SYNTHESIS OF 2-METHYL-3-CARBETHOXYPYRYLIUM SALTS BY THE CONDENSATION OF ETHOXYMETHYLENEACETOACETIC ESTER WITH KETONES

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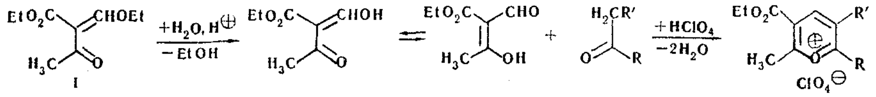
A method is proposed for the synthesis of 2-methyl-3-carbethoxypyrylium salts by the acid condensation of ethoxymethyleneacetoacetic ester with alkyl aryl, heterocyclic, and cyclic ketones or resorcinol. 2-Methyl-3-carbethoxy-6-phenylpyrylium perchlorate was condensed with benzaldehyde, and the product was subjected to acid hydrolysis and decarboxylation to 2-methyl-6-phenylpyrylium perchlorate to confirm the structure of the synthesized salts.

One of us and co-workers previously investigated a method for the synthesis of pyrylium salts on the basis of the acid condensation of carbocyclic hydroxymethylene ketones with methyl and methylene ketones and cross condensation of cyclic and alkyl aryl ketones with ethyl orthoformate [1, 2]. In order to obtain pyrylium salts with a free γ position, we studied the acid condensation of ethoxymethyleneacetoacetic ester (I) with several alkyl aryl (acetophenone, 4-methoxyacetophenone, 3,4-dimethoxyacetophenone, 4-hydroxyacetophenone, propiophenone, methyl α-naphthyl ketone, and benzalacetone), carbocyclic (cyclopentanone, cycloheptanone, and tetralone), and heterocyclic (2-acetothienone) ketones and with resorcinol. Pyrylium salts which contain a carbethoxy group in the 3-position of the pyrylium ring were thus obtained.

The condensation of I with the indicated ketones proceeds smoothly by heating a mixture of equimolecular amounts of the components and 70% perchloric acid in glacial acetic acid for 30 min. However, the yield of the pyrylium salts does not exceed 20% under these conditions. When the reaction is carried out at room temperature in dehydrating agents (acetic anhydride or ethyl orthoformate) in amounts necessary for tying up the water contained in the 70% perchloric acid and that liberated during the condensation at room temperature, the yields of salts increase to 60%. These facts indicate two possible schemes for the formation of the pyrylium salts as a function of the conditions used to carry out the condensation. In the first case, the water contained in the 70% perchloric acid hydrolyzes I to a β-keto-aldehyde which exists in the hydroxymethylene and aldehyde forms, and the aldehyde form [3], which is present in low concentrations under these conditions, primarily enters into the condensation.



The second scheme includes the formation of a methyleneacetoacetic ester carbonium ion (II) on treatment of I with anhydrous perchloric acid which, by reacting with the enol form of the methyl ketone, gives an unsaturated 1,5-diketone (III) which is cyclized to a pyrylium salt.

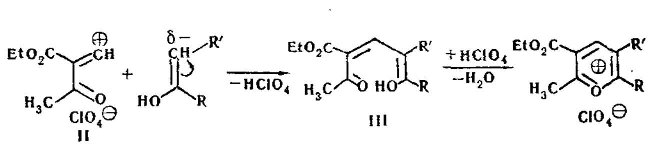


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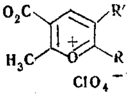
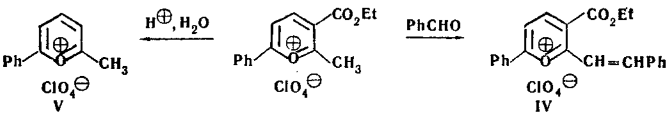
TABLE 1. 2-Methyl-3-carbethoxypyrylium Perchlorates



