AROMATIC CATIONS FROM PYRONES AND SIMILAR COMPOUNDS

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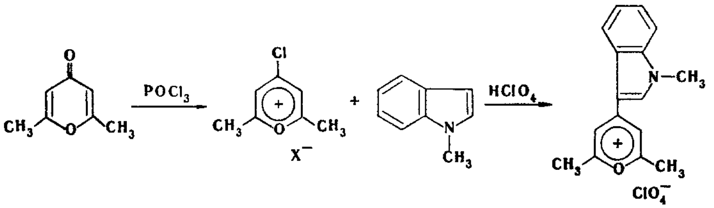
Various pyrones and flavone, xanthone, and diphenylcyclopropenone react with organic nucleophiles in the presence of phosphorus oxychloride in nitromethane with the formation of the corresponding aromatic cations, which have been isolated in the form of the perchlorates.

Syntheses of pyrylium salts with pyrones are extremely numerous [1]. The most convenient route to them is organomagnesium synthesis (see, for example, [2]). Recently, in order to obtain alkoxycarbonylmethyl-substituted pyrylium salts [3], the use of the Reformatskii reaction has been proposed. However, none of the known methods permit the attachment of many heterocyclic and aromatic substituents to pyrones because of the difficulty or impossibility of obtaining their organometallic derivatives. We have described a method for the synthesis of pyrylium salts with such substituents from chlorine-substituted pyrylium salts [4, 5]. Although the latter are readily obtained from pyrones, this method also has its limitations, since some pyrones and similar compounds (for example, dimethylpyrone, dimethylcoumalin, xanthone, diphenylcyclopropenone, etc.) cannot be converted into stable chlorine-substituted aromatic cations. Further investigations in this field have shown that in the presence of phosphorus oxychloride the direct interaction of pyrones with nucleophilic agents leads to new pyrylium salts. We suggest the intermediate formation of a chloropyrylium salt from the pyrone and the $POCl_3$ and the subsequent pyrylation of the nucleophile by the type of reaction described previously [5]. For example, the reaction of 2,6-dimethylpyrone with N-methylindole can be represented in the following way:



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It is likely that in the formation of (II) the anion will have the structure $(PO_2Cl_2)^-$. The pyrylation stage takes place under conditions analogous to the pyrylation of chlorine-substituted pyrylium salts (brief boiling or standing at room temperature of a mixture of the components in nitromethane). The final products are isolated in the form of well-crystallizing perchlorates. As nucleophiles may be used any reactive organic compounds (for example, N-methyl- and N-ethylindoles, N-methylpyrrole, and resorcinol). In addition to its application to dimethylpyrone, this reaction can be extended to 2,6-diphenylpyrone, 2,4-dimethyl-, and 2,4-diphenylcoumalins, 3-methylcoumarin, xanthone, and diphenylcyclopropene, to judge from their reactions with (III). In the case of diphenylpyrone and diphenylcoumalin, pyrylium salts identical with those described previously [5] are obtained. As well as by independent syntheses, the aromatic salts obtained were identified by means of their IR spectra [6].

Apparently, the proposed pyrylation reaction with pyrones has a general nature and can be applied to the synthesis of various aromatic cations, which will find applications in organic synthesis.

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TABLE 1. Characteristics of the Salts Synthesized

Compound	mp, °C	Empirical formula	Found, %			Calc., %			IR spectra of the compounds			Yield, %
			C	H	Cl	C	H	Cl	8a	8b	19a	
2,6-Dimethyl-4-(1-methylindol-3-yl)pyrylium perchlorate	254	$C_{16}H_{16}ClNO_5$	57,2	4,5	10,8	57,0	4,7	10,5	1655 s	1545s	1450m	62
4-(1-Ethylindol-3-yl)-2,6-dimethylpyrylium perchlorate	242	$C_{17}H_{18}ClNO_5$	58,1	5,3	10,6	58,1	5,1	10,1	1660 s	1545 s	1460m	66
2,6-Dimethyl-4-(1-methylpyrrol-2-yl)pyrylium perchlorate	218	$C_{12}H_{14}ClNO_5$	49,8	5,1	12,0	50,2	4,9	12,4	1660s	1560s	1465m	35
4-(2,4-Dihydroxyphenyl)-2,6-dimethylpyrylium perchlorate	175	$C_{13}H_{13}ClNO_7$	49,1	4,9	10,9	48,9	4,1	11,2	1650s	1550 s	1460m	42
4,6-Dimethyl-2-(1-methylindol-3-yl)pyrylium perchlorate	254	$C_{16}H_{16}ClNO_5$	56,3	5,2	10,5	57,0	4,7	10,5	1660s	1550 s	1480m	51
9-(1-Methylindol-3-yl)xanthylium perchlorate	274	$C_{22}H_{16}ClNO_5$	63,9	4,0	7,9	64,5	3,9	8,7	1630c	1520 s	1480m	63
4-Methyl-2-(1-methylindol-3-yl)benzopyrylium perchlorate	286	$C_{19}H_{16}ClNO_5$	60,8	4,5	9,8	61,1	4,3	9,4	1635 s	1540 s	1460m	85
4-(1-Methylindol-3-yl)-2,6-diphenylpyrylium perchlorate	293	$C_{26}H_{20}ClNO_5$	67,3	4,6	7,5	67,7	4,3	7,7	1640 s	1545 s	—	84
2-(1-Methylindol-3-yl)-4,6-diphenylpyrylium perchlorate	276	$C_{26}H_{20}ClNO_5$	67,1	4,5	7,6	67,7	4,3	7,7	1630s	1525 s	—	79
(1-Methylindol-3-yl)diphenylcyclopropenylium perchlorate	237	$C_{24}H_{18}ClNO_4$	68,3	4,4	8,8	68,7	4,3	8,5				45

EXPERIMENTAL

The IR spectra of the compounds synthesized were taken on a UR-20 spectrophotometer in KBr tablets.

2,6-Dimethyl-4-(1-methylindol-3-yl)pyrylium Perchlorate. A mixture of 1.24 g (0.01 mole) of 2,6-dimethyl-γ-pyrone, 1.31 g (0.01 mole) of N-methylindole, 1.53 g (0.01 mole) of $POCl_3$, and 10 ml of nitromethane was kept at room temperature for 12 h. Then 1.5 ml of perchloric acid was added and the mixture was heated until a vigorous evolution of HCl began. The addition of ether precipitated dark brown crystals, which were filtered off, washed with ether, and crystallized from acetonitrile.

The other salts given in Table 1 were obtained similarly. In some cases (for example, in the cases of diphenylcyclopropenone, diphenylcoumalin, etc.) the reaction mixture was first heated to the boil and was then left for 12 h.

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