H), 2.60 (d of t, J_{aa} = 11, J_{ae} = 4 Hz, 1 H, C_4 H), 0.80 (s, 9 H, *tert*-butyl).

Anal. Calcd for $C_{17}H_{24}O_4S$: C, 62.93; H, 7.46. Found: C, 62.83; H, 7.66.

Dispiro[bis(4-*tert*-butylcyclohexane-1,2',5',1''-oxazolid-4'-one)] (20). 4-*tert*-Butylcyclohexanone cyanohydrin (**19**, 2 g) was dissolved in a mixture of 95% EtOH (5 ml) and concentrated HCl (5 ml). The solution was boiled under reflux for 13 h. The precipitated oxazolidone (0.20 g, 9%) was filtered and had mp 330 °C; ir 3400, 3290, 1685 (C=O), 1090 cm^{-1}; the NMR spectrum could not be determined owing to the insolubility of this compound in the usual solvents; mass spectrum (70 eV) *m/e* (rel intensity) 336 (0.8), 335 ($M\cdot^+$, 2.4), 320 (2.6) 236 (100), 182 (3.4), 180 (4.6), 164 (70), 154 (9.2), 138 (9.2).

Anal. Calcd for $C_{21}H_{37}NO_2$: C, 75.17; H, 11.12; N, 4.18. Found: C, 75.55; H, 11.14; N, 4.23.

The same compound (identical ir spectra) could be obtained, albeit in even lower yield (3.5%), by keeping a mixture of the cyanohydrin and polyphosphoric acid at room temperature.[13]

Acknowledgments. Part of this work was carried out during the tenure (by S.S.S.) of an NDEA Fellowship (1970–1971). Thanks are due to the Dow Chemical Co. for the gift of 4-*tert*-butylcyclohexanone.

Registry No.—**1**, 23022-33-5; **9**, 35905-86-3; **10**, 58463-38-0; **10** 4-*c* isomer, 58463-39-1; **11**, 58463-32-4; **12**, 58463-40-4; **13**, 58463-41-5; **14**, 58463-42-6; **15**, 58463-43-7; **16**, 58463-44-8; **17**, 58463-45-9; **18**, 58463-46-0; **19**, 941-44-6; **20**, 58463-47-1; ethyl *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxamide, 58463-48-2; *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carbonitrile, 35905-99-8; *r*-1-*tert*-butyl-*c*-3-phenylsulfonylcyclohexane-*c*-4-carboxylic acid, 58463-49-3; methyl 1-*r*-*tert*-butyl-*t*-3-thiophenoxycyclohexane-*t*-4-carboxylate, 58463-50-6; thiophenol, 108-98-5.

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(6) Equilibration appears to occur, at least partly, via retro-Michael addition followed by readdition.[3] The isolation of olefin **1** from some equilibration experiments supports this suggestion. Since elimination from **4** would be expected to be more difficult than from **5** this could explain slight differences observed between the ratio obtained starting from pure **5** and from the addition under thermodynamic control conditions, and also the different ratio obtained in the dipolar aprotic solvent, DMF, used.[1]
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Reaction of Pyridine 1-Oxides and *N*-Iminopyridinium Ylides with Diazonium Salts. *N*-Aryloxypyridinium Salts and Their Base-Catalyzed Rearrangement

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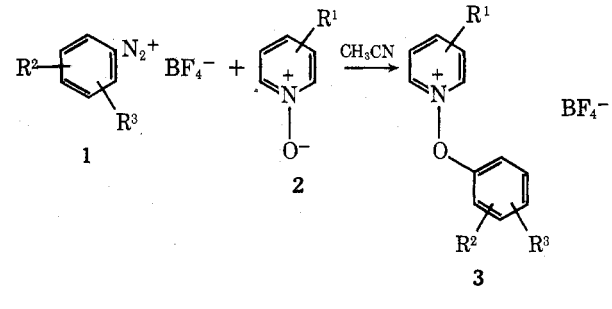
N-Aryloxypyridinium tetrafluoroborates are prepared by the reaction of pyridine 1-oxides with aryldiazonium tetrafluoroborates bearing an electron-withdrawing substituent in the aryl ring. The scope, limitations, and possible mechanism of the reaction are discussed. The salts undergo base-catalyzed rearrangement to give 2-*o*-hydroxyarylpyridines. *N*-Aminopyridinium tetrafluoroborates react with aromatic diazonium salts in acetonitrile to give 1-[(*N*-arylacetimidoyl)amino]pyridinium tetrafluoroborates (**14**) but no *N*-arylaminopyridinium tetrafluoroborates. Related compounds are formed in propionitrile and malononitrile, but not in butyronitrile and benzonitrile. In butyronitrile, for example, 1-(*N*-butyrimidoylamino)iminopyridinium tetrafluoroborate (**16**) is formed. Compounds **14** give the corresponding ylides with base. Treatment of *N*-aryliminopyridinium ylides with base does not lead to their rearrangement to 2-*o*-aminoarylpyridines.

