# SYNTHESIS OF PYRYLIUM SALTS BY CONDENSATION OF β-CHLOROCINNAMALDEHYDES WITH CARBONYL COMPOUNDS

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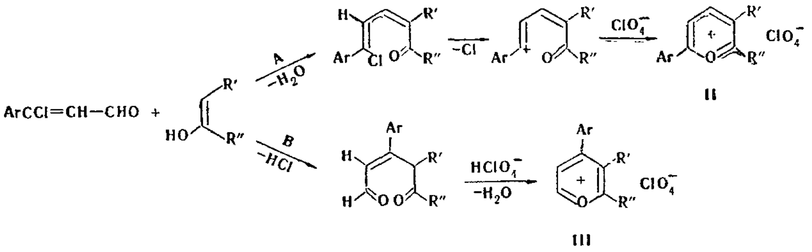
A method is proposed for the synthesis of unsymmetrical unsubstituted pyrylium salts by condensation of β-chlorocinnamaldehydes with methyl and methylene ketones and β-dicarbonyl compounds in the presence of $HClO_4$ or Lewis acids. The probable scheme of the reaction is examined.

Pyrylium salts of various structure were obtained by condensation of β-chlorovinyl ketones with phenols [1] activated by ketones [2] or enamines [3]. We have used the more active β-chlorocinnamaldehydes (Ia-c), which are readily obtained from the corresponding acetophenones and the Vilsmeier reagent [4].

In the condensation of such aldehydes with ketones one might have expected the formation of pyrylium salts via one of the following schemes:



I a $Ar=C_6H_5$; b $Ar=4\text{-}O_2NC_6H_4$; c $Ar=3,4\text{-}(CH_3O)_2C_6H_3$

Scheme A might have been realized by electrophilic attack of the methylene group of the ketone by the carbon atom of the aldehyde group and subsequent formation of γ-unsubstituted pyrylium salts (II), while scheme B, in analogy with condensations of β-chlorovinyl ketones, should lead to α-unsubstituted pyrylium salts III.

It was found that only the known 2,6-diphenylpyrylium perchlorate is obtained in the reaction of β-chlorocinnamaldehyde Ia with acetophenone; this corresponds to scheme A.

The occurrence of the reaction via scheme A is confirmed by the fact that compounds 16, 19, and 23 (see Table 1) are identical to known samples obtained by other methods.

β-Chlorocinnamaldehydes proved to be convenient reagents for the synthesis of unsymmetrical pyrylium salts with an activated γ-position, including also compounds containing functional substituents; previous attempts to accomplish this synthesis were unsuccessful.

The use of aldehydes Ia and Ib makes it possible to obtain pyrylium salts from dimedone and indanedione (compounds 20, 21, and 22); this cannot be accomplished when other β-dicarbonyl compounds and their analogs are used. The presence in the aryl residue of electron-donor substituents (Ic) passivates the

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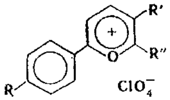
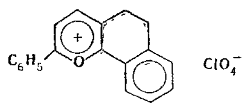
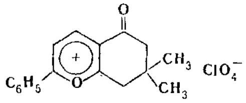
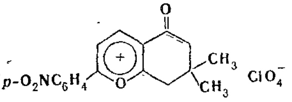
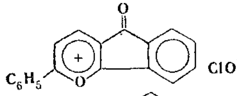
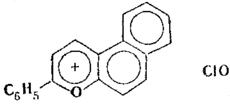
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1031-1035, August, 1974. Original article submitted July 31, 1973.

