SYNTHESIS OF 2-METHYL-4,6-DIARYLPYRILIUM TETRAFLUOROBORATES

T. A. Markina and N. N. Boiko

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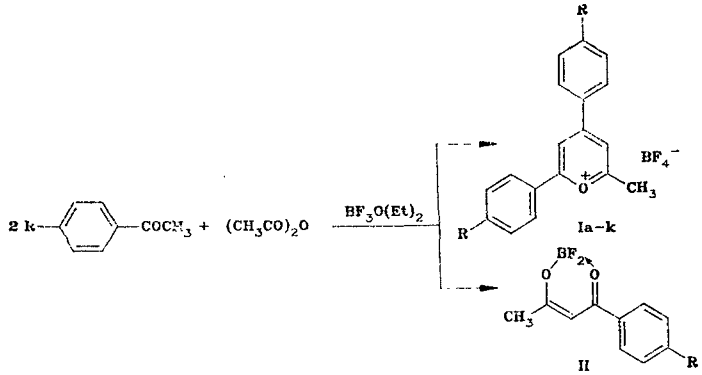
Condensation of acetophenones with acetic anhydride in the presence of boron trifluoride etherate has given some 2-methyl -4,6-diarylpyrilium tetrafluoroborates. The optimum conditions for the synthesis of 2-methyl-substituted pyrilium salts have been established.

Pyrilium salts with a methyl group in the 2 position are intermediates in the synthesis of various types of pyrilium dyes, which are of interest in many areas of science and technology [1, 2].

Methods are known for the synthesis of 2-methyl-substituted pyrilium salts involving the acylation of α,β-unsaturated and aromatic ketones in the presence of acidic catalysts. Most of the pyrilium salts obtained in this way contain perchlorate, tetrachloroferrate, or sulfate anions as the counterions [3], and there is little information on the synthesis of 2-methylpyrilium tetrafluoroborates [4, 5]. However, in view of their thermal stability, nonexplosive nature, and high solubility in organic solvents, the fluoroborates are preferred in practical applications.

The object of the present investigation was to develop a convenient method for the synthesis of 2-methyl-4,6-diarylpyrilium tetrafluoroborates. A method has beeen described [4] for the preparation of (I) by reacting aromatic ketones with acetic anhydride in the presence of boron trifluoride etherate. Under these conditions, a mixture of the pyrilium salts (I) and the boron complexes (II) are obtained, the yields of the salts being low.



We have examined the effects of the reaction conditions in the yields of the pyrilium tetrafluoroborates (Ia-j). It has been found found that when the amount of acetic anhydride is increased to more than 2 moles per mole of acetophenone, the yields are not increased, by an excess of boron trifluoride etherate decreases the yields of the desired products. Increasing the temperature and reaction time results in a decrease in the amounts of boron complexes formed, thereby increasing the yields of the pyrilium salts. The optimum conditions for the synthesis of the pyrilium salts were found to be boiling the reaction mixture of the substituted aromatic ketone, acetic anhydride, and boron trifluoride etherate (molar ratio 2:4:1.4) for 2 h. The course of the reaction with respect to the formation of pyrilium tetrafluoroborates is largely dependent on the nature of the substituent in the aromatic ring. For instance, the pyrilium salt containing a nitrogroup was obtained in 19% yield, whereas in the case of p-hydroxyacetophenone the yield of 2-methyl-4,6-di(p-hydroxyphenyl) pyrilium tetrafluoroborate reached 78%, no traces of the complex (II) being present. In the

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TABLE 1. 2-Methyl-4,6-diarylpyrilium Tetrafluoroborates

Compound	R	mp, deg C*	UV spectrum, λ_{max}, nm (log ε)	Found, %		Empirical formula	Found, %		Yield†, %
				C	H		C	H	
Ia	H	247—250	350 (4,57), 385 (4,62)	—	—	$C_{18}H_{16}BF_4O$	—	—	40,0 (31 [4])
Ib	CH_3	256—258	360 (4,38), 405 (4,51)	66,5	5,4	$C_{20}H_{19}BF_4O$	66,3	5,3	44,8
Ic	OH	216—217	355 (4,50), 400 (4,68)	—	—	$C_{18}H_{15}BF_4O_3$	—	—	78,2 (70 [4])
Id	OCH_3	239—240	370 (4,30), 420 (4,61)	61,1	5,1	$C_{20}H_{19}BF_4O_3$	61,0	4,9	40,0
Ie	OC_2H_5	239—241	385 (4,45), 450 (4,82)	—	—	$C_{22}H_{23}BF_4O_3$	—	—	38,0 (39 [5])
If	i-OC_3H_7	200—201	390 (4,31), 450 (4,73)	64,2	5,7	$C_{24}H_{27}BF_4O_3$	64,0	6,0	30,0
Ig	C_6H_5	267—269	445 (4,48)	74,4	4,8	$C_{30}H_{23}BF_4O$	74,1	4,8	40,0
Ih	Cl	266—268	360 (4,40), 400 (4,57)	—	—	$C_{18}H_{13}BCl_2F_4O$	—	—	42,6 (17 [4])
Ii	Br	263—265	365 (4,42), 405 (4,76)	43,6	2,8	$C_{18}H_{13}BBr_2F_4O$	43,9	2,7	46,3
Ij	NO_2	238—240	335 (4,52)	51,4	3,0	$C_{18}H_{13}BF_4N_2O_5$	51,0	3,1	19,3

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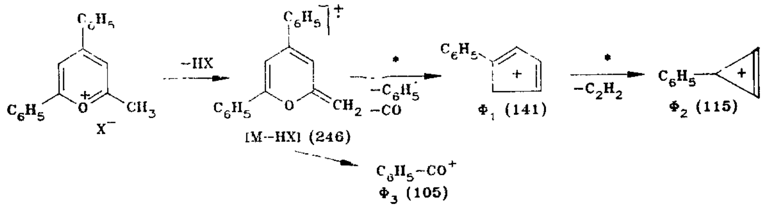
*Compounds (Ia–f) were crystallized from acetic acid, (Ig) from formic acid, (Ih) from acetic anhydride, and (Ii) from a mixture of acetic anhydride and acetic acid (1:1).

