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REACTIONS OF HETEROCYCLIC CATIONS WITH NITROGEN-CONTAINING NUCLEOPHILES.

12.* REACTION OF PYRYLIUM SALTS WITH AZOMETHINES

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The reaction of pyrylium salts with azomethines leads to the formation of styrylpyrylium, styrylpyridinium, and 4-arylbenzylaminopyrylium salts. The reaction of the latter with ammonia and amines gave pyridines and pyridinium salts with a tertiary amino group as a substituent.

We have previously shown that 2,4,6-triarylpyrylium salts react in dimethylformamide (DMF) with azomethines in the 2 position of the ring to give, after ring opening and recyclization, the corresponding pyridinium salts, whereas 2-methyl-substituted salts form 1-aryl-2-styrylpyridinium perchlorates [2, 3].

In the present research in the case of 1,3-dimethyl-6,7-dimethoxy-2-benzopyrylium perchlorate (I) we established that azomethines II initially attack the ring methyl group in the 1 position. (The PMR spectrum of III does not contain the singlet at δ 2.6 ppm that is characteristic for this methyl group.) The liberated aniline then reacts with styrylpyrylium salt III to give isoquinolinium salt IV. In contrast to the reactions of triarylpyrylium salts with azomethines, this reaction takes place in ethanol. In the case of initial attack on the ring the final products would have been the corresponding N-arylisoquinolinium salt and benzaldehyde. However, in separate experiments we showed that methylpyridinium and isoquinolinium salts do not react with benzaldehyde in alcohol. At the same time, salt III and 2-styryl-4,6-diphenylpyrylium perchlorate (V) readily form IV and VI with aniline in alcohol solution.

It is interesting to note that styrylpyrylium salts III and V react with azomethines in the same way as triarylpyrylium salts not only in dimethylformamide (DMF) but also in ethanol (in the latter the degree of conversion is 50% after 1 h).

4-Unsubstituted 2,6-diphenylpyrylium salt VII in acetic acid undergoes attack by azomethines in the 2 position, which leads to the previously described 1,2,6-triarylpyridinium

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*See [1] for Communication 11.
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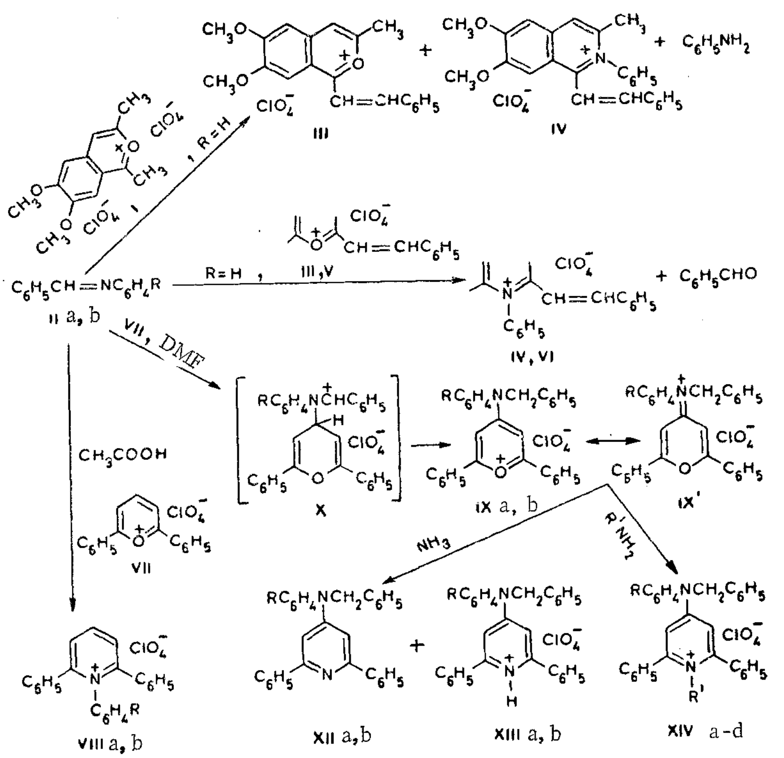
perchlorates (VIII) [1]. The reaction of salt VII with azomethines in DMF takes place primarily in the 4 position of the ring to give dark-crimson perchlorates IX with a tertiary amino group as the substituent. The formation of the latter can be explained by intramolecular rearrangement of the intermediately formed 4H-pyran X, i.e., ultimately by migration of a hydride ion from the pyran ring to the > $\mathrm{N{-}C^{+}H}$ fragment of the substituent. The presence of CH_2 group was confirmed by the PMR spectroscopic data (singlet, δ 3.40 ppm).

