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.

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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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TABLE 1. Difurylphenyl- and Trifurylmethanes I-XVIII

Compound	bp, °C (mm)	n_D^{20}	d_4^{20}	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
I	163—165 (4)	1,5518	1,0978	81,0	6,5	$C_{17}H_{16}O_2$	80,9	6,4	91
II	200—205 (8)	1,5202	1,0000	82,4	8,8	$C_{23}H_{28}O_2$	82,1	8,4	76
III	215—220 (8)	1,5181	0,9985	82,5	8,4	$C_{25}H_{32}O_2$	82,4	8,9	74
IV	230—235 (8)	1,5141	0,9833	82,1	9,0	$C_{27}H_{36}O_2$	82,6	9,3	74
V	245—248 (8)	1,5118	0,9754	81,7	9,0	$C_{29}H_{40}O_2$	82,8	9,5	74
VI	259—260 (3)	1,5585	—	68,2	5,1	$C_{21}H_{20}O_6$	68,5	5,4	48
VII	45[a]	—	—	71,5	5,5	$C_{17}H_{15}ClO_2$[b]	71,2	5,3	76
VIII	52[a]	—	—	61,0	4,4	$C_{17}H_{15}BrO_2$[c]	61,7	4,6	92
IX	196—199 (4)	1,5597	1,1313	69,0	5,3	$C_{17}H_{15}NO_4$[d]	68,7	5,1	74
X	202 (4)	1,5678	1,2648	68,6	5,0	$C_{17}H_{15}NO_4$[d]	68,7	5,1	71
XI	78[a]	—	—	68,7	5,3	$C_{17}H_{15}NO_4$[e]	68,7	5,1	82
XII	55[a]	—	—	76,9	6,4	$C_{18}H_{18}O_3$	76,6	6,4	94
XIII	136 (5)	1,5271[f]	1,1245	75,0	6,0	$C_{15}H_{14}O_3$	74,4	5,8	81
XIV	170—174 (5)	1,5082	1,0283	77,4	8,4	$C_{21}H_{26}O_3$	77,3	8,0	78
XV	184—186 (5)	1,5038	1,0077	78,1	8,9	$C_{23}H_{30}O_3$	77,9	8,5	79
XVI	264—268 (13)	1,5002	0,9895	78,8	8,9	$C_{25}H_{34}O_3$	78,5	9,0	77
XVII	226—228 (5)	1,4978	0,9877	78,4	9,4	$C_{27}H_{38}O_3$	79,0	9,4	77
XVIII	38[a]	—	—	75,1	6,4	$C_{16}H_{16}O_3$	75,0	6,3	84

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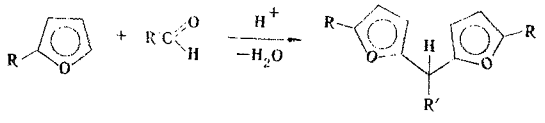
[a] Melting point. [b] Found: Cl 12.3%. Calculated: Cl 12.4%. [c] Found: Br 24.0%. Calculated: Br 24.1%. [d] Found: N 4.9%. Calculated: N 4.7%. [e] Found: N 4.5%. Calculated: N 4.7%. [f] This compound had n_D^{20} 1.5280 and bp 152°C (10 mm) [5].

We have established that the corresponding difurylphenyl- and trifurylmethanes I-XVIII are formed in high yields in the reaction of aromatic and heteroaromatic aldehydes with furan derivatives in benzene in the presence of catalytic amounts of 58% $HClO_4$ (Table 1).

Their UV spectra contain broad absorption bands at 226-231 nm as a result of superimposition of the absorption of the individual chromophore groups of the furan or phenyl fragments of the molecule.



I-XVIII

I—VI $R'=C_6H_5$; I $R=CH_3$; II $R=C_4H_9$; III $R=C_5H_{11}$; IV $R=C_6H_{13}$; V $R=C_7H_{15}$; VI $R=COOC_2H_5$; VII—XII $R=CH_3$; VII $R'=4\text{-}ClC_6H_4$; VIII $R'=4\text{-}BrC_6H_4$; IX $R'=2\text{-}NO_2C_6H_4$; X $R'=3\text{-}NO_2C_6H_4$; XI $R'=4\text{-}NO_2C_6H_4$; XII $R'=4\text{-}CH_3OC_6H_4$; XIII—XVI R'=2-furyl ; XIII $R=CH_3$; XIV $R=C_4H_9$; XV $R=C_5H_{11}$; XVI $R=C_6H_{13}$; XVII $R=C_7H_{15}$;
XVIII $R=CH_3$; R'=5-methyl-2-furyl

