SYNTHESIS OF 2,6-DIARYL-SUBSTITUTED PYRYLIUM AND 4-ALKOXYCHROMYLIUM SALTS WITH VARIOUS ANIONS

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UDC 547.814.07

A method is proposed for the synthesis of 2,6-diphenyl-substituted pyrylium salts and 7-hydroxy-4-ethoxychromylium salts with various anions on the basis of the condensation of ethyl orthoformate with aliphatic–aromatic ketones in the presence of acid catalysts (hydrogen chloride, hydrogen bromide, hydrogen iodide, and 92% sulfuric acid) and Lewis acids (aluminum chloride, ferric chloride, and stannic chloride).

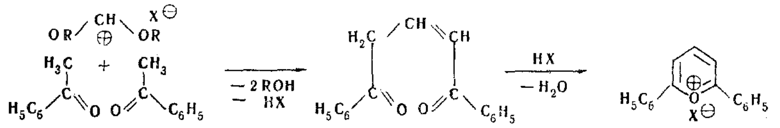
The previously described methods for the synthesis of 2,6-diphenylpyrylium salts which have an active γ-position were based on the condensation of phenylpropargyl aldehyde or β-chlorovinyl phenyl ketone [2] with acetophenone. Later a method was found for preparing 2,6-diaryl-substituted pyrylium salts by condensation of ethyl orthformate with aliphatic–aromatic and heterocyclic ketones in the presence of perchloric acid or boron trifluoride etherate [3].

In this paper we propose a method for obtaining 2,6-diphenyl-substituted pyrylium salts and 4-ethoxychromylium salts on the basis of the condensation of ethyl orthoformate with aliphatic–aromatic ketones (acetophenone and 2,4-dihydroxyacetophenone) in the presence of various acid catalysts (hydrogen chloride, hydrogen bromide, hydrogen iodide, and concentrated sulfuric acid) and strong and weak Lewis acids (aluminum chloride, ferric chloride, and stannic chloride).

As was previously shown in [3], the intermediates in this reaction are the perchlorates of dialkoxycarbonium ions which have C-alkylating ability and are obtained by the reaction of ethyl orthoformate with anhydrous perchloric acid.

We have observed that not only the perchlorates of the dialkoxycarbonium ions, but also their chlorides, bromides, iodides, sulfates, etc. can be C-alkylating agents in this reaction (Table 1); this opens possibilities for the development of a very simple and convenient method for the synthesis of 2,6-diaryl-substituted pyrylium salts with the indicated anions according to the scheme

$$CH(OR_3) + HX \longrightarrow [CH(OR)_2]^{\oplus} X^{\ominus} + ROH$$



$X^- = Cl^-, Br^-, I^-, HSO_4^-, AlCl_4^-, FeCl_4^-, {}^1/_2 SnCl_6$

Of significant interest is the fact that the dialkoxycarbonium chlorides, bromides, and iodides have high C-alkylating ability; alkylation of aliphatic–aromatic ketones with these salts is readily accomplished under comparatively mild conditions in the absence of any Friedel-Crafts reaction catalysts. The reaction is carried out with heating (60-75 deg) for 1 h of a mixture of components with subsequent bubbling of gaseous hydrogen halide through the mixture for 3 to 6 h. The yields of the salts decreased considerably on shortening the time of passage of the hydrogen halides.

Rostov-on-Don State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 160-163, February, 1971. Original article submitted November 5, 1969.

TABLE 1. Characteristics of the Synthesized Compounds

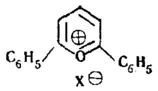
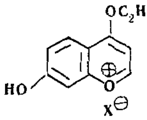
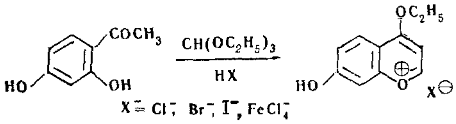
Compound	X	mp, °C	Appearance	Empirical formula	Found, %			Calculated, %			Yield, %
					C	H	X	C	H	X	
											
I	Cl	113	Light-rose plates	$C_{17}H_{13}ClO$	75,4	4,7	12,5	76,0	4,8	13,2	63
II	Br	182	Light-brown plates	$C_{17}H_{13}BrO$	64,9	3,9	25,0	65,2	4,2	25,5	20
III	I	152	Dark-violet plates	$C_{17}H_{13}IO$	56,4	3,2	35,0	56,7	3,6	35,2	80
IV	HSO_4	169	Yellow-brown plates	$C_{17}H_{14}O_5S$	61,8	4,0	S 8,9	61,8	4,3	S 9,1	92
V	$AlCl_4$	300	Orange plates	$C_{17}H_{13}AlCl_4O$			Al 8,1			Al 8,7	97
VI	$FeCl_4$	182—183	Red-violet plates	$C_{17}H_{13}Cl_4FeO$			Fe 12,1			Fe 13,0	93
VII	$^1/_2$ $SnCl_6$	268	Yellow needles	$C_{34}H_{26}Cl_6O_2Sn$			Sn 12,1			Sn 14,9	68
											
