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# Molecular Complexes of 4-Nitropyridine and 4-Nitroquinoline *N*-Oxides with Boron Trifluoride and Hydrogen Chloride as Intermediates in $S_NAr$ Reactions

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**Abstract**—Complexation of 4-nitropyridine *N*-oxides with *v*- ($BF_3$, HCl) and π-acceptors (tetracyanoethylene, chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 7,7,8,8-tetracyanoquinodimethane) activates the nitro group to nucleophilic replacement by chlorine. Adducts formed by 4-nitropyridine and 4-nitroquinoline *N*-oxides with boron trifluoride and hydrogen chloride were studied by IR spectroscopy. It was shown that these complexes belong to the *n*,*v* type and that the donor–acceptor interaction therein involves the oxygen atom of the *N*-oxide group.

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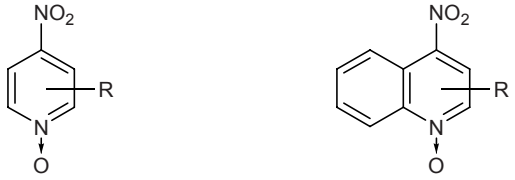
Nucleophilic replacement in the series of heteroaromatic *N*-oxides underlies synthesis of various pyridine and quinoline derivatives. However, despite activating effect of the *N*-oxide group, $S_NAr$ reactions with weak nucleophiles are slow. For example, in the reaction of 4-nitroquinoline *N*-oxides with $Et_3BuNCl$ as source of chloride ions at 40°C the yield of the corresponding replacement product, 4-chloroquinoline *N*-oxide did not exceed 3% even after 72 h [1]. The use of π- (tetracyanoethylene [2, 3]) or *v*-acceptors ($BF_3$ [1], $AlCl_3$ [4], $H^+$ [5]) as catalysts makes it possible to complete replacement of the nitro group by chlorine in 30 min. Addition of boron trifluoride–ether complex to a mixture containing 4-nitroquinoline *N*-oxide and $Et_3BuNCl$ in acetonitrile ensures reaction completion in 1 h at room temperature. Analogous result is obtained when solid 4-nitroquinoline *N*-oxide–$BF_3$ adduct is used. These data indicate that the nucleophilic replacement process involves molecular complex of the *N*-oxide with $BF_3$. Presumably, the reaction of *N*-oxide **IIa** with hydrogen chloride also occurs under very mild conditions due to intermediate formation of **IIa**·HCl. Such intermediates have not been reported, and we believe that their study will provide better understanding of the mechanism of $S_NAr$ reactions in the series of heteroaromatic *N*-oxides and that activation by external acceptor can be extended to other heterocyclic systems.

The goal of the present work was to compare the efficiency of activation of $S_NAr$ reactions of 4-nitropyridine *N*-oxides **Ia**–**Id** and 4-nitroquinoline *N*-oxides **IIa** and **IIb** by external acceptor and examine properties of donor–acceptor complexes of these *N*-oxides with $BF_3$ and HCl, which are likely to be formed as intermediates.

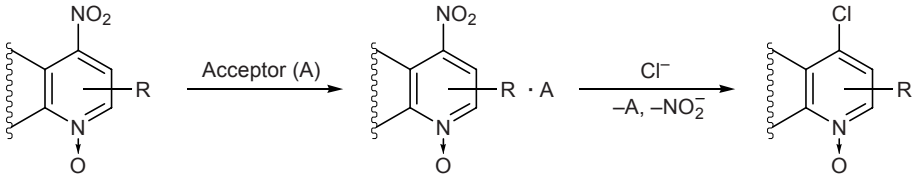



**Ia–Id** **IIa**, **IIb**

**I**, R = H (**a**), 2-Me (**b**), 3-Me (**c**), 2,6-$Me_2$ (**d**);
**II**, R = H (**a**), 2-Me (**b**).

We have found that nucleophilic replacement of the nitro group in 4-nitropyridine *N*-oxides by chlorine is activated by electron acceptors to a much lesser extent as compared to 4-nitroquinoline *N*-oxides (Table 1). A probable reason is smaller contribution of the quinoid structure in 4-nitroquinoline *N*-oxides. Hydrogen atom in position *5* of the quinoline ring is capable of

