66. D. P. Kunchuliya, N. I. Bekasova, and V. V. Korshak, Vysokomol. Soedin., A12, 1403 (1970).
67. D. P. Kunchuliya, V. V. Korshak, and N. I. Bekasova, Vysokomol. Soedin., A12, 2467 (1970).
68. É. M. Akovbyan, E. A. Chaikina, L. S. Gal'braikh, V. I. Bregadze, O. Yu. Okhlobystin, and and Z. A. Rogovin, Vysokomol. Soedin., B9, 566 (1967).
69. É. M. Akovbyan, E. A. Chaikina, L. S. Gal'braikh, V. I. Bregadze, O. Yu. Okhlobystin, and Z. A. Rogovin, Vysokomol. Soedin., B10, 428 (1968).
70. G. Markl. Angew. Chem., 78, 907 (1966).
71. A. I. Tolmachev and E. S. Kozlov, Zh. Obshch. Khim., 37, 1822 (1967).
72. C. L. Pedersen, Acta Chem. Scand., B29, 791 (1975).
73. M. P. Zhdanova, Master's Dissertation, Rostov State University, Rostov-on-Don (1980).
74. É. A. Zvezdina, M. P. Zhdanova, and G. N. Dorofeenko, Usp. Khim., 51, 817 (1981).
75. W. Kliegel, Pharmazie, 27, 1 (1972).
76. R. A. Nurgatroyd and B. T. Kelly, Atom. Energy Rev., 15, 3 (1977).
77. K. Nidenzu, Naturwissenschaften, 64, 378 (1977).
78. R. Thompson, Pure Appl. Chem., 39, 547 (1974).

POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES. 2.* TRIFURYLALKANES AND MECHANISM OF THEIR FORMATION

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Alkylfurans react with carboxylic acid anhydrides and chlorides in benzene in the presence of catalytic amounts of perchloric acid to give trifurylalkanes. The mechanism of the reaction, which is a consecutive process with the successive formation of an acylfuran, an alkyldifurylcarbinol, and a trifurylalkane, is examined. Intermediates, including an alkyldifurylcarbonium perchlorate, were isolated and characterized.

Of the trifurylalkanes, only 1,1,1-tri(5-methyl-2-furyl)ethane, which was isolated by one of us in collaboration with Shapiro [2] from the side products of the acetylation of α-methylfuran by the method in [3], has been described.

We obtained trifurylalkanes I-VIII by the reaction of alkylfurans with acetic anhydride or with caproyl and α-bromopropionyl chlorides in the presence of a catalytic amount of perchloric acid [4]. The most active 2-alkyl- and 2,4-dialkylfurans were used as the starting compounds. Considering the tendency of alkylfurans to undergo self-condensation in the presence of mineral acids, we carried out the reaction in benzene. This makes it possible to carry out the transformation regardless of the nature of the aggregate state of the substances and to obtain trifurylalkanes I and IV-VII in high yields (Tables 1, 2, and 4). The use of any halides leads to partial resinification and a decrease in the yields to 60% (II, III, and VIII). The corresponding 5-alkyl-2-acylfuran, the amount of which depends on the nature of the reagents, their ratio, and the order of mixing, is always formed as a side product.

The electronic spectra of trifurylalkanes I-VIII are similar to the UV spectra of alkylfurans but differ with respect to higher intensities.

The absorption bands of the alkyl substituents (1345-1470 cm^{-1} and characteristic vibrations of the furan ring are the most intense bands in the IR spectra of I-VIII.

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*See [1] for Communication 1.

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TABLE 1. Trifurylalkanes I-VIII

Compound	bp, °C (mm)	n_D^{20}	M*	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
I	240 (5)	1,5080	270	75,2	7,0	$C_{17}H_{18}O_3$	75,6	6,7	92
II	270 (1)	1,5480	363	60,1	5,0	$C_{18}H_{19}BrO_3$ †	59,5	5,2	60
III	280 (11)	1,5122	326	77,2	8,1	$C_{21}H_{26}O_3$	77,3	8,0	61
IV	267 (9)	1,4895	438	79,1	9,6	$C_{29}H_{42}O_3$	79,4	9,6	88
V	321 (11)	1,4892	522	80,7	10,4	$C_{35}H_{54}O_3$	80,5	10,3	87
VI	290 (9)	1,4950	480	79,7	10,0	$C_{32}H_{48}O_3$	80,0	10,0	83
VII	265 (3)	1,4955	564	81,2	10,6	$C_{38}H_{60}O_3$	80,9	10,6	81
VIII	260 (3)	1,4968	536	80,4	10,4	$C_{36}H_{56}O_3$	80,6	10,4	61

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*By cryoscopy in benzene (by mass spectrometry in the case of IV).

