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REACTIVITY OF PYRYLIUM SALTS TOWARD BASIC REACTANTS

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16. Abstract

The reactivity of some N-acyl and N-sulfonyl-hydrazines 2-4, 10a-10g, 12, 13, 16a, 16b and of hydrazones 18, benzyl-dihydrazone 21 towards pyrylium salts 1 was examined. By reaction of 2,4,6-trimethyl-pyrylium salt 1 with substituted hydrazines some pyridinium salts were obtained. Relationships between basicity and reactivity were discussed.

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REACTIVITY OF PYRYLIUM SALTS TOWARD BASIC REACTANTS

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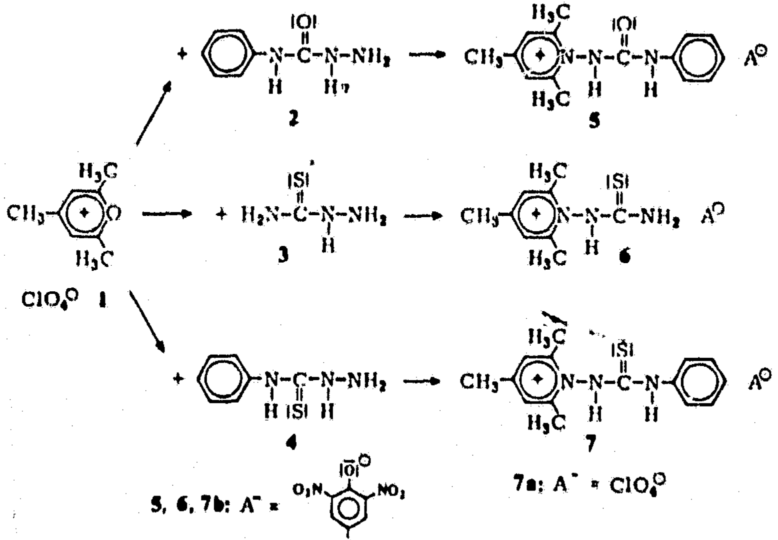
We reported recently on the synthesis of substituted pyridinium salts[1]; /649* for several years now bis-pyridiniumaldoximes with aliphatic residues -- bonding member between nitrogen atoms -- have been used as antidotes in intoxications with organic phosphates /650 and thiophosphates[2,3]. Bis-pyridinium salts proved to be much more effective than pyridin-aldoxim-methiodide (PAM)[4,5] which has been known for a long time, whereby the effects consist in reactivation of acetylcholine esterase inhibited by phosphorylation or phosphonylation -- with the oxim grouping representing the actually active part of the molecule.

In the framework of these studies as well as those regarding the reactivity of substituted pyrylium salts we endeavored to synthetize acylated aminopyridinium and bis-aminopyridinium salts; thus, e.g., 2,4,6-trimethyl-pyryliumperchlorate (1) reacted with 4-phenyl-semicarbazide (2), with thio-semicarbazide (3), and with N-4-phenyl-thio-semicarbazide (4) in aqueous or alcoholic solution toward the substituted pyridinium salts 5, 6, 7:



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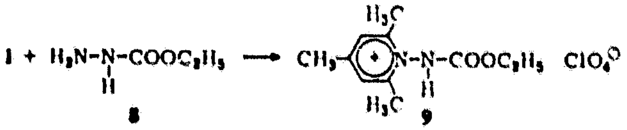
The NMR spectrum of 7 in CF_3COOH contains two signals at τ = = 7.26 and τ = 7.1 corresponding to the α and γ-methylprotons of the pyridinium nucleus (9 H); the β-protons yield a signal at τ = = 2.3. The five aromatic phenylprotons appear as a sharp singlet at τ = 2.42.