N-Alkoxypyridinium salts are well-known compounds whose preparation[1] and properties[1,2] have recently been reviewed. They are usually readily made from the *N*-oxide and an alkyl halide, dialkyl sulfate, or alkyl sulfonate. In contrast, the *N*-aryloxy compounds were not known when this work was initiated.[3] Attempts to phenylate pyridine 1-oxide with diphenyliodonium bromide or benzenediazonium tetrafluoroborate failed.[4] We now report[3] a convenient synthesis of such compounds and a novel molecular rearrangement which they undergo.

It was expected that, for a direct arylation to occur between a diazonium salt and an *N*-oxide, the salt would have to be more electrophilic than unsubstituted benzenediazonium tetrafluoroborate, rather than going the other way and making the *N*-oxide more nucleophilic. It was felt that if the latter were the case the *N*-oxide might induce a homolytic decomposition via the diazo compound[5] which would defeat the purpose. To this end, the diazonium tetrafluoroborate (**1**) of



an aromatic amine bearing an electron-withdrawing substituent was added to a solution of a pyridine 1-oxide (**2**) in acetonitrile and the solution was either stirred at room temperature or warmed gently to give the desired *N*-aryloxypyridinium tetrafluoroborate (**3**). The salts so prepared are listed in Table I.

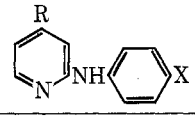
The structures of the salts **3** were established by spectro-

Table I. 1-Aryloxypyridinium Tetrafluoroborates (3)[g]

Registry no.	R^1	R^2	R^3	% yield	Mp, °C	Molecular formula
33393-61-2	H	4-NO_2	H	75	157.5–159	$C_{11}H_9BF_4N_2O_3$
33393-60-1	H	4-CN	H	70	214–215	$C_{12}H_9BF_4N_2O$
33393-59-8	H	4-CF_3	H	36	135–136	$C_{12}H_9BF_7NO$
33395-25-4	H	3-NO_2	H	24	149–150	$C_{11}H_9BF_4N_2O_3$
33395-26-5	H	2-NO_2	H	27	161–162	$C_{11}H_9BF_4N_2O_3$
33395-27-6	H	2-CF_3	H	44	169–170	$C_{12}H_9BF_7NO$
55165-47-4	H	2-CN	H	19	160.5–162	$C_{12}H_9BF_4N_2O$
58408-63-2	H[a,b]	2-NO_2	4-NO_2	86	182–184	$C_{11}H_8BF_4N_3O_5$
58408-65-4	H[b]	3-NO_2	5-NO_2	56	190–192	$C_{11}H_8BF_4N_3O_5$
58408-67-6	4-CH_3	4-NO_2	H	22	136–137	$C_{12}H_{11}BF_4N_2O_3$
58408-69-8	4-CH_3	4-CN	H	37	177–179	$C_{13}H_{11}BF_4N_2O$
58408-71-2	4-CH_3	2-NO_2	H	34	147–148	$C_{12}H_{11}BF_4N_2O_3$
58408-73-4	4-C_6H_5	4-CN	H	75	193–194	$C_{18}H_{13}BF_4N_2O$
58408-75-6	4-C_6H_5	4-NO_2	H	87	188–189	$C_{17}H_{13}BF_4N_2O_3$
58408-77-8	4-OCH_3	4-NO_2	H	61	151.5–153	$C_{12}H_{11}BF_4N_2O_4$
58408-79-0	4-OC_6H_5	4-NO_2	H	59	209–211	$C_{17}H_{13}BF_4N_2O_4$
58408-81-4	4-Cl[d]	4-NO_2	H	64	170	$C_{11}H_8BClF_4N_2O_3$
58408-83-6	4-CN[e]	4-CN	H	5	166–167	$C_{13}H_8BF_4N_3O$
58408-85-8	2-OCH_3	4-NO_2	H	87	168.5–170	$C_{12}H_{11}BF_4N_2O_4$
58408-87-0	4-OCH_3[f]	2-NO_2	4-NO_2	71	125–127	$C_{12}H_{10}BF_4N_3O_6$
58408-89-2	4-CN[b]	2-NO_2	4-NO_2	84	208–209	$C_{12}H_7BF_4N_4O_5$
58408-91-6	4-[b]	2-NO_2	4-NO_2	77	217–218.5 dec	$C_{22}H_{14}B_2F_8N_6O_{10}$