**Scheme 1.**




**Ia–Id**, **IIa**, **IIb**

A = $BF_3$, $H^+$, tetracyanoethylene (**III**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (**IV**), 2,3,5,6-tetrachlorobenzoquinone (**V**), 7,7,8,8-tetracyanoquinodimethane (**VI**).

interacting with the 4-nitro group, forcing the latter to deviate from the quinoline ring plane. As a result, conjugation between the nitro group and the aromatic system becomes weaker, and the double character of the C–$NO_2$ bond decreases.

There are no crystallographic data on the structure of 4-nitroquinoline and its *N*-oxide [6]. However, a considerable torsion angle between the nitro group and aromatic ring plane is observed in 1-nitronaphthalene (23.99° for its clathrate with guanidinium biphenyldisulfonate [7]) and some its derivatives: 49.93° for 1,5-dinitronaphthalene [8], 15.40° for ammonium 2,4-dinitronaphthoxide [9], 14.66° for 1-hydroxy-2,4-dinitronaphthalene-7-sulfonic acid [10], and 32.37° for 4-nitro-*N*-phenylnaphthalene-1,8-dicarboximide [11].

The reactivity of 4-nitropyridine *N*-oxide in the replacement of the nitro group by chlorine, activated by external acceptor, changes in the following series (Table 1): **Id** < **Ib** < **Ia** < **Ic**. Introduction of a methyl group into position *2* of molecule **Ia** and of two methyl groups into positions *2* and *6* strongly decelerates the substitution process in the presence of HCl, while only traces of the corresponding 4-chloropyridine *N*-oxides were detected in the reactions of *N*-oxides **Ib** and **Id** with $Et_3BuNCl$ in the presence of $BF_3$ (65°C, 5 h). Presumably, methyl groups hamper interaction of the acceptor with the *N*-oxide group for steric reasons. Although methyl group in the 3-position of compound **Ic** should create steric hindrances to attack by nucleophile and reduce electrophilicity of the heteroring, the reaction with **Ic** is faster. This may also result from some deviation of the nitro group from the heteroring plane due to steric interaction with the substituent on $C^3$. Analogous explanation was proposed in [12] for ready replacement of the nitro group by chlorine or bromine in 3-substituted 4-nitro-1,3-dihydro-2*H*-imidazo[4,5-*c*]pyridin-2-ones.

We previously revealed a good correlation between the logarithms of the stability constants of Zn-tetraphenylporphyrin complexes with pyridine *N*-oxides and Hammett constants σ; deviation of the point for compound **Ic** from the straight line may be rationalized in the same way [13]. In fact, according to the X-ray diffraction data, the dihedral angle between the planes passing through the nitro group and pyridine ring in

**Table 1.** Replacement of the nitro group in 4-nitropyridine and 4-nitroquinoline *N*-oxides by chlorine atom in acetonitrile at 65°C in the presence of electron acceptors[a]

| Compound no. | Activator | Reaction time, min | Yield, % |
|---|---|---|---|
| **Ia** | $BF_3$ | 300 | 30 |
| **Ic** | $BF_3$ | 300 | 59 |
| **IIa** | $BF_3$ | 30 | >99 |
| **Ia** | **III** | 300 | 43 |
| **Ib** | **III** | 300 | 24 |
| **Ic** | **III** | 120 | 38 |
| **Id** | **III** | 300 | 17 |
| **IIa** | **III** | 15 | 37 |
| **Ia** | **IV** | 300 | 33 |
| **Ic** | **IV** | 300 | 47 |
| **IIa** | **IV** | 120 | 96 |
| **Ic** | **V** | 300 | 41 |
| **IIa** | **V** | 60 | >99 |
| **Ic** | **VI** | 300 | 19 |
| **IIa** | **VI** | 120 | 39 |
| **Ia** | HCl | 600 | 73 |
| **Ib** | HCl | 600 | 18 |
| **Ic** | HCl | 600 | 94 |
| **Id** | HCl | 600 | 13 |
| **IIa** | HCl | 30 | >99 |
| **IIb** | HCl | 30 | >99 |

[a] The reaction of *N*-oxide **IIa** with $Et_3BuNCl$ in the presence of tetracyanoethylene (**III**) in the system acetonitrile–dioxane (1 : 1) was complete in 3 h at room temperature [3].

