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SYNTHESIS OF PYRYLIUM SALTS AND HETEROCYCLIC NITROGEN BASES FROM CYCLOALKENYLACETIC ACID ESTERS

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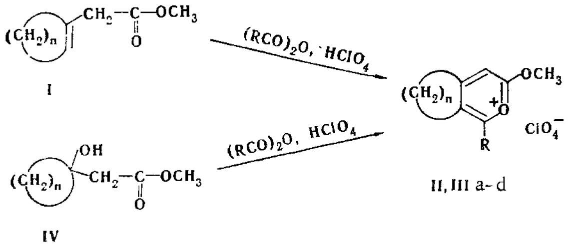
2-Alkyl-6-methoxy-3,4-tetramethylene- and 3,4-pentamethylenepyrylium perchlorates were obtained by acylation of cycloalkenylacetic acid esters with aliphatic acid anhydrides. 2-Methyl-6-methoxy[2,3-c]cholestanopyrylium perchlorate was similarly synthesized. 2-Alkyl-3,4-tetramethylene-6-pyridones were isolated by treatment of 2-alkyl-6-methoxy-3,4-tetramethylenepyrylium perchlorates with excess concentrated ammonium hydroxide. 2-Methyl-3,4-pentamethylene-6-aminopyridine was obtained by the action of excess concentrated ammonium hydroxide on 2-methyl-6-methoxy-3,4-pentamethylenepyrylium perchlorate.

In a continuation of our study of the acylation of β,γ-unsaturated compounds [1, 2] and homoveratric acid esters [3] and in order to synthesize previously unknown 2-alkyl-6-methoxy-3,4-tetramethylene- and 3,4-pentamethylenepyrylium salts and their nitrogen derivatives we studied the acylation of methyl cycloalkenylacetates (I) with aliphatic acid anhydrides (acetic, propionic, butyric, and valeric) in the presence of 70% perchloric acid.

As a result of the reaction we obtained 2-alkyl-6-methoxy-3,4-tetramethylenepyrylium perchlorates (IIa-d) and 3,4-pentamethylenepyrylium perchlorates (IIIa-d) in 25-50% yields.



I-IV $n=4,5$; II, III a $R=CH_3$; b $R=C_2H_5$; c $R=n\text{-}C_3H_7$; d $R=n\text{-}C_4H_9$

We were unable to isolate pyrylium salts in the acylation of cyclopentenylacetic esters in view of their extreme hygroscopic character. Cyclic hydroxy esters IV, obtained directly via the Reformatskii reaction, are readily dehydrated under the conditions of the acylation to olefins and subsequently undergo diacylation. The pyrylium salts formed in this case were isolated in the form of oils, which were converted to the corresponding nitrogen bases without further purification by the action of excess concentrated ammonium hydroxide. The yields of the nitrogen compounds ranged from 74 to 83%.

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TABLE 1. 2-Alkyl-6-methoxypolymethylenepyrylium Perchlorates

Compound	R	mp, °C*	Empirical formula	Found, %			Calculated, %			Characteristic bands in the IR spectrum, ν, cm⁻¹	Yield, %
				C	H	Cl	C	H	Cl		
IIa	CH_3	83—85	$C_{11}H_{15}O_6Cl$	47.49	5,43	12,89	47,39	5.38	12,74	1090, 1200, 1530, 1645	25
IIb	C_2H_5	94—95	$C_{12}H_{17}O_6Cl$	49,35	5,73	12,13	49,23	5,81	12,13	1090, 1200, 1520, 1640	34
IIc	n-C_3H_7	286	$C_{13}H_{19}O_6Cl$	51,31	6,13	11,48	50,89	6,19	11,58	1100, 1250, 1535, 1610, 1635	25
IId	n-C_4H_9	273—275	$C_{14}H_{21}O_6Cl$	52,12	6,89	11,13	52,42	6,55	11,07	1100, 1250, 1535, 1610, 1635	25
IIIa	CH_3	138—140	$C_{12}H_{17}O_6Cl$	49,34	6,01	12,18	49,23	5,81	12,15	1090, 1200, 1225, 1535, 1650	25
IIIb	C_2H_5	85—86	$C_{13}H_{19}O_6Cl$	50,60	6,40	11,20	50,91	6,20	11,58	1080, 1210, 1225, 1520, 1630	50
IIIc	n-C_3H_7	129—130	$C_{14}H_{21}O_6Cl$	52,54	6,53	11,43	52,41	6,55	11,07	1100, 1200, 1220, 1530, 1645	50
IIId	n-C_4H_9	109,5—110	$C_{15}H_{23}O_6Cl$	53.67	6,90	9,97	53,81	6,87	10,43	1090, 1200, 1220, 1525, 1645	25

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*All of the salts were purified by reprecipitation from acetone by the addition of ether.

