2,6-Diarylpyrylium Tetrafluoroborates (I-X). A mixture of 0.2 mole of the corresponding substituted acetophenone, 0.2 mole of ethyl orthoformate, and 0.3 mole of boron trifluoride etherate was stirred at 100°C for 15 min, after which it was cooled and diluted with a tenfold amount of ether, and the precipitate was removed by filtration, washed with ether, and dried. The salts were purified by reprecipitation from solution in acetone by the addition of ether or by recrystallization from acetic acid or alcohol.

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REACTIONS OF ARYLFURANS WITH ACETYLENEDICARBOXYLIC ACID

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A mixture of substances consisting of anhydrides of substituted phthalic acids (products of the diene synthesis) and 2-(5-aryl-2-furyl)but-2-ene-1,4-dioic acids (products of substitutive addition) is formed in the reaction of arylfurans with acetylenedicarboxylic acid.†

The diene synthesis of furan and its derivatives with acetylenic dienophiles that are activated by one electronegative group takes place in the presence of catalysts [2]. Ethylene dienophiles that have one electronegative grouping do not undergo the diene synthesis with furans and their homologs [3]. The reaction of furan with α,β-unsaturated aldehydes and ketones proceeds via a different pathway: substitutive addition takes place [3].‡

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*Deceased.

†The data on the two pathways of the reaction of arylfurans with acetylenedicarboxylic acid were presented by the authors at the 7th Symposium on the Chemistry of Heterocycles in Bratislava (September 1981) [1].

‡As the present paper was being prepared for publication, a communication [4] regarding the reaction of furan and its derivatives with diformylacetylene to give a mixture of substances consisting of Diels—Alder adducts and products of substitutive addition appeared.

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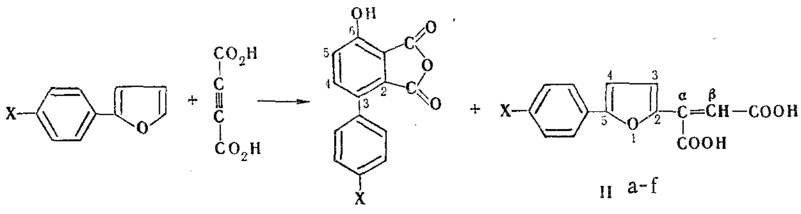
We have previously shown that dimethyl 3-aryl-3,6-endoxo-3,6-dihydrophthalates, which are converted to esters of 6-hydroxyphthalic acids by the action of acidic agents, are formed in the reaction of aryl- and arylhydroxyfurans with acetylenedicarboxylic ester [5].

In the present research we used acetylenedicarboxylic acid as the dienophile in the diene synthesis with arylfurans. We established that a mixture of products consisting of anhydrides of substituted phthalic acids (I) and 2-(5-aryl-2-furyl)but-2-ene-1-4-dioic acids (II) is formed in the reaction of arylfurans with this acid.



I a-f

II a-f

I-II a $X=NHCOCH_3$; b $X=CH_3$; c $X=OCH_3$ d $X=H$; e $X=Cl$; f $X=Br$

Anhydrides I are formed from 3-aryl-6-hydroxyphthalic acids, which are obtained, in turn, by aromatization of the adducts of arylfurans with acetylenedicarboxylic acid.

The formation of substitutive addition products II reveals an analogy with pyrrole. In a number of papers [6-8] it has been shown that substituents that increase the diene character of the pyrrole ring promote the diene synthesis, while, on the other hand, the introduction of substituents that diminish the diene character of pyrrole promotes substitutive addition. Similar conclusions [4] have been drawn relative to the dependence of the direction of the reaction of diformylacetylene with various dienes. In our opinion, the observed substitutive addition of acetylenedicarboxylic acid to arylfurans is also a consequence of the decrease in the diene character of the furan ring when an aryl residue is introduced into it.

According to the PMR data, the ratio of I and II in the unpurified product was ∿2:1* and did not depend on the solvent used; however, the latter did affect the amounts of isomers isolated in the individual state.

Signals of aromatic protons in the form of multiplets at 7.2-7.7 ppm were observed in the PMR spectra of 3-aryl-6-hydroxyphthalic acid anhydrides I. A signal of a methylidyne proton at 6.75-6.85 ppm, signals of furan protons in the form of two doublets with spin-spin coupling constant (SSCC) J_{34} = 3.5-3.8 Hz, and signals of protons of the benzene ring at 7.0-7.7 ppm were observed in the spectra of substitutive addition products II.

