PYRYLIUM SALTS FROM PYRONES AND SOME ORGANOMETALLIC COMPOUNDS

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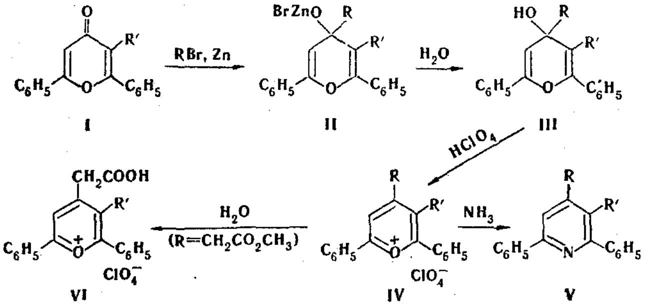
Pyrones and their analogs react with methyl bromoacetate and methyl γ-bromocrotonate in the presence of activated zinc to give, ultimately, carbomethoxymethyl- or (3-carbomethoxy-2-propenyl)-substituted pyrylium salts. The Ivanov reagent from phenylacetic acid reacts with pyrones to give carboxybenzyl-substituted pyrylium salts.

The conversion of pyrylium salts to compounds of the aromatic and heterocyclic series is well known [1]. Their direct practical application (see [2], for example) has recently been investigated. The possibility of chemical bonding of pyrylium salts with other organic compounds with retention of the pyrylium ring (for example, copolymerization during the creation of modified plastics) extends their application considerably. Pyrylium cations with isolated carboxy or carbethoxy groups can probably be considered to be most convenient for this purpose. The well-known organometallic syntheses of pyrylium salts from pyrones [2] do not make it possible to attach functional groups to heteroaromatic systems, but they have led us to the idea of using the Reformatskii reaction for this purpose [3].



The reaction of 2,6-diphenyl-4-pyrone (I), 2,6-diphenyl-4-thiapyrone, 2,6-diphenyl-3-bromo-4-pyrone, flavone, and xanthone with methyl bromoacetate (or ethyl iodoacetate) in the presence of activated zinc in dry benzene gives the typical (for the Reformatskii reaction) organometallic complex II, which is hydrolyzed to pyranol III on hydrolysis with dilute acetic acid. Pyranol III is converted to pyrylium perchlorate IV on treatment with perchloric acid. The 2,6-diphenyl-4-carbomethoxymethylpyrylium salt is converted to carboxymethyl-substituted pyrylium perchlorate VI by hydrolysis, but it is converted to pyridine V by the usual method.

The reaction of methyl γ-bromocrotonate with pyrones (IV, when $R = CH_2CH{=}CHCOOCH_3$, $R' = H$) proceeds similarly and without any complications.

This success naturally induced us to search for syntheses of pyrylium salts by means of other organometallic compounds. It was found that the Ivanov reagent obtained from sodium phenylacetate and isopropylmagnesium chloride by the method in [4] reacts with pyrones, flavones, and xanthone as with ordinary carbonyl compounds, and product VII is hydrolyzed to give pyranol VIII, from which it is easy to pass to pyrylium salt IX. The latter in turn can be converted to pyridine X.

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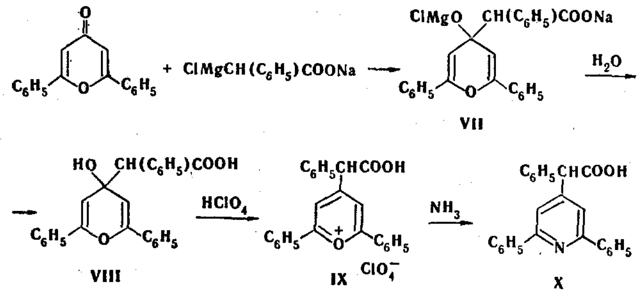

We were unable to introduce a new reagent obtained from β-chloropropionic acid [5] into the reaction. Neither the Reformatskii reaction nor the Ivanov reagent could be used for the synthesis of pyrylium salts from 2,6-dimethylpyrone and 2,4-dimethyl- and 2,4-diphenylcoumalin or for the preparation of cyclopropenylium salts from diphenylcyclopropenone.