**Table 2.** Yields, melting points, and UV spectra of complexes formed by 4-nitropyridine and 4-nitroquinoline *N*-oxides with HCl and $BF_3$

| Compound no. | Acceptor | Yield, % | mp, °C | UV spectrum ($CHCl_3$), $\lambda_{max}$, nm (log ε) | Δλ,[a] nm |
|---|---|---|---|---|---|
| **Ia** | – | 72 | 159 [17] | 343 (4.29) | – |
| | HCl | 92 | 128 | 283 (3.87) | –60 |
| | $BF_3$ | 88 | 143–145 | 278 (3.71) sh | –65 |
| **Ib** | – | 76 | 155 [18] | 347 (4.22) | – |
| | HCl | 81 | 137–138 | 296 (3.87) | –51 |
| | $BF_3$ | 79 | 127 | 295 (3.61) sh | –52 |
| **Ic** | – | 76 | 136–137 [19] | 339 (4.27) | – |
| | HCl | 52 | 82–85 | 285 (3.85) sh | –54 |
| | $BF_3$ | 61 | 100–103 | 279 (3.70) | –60 |
| **Id** | – | 80 | 163–164 [20] | 347 (4.25) | – |
| | HCl | 78 | 143 | 300 (3.88) | –47 |
| | $BF_3$ | [b] | [b] | 298 (3.73) | –49 |
| **IIa** | – | 67 | 153–154 [17] | 388 (4.11) | – |
| | HCl | [c] | [c] | 336 (3.75) | –52 |
| | $BF_3$ | 81 | 127–131 | 332 (3.77) | –56 |
| **IIb** | – | 64 | 155–157 [17] | 391 (4.03) | – |
| | HCl | [c] | [c] | 333 (3.83) | –57 |
| | $BF_3$ | 67 | 193–195 | 334 (3.83) | –58 |

[a] $\Delta\lambda = \lambda_{max}(N\text{-oxide}) - \lambda_{max}(N\text{-oxide}\cdot A)$.
[b] The complex decomposed during isolation.
[c] We failed to isolate the complexes as individual substances.

*N*-oxide **Ic** is 14.68° [14] (31.98° in the complex of **Ic** with $ZnBr_2$ [15]).

The effect of π-acceptors as activators of nucleophilic substitution in the series of nitropyridine *N*-oxides is similar to the effect of $BF_3$. An exception is tetracyanoethylene (**III**) which almost equally accelerates the reactions of $Et_3BuNCl$ with all the examined 4-nitropyridine *N*-oxides **Ia**–**Id** (Table 1). These findings require special consideration, taking into account that the acceptor power of **III** is much weaker than the acceptor power of quinone **IV** [16] and that the latter does not promote reaction of $Et_3BuNCl$ with *N*-oxides **Ib** and **Id** under the above conditions.

Thus we have found that coordination of 4-nitropyridine and 4-nitroquinoline *N*-oxides with electron acceptors considerably accelerates $S_NAr$ reactions and that the efficiency of such activation depends on the *N*-oxide structure. Therefore, in the next step of our study we synthesized probable intermediates in these reactions, i.e., complexes of *N*-oxides with HCl and $BF_3$, and examined their structure.

Our attempts to obtain *N*-oxide **IIa** hydrohalides by reaction with hydrochloric or hydrobromic acid or gaseous hydrogen halides showed that the nitro group in **IIa** is very readily replaced by chlorine or bromine atom. For example, the replacement was complete in 15–30 min when gaseous hydrogen chloride was passed through a solution of **IIa** in chloroform at room temperature [5]. Even fast isolation (within 30 s) of the reaction product of **IIa** with gaseous HCl in a hexane–chloroform mixture gave a crystalline substance containing about 8% of the corresponding chloro derivative whose fraction continuously increased with time (20% in 24 h). Obviously, nucleophilic substitution of the nitro group by chlorine occurs even in the solid phase.

