SYNTHESIS OF β-ACETYL- AND β-CARBETHOXYPYRYLIUM SALTS

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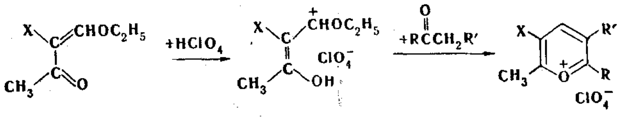
Adducts of ethoxymethyleneacetylacetone and ethoxymethyleneacetoacetic ester with perchloric acid were obtained. β-Acetyl- and β-carbethoxypyrylium salts were synthesized by condensation of these compounds with ketones and phenols.

It has been found that ethoxymethyleneacetylacetone and ethoxymethyleneacetoacetic ester react quantitatively with perchloric acid to give salt adducts with a molar ratio of 1 : 1. These adducts are extremely hygroscopic and cannot be identified by the usual methods (elementary analysis and IR spectroscopy). However, proceeding from the transformations that these compounds undergo and the PMR spectroscopic data, structure I can be proposed as the most likely structure.

When perchlorates I are heated in acetic acid or acetic anhydride with methyl or methylene ketones and certain phenols, they form pyrylium salts IIa-j, which contain functional substituents in the β-position of the pyrylium ring.



I

II a-j

IIa–d X=$COCH_3$; a R=C_6H_5, R'=H; b R=4-BrC_6H_4, R'=H; c R=4-$CH_3OC_6H_4$, R'=H; d α,β-dihydronaphtho
II e–j X=$COOC_2H_5$; e R=C_6H_5, R'=H; f R=4-BrC_6H_4, R'=H; g R=4-$C_6H_5C_6H_4$, R'=Cl; h R=2,5-$(HO)_2C_6H_3$, R'=H; i R=CH_3, R'=H; j R=C_2H_5, R'=CH_3

This path was used to synthesize the hard-to-obtain (for example, see [1]) β-acetylpyrylium salts IIa-d from I (X = $COCH_3$) and aliphatic aromatic ketones. In addition to the bands characteristic for substituted pyrylium salts [2], the IR spectra of these perchlorates (IIa-d) contain an intense band at 1705-1710 cm^{-1}, which is assignable to an acetyl grouping bonded to an aromatic ring. Perchlorate IIc reacts with concentrated ammonium hydroxide to give 2-methyl-3-acetyl-6-(4-methoxyphenyl)pyridine.

Thus, condensation of ethoxymethyleneacetylacetone perchlorate with ketones and subsequent treatment of the resulting pyrylium salts with ammonia may be a convenient method for the synthesis of difficult-to-obtain ketones of the pyridine series.

Reaction of I (X = $COOC_2H_5$) with ketones or phenols (resorcinol, resorcinol monomethyl ether, and m-cresol) gives substituted 3-carbethoxypyrylium (IIe-j) or 3-carbethoxychromylium perchlorates. The previously described [3] IIe and 2-methyl-3-carbethoxy-7-hydroxychromylium perchlorate were thus obtained with acetophenone and resorcinol. The IR spectra of the 3-carbethoxypyrylium salts contain bands characteristic for the pyrylium cation at 1622-1638 cm^{-1} and 1530-1567 cm^{-1} and a band at 1738-1760 cm^{-1}, which is assignable to an ester group bonded to the pyrylium cation.

EXPERIMENTAL

The PMR spectrum was recorded with an RYa-2305 spectrometer (60 MHz). The IR spectra of mineral oil suspensions were recorded with a UR-20 spectrometer.