[a] Isolated as the perchlorate, a rather explosive compound. [b] Sulfolane was used as the reaction solvent, while acetonitrile was the solvent in other cases. [c] Also from the 4-chloro derivative by repeated recrystallization from methanol. [d] 4-Chloro-2-*p*-nitroanilinopyridine (7%) was also isolated. [e] 4-Cyano-2-*p*-cyanoanilinopyridine (29%) was also isolated (see Experimental Section). [f] Could not be purified because of its slow rearrangement to 6 on recrystallization. [g] Satisfactory analytical data (±0.3% for C, H) were reported for all compounds except the 4-methoxyphenyl derivative. Ed.

Table II. 2-Anilinopyridines[a]

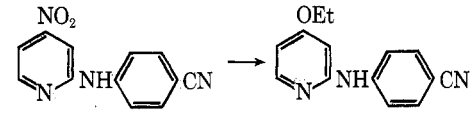


Registry no.	R	X	% yield	Mp, °C	Molecular formula
58408-92-7	NO_2	CN	29	222–224	$C_{12}H_8N_4O_2$
58408-93-8	CN	CN	29	238–240	$C_{13}H_8N_4$
58408-94-9	CN	NO_2	12	243–244	$C_{12}H_8N_4O_2$
58408-95-0	CN	CF_3	44	184–186	$C_{13}H_8N_3F_3$
58408-96-1	NO_2	CF_3	27	162–163.5	$C_{12}H_8F_3N_3O_2$
58408-97-2	NO_2	NO_2	20	264–267	$C_{11}H_8N_4O_4$
58408-98-3	Cl	NO_2	9	201–204	$C_{11}H_8N_3O_2Cl$
58408-99-4	Cl	CN	15	206–208	$C_{12}H_8N_3Cl$

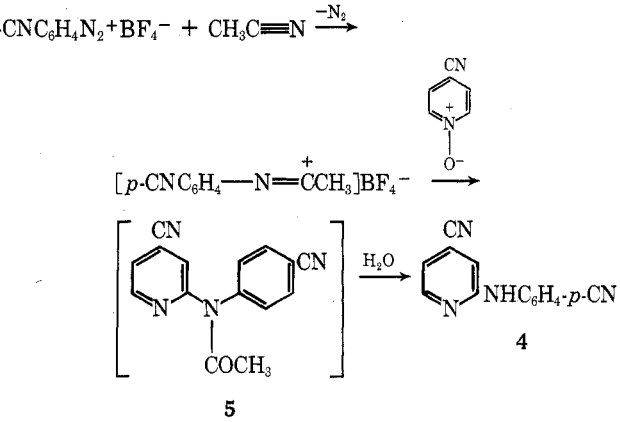
[a] Satisfactory analyses (±0.3% for C, H) were reported for all compounds in table. Ed.

scopic methods and by microanalysis. In particular, the NMR spectra indicated that arylation had occurred at oxygen. For example, 1-(4-nitrohenoxy)pyridinium tetrafluoroborate (**3**, $R^1 = R^3 = H$; $R^2 = p$-NO_2) exhibited bands at δ 9.65 (2 H, d, $J_{2,3} = J_{5,6} = 6$ Hz, H-2,6), 9.00 (1 H, t, $J_{3,4} = J_{4,5} = 7$ Hz, H_4), 8.56 (2 H, d of d, H-3,5), 8.39 (2 H, d, $J_o = 9$ Hz, phenyl meta hydrogens), and 7.50 (2 H, d, $J_o = 9$ Hz, phenyl ortho hydrogens).