Insofar as the rate of replacement of the nitro group in nitropyridine *N*-oxides by the action of hydrogen halides is much lower than in the reactions with their quinoline analogs, we made an attempt to isolate nitropyridine *N*-oxide adducts with HCl, which were not reported previously. Unlike 4-nitroquinoline *N*-oxide,

passing of hydrogen chloride over a period of 5 min through solutions of pyridine *N*-oxides **Ia**–**Id** in chloroform resulted in separation of stable crystalline 1:1 hydrochlorides (Table 2).

The reactions of *N*-oxides with HCl were accompanied by considerable blue shift of the long-wave absorption maximum of the initial *N*-oxide in the electronic absorption spectra with simultaneous decrease in the absorption intensity (Table 2). This is consistent with published data. According to [21], protonation of pyridine, quinoline, and isoquinoline *N*-oxides at the oxygen atom of the *N*-oxide group induces blue shift of the long-wave π–π* band [21]. Furthermore, the electronic absorption spectra of *N*-oxide **Id** in $CH_3CN$ ($\lambda_{max}$ 349.5 nm) and in a 1 M solution of $HClO_4$ in $CH_3CN$ ($\lambda_{max}$ 299.5 nm) [22] are very consistent with our data ($\lambda_{max}$ 347 and 300 nm, respectively).

It is known that the presence of electron-donating substituents in heteroaromatic ring reduces the blue shift of the π–π* band; moreover, in some cases bathochromic shift is observed. For instance, the Δλ value for protonated 2,4,6-trimethylpyridine and 4-chloro-2,6-dimethylpyridine *N*-oxides in $CH_3CN$ is fairly small, 0.6 and –6.5 nm, respectively, but it becomes very strong in going to pyridine *N*-oxides in which the substituent is capable of conjugation with the heteroaromatic ring: Δλ = 43.5 and –50 nm, respectively, for protonated 4-methoxy-2,6-dimethylpyridine *N*-oxide and compound **Id** [22].

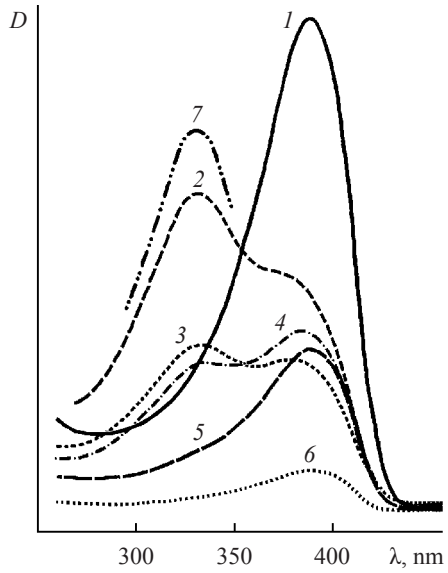
The IR spectrum of **Id**·HCl conforms well to that reported for 2,6-dimethylpyridine *N*-oxide hydrochloride; the spectrum contains a weak ν(N–O) band from the free base at 1251 $cm^{-1}$ and two ν(N–O) bands from the bound molecules at 1188 and 1232 $cm^{-1}$ [23].

The position of the ν(AH) stretching vibration band in the IR spectra of salts like A–H···B, depending on the acid and base strength, can be used as an indication of hydrogen bond formation [24]. For example, the ν(O–H) band in the IR spectra of *N*-oxide molecular complexes with a very weak hydrogen bond is located at 3000–2300 $cm^{-1}$ (4-nitropyridine *N*-oxide–4-nitrobenzoic acid complex). In going to stronger hydrogen bond (the O–H bond shortens), the absorption band shifts to lower frequencies (by 400 $cm^{-1}$ for the complex of 4-methoxy-2,6-dimethylpyridine *N*-oxide with pentachlorophenol). Complete proton transfer to the *N*-oxide oxygen atom leads to the reverse shift of the ν(O–H) band toward higher frequencies (4-dimethylamino-2,6-dimethylpyridine *N*-oxide complex with *p*-toluenesulfonic acid) [25].