TABLE 1. Properties of 2-Phenylpyrylium Salts



| No. | R | R′ | R″ | mp, °C | Empirical formula | Found, % |  |  | Calculated, % |  |  | IR spectrum, cm⁻¹ | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | C | H | Hal | C | H | Hal |  |  |
| 1 | H | H | $C_6H_5$ | $222^5$ | $C_{17}H_{13}ClO_5$ | — | — | — | — | — | — | 1616, 1602, 1538, 1500, 1090 | 75 |
| 2 | $NO_2$ | H | $C_6H_5$ | 282 | $C_{17}H_{12}ClO_7$ | 54,2 | 3,2 | 9,7 | 54,0 | 3,2 | 9,4 | 1630, 1535, 1100 | 73 |
| 3 | H | H | $4\text{-}CH_3OC_6H_4$ | 241—242 | $C_{18}H_{15}ClO_6$ | 58,5 | 4,2 | 9,5 | 58,3 | 4,1 | 9,8 | 1615, 1580, 1100 | 58 |
| 4 | H | H | $3,4\text{-}(CH_3O)_2C_6H_3$ | 226—228 | $C_{19}H_{17}ClO_7$ | 58,4 | 4,2 | 9,3 | 58,0 | 4,4 | 9,0 | 1620, 1535, 1090 | 33 |
| 5 | H | H | $2\text{-}C_4H_3S$ | 190 | $C_{15}H_{11}ClO_5S$ | 52,9 | 3,3 | 19,6* | 53,1 | 3,3 | 20,0 | 1625, 1605, 1090 | 44 |
| 6 | H | H | $4\text{-}BrC_6H_4$ | 240 | $C_{17}H_{12}ClBrO_5$ | 52,2 | 3,0 | 27,5 | 52,5 | 2,9 | 28,0 | 1615, 1590, 1100 | 51 |
| 7 | $NO_2$ | H | $4\text{-}CH_3C_6H_4$ | 276 | $C_{18}H_{14}ClO_7$ | 54,9 | 3,8 | 9,3 | 55,1 | 3,9 | 9,1 | 1630, 1530, 1100 | 52 |
| 8 | $NO_2$ | H | $4\text{-}NO_2C_6H_4$ | 241 | $C_{17}H_{11}N_2ClO_9$ | 48,0 | 2,9 | 8,7 | 48,2 | 2,6 | 8,4 | 1630, 1605, 1100 | 42 |
| 9 | H | $CH_3$ | $C_6H_5$ | 162—163 | $C_{18}H_{15}ClO_5$ | 59,9 | 4,2 | 9,7 | 59,5 | 4,1 | 9,8 | 1605, 1550, 1100 | 39 |
| 10 | H | $COC_6H_5$ | $C_6H_5$ | 206 | $C_{24}H_{17}ClO_6$ | 65,6 | 3,9 | 8,3 | 65,9 | 3,9 | 8,1 | 1665, 1605, 1090 | 100 |
| 11 | $NO_2$ | $COC_6H_5$ | $C_6H_5$ | 265 | $C_{24}H_{16}ClO_8$ | 59,4 | 3,1 | 6,9 | 59,7 | 3,3 | 7,4 | 1680, 1615, 1530, 1100 | 97 |
| 12 | H | $CH_2COOH$ | $C_6H_5$ | 264 | $C_{19}H_{15}ClO_7$ | 58,0 | 3,8 | 9,0 | 58,2 | 3,8 | 9,1 | 1735, 1607, 1100 | 83 |
| 13 | H | $C_6H_5$ | $4\text{-}C_6H_5C_6H_4$ | 224 | $C_{29}H_{21}ClO_5$ | 71,5 | 4,0 | 7,7 | 71,5 | 4,3 | 7,9 | 1615, 1590, 1090 | 64 |
| 14 | H | Cl | $4\text{-}C_6H_5C_6H_4$ | 243 | $C_{23}H_{16}Cl_2O_5$ | 62,0 | 3,7 | 16,4 | 62,1 | 3,6 | 16,0 | 1620, 1585, 1090 | 57 |
| 15 | H | H | $1\text{-}C_{10}H_7$ | 212 | $C_{21}H_{15}ClO_5$ | 66,0 | 4,1 | 9,3 | 65,8 | 3,9 | 9,4 | 1615, 1540, 1100 | 50 |
| 16 | H | $COOC_2H_5$ | $CH_3$ | $185^6$ | $C_{15}H_{15}ClO_7$ | 52,4 | 4,5 | 10,8 | 52,5 | 4,4 | 10,4 | 1725, 1615, 1095 | 53 |
| 17 | H | H | COOH | 229 | $C_{12}H_9ClO_7$ | 48,0 | 3,2 | 11,0 | 47,8 | 3,0 | 11,4 | 1755, 1625, 1100 | 33 |
| 18 | H | $CH_3$ | $C_2H_5$ | 150 | $C_{14}H_{15}ClO_5$ | 55,9 | 5,0 | 13,3 | 56,2 | 5,0 | 13,9 | 1610, 1560, 1095 | 25 |
| 19 |  |  |  | 215—216† | $C_{19}H_{15}ClO_5$ | 63,8 | 4,0 | 10,4 | 63,5 | 4,2 | 9,9 | 1610, 1602, 1575, 1500, 1090 | 42 |
| 20 |  |  |  | 223 | $C_{17}H_{17}ClO_6$ | 57,8 | 4,9 | 10,4 | 57,8 | 4,8 | 10,8 | 1705, 1615, 1090 | 64 |
| 21 |  |  |  | 175—185 | $C_{17}H_{16}ClO_8$ | 51,0 | 4,1 | 8,6 | 51,3 | 4,0 | 8,9 | 1715, 1625, 1530, 1100 | 58 |
| 22 |  |  |  | 172 | $C_{18}H_{11}ClO_6$ | 63,9 | 3,3 | 9,5 | 63,5 | 3,1 | 9,9 | 1705, 1620, 1090 | 62 |
| 23 |  |  |  | $188^8$ | — | — | — | — | — | — | — | 1610, 1590, 1095 | 28 |

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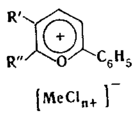
*The sum of Cl and S.

