SYNTHESIS OF PYRYLIUM SALTS BY CONDENSATION OF BENZALACETOPHENONE WITH ALIPHATIC CARBONYL COMPOUNDS

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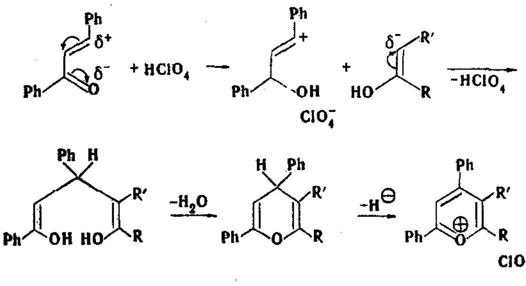
The acid condensation of chalcone with aliphatic ketones, aldehydes, and β-dicarbonyl compounds was studied for the first time. Tri- and tetrasubstituted pyrylium salts, including compounds containing functional substituents, were obtained.

It is known that symmetrical triaryl-substituted pyrylium salts have been obtained by the reaction of chalcones with aliphatic-aromatic and aromatic ketones in the presence of Lewis acids, strong mineral acids, or dehydrating agents such as polyphosphoric acid, $H_2SO_4 + POCl_3$ [1], $ZnCl_2$, $PbCl_2$ [2], $HClO_4$ [3], $BF_3 \cdot Et_2O$ [4,5], Ph_3CClO_4 [6], and CH_3COClO_4 [7]. The mechanism of their formation includes the addition of the methyl or methylene ketone to the chalcone via the Michael reaction to give a 1,5-diketone with subsequent cyclization and dehydrogenation, based on the properties of the chalcone salt as a hydride-ion acceptor [8]. There is no information on the reaction of chalcones with aliphatic compounds in the literature available to us. The preparation of 2-methyl-3-carbethoxy-4,6-phenylpyrylium salt by the reaction of benzalacetophenone with acetoacetic ester in the presence of boron trifluoride etherate as the dehydrating agent is described only in one of the latter papers [8].

In order to extend the possibilities of this method, we studied the condensation of benzalacetophenone with aliphatic ketones (acetone and diethyl ketone), acetaldehyde, and β-dicarbonyl compounds (dibenzoylmethane, acetylacetone, and acetoacetic ester) in the presence of perchloric acid. We have demonstrated that this route can be used to obtain tri- and tetrasubstituted pyrylium salts, as well as difficult-to-obtain pyrylium compounds that contain carbonyl and carboxyl groups. The reaction probably proceeds via the following scheme:



R=H, CH_3, C_2H_5, C_6H_5; R′=H, CH_3, $COCH_3$, COC_6H_5, $CO_2C_6H_5$

To obtain pyrylium salts via this method, a mixture of benzalacetophenone and the appropriate carbonyl compound is allowed to stand for 5-10 h in the presence of anhydrous perchloric acid, which is obtained by tying up the water in 72% $HClO_4$ by means of acetic anhydride. The pyrylium salts formed are readily isolated from the reaction mixture in the crystalline state in yields of 8-45%. Owing to the mild conditions involved in carrying out this reaction, we were able to synthesize the previously unknown pyrylium salts containing acetyl and benzoyl groups in the 3 position of the pyrylium ring. Earlier attempts

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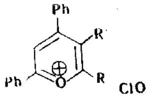
TABLE 1