To effect a transition of the above described substances -- which are to be considered as hydrazides of carbamic or thiocarbamic acid -- to pure carbonic acid hydrazides we precipitated a /651 reaction between hydrazine carbonic acid ethyl ester and the pyrilium salt 1. The electron attracting effect of the carbonyl group was partly compensated by the (+)-M-effect of the $-OC_2H_5$ group. As the mesomeric effect of -OR groups does not equal that of $-N(R)_2$ groups, the basicity of the hydrazine carbonic acid ester ranges between that of semicarbazide and acetylhydrazide (pK_a = 3.24). Heating of equimolar amounts of 1 and 8 in methanolic solution yields 1-ethoxycarbonyl-amino-2,4,6-trimethyl-pyridinium-perchlorate (9):



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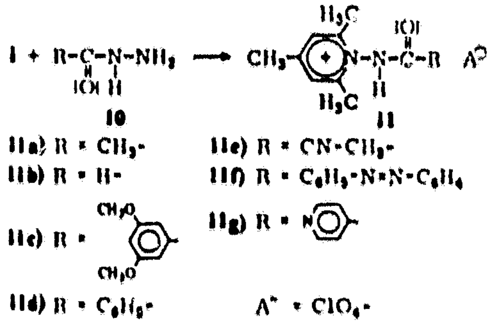
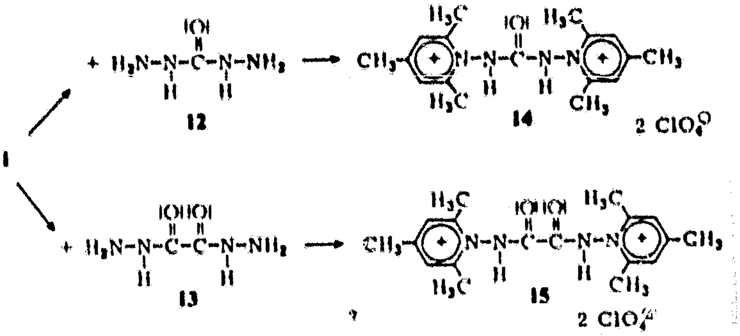
9 can be scrubbed with an ethanol/ether mixture, however it is subject to fast oleaginous separation and crystalizes only after thorough refrigeration.

The basicity of hydrazides can be lowered further by introducing other electron attracting substituents into the molecule. To find out the gradation in regards to reactivity, the residue R of hydrazide was varied in such a manner as to obtain a sequential series with declining basicity. Thus, formic acid hydrazide without the inductive effect of the methyl group has a lower basicity than acetyl hydrazide. Proceeding further to benzoic acid hydrazide, basicity changes only slightly (pK_a = 3.03), on the other hand, it diminishes considerably with introduction of a cyanogen group; cyanogen acetyl hydrazide has a pK_a value of 2.34. Compounds with lowest basicity in this series are azobenzol carbonic acid hydrazide[6] and isonicotinic acid hydrazide[7] (pK_a = 1.82).

Conversion of hydrazides 10 in a molar ratio of 1:1 or slightly over that in alcoholic or aqueous solution with pyrylium salts yields stabile, crystalline pyridinium perchlorate 11:

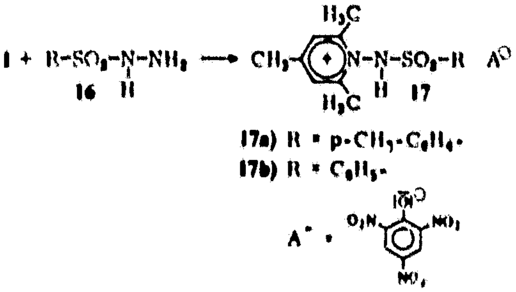


In continuation of the studies we became interested also in aminosubstituted bis-pyridinium salts 14 and 15 available from the bifunctional acid hydrazides 12, 13 and 2 mol pyrylium salt: /652



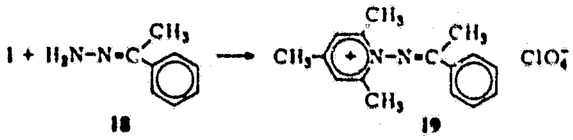
It must be assumed that only two-stage reactions are involved. All compounds obtained in this manner show simple and clear NMR spectra which correspond with the requisite structures. The characteristic absorptions of the pyridinium nucleus are reflected also in the IR spectra; in analogy to 5, all substances -- due to positive change in the molecule -- show a shift of the -CO-absorption bands to higher frequencies. In the case of simple 1-N-acyl-aminopyridinium salts the difference amounts to 20-40 cm^{-1}, but, in the case of compound 15 it is 50 cm^{-1} and in the case of compound 14 the difference is as much as 80 cm^{-1}.