The IR data showed that the isolated pyridine *N*-oxide hydrochlorides are characterized by almost complete proton transfer to the oxygen atom of the N→O group. Broadened ν(O–H) bands appear in the IR spectra of pyridine *N*-oxide hydrochlorides in the region 2330–1795 $cm^{-1}$ (Table 3). Here, in going from **Ia**·HCl (hydrochloride of the weakest base, p$K_a$ = –1.7 [26]) to stronger bases **Ib** (p$K_a$ = –0.967 [17]) and **Ic**

**Table 3.** IR spectra of complexes of 4-nitropyridine and 4-nitroquinoline *N*-oxides with HCl and $BF_3$

| Compound no. | $\nu_{as}(NO_2)$ | $\nu_s(NO_2)$ | ν(N→O) | ν(OH) (B–O, B–F) |
|---|---|---|---|---|
| **Ia** | 1517 v.s | 1348 v.s | 1272 v.s | – |
| **Ia**·HCl | 1544 v.s, 1514 v.s | 1348 v.s | 1272 v.s, 1196 s | 2178 br.s, 1930 br.s, 1794 br.s |
| **Ia**·$BF_3$ | 1516 v.s | 1348 v.s | 1276 s, 1176 s | (1124 v.s), (1084 v.s), (1040 v.s) |
| **Ib** | 1516 v.s | 1343 v.s | 1288 v.s, 1270 v.s | – |
| **Ib**·HCl | 1518 v.s | 1346 v.s, 1338 v.s | 1286 v.s, 1270 v.s | 2360 m, 2342 m |
| **Ib**·$BF_3$ | 1520 s | 1348 v.s | 1288 s, 1272 s, 1144 s | (1092 v.s), (1048 v.s) |
| **Ic** | 1510 s | 1344 v.s | 1264 v.s | – |
| **Ic**·HCl | 1510 s | 1344 v.s | 1264 s | 2334 br.s |
| **Ic**·$BF_3$ | 1548 v.s | 1360 s | 1256 s, 1180 m, 1148 s | (1084 v.s), (1044 m) |
| **Id** | 1518 v.s | 1341 v.s | 1274 v.s | – |
| **Id**·HCl | 1543 v.s, 1522 v.s | 1344 s | 1281 m, 1228 m | 2252 br.m, 1972 br.m, 1815 br.m |
| **IIa** | 1521 v.s | 1344 s | 1307 v.s | – |
| **IIa**·$BF_3$ | 1536 s, 1520 s | 1344 m | 1308 s, 1124 s | 1084 v.s, 1054 s |
| **IIb** | 1520 v.s | 1344 m | 1308 v.s | – |
| **IIb**·$BF_3$ | 1548 s, 1528 s | 1360 m | 1308 m, 1144 v.s | (1108 v.s), (1084 v.s), (1040 s) |




Electronic absorption spectra in chloroform of (*1*) *N*-oxide **IIa** ($c = 1.7 \times 10^{-4}$ M, $d = 0.5$ cm), complex **IIa**·$BF_3$ at a concentration $c$ of (*2*) $1.2 \times 10^{-3}$ M ($d = 0.1$ cm), (*3*) $6.0 \times 10^{-4}$ M ($d = 0.1$ cm), (*4*) $1.2 \times 10^{-4}$ M ($d = 0.5$ cm), (*5*) $6.0 \times 10^{-5}$ M ($d = 0.5$ cm), and (*6*) $1.2 \times 10^{-5}$ M ($d = 0.5$ cm), and (*7*) *N*-oxide **IIa** in the presence of excess $BF_3$ ($c = 1.2 \times 10^{-3}$ M, $d = 0.1$ cm).