The most notable failure of this arylation occurred with 4-nitro- and 2-methylpyridine 1-oxides. The *N*-oxide function in 4-nitropyridine 1-oxide is, presumably, not basic enough to react with the diazonium ion (what may be an impure form of the desired salt was isolated). Some 2-(*p*-nitroanilino)-4-nitropyridine was formed. Arylation of 4-nitro- and 4-cyanopyridine 1-oxides in acetonitrile with other diazonium salts gave only the corresponding 2-anilinopyridines and these results are collected in Table II. The nitro group in 2-(*p*-cyanoanilino)-4-nitropyridine underwent the expected displacement with ethoxide ion. An intermediate situation was observed with the somewhat more basic 4-cyanopyridine 1-oxide in acetonitrile solution, using *p*-cyanobenzenediazonium tetrafluoroborate as the arylating agent. A low (5%) yield of



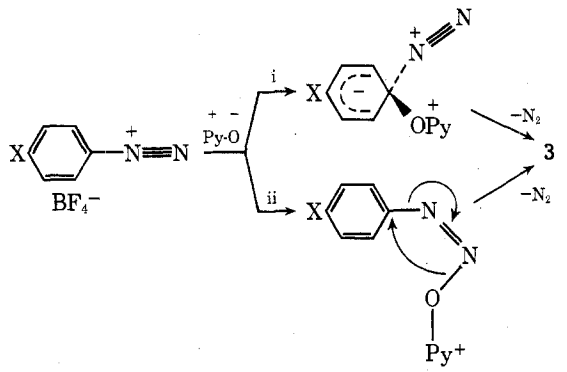
the desired salt (**3**, R^1 = 4-CN; R^2 = 4-CN; R^3 = H) was obtained, together with a 29% yield of 2-(*p*-cyanoanilino)-4-cyanopyridine (**4**). The latter was presumably formed by the hydrolysis of the initially formed acetamide (**5**).[6]



A similar situation was found with 4-chloropyridine 1-oxide. Reaction with *p*-nitrobenzenediazonium tetrafluoroborate in acetonitrile gave a mixture of **3** (R^1 = 4-Cl; R^2 = 4-NO_2; R^3 = H) and 4-chloro-2-*p*-nitroanilinopyridine (7%). Attempted purification of the pyridinium salt from hot methanol led to a mixture of the 4-chloro- and 4-methoxypyridinium derivatives. More prolonged heating with methanol led to complete nucleophilic displacement of the chlorine atom and the formation of **3** (R^1 = 4-OMe; R^2 = 4-NO_2; R^3 = H). When *p*-cyanobenzenediazonium tetrafluoroborate was used, 4-chloro-2-*p*-cyanoanilinopyridine could be obtained pure following methanolic workup, together with a mixture of the corresponding 4-chloro- and 4-methoxypyridinium salts. No attempt was made to separate these.

4,4′-Bipyridyl 1,1′-dioxide was not arylated by *p*-nitro-

Scheme I

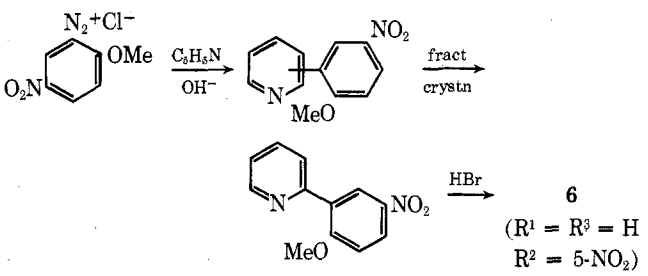


benzenediazonium tetrafluoroborate, probably because it was not basic enough, but was arylated in good yield (Table I) by using the more electrophilic 2,4-dinitrobenzenediazonium tetrafluoroborate in sulfolane solution (to avoid nitrilium ion formation in acetonitrile with the more electrophilic cation); other examples are given in Table I.

2-Picoline 1-oxide was not O-arylated and it is hard to imagine that the *N*-oxide function would be sufficiently sterically hindered by the 2 substituent to prevent attack, but no alternate explanation can be advanced at this time (vide infra).

The O-arylations occur at temperatures (usually room temperature) well below those at which unimolecular decomposition of the diazonium salts occur. Indeed, in the absence of *N*-oxide, the diazonium salts are stable in solution under these conditions. This suggests either that an SNAr displacement (path i) (or a direct SN2 process) is taking place[7] or that a diazo oxide is first formed which collapses to **3** with loss of nitrogen (path ii) (Scheme I).

