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REACTIONS OF ACETOPHENONES AND BORON TRIFLUORIDE ETHERATE IN THE PRESENCE OF HOMOLOGS OF ORTHOFORMIC ESTER

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It was established that homologs of orthoformic ester (orthoacetic and orthopropionic esters), in contrast to it, do not undergo reaction with substituted acetophenones and boron trifluoride etherate to give γ-alkylpyrylium salts; the products obtained are 2,4,6-triarylpyrylium tetrafluoroborates.

It is known that pyrylium salts with an active methyl group are starting compounds for the synthesis of a number of polymethine dyes. The preparation of 2,6-diarylpyrylium tetrafluoroborates [1] via the Dorofeenko–Mezheritskii reaction [2] from substituted acetophenones, orthoformic ester, and boron trifluoride etherate, has been described in the literature.

In the present research we set out to ascertain the possibility of the use of homologs of orthoformic ester in the Dorofeenko–Mezheritskii reaction for obtaining pyrylium tetrafluoroborates I with an active methyl or methylene group in the 4 position of the pyrylium ring.

A mixture of the corresponding substituted acetophenone, orthoacetic or orthopropionic ester, and boron trifluoride etherate was heated for 1 h on a boiling-water bath. At the end of the process, from the reaction mass, by the usual methods, we isolated crystalline reaction products which, on the basis of the IR spectral data, can be classified as pyrylium salts. However, the PMR spectra indicated the absence of a methyl group in the pyrylium

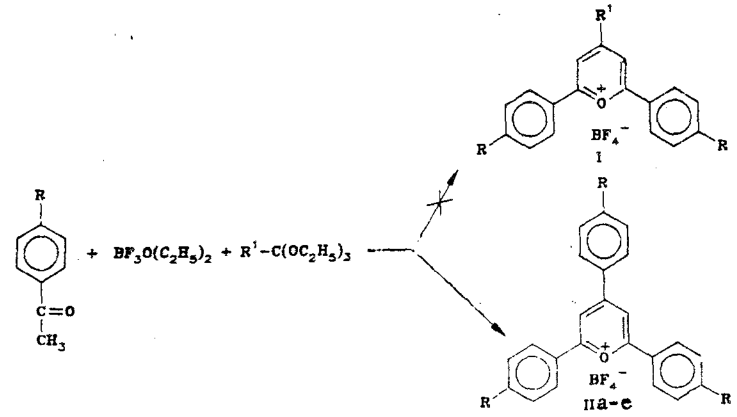

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TABLE 1. 2,4,6-Triarylpyrylium Tetrafluoroborates

Compound	R	T_{mp}, °C	IR spectrum, cm^{-1}		Electronic spectrum, λ_{max}, nm (log ε)	Mass spectrum, M^+
			pyrilium ring	BF_4^-		
IIa	H	251—252	1620, 1545, 1480	1060	370 (4,48); 420 (4,36)	309
IIb	CH_3	272—274	1630, 1545, 1480	1060	390 (4,65); 440 (4,46)	351
IIc	OCH_3	311—312	1630, 1540, 1485	1060	425 (4,81)	399
IId*	Cl	280—282	1635, 1550, 1470	1065	390 (4,40); 435 (4,23)	
IIe	C_6H_5	190—192	1690, 1570, 1485	1065	450 (4,72)	537

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*Found, %: C 55.52, H 2.73. $C_{23}H_{14}OBCl_3F_4$. Calculated, %: C 55.30, H 2.82.

ring. On the basis of the mass spectra of the isolated compounds, the electronic absorption spectra, and data on the melting points of these compounds and 2,6-diaryl-4-methylpyrylium tetrafluoroborates [3] and 2,4,6-triarylpyrylium tetrafluoroborates [4] it was established that orthoacetic and orthopropionic esters, in contrast to orthoformic ester, do not undergo condensation via the mechanism of the Dorofeenko—Mezheritskii reaction and that the isolated substances are 2,4,6-triarylpyrylium tetrafluoroborates IIa-e.

When thoroughly purified orthoacetic etherate was used, the yields of the reaction products were 11-43% based on acetophenone. However, the same final products were obtained in 7-10% yields when the reaction was carried out in the presence of orthopropionic ester, as well as in the absence of the orthoester.

The fact of the isolation of 2,4,6-triphenylpyrylium tetrafluoroborate in 10% yield in a study of the reaction of acetophenone with boron trifluoride etherate has been noted in the literature [5].