($pK_a$ = –0.97 [27]), the broad absorption band shifts toward higher frequencies. Despite the presence of two electron-donating groups in the molecule of *N*-oxide **Id** (which should increase the basicity), the shift in the IR spectrum of **Id**·HCl is smaller than in the spectra of **Ib**·HCl and **Ic**·HCl, and the absorption band is very broad (it includes three maxima).

The $\nu_{as}(NO_2)$ band in the spectra of **Ia**·HCl and **Id**·HCl is split into two peaks, in contrast to the only band present in the spectra of the initial *N*-oxides. No such splitting is observed in the IR spectra of **Ib**·HCl and **Ic**·HCl; however, in the spectrum of **Ic**·HCl the $\nu_s(NO_2)$ band is doubled. This pattern may be due to hydrogen bonding between the proton linked to the *N*-oxide oxygen atom and oxygen atoms of the nitro group in the neighboring molecule. As a result, oxygen atoms in the nitro group become nonequivalent, and the $\nu(NO_2)$ band in the IR spectrum is split. Likewise, Hanuza et al. [28] rationalized doubling of the $\nu_s(NO_2)$ band in the IR spectrum of a single crystal of compound **Id**.

It was reported in [29] that *N*-oxide **Ia** does not form complexes with $BF_3$, presumably because of its low basicity. Nevertheless, we succeeded in isolating individual boron trifluoride adducts with five of the six *N*-oxides from solutions in $CHCl_3$, the ratio *N*-oxide–$BF_3$ being 1 : 1. An exception was the adduct with *N*-oxide **Id**, which decomposed during isolation.

In the electronic absorption spectra of the complexes with $BF_3$, as in the spectra of hydrochlorides, the long-wave absorption band was displaced by 50–65 nm to shorter wavelengths, and its intensity was lower as compared to the spectra of the initial *N*-oxides. A good correlation was observed between $\Delta\lambda$ for the complexes with $BF_3$ and $\Delta\lambda$ for the corresponding hydrochlorides. The largest blue shift ($\Delta\lambda$ = –65 nm) was found for unsubstituted pyridine *N*-oxide **Ia** ($\Delta\lambda$ = –60 nm for **Ia**·HCl), and the smallest (–49 nm), for **Id** (–47 nm for **Id**·HCl). Similar trends in the variation of the electronic absorption spectra of pyridine *N*-oxide complexes with HCl and $BF_3$ imply that the coordination involves the same center. Somewhat larger $\Delta\lambda$ values for the complexation with $BF_3$ must be noted.

The electronic absorption spectrum of a saturated solution of complex **IIa**·$BF_3$ in chloroform displayed a band at λ 332 nm due to the complex and a shoulder at about λ 380 nm due to free *N*-oxide **IIa** (see figure). Dilution leads to dissociation of the complex, the band at 332 nm gradually disappears, and the final spectrum becomes identical to the spectrum of *N*-oxide **IIa**.

The complexes with $BF_3$ showed in the IR spectra strong broadened absorption bands in the region 1125–1050 $cm^{-1}$, which were assigned to vibrations of the B–F bonds [30] and newly formed B–O bond [31]; new ν(N–O) bands originating from the N→O group bound to the acceptor also appeared at 1150–1120 $cm^{-1}$. The ν(N–O) bands typical of the initial *N*-oxides (1264–1288 $cm^{-1}$) were also present in the spectra, but their intensity was lower. The ν(N–O) band in the spectrum of **Ic**·$BF_3$ shifts to 1256 $cm^{-1}$ (1264 $cm^{-1}$, v.s, in the spectrum of **Ic**), and its intensity decreases. The observed variations in the IR spectra are consistent with coordination of the acceptor molecule at the oxygen atom of the N→O group [26, 32].

Thus using electronic absorption and IR spectroscopy we showed that 4-nitropyridine and 4-nitroquinoline *N*-oxides form *n*,*v*-complexes with $BF_3$ and HCl via coordination of the acceptor at the oxygen atom of the *N*-oxide group.