Only two pyridinium salts could be obtained with N-sulfonyl hydrazides; because of the stronger electron attraction of the sulfonyl group these substances are less reactive than the N-acyl hydrazides p-toluene-sulfonyl hydrazide (16a) and benzol-sulfonyl hydrazide (16b)



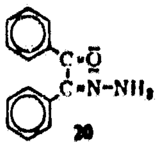
and yield through heating with 1 in aqueous or alcoholic solution the corresponding pyridinium salts 17a and 17b. As the N-sulfonyl hydrazides become subject to cleavage when heated for longer periods in water or alcohol, the reaction must not last long. The compounds were precipitated as picrates, as the corresponding perchlorates /653 could not be isolated. However, the yields are only moderate; the p-chlorobenzol-sulfonyl hydrazide and m-nitro-benzol-sulfonyl hydrazide could not be made to react. Namely, heating both compounds with 2,4,6-trimethyl-pyrylium perchlorate in ethanol or water with subsequent precipitation with picric acid yields merely the picrate of 2,4,6-trimethyl-pyrylium cation, a proof that no reaction whatsoever took place.

Hydrazones, as relatively basic substances -- e.g., aceton hydrazone: pK$_a$ = 5.1[8] -- should yield with pyrylium salts in a smooth reaction pyridinium compounds. The greatest basicity from among the selected compounds shows acetophenon hydrazone (18) with a pK$_a$ value of 4.70[8]. It is proximatively comparable to aniline (pK$_a$ = 4.60)[9], the reactions of which with pyrylium salts are sufficiently known[10].



Less basicity is evinced with pK$_a$ = 3.85 by benzophenon hydrazone (18) due to expanded conjugation potential of the molecule. The basicity of benzyl-mono-hydrazone (20) could be somewhat lower;

with the aim to also provide availability of bis-pyridinium salts in this series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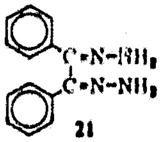
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benzyl dihydrazone (21) was included.

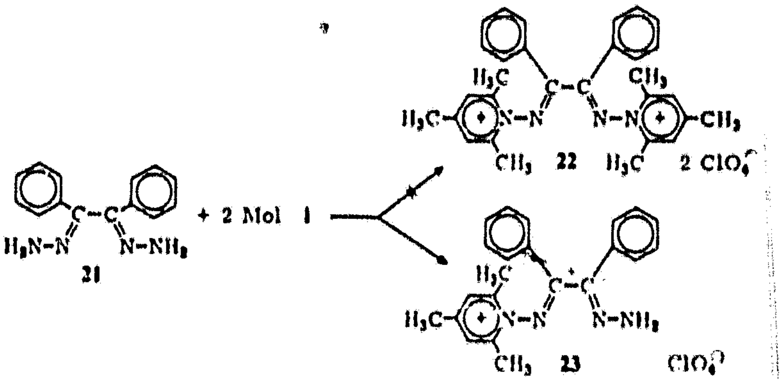
Nevertheless, the reactions do not progress so smoothly as, e.g., in the case of N-acyl hydrazides. If pyrylium salt in an etheric solution is left to react with an acetophenon hydrazone, it becomes essentially possible to isolate the unchanged pyrylium salt and the corresponding acetophenon azine. On the other hand, if an alcoholic solution of hydrazone is precipitated into a warm alcoholic solution of pyrylium salt, it is possible to obtain a 30% yield of the corresponding pyridinium salt 19; azine is also isolated as a byproduct in a 16% yield.

