REACTION OF PYRYLIUM SALTS WITH AMIDINES

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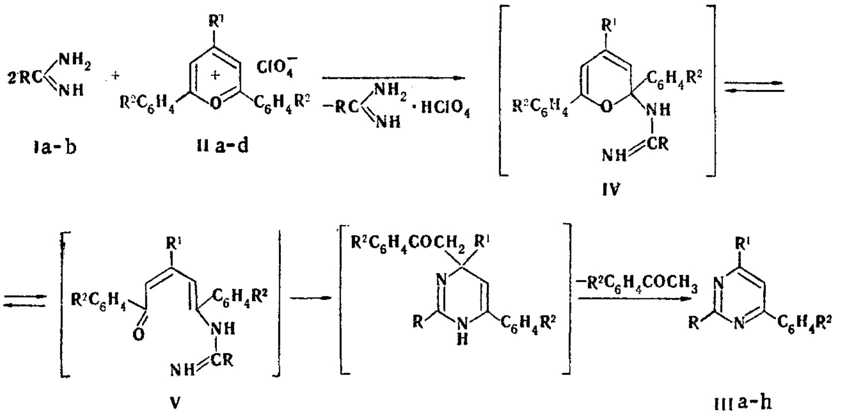
2,4,6-Substituted pyrimidines were obtained by reaction of 2,4,6-triarylpyrylium perchlorates with amines. 2,4-Substituted pyrimidines were similarly synthesized from 2,6-diphenylpyrylium perchlorate.

It is known that isoxazoles and pyrazoles are formed in the reaction of pyrylium salts with hydroxylamine, phenylhydrazine, and hydrazine [1, 2]. We recently found that it is possible to obtain pyrimidine structures from pyrylium salts and guanidine [3] or 2-aminobenzimidazoles [4].

The aim of the present research was to study the reaction of pyrylium salts with amidines It was established that acetamidines and benzamidines (Ia, b) react at 0°C with 2,4,6-triarylsubstituted pyrylium salts (II) to give pyrimidines IIIa-h in 56-93% yields:



I a $R=CH_3$; b $R=C_6H_5$; II a $R^1=C_6H_5$, $R^2=H$; b $R^1=p\text{-}OCH_3C_6H_4$, $R^2=H$; c $R^1=p\text{-}NO_2C_6H_4$, $R^2=H$; d $R^1=R^2=H$; III a $R=CH_3$, $R^1=C_6H_5$, $R^2=H$; b $R=CH_3$, $R^1=p\text{-}OCH_3C_6H_4$, $R^2=H$; c $R=CH_3$, $R^1=p\text{-}NO_2C_6H_4$; $R^2=H$; d $R=R^1=C_6H_5$, $R^2=H$; e $R=C_6H_5$, $R^1=p\text{-}OCH_3C_6H_4$, $R^2=H$, f $R=C_6H_5$, $R^1=p\text{-}NO_2C_6H_4$, $R^2=H$; g $R=CH_3$, $R^1=R^2=H$; h $R=C_6H_5$, $R^1=R^2=H$

The reaction goes to completion more rapidly when the mixtures are heated, and the yields of pyrimidines are not reduced. The structures of the III obtained were confirmed by IR spectroscopic data and by alternative synthesis of the known 2-methyl-4,6-diphenylpyrimidine from 2-chloro-4,6-diphenylpyrimidine and malonic ester [5].

The reaction probably begins with attack by the amino group of the amidine on the position of the pyrylium ring to give substituted α-pyran IV, which exists in tautomeric equilibrium with its open form V. The subsequent formation of a new heteroring with splitting out of acetophenone leads to pyrimidines III.

2,6-Diarylpyrylium perchlorates react similarly with amidines to give 2,4-disubstituted pyrimidines IIIg, h.

The reaction of 2-methyl-4,6-diphenyl- and 4-methyl-2,6-diphenylpyrylium perchlorates with amidines is accompanied by deprotonation of the pyrylium salt and the formation of red dimers of the corresponding methylenepyrans [6] instead of pyrimidines.

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TABLE 1. Characteristics of the Synthesized Pyrimidines IIIa-h

Compounds III	mp, °C (crystallization solvent)	Found, %		Empirical formula	Calc., %		IR spectrum, cm⁻¹	Yield, %
		C	H		C	H		
a	88—89[a] (methanol)	82,6	5,9	$C_{17}H_{14}N_2$	82,9	5,7	1535, 1580, 1590	56
b	103—104[b] (heptane)	77,8	5,5	$C_{18}H_{16}N_2O$	78,3	5,8	1240, 1260 (OCH_3), 1530, 1580, 1590	60
c	198—199 (heptane)	69,6	4,4	$C_{17}H_{13}N_3O_2$	70,1	4,5	1350 (NO_2), 1515, 1542, 1580	89
d	187—188[c] (ethanol with benz.)	85,6	5,3	$C_{22}H_{16}N_2$	85,7	5,2	1535, 1575, 1592	85
e	138—140 (ethanol)	81,0	5,6	$C_{23}H_{18}N_2O$	81,6	5,4	1240, 1260 (OCH_3), 1533, 1575, 1590	86
f	213—215[d] (benzene)	74,9	4,3	$C_{22}H_{15}N_3O_2$	74,8	4,3	1352 (NO_2), 1515, 1540, 1582	93
g	53,5—54[e]	77,9	5,8	$C_{11}H_{10}N_2$	77,6	5,9	1560, 1580	51
h	71—72[f] (methanol)	83,1	5,6	$C_{16}H_{12}N_2$	82,7	5,2	1555, 1573, 1595	43

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a) According to the data in [5], this compound has mp 87-89°C. b) PMR spectrum (in CCl_4): 2.65 (3H, s, $C-CH_3$), 3.7 (3H, s, $O-CH_3$), and 6.65-8.0 ppm (10H, m, aromatic protons). c) According to the data in [7], this compound has mp 185-186°C. d) According to the data in [7], this compound has mp 212-215°C. e) According to the data in [8], this compound has mp 53°C. f) According to the data in [9], this compound has mp 71-72°C.