EXPERIMENTAL

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

2,6-Diphenyl-4-methylpyrylium Tetrafluoroborate. A Grignard reagent obtained from 3.7 ml of methyl iodide and 1.5 g of magnesium in 45 ml of absolute ether was added rapidly to a suspension of 5.12 g (16 mmole) of 2,6-diphenylpyrylium tetrafluoroborate [1] in 60 ml of dry ether, after which the reaction mixture was stirred at room temperature for 20 min, cooled with ice, and decomposed with ammonium chloride solution. The ether layer was separated, washed with 1 N sodium carbonate solution and water, and dried with anhydrous sodium sulfate. The dry ether solution was treated successively with 9 ml of acetic anhydride and (cautiously) with 3 ml of 45% aqueous hydrogen tetrafluoroborate, and the resulting precipitate was removed by filtration, washed with ether, and recrystallized from acetic acid to give 1.9 g (35.6%) of a product that did not melt up to 350°C. Electronic spectrum, λ_{max} (log ε): 400 nm (4.44). Found, %: C 65.07, H 4.64. $C_{18}H_{15}OBF_4$. Calculated, %: C 64.71, H 4.49.

2,6-Bis(4-methylphenyl)-4-methylpyrylium Tetrafluoroborate. This compound was similarly obtained in 35% yield from 2,6-bis(4-methylphenyl)pyrylium tetrafluoroborate and did not melt up to 350°C. Electronic spectrum, λ_{max} (log ε): 425 nm (4.77). Found, %: C 66.43, H 5.01. $C_{20}H_{19}OBF_4$. Calculated, %: C 66.33, H 5.25.

2,4,6-Triarylpyrylium Tetrafluoroborates. A) In the presence of an orthoester. A mixture of 2 mmole of the corresponding acetophenone, 1 mmole of orthoacetic or orthopropionic ester, and 1.5 mmole of boron trifluoride etherate was heated for 1 h on a boiling-water bath, after which the reaction mass was diluted with ether until the addition of a new portion of ether did not give rise to the new formation of a precipitate. The precipitate was removed by filtration, washed with ether, and recrystallized from acetic acid.

B) In the absence of an orthoester. A mixture of 2 mmole of the corresponding acetophenone and 1.5 mmole of boron trifluoride etherate was heated and then worked up as in the preceding method.

Alternative Synthesis (carried out as in [4]). A mixture of 3 mmole of the corresponding acetophenone, 2 mmole of the corresponding benzaldehyde, 1.5 mmole of boron trifluoride etherate, and 25 ml of toluene was refluxed for 2 h with a Dean-Stark trap. The reaction mass was cooled and worked up via the method described above. The yields of 2,4,6-triarylpyrylium tetrafluoroborates ranged from 31 to 50%.

The characteristics of the 2,4,6-triarylpyrylium tetrafluoroborates synthesized in the presence of an orthoester are presented in Table 1.

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ACETALS OF LACTAMS AND ACID AMIDES.

48.* REACTION OF ENAMINO DIKETONES WITH AMIDE CRYSTALS. SYNTHESIS OF DERIVATIVES OF COUMARIN AND CARBOSTYRIL

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It was established that the reaction of derivatives of 2-aminomethylenecyclohexane-1,3-dione with N,N-dimethyl-diethylacetal gives dienediamines, heating of which in aqueous hydrochloric acid leads, depending on the structure, to derivatives of carbostyril and/or coumarin. This unusual reaction is based on initial attack at the α position of the enamino diketone by the ketone acetal, which exists in equilibrium with the starting amide acetal.

It has been previously established that acetals of amides and lactams are capable of undergoing condensation at the amino group of the primary enamines to give enamidines [2]. In continuing this research, in the present paper we studied the reaction of amide acetals with an enamino diketone – 2-aminomethylene-5,5-dimethylcyclohexane-1,3-dione (I), which was obtained by transamination with ammonia of 2-(N,N-dimethylaminomethylene)-5,5-dimethylcyclohexane-1,3-dione (II). The latter is readily formed in the reaction of dimedone (III) with dimethylformamide diethylacetal (IV).

The reaction of primary enamino diketone I with N,N-dimethylacetamide diethylacetal (V) proceeds extremely readily, and brief heating of the components in toluene leads to complete conversion of starting I to the reaction products; according to TLC and PMR data, two principal substances, VI and VII, the relative percentage of which is 7:3, and a small amount of a third compound (VIII) are formed in this case. Compound VIII was isolated owing to its relatively low solubility, whereas we were able to separate VI and VII by fractional crys-

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*See [1] for Communication 47.

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