The IR spectrum of 19 shows the usual oscillation frequencies /654 of the pyridinium ring; the bands at 1,615 cm^{-1} can be ascribed to the -C=N-bond.

The NMR spectrum of 19 shows an inversion of signals for the α- and γ-methyl protons. The signal for the γ-methyl protons appears at $\tau = 7.22$, that for the α-methyl proton at $\tau = 7.28$. The signal at = 7.61 is ascribed to the single methyl group which in this case is not bonded to a hetero-atom. In the reaction with benzophenon hydrazone, dimerization of the hydrazone to azine constituted the main reaction. In spite of the given adequate basicity, it was not possible to isolate any pyridinium salt, and even benzyl monohydrazon produced no reaction; the reaction components were almost quantitatively recovered.

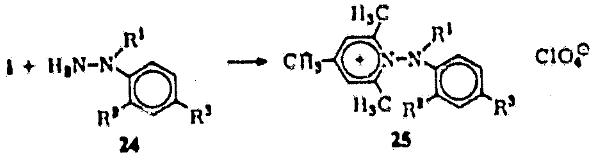
Benzyl dihydrazone 21 with two mol 1 should yield a bis-pyridinium salt of the structure 22.

If both components 21 and 1 are left to react in an alcoholic solution in a mol ratio of 1:2, the yield is a mixture of 1 and the monoreaction product 23; approximately 50% of the used 1 could be recovered. The same compound is obtained in a 90% yield when the conversion is done at a mol ratio of 1:1.



Schneider et al.[11, 12] converted phenyl hydrazine and substituted phenyl hydrazines with pyrylium salts whereby methyl, methoxyl, as well as bromine and chlorine were bonded to the benzol nucleus as substituents. Phenyl hydrazine has a pK_a value of 5.27[13]. Lower basicity is produced by introduction of a methyl group to an -stabile N-atom. 1-methyl-1-phenyl hydrazine has a lower basicity (with pKa = 4.98)[13] than nonsubstituted phenyl hydrazine. There is a reversal of conditions here in comparison to alkyl-substituted ani- /655 lines; however, the same basicity conditions are found also in the case of alkyl-substituted hydrazines[14].

A further decrease in basicity occurs also through substitution of the phenyl nucleus with a nitro group strongly attracting electrons. Thus, p-nitro-phenyl hydrazine has a pK_a value of 3.94[15] and that of 2,4-dinitro-phenyl hydrazine is 2.68[13].



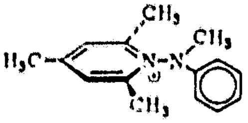
25a) R^1 = CH_3-; R^2 = H-; R^3 = H-
25b) R^1 = H-; R^2 = H-; R^3 = -NO_2
25c) R^1 = H-; R^2 = NO_2-; R^3 = -NO_2
25d) R^1 = H-; R^2 = H-; R^3 = -SO_3H

All three hydrazine derivatives 24a-24c yield with 1 crystalline pyridinium salts 25a-25c. The results show clearly a gradation of reactivity in relation to basicity. On the other hand, no reaction occurs when the benzol nucleus in the 4th position is substituted by a sulfonic acid grouping. Phenyl-hydrazine-p-sulfonic acid (24d) even in prolonged heating with 1 in ethanol or benzol yields no crystalline product 25d that could be isolated. The electron attraction effect of the p-stabile sulfonic acid group is obviously so strong that no reaction can be forced any more.

The NMR spectra of the three compounds show signals for the methyl protons on pyridinium nucleus at $\tau = 7.1-7.3$. The correlation for the α- and γ-methyl protons occurs very simply following the integration ratio. The positionally constant signals for -protons appear for all three compounds at approximately $\tau = 2.1$.

The spectrum of compound 25a shows an inversion of signals for α- and γ-protons (α-CH_3-: $\tau = 7.27$; γ-CH_3-: $\tau = 7.23$), while compound 25b shows the normal chemical displacement for these protons, such as it is known also for other N-alkylated 2,4,6-trimethyl pyridinium salts. In the spectrum of compound 25c the signals for α- and γ-methyl groups coincide.