The IR spectra of these compounds contain bands at 3110-3145 cm⁻¹, which are characteristic for furan CH bonds, as well as bands at 3030-3080 cm^{-1} (I-XII), which are characteristic for the vibrations of phenyl CH bonds. Bands of stretching vibrations of aromatic (1593-1620 cm^{-1}) and heteroaromatic (1571-1575 and 1489-1506 cm^{-1}) rings are present at 1489-1620 cm^{-1}. Corresponding bands are present in the region of pulsation vibrations of the furan ring: two bands at 1010 and 1025-1029 cm^{-1} for molecules that contain two furan rings (VII-XII), and three bands at 995-996, 1002-1010, and 1012-1030 cm^{-1} for trifurylmethanes XIII and XVIII. This band is very intense and broadened in the spectrum of difurylphenylmethane VI. The spectra of VI and IX-XII contain corresponding bands of stretching vibrations of the substituents, viz., CO (1720, 1745 cm^{-1}) and NO_2 (1523-1542 and 1355-1366 cm^{-1}), as well as COC (1045 cm^{-1}).

The signal of the methylidyne proton in the PMR spectrum of IX "goes beyond" the signals of the furan protons to the weaker-field region and is recorded at 6.70 ppm (Table 2). This anomaly is evidently explained by the possibility of the formation of a hydrogen bond between this proton and the oxygen atom of the o-nitro group.

TABLE 2. Spectral Properties of Difurylphenyl- and Trifurylmethanes I-XVIII

Compound	UV spectrum		IR spectrum, cm^{-1}						PMR spectrum, ppm			
	λ_{max}, nm	lg ε	$=CH_{furan}$	$=CH_{phenyl}$	furyl ring	phenyl ring	furan ring pulsations	substituent	furyl	phenyl	≥CH (s)	substituent
I	230	4,14	3119	3038	1574, 1504	1620	1010, 1029	—	5,68 (s, 4H)	7,08 (s, 5H)	5,16	2,11 (s, 6H)
II	227	4,38	3118	3035	1576, 1506	1620	1021	—	5,63 (s, 4H)	7,03 (s, 5H)	5,13	0,81 (t, 6H); 2,48 (t, 4H); 1,44 (m, 8H)
III	227	4,37	3116	3038, 3073	1574, 1505	1619	1020	—	5,63 (s, 4H)	7,01 (s, 5H)	5,11	0,78 (t, 6H); 2,45 (t, 4H); 1,28 (m,12H)
IV	227	4,36	3115	3038, 3073	1573, 1502	1618	1021	—	5,63 (s, 4H)	7,01 (s, 5H)	5,12	0,78 (t, 6H); 2,45 (t, 4H); 1,21 (m,16H)
V	227	4,35	3114	3038, 3072	1573, 1503	1618	1022	—	5,63 (s, 4H)	7,03 (s, 5H)	5,12	0,78 (t, 6H); 2,45 (t, 4H); 1,18 (m,20H)
VI	263	4,46	3135	3035, 3070	1540, 1503	1602	1024	1720, 1745	6,50 (dd, 4H)	7,13 (m, 5H)	5,44	1,23 (t, 6H); 4,15 (q, 4H)
VII	224	4,37	3114	3038	1573, 1500	1620	1010, 1025	—	5,71 (s, 4H)	7,06 (dd, 4H)	5,14	2,13 (s, 6H);
VIII	225	4,31	3116	3040	1572, 1491	1620	1010, 1028	—	5,70 (s, 4H)	7,12 (dd, 4H)	5,11	2,16 (s, 6H);
IX	—	—	3115, 3145	3085	1573, 1489	1619	1010, 1029	1539, 1366	5,75 (s, 4H)	7,77 (m,1H); 7,29 (m,3H)	6,70	2,10 (s, 6H)
X	231	4,24	3115, 3145	3079	1573, 1489	1620	1010, 1029	1542, 1355	5,76 (s, 4H)	8,01 (m,1H); 7,41 (m,3H)	5,29	2,16 (s, 6H)
XI	223	4,26	3110, 3138	3050, 3080	1573, 1500	1608	1010, 1028	1523, 1364	5,78 (s, 4H)	7,65 (dd, 4H);	5,26	2,19 (s, 6H)
XII	230	4,40	3145	3050, 3080	1573, 1470	1620	1010, 1029	1045	5,66 (s, 4H)	6,81 (dd, 4H)	5,09	2,13 (s, 6H); 3,64 (s, 3H)
XIII	226	4,38	3119	—	1565, 1495	—	1012, 1002 995	—	5,78 (s, 4H); 6,05 (tt, 2H); 7,2 (m 1H)	—	5,21	2,16 (s, 6H)
XIV	227	4,23	3120	—	1573, 1512	—	1020	—	5,71 (s, 4H); 6,05 (tt, 2H); 7,21 (m, 1H)	—	5,25	0,88 (t, 6H); 1,51 (m,8H); 2,53 (t, 4H)
XV	227	4,25	3120	—	1573, 1512	—	1020	—	5,74 (s, 4H); 6,02 (tt, 2H); 7,23 (m,1H)	—	5,28	0,86 (t, 6H); 1,36 (m,12H); 2,53 (t, 4H)
XVI	227	4,29	3120	—	1573, 1512	—	1020	—	5,74 (s, 4H); 6,05 (tt, 2H); 7,23 (m, 1H)	—	5,28	0,85 (t, 6H); 1,25 (m,16H); 2,53 (t, 4H)
XVII	227	4,34	3120	—	1573, 1513	—	1019	—	5,74 (s, 4H); 6,05 (tt, 2H); 7,23 (m, 1H)	—	5,29	0,85 (t, 6H); 1,23 (m,20H); 2,54 (t, 4H)
XVIII	226	4,32	3114	—	1573, 1512	—	1030, 1010, 996	—	5,72 (dd, 6H)	—	5,15	2,16 (s, 9H)

