CONDENSATION OF ACETALS OF AROMATIC β-KETO ALDEHYDES WITH KETONES AND PHENOLS

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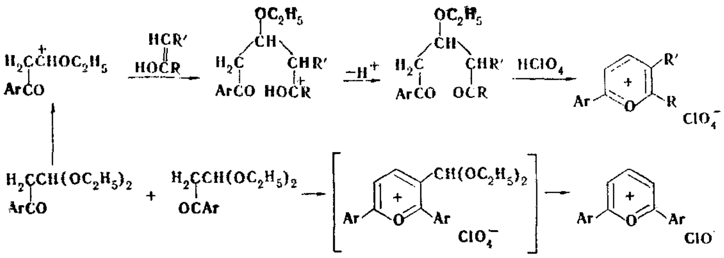
Pyrylium salts with a free (active) γ position and different kinds of substituents in the α,α' positions of the pyrylium ring were obtained by the reaction of acetals of aroylacetaldehydes with ketones and phenols.

It is known that in the condensation of α-formyl ketones with ketones, which proceeds with the formation of pyrylium salts, the yields of salts and often the very possibility of obtaining the desired product depend to a considerable degree on the percentage of the enol form of the formyl ketone in the equilibrium mixture of tautomers. The higher the degree of enolization of the aldehyde group, the lower the yield and the probability of obtaining the pyrylium salt [1]. It is apparent that replacement of the aldehyde group by an unenolized formyl fragment makes it possible to avoid the indicated difficulties. This requirement is satisfied when the aldehydes are replaced by their diethylacetals. It is known that the condensation of acetals of some β-keto aldehydes with phenols leads to pyrylium salts [2]. In addition, we have previously demonstrated that malondialdehyde tetraethylacetal [3] and benzoylacetaldehyde diethylacetal [4] are capable, under acid catalysis conditions, of reacting with ketones to form 2-aryl-substituted pyrylium salts.

Continuing our research in this direction, we studied the reaction of the diethylacetals of several aroylacetaldehydes (benzoylacetaldehyde, p-methoxybenzoylacetaldehyde, and p-ethoxybenzoylacetaldehyde) with aliphatic, alicyclic, and aliphatic-aromatic ketones and phenols under acid catalysis conditions, which leads to pyrylium and benzopyrylium salts. The reaction was carried out by brief refluxing (5-6 min) of a mixture of the appropriate β-keto acetal with a slight excess of the ketone or phenol in the presence of an equimolecular amount of perchloric acid, previously mixed with the calculated amount of acetic anhydride (to tie up the water present in 70% $HClO_4$) in glacial acetic acid. The reaction probably proceeds in accordance with the scheme



The synthesized salts (Table 1) are high-melting, colored compounds that fluoresce in solution in the green region. Unsymmetrical 2,6-diaryl-substituted pyrylium salts can be readily obtained by this method. As a result, we found a route to the synthesis of pyrylium salts with a free (active) γ position and different kinds of substituents in the α,α' positions of the pyrylium ring. It is interesting that the autocondensation of diethylacetals of aroylacetaldehydes in the presence of an equimolecular amount of perchloric acid proceeds with splitting out of a formyl fragment from the β-carbon atom of the pyrylium ring and leads to symmetrical 2,6-diarylpyrylium salts.

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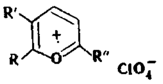
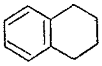
TABLE 1



Comp.	R	R′	R″	mp, °C*	Empirical formula
I	C_6H_5	H	C_6H_5	222	$C_{17}H_{13}ClO_5$
II	C_6H_5	H	$4\text{-}CH_3OC_6H_4$	241—242	$C_{18}H_{15}ClO_6$
III	C_6H_5	H	$4\text{-}C_2H_5OC_6H_4$	208—210	$C_{19}H_{17}ClO_6$
IV	C_6H_5	H	$3,4\text{-}(CH_3)_2C_6H_3$	220—222	$C_{19}H_{17}ClO_7$
V	$4\text{-}CH_3OC_6H_4$	H	$4\text{-}CH_3OC_6H_4$	249	$C_{19}H_{17}ClO_7$
VI	$4\text{-}CH_3OC_6H_4$	H	$4\text{-}C_2H_5OC_6H_4$	205—208	$C_{20}H_{19}ClO_7$
VII	$4\text{-}C_2H_5OC_6H_4$	H	$4\text{-}C_2H_5OC_6H_4$	220—221	$C_{21}H_{21}ClO_7$
VIII	C_2H_5	CH_3	C_6H_5	150—151	$C_{14}H_{15}ClO_5$
IX	CH_3	$COOC_2H_5$	C_6H_5	180—182	$C_{15}H_{15}ClO_7$
X	$(CH_2)_4$		C_6H_5	172—173	$C_{15}H_{15}ClO_5$
XI	1,2-Naphtha		C_6H_5	188	$C_{19}H_{13}ClO_5$
XII			C_6H_5	201—203	$C_{19}H_{15}ClO_5$