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TABLE 1. β-Acetyl- and β-Carbethoxypyrylium Perchlorates

Comp.	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	Cl	C	H	Cl	
IIa	165	$C_{14}H_{13}ClO_6$	54,1	4,3	11,1	53,8	4,2	11,4	49
IIb	152—153	$C_{14}H_{12}BrClO_6$	43,2	3,0	29,4	43,0	3,1	29,5	61
IIc	169—171	$C_{15}H_{15}ClO_7$	53,8	4,7	10,4	54,1	4,4	10,4	41
IId	173—174	$C_{16}H_{15}ClO_6$	59,0	4,7	10,2	59,3	4,4	10,5	27
IIe	187—189*	$C_{15}H_{15}ClO_7$	52,3	4,4	10,2	52,5	4,4	10,4	74
IIf	170—171	$C_{15}H_{14}BrClO_7$	42,6	3,4	27,3	42,7	3,3	27,4	86
IIg	191	$C_{21}H_{18}Cl_2O_7$	55,6	4,2	15,5	55,7	4,0	15,7	82
IIh	216	$C_{15}H_{15}ClO_9$	48,1	4,2	10,0	48,1	4,0	9,5	23
IIi	106	$C_{10}H_{13}ClO_7$	42,8	4,6	12,5	42,9	4,6	12,7	95
IIj	119	$C_{12}H_{17}ClO_7$	46,6	5,8	11,4	46,7	5,5	11,5	87

*According to [3], this compound has mp 187-189°.

Ethoxymethyleneacetylacetone. This compound was obtained by our modification of the method in [4]. A mixture of 100 g (1 mole) of acetylacetone, 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, after which the unchanged ethyl orthoformate and acetic anhydride were removed by distillation, and the residue was vacuum distilled to give 117-125 g (75-80%) of a fraction with bp 146-150° (24 mm).

Ethoxymethyleneacetoacetic ester [3] was similarly synthesized.

Ethoxymethyleneacetoacetic Ester Perchlorate (I, X = $COOC_2H_5$). A 1 ml (0.01 mole) sample of 70% perchloric acid was added dropwise to 3 ml of cooled (to 0°) acetic anhydride, and the mixture was added to a solution of 1.86 g (0.01 mole) of ethoxymethyleneacetoacetic ester in 3 ml of acetic anhydride. After 2 min, the mixture was diluted with absolute ether and crystallization was initiated by friction to give 2.96 g (quantitative yield) of product. The colorless crystalline product deliquesced in air.

PMR spectrum (in CF_3COOH): 2.40 (singlet, CH_3), 8.95 (singlet, CH), 0.91-1.10 (multiplet, CH_3CH_2), 4.00-4.40 ppm (multiplet, CH_3CH_2). The multiplets at 0.91-1.10 and 4.00-4.40 ppm are the result of the superimposition of the signals of the protons of the ethoxymethylene and carbethoxy groups.

Perchlorate I (X = $COCH_3$) was similarly obtained.

2-Methyl-3-acetyl-6-phenylpyrylium Perchlorate (IIa). A 1 ml (0.01 mole) sample of 70% perchloric acid and 1.56 g (0.01 mole) of ethoxymethyleneacetylacetone were added successively dropwise to 5 ml of cooled (to 0°) acetic anhydride. After 1 min, 1.2 ml (0.01 mole) of acetophenone was added, and the mixture was heated on a water bath for 2.5 min. It was then cooled and diluted with a fivefold amount of ether. After 5 min, the ether solution was decanted, 1 ml of glacial acetic acid was added, and crystallization was initiated by friction. The resulting crystals were removed by filtration, washed with ether, and purified by reprecipitation from nitromethane by the addition of ether to give 1.5 g (49%) of a product with mp 165°. IR spectrum: 1707, 1610, 1577, 1555, 1503, and 1100 cm^{-1}.

Perchlorates IIb-d (see Table 1) were similarly obtained.