†According to [7], this compound has mp 204-206°C.

TABLE 2



| No. | R′ | R″ | Hexachlorostibiates | | Pentachlorostannates | |
|---|---|---|---|---|---|---|
| | | | mp, °C | Yield, % | mp, °C | Yield, % |
| 24 | H | $C_6H_5$ | 242 | 18 (13)* | 267 | 19† |
| 25 | $COC_6H_5$ | $C_6H_5$ | 147 | 60 (64) | 133 | 72 |
| 26 | H | $CH_3$ | 160 | 10 (20) | 170 | 33 |
| 27 | $CH_3$ | $C_2H_5$ | 130 | 12 (10) | 196 | 29 |
| 28 | $COOC_2H_5$ | $CH_3$ | 140 | 15 (51) | 173 | 66 |

* These are the yields for reaction in $CH_3COOH$ (in $CH_2Cl_2$).

† This is the yield for reaction in $CH_2Cl_2$.

aldehyde group, and this leads to a decrease in the yield of the pyrylium salt and an increase in the reaction time.

As the electron density in the aryl ring of aliphatic-aromatic ketones increases, their ability to undergo condensation with β-chlorocinnamaldehyde decreases. Only polymeric products are isolated when phenols are used as the ketone component during acid catalysis, but the corresponding naphthopyrylium salt is formed in the condensation of Ia with β-naphthol (1 : 1), apparently as a consequence of predominant reaction at the more active α-position.

Admixtures of isomeric pyrylium salt III were not detected in a single case, and aldehydes Ia-c, in contrast to β-chlorovinyl ketones, consequently undergo condensation with ketones in the presence of $HClO_4$ exclusively at the carbon atom of the carbonyl group. Complexing catalysts ($SnCl_4$ and $SbCl_5$) in protic and aprotic solvents can be used in place of perchloric acid, but even this does not make it possible to direct the process via scheme B.

The pyrylium pentachlorostannates and hexachlorostibiates obtained in this manner (Table 2) were converted to perchlorates and proved to be identical to samples obtained when perchloric acid was used.

The $SnCl_4$ catalyst is somewhat more active than $SbCl_5$. Perchloric acid is more favorable for condensation of β-chlorocinnamaldehyde with aliphatic-aromatic ketones and some dicarbonyl compounds. However, the use of $SnCl_4$ provides broader synthetic possibilities, inasmuch as the reaction proceeds under very mild conditions.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-10 spectrometer.

Synthesis of Pyrylium Salts by Condensation of β-Chlorocinnamaldehydes (I) with Ketones. A. In the presence of perchloric acid. Acetic anhydride (3 ml) was added to a mixture of 0.012 mole of the ketone, 10 ml of glacial acetic acid, 0.01 mole of I, and 1 ml of 70% $HClO_4$, and the resulting solution was refluxed for 5-10 min (in the case of Ia) or 10-20 min (Ib, c) until vigorous HCl evolution ceased. The crystals that formed when the solutions were cooled were removed by filtration and washed successively with ethyl acetate and ether. An additional amount of pyrylium salt precipitated from the filtrate. The IR spectra of the synthesized compounds contain intense bands at 1600-1620, 1580-1600, and 1090-1100 $cm^{-1}$, which are related to the vibrations of the pyrylium cation, the aromatic substituents, and the $ClO_4^-$ anion, respectively. Intense absorption bands at 1660-1705 $cm^{-1}$ also appeared for compounds containing carbonyl groups in the β-position of the pyrylium ring.

The introduction of a nitro group into the 4-position of the aryl substituent causes a short-wave shift at 10-20 $cm^{-1}$ of the stretching vibrations of the pyrylium cation.

B. In the presence of complexing catalysts. A 0.003-mole sample of $SnCl_4$ or $SbCl_5$ was added slowly to a mixture of 0.002 mole of aldehyde Ia, 0.002 mole of the ketone, 10 ml of glacial acetic acid, and 10 ml of ether, during which the mixture began to boil. The solution was allowed to stand for 10-12 h, and the precipitated crystals were removed by filtration and washed with dry ether. The reaction was carried out similarly by replacing the acetic acid by 5 ml of methylene chloride.

In order to synthesize the pyrylium perchlorates, the pentachlorostannates or hexachlorostibiates were dispersed in acetone or acetic acid with excess 70% $HClO_4$. The mixture was refluxed for 10 min and diluted with ether, and the precipitated crystals were removed by filtration. The perchlorates formed in this manner did not depress the melting point of the samples described above.

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