SYNTHESIS OF 2,6-DIARYLPYRYLIUM TETRAFLUOROBORATES

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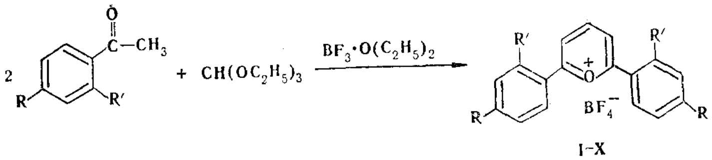
A number of previously unknown 2,6-diarylpyrylium tetrafluoroborates was obtained by the reaction of substituted acetophenones with ethyl orthoformate and boron trifluoride etherate.

Pyrylium salts have found extensive application as sensitizers of organic silverless photographic materials [1]. In order to search for new effective sensitizers we worked out a method for the synthesis of 2,6-diarylpyrylium tetrafluoroborates.

2,6-Diarylpyrylium salts can be obtained by cyclization of 1,5-dicarbonyl compounds of their derivatives in the presence of acidic catalysts and also by condensation of β-chloro carbonyl compounds with aromatic ketones or acetylenes [2]. These methods are inconvenient because they require several steps. In our opinion, the one-step condensation of orthoesters with aromatic ketones in the presence of acids is a more convenient method for the synthesis of 2,6-diarylpyrylium salts. Most of the pyrylium salts synthesized in this way have a perchlorate anion as the gegenion [3, 4]. Hydrochloric acid, HBr, HI, concentrated H_2SO_4, or Lewis acids such as $AlCl_3$, $FeCl_3$, and $SnCl_4$ have also been used as the acids [5, 6]; in [6] the sulfate anion of a pyrylium salt was exchanged for the tetrafluoroborate anion by means of an aqueous solution of sodium tetrafluoroborate, and 2,6-diarylpyrylium tetrafluoroborates with alkyl substituents in aryl rings containing six or more carbon atoms were isolated. The synthesis of 2,6-di(p-chlorophenyl)pyrylium tetrafluoroborate in 19% yield with the methanol complex of boron trifluoride as the Lewis acid was described in [7], while the synthesis of 2,6-diphenylpyrylium tetrafluoroborate in 63% yield from acetophenone, a six-fold excess of ethyl orthoformate, and a 48% aqueous solution of HBF_4 in acetic anhydride was described in [8].

We have synthesized a number of 2,6-diarylpyrylium tetrafluoroborates (I-X) by the reaction of the corresponding substituted acetophenones, ethyl orthoformate, and boron trifluoride etherate; reaction conditions that make it possible to use 0.2 mole (or more) of the aromatic ketone were selected.



The structure of salts I-X was confirmed by the results of elementary analysis (Table 1) and data from the IR and electronic spectra; the data from the IR spectra were in agreement with the literature data [9].

EXPERIMENTAL

The IR spectra of KBr pellets of the synthesized compounds were recorded with a UR-20 spectrometer. The electronic absorption spectra of solutions of the compounds in methylene chloride and acetone were recorded with an SF-4A spectrophotometer.

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TABLE 1. 2,6-Diarylpyrylium Tetrafluoroborates

Compound	R	R′	mp, °C	IR spectrum, cm^{-1}		Electronic absorption spectrum		Found, %		Empirical formula	Calculated, %		Yield, %
				pyrylium ring vibrations	BF_4^- vibrations	λ_{max}, nm (in CH_2Cl_2)	$\varepsilon_{max} \cdot 10^{-4}$ liter · cm^{-1} · $mole^{-1}$	C	H		C	H	
I [8]	H	H	203—205	1620, 1545, 1480	1060	415	2,8	63,8	4,2	$C_{17}H_{13}BF_4O$	63,8	4,1	52
II	CH_3	H	214—216	1630, 1545, 1480	1060	440	3,2	65,5	4,9	$C_{18}H_{15}BF_4O$	65,5	4,9	48
III	CH_3	CH_3	178—180	1630, 1545, 1480	1060	430	2,5	67,0	5,9	$C_{20}H_{17}BF_4O$	66,7	6,1	44
IV	OH	H	260—262	1610, 1540, 1485	1055	470	3,3	58,2	3,8	$C_{17}H_{13}BF_4O_3$	58,0	3,7	64
V	OCH_3	H	247—248	1630, 1540, 1480, 1430	1060	(in acetone) 485	3,7	60,3	4,5	$C_{19}H_{17}BF_4O_3$	60,0	4,5	84
VI	OC_2H_5	H	229—231	1620, 1540, 1470	1050	490	3,7	61,9	5,3	$C_{21}H_{21}BF_4O_3$	61,8	5,2	75
VII	F	H	238—240	1635, 1550, 1470, 1420	1060	410	2,7	57,3	3,1	$C_{17}H_{11}BF_6O$	57,3	3,1	62
VIII [7]	Cl	H	236—238	1630, 1550, 1475, 1410	1065	430	3,0	52,5	2,9	$C_{17}H_{11}BCl_2F_4O$	52,5	2,8	46
IX	Br	H	226—228	1630, 1545, 1470, 1405	1070	435	3,3	42,8	2,5	$C_{17}H_{11}BBr_2F_4O$	42,7	2,3	46
X	I	H	233—235	1690, 1600, 1570, 1485	1065	445	3,3	35,5	2,0	$C_{17}H_{11}BF_4I_2O$	35,7	1,9	65

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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