INTRODUCTION OF THE PYRYLIUM RING INTO COMPOUNDS OF THE AROMATIC AND HETEROCYCLIC SERIES

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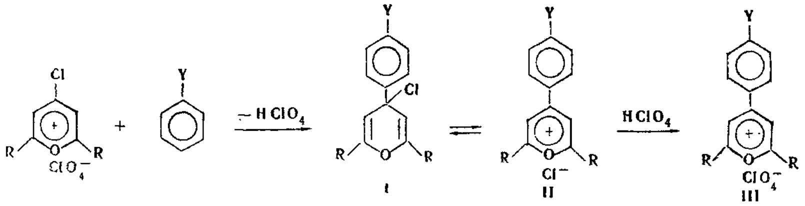
Halogen-substituted pyrylium cations react with organic nucleophilic compounds via an electrophilic mechanism to form new pyrylium salts. The reaction is extended to aromatic, heterocyclic, and nonbenzoid aromatic systems. Pyrylium salts that contain other functional groups do not enter into this reaction. The IR spectra of the compounds obtained are presented.

The syntheses of diverse pyrylium salts were substantially simplified by the discovery of the reaction of α- or γ-unsubstituted pyrylium cations with nucleophilic agents, which leads to new pyrylium compounds (the pyrylation reaction) [1, 2].

We have observed that halogen-substituted pyrylium salts are also capable of reacting with various nucleophiles via an electrophilic mechanism to give new pyrylium salts with a substituent corresponding to the nucleophile used [3]. An investigation of this reaction in the case of the pyrylation of aromatic (dialkylanilines and phenolic ethers), heterocyclic compounds (N-methylindole), and azulenes with various pyrylium, thiapyrylium, benzopyrylium, and xanthylium salts has shown that it is a general reaction and can also be used in those cases where the pyrylation reaction is unsuccessful. Purer pyrylation products are obtained from halogen-substituted pyrylium cations.

It can be assumed that pyranylation of the nucleophilic agent occurs in the first step of this reaction (as in the case of pyrylation) to form pyran I, the halogen atom of which becomes the anion of pyrylium cation II (aromatization), and the presence of a Lewis acid (for example, perchloric acid when pyrylium perchlorates are used) results in replacement of the halide ion by the anion of the acid that is present:



The fact that bromine-substituted salts react to give lower yields than chlorine-substituted salts may serve as a confirmation of this. 2,6-Diphenyl-4-(p-dimethylaminophenyl)pyrylium perchlorate is obtained in 65% yield from 2,6-diphenyl-4-chloropyrylium perchlorate but in only 23% yield from 2,6-diphenyl-4-bromopyrylium perchlorate. Pyrylium salts with hydroxy, carboxy, acetoxy, methoxy, and cyano substituents do not react at all with reactive organic compounds or form only traces of the expected products.

The optimum conditions for the reaction of halogen-substituted pyrylium cations with organic nucleophilic compounds consist in refluxing the pyrylium salts with a small excess of the compound to be pyrylated in dimethylformamide or nitromethane. Acetic acid is unsuitable for this reaction, since it forms acetoxypyrylium salts.

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TABLE 1. Characteristics of the Synthesized Pyrylium Salts