TABLE 2. 2-Alkyl-3,4-tetramethylene-6-pyridones

Compound	R	mp, °C*	Empirical formula	Found, %			Calculated, %			Characteristic bands in the IR spectrum, ν, cm⁻¹	Yield, %
				C	H	N	C	H	N		
VIa	CH_3	230—231	$C_{10}H_{13}O$	74.00	7,68	8,71	73,70	7,98	8,58	1645, broad band, 2600—3300	89,0
VIb	C_2H_5	217	$C_{11}H_{15}O$	74,58	8,64	8,10	74,50	8,48	7,91	1640, 2600—2700	90,0
VIc	n-C_3H_7	159—160	$C_{12}H_{17}O$	75,13	8,57	7,55	75,40	8,90	7,34	1645, 2400—3400	88,5
VId	n-C_4H_9	192—193	$C_{13}H_{19}O$	75,90	9,55	6,60	76,10	9,27	6,84	1650, 2400—3450	86,0

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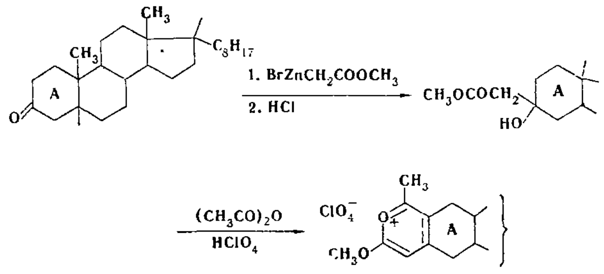
*These compounds were purified by chromatography with a column filled with aluminum oxide [elution with ethyl acetate–ethyl ether (8 : 2)].

The compositions and structures of II and III were confirmed by the results of elementary analysis and IR spectroscopy (see Table 1).

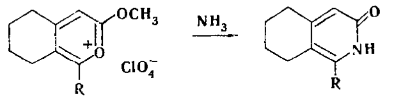
We were similarly able to bring about rearrangement of the pyrylium ring to the A ring of the cholestanone molecule via the scheme



V

An attempt to synthesize pyrylium salts from unsaturated esters obtained from acetophenone and desoxybenzoin did not give the desired results. We were unable to carry out the diacylation of cycloalkenylacetic esters with aromatic acid chlorides, nor were we able to formylate them with dichloromethyl butyl ether in the presence of anhydrous aluminum chloride.

The corresponding nitrogen bases were obtained in 84-90% yields by treatment of the synthesized salts with concentrated ammonium hydroxide.



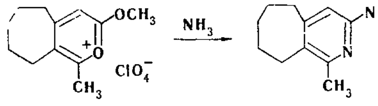
II a-d VI a-d

II, IV a R=CH_3; b R=C_2H_5; d R=n-C_3H_7; e R=n-C_4H_9

It might be noted that the character of the products obtained probably depends on the structure of the pyrylium salt.

Thus 2-alkyl-6-methoxy-3,4-tetramethylenepyrylium perchlorates are converted to 2-alkyl-3,4-tetramethylene-6-pyridones (VIa-d) by the action of ammonia. Data on the properties of VI are presented in Table 2.

The reaction of 2-methyl-6-methoxy-3,4-pentamethylenepyrylium perchlorate with ammonia leads to 2-methyl-3,4-pentamethylene-6-aminopyridine VII.



III a VII

EXPERIMENTAL

The PMR spectra were recorded with an RYa-2305 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

The cycloalkenylacetic acid esters were obtained via the Reformatskii reaction [4].

General Method for the Preparation of 2-Methyl-6-methoxy-3,4-polymethylenepyrylium Perchlorates. A 3-mmole sample of 70% perchloric acid was added dropwise at room temperature to a solution of 3 mmole of methyl cycloalkenylacetate in 20 mmole of acetic anhydride, and the mixture was allowed to stand at room temperature for 2.5-3 h, after which it was diluted with ether. The liberated yellow oil began to crystallize on standing in a refrigerator. The product was removed by filtration, washed thoroughly with ether, dried, and reprecipitated several times from acetone by the addition of ether. This method was used to obtain salts IIa-d and IIIa-d (Table 1).

2-Methyl-3,4-tetramethylene-6-pyridone. An excess amount of 22% ammonium hydroxide was added to 0.25 g (8.9 mmole) of 2-methyl-6-methoxy-3,4-tetramethylenepyrylium perchlorate, and the mixture was allowed to stand for 3 days. Workup gave 0.13 g of crystalline product.

Compounds VIb-d were similarly obtained (Table 2).

2-Methyl-3,4-pentamethylene-6-aminopyridine. An excess amount of 22% ammonium hydroxide was added to 0.2 g (7 mmole) of 2-methyl-6-methoxy-3,4-pentamethylenepyrylium perchlorate, and the mixture was allowed to stand for 3 days. Workup gave 0.1 g (77%) of a colorless crystalline product with mp 86.5° (petroleum ether). Found: C 74.88; H 9.06; N 16.00%. $C_{11}H_{16}N_2$. Calculated: C 75.00; H 9.11; N 15.9%. IR spectrum: 3300 and 3460 cm^{-1}. PMR spectrum, δ, ppm: 1.56 (CH_2), 2,22 (CH_3), 2.5 (CH_2), 4.6 (NH_2), 5.83 (CH).

The signal of the protons of the amino group in the PMR spectrum vanished when a solution of the aminopyridine was deuterated.

2-Methyl-6-methoxy[2,3-c]cholestanopyrylium Perchlorate (V). A mixture of 0.47 g (1 mmole) of methyl hydroxycholestanoacetate [4, 5], 0.5 ml (5 mmole) of acetic anhydride, and 0.66 ml (1 mmole) of 70% perchloric acid was heated on a boiling-water bath for 30 min, after which it was cooled and diluted with ether. The resulting dark-brown precipitate was removed by filtration, washed with ether, and dried to give 0.28 g (50%) of shiny brown crystals with mp > 350° (glacial acetic acid). Found: C 68.35; H 9.30; Cl 5.64%. $C_{32}H_{51}ClO_6$. Calculated: C 68.00; H 9.00; Cl 6.02%. IR spectrum: 1100, 1270, and 1630 cm^{-1}.

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