R	R′	mp, °C	Appearance	Empirical formula	Found, %			Calc., %			IR spectrum, , cm^{-1}	Yield,%
					C	H	Cl	C	H	Cl		
H	H	249*	Yellow crystals	$C_{17}H_{13}ClO_5$	61,1	4,0	10,9	61,5	4,1	10,5	1630, 1590, 1540, 1480, 1380, 1090	8
CH_3	H	259	Red-yellow crystals	$C_{18}H_{15}ClO_5$	62,7	3,7	10,4	62,4	4,0	10,1	1630, 1590, 1540, 1460, 1100	45
C_2H_5	CH_3	223—225	Yellow needles	$C_{20}H_{19}ClO_5$	64,3	5,3	9,5	64,2	5,1	9,3	1610, 1570, 1500, 1400, 1100	23,5
CH_3	$COCH_3$	204—205	Yellow needles	$C_{20}H_{17}ClO_6$	61,8	4,3	9,4	61,9	4,3	9,1	1700, 1630, 1570, 1480, 1400, 1100	7,5
C_6H_5	COC_6H_5	235—236	Dark-yellow crystals	$C_{30}H_{21}ClO_6$	70,9	4,5	7,0	70,9	4,1	6,9	1670, 1630, 1570, 1510, 1400	25
CH_3	$COOC_2H_5$	176†	Yellow crystals	$C_{21}H_{19}ClO_7$	60,9	4,8	8,4	60,0	4,6	8,3	1720, 1610, 1570, 1500, 1400, 1100	28

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*According to [6], mp 240°.

† According to [8], mp 178°.

to synthesize such compounds did not give positive results, since the acyl groups were cleaved under the reaction conditions [9, 10].

The synthesized pyrylium salts are readily converted to the corresponding pyridines in quantitative yield by the action of 25% ammonium hydroxide. The structures and compositions of the synthesized compounds were confirmed by the results of elementary analysis and IR spectroscopy (Table 1). The IR spectra of the salts contain absorption bands at 1620-1630, 1540-1560, 1480-1510, and 100 cm^{-1} (ClO_4^- ion), which are characteristic for pyrylium perchlorates, and at 1670-1720 cm^{-1}, which are characteristic for salts that contain benzoyl, acetyl, and carbethoxy groups in the 3 position of the pyrylium ring [11].

EXPERIMENTAL

Synthesis of Pyrylium Salts (Table 1). A 4.16-g (0.02 mole) sample of benzalacetophenone was dissolved in 20 ml of ether, and a previously prepared mixture of 2.5 ml (0.025 mole) of 70% $HClO_4$ and 7.5 ml of acetic acid was added dropwise with cooling, followed by the addition of 0.02 mole of the carbonyl compound. The solution was allowed to stand in the cold for 5 h, and the precipitated salt was removed by filtration, washed with ether, and crystallized from acetic acid.

2-Ethyl-3-methyl-4,6-diphenylpyridine Hydrochloride. Excess (0.2 mole) 25% ammonium hydroxide was added to 0.79 g (0.002 mole) of 2-ethyl-3-methyl-4,6-diphenylpyrylium perchlorate, and the mixture was allowed to stand at room temperature for 2-3 h to give 0.4 g (75%) of red-yellow crystals. The product was washed with water, dried, and dissolved in dry ether. Anhydrous hydrogen chloride was passed through the solution to precipitate 0.24 g (52%) of colorless crystals with mp 132° (from acetone). Found: C 77.9; H 6.2; Cl 10.6%. $C_{20}H_{20}ClN$. Calculated: C 78.0; H 6.5; Cl 11.3%. The product was quite soluble in water and, like the previously studied 2-alkyl-3,4;5,6-bistrimethylenepyridine salts [12], had respiratory stimulating action, sedative properties, and a weak analgesic effect.

2,4,6-Triphenyl-3-benzoylpyridine. Treatment of 0.52 g (0.001 mole) of 2,4,6-triphenyl-3-benzoylpyridine perchlorate with excess (0.1 mole) 25% ammonium hydroxide gave 0.32 g (78%) of red-yellow crystals with mp 165° (from acetic acid). IR spectrum: 1680, 1620, 1600, 1550, and 1500 cm^{-1}. Found: C 87.8; H 5.0%. $C_{30}H_{21}ON$. Calculated: C 87.6; H 5.1%.

The IR spectra of mineral-oil pastes of the synthesized compounds were recorded with a UR-20 spectrophotometer at 600-1800 cm^{-1} (NaCl prism).

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