2-Methyl-3-carbethoxy-6-(4-bromophenyl)pyrylium Perchlorate (IIf). A 1 ml (0.01 mole) sample of 70% perchloric acid and 1.86 g (0.01 mole) of ethoxymethyleneacetoacetic ester were added successively dropwise to 5 ml of cooled (to 0°) acetic anhydride, after which 2.6 g (0.013 mole) of 4-bromoacetophenone was added, and the mixture was heated on a water bath for 1.5 min. It was then cooled and diluted with ether, and the precipitated crystals were removed by filtration and crystallized from acetic acid to give 3.6 g (86%) of a product with mp 170-171°. IR spectrum: 1742, 1624, 1600, 1580, 1560, 1508, and 1100 cm^{-1}.

Perchlorates IIe, g, h (see Table 1) were similarly obtained.

2,6-Dimethyl-3-carbethoxypyrylium Perchlorate (IIi). A 1 ml (0.01 mole) sample of 70% perchloric acid and 1.86 g (0.01 mole) of ethoxymethyleneacetoacetic ester were added successively dropwise to 5 ml of cooled (to 0°) acetic anhydride, after which 7 ml (0.1 mole) of acetone was added, and the mixture was heated on a water bath until it became turbid. It was then cooled rapidly and diluted with a 10-fold quantity of ether; crystallization was initiated by friction to give 2.65 g (95%) of a product with mp 106° (reprecipitated from warm acetic acid by the addition of ether). IR spectrum: 1747, 1636, 1530, 1502, and 1100 cm^{-1}.

Perchlorate IIj (see Table 1) was similarly obtained.

2-Methyl-3-carbethoxy-7-hydroxychromylium Perchlorate. A 1 ml (0.01 mole) sample of 70% perchloric acid and 1.86 g (0.01 mole) of ethoxymethyleneacetoacetic ester were added successively dropwise in the cold to 5 ml of acetic anhydride, after which 1.43 g (0.013 mole) of resorcinol was added, and the mixture was heated on a water bath until it darkened. It was then cooled rapidly and diluted with ether to give 2.39 g (72%) of a salt with mp 184° (from acetic acid) [3].

2-Methyl-3-carbethoxy-7-methylchromylium Perchlorate. This compound with mp 147-149° (from acetic acid), was similarly obtained in 12% yield from m-cresol. IR spectrum: 1737, 1639, 1586, 1538, 1502, 1095 cm^{-1}. Found, %: C 50.4; H 4.8; Cl 10.5. $C_{14}H_{15}ClO_7$. Calculated,%: C 50.8; H 4.5; Cl 10.7.

2-Methyl-3-carbethoxy-7-methoxychromylium Perchlorate. This compound, with mp 133-135° (from acetic acid), was similarly obtained in 9% yield from resorcinol monomethyl ether. IR spectrum: 1735, 1643, 1622, 1584, 1550, and 1095 cm^{-1}. Found,%: C 49.0; H 4.8; Cl 10.7. $C_{14}H_{15}ClO_8$. Calculated,%: C 48.5; H 4.3; Cl 10.3.

2-Methyl-3-acetyl-6-(4-methoxyphenyl)pyridine. Concentrated ammonium hydroxide solution was added to 3.42 g (0.01 mole) of perchlorate IIc, and after 5-6 h the mixture was extracted with ether. The ether extract was dried over anhydrous sodium sulfate, and the ether was evaporated to give 1.89 g (90%) of a product with mp 109° (from petroleum ether). IR spectrum: 1690, 1613, 1580, 1560, and 1515 cm^{-1}. Found,%: C 75.0; H 6.4; N 5.9. $C_{15}H_{15}NO_2$. Calculated,%: C 74.7; H 6.2; N 5.8.

LITERATURE CITED

1. A. G. Ismailov and G. I. Safarov, Zh. Organ. Khim., 2, 1624 (1966).
2. A. D. Semenov, G. N. Dorofeenko, and V. I. Dulenko, Khim. Geterotsikl. Soed., 14 (1966).
3. G. N. Dorofeenko, E. P. Olekhnovich, and L. I. Laukhina, Khim. Geterotsikl. Soed., 435 (1971).
4. R. G. Jones, J. Am. Chem. Soc., 73, 3684 (1951).