The displacement of signals for the α-methyl protons to a higher field can be explained by transposition of the pyridinium ring in relation to the substituents in amino nitrogen (A).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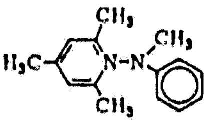
B

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The mutual position of both planes (pyridinium ring and the "aminobond plane") is determined by two mutually inverse effects:

1. Electronic effects that strive for an even plane of the entire molecule, and

2. steric effects which strive for a transposition of both planes.

Taking into consideration Stuart's calotte models of the three molecules, it can be seen that at a level position (B) the interaction of the methyl-phenyl-amine grouping with the α-stabile methyl groups is very strong. This shifts both planes into a vertical apposition, thus practically cancelling free rotation around the N-N bond axis. The phenyl ring and the methyl group are both above and below the pyridinium ring which results in strong screening of the α-methyl protons and, thus, in inversion of signals.

Conditions are similar in compound 25c in which the ortho-stabile nitro group hinders the rotation around the N-N bond. However, as the effect is not as pronounced as it is in 25a, the signal displacement for α-methyl is smaller. On the other hand, in compound 20b rotation around the N-N bond is possible, screening is not excessive, i.e., adsorption progresses at "normal" values.

Description of Experiments

Melting point: Lindstrom apparatus (uncorrected). IR spectra: spectrophotometer 257 Perkin-Elmer. NMR spectra: instrument of the Jeol company, Japan, model JNM-MH-60 Mark 2 (60 MHz, TMS as inner standard). Elementary analysis: automatically operating CHN-microanalyzer of the Heraeus company, Hanau.

1-(3-phenyl-ureido-)-2,4,6-trimethyl-pyridinium-picrate (5)

2.2 g (10 mmol) 2,4,6-trimethyl-pyrylium-perchlorate (1) and 1.5 g (10 mmol) of 4-phenyl-semicarbazide (2) are fast brought to boil in 150 ml water. A warm solution of 2.3 g (10 mmol) of picric acid in ethanol is added to the reaction mixture; cooling produces yellow crystalline flakes. From aqueous ethanol, melting point 203-205 degrees (decomp.); yield: 2.5 g = 74%.

$C_{21}H_{20}N_6O_8$ (484.42) calculated: C 52.07 H 4.16 N 17.35; found: C 52.21 H 4.17 N 17.18.

1-(thio-ureido-)-2,4,6-trimethyl-pyridinium-picrate (6) /657

From 2.2 g (10 mmol) of 1, 1.0 g (11 mmol) of thiosemicarbazide (3) and 2.3 g (10 mmol) of picric acid in aqueous solution analogously to (5), yellow needles from aqueous ethanol. Melting point 165-166 degrees (decomp.); yield: 2.8 g = 66%.

$C_{15}H_{16}N_6O_7S$ (424.39) calculated: C 42.45 H 3.80 N 19.80; found: C 42.73 H 4.19 N 19.88

1-(3-phenyl-thio-ureido-)-2,4,6-trimethyl-pyridinium-perchlorate (7a)

2.2 g (10 mmol) of 1 and 1.7 g (10 mmol) of 4-phenyl-thi-semicarbazide (4) are heated for ½ hr in ethanol. Boiling down of the solution produces white crystals, recrystallization from ethanol. Melting point 152-154 degrees; yield: 1.6 g = 43%.

C H Cl N O S (371.84) calculated: C 48.46 H 4.88 N 11.31; found: C 48.51 H 5.00 N 11.38.

1-(3-phenyl-thio-ureido-)-2,4,6-trimethyl-pyridinium-picrate (7b)

Analogously to (7a) from 1.1 g (5 mmol) of 1, 0.85 g (5 mmol) of 4-phenyl-thio-semicarbazide (4) and 1.15 g (5 mmol) of picric acid. Yellow flakes from ethanol, melting point 152-154 degrees (decomp.); yield: 1.7 g = 68%. $C_{21}H_{20}N_6O_7S$ (500.5) calculated: C 50.39 H 4.03 N 16.80; found: C 50.41 H 4.05 N 16.82.