## EXPERIMENTAL

The IR spectra of pyridine and quinoline *N*-oxides and their complexes with electron acceptors were recorded in KBr on a Specord M-80 spectrometer. The electronic absorption spectra were measured on

a Specord UV-Vis spectrophotometer. Taking into account that dissolution of the complexes in chloroform was accompanied by their dissociation into initial components, excess boron trifluoride–ether complex was added to or gaseous hydrogen chloride was passed through their solutions to obtain electronic absorption spectra.

The reaction mixtures were analyzed (qualitatively and quantitatively), and the purity of the products was checked, by HPLC using a Laboratorni Přistroje chromatograph (Praha) equipped with an UV LCD 2040 detector (λ 280 nm for 4-nitropyridine *N*-oxides or 335 nm for 4-nitroquinoline *N*-oxides); Separon SGX $C_{18}$ column (3×150 mm); eluent acetonitrile–water, 84:16, flow rate 0.2 ml/min. A 0.05-ml portion of the reaction mixture was placed in a test tube charged with 0.45 ml of a 3% solution of trimethylamine in ethanol, and a 0.5-μl sample was withdrawn and injected. A standard reaction mixture contained 0.3 ml of acetonitrile, 0.1 mmol of *N*-oxide **I** or **II**, 0.1 mmol of $Et_3BuNCl$, and 0.02 ml of $BF_3 \cdot Et_2O$, 0.02 ml of concentrated hydrochloric acid, or 0.1 mmol of solid π-acceptor **III**–**VI**.

*N*-Oxides **Ia**–**Id**, **IIa**, and **IIb** were synthesized according to the procedures described in [17, 18]. Chloroform was purified by standard method [33].

**4-Nitropyridine *N*-oxide complex with $BF_3$.** Boron trifluoride–ether complex, 0.4 ml, was added to a solution of 280 mg (0.002 mol) of 4-nitropyridine *N*-oxide in 6 ml of chloroform. The precipitate was filtered off, washed with diethyl ether (2×2 ml), and dried in air. Yield 0.366 g (88%), colorless powder, mp 143–145°C. Found, %: C 28.79; H 2.06; N 13.71. $C_5H_4BF_3N_2O_3$. Calculated: %: C 28.87; H 1.94; N 13.53.

Complexes of *N*-oxides **Ib**–**Id** with $BF_3$ were synthesized in a similar way. In the reactions with *N*-oxides **Ib** and **Id** the resulting complexes separated as oily substances which crystallized on storage.

**4-Nitroquinoline *N*-oxide complex with $BF_3$.** Boron trifluoride–ether complex, 0.4 ml, was added to a solution of 190 mg (0.001 mol) of 4-nitroquinoline *N*-oxide in 5 ml of chloroform, the solvent was distilled off under reduced pressure, the brown oily residue was treated with 7 ml of diethyl ether, and the precipitate was filtered off, washed with 5 ml of diethyl ether, and dried in air. Yield 0.209 g (81%), light yellow powder, mp 127–131°C. Found, %: C 41.69; H 2.46; N 10.69. $C_9H_6BF_3N_2O_3$. Calculated, %: C 41.88; H 2.34; N 10.90.

The complex of *N*-oxide **IIb** with $BF_3$ was synthesized in a similar way. The *N*-oxide–$BF_3$ ratio in the complexes was determined by titration (after preliminary hydrolysis) as described in [34].

**4-Nitropyridine *N*-oxide hydrochloride.** Gaseous hydrogen chloride was passed through a solution of 0.07 g (0.5 mmol) of 4-nitropyridine *N*-oxide in 2 ml of chloroform. The precipitate was separated by centrifugation and washed with chloroform (3×1 ml). Yield 0.096 g (92%), colorless powder, mp 128°C. Found, %: C 34.12; H 3.04; N 15.69. $C_5H_5ClN_2O_3$. Calculated, %: C 33.98; H 2.85; N 15.92.

*N*-Oxides **Ib**–**Id** hydrochlorides were obtained in a similar way. In the reactions with *N*-oxides **Ib** and **Id**, oily substances separated from the solution and crystallized on storage. The ratio *N*-oxide–HCl was determined by titration using Methyl Red as indicator.

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