REACTION OF 2,4,6-SUBSTITUTED PYRYLIUM SALTS WITH COMPOUNDS CONTAINING A C = N BOND

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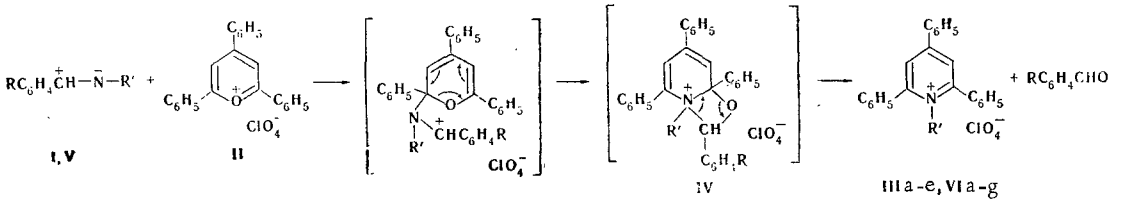
2,4,6-Substituted pyrylium salts add azomethines to give pyridinium salts and aromatic aldehydes. The latter can be condensed with the methyl groups of the pyridinium salts. Benzaldoxime, benzalazine, benzalphenylhydrazine, urea, thiourea, and phenyl isothiocyanate react with 2,4,6-triphenylpyrylium perchlorate similarly to give, respectively, 2,4,6-triphenylpyridine N-oxide, 2,4,6-triphenylpyridine, or N-substituted 2,4,6-triphenylpyridinium perchlorates.

It was recently shown that thionylamines react in an "ylid-like" structure with pyrylium salts via a dipolar 1,2-cycloaddition scheme [1]. As we have already reported [2], azomethines of aromatic amines (I), for which an "ylid-like" structure is also possible, react similarly with 2,4,6-substituted pyrylium salts. In this case, 1-arylpyridinium salts (III) and aromatic aldehydes are formed from 2,4,6-triphenylpyrylium perchlorate (II):



I, V II IV IIIa-e, VIa-g

I, III: a) R = H, R' = phenyl; b) R = H, R' = p-tolyl; c) R = H, R' = o-tolyl; d) R = H, R' = p-anisyl; e) R = H, R' = p-nitrophenyl. V, VI: a) R = p-NO_2, R' = 2-pyridyl; b) R = p-NO_2, R' = 4-pyridyl; c) R = p-NO_2, R' = 2-benzimidazolyl; d) R = m-NO_2, R' = 1-methyl-2-benzimidazolyl; e) R = p-NO_2, R' = 1-ethyl-2-benzimidazolyl; f) R = p-NO_2, R' = 1-nonyl-2-benzimidazolyl; g) R = NO_2, R' = 1,5,6-trimethyl-2-benzimidazolyl.

The reaction apparently proceeds by nucleophilic attach of the azomethine at the α-position of the pyrylium ring with subsequent ring opening, 1,2-cycloaddition, and, finally, thermal cleavage of four-membered complex IV. The absence of water in the reaction mixture excludes the possibility of hydrolysis of the azomethines and, consequently, the presence of an aromatic amine. The reaction proceeds quantitatively when the components are refluxed in absolute dimethylformamide (DMF) for 1 h. In the case of perchlorate II and benzalaniline, it was shown that the reaction in glacial acetic acid is 70% complete after 3 h, is 55% complete in absolute nitromethane after the same time, and does not occur at all in absolute ethanol. Inasmuch as the reaction goes to completion much more rapidly in absolute DMF, all of the reactions were studied primarily in this solvent.

We have also extended the reaction to azomethines of heteroaromatic amines (V).

2-Methyl-4,6-diphenylpyrylium perchlorate (VII) reacts via this same scheme, but the aldehyde formed in the reaction condenses at the methyl group to give styryl derivatives VIII:

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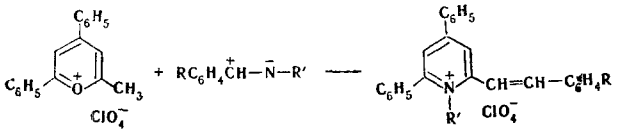


VII VIII a-d

VIII: a) R = H, R' = phenyl; b) R = H, R' = p-tolyl; c) R = p-NO_2, R' = 1-ethyl-2-benzimidazolyl; d) R = p-NO_2, R' = 1,5,6-trimethyl-2-benzimidazolyl.

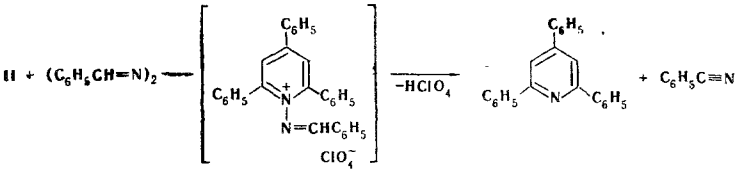
The fact that the reaction does not occur in ethanol excludes the possibility of carrying it out with perchlorate VII without simultaneous condensation at the methyl group.

