REACTIONS OF PYRYLIUM SALTS WITH NUCLEOPHILIC AGENTS

S. N. Baranov, M. A. Dumbai,
and S. V. Krivun

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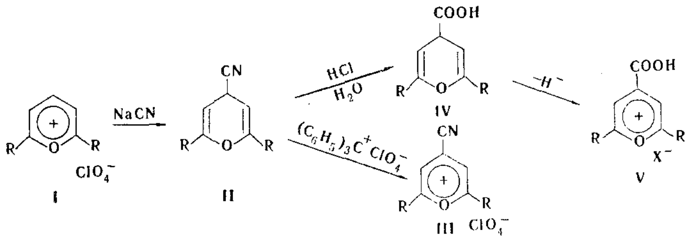
The reaction of γ-unsubstituted pyrylium salts with alkali-metal cyanides gives cyano- and carboxy-substituted pyrans and pyrylium salts, while the reaction with sodium sulfide gives dipyranyl sulfides. A phthalimide derivative of pyran is obtained from 2,6-diphenylpyrylium perchlorate and potassium phthalimide, while pyrylium cations react with zinc to give the corresponding dipyranyls.

It has been demonstrated in a number of papers [1-4] that α- or γ-unsubstituted pyrylium salts, in contrast to 2,4,6-trisubstituted salts, react with nucleophilic agents with retention of the pyran ring. In a continuation of these investigations, in the present research we have studied the reaction of 2,6-substituted pyrylium salts (I) with several inorganic nucleophiles, potassium phthalimide, and zinc.

The reaction of pyrylium salts with potassium cyanide (or sodium cyanide) in aqueous ether proceeds almost quantitatively to give the corresponding γ-cyanopyrans (II). As expected, the latter readily split out a hydride ion on refluxing with triphenylmethyl perchlorate to give γ-cyano-substituted pyrylium salts (III). On the other hand, the hydrolysis of the pyrans with dilute hydrochloric acid gives carboxypyrans IV in high yields, and they are converted to carboxypyrylium salts V under the influence of hydride-ion acceptor. The structure of 2,6-diphenyl-4-carboxypyrylium perchlorate was confirmed by alternative synthesis from diphenacylacetic acid [5].



a $R{=}C_6H_5$; b $R{=}p\text{-}CH_3OC_6H_4$

The reaction with cyanide is somewhat analogous to the synthesis of quinaldinic acid from acylquinolinium salts and KCN (the Reissert reaction [6]). The reaction of KCN with 2,4,6-trisubstituted pyrylium cations [7] has been studied in a number of pyrylium salts, but in this case the transformation of the initially formed cyano-substituted pyrans to either carboxypyrans or, especially, to cyano- and carboxypyrylium salts was not possible.

In investigating the reaction of 2,6-diphenylpyrylium perchlorate and its derivatives with sodium sulfide in aqueous ether it was expected that the corresponding dipyranyl sulfide would be formed (in analogy to the previously obtained dipyranyl ether [4]). However, we found that a mercaptopyran is formed under these conditions. Since the latter decomposes on heating (and even on prolonged storage), it could

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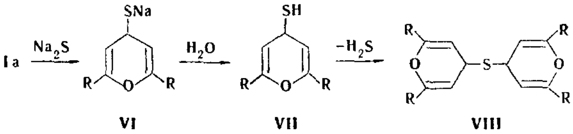
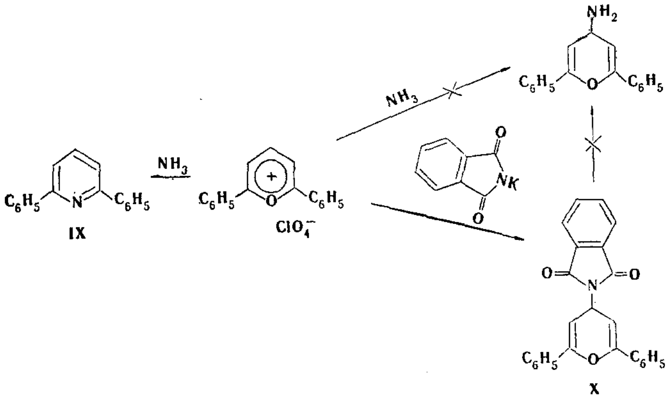
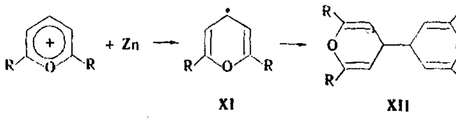
not be obtained in chemically pure form. The α,α′-diphenyl-γ-mercaptopyran structure (VII) was judged from the UV spectrum (in ethanol, λ_{max} 250, 368 nm; log ε 4.44, 4.14), which proved to be similar to the spectrum of 2,6-diphenyl-4-methoxy-4H-pyran (λ_{max} 246, 355 nm; log ε 4.13, 4.01). The IR spectra also fully confirm structure VII. When VII is heated in inert solvents, H_2S is split out, and dipyranyl sulfide VIII is obtained.