The most characteristic bands in the IR spectra of the perchlorates obtained are affiliated with the symmetrical and asymmetrical vibrations of the pyrylium ring [6]. These are the strong 8a band (in the Wilson classification) at 1610-1630 cm^{-1} and the bands at 1520-1540 cm^{-1} (8b) and 1470-1480 cm^{-1} (19a). The PMR spectra of the synthesized compounds also confirm their structure. Thus, for example, the spectrum of IX contains the singlet of a methylidyne proton at δ 7.04 ppm. The somewhat elevated chemical shift of this group is explained by the decrease in the electron density on it due to concentration of electrons on the carboxyl group and the pyrylium ring. The signals of the pyrylium ring and the protons of the 2,6-phenyl substituents are found at 7.5-8.2 ppm, while the signal of the OH group is situated at 8.43 ppm. The singlet of the phenyl protons of the benzyl substituent is observed at 6 ppm. Pyrylium salts with carbomethoxymethyl and carbomethoxypropenyl substituents also have similar spectra. Thus the singlet at 6.46 ppm (IV, R = CH_2COOCH_3) probably corresponds to the methylene group. Here a pronounced shift to weak field due to the electron-acceptor properties of the carbomethoxy group and the pyrylium ring is also observed. The group of overlapping signals at 7.14-7.94 ppm corresponds to the chemical shifts of the protons of the pyrylium ring and the 2,6-phenyl substituents.

EXPERIMENTAL

The IR spectra of KBr pellets were recorded with a UR-20 spectrophotometer. The PMR spectra* were recorded with a YaMR-5535 spectrometer (40 MHz); the internal standard was cyclohexane, the solvent was dimethyl sulfoxide (DMSO), and the chemical shifts are converted to the δ scale.

2,6-Diphenyl-4-carbomethoxymethylpyrylium Perchlorate (IV). A mixture of 2.5 g (0.01 mole) of 2,6-diphenyl-γ-pyrone, 3 g (0.1 g-atom) of zinc, and 3 g (0.02 mole) of methyl bromoacetate in 5 ml of dry benzene was heated until it began to boil spontaneously, after which it was refluxed for another 10-15 min, cooled, and decomposed with 50 ml of 4% acetic acid. The pyranol was extracted with ether, and the extract was dried and treated with 1.5 ml of 70% perchloric acid. Workup gave 2.9 g (7.3%) of a product with mp 235°.

Pyrylium salts were similarly obtained from thiapyrone, flavone, xanthone, and methyl bromoacetate, ethyl iodoacetate, and methyl bromocrotonate (see Table 1).

2,6-Diphenyl-4-hydroxy-4-carbomethoxymethyl-4H-pyran (III). This compound was isolated after evaporation of the ether extract of the preceding experiment and was crystallized twice from hexane to give colorless needles with mp 133° in 70% yield. Found,%: C 62.3; H 5.3. $C_{20}H_{18}O_4$. Calculated,%: C 62.1; H 5.6.

2,6-Diphenyl-4-hydroxy-4-carboxymethyl-4H-pyran. A solution of 1.2 g (0.021 mole) of KOH in 1.7 ml of water was added slowly to a solution of 2.25 g (0.007 mole) of carbomethoxymethylpyran III in 35 ml of ethanol, after which the mixture was refluxed for 4 h. The resulting potassium salt was dissolved in the minimum amount of water and acidified to pH 1 with hydrochloric acid. The reaction product was extracted with ether, and the extract was washed with concentrated NaCl solution, dried, and evaporated to give 1.6 g (74%) of a product with mp 73° (from hexane). Found,%: C 74.2; H 5.2. $C_{19}H_{16}O_4$. Calculated,%: C 74.0; H 5.2.

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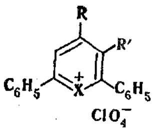
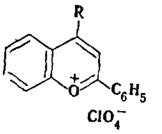
*We sincerely thank L. M. Kaplan for recording the spectra and assisting us in their interpretation.