†Found: Br 21.7%. Calculated: Br 22.0%.

TABLE 2. Spectral Properties of Trifurylalkanes I-VIII

Compound	UV spectrum (ethanol)		IR spectrum, cm⁻¹			PMR spectrum, ppm		
	λ_{max}, nm	lg ε	$=CH_{fur}$	furan ring	furan ring vibrations	furan	$-\overset{\vert}{\underset{\vert}{C}}-CH_3$	substituent
I	229	4,31	3090	1600, 1510	1010	5,37 (m 6H)	1,85 (s 3H)	2,20 (s, 9H)
II	227	4,37	3100	1590, 1500	1020	—	—	—
III	223	4,41	3095	1605, 1503	1012	—	—	—
IV	228	4,35	3100	1560, 1520	1018	5,39 (m 6H)	1,82 (s, 3H)	2,42 (t, 6H); 1,22 (m, 18H); 0,85 (t, 9H)
V	230	4,34	3105	1620, 1560	1028	5,40 (m, 6H)	1,82 (s, 3H)	2,42 (t, 6H); 1,22 (m, 30H); 0,83 (t, 9H)
VI	226	4,36	3085	1660, 1570	1060	5,33 (s, 3H);	1,82 (s, 3H)	2,42 (t, 6H); 1,25 (m, 18H); 1,42 (m, 9H); 0,89 (t, 9H)
VII	227	4,35	3080	1620, 1560	1055	1,23 (m, 9H)		2,42 (t, 6H); 1,25 (m, 30H);
VIII	233	4,36	3095	1640, 1530	1040	5,35 (s, 3H)	1,82 (s, 3H)	1,42 (m, 9H); 0,89 (t, 9H)

The mass spectrum of 1,1,1-tri(5-n-pentyl-2-furyl)ethane (IV) does not contain a molecular ion (Table 3), and this indicates that the molecule is unstable with respect to electron impact (W_M = 0). Primary fragmentation gives stable ions with peaks with high intensities in the spectrum:

$$F_1 = F_2 = F_3 (\overset{+}{C}_9H_{13}O,\ m/z\ 137) \text{ and } F_4 = C_2H_3 + H = \overset{+}{C}_2H_4\ (m/z\ 28)$$

The $\overset{+}{C}_2H_4$ peak is the maximum peak. Secondary fragmentation of the resulting ions proceeds in the same way as the fragmentation of alkyl-substituted furans with retention of the charge on the alkyl or oxygen-containing fragment. In connection with the fact that there is a substituent with an alkyl chain in the 5 position, peaks with m/z 56 and 82, which are due to the McLafferty rearrangement [5], are present in the mass spectrum. (See scheme on next page.)

A peculiarity of the synthesis under consideration is its multistep character.* Acylation of the alkylfuran to give a ketone, which is alkylated (2) to give an alkyldifurylcarbinol by excess alkylfuran under the influence of acid, occurs in step (1). The carbinol is readily dehydrated (3) to give a carbonium ion, which reacts with yet another molecule of alkylfuran (4). In fact, it is sufficient to decrease the alkylfuran:anhydride ratio, and an 5-alkyl-2-acylfuran (50-80%) becomes the principal reaction product.

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*Ideas regarding the consecutive character of the reaction of furan with acetone were expressed by Brown and co-workers for the first time in [6] and were discussed by one of us [7] but were not confirmed experimentally.