Proceeding from these and previously described observations that γ-unsubstituted pyrylium salts react with various nucleophiles (organic and inorganic) with retention of the pyran ring, we assumed that their reaction with ammonia should lead to the formation of 4-aminopyrans (or dipyranyl- and tripyranylamines when excess pyrylium salt is present, as occurs in the reaction of NH_3 with tropylium salts [8]). However, the final product of this reaction is a 2,6-diarylpyridine (IX). The reaction of I with potassium phthalimide under the conditions of the reaction of such salts with KCN and Na_2S gave a phthalide derivative (X) of the pyran, but hydrolysis of the latter by the Gabriel method [9] (both by heating in an ampul with hydrochloric acid and by hydrazinolysis) results in pronounced resinification, and substantial amounts of an aminopyran could not be isolated.



It has previously been shown [10] that 2,4,6-triphenylpyrylium perchlorate forms a stable radical with active powdered metals (zinc and magnesium). We have observed that if this sort of reaction is carried out with γ-unsubstituted pyrylium salts in a polar solvent, the resulting radicals (XI) recombine, and dipyranyls (XII) are obtained:



The structures of the pyrylium salts were confirmed by the IR spectra using the data from the excellent study in [11] and, in some cases, by alternative syntheses.

EXPERIMENTAL

2,6-Diphenyl-4-cyano-4H-pyran (IIa). A mixture of 19.9 g (0.06 mole) of 2,6-diphenylpyrylium perchlorate (Ia), 4.9 g (0.09 mole) of sodium cyanide, 400 ml of ether, and 400 ml of water was stirred vigorously until the pyrylium-salt suspension vanished. The ether layer was separated and washed with water, and the ether was evaporated to give 15 g (97%) of IIa with mp 96-97° (from hexane). Found: C 83.5; H 5.3; N 5.6%. $C_{18}H_{13}NO$. Calculated: C 83.4; H 5.0; N 5.4%.

2,6-Di(p-anisyl)-4-cyano-4H-pyran (IIb). This compound was similarly obtained in 99% yield from Ib and had mp 124-126° Found: C 75.9; H 5.6%. $C_{20}H_{17}NO_3$. Calculated: C 75.2; H 5.3%.

2,6-Diphenyl-4-cyanopyrylium Perchlorate (IIIa). A mixture of 1.7 g (7 mmole) of IIa, 2.7 g (8 mmole) of trityl perchlorate, and 15 ml of glacial acetic acid was refluxed for 5 min. It was then cooled, and the yellow precipitate was removed by filtration and washed to give 1.1 g (44%) of IIIa with mp 296-297° (from nitromethane). Found: C 59.9; H 3.7; Cl 10.6%. $C_{18}H_{12}ClNO_5$. Calculated: C 60.3; H 3.4; Cl 10.1%.

2,6-Di(p-anisyl)-4-cyanopyrylium Perchlorate (IIIb). This compound was similarly obtained in 38% yield from IIb and had mp 284-286°. Found: C 57.3; H 4.2; Cl 8.0%. $C_{20}H_{16}ClNO_7$. Calculated: C 57.4; H 3.8; Cl 8.6%.

2,6-Diphenyl-4-carboxy-4H-pyran (IVa). A 1.7-g (7 mmole) sample of IIa was refluxed with 25 ml of concentrated hydrochloric acid for 7 h, and the resinous reaction product was separated from the acid and converted to the sodium salt by refluxing for 10 min with sodium bicarbonate solution. The solution of the sodium salt of the acid was washed with benzene and acidified with hydrochloric acid. The white precipitate of pyranylcarboxylic acid was removed by filtration, washed with a small amount of water, and dried to give 1.2 g (63%) of IVa with mp 133-134° (from benzene). Found: C 77.4; H 5.2%. $C_{18}H_{14}O_3$. Calculated: C 77.7; H 5.0%.