Pyridine 1-oxides and pyridinium salts undergo base-catalyzed proton abstraction from the 2 position of the pyridine ring.[8] Treatment of the salts **3** in hot acetonitrile solution either with potassium phenoxide or with triethylamine gave the corresponding 2-(2-hydroxyaryl)pyridine (**6**). For example, **3** ($R^1 = R^3 = H$; R^2 = 4-NO_2) gave **6** ($R^1 = R^3 = H$, 5-NO_2)

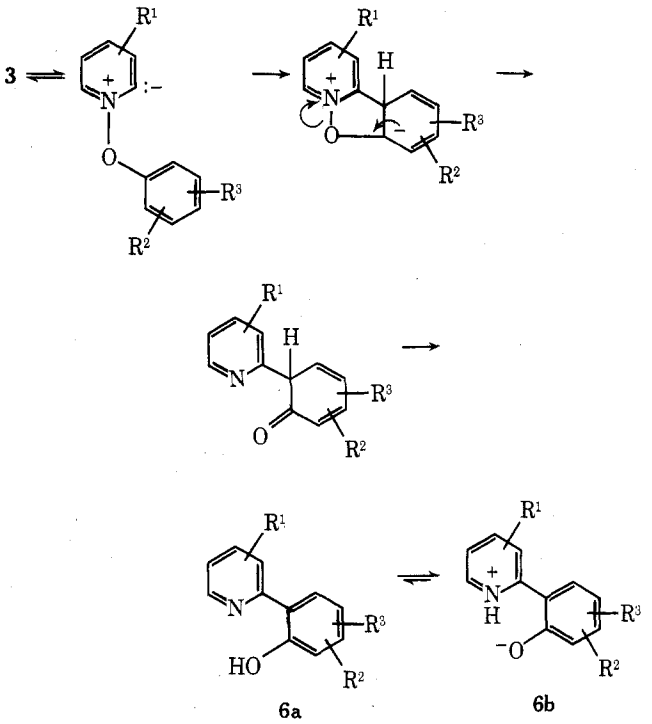


whose structure was established by its spectral properties and by its synthesis by an unambiguous route. Thus, Gomberg–Hey arylation of pyridine with the diazonium salt from 2-amino-4-nitroanisole gave a mixture of the three possible arylation products which were fractionally crystallized to give 2-(2-methoxy-5-nitrophenyl)pyridine.[9] This was demethylated with hydrobromic acid to give authentic 2-(2-hydroxy-5-nitrophenyl)pyridine (**6**), identical with the compound obtained above. The spectral properties of the other rearrangement products **6** permitted unambiguous assignment of their structure. A possible mechanism for the base-catalyzed rearrangement is given in Scheme II.

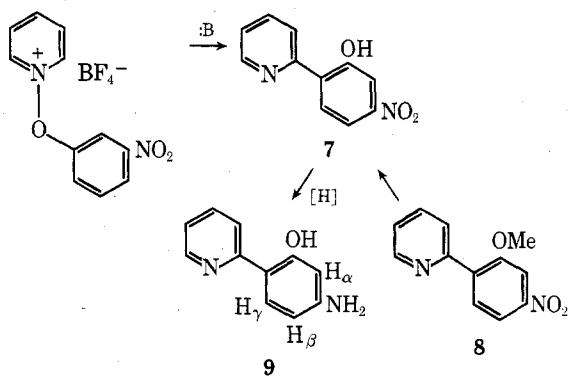
The phenols **6** do not exhibit an O–H stretching band in the infrared (or only a very weak broad band) either in the solid state or in solution, but do show a broad $-^+NH=$ band at ca. 2600 cm^{-1}, indicating that they exist mainly in the zwitterionic form **6b**.

The base-catalyzed rearrangement of 1-(3-nitrophenoxy)pyridinium tetrafluoroborate (**3**, $R^1 = R^3 = H$; R^2 = 3-NO_2) can, in principle, lead to two isomeric 2-*o*-hydroxyphenylpyridines via attack either ortho or para to the nitro group. In practice, only one product was obtained, namely **7** resulting from attack at the sterically less hindered para position. The NMR spectrum of the product could not be used to distinguish between the two possibilities as the protons on the nitrophenyl ring appeared as a broad singlet, probably owing to the compensating effects on the chemical shifts by the nitro and hydroxyl groups meta to each other. The rearranged product was reduced to the corresponding primary amine (**9**). This exhibited a narrow one-proton doublet ($J_{\alpha,\beta}$ = 2 Hz) at δ 6.57 (H_α), a 1 H quartet ($J_{\beta,\gamma}$ = 9.0, $J_{\alpha,\beta}$ = 2 Hz) at δ 6.66 (H_β), and a 1 H doublet ($J_{\beta,\gamma}$ = 9.0 Hz) at δ 8.07 (H_γ), clearly eliminating the alternate possibility which would have vicinal protons. This proposed structure was confirmed by the synthesis of authentic **7** by demethylation of 2-(2-methoxy-4-nitrophenyl)pyridine (**8**).