EXPERIMENTAL

The UV spectra of solutions of the compounds in ethanol were recorded with a Specord UV-vis spectrophotometer. The IR spectra of thin layers or mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 were recorded with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

Bis(5-methyl-2-furyl)phenylmethane (I). A 0.1-ml sample of 58% $HClO_4$ was added to a refluxing solution of 10 ml (0.1 mole) of benzaldehyde in 80 ml of benzene, 25 ml (0.27 mole) of 2-methylfuran was then added dropwise, and the mixture was refluxed until 1.8 ml of water had been removed by distillation. 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 163-165°C (4 mm). The yield was 22.9 g (91%). Compounds II-XVIII were similarly obtained. In the synthesis of VI the furan component was added all at once. In the isolation of VII, VIII, XI, XII, and XVIII the residue obtained after removal of the solvent was purified by recrystallization from hexane.

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ACYLATION OF 2-AMINO-5-PHENYL-4-OXAZOLINONE AND 2-AMINO-4-IMIDAZOLINONES

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5:542.951.1:543.422.51

The acylation of 2-amino-5-phenyl-4-oxazolinone and 2-amino-1-methyl-4-imidazolinone with acetyl chloride in benzene in the presence of triethylamine leads to the formation of 2-acetamido-5-phenyl-4-oxazolinone and 2-acetamido-1-methyl-4-imidazolinone. The acylation of 2-amino-4-imidazolinone under the indicated conditions, as well as with acetic anhydride, gives 1-acetylimidazolidine-2,4-dione. 3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid) is formed as a side product in the acylation of 2-amino-4-azolinones with acetyl chloride in benzene in the presence of triethylamine. The IR and PMR spectra of the compounds obtained are presented.

It is known that 2-amino-4-thiazolinone [pseudothiohydantoin (I, X = S, R = H)] reacts readily with acetic anhydride to give a 2-acetyl derivative [1]; however, it is not acylated with acetyl chloride in benzene in the presence of triethylamine [2]. One might have assumed that the lack of a reaction in the latter case is explained by the peculiar acid-base properties of pseudothiohydantoin, which is an amphoteric compound with very weak acid (pK_a 11.7) and base (pK_a 2.1) functions [3]. The low basicity constitutes evidence that this compound is a very weak nucleophile, while the low acidity hinders its activation in acylation via a general-base-catalysis scheme; moreover, the pseudothiohydantoin anion has anomalously low nucleophilicity [2].

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