Comp.	Found, %			Calc., %			IR spectrum, cm^{-1}	Yield, % (method)
	C	H	Cl	C	H	Cl		
I	—	—	—	—	—	—	1662	42,5 (D)
II	58,4	4,2	9,5	58,3	4,1	9,8	1620	53 (A), 20 (B)
III	60,6	4,7	9,7	60,6	4,6	9,4	1620	40 (A), 16 (C)
IV	58,2	4,3	8,8	58,0	4,4	9,0	1620	40 (A)
V	—	—	—	—	—	—	1624	25 (B), 20 (D)
VI	59,7	5,0	8,6	59,0	4,7	8,7	1609	35 (B), 40 (C)
VII	—	—	—	—	—	—	1609	35 (C), 25 (D)
VIII	55,9	5,0	12,4	56,2	5,0	11,9	1612	50 (A)
IX	—	—	—	—	—	—	1616	76,5 (A)
X	—	—	—	—	—	—	1620	58,8 (A)
XI	63,2	3,7	9,8	63,9	3,6	10,1	1612	28
XII	—	—	—	—	—	—	1611	97 (A)

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*The melting points were in agreement with those presented in [4,7], and the products did not depress the melting points of genuine samples. All of the substances were recrystallized from acetic acid.

The IR spectra of the compounds obtained were studied. It is known [8, 9] that the shift of the 8a and 8c bands (according to the Wilson classification [10]) in the spectra of substituted pyrylium salts correlates with the stability of the pyrylium ring. Nucleophilic substituents in the α and γ positions usually shift the 8a and 8c bands to higher frequencies, while, on the other hand, substituents in the β,β' position shift the 8a and 8c absorption bands of the pyrylium ring in the opposite direction.

The IR spectra of the salts that we synthesized contain an intense 8a band at 1609-1620 cm^{-1} and an 8c band at 1530-1560 cm^{-1}, which correspond to the symmetrical and asymmetrical vibrations of the pyrylium ring. No substantial stabilization of the pyrylium ring, as compared with the unsubstituted pyrylium cation [9] (8a 1620 cm^{-1}, 8c 1557 cm^{-1}), occurs on introduction of aromatic substituents into the α position of the pyrylium ring. A slight shift of the 8a band to lower frequencies is observed for salts I, III, VI, and VIII, which can be ascribed to the appearance of β-substituents in the pyrylium ring [9]. The remaining bands correspond to the vibrations of the aromatic substituents and the ClO_4^- ion.

EXPERIMENTAL

2-Ethyl-3-methyl-6-phenylpyrylium Perchlorate (VIII) (Method A). A 0.3-ml (3 mmole) sample of 70% $HClO_4$, mixed with 0.9 ml (9 mmole) of acetic anhydride, was added to a mixture of 0.4 ml (4 mmole) of diethyl ketone and 0.6 ml (3 mmole) of benzoylacetaldehyde diethylacetal in anhydrous acetic acid. The mixture was refluxed for 5-6 min and cooled, and the precipitate was removed by filtration, washed with ether, and dried to give 0.4 g (50%) of orange needles with mp 150-151° (from acetic acid).

In method B, the 2,6-diarylpyrylium salts were obtained by the condensation of p-methoxybenzoylacetaldehyde diethylacetal with ketones under the conditions of method A.

In method C, the pyrylium salts were synthesized under the conditions of the condensation of p-ethoxybenzoylacetaldehyde diethylacetal with ketones.

2,6-Di(p-methoxyphenyl)pyrylium Perchlorate (V) (Method D). A solution of 0.2 ml (2 mmole) of 70% $HClO_4$ in 0.6 ml (6 mmole) of acetic anhydride was added to 1 ml (4 mmole) of p-methoxybenzoylacetaldehyde diethylacetal, and the mixture was refluxed for 2-3 min. Cooling precipitated 0.3 g (20%) of red needles of V with mp 249° (mp 248-250°) [3].

3-Phenylbenzo[*f*]chromylium Perchlorate (XI). An 8-ml (80 mmole) sample of acetic anhydride and 8 ml of ether were added to a mixture of 5 ml (22 mmole) of benzoylacetaldehyde diethylacetal and 3.2 g (22 mmole) of β-naphthol, and 2.4 ml (22 mmole) of 70% $HClO_4$ was then added dropwise. The mixture darkened and warmed up slightly. A precipitate of XI began to form after a certain time. The mixture was worked up to give 2 g (25%) of orange needles with green fluorescence and mp 188°.

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