In the reaction of perchlorate VII with benzal-p-toluidine in DMF the latter attacks not only the 4 position but also the 2 position of the ring, which leads to colorless 2,2,6,6-tetraphenyl-1,1-di(p-tolyl)-3,4-bispyridinium bisperchlorate (XI, 13% yield), which was previously described [1], in addition to salt IXb (in 68% yield).



II, VIII, IX, XII, XIII a R=H, b R=p-CH_3; XIV a R=H, R'=CH_3; b R=R'=CH_3; c R=H, R'=C_6H_5; d R=CH_3; R'=C_6H_5

Inasmuch as they are pyrylium salts, IX react with the simplest nitrogen-containing nucleophiles, viz., ammonia and aniline, to give the corresponding pyridines XII and pyridinium salts XIII and XIV. The structure of salts IX can be represented by two resonance forms IX and IX'. The positive charge may be located both in the ring and on the exocyclic nitrogen atom. The presence of a positive charge on the nitrogen atom and the double bond with the ring explain the deep color of the compounds obtained. However, the presence in the IR spectra of absorption bands that are characteristic for a heteroaromatic cation and the facile replacement of the oxygen atom by a nitrogen atom constitute evidence in favor of the pyrylium structure of salts IX. Calculations* of the electron density distribution and the bond orders in these salts show that ~60% of the positive charge is distributed in the pyridium ring; the nitrogen atom is also positively charged. The double bond character of the nitrogen—ring bond is rather great (bond length 1.39 Å). (See top, following page.)

Thus the structure of salts IX is more accurately depicted by a set of two resonance structures (IX and IX'). The same may also apply to the structure of pyridinium salts XIV obtained from them; salts XIV are red, and their IR spectra contain absorption bands that are characteristic for a heteroaromatic cation.

It must be pointed out that several 4-aminopyrylium salts with secondary and tertiary amino groups, which were obtained by replacement of the functional groups in the 4 position

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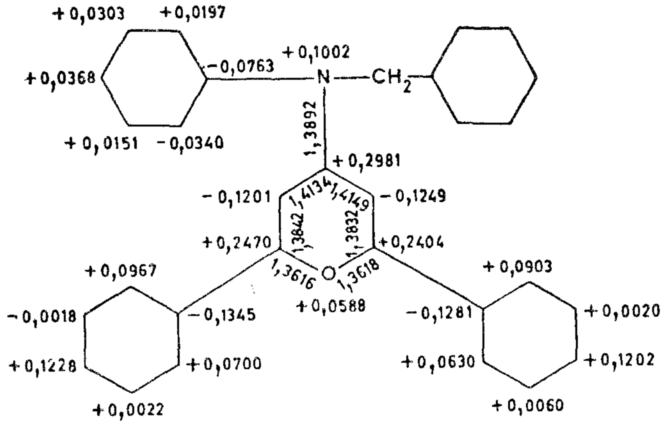
*The calculations were made by B. Ya. Simkin [by the Pariser—Parr—Pople (PPP) method], for which the authors extend their sincere thanks.



of pyrylium salts [4], have been described in the literature. However, we have developed a method for the direct introduction of a tertiary amino group in more accessible pyrylium salts with a free 4 position.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71-IR spectrometer. The PMR spectra of solutions of the compounds in CF_3COOH and CCl_4 were measured with a Tesla BS-467C spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The purity of the compounds obtained was monitored by thin-layer chromatography (TLC) on plates with silicic acid or aluminum oxide. Data for all of the compounds are presented in Table 1.