Scheme II



6a **6b**



7 **8** **9**

The yield of rearranged product from 4-methyl-1-(4-nitrophenoxy)pyridinium tetrafluoroborate (**3**, R^1 = 4-Me; R^2 = 4-NO_2; $R^3 = H$) was exceptionally low (9.6%). It is possible that base-catalyzed proton abstraction occurs from the methyl side chain which could lead to elimination of *p*-nitrophenol, as is observed. The pyridine-containing fragment was not isolated. The results of the base-catalyzed rearrangements are summarized in Table III. The phenols could be brominated readily, e.g., 2-(5-cyano-2-hydroxyphenyl)pyridine gave 2-

Table III. 2-(2-Hydroxyaryl)pyridines (6)

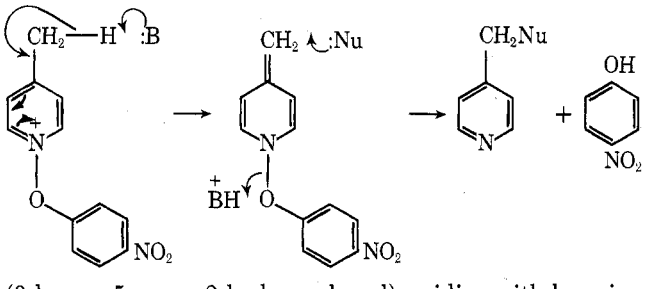
Registry no.	R^1	R^2	R^3	% yield	Mp, °C	Molecular formula
33400-82-7	H	5-NO_2	H	65	216–217	$C_{11}H_8N_2O_3$
33400-78-1	H	3-NO_2	H	66	167–168	$C_{11}H_8N_2O_3$
58409-00-0	H	4-NO_2[a]	H	33	186.5–187.5	$C_{11}H_8N_2O_3$
33400-81-6	H	5-CN	H	69	198–199	$C_{12}H_8N_2O$
33400-80-5	H	5-CF_3	H	40	92–93	$C_{12}H_8F_3NO$
33400-79-2	H	3-CF_3	H	49	87–88	$C_{12}H_8F_3NO$
55165-48-5	H	3-CN	H	28	180–182	$C_{12}H_8N_2O$
58409-01-1	4-C_6H_5	5-CN	H	53	164.5–165.5	$C_{18}H_{12}N_2O$
58409-02-2	4-CH_3[b]	5-NO_2	H	10	204–205.5	$C_{12}H_{10}N_2O_3$
58409-03-3	4-OCH_3	5-NO_2	H	68	191.5–192.5	$C_{12}H_{10}N_2O_4$
58409-04-4	4-OC_6H_5	5-NO_2	H	81	147–148	$C_{17}H_{12}N_2O_4$
58409-05-5	4-OCH_3	3-NO_2	5-NO_2	69	289–291 dec	$C_{12}H_9N_3O_6$

[a] From 3 (R^2 = 3-NO_2). [b] *p*-Nitrophenol was the major product (49.7%). [c] Satisfactory analyses (±0.3% for C, H) were reported for all compounds in table. Ed.

Table IV. 1-[(*N*-Arylacetimidoyl)amino]pyridinium Tetrafluoroborates (14)[a]