The configuration of II was established by means of the ^{13}C NMR spectra. It is known [9] that the $^{3}J_{H^{13}C=O}$ SSCC in the carbalkoxyethylene fragment is stereospecific: $^{3}J_{H^{13}C=O}$ ∿ 13-14 Hz for the trans orientation, whereas it is ∿6-7 Hz for the cis orientation. In the spectrum of IIa, $\delta_{\alpha\text{-COOH}}$ is 165.07 ppm and $^{3}J_{H\beta,\alpha\text{-COOH}}$ = 7.5 Hz, which corresponds to a transoid orientation of the acidic groups attached to the $C_\alpha{=}C_\beta$ bond. Acid II cannot be converted to the anhydride, and this conforms the trans configuration of II.

The structure of anhydrides I was also confirmed by their hydrolysis to the corresponding 3-aryl-6-hydroxyphthalic acids (III).

EXPERIMENTAL

Thin-layer chromatography (TLC) was carried out on Silufol UV-254 plates with development in UV light; the solvent system was benzene-dioxane-acetic acid (95:25:4). The NMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Varian XL-100 spectrometer with tetramethylsilane (TMS) as the internal standard.

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*When the reaction of arylfurans with acetylenedicarboxylic acid was carried out in a mixture of benzene with ether or with acetone, substituted phthalic acids and products of substitutive addition were identified in the reaction mixture by means of PMR spectroscopy prior to recrystallization.

TABLE 1. 3-Aryl-6-hydroxyphthalic Acid Anhydrides (Ia-f)

Compound	mp, °C (from acetic acid)	R_f	PMR spectrum, ppm			Aromatic protons, ppm	Found, %		Empirical formula	Calc., %		Yield, %
			4-H	5-H	CH_3		C	H		C	H	
I a	292—293	0,44	7,71	7,73	2,07	7,40—7,66	64,5	3,9	$C_{16}H_{11}NO_5$[a]	64,6	3,7	31
I b	225—227	0,85	7,69	7,38	2,37	7,25—7,44	70,7	3,9	$C_{16}H_{10}O_4$	70,8	3,9	31
I c	275—277	0,81	7,69	7,38	3,82	7,38—7,69	67,0	4,0	$C_{15}H_{10}O_5$	66,7	3,7	30
I d	197—199	0,80	7,72	7,40	—	7,39—7,57	69,7	3,3	$C_{14}H_8O_4$	70,0	3,3	58
I e	241—243	0,80	7,72	7,40	—	7,54	61,2	2,7	$C_{14}H_7ClO_4$[b]	61,2	2,6	37
I f	241—243	0,83	7,71	7,43	—	7,49—7,65	52,7	2,3	$C_{14}H_7BrO_4$[c]	52,7	2,2	44

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[a] Found: N 4.5%. Calculated: N 4.7%. [b] Found: Cl 12.9%. Calculated: Cl 12.9%. [c] Found: Br 25.4%. Calculated: Br 25.1%.

TABLE 2. 2-(5-Aryl-2-furyl)but-2-ene-1,4-dioic Acids (IIa-f)

Compound	mp, °C (from acetic acid)	R_f	PMR spectrum, ppm				$J_{H_3H_4}$, Hz	Found, %		Empirical formula	Calc., %		Yield, %
			H_β	3-H, 4-H	CH_3	aromatic protons, ppm		C	H		C	H	
IIa	198—200	0,25	6,74	6,89—7,01	2,06	7,64	3,8	60,6	4,1	$C_{16}H_{13}NO_6$[a]	61,0	4,1	40
IIb	185—186	0,83	6,76	6,94—7,02	2,34	7,24—7,63	3,6	66,3	4,5	$C_{15}H_{12}O_5$	66,2	4,4	40
IIc	178—179	0,58	6,76	6,88—6,97	3,8	7,00—7,68	3,5	62,1	4,1	$C_{15}H_{12}O_6$	62,1	4,2	16
IId	178—179	0,48	6,80	7,03		7,00—8,00	—[b]	65,2	4,1	$C_{14}H_{10}O_5$	65,1	3,9	23
IIe	196—198	0,50	6,82	7,02—7,09		7,48—7,74	3,6	57,3	3,1	$C_{14}H_9ClO_5$	57,4	3,1	7
IIf	197—198	0,71	6,83	7,06		7,64	—[b]	49,7	2,8	$C_{14}H_9BrO_5$	49,8	2,7	10

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[a] Found: N 4.5%. Calculated: N 4.4%. [b] The signals of the 3-H and 4-H protons form an AA' system; we were unable to determine $^3J_{3\text{-}H\text{-}4\text{-}H}$.