Reaction of Perchlorate I with Benzalaniline (IIa). A 0.32-g (1 mmole) sample of perchlorate I was refluxed with 0.22 g (1.2 mmole) of benzalaniline in 5 ml of absolute ethanol for 1 h, after which the hot reaction mixture was filtered to give 0.12 g of red 1-styryl-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate (III). The filtrate was cooled to precipitate 0.22 g of yellow 1-styryl-2-phenyl-3-methyl-6,7-dimethoxy-isoquinolinium perchlorate (IV). It was demonstrated by chromatography that aniline was present in the mother liquor.

Reaction of 2-Styryl-4,6-diphenylpyrylium Perchlorate (V) with Benzalaniline. This reaction was carried out in absolute ethanol for 1 h with a reagent ratio of 1:1.2. Perchlorate VI precipitated when the mixture was cooled.

The reaction of perchlorate III with benzalaniline was carried out similarly.

1-(p-Tolyl)-2,6-diphenylpyridinium Perchlorate (VIIIb). A 0.33-g (1 mmole) sample of salt VII was heated with 0.24 g (1.2 mmole) of azomethine IIb in 5 ml of acetic acid until the salt dissolved completely. The solution was cooled and treated with ether to precipitate 0.28 g (66%) of perchlorate VIIIb with mp 210-211°C [1].

The reaction of perchlorate VII with benzalaniline was carried out similarly.

2,6-Diphenyl-4-phenylbenzylaminopyrylium Perchlorate (IXa). A 4-g (12 mmole) sample of salt VII and 2.52 g (14.4 mmole) of benzalaniline were refluxed in 20 ml of DMF for 1 h, after which the mixture was cooled and treated with heptane, and the liberated oil was crystallized by successive trituration with ether and water to give 5.7 g of dark-crimson perchlorate IXa. The latter was purified by chromatography on plates with silicic acid by elution with benzene.

Reaction of Perchlorate VII with Benzal-p-toluidine (IIb) in DMF. This reaction was carried out similarly. Workup gave 5.2 g of a dark-crimson precipitate, which was treated with chloroform. Filtration gave 0.7 g (13%) of insoluble colorless bisperchlorate XI with mp 295-296°C (from ethanol with acetonitrile) [1]. The chloroform was evaporated, and the residual perchlorate IXb was purified by chromatography, as in the case of IXa.

Reaction of Perchlorate IXa with Ammonia. A stream of ammonia was passed into a suspension of 0.5 g (1 mmole) of salt IXa in ethanol for 1 h, after which the alcohol was evaporated to give 0.5 g of a residue, which was separated by means of TLC on silicic acid (elution with benzene) to give 2,6-diphenyl-4-phenyl-benzylaminopyridine (XIIa, 0.07 g) and 2,6-diphenyl-4-phenylbenzylaminopyridinium perchlorate (XIIIa, 0.35 g), which was converted to pyridine XIIa by the action of an alcohol solution of alkali. PMR spectrum of XIIa: δ 4.28 (s, 2H, CH_2) and 6.48-8.25 ppm (m, 22H).

