7. R. Mat'yakubov, Yu. M. Mamatov, N. Kh. Mukhamadaliev, and E. G. Abduganiev, Khim. Geterotsikl. Soedin., No. 4, 462 (1979).
8. R. Mat'yakubov and Yu. M. Mamatov, Khim. Geterotsikl. Soedin., No. 7, 889 (1981).

POLYFURYL(ARYL)ALKANES AND THEIR DERIVATIVES.

1. SYNTHESIS OF TRI- AND TETRAFURYLMETHANES

V. G. Kul'nevich, S. V. Zhuravlev,
and L. A. Solonenko

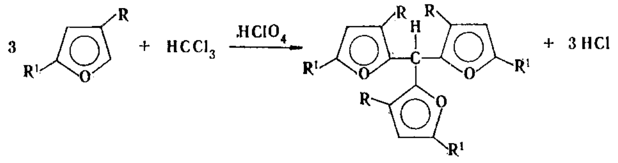
UDC 547.727.07:543.422.51

Derivatives of tri- and tetrafurylmethane were obtained by the reaction of alkylfurans with chloroform and carbon tetrachloride in benzene in the presence of catalytic amounts of 58% $HClO_4$.

Compounds of the furan series are widely used in industry, agriculture, and medicine, and the development of methods for the synthesis of compounds that contain several furan rings is therefore an important trend in the chemistry of heterocycles. Little study has been developed to tri- and tetrafurylalkanes, and methods for their synthesis have not been developed.

It is known that a substituted trifurylmethyl chloride is formed in the reaction of carbon tetrachloride with methyl pyromucate [1]. The preparation of polyfurylmethanes by alkylation of furan derivatives with donor substituents by means of chloroform and carbon tetrachloride has not been described. This is understandable, since the furan ring is readily destroyed by the action of protic and aprotic acids [2].

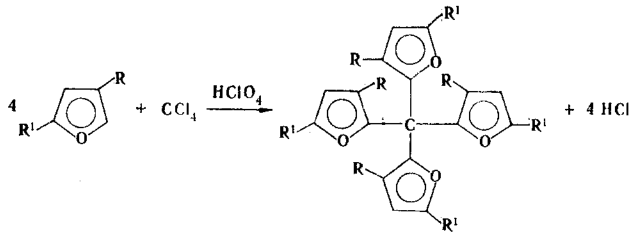
We have established that the reaction of alkylfurans with chloroform in benzene in the presence of catalytic amounts of 58% $HClO_4$ leads to the formation of trifurylmethanes in 75-87% yields.



I–V

I–IV R=H; I $R^1=CH_3$; II $R^1=C_4H_9$; III $R^1=C_5H_{11}$; IV $R^1=C_7H_{15}$; V $R=CH_3$, $R^1=C_7H_{15}$

The reaction of alkylfurans with CCl_4 under similar conditions makes it possible to obtain tetrafurylmethane derivatives in 78-87% yields.



VI–IX

R=H; VI $R^1=C_4H_9$; VII $R^1=C_5H_{11}$; VIII $R^1=C_7H_{15}$; IX $R=CH_3$, $R^1=C_7H_{15}$

Krasnodar Polytechnic Institute, Krasnodar 350006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 450-453, April, 1983. Original article submitted March 25, 1982.

TABLE 1. Tri- and Tetrafurylmethanes I-IX

Compound	bp, °C (mm)	n_D^{20}	d_4^{20}	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
I	38*	—	—	74,5	6,1	$C_{16}H_{16}O_3$	75,0	6,2	81
II	275—310(4)	1,5182	1,0730	79,0	9,1	$C_{25}H_{34}O_3$	78,5	9,0	78
III	305—320(3)	1,5078	1,0320	80,0	10,0	$C_{28}H_{40}O_3$	79,2	9,5	75
IV	270—300(2)	1,4837	0,9542	80,4	10,4	$C_{34}H_{52}O_3$	80,3	10,2	81
V	290—320(2)	1,4981	0,9267	80,7	10,7	$C_{37}H_{58}O_3$	80,7	10,5	87
VI	307—312(3)	1,5183	1,0360	79,1	8,9	$C_{33}H_{44}O_4$	78,5	8,8	86
VII	310—325(3)	1,5146	1,0070	80,1	10,0	$C_{37}H_{52}O_4$	79,3	9,3	81
VIII	290—320(2)	1,5013	0,9624	81,0	10,5	$C_{45}H_{68}O_4$	80,3	10,2	78
IX	205—240(0,6)	1,4956	0,9345	81,1	9,7	$C_{49}H_{76}O_4$	80,7	10,5	87

*This is the melting point, °C.