R	R′	Mp °C	Empirical formula	Found %			Calc., %			Yield, %
				C	H	Cl	C	H	Cl	
4-$CH_3OC_6H_4$	H	162	$C_{16}H_{17}ClO_8$	51,4	4,5	9,4	51,5	4,6	9,5	60
3,4-$(CH_3O)_2C_6H_3$	H	160	$C_{17}H_{19}ClO_9$	50,1	4,8	8,3	50,6	4,7	8,8	50
4-HOC_6H_4	H	201	$C_{15}H_{15}ClO_8$	50,1	4,2	10,2	50,1	4,2	10,0	48
α-$C_{10}H_7$	H	178	$C_{19}H_{17}ClO_7$	57,7	4,3	8,8	58,0	4,3	8,5	40
C_6H_5	CH_3	195	$C_{16}H_{17}ClO_7$	54,0	5,0	10,4	53,8	4,8	10,0	53
CH=CH—C_6H_5	H	190	$C_{17}H_{17}ClO_7$	55,5	4,5	9,4	55,3	4,6	9,6	34
α,β-Dihydronaphtho		180	$C_{17}H_{17}ClO_7$	54,9	4,7	9,4	55,3	4,6	9,6	49
Pentamethylene		140	$C_{14}H_{19}ClO_7$	49,8	5,7	10,6	50,1	5,7	10,5	40

The thus synthesized pyrylium salts display CH acid properties from the methyl group in the 2-position by reacting with benzaldehyde. Thus 2-methyl-3-carbethoxy-6-phenylpyrylium perchlorate readily forms 2-styryl-3-carbethoxy-6-phenylpyrylium perchlorate (IV) with benzaldehyde. 2-Methyl-3-carbethoxy-6-phenylpyrylium perchlorate undergoes hydrolysis and decarboxylation on refluxing in a mixture of concentrated hydrochloric and glacial acetic acids to form the previously reported [4] 2-methyl-6-phenylpyrylium perchlorate (V). These facts confirm the proposed structures of the pyrylium salts.



In anhydrous media, compound I also condenses smoothly with resorcinol to give 2-methyl-3-carbethoxy-7-hydroxychromylium perchlorate in 48% yield. All of the synthesized perchlorates are crystalline substances which are soluble in polar solvents to give solutions with green opalescence. The IR spectra of the 3-carbethoxypyrylium salts contain, in addition to bands which are characteristic for substituted pyrylium salts [5], a very intense band at 1720-1730 cm^{-1}, which is due to an ester grouping bonded to an aromatic ring [6, 7].

In contrast to the previously described two special cases of the synthesis of pyrylium salts which contain a carbethoxy group [8, 9], our proposed method is a general one, since it makes it possible to synthesize compounds of this type with diverse substitutents (see Table 1).

EXPERIMENTAL

Ethoxymethyleneacetoacetic Ester (I). This was obtained by our modification of the method in [10]. A mixture of 120 g (1 mole) of acetoacetic ester, 240 g (1.75 mole) of ethyl orthoformate, and 285 g (2.85 mole) of acetic anhydride was heated at 120° for 1 h and at 140° for 1 h. The unchanged ethyl orthoformate and acetic anhydride were removed by distillation, and the residue was vacuum distilled to give 145-155 g (80-85%) of a fraction with bp 140-145° (14 mm).

2-Methyl-3-carbethoxy-6-phenylpyrylium Perchlorate. A total of 4 ml of 70% perchloric acid was added dropwise with cooling to a mixture of 7.2 g (0.04 mole) of I and 5 g (0.04 mole) of acetophenone in 16 g of acetic anhydride and 20 ml of absolute ether. The mixture was allowed to stand at room temperature for 2 h. It was then diluted with ether, and 8.5 g (61%) of fine crystals with mp 187-189° (from acetic acid) were filtered. IR spectrum: 1720, 1618, 1480, 1560, and 1095 cm^{-1}. Found %: C 52.3; H 4.4; Cl 10.1. $C_{15}H_{15}ClO_7$. Calculated %: C 52.5; H 4.4; Cl 10.4.

Compound I was similarly condensed with 4-methoxyacetophenone, 3,4-dimethoxyacetophenone, 4-hydroxyacetophenone, propiophenone, methyl α-naphthyl ketone, and tetralone.