TABLE 3. Characteristics of the Synthesized IX-XVII

Compound	mp,* °C	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm⁻¹		Found, %			Empirical formula	Calc., %			Yield, %
			OH	ClO_4	C	H	Cl		C	H	Cl	
IX	160	218 (4,00)	3444	—	67,1	5,6	—	$C_{10}H_{10}O_3$	67,4	5,62	—	93
X	138	226 (3,95)	3360	—	69,5	6,7	—	$C_{12}H_{14}O_3$	69,9	6,79	—	80
XI	360	245 (4,10)	3430	—	53,8	3,7	—	$C_{12}H_{10}O_7$	54,1	3,76	—	60
XII	260	249 (3,4)	3400	—	60,8	8,2	—	$C_{12}H_{12}O_5$	61,0	8,33	—	61
XIII	78—80†	432	—	1100	45,7	3,4	13,10	$C_{10}H_9ClO_6$	46,0	3,45	13,60	85
XIV	203—204†	286, 343	—	1093	50,2	4,5	11,91	$C_{12}H_{13}ClO_6$	49,9	4,51	12,30	90
XV	152,5—153†	203, 249, 338	—	1080	41,1	2,5	9,97	$C_{12}H_9ClO_{10}$	41,3	2,58	10,18	80
XVI	198†	204, 252, 341	—	1095	47,1	4,2	8,37	$C_{16}H_{17}ClO_{10}$	47,4	4,22	8,77	91
XVII	126—128†	213 (4,67), 294 (4,53), 349 (4,46) (H_2SO_4)	—	1090	46,3	3,8	10,40	$C_{13}H_{13}ClO_8$	46,9	3,90	10,68	78

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*Crystallization solvents: water for IX-XI, H_2SO_4 for XIII, and CH_3COOH for XIV-XVI.

†With fulmination.

TABLE 4. Mass Spectra of IV and XIV at an Electron Energy of 70 eV*

Compound	m/z values (relative intensities of the peaks in percent of the maximum peak)
IV	221 (3,1), 220 (2,0), 194 (4,1), 193 (24,5), 180 (5,1), 180 (5,1), 179 (29,6), 166 (3,1), 165 (10,2), 152 (4,1), 151 (10,2), 138 (11,2), 137 (51,0), 125 (6,1), 123 (10,2), 122 (2,0), 121 (7,1), 109 (14,3), 96 (4,1), 95 (25,5), 91 (3,6), 82 (6,1), 81 (5,1), 71 (3,6), 69 (11,2), 68 (4,1), 67 (9,2), 66 (6,1), 65 (6,1), 57 (4,1), 56 (3,1), 45 (5,1), 44 (16,3), 43 (51,0), 42 (4,1), 41 (23,5), 40 (5,6), 39 (14,8), 32 (21,9), 31 (4,1), 30 (4,1), 29 (8,2), 28 (100)
XIV	190 (14,7), 189 (19,1), 188 (98,5), 187 (23,5), 175 (27,9), 173 (23,5), 162 (2,9), 159 (13,2), 152 (4,4), 149 (13,2), 148 (4,4), 145 (45,6), 137 (4,4), 135 (5,1), 131 (8,8), 120 (5,9), 117 (13,2), 116 (5,9), 115 (12,5), 109 (7,3), 107 (5,9), 100 (5,1), 95 (5,1), 91 (14,7), 85 (35,3), 83 (60,3), 82 (32,3), 81 (20,6), 80 (4,4), 79 (11,8), 78 (10,3), 77 (20,6), 69 (16,2), 67 (17,6), 53 (23,5), 44 (44,0), 43 (100), 41 (20,6), 39 (23,5), 38 (11,8), 35 (11,8), 30 (8,8), 29 (25,0), 28 (54,4), 27 (35,3)

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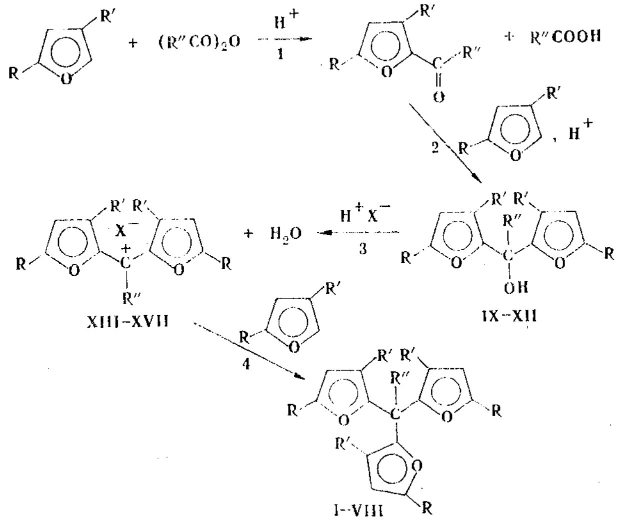
*The peaks with intensities >1% of the maximum peak are indicated.