The structure of VIIIa was confirmed by alternative synthesis [3]. Intense absorption bands of the pyridinium ring (1620-1640 and 1555-1580 cm^{-1}), bands of the ClO_4^- anion (110 cm^{-1}), and, for VIc, absorption bands of a benzimidazole NH group at 3200 cm^{-1} are present in the IR spectra of the pyridinium perchlorates obtained in this study.

2,4,6-Trimethylpyrylium perchlorate reacts with azomethines to give a mixture of substances that are difficult to separate.

We also subjected other compounds for which the "quasi-ylid" structure is possible to the reaction under consideration. Benzaldehyde and 2,4,6-triphenylpyridine are isolated from the reaction of perchlorate II with benzaldoxime in DMF. It can be assumed that the initially formed 2,4,6-triphenylpyridine N-oxide, which is unstable [4], is deoxygenated. In fact when the reaction is carried out in glacial acetic acid (it is ~40% complete after 5 h), the N-oxide can be isolated. Up until now, only alkyl-substituted pyrylium salts could be converted to pyridine N-oxides [5-7]. However, in an attempt to obtain the N-oxide from perchlorate II and hydroxylamine we isolated 3,5-diphenylisoxazole [8]. Thus, 2,4,6-triphenylpyridine N-oxide can be obtained by means of this reaction also from perchlorate II, which contains phenyl substituents.

Intermediate IX in the reaction of perchlorate II with benzalazine is apparently unstable. It decomposes to give 2,4,6-triphenylpyridine and benzonitrile:



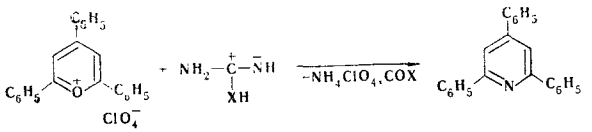
IX

This conversion represents an example of an aminonitrile rearrangement [9] in which the excess benzalazine acts as the base. The reaction practically does not occur in glacial acetic acid.

The reaction of perchlorate II with benzalphenylhydrazine in DMF gives an easily resinified substance that reddens on standing, does not contain chlorine, and could not be purified. The reaction in glacial acetic acid goes to ~60% completion after 5 h to give N-anilino-2,4,6-triphenylpyridinium perchlorate.

The reactions under consideration apparently proceed via the same mechanism as in the case of azomethines, but in DMF go to completion in the presence of a twofold excess of the "ylid-like" compounds; the excess amount is probably necessary to tie up the perchloric acid.

In the reaction of perchlorate II with urea and thiourea, the resonance structures of which can also be considered to be of the ylid type, 2,4,6-triphenylpyridine is formed:



X = O or S

Addition at the C = S bond does not occur in the case of thiourea. The reaction with phenyl isothiocyanate also proceeds preferably at the C = N group, and thiopyrylium salts therefore cannot be obtained via this path.

TABLE 1. Azomethines of Heterocyclic Amines (V)

Compound	mp, °C (from ethanol)	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	N	C	H	N	
Va	143[10]	$C_{12}H_9N_3O_2$	58,6	4,7	17,3	58,8	4,5	17,1	82
Vb	108	$C_{12}H_9N_3O_2 \cdot H_2O$	58.7	4,8	16,9	58,8	4,5	17,1	75
Vc	253*	$C_{14}H_{10}N_4O_2$	63,7	4,2	20,9	63,2	3,8	21,0	73
Vd	178	$C_{15}H_{12}N_4O_2$	64,2	4,7	20,4	64,3	4,3	20,0	70
Ve	178[11]	$C_{16}H_{14}N_4O_2$	65,4	5,0	19,2	65,3	4,8	19,0	68
Vf	118	$C_{23}H_{28}N_4O_2$	70,4	7,6	14,6	70,4	7,2	14,3	78
Vg	227	$C_{17}H_{16}N_4O_2$	66,3	5,1	18,7	66,2	5,2	18,2	70

*From xylene.

TABLE 2. Pyridinium Perchlorates (III, VI, and VIII)