The electronic spectra of tri- and tetrafurylmethanes contain absorption maxima at 220-231 nm. The forms of the absorption curves are virtually identical, but the bands have different intensities. As noted in [3], the extinction coefficients increase as the number of furan rings in the molecules increase. This is associated with the fact that, because of the absence of conjugation between the furan rings, the principal chromophore is the furan ring (Table 2).

The IR spectra of II-IX are characterized by a band of medium intensity of the pulsation vibrations of the furan ring at 1020-1030 cm^{-1}. All of the remaining absorption bands have low intensities. Typical frequencies related to the stretching vibrations of the C—H bond of the furan ring (3110-3119 cm^{-1}), a double bond (1612-1620 cm^{-1}), and the ring as a whole (two bands at 1571-1575 and 1462-1473 cm^{-1}) are presented in Table 2. The IR spectrum of trifurylmethane I is of greatest interest. All of the absorption bands of this compound have high intensities and are well resolved. The band corresponding to the ring pulsation vibrations is split into three bands at 995, 1010, and 1030 cm^{-1}. The assignment of the frequencies of the vibrations of the various groups in tri- and tetrafurylmethanes is in agreement with [4, 5].

The signals of the β protons of the furan rings in the PMR spectra are shifted to the stronger-field region (5.6-5.8 ppm) as compared with the signals of monosubstituted furans [6]. The 3-H and 4-H protons in I-IV are equivalent and resonate in the form of double doublets at 5.74-5.77 and 5.64-5.66 ppm (Table 2). The signals of the β protons in the spectra of tetrafurylmethanes VI-VIII are two poorly resolved doublets at 5.68-5.69 and 5.64-5.66 ppm. The signals of 3-H protons vanish in the spectra of V and IX; singlets of protons of a methyl group appear in place of them at 1.50 and 1.51 ppm (this is not reflected in Table 2), i.e., at stronger field than in the case of 3-methylfuran (1.97 ppm) [7]. In the spectra of these compounds the 4-H protons give singlets at 5.56 and 5.64 ppm, respectivel The signals of the methylidyne protons in trifurylmethanes I-V are shifted to the weak-field region and are singlets at 5.15-5.30 ppm.

The signals of the protons of the alkyl substituents of II-IX are located in the stronger-field region. They can be united in three groups: signals of the protons attached to the α-carbon atom (triplet at 2.40-2.50 ppm), signals of terminal methyl groups (triplet at 0.80-0.83 ppm), and, finally, signals of protons of methylene groups (multiplet at 1.21-1.38 ppm).

The fragmentation of polyfurylmethanes under the influence of electron impact has not been described. We investigated the principles of the fragmentation of trifurylmethane I. We found that the stability of the molecule is high (W_M = 61%). Two groups of ions are recorded in the mass spectrum of this compound. The first group corresponds to splitting out of the $CH_3CO^{\cdot}$ radical, which is characteristic for most furans [8]. The subsequent fragmentation is accompanied by the formation of rearranged F_1, F_2, and F_3 ions. The second group of ions is associated with cleavage of the bond between the furan ring and the methane carbon atom. The stability of the resulting cation is due to the possibility of delocalization of the positive charge by conjugation with the aromatic system of furan rings.