X=ClO_4, R'=H, R''=CH_3; IX andXIII R=H; X and XIV R=CH_3; XI andXV R=COOH; XVI R=$COOC_2H_5$ and unsymmetrical — carbinol XII R=CH_3 and R=COOH, perchlorate XVIII R=CH_3 and R=$COOC_2H_5$

We isolated and characterized intermediates, viz., 5-alkyl-2-acylfurans and alkylbis-(5-alkyl-2-furyl)carbinols IX-XII (Tables 3 and 4) and also demonstrated the formation of alkylbis(5-alkyl-2-furyl)carbonium cations, which were isolated from the reaction mixture in the form of perchlorates XIII-XVII.

The electronic spectra of alkyldifurylcarbinols IX-XII are similar to the spectra of the starting furan compounds. The presence of a carboxy group conjugated with a furan ring in carbinols XI and XII gives rise to a 20-25 nm bathochromic shift of the absorption maximum as compared with methylbis(5-methyl-2-furyl)carbinol (X), the spectrum of which is similar to the spectra of the starting α-methylfuran and the corresponding triphenylalkane I, which differ only with respect to their intensities.

The UV spectra of perchlorates XIII-XVII are distinguished by the presence of several intense absorption bands that are shifted bathochromically to the boundary with the visible region; this constitutes evidence for an oriented conjugation system.

The IR spectra of alcohols IX-XII contain characteristic OH absorption at 3360-3444 cm^{-1} and a C—O band corresponding to a tertiary alcohol at 1220 cm^{-1} [8]. A markedly split intense band of a ClO_4^- ion (1090-1100 cm^{-1}) is observed in the spectra of perchlorates XIII-XVII, and characteristic absorption of a furan ring appears in the spectra without special changes.

The methylbis(5-carboxy-2-furyl)carbinol (XI) structure was confirmed by data from the PMR spectrum. The singlet at strong field (2.10 ppm) corresponds to the methyl group, and the 3-H and 4-H protons of the two furan rings give two doublets at 7.05 and 6.25 ppm. The spectrum also contains the signal of an OH proton at weaker field at 7.25 ppm.

The PMR spectrum of methylbis(5-methyl-2-furyl)carbonium perchlorate (XIV) contains a CH_3—C singlet at 2.73 ppm. The 3-H and 4-H protons of the furan rings are represented by doublets at 8.0 and 6.53 ppm, which constitutes evidence for the presence of positive charge on the methylene carbon atom. The protons of the CH_3 group attached to the furan ring give a singlet at 2.58 ppm.

A molecular-ion peak is absent in the mass spectrum of perchlorate XIV (Table 4). The intense peak with m/z 188 indicates dissociation of the molecule to give a stable $\overset{+}{C}_{12}H_{13}O_2$ primary ion (m/z 188) and a ClO_4^- ion (m/z 100). Its subsequent fragmentation takes place via a known pathway. The splitting out of a $CH_3\overset{+}{C}$ ion (m/z 27) and the formation of a C—C bond explain the appearance of the characteristic (for difuryl) peak with m/z 162, which then undergoes fragmentation to give C_5H_5O ions (m/z 81). A CH_3C fragment may also be ejected from the ion with m/z 173, as a result of which a peak with high intensity with m/z 145 and a doubly charged $\overset{++}{C}_4H_2O$ ion, which adds two H to give a stable particle with m/z 83, are present in the spectrum. The $\overset{+}{C}_3H_7$ ion (m/z 43), which has the maximum intensity in the spectrum ($\overset{+}{C}H_2C + CH_3 + H \rightarrow \overset{+}{C}_3H_7$), although it also is not characteristic for the given compound, is obtained by recombination of the individual fragments. The fragmentation of the furan ring proceeds typically with the formation of ions with m/z 39.29.

EXPERIMENTAL

The UV spectra were recorded with a Specord UV-vis spectrophotometer. The IR spectra were obtained with a UR-20 spectrometer. The PMR spectra were recorded with an RYa-203 spectrometer (60 MHz) from the Special Design Office of Analytical Instrument Making of the Academy of Sciences of the USSR. The mass spectra were obtained with a Varian MAT CH-6 spectrometer with a system for direct introduction of the samples into the ion source at 100 and 120°C and an ionizing voltage of 70 eV.