Compound	mp, °C*	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	Cl	N	C	H	Cl	N	
IIIa	265—266[12]	$C_{29}H_{22}ClNO_4$	72,3	4,5	7.7	2,8	72,0	4,6	7,3	2,9	80
IIIb	244[12]	$C_{30}H_{24}ClNO_4$	72,6	4,7	7,5	3,0	72,3	4,9	7,1	2,8	90
IIIc	253[12]	$C_{30}H_{24}ClNO_4$	72,5	4,7	7,4	2,7	72,3	4,9	7,1	2,8	80
IIId	241[12]	$C_{30}H_{24}ClNO_5$	69,9	4,5	7,0	2,7	70,1	4,7	6,9	2,7	90
IIIe	242	$C_{29}H_{21}ClN_2O_6$	65,3	4,3	6,4	5,8	65,8	4,0	6,7	5,3	82
VIa	230—231	$C_{28}H_{21}ClN_2O_4$	69,7	4,7	7,2	6,1	69,4	4,4	7,3	5,8	89
VIb	300—301	$C_{28}H_{21}ClN_2O_4$	69,4	4,8	7,3	6,0	69,4	4,4	7,3	5,8	83
VIc	255	$C_{30}H_{22}ClN_3O_4$	69,0	4,6	6,5	8,2	68,8	4,2	6,8	8,0	65
VId	144—146	$C_{31}H_{24}ClN_3O_4 \cdot H_2O$	67,2	4,9	6,5	7,5	66,9	4,7	6,4	7,6	70
VIe	140—142	$C_{32}H_{26}ClN_3O_4 \cdot H_2O$	67,8	5,6	5,7	7,4	67,4	5,1	6,2	7,4	94
VIf	103—105	$C_{39}H_{40}ClN_3O_4$	72,4	6,6	5,2	6,3	72,0	6,2	5,5	6,5	47
VIg	300	$C_{33}H_{28}ClN_3O_4$	70,2	5,2	5,9	7,5	70,0	5,0	6,3	7,4	75
VIIIa	145—150[3]	$C_{31}H_{24}ClNO_4$	72.8	4,7	6,9	2,7	73,0	4,7	7,0	2,8	88
VIIIb	145—150	$C_{32}H_{26}ClNO_4$	73,0	5,4	6,5	—	73,4	5,0	6,8	—	83
VIIIc	168—170	$C_{34}H_{27}ClN_4O_6 \cdot H_2O$	64,0	4,8	5,1	8,5	63.7	4,6	5,5	8.7	49
VIIId	213—214	$C_{35}H_{29}ClN_4O_6$	65,6	4,9	5,1	9,1	66,0	4,6	5,6	8,8	47

*The following solvents were used to recrystallize the products: glacial acetic acid (IIIa-c, VIa-b, VIg, and VIIId), ethanol (IIId, e), butanol (VIc), chloroform–ether (VId, e, VIIIa-c), and methanol (VIf).

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

The azomethines were obtained by refluxing alcohol solutions of equimolecular amounts of the aldehyde and amine for 1-10 h [10] (Table 1).

Reaction of Perchlorate II with Azomethines. A 2.5-mmole sample of perchlorate II was refluxed with 3 mmole of azomethine in 10 ml of absolute DMF for 1 h. The addition of ether precipitated the solid reaction product. However, if the product separated out as an oil, it was crystallized by the addition of water (Table 2). The mother liquor formed a yellow-orange precipitate of benzaldehyde 2,4-dinitrophenylhydrazone with mp 235-236°.

The reaction of VII with azomethine proceeds similarly, except that a hydrazone was not formed in the mother liquor. The styryl derivatives (Table 2) were purified by two to three reprecipitations from cold solvents.

Reaction of Perchlorate II with Benzaldoxime. A) A 0.51-g (125 mmole) sample of perchlorate II was refluxed with 0.3 g (2.5 mmole) of benzaldoxime in 3 ml of absolute DMF for 2 h. The addition of absolute ether precipitated the perchlorate of the starting benzaldoxime, after which the mother liquor was evaporated by heating in vacuo (water aspirator). The addition of a few drops of alcohol crystallized out 0.32 g (84%) of 2,4,6-triphenylpyridine with mp 137° (from alcohol) [13].

B) The reaction was carried out in 3 ml of glacial acetic acid with the same amount of reaction substances for 5 h. Cooling precipitated 0.31 g of starting perchlorate II. The excess solvent was removed by vacuum distillation (water aspirator), and a few drops of alcohol were added to the cold residue to give 0.07 g (18%) of 2,4,6-triphenylpyridine N-oxide with mp 184° (from alcohol) [4]. IR spectrum: 1250 cm^{-1} (N-oxide).

The reaction of perchlorate II with benzalazine was carried out as in method A, and the yield of 2,4,6-triphenylpyridine was 82%.

N-Anilino-2,4,6-triphenylpyridinium Perchlorate. A 0.51-g (1.25 mmole) sample of perchlorate II was refluxed with 0.49 g (2.5 mmole) of benzalphenylhydrazine in 5 ml of glacial acetic acid for 5 h. Cooling gave a black resinous precipitate, from which 0.21 g of unchanged perchlorate II was isolated after treatment with ether and chloroform. The addition of ether to the chloroform solution precipitated 0.31 g (50%) of green N-anilino-2,4,6-triphenylpyridinium perchlorate with mp 175° (from chloroform–ether). Found: C 70.2; H 4.7; Cl 7.0; N 5.7%. $C_{29}H_{23}ClN_2O_4$. Calculated: C 69.9; H 4.7; Cl 7.1; N 5.6%.

Reaction of Perchlorate II with Urea. A 2.04-g (5 mmole) sample of perchlorate II was refluxed with 0.3 g (5 mmole) of urea in 20 ml of absolute DMF for 1 h, after which the mixture was cooled, diluted with water, and extracted with ether to give 1.44 g (93%) of 2,4,6-triphenylpyridine.

Perchlorate II reacted similarly with thiourea, and the yield of 2,4,6-triphenylpyridine was 90%.

The reaction of perchlorate II with phenyl isothiocyanate was carried out under the same conditions but for 10 h. The mixture was then cooled and diluted with ether to give 1.72 g (73%) of 1,2,4,6-tetraphenylpyridinium perchlorate with mp 265-266° [2].

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