## SYNTHESIS OF PYRYLIUM SALTS WITH FUNCTIONAL SUBSTITUENTS

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UDC 547.812

We have found that the acylation of methallyl chloride with acyl perchlorates gives 2,6-dialkyl-4-chloromethylpyrylium salts (I) in 25-30% yields.

$$\begin{array}{c} \text{CH}_2\text{CI} \\ \text{CH}_2 \\ \text{CH}_3 \end{array} \xrightarrow{\text{RCO}^+\text{CIO}_4^-} \begin{array}{c} \text{CH}_2\text{CI} \\ \text{+} \\ \text{0} \\ \text{R} \end{array} \begin{array}{c} \text{CIO}_4^- \\ \text{I} \end{array}$$

Acylation with acetyl chloride in the presence of  $AlCl_3$  makes it possible to raise the yield of I (R =  $CH_3$ , mp 174°) to 42%.

A number of tetrahydro-2-benzopyrylium perchlorates (II) containing an anhydride grouping were obtained by diacylation of cis-4-methyl-1,2,3,4-tetrahydrophthalic anhydride.

For example, 1,3-dimethyl-5,6,7,8-tetrahydro-6,7-anhydrodicarboxy-2-benzopyrylium perchlorate (II,  $R = CH_3$ ), with mp 280° (dec., from glacial acetic acid), was obtained in 25% yield. The IR and PMR spectra and the results of elementary analysis correspond to their assumed structure. PMR spectrum (80 MHz, in  $CF_3COOH$ ) of  $I(R = CH_3)$ ,  $\delta$ : 3.03 (s, 2,6- $CH_3$ ), 4.90 (s, 4- $CH_2$ ), and 7.96 ppm (s, 3-H, 5-H). The PMR spectra of  $I(R = C_2H_5, C_3H_7)$  differ only with respect to the appearance of multiplets from  $C_2H_5$  and  $C_3H_7$ . For proof of the structure of II, the latter was converted to III, the PMR spectrum of which (in  $CCl_4$ ) contains singlet signals at 2.34 and 2.36 (1- $CH_3$ , 3- $CH_3$ ), 3.58 and 3.62 (6, 7- $COOCH_3$ ), and 6.58 ppm (4-H) and a complex multiplet at 3 ppm from the protons of the saturated ring. The presence of the latter multiplet in the absence of a similar signal at stronger field excludes alternative structure IV.

Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1424, October, 1975. Original article submitted September 10, 1974.

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