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp,[*] °C	IR spectra, cm^{-1}	Found, %				Empirical formula	Calculated, %				Yield, %
			C	H	Cl	N		C	H	Cl	N	
III	276[†]	1630, 1590, 1560, 1510, 1280, 1240, 1180, 1100	58,8	4,8	8,6	—	$C_{20}H_{19}ClO_7$	59,1	4,7	8,7	—	30
IV	296 (dec.)	1640, 1620, 1578, 1519, 1270, 1240, 1180, 1096	63,7	5,3	7,6	3,2	$C_{26}H_{24}ClNO_6$	64,0	5,0	7,3	2,9	45
VI	184—185	1630, 1600, 1580, 1100	73,0	5,0	7,3	2,7	$C_{31}H_{24}ClNO_4$	73,0	4,7	7,0	2,7	90
IXa	188	1680, 1630, 1600, 1580, 1100	69,8	4,9	6,8	3,0	$C_{30}H_{24}ClNO_5$	70,1	4,7	7,0	2,7	90
IXb	186—187	1680, 1630, 1600, 1580, 1100	70,8	4,9	6,6	3,0	$C_{31}H_{26}ClNO_5$	70,5	5,0	6,7	2,7	68
XIIa	111—112	1590, 1580, 1180	87,5	5,8	—	6,6	$C_{30}H_{24}N_2$	87,3	5,9	—	6,8	14
XIIb	118—119	1590, 1580, 1180	87,4	6,0	—	6,5	$C_{31}H_{26}N_2$	87,3	6,1	—	6,6	13
XIIIa	189—190	3328, 1680, 1620, 1600, 1580, 1100	70,0	4,8	7,0	5,2	$C_{30}H_{25}ClN_2O_4$	70,2	4,9	6,9	5,5	70
XIIIb	190—191	3308, 1680, 1620, 1600, 1580, 1100	70,5	5,2	6,9	5,1	$C_{31}H_{27}ClN_2O_4$	70,7	5,1	6,7	5,3	64
XIVa	179—180	1680, 1620, 1600, 1580, 1100	70,9	5,2	6,4	5,2	$C_{31}H_{27}ClN_2O_4$	70,7	5,1	6,7	5,3	96
XIVb	180—181	1680, 1620, 1600, 1580, 1100	71,3	5,4	7,0	5,0	$C_{32}H_{29}ClN_2O_4$	71,0	5,4	6,7	5,2	98
XIVc	194—195	1680, 1630, 1600, 1570, 1100	73,2	5,0	6,3	4,9	$C_{36}H_{29}ClN_2O_4$	73,4	4,9	6,0	4,8	74
XIVd	201—202	1680, 1630, 1600, 1570, 1100	73,8	4,9	6,2	4,5	$C_{37}H_{31}ClN_2O_4$	73,7	5,2	5,9	4,7	80

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[*] The compounds were purified by crystallization from glacial acetic acid (III, XIIIa, XIVa), ethanol (IV, XIIa,b, XIIIb, and XIVc, d), chloroform–ether (VI), and butanol (IXa,b and XIVb).

[†] This compound had mp 290-293°C [5].

Perchlorate IXb reacted similarly with ammonia. The indicated transformations also took place when salts IX were refluxed with excess ammonium acetate in acetic acid for 10 h. The yields of reaction products were approximately the same.

1-Methyl-2,6-diphenyl-4-phenylbenzylaminopyridinium Perchlorate (XIVa). A stream of methylamine was passed with stirring into a suspension of 0.5 g (1 mmole) of salt IXa in ethanol for 1 h, after which the alcohol was evaporated to give 0.51 g of salt XIVa, which was purified by chromatography on plates with silicic acid (elution with benzene).

The reaction of perchlorate IXb with methylamine took place similarly.

1,2,6-Triphenyl-4-phenylbenzylaminopyridinium Perchlorate (XIVc). A 0.5-g (1 mmole) sample of perchlorate IXa and 0.12 g (1.3 mmole) of aniline were refluxed in 5 ml of DMF for 1 h, after which the mixture was treated with ether, and the liberated oil was crystallized by trituration with water. Precipitated salt XIVc (0.43 g) was purified by chromatography on plates with silicic acid (elution with benzene).

Perchlorate IXb reacted similarly with aniline.

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