}C_{(23)}C_{(22)}$	113,8(2)	$C_{(21)}C_{(23)}C_{(25)}$	102,3(2)
$C_{(22)}C_{(23)}C_{(25)}$	105,1(2)	$O_{(4)}C_{(24)}N_{(2)}$	124,4(2)
$O_{(4)}C_{(24)}C_{(25)}$	126,6(2)	$N_{(2)}C_{(24)}C_{(25)}$	108,9(2)
$C_{(18)}C_{(25)}C_{(23)}$	101,4(2)	$C_{(18)}C_{(25)}C_{(24)}$	114,8(2)
$C_{(23)}C_{(25)}C_{(24)}$	105,4(2)	$N_{(2)}C_{(26)}C_{(27)}$	118,7(2)
$N_{(2)}C_{(26)}C_{(31)}$	120,5(2)	$C(27)\,C_{(26)}C_{(31)}$	120,8(2)
$C_{(26)}C_{(27)}C_{(28)}$	118,5(2)	$Cl_{(3)}C_{(28)}C_{(27)}$	118,4(2)
$Cl_{(3)}C_{(28)}C_{(29)}$	119,1(2)	$C_{(27)}C_{(28)}C_{(29)}$	122,5(2)
$C_{(28)}C_{(29)}C_{(30)}$	117,3(2)	$Cl_{(4)}C_{(30)}C_{(29)}$	118,2(2)
$Cl_{(4)}C_{(30)}C_{(31)}$	119,2(2)	$C_{(29)}C_{(30)}C_{(31)}$	122,5(2)
$C_{(26)}C_{(31)}C_{(30)}$	118,3(2)		

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