1,1,1-Tri(5-n-pentyl-2-furyl)ethane (IV). A mixture of 0.2 ml of 58% perchloric acid in 15.3 g (0.15 mole) of acetic anhydride was added dropwise with vigorous stirring in the course of 30 min to a heated (to 80°C) solution of 25.2 g (0.15 mole) of 2-n-pentylfuran in 60 ml of benzene, and the mixture was stirred at this temperature for 2 h. It was then cooled, washed with 5% sodium carbonate solution, and dried with anhydrous Na_2SO_4. The solvent was removed, and the residue was fractionated in vacuo with collection of the fraction with bp 267°C (9 mm). The yield was 22.8 g (88%). Compounds I-VIII were obtained by a similar method.

Methylbis(5-carboxyl-2-furyl)carbinol (XI). A) A 0.2-ml sample of 58% perchloric acid was added with stirring to heated (to 80°C) solution of 15.4 g (0.1 mole) of 5-carboxyl-2-

acetylfuran in 50 ml of benzene, after which a solution of 22.4 g (0.2 mole) of furan-2-carboxylic acid in benzene was added dropwise in the course of 15 min, and the reaction mixture was stirred at this temperature for 8 h. It was then cooled and poured into 200 ml of water, and the organic layer was separated. The aqueous layer was evaporated to one third of its original volume and subjected to steam distillation until the condensate was neutral. The residue in the distilling flask was evaporated to give 16 g (60%) of colorless crystals with mp 360°C (from water).

B) A solution of 61.2 ml (0.3 mole) of acetic anhydride and 0.1 ml of 58% of perchloric acid in 50 ml of benzene was heated to 80°C, and a solution of 22.4 g (0.2 mole) of furan-2-carboxylic acid in the minimum volume of benzene was added dropwise with vigorous stirring. The reaction mixture was stirred at this temperature for 8 h, after which it was cooled and worked up as in method A to give 13.5 g (50%) of carbinol XI.

LITERATURE CITED

1. V. G. Kul'nevich, S. V. Zhuravlev, and L. A. Solonenko, Khim. Geterotsikl. Soedin., No. 4, 450 (1983).
2. Yu. M. Shapiro and L. A. Solonenko, in: The Chemistry and Technology of Furan Compounds [in Russian], Vol. 66, Krasnodar (1975), p. 88.
3. G. N. Dorofeenko, V. I. Karban, L. V. Dulenko, and V. N. Novikov, Izv. Vyssh. Uchebn. Zaved., Khim. Tekhnol., 7, 432 (1974).
4. V. G. Kul'nevich, L. A. Solonenko, and M. I. Ibragimov, USSR Inventor's Certificate No. 794018; Byull. Izobret., No. 1 (1981).
5. R. Silverstein, G. Bassler, and T. Morrill, Spectrometric Identification of Organic Compounds, Wiley (1974).
6. R. G. Ackman, W. H. Brown, and G. F. Wright, J. Org. Chem., 20, 1147 (1955).
7. Yu. M. Shapiro and V. G. Kul'nevich, in: The Chemistry and Technology of Furan Compounds [in Russian], Vol. 66, Krasnodar (1975), p. 75.
8. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 138.

POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

3.* SYNTHESIS OF DERIVATIVES OF DIFURYLPHENYL- AND TRIFURYLMETHANE

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Previously unknown difurylphenyl- and trifurylmethanes were obtained by the reaction of aromatic and heteroaromatic aldehydes with furan derivatives in benzene in the presence of perchloric acid.

Heating pyromucic acid esters with nitrofurfural or benzaldehydes in concentrated sulfuric acid [2, 3] and in a mixture of the latter with acetic acid [4] leads to difurylphenyl- or trifurylmethanes, but their yields are low, and the assortment is limited. The reaction of oxo compounds with α-methylfuran without a solvent [5] does not make it possible to use crystalline reagents, while the condensation of ethyl furoate with furfural diacetate in the presence of sulfuric acid in benzene [6] gives a mixture of products, also in low yields.

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*See [1] for Communication 2.

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