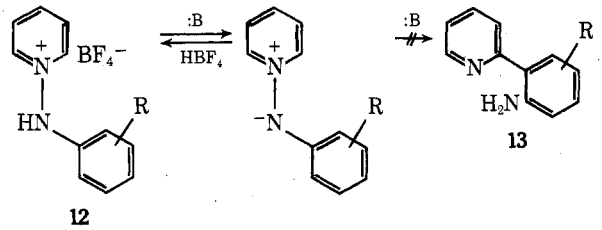
Registry no.	R	X	% yield	Mp, °C	Molecular formula
58409-07-7	H	4-CN	54	282–283	$C_{14}H_{13}BF_4N_4$
58409-09-9	H	4-NO_2	40	268–270	$C_{13}H_{13}BF_4N_4O_2$
58409-11-3	H	4-CF_3	58	253–255	$C_{14}H_{13}BF_7N_3$
58409-13-5	H	3-Cl	45	190–192	$C_{13}H_{13}BClF_4N_3$
58409-15-7	H	H	52	202–204	$C_{13}H_{14}BF_4N_3$
58409-17-9	H	3-NO_2	40.5	155–156	$C_{13}H_{13}BF_4N_4O_2$
58409-19-1	H	4-Cl	30	217–218.5	$C_{13}H_{13}BClF_4N_3$
58409-21-5	2-CH_3	4-CN	38	210–211	$C_{15}H_{15}BF_4N_4$
58409-23-7	2-CH_3	H	38	239–240	$C_{14}H_{16}BF_4N_3$
58409-25-9	3,5-Me_2	4-NO_2	77	262–266	$C_{15}H_{17}BF_4O_2$
58409-27-1	3,5-Me_2	3-Cl	41	254–255	$C_{15}H_{17}BClF_4N_3$
58409-29-3	2,6-Me_2	3-Cl	49	228–229	$C_{15}H_{17}BClF_4N_3$

[a] Satisfactory analytical values (±0.3% for C, H) were reported for all compounds. Ed.



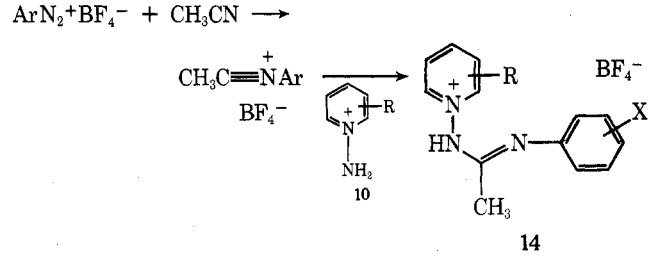
(3-bromo-5-cyano-2-hydroxyphenyl)pyridine with bromine in acetic acid.

The above reactions thus provide convenient routes to both *N*-aryloxypyridinium salts and, via a new molecular rearrangement, to 2-*o*-hydroxyphenylpyridine derivatives. It was of considerable interest, therefore, to see if these reactions could be extended to the N-arylation of either 1-aminopyridinium salts [$RC_5H_4{}^+NNH_2$] BF_4^- (**10**) or of the corresponding 1-imino ylide $RC_5H_4N^+N^-H$ (**11**) to give *N*-arylaminopyridinium salts (**12**). It was also of interest to determine whether these, if formed, would undergo base-catalyzed rearrangement to the corresponding 2-*o*-aminophenylpyridines (**13**) which are difficult to prepare by conventional routes. In contrast to the *N*-aryloxypyridinium salts, the pyridine *N*-phenylimines are known compounds[10,11] and, indeed, N-arylation of **10** has been achieved using an activated aryl halide.[12]



12 13

The reaction of 1-aminopyridinium tetrafluoroborates (**10**) with aryldiazonium tetrafluoroborates (bearing electron-withdrawing groups in the aryl ring) in acetonitrile solution did not yield any of the desired *N*-aryliminopyridinium salts (**12**). The only products isolated were the 1-[(*N*-arylacetimidoyl)amino]pyridinium tetrafluoroborates (**14**) (Table IV).



14

These are probably formed via the nitrilium ion resulting from the N-arylation of solvent acetonitrile followed by attack at the *N*-amino group. It is interesting that in these cases, as opposed to the *N*-oxide situation, reaction does occur at nitrogen in the 2-picoline derivative. There is, therefore, no apparent undue steric hindrance by a 2-methyl group to attack by a carbenium ion at the *N*-imino nitrogen atom, which would suggest that in the arylations at oxygen, path i (Scheme I), may be operating in the formation of **3**, since much more steric hindrance would be anticipated in this pathway than in path ii.