EXPERIMENTAL

The PMR spectrum was recorded with a Tesla BS-487c spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

Reaction of Perchlorate IIa with Acetamidine. A 1.02-g (2.5 mmole) sample of perchlorate Ia was added to an alcohol solution of acetamidine isolated from 0.48 g (5 mmole) of its hydrochloride with an equivalent amount of sodium ethoxide, and the mixture was refluxed for 1 h. The solvent was removed by evaporation, and a mixture of pyrimidine, acetophenone, and 1,3,5-triphenylpentene-1,5-dione was separated by dissolving the residue in benzene. The benzene solution was concentrated, and petroleum ether was added to precipitate 2-methyl-4,6-diphenylpyrimidine (IIIa). 2-Methyl-4-phenyl-6-(p-methoxyphenyl)pyrimidine (IIIb), 2,4-diphenylpyrimidine (IIIh), and 2-methyl-4-phenylpyrimidine (IIIg) were similarly obtained. The latter was obtained in the individual state by vacuum sublimation.

Reaction of Perchlorate IIa with Benzamidine. An alcohol solution of sodium ethoxide, prepared from 0.12 g (5.0 mg-atom) of sodium, was added to a solution of 0.96 g (5.0 mmole) of benzamidine hydrochloride in absolute ethanol, the precipitated sodium chloride was removed by filtration, and 1.02 g (2.5 mmole) of perchlorate IIa was added to the resulting solution of benzamidine. The mixture was refluxed for 1 h, cooled, and filtered to give 0.65 g (82%) of 2,4,6-triphenylpyrimidine (IIId).

The reaction of benzamidine with other 2,4,6-triaryl-substituted pyrylium salts and of acetamidine with 4-(p-nitrophenyl)-2,6-diphenylpyrylium perchlorate was carried out under similar conditions.

Data on the pyrimidines IIIa-h are presented in Table 1.

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PYRYLATION OF 1,2-DIPHENYLBENZO[b]CYCLOPENTA[e]PYRAN

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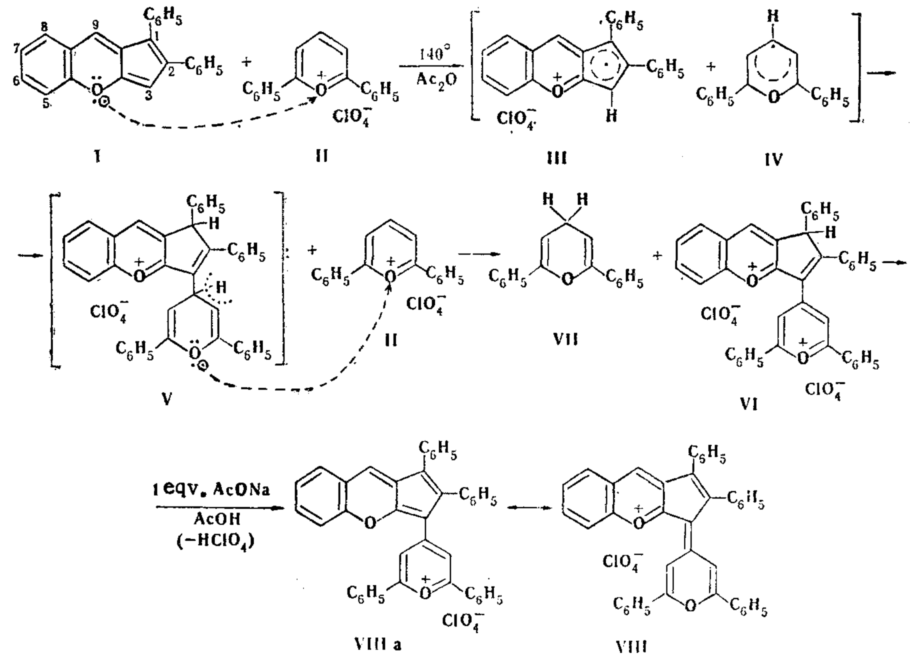
1,2-Diphenylbenzo[b]cyclopenta[e]pyran was pyrylated with 2,6-diphenylpyrylium perchlorate. The structures of the singly and doubly charged 2,6-diphenyl-4-(1,2-diphenylbenzo[b]cyclopenta[e]-3-pyrania)pyrylium cations are confirmed by data from the electronic absorption spectra. A radical mechanism for the pyrylation is proposed on the basis of the ESR spectrum.

Radical substitution reactions in the benzo[b]cyclopenta[e]pyran series have not been studied at all, although it might be assumed *a priori* that, as in the case of azulenes, they would be directed to the 1 and 3 positions. An attempt to subject a substrate to substitution by cations that usually do not react at low temperatures but form radicals at temperatures that cause one-electron transfer, i.e., in the final analysis, to subject the substrate to radical substitution, would seem of great theoretical interest. The 2,6-diphenylpyrylium cation [1], for example, may serve as a one-electron oxidizing agent of this type. Organic compounds that either have increased electron density on at least one of the carbon atoms (N,N-dimethylaniline [2, 3], 1-methylindole [4], and 2-methylindole [5]) or are capable of easily undergoing oxidation to relatively stable cation radicals (ferrocene [6]) are usually substrates in this reaction.



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