TABLE 2. Spectral Properties of Polyfurylmethanes I-IX

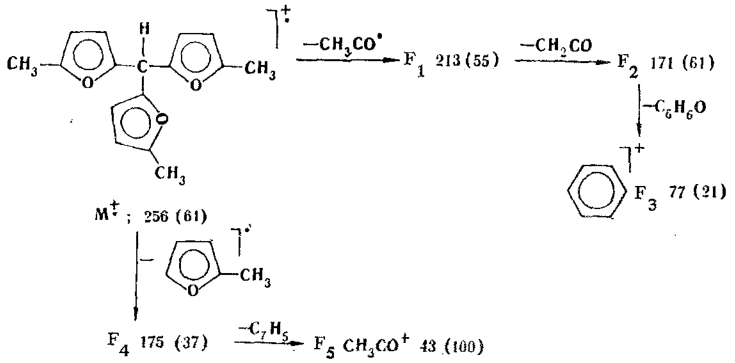
Compound	UV spectrum*		IR spectrum, cm^{-1}				PMR spectrum, ppm					
	λ_{max}, nm	lg ε	=CH	C=C	ring	ring pulsations	3-H	4-H	$>$CH	–CH_2	$(CH_2)_n$	CH_3
I	226	4,32	3112	1620	1571, 1462	1030, 1010, 995	5,77 d (3H)	5,69 d (3H)	5,15 s (1H)	2,16 s (9H)	—	
II	220	3,29	3118	1615	1575, 1473	1020	5,74 d (3H)	5,63 d (3H)	5,21 s (1H)	2,40 t (6H)	1,21 m (12H)	0,80 t (9H)
III	221	3,17	3119	1615	1575, 1473	1020	5,75 d (3H)	5,61 d (3H)	5,25 s (1H)	2,41 t (6H)	1,21 m (18H)	0,82 t (9H)
IV	227	3,31	3118	1612	1575, 1473	1020	5,75 d (3H)	5,60 d (3H)	5,30 s (1H)	2,48 t (6H)	1,21 m (30H)	0,83 t (9H)
V	231	3,15	3115	1613	1573, 1475	1021	—	5,56 s (3H)	5,30 s (1H)	2,48 t (6H)	1,21 m (30H)	0,84 t (9H)
VI	227	4,29	3110	1613	1575, 1471	1029	5,69 d (4H)	5,66 d (4H)	—	2,48 t (8H)	1,20 m (16H)	0,85 t (12H)
VII	229	4,27	3110	1612	1574, 1473	1028	5,69 d (4H)	5,65 d (4H)	—	2,48 t (8H)	1,20 m (24H)	0,85 t (12H)
VIII	230	4,22	3112	1614	1573, 1473	1028	5,68 d (4H)	5,64 d (4H)	—	2,50 t (8H)	1,21 m (40H)	0,83 t (12H)
IX	231	4,33	3115	1612	1575, 1473	1029	—	5,64 s (4H)	—	2,50 t (8H)	1,21 m (40H)	0,83 t (12H)

*Solvents: ethanol for I and VI-IX, and hexane for II-V.

TABLE 3. Mass Spectrum of Trifurylmethane I

M	m/z values (relative intensities of the ion peaks in percent relative to the maximum peak)*
256	256 (61), 214 (31,5), 213 (54,4), 199 (11,9), 175 (37), 172 (12,6), 171 (61), 143 (17), 131 (11,8), 129 (13,6), 128 (15,7), 115 (14,1), 77 (21), 53 (12,6), 44 (17,8), 43 (100)

*The peaks with relative intensities greater than 10% are presented.



EXPERIMENTAL

The IR spectra of thin layers of II-IX and a mineral oil suspension of I were recorded with a UR-20 spectrometer. The UV spectra of solutions in hexane (II, III) and ethanol were recorded with a Specord UV-vis spectrophotometer. The PMR spectra of solutions in CCl_4 were obtained with a Varian HA-100D spectrometer with hexamethyldisiloxane as the internal standard. The mass spectrum was recorded with a Varian MAT-6M mass spectrometer (70 eV).

Tris(5-H-butyl-2-furyl)methane (II). A 0.1-ml sample of 58% $HClO_4$ was added to a heated (to 60°C) solution of 18.6 g (0.15 mole) of n-butylfuran and 5 ml (0.06 mole) of chloroform in 100 ml of benzene, and the mixture was stirred for 2 h. It was then cooled, washed with 5% sodium carbonate solution, and dried with Na_2SO_4. The solvent was removed, and the residue was fractionated in vacuo with collection of the fraction with bp 275-310°C (4 mm). The yield was 15.5 g (81%). Compounds I and III-V were similarly obtained.

Tetra(5-H-butyl-2-furyl)methane (VI). A 0.1-ml sample of 58% $HClO_4$ was added to a heated (to 50°C) solution of 24.8 g (0.2 mole) of n-butylfuran and 5 ml (0.05 mole) of CCl_4 in 50 ml of benzene, and the mixture was stirred for 2 h. It was then cooled, washed with 5% sodium carbonate solution, and ried with Na_2SO_4. The solvent was removed, and the residue was fractionated in vacuo with collection of the fraction with bp 307-312°C (3 mm). The yield was 21.7 g (86%).

Compounds VII-IX were similarly obtained.

LITERATURE CITED

1. S. J. Pennanen, Acta Chem. Scand., 26, No. 5, 1981 (1972).
2. R. Elderfield (editor), Heterocyclic Compounds, Vol. 1, Wiley.
3. Yu. M. Shapiro and V. G. Kul'nevich, in: The Chemistry and Technology of Furan Compounds [in Russian], Krasnodar (1975), p. 75.
4. A. R. Katritsky and J. Lagowski, J. Chem. Soc., No. 2, 657 (1959).
5. R. A. Stepen' and T. V. Barakov, in: Research on the Chemistry of Wood [in Russian], Krasnoyarsk (1973), p. 112.
6. É. Ya. Lukevits (editor), Advances on the Chemistry of Furan [in Russian], Zinatne, Riga (1978), p. 19.
7. D. Miller, J. Chem. Soc., C, No. 1, 12 (1969).
8. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972), p. 140.