1-ethoxycarbonyl-amino-2,4,6-trimethyl-pyridinium-perchlorate (9)

1.1 g (5 mmol) of 1 and 0.6 g (5.7 mmol) of hydrazoic carbonic acid ester (8) are heated in 50 ml of methanol. After boiling down of the solution and strong cooling appears a white crystalline mass which is several times recrystallized from ethanol/ether. Melting point 84-86 degrees; yield: 900 mg = 58%. $C_{11}H_{17}ClN_2O_6$ (308.7) calculated: C 42.79 H 5.55 N 9.08; found: C 43.13 H 5.46 N 9.31.

1-(acetylamino-)-2,4,6-trimethyl-pyridinium-perchlorate (11a)

2.2 g (10 mmol) of 1 and 1.2 g (16 mmol) of N-acetyl hydrazide are shortly heated in 50 ml of ethanol. White crystals form during cooling, recrysrallized from ethanol. Melting point 151-152 degrees; yield: 1.9 g = 68%. $C_{10}H_{15}ClN_2O_5$ (278.7) calculated C 43.10 H 5.42 N 10.05; found: C 42.88 H 5.50 N 10.11.

Picrate of 11a

From 1.1 g (5 mmol) of 1, 0.5 g (6.8 mmol) of N-acetyl hydrazide (10a) and 1.1 g picric acid in aqueous solution analogously to (5), yellow needles after recrystallization from ethanol. Melting point 193-195 degrees (decomp.); yield 1.45 g = 72%. $C_{16}H_{17}N_5O_8$ (407.34) calculated: C 47.18 H 4.21 N 17.20; found: C 47.52 H 4.32 N 16.94.

1-(formyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (11b)

From 22.4 g (0.1 mol of 1 and 6.2 g (0.1 mol) of formyl hydrazide (11b), ½ hr heating in ethanol analogously to (11a); white flakes after recrystallization from ethanol. Melting point 150-152 degrees; yield: 22 g = 83%. $C_9H_{13}ClN_2O_5$ (264.7) calculated: C 40.84 H 4.95 N 10.58; found: C 41.03 H 5.08 N 10.56.

1-(3',5'-dimethoxy-benzoyl-amino)-2,4,6-trimethyl-pyridinium-perchlorate (11c) /658

From 2.2 g (10 mmol) of 1 and 2 g (10 mmol) of 3,5-dimethoxy-benzoic acid hydrazide (10 c) heated for 3 min in ethanol produce white flakes recrystallized from ethanol. Melting point 238 deg.; yield 3.4 g = 85%. $C_{17}H_{21}ClN_2O_7$ (400.8) calculated: C 50.95 H 5.28 N 6.99; found: C 51.21 H 5.32 N 7.12.

1-(benzoyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (11d)

2.2 g (10mmol) of 1 and 1.4 g (10 mmol) of N-benzoyl hydrazide (11d) are heated for a short time in water. The warm solution is concentrated in vacuum; colorless crystals from methanol. Melting point 145-147 degrees; yield: 2.1 g = 62%. $C_{15}H_{17}ClN_2O_5$ (340.77) calculated: C 52.69 H 5.03 N 8.22; found: C 52.68 G 5.11 N 8.31.

Picrate of 11d

Analogously to (5) from 2.2 g (10 mmol) of 1, 1.4 g (10 mmol) of N-benzoyl hydrazide (10d) and 2.3 g picric acid in 150 ml water; yellow crystals from ethanol. Melting point 198-200 degrees (decomp.); yield: 3.3 g = 70%. $C_{21}H_{19}N_5O_8$ (469.40) calculated C 53.73 H 4.08 N 14.92; found: C 53.40 H 4.04 N 14.81.