2-Methyl-3-carbethoxy-5,6-trimethylenepyrylium Perchlorate. A total of 0.9 g (0.01 mole) of cyclopentanone, 5 ml of acetic anhydride, 8 ml of absolute ether, and 1 ml (0.01 mole) of 70% perchloric acid were added dropwise with cooling to 1.8 g (0.01 mole) of I. The mixture was allowed to stand for 2 h, and crystallization was initiated by rubbing or by dilution with ether to give 1.63 g (54%) of a product which was purified by reprecipitation from nitromethane by ether to give silvery platelets with mp 169° which decomposed on prolonged storage. IR spectrum: 1730, 1620, 1584, 1470, and 1096 cm^{-1}. Found %: C 46.6; H 5.1; Cl 12.0. $C_{12}H_{15}ClO_7$. Calculated %: C 46.9; H 4.9; Cl 11.6.

2-Methyl-3-carbethoxy-5,6-pentamethylenepyrylium perchlorate was similarly synthesized.

2-Methyl-3-carbethoxy-6-(α-thienyl)pyrylium Perchlorate. A total of 1 ml (0.01 mole) of 70% perchloric acid, 1.3 g (0.01 mole) of 2-acetothienone, and 1.8 g (0.01 mole) of I were added dropwise with cooling to 4 ml of acetic anhydride. The mixture began to crystallize on standing for 2 h. The precipitate was filtered and washed with a small amount of acetic acid and ether to give 1.6 g (50%) of salt with mp 188° (from acetic acid). IR spectrum: 1724, 1620, 1565, 1478, and 1102 cm^{-1}. Found %: C 44.8; H 3.8; Cl 9.9; S 8.9. $C_{13}H_{13}ClO_7S$. Calculated %: C 44.7; H 3.7; Cl 10.2; S 9.2.

2-Methyl-3-carbethoxy-6-styrylpyrylium perchlorate was similarly synthesized.

2-Methyl-3-carbethoxy-7-hydroxychromylium Perchlorate. A total of 1 ml (0.01 mole) of 70% perchloric acid was added dropwise with cooling and stirring to a mixture of 4 ml of acetic anhydride, 1.8 g (0.01 mole) of I, 1.1 g of resorcinol, and 15 ml of absolute ether. The precipitation of a crystalline product was immediately observed. After 30 min, the mixture was diluted with 40 ml of absolute ether, and 1.6 g (48%) of silvery-gray plates with mp 184° (from acetic acid) was obtained by filtration. IR spectrum: 1724, 1625, 1580, 1555, 1468, 1422, and 1105 cm^{-1}. Found %: C 47.0; H 4.0; Cl 10.4. $C_{13}H_{13}ClO_8$. Calculated %: C 46.8; H 3.9; Cl 10.7.

2-Styryl-3-carbethoxy-6-phenylpyrylium Perchlorate. A mixture of 3.4 g (0.01 mole) of 2-methyl-3-carbethoxy-6-phenylpyrylium perchlorate and 1.6 g (0.015 mole) of benzaldehyde in 6 ml of glacial acetic acid was refluxed for 1.5 h, cooled, and poured into 100 ml of absolute ether. The mixture was allowed to stand overnight in a refrigerator to give 4 g (93%) of fine red crystals with mp 193° (from acetic acid). IR spectrum: 1722, 1634, 1618, 1570, 1559, 1480, 1405, and 1103 cm^{-1}. Found %: C 61.4; H 4.4; Cl 8.0. $C_{22}H_{19}ClO_7$. Calculated %: C 61.2; H 4.4; Cl 8.2.

2-Methyl-6-phenylpyrylium Perchlorate. A mixture of 3.4 g (0.01 mole) of 2-methyl-3-carbethoxy-6-phenylpyrylium perchlorate, 20 ml of acetic acid, and 12 ml of concentrated hydrochloric acid was refluxed for 2.5 h, cooled, 1 ml (0.01 mole) of 70% perchloric acid and 20 ml of ether were added, and the resulting mixture was allowed to stand overnight in a refrigerator to give 0.6 g (13%) of salt with mp 139° (from acetic acid) [4].

The IR spectra of mineral oil pastes of the synthesized samples were obtained with an IKS-14 spectrophotometer at 600-1800 cm^{-1} (NaCl prism).

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