Comp.	Name	Mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	Cl	C	H	Cl	
1	2,6-Diphenyl-4-(p-dimethylaminophenyl)pyrylium perchlorate	Above 380	$C_{25}H_{22}ClNO_5$	66,83	5,01	8,12	66,51	4,87	7,87	65
2	2,6-Diphenyl-4-(p-dipropylaminophenyl)pyrylium perchlorate	284	$C_{29}H_{30}ClNO_5$	69,12	5,98	7,94	68,63	5,91	7,00	56
3	2,6-Diphenyl-4-azulenylpyrylium perchlorate	250—251	$C_{27}H_{19}ClO_5$	70,85	4,37	7,88	70,74	4,14	7,75	51
4	2,6-Diphenyl-4-(4',6',8'-trimethylazulenyl)pyrylium perchlorate	255	$C_{30}H_{25}ClO_5$	72,20	5,27	7,65	72,00	5,00	7,00	45
5	2,6-Diphenyl-4-(guaiazulenyl)pyrylium perchlorate	259	$C_{32}H_{29}ClO_5$	73.22	5,19	7,01	72,72	5,49	6,62	42
6	2,6-Diphenyl-4-(1'-methyl-3'-indolyl)pyrylium perchlorate	292—293	$C_{26}H_{20}ClNO_5$	67,34	4,45	7,51	67,67	4,33	7,70	82
7	2,6-Diphenyl-4-(2',4'-dimethoxyphenyl)pyrylium perchlorate	258	$C_{25}H_{21}ClO_7$	64,43	4,62	8,21	64,10	4,49	7,57	91
8	2,6-Diphenyl-4-(p-dimethylaminophenyl)thiapyrylium perchlorate	254	$C_{25}H_{22}ClNO_4S$*	64,52	5,01	7,92	64,24	4,71	7,60	89
9	2,6-Diphenyl-4-(1'-methyl-3'-indolyl)thiapyrylium perchlorate	273—273,5	$C_{26}H_{20}ClNO_4S$†	64,98	4,32	7,22	65,48	4,20	7,34	90
10	4,6-Diphenyl-2-(p-dimethylaminophenyl)pyrylium perchlorate	287—288	$C_{25}H_{22}ClNO_5$	67,09	5,14	8,17	66,51	4,87	7,81	60
11	4,6-Diphenyl-2-(1'-methyl-3'-indolyl)pyrylium perchlorate	276—276,5	$C_{26}H_{20}ClNO_5$	67,91	4,59	7,90	67,67	4,33	7,70	70
12	4-Methyl-2-(p-dimethylaminophenyl)benzopyrylium perchlorate	318	$C_{18}H_{18}ClNO_5$	60,08	4,62	10,24	59,50	4,96	9,64	68
13	4-Methyl-2-(1'-methyl-3'-indolyl)benzopyrylium perchlorate	286	$C_{19}H_{16}ClNO_5$	64,51	4,52	9,21	61,12	4,26	9,38	82
14	2-Phenyl-4-(p-dimethylaminophenyl)benzopyrylium perchlorate	241	$C_{23}H_{20}ClNO_5$	64,54	4,80	9,04	61,12	4,26	8,35	69
15	2-Phenyl-4-(1'-methyl-3'-indolyl)benzopyrylium perchlorate	273	$C_{24}H_{18}ClNO_5$	65,84	4,41	8,46	66,20	4,13	8,16	84
16	9-(1'-Methyl-3'-indolyl)xanthylium chloroferrate	268	$C_{22}H_{16}Cl_4NOFe$	52,45	3,22	27,14	51,97	3,18	27,95	63
17	9,9-Bis(p-dimethylaminophenyl)xanthene	233	$C_{29}H_{28}N_2O$	80,44	6,75		80,27	6,67		65

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* Found: S 7.13%. Calculated: S 6.85%.

† Found: S 6.54%. Calculated: S 6.70%.