1-(cyanogen-acetyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (11e)

Analogously to (11a) from 2.2 g (10 mmol) of 1 and 1 g (10 mmol) of cyanogen-acetyl hydrazide (10e), heated for 10 min in 40 ml of ethanol; white needles from ethanol. Melting point 187-189 degrees; yield: 2.5 g = 82%. $C_{11}H_{14}ClN_3O_5$ (303.7) calculated: C 43.50 H 4.64 N 13.84; found: C 43.50 H 4.59 N 13.81.

1-(p-phenyl-azo-benzoyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (11f)

From 1.1g (5 mmol) of 1 and 1.2 g (5 mmol) of azobenzol-carbonic acid hydrazide (10f), heated in ethanol for 15 min; orange-red crystals from ethanol. Melting point 189-191 degrees (decomp.); yield 1.15 g = 52%. $C_{21}H_{21}Cl N_4O_5$ (444.9) calculated: C 56.70 H 4.76 N 12.60; found: C 57.01 H 4.79 N 12.59.

1-(isonicotinoyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (11g)

From 2.2 g (10 mmol) of 1 and 1.4 g (10 mmol) of isonicotinic acid hydrazide (10g) in aqueous solution analogously to (11d); white crystals from methanol/water. Melting point 283-285 degrees (decomp.); yield: 2.5 g = 73%. $C_{14}H_{16}Cl N_3O_5$ (341.74) calculated: C 49.20 H 4.72 N 12.30; found: C 48.99 H 4.76 N 12.45.

Dipicrate of 11g

From 2.2 g (10 mmol) of 1, 1.4 g (10 mmol) of isonicotinic acid hydrazide (10a) and excess of picric acid in 50 ml water analogously to (5); long yellow needles from ethanol. Melting point 221-224 deg. (decomp.); yield: 3.2 g = 45%. $C_{26}H_{21}N_9O_{15}$(699.5) calculated: C 44.64 H 3.02 N 18.01; found: C 44.70 H 3.07 N 18.02.

N,N'-bis-(2,4,6-trimethyl-pyridino-)-ureido-diperchlorate (14)

2.2 g (10 mmol) of 1 and 0.45 g (5 mmol) of carbohydrazide (12) are heated in 40 ml of ethanol overnight. After boiling down and cooling of the solution there appears a white crystalline mass; from glacial acetic acid/water melting point 226-230 degrees (decomp.); yield 1.1 g = 44%. $C_{17}H_{24}Cl_2N_4O_9$ (499.3) calculated: C 40.89 H 4.85 N 11.23; found: C 40.86 H 4.80 N 11.02.

N,N'-bis-(2,4,6-trimethyl-pyridino-)-oxamide-diperchlorate (15) /659

From 2.2 g (10 mmol) of 1 and 0.6 g (5 mmol) of oxalic acid hydrazide (13) heated in ethanol in analogy to (14); white crystals from aqueous ethanol. Melting point 302-304 degrees (decomp.); yield: 1.7 g = 64%. $C_{18}H_{24}Cl_2N_4O_{10}$ (527.3) calculated: C 41.00 H 4.59 N 10.62; found: C 40.77 H 4.67 N 10.69.

1-(p-tolylsulfonyl-amino-)-2,4,6-trimethyl-pyridinium-picrate (17a)

From 1.1 g (5 mmol) of 1, 0.9 g (5 mmol) of p-tolyl-sulfonyl hydrazide (16a) and 1.1 g (5 mmol) of picric acid in aqueous solution analogously to (5); yellow needles from ethanol. Melting point

206-209 degrees (decomp.); yield: 1.3 g = 50%. $C_{21}H_{21}N_5O_9S$ (%19.48) calculated: C 48.55 H 4.08 N 13.48; found: C 48.47 H 4.11 N 13.51.