†Best yields previously obtained shown in brackets.

other cases, the reaction followed both possible courses.

Optimization of the reaction enabled the reaction time to be reduced from 24 [5] to 2 h, and the yields to be increased in some instances by a factor of 2.5 over those previously obtained (Table 1). In addition, a series of novel pyrilium tetrafluoroborates have been obtained.

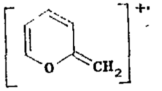
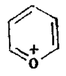
The structures of the products were confirmed by mass spectroscopy. The mass spectra of 2-methyl-4,6-diarylpyrilium salts have not hitherto been described. It has, however, been found [6] that a typical route for the breakdown of the 2-methyl-4,6-diphenylpyrilium ion may be represented as follows:



Similarly, for the pyrilium tetrafluoroborates examines (Ib, d, e, i, j), the major peak was that for the pyrilium salt fragment with loss of the anion BF_4 and one hydrogen atom of the methyl group $[M - HBF_4]^+$ (Table 2). These peaks had the greatest intensity, indicating the stability of the molecule to electron impact. In contrast to the salts which did not contain a substituent in the benzene ring, (I) showed a primary fissure due to the successive elimination of the aryl radical residues of the pyrilium nuclei to give the ions $[M - HBF_4]^+$ R]$^+$ and $[M - NBF_4 - 2R]^+$. The further degradation of the pyrilium salts is in accordance with the fragmentation sequence. Thus, the mass spectra contain peaks attributed to ions with structures analogous to the fragments Φ_1, Φ_2, Φ_3, but containing substituents (R) in the benzene ring. The possibility of subsequent fission of the radical is confirmed by the presence of peaks for fragments with m/z 140, 114, and 104. In addition to these peaks, peaks corresponding to the pyrilium cation and methylenepyran are common to the whole series [7].

The UV absorption spectra of (Ia–j) show that the introduction of electron donor substituents into the aryl nucleus results in a bathochromic shift of the absorption maximum in comparison with 2-methyl-4,6-diphenylpyrilium tetrafluoroborate. The absorption maxima of the compound with an electron-acceptor group (nitro) occurs at a shorter wavelength. The wavelengths of the absorption maxima of pyrilium salts containing halo, hydroxy, or

TABLE 2. Mass Spectra of (I)

Compound	m/z Values (relative intensity of peaks for characteristic fragments as % of the maximum)										
	$[M-HBF_4]^{+\cdot}$	$[M-HBF_4-R]^+$	$[M-HBF_4-2R]^+$	$[R-C_6H_4-C_5H_4]^+$	$[R-C_6H_4-C_3H_2]^+$	$[C_6H_4-C_5H_4]^+$	$[C_6H_4-C_3H_2]^+$	$[R-C_6H_4-CO]^+$	$[C_6H_4-CO]^+$		
Ib	100 (274)	32,5 (259)	14,5 (244)	12,1 (155)	16,8 (129)	11 (140)	11 (114)	24 (119)	7,2 (104)	8,4 (94)	9,6 (81)
Id	100 (306)	7,6 (275)	7,6 (244)	7,5 (171)	5,1 (145)	5,7 (140)	6,3 (114)	26,6 (135)	—	7,6 (94)	10,1 (81)
Ie	100 (333)	14,8 (288)	15,7 (244)	10,2 (185)	13,9 (159)	44,4 (140)	3,7 (114)	—	5,6 (104)	26,9 (94)	4,6 (81)
Ii	100 (404)	7,4 (324)	12,2 (244)	—	—	11,2 (140)	4,1 (114)	5,6 (184)	2,6 (104)	4,8 (94)	6,3 (81)
Ij	100 (337)	29,8 (291)	40 (244)	16,4 (186)	15,1 (160)	15,5 (140)	40 (114)	38,7 (150)	40 (104)	21,8 (94)	6,7 (81)

methyl groups as substituents occupy an intermediate position, ranging from 400 to 405 nm.

EXPERIMENTAL

The UV spectra were obtained on an SF-4A instrument (in methylene chloride); the mass spectra, under standard electron impact conditions (ionizing voltage 70 eV, cathode emission current 300 μA, accelerating voltage 3 kV) on a Varian MAT-311A. The course of the reactions was followed and the purity of the compounds obtained were determined by TLC on Silufol UV-254 plates in the system acetic acid—chloroform—nitromethane (1:1:1).

General Method of Synthesis of 2-Methyl-4,6-diarylpyrilium Tetrafluoroborates (Ia-j). A mixture of 0.2 mole of the substituted acetophenone, 0.4 mole of acetic anhydride, and 0.14 mole of boron trifluoride etherate was boiled for 2 h (in the case of (Ih), for 1 h). The hot reaction mixture was poured into 300 ml of ethyl acetate, and boiled for 5 min. The insoluble solid was filtered off and washed on the filter with boiling ethyl acetate until all the complex (II) had been removed (chromatographic analysis). The product was recrystallized from an appropriate solvent. The properties of (Ia-j) are given in Table 1.

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