TABLE 3. 3-Aryl-6-hydroxyphthalic Acid (IIIa-c)

Compound	mp, °C	R_f	PMR spectrum, ppm[a]		Found, %		Empirical formula	Calc., %		Yield, %
			H_4	H_5	C	H		C	H	
III a[b]	300—302	0,19	7,35	7,05	61,3	4,1	$C_{16}H_{13}NO_6$[c]	61,0	4,1	69
III b	225—227	0,71	—	7,04	66,4	4,9	$C_{15}H_{12}O_5$	66,2	4,4	70
III c	275—277	0,70	7,33	7,03	62,1	4,3	$C_{15}H_{12}O_6$	62,2	4,2	43

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[a] The signals of the aromatic protons of the benzene ring in the 3 position are similar to the analogous signals in the spectra of the anhydrides (see Table 1). [b] Acids IIIb,c are converted to the anhydrides when they are melted. [c] Found: N 4.4%. Calculated: N 4.4%.

3-(Acetamidophenyl)-6-hydroxyphthalic Acid Anhydride (Ia). A suspension of 2 g (10 mmole) of 2-(p-acetamidophenyl)furan [5] and 1.1 g (10 mmole) of acetylenedicarboxylic acid in 20 ml of acetic acid was heated at 100°C for 2 h, after which the precipitated Ia (0.9 g) was removed by filtration. Anhydrides Ib-f were similarly obtained. The physicochemical constants of the compounds obtained are presented in Table 1.

2-{[5-(p-Acetamidophenyl)-2-furyl]}but-2-en-1,4-dioic Acid (IIa). A solution of 1.1 g (10 mmole) of acetylenedicarboxylic acid in 20 ml of a mixture of benzene and acetone (1:1) was added to a suspension of 2.0 g (10 mmole) of 2-(p-acetamidophenyl)furan in 20 ml of benzene, and the mixture was heated at 100°C. The resulting crystals, which were a mixture of I and II (1.5 g), were removed by filtration and recrystallized from acetic acid until they had a constant melting point (three times) to give 1.2 g of IIa. The mother liquor was evaporated, and the precipitate (0.4 g) was found to be a mixture of equal amounts of I and

II according to the PMR data. Acids IIb-f were similarly obtained. The physicochemical constants of the compounds obtained are presented in Table 2.

3-(p-Acetamidophenyl)-6-hydroxyphthalic Acid (IIIa). A 0.5-g sample of anhydride Ia was dissolved by heating in 5 ml of 10% NaOH, after which the solution was cooled and acidified with 2 N HCl. The resulting crystals were removed by filtration, washed with water, and dissolved in ether. The ether solution was dried over $CaCl_2$ and evaporated, and the precipitated IIIa was removed by filtration and washed with petroleum ether. Acids IIIb,c were similarly obtained. The physicochemical constants of the compounds obtained are presented in Table 3.

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PYRYLOCYANINES.

15.* BENZOPYRYLO-2-CYANINES

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Symmetrical 4,4'-diphenyl-substituted benzopyrylo-2-monomethylidyne, carbo-, and dicarbocyanines and their thio analogs, as well as unsymmetrical carbocyanines that contain, in addition to 4-phenylbenzopyrylium or 4-phenylbenzothiopyrylium rings, 3-ethylbenzothiazolium or 1,3,3-trimethyl-3H-indolium residues, were synthesized. The indicated dyes were more highly colored than their isomers that contain flavylium or thioflavylium residues. On the basis of the deviations calculated from the centers of the absorption bands it was concluded that the benzopyran residues in the dyes of the α series have greater electron donor character than those in the dyes of the γ series.

In the present research we set out to synthesize and investigate the color of benzopyrylo-2-cyanines, which, in contrast to the corresponding 4-substituted isomers [2], have not been investigated systematically. The synthesis of such dyes is fraught with certain difficulties because of the ease of self-condensation of 2-methylbenzopyrylium salts in the 4 position. This was evidently precisely the reason for the color ascribed to the 2-methylbenzopyrylium salt (λ_{max} 590 nm [3]). Considering the information stated above, we dealt with 4,4'-diphenyl-substituted dyes, of which only benzopyrylo-2-monomethylidynecyanine was previously known [4]. In the synthesis of the indicated dyes we used 2-methyl-4-phenylbenzopyrylium salts (I) [5] and benzothiopyrylium salts (II), as well as their analogs without substituents in the 2 position, viz., III and IV [6], respectively, and, in addition, 2-formylmethylene-4-benzopyran (V) and benzothiopyran (VI).

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*See [1] for communication 14.

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