1-(benzolsulfonyl-amino-)-2,4,6-trimethyl-pyridinium-picrate (17b)

2.2 g (10 mmol) of 1 and 1.7 g (10 mmol) of benzol-sulfonyl hydrazide (16b) are fast brought to boiling in 100 ml of ethanol. The salt is precipitated by addition of a warm ethanolic solution of 2.3 g (10 mmol) of picric acid; approximately 1 g of nonconverted pyrilium salt can be recovered from the mother lye. Yellow needles from aqueous ethanol. Melting point 220-224 degrees (dec.); yield: 1 g = 20%. $C_{20}H_{19}N_5O_9S$ (505.5)calculated: C 47.52 H 3.79 N 13.86; found: C 47.49 H 3.82 N 13.57.

1-(phenyl-methyl-methylene-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (19)

2.2 g (10 mmol) of 1 are heated in 40 ml of ethanol to 60 deg.; to this is added by drops a solution of 1.4 g (10 mmol) of acetophenone hydrazone (18) in 20 ml of ethanol; the mixture slowly assumes a dark red coloring. Dark brown crystals are obtained from the solution after condensing and cooling, which are recrystallized from ethanol. It is possible to isolate from the mother lye 200 mg of acetophenone in the form of yellow flakes with a melting point of 120 degrees; light yellow crystals from ethanol. Melting point 163-165 degrees; yield: 1.1 g = 33%. $C_{16}H_{19}ClN_2O_4$ (338.8) calculated C 56.72 H 5.65 N 8.27; found: C 56.78 H 5.71 N 8.31.

1-(hydrazono-phenyl-methyl-)-phenyl-methylenamino-N-2,4,6-trimethyl-pyridinium-perchlorate (23)

2.2 g (10 mmol) of 1 and 2.4 g (10 mmol) of benzyl hydrazone (21) are heated under reverse flow in 90 ml of ethanol for 2 hrs; long, white needles are separated during cooling which are recrystallized from ethanol. Melting point 208-211 degrees (decomp.); yield: 4.1 g = 92%. $C_{22}H_{23}ClN_4O_4$ (442.5) calculated: C 59.66 H 5.23 N 12.65; found: C 59.71 H 5.37 N 12.80.

1-(phenyl-methyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (25a)

2.2 g (10 mmol) of 1 are made into a paste with 20 ml of waterless ether. To this suspension is added in drops 1.6 g (13 mmol) of

1-methyl-1-phenyl hydrazine (24a). After the reaction dies down, heating with reverse flux continues for 1 hr; the white pyryllium salt forms yellow crystals that are extracted and recrystallized from ethanol. Melting point 97-98 degrees, yield: 3.0 g = 94%. $C_{15}H_{19}ClN_2O_4$ (326.77 calculated: C 55.12 H 5.86 N 8.57; found: C 54.82 H 5.62 N 8.26.

1-(4-nitro-phenyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (25b)

2.2 g (10 mmol) of 1 are warmed in 40 ml ethanol. To this is added in drops, while mixing, a solution of 1.5 g (10 mmol) of 4-nitro-phenyl hydrazine (24b) in 60 ml ethanol. The solution turns yellow, condenses after some time and it is let to crystal- /660
lize under refrigeration; yellow crystalline powder, after recrystallization from aqueous ethanol yellow flakes. Melting point 239 degrees (decomp.); yield: 2 g = 56%. $C_{14}H_{16}ClN_3O_6$ (357.75) calculated: C 47.01 H 4.51 N 11.72; found: C 47.07 H 4.60 N 11.24.

1-(2,4-dinitro-phenyl-amino-)-2,4,6-trimethyl-pyridinium-perchlorate (25c)

0.55 g (2.5 mmol) of 1 are made into a paste with 30 ml of boiling benzol. To this is added in drops a solution of 0.5 g (2.5 mmol) of dinitro-phenyl hydrazine in 110 ml of benzol. After heating with reverse flux overnight occurs formation of light yellow crystals, light yellow colored crystals are obtained after recrystallization from ethanol. Melting point 270-271 degrees (decomp.); yield 500 mg = 50%. $C_{14}H_{15}ClN_4O_8$ (402.8) calculated: C 41.75 H 3.75 N 13.91; found: C 41.85 H 3.80 N 14.08.

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