VIII	Cl	211	Light-brown needles	$C_{11}H_{11}ClO_3 \cdot H_2O$	53,7	4,9	13,8	54,0	5,3	14,5	70
IX	Br	285	Dark-brown needles	$C_{11}H_{11}BrO_3$	48,3	3,7	29,0	48,7	4,0	29,5	70
X	I	189—190	Dark-violet needles	$C_{11}H_{11}IO_3$	43,6	3,1	37,6	43,7	3,3	38,4	95
XI	$FeCl_4$	300	Red-brown plates	$C_{11}H_{11}Cl_4FeO_3$			Fe 14,0			Fe 14,3	60

TABLE 2. Major Absorption Bands in the IR Spectra of 2,6-Diphenylpyrylium and 7-Hydroxy-4-ethoxychromylium Salts

Compound	Major vibration bands of the pyrylium ring, cm^{-1}				Vibrations of the benzene ring, cm^{-1}	Vibrations of the alkoxy group, cm^{-1}
	8a	8b	19a	19b		
I	1616	1540	1462	1443	1592	—
II	1618	1567	1484	1410	1596	—
III	1616	1538	1460	1412	1588	—
IV	1620	1515	1497	1410	1595	—
V	1618	1536	1446	1410	1600	—
VI	1618	1540	1460	1410	1580	—
VII	1618	1546	1460	1410	1596	—
VIII	1625	1568	1461	—	1606	1240
IX	1631	1578	1463	—	1592	1260
X	1626	1572	1464	—	1611	1240
XI	1626	1580	1463	—	1602	1259

The structures of the pyrylium salts were proved by converting them, by the action of ammonium hydroxide, to 2,6-diphenylpyridine and, by reaction with 70% perchloric acid, to the previously described 2,6-diphenylpyrylium perchlorate [1-3].

Under similar conditions 7-hydroxy-4-ethoxychromylium salts are formed in high yields by the condensation of 2,4-dihydroxyacetophenone with ethyl orthoformate.



The structures of the compounds obtained were proved by converting them to the previously described perchlorate [4] and to the corresponding 7-hydroxychromone by the action of water.

The IR spectra of the synthesized salts (Table 2) contain intense absorption bands which correspond to the valence vibrations of the pyrylium and benzene rings.

EXPERIMENTAL

2,6-Diphenylpyrylium Sulfate. Concentrated (92%) sulfuric acid [4 ml (0.08 mole)] was added to a solution of 2.4 ml (0.02 mole) of acetophenone in 20 ml of freshly distilled ethyl orthoformate. The solution was allowed to stand for 12 h and then diluted with ether. The resulting yellow-brown crystals, which fluoresced strongly, both in solution and in the solid state, were filtered to give 3.1 g (92%) of a product with mp 169 deg (from glacial acetic acid).

2,6-Diphenylpyrylium Chloride. A mixture of 2.4 g (0.02 mole) of acetophenone and 20 ml of freshly distilled ethyl orthoformate was heated for 1 h on a water bath at 60 deg with passage of a stream of hydrogen chloride through the mixture. The solution was then saturated for another 2 h with hydrogen chloride and allowed to stand for 12 h. Pale-rose plates formed on extreme dilution with ether and were filtered and dried.

2,6-Diphenylpyrylium perchlorate formed in quantitative yield by treatment of the solution of the chloride in glacial acetic acid with 70% perchloric acid. The orange crystals had mp 220 deg [3]. This sample did not depress the melting point of an authentic sample of 2,6-diphenylpyrylium perchlorate. 2,6-Diphenylpyridine was obtained in 86% yield by treatment of the chloride with ammonium hydroxide and had mp 81 deg [5].

7-Hydroxy-4-ethoxychromylium Bromide. A solution of 1.52 g (0.01 mole) of 2,4-dihydroxyacetophenone in 30 ml of freshly distilled ethyl orthoformate was heated for 1 h at 70 deg on a water bath while passing a stream of hydrogen bromide through the mixture. The solution was then saturated for another 6 h with hydrogen bromide and allowed to stand for 12 h. Extreme dilution of the mixture with ether yielded brown crystals which were filtered, washed with ether, and dried to give 1.9 g (70%) of a product with mp 285 deg (from alcohol).

A quantitative yield of 7-hydroxychromone with mp 218 deg [4] was formed by heating the bromide with water.

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