TABLE 2. IR Spectra of the Synthesized Pyrylium Salts

Comp.*	Pyrylium ring vibrations, cm^{-1}				Phenyl ring vibrations, cm^{-1}		
	8a	8b	19a	19b	8a	8b	19a
1	1645 s	1530 s	—	1425 s	1595 †	1557 m	1495 s
2	1645 s	1540 s	1465 m	1430 s	1600 s	1580 †	1500 s
3	1632 s	1540 †	1470 m	1415 †	1600 †	1585 m	1510 s
4	1632 s	1525 †	1460 s	1425 m	1590 m	—	1505 s
5	1635 s	1550 s	1465 s	1430 †	1605 †	1585 s	1505 s
6	1640 s	1545 s	—	1425 s	1590 m	—	1500 s
7	1630 m	1540 m	1488 s	1420 m	1600 s	1560 m	1517 m
8	1620 s	1540 †	1475 s	1425 s	1590 s	1565 s	1500 s
9	1600 s	1535 s	—	1420 †	—	1545 s	1505 †
10	1630 s	1530 †	1480 †	1425 s	1612 s	—	1500 s
11	1630 s	1525 s	—	—	1600 m	1585 m	1500 s
12	1645 m	1530 s	1460 †	1420 s	1595 s	1575 †	1500 s
13	1635 s	1540 s	1460 s	1420 s	—	1580 s	1495 s
14	1610 s	1535 s	1475 s	1420 s	1590 s	1575 s	1503 s
15	1620 s	1535 s	1490 s	1420 s	1600 s	1560 s	1495 s
16	1620 m	1550 m	1480 s	1415 s	1603 s	1585 s	1495 †

* The numbering corresponds to that in Table 1.

† Inflection.

Note: s is strong and m is medium.

The pyrylium salts obtained (the compounds obtained in nitromethane are presented in Table 1, while examples of syntheses in dimethylformamide are presented in the Experimental section) are similar in properties to trisubstituted salts [2,4]. The compounds were identified from the results of elementary analysis, conversion to pyridines, IR spectra, and, in some cases, by alternative synthesis.

The IR spectra of the synthesized substituted pyrylium salts have a number of characteristic bands that are similar in many respects to the absorption bands in the spectra of substituted pyrylium [5] and isobenzopyrylium salts [6]. Thus, with respect to position, intensity, and behavior for various substitutions, the group of bands at 1420-1650 cm^{-1} is related to the stretching vibrations of the C =C bonds of the pyrylium, benzene, and nonbenzoid aromatic rings. The band at 1620-1640 cm^{-1} apparently belongs to the vibrations of the pyrylium cation (8a in the Wilson classification [7]) and can serve for the identification of this heterocycle. The bands at 1530-1550 cm^{-1} (8b), 1470-1490 cm^{-1} (19a), and 1415-1425 cm^{-1} (19b), which are related to the stretching and deformation vibrations of the pyrylium cation [7] and also confirm the structures of the compounds obtained, are also intense and characteristic. In addition, there are a number of bands (8a, 8b, and 19a) that are characteristic for phenyl substituents and nonbenzoid aromatic systems of the azulene type (Table 2).

EXPERIMENTAL

The IR spectra of KBr pellets of the synthesized compounds were recorded with a UR-20 spectrophotometer.*

2,6-Diphenyl-4-(1'-methyltetrahydro-5'-quinolinyl)pyrylium Perchlorate. A mixture of 1.8 g (0.005 mole) of 2,6-diphenyl-4-chloropyrylium perchlorate (DCPP) and 0.74 g (0.005 mole) of N-methyl-1,2,3,4-tetrahydroquinoline in 10 ml of dimethylformamide (DMF) was refluxed for 30 min and cooled. The crystalline product was removed by filtration, washed with ether, and dried to give 1.4 g (57%) of a product with mp 290° (from nitromethane).

The pyrylation was similarly carried out in DMF with N,N-dimethylaniline (63% yield of a product with mp >380°), N-methylindole (80% yield of a product with mp 291°), N-methylindoline (78% yield of a product with mp 292°), etc.

2,6-Diphenyl-4-(p-dimethylaminophenyl)pyrylium Perchlorate (1). This compound [1.5 g (65%)] was obtained via the above method using nitromethane as the solvent and melted above 380° (from nitromethane).

9,9-Bis(p-dimethylaminophenyl)xanthene (17). A mixture of 1.6 g (0.005 mole) of 9-chloroxanthylium perchlorate and 1.2 g (0.01 mole) of N,N-dimethylaniline in 10 ml of nitromethane was refluxed for 1 h and

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cooled. The resulting crystalline precipitate was separated, washed with ether, and dried to give 1.4 g (65%) of a product with mp 233° (from nitromethane).

Other reactive nucleophilic reagents were similarly pyrylated (Table 1).

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