TABLE 1

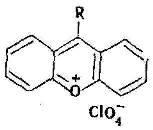


IV a, b

a X=O; b X=S



XI



XII

Comp.	R	R′	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	Cl	C	H	Cl	
IVa	CH_2COOCH_3	H	235	$C_{20}H_{17}ClO_7$	59,3	4,8	8,8	59,4	4,2	8,7	73
XI	CH_2COOCH_3		208—209	$C_{18}H_{15}ClO_7$	56,6	4,2	9,0	57,1	3,9	9,2	92
XII	CH_2COOCH_3		220—221	$C_{16}H_{13}ClO_7$	54,3	4,0	10,7	54,5	3,8	10,0	68
IVa	$CH_2COOC_2H_5$	H	249	$C_{21}H_{19}ClO_7$	60,6	5,8	8,8	60,2	4,5	8,4	71
IVb	CH_2COOCH_3	H	229	$C_{20}H_{17}ClO_6S$[a]	57,3	4,3	7,6	57,1	4,0	8,4	62
IVa	CH_2COOCH_3	Br	222	$C_{20}H_{16}BrClO_7$[b]	49,6	3,4	7,9	49,7	3,3	7,4	51
IX	$C_6H_5CHCOOH$	H	255	$C_{25}H_{19}ClO_7$	64,5	4,3	7,5	64,4	4,1	7,6	60
XI	$C_6H_5CHCOOH$		225	$C_{23}H_{17}ClO_7$	62,5	3,8	8,5	62,3	3,9	8,1	53
XII	$C_6H_5CHCOOH$		201	$C_{21}H_{15}ClO_7$	60,3	3,9	7,7	60,9	3,6	8,4	64
IV b	$C_6H_5CHCOOH$	H	221	$C_{25}H_{19}ClO_6S$[c]	62,2	3,9	7,4	61,8	4,8	7,5	52
IVa	$C_6H_5CHCOOH$	Br	171	$C_{25}H_{19}BrClO_7$[d]	54,7	4,2	6,1	55,0	3,3	6,5	53
IVa	$CH_2CH{=}CHCOOCH_3$	H	252	$C_{22}H_{19}ClO_7$	60,8	4,2	8,7	61,4	4,4	8,2	62
IV b	$CH_2CH{=}CHCOOCH_3$	H	222	$C_{22}H_{19}ClO_6S$[e]	59,8	4,0	7,9	59,2	4,3	8,0	64

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[a] Found,%: S 7.8. Calculated,%: S 7.9. [b] Found,%: Br 17.5. Calculated,%: Br 16.6. [c] Found,%: S 6.7. Calculated,%: S 6.6. [d] Found,%: Br 13.7. Calculated,%: Br 14.5. [e] Found,%: S 7.7. Calculated,%: S 7.2.

2,6-Diphenyl-4-carboxymethylpyrylium Perchlorate (VI). A mixture of 4.04 g (0.01 mole) of perchlorate IV and 1.2 g (0.02 mole) of KOH in 30 ml of 70% ethanol was refluxed for 15 min, after which the hot solution was filtered and diluted with 50 ml of 4% acetic acid. The precipitated crystals were removed by filtration, dried, and converted to the pyrylium salt in dry ether by addition of perchloric acid. Workup gave 3.2 g (84%) of a product with mp 250-251° (from nitromethane). Found,%: C 58.0; H 4.3; Cl 9.4. $C_{19}H_{15}ClO_7$. Calculated,%: C 58.5; H 3.8; Cl 9.1.

2,6-Diphenyl-4-(α-carboxybenzyl)pyrylium Perchlorate (IX). A solution of 2.5 g (0.01 mole) of 2,6-diphenyl-γ-pyrone in 5 ml of dry benzene was added to an Ivanov reagent obtained from 1.6 g (0.01 mole) of sodium phenylacetate and 0.011 mole of isopropylmagnesium chloride, after which the mixture was heated for 1 h, cooled, and decomposed with 100 ml of 4% acetic acid. The pyranol was extracted with ether, and the extract was dried and treated with 1.5 ml of 70% perchloric acid. The salt was separated and crystallized from nitromethane to give 2.8 g (60%) of a product with mp 254-255°. The characteristics of the pyrylium salts obtained from thiapyrone, xanthone, flavone, and the Ivanov reagent are presented in Table 1.

2,6-Diphenyl-4-carbomethoxymethylpyridine (V). A suspension of 4 g (0.01 mole) of perchlorate IV in 20 ml of methanol was saturated with gaseous ammonia. It was then cooled to precipitate crystalline pyridine V. A portion of the product was precipitated from the filtrate by addition of water. The yield of product with mp 129° (from hexane) was 2.4 g (80%). Found, %: C 79.6; H 5.8; N 4.2. $C_{20}H_{17}NO_2$. Calculated,%: C 79.2; H 5.6; N 4.6.

The same method was used to obtain 2,6-diphenyl-4-(3-carbomethoxy-2-propenyl)pyridine (V, R = $CH_2CH{=}CHCOOCH_3$, R′ = H) in 50% yield (mp 135.5°. Found,%: C 80.6; H 5.2; N 4.0. $C_{22}H_{19}NO_2$. Calculated,%: C 80.2; H 5.2; N 4.1) and 2,6-diphenyl-4-α-carboxybenzyl)pyridine (X) in 55% yield (mp 138°. Found,%: C 82.2; H 5.1; N 3.4. $C_{25}H_{19}NO_2$. Calculated,%: C 82.1; H 5.2; N 3.8).

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