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SYNTHESIS OF 4-CHLOROMETHYL-SUBSTITUTED PYRYLIUM SALTS

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The diacylation of methallyl chloride gave 2,6-dialkyl-4-chloromethylpyrylium salts, which were isolated in the form of stable perchlorates.

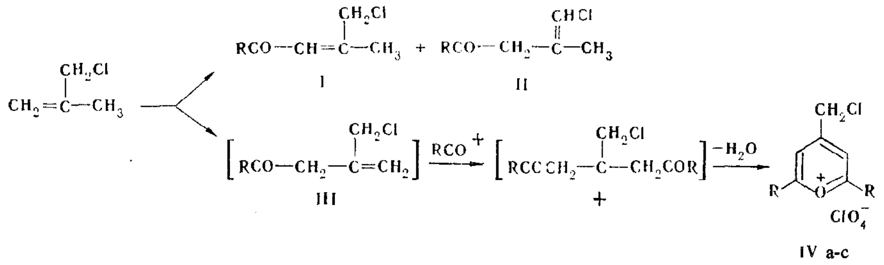
One of the principal methods for the synthesis of pyrylium salts is the diacylation of olefins [1]. In order to synthesize chloromethyl-substituted pyrylium salts and study their properties we carried out the diacylation of methallyl chloride for the first time.*

Monoacylation of methallyl chloride by the Kondakov method [3] gave alkyl γ-chloropropenyl ketones I, which proved to be intermediates in the syntheses of furans and pyrroles [4, 5].

In the present paper we describe the synthesis of 2,6-dialkyl-4-chloromethylpyrylium salts. The latter are of interest in connection with their ability to undergo three types of transformations, viz., recyclization with retention of the number of atoms in the ring, ring contraction [6], and reactions at the chloromethyl group [7], detailed information regarding which will be presented in a separate communication.

The diacylation of methallyl chloride makes it possible to obtain 2,6-dialkyl-4-chloromethylpyrylium salts IV, which were isolated in the form of crystalline perchlorates, in satisfactory yields.

In conformity with the generally accepted mechanism of the diacylation of olefins [8], the formation of the IV cations proceeds through intermediate β,γ-unsaturated ketones III.



IV a $R=CH_3$, b $R=C_2H_5$, c $R=C_3H_7$

Carboxylic acid anhydrides and 70% perchloric acid or acid chlorides and $AlCl_3$ were used as the acylating agents.

The IR and UV spectra of perchlorates IV are similar to the spectra of 2,4,6-trimethylpyrylium perchlorate. The PMR spectra contain signals of 2,6-dialkyl substituents at strong field, as well as singlets of CH_2Cl and ring protons.

In addition to salts IV, we also isolated liquid products that undergo partial decomposition during distillation *in vacuo* and darken on storage. The IR spectra of these products in the region of stretching vibrations contain strong absorption bands at 1720, 1690, 1665, and 1625 cm^{-1}, the first two of which we assigned to the vibrations of unconjugated (1720

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*See [2] for our preliminary communication.

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TABLE 1. 2,6-Dialkyl-4-chloromethylpyrylium Perchlorates

Compound	mp, deg C	Chemical shifts, ppm			Found, %			Empirical formula	Calc., %			Yield, %
		2,6-R	4-CH_2Cl	3,5-H	C	H	Cl		C	H	Cl	
IVa	174–175	3,03 (s, 6H)	4,91 (s, 2H)	8,00 (s, 2H)	37,6	4,1	27,8	$C_8H_{10}Cl_2O_5$	37,4	3,9	27,6	27
IVb	226–227	1,56 (t, 6H); 3,70 (q, 4H)	4,91 (s, 2H)	8,00 (s, 2H)	42,2	5,2	25,0	$C_{10}H_{14}Cl_2O_5$	42,1	4,9	24,9	24
IVc	149–150	1,03 t (6H), 2,17 (m, 4H, β-CH_2); 3,80 (t, 4H, α-CH_2)	4,91 (s, 2H)	8,00 (s, 2H)	46,2	6,0	22,5	$C_{12}H_{18}Cl_2O_5$	46,0	5,8	22,7	25

cm^{-1}) and conjugated (1690 cm^{-1}) carbonyl groups, whereas we assigned the other two to vibrations of double bonds. On the basis of this, it may be assumed that the substances are mixtures of ketones I and II. These products were not investigated in greater detail.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in trifluoroacetic acid were obtained with a Tesla BS-487B (80 MHz) spectrometer with hexamethyldisiloxane as the standard. The IR spectra of KBr pellets and mineral oil suspensions were recorded with a UR-20 spectrometer.

2,6-Dialkyl-4-chloromethylpyrylium Perchlorates (IVa-c). A) An 8-ml (0.1 mole) sample of 70% perchloric acid was added in the course of 5 min to a mixture of 0.72 mole of the carboxylic acid anhydride and 20 ml (0.24 mole) of methallyl chloride at such a rate that the temperature of the reaction mixture did not rise above 65°C, after which it was cooled and treated with 100 ml of ether. The resulting lower layer was separated by decantation and mixed with 10 ml of propyl alcohol. After 20 min, the crystalline precipitate was removed by filtration and washed with ether. The properties of the synthesized compounds are presented in Table 1.

For the separation of I and II (R = CH_3) the ether solution that was separated by decantation was neutralized with a solution of sodium carbonate, washed with water, and dried over $CaCl_2$. The ether was evaporated, and the residue was distilled *in vacuo*; 5 g of a fraction with bp 70-80°C (1-2 mm) was collected.

B) A 30-g (0.22 mole) sample of $AlCl_3$ was added in portions at 0°C to a mixture of 10 ml (0.12 mole) of methallyl chloride in 72 ml (1 mole) of acetyl chloride, and the mixture was then allowed to stand overnight. It was then heated at 60°C for 1.5 h, after which it was cooled and poured over 100 g of ice with 5 ml of concentrated HCl. This mixture was then extracted with ether. A 20-ml sample of 70% perchloric acid was added to the aqueous solution. After prolonged cooling, the precipitated crystals of IVa were removed by filtration and dried to give 10.6 g (40%) of a product with mp 174-175°C (from acetic acid).

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