2,6-Di(p-anisyl)-4-carboxypyran (IVb). This compound was similarly obtained in 50% yield and had mp 91-92°. Found: C 71.3; H 5.5%. $C_{20}H_{18}O_5$. Calculated: C 71.0; H 5.3%.

2,6-Diphenyl-4-carboxypyrylium Perchlorate (Va). This compound was obtained by the method used to prepare IIIa from 1.55 g (6 mmole) of IVa and 2.02 g (6 mmole) of trityl perchlorate and had mp 276-277° (from glacial acetic acid). The yield was 0.8 g (39%). Found: C 57.0; H 3.6; Cl 9.0%. $C_{18}H_{13}ClO_7$. Calculated: C 57.3; H 3.4; Cl 9.6%.

2,6-Di(p-anisyl)-4-carboxypyrylium Perchlorate (Vb). This compound was obtained in 63% yield by the method used to prepare IVb and had mp 262-264°. Found: C 54.6; H 4.2; Cl 8.5%. $C_{20}H_{17}ClO_9$. Calculated: C 54.9; H 3.9; Cl 8.2%.

Bis(2,6-diphenyl-4H-pyranyl) Sulfide (VIII). A mixture of 6.64 g (0.02 mole) of Ia and 7.20 g (0.03 mole) of $Na_2S \cdot 9H_2O$ was stirred vigorously in aqueous ether (800 ml of a 1 : 1 solution) at room temperature until the pyrylium-salt suspension had vanished. The newly formed yellowish precipitate (5.3 g) was removed by filtration, washed with water, and dried. The crude 2,6-diphenyl-4-mercaptopyran (VII) melted at 126°. It was refluxed in 25 ml of benzene until the odor of hydrogen sulfide had vanished, and the solution was cooled to precipitate 3.83 g (77%, based on salt Ia) of dark-red crystals of VIII with mp 155° (dec., from isopropyl alcohol). Found: C 81.6; H 5.4; S 6.4%. $C_{34}H_{26}O_2S$. Calculated: C 81.9; H 5.2; S 6.4%.

N-(2,6-Diphenyl-4-pyranyl)phthalimide (X). A mixture of 3.32 g (0.01 mole) of Ia, 5.55 g (0.03 mole) of potassium phthalimide, 400 ml of ether, and 400 ml of water was stirred vigorously at room temperature until the pyrylium salt had vanished. The white amorphous precipitate (1.8 g) was removed by filtration and dried, and the ether layer was separated, washed with water, and evaporated to give 1.1 g of a white precipitate that was identical to the first precipitate. The overall yield of X with mp 185° (from benzene) was 79%. Found: C 80.0; H 4.5; N 3.3%. $C_{25}H_{17}NO_3$. Calculated: C 79.2; H 4.5; N 3.7%.

2,2',6,6'-Tetraphenyl-4,4'-dipyranyl (XII). A 4-g (0.06 g-atom) sample of zinc dust was added in portions with stirring under dry nitrogen to a solution of 6.64 g (0.02 mole) of Ia in 25 ml of dry acetonitrile (the mixture warmed up during the addition of the zinc dust). The solid material was removed by filtration, washed with 5 ml of cold acetonitrile, and dried. The material was extracted with toluene in a Soxhlet apparatus, and the solution was evaporated to 7 ml and filtered to give 1.8 g (40%) of dark-red needles of XII with mp 320° (dec.). Found: C 87.3; H 5.8%. $C_{34}H_{26}O_2$. Calculated: C 87.6; H 5.6%.

2,2',6,6'-Tetraphenyl-4,4'-dithiapyranyl. This compound [0.9 g (36%)] was similarly obtained from 3.48 g (0.01 mole) of 2,6-diphenyl-4-thiapyrylium perchlorate in 20 ml of acetonitrile and 1.95 g (0.03 g-atom) of zinc and had mp 315° (dec.). Found: C 81.7; H 5.5; S 12.4%. $C_{34}H_{26}S_2$. Calculated: C 81.9; H 5.2; S 12.8%.

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