When the reactions were carried out in propionitrile or malononitrile the corresponding 1-[(*N*-arylimidoyl)amino]pyridinium tetrafluoroborates (**15**) were usually obtained, though the yields were rather poor (Table V). Butyronitrile appeared to be an exception. When 1-aminopyridinium tetrafluoroborate in butyronitrile was treated either with *p*-nitro- or *p*-trifluoromethylbenzenediazonium tetrafluoroborate no **15** was formed. Instead, the same product was obtained in each

Table V. Products (15) of Reaction of 1-Aminopyridinium Tetrafluoroborates with Aryldiazonium Tetrafluoroborates in Various Nitriles[d]

Solvent	Registry no.	R^1	X	R^2	% yield	Mp, °C	Molecular formula
Propionitrile	58409-31-7	H	4-CNC_6H_5	CH_3CH_2	23	206–207	$C_{15}H_{15}BF_4N_4$
Propionitrile	58409-33-9	H	4-$NO_2C_6H_5$	CH_3CH_2	31.5	200–201	$C_{14}H_{15}BF_4N_4O_2$
Propionitrile	58425-88-0	3,5-Me_2	4-$NO_2C_6H_5$	CH_3CH_2	20	187–188	$C_{16}H_{19}BF_4N_4O_2$
Malononitrile	58425-90-4	H[a]	4-$NO_2C_6H_5$	N≡C–CH_2	57	187–188	$C_{14}H_{12}BF_4N_5O_2$
Butyronitrile	58548-79-1	H[b]	H	$CH_3CH_2CH_2$	28	159–160	$C_9H_{14}BF_4N_3$
Benzonitrile	58425-92-6	H[c]	H	C_6H_5	9	178–179	$C_{12}H_{12}BF_4N_3$

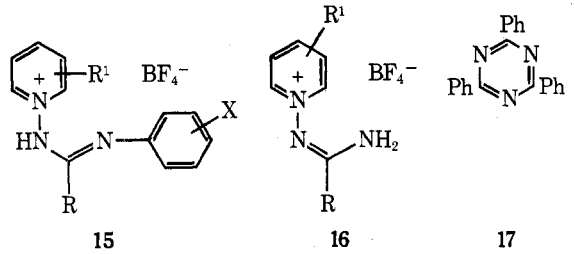
[a] ω-Cyano-*p*-nitroacetanilide (9%) was also isolated. [b] From *p*-nitro- or *p*-trifluoromethylbenzenediazonium tetrafluoroborate. A small amount of 2,4,6-triphenyl-*s*-triazine was also isolated. [c] From *p*-nitrobenzenediazonium tetrafluoroborate. [d] Satisfactory analytical values were reported for all compounds in Table. Ed.

Table VI. 1-[(*N*-Arylacetimidoyl)imino]pyridinium Ylides (19)[a]

Registry no.	R	X	% yield	Mp, °C	Molecular formula
58425-93-7	H	4-NO_2	71.5	157–159	$C_{13}H_{12}N_4O_2$
58425-94-8	H	4-CN	67	159–160	$C_{14}H_{12}N_4$
58425-95-9	3,5-Me_2	4-NO_2	72	136–137	$C_{15}H_{16}N_4O_2$

[a] Satisfactory analytical values (±0.3%) were reported for all compounds in Table . Ed.

case, whose spectral properties and analysis showed it to be the salt **16** (R = *n*-Pr; R^1 = H). In the reaction with the *p*-nitrodiazonium salt some *p*-nitrobutyranilide was also obtained. No reaction occurred between 1-aminopyridinium tetrafluoroborates and butyronitrile in the absence of diazonium salt. A similar product (12.5%) was obtained from 1-aminopyridinium tetrafluoroborate and *p*-trifluoromethylbenzenediazonium tetrafluoroborate (but *not* from the *p*-nitrodiazonium salt) in boiling propionitrile. Unfortunately, it could not be obtained analytically pure. A low (9%) yield of **16** (R = Ph; R^1 = H) was obtained from the amine, *p*-nitrobenzenediazonium tetrafluoroborate, and benzonitrile, together with small amounts of 2,4,6-triphenyl-*s*-triazine (**17**).

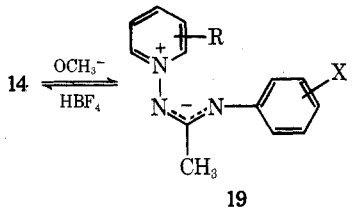


15 **16** **17**

The latter was also isolated when *p*-cyano- and *p*-trifluoromethylbenzenediazonium tetrafluoroborate were used. These reactions may be rationalized if it is assumed that decomposition of the diazonium tetrafluoroborates in the higher boiling solvents gives some boron trifluoride (via the Schiemann reaction) which now reacts with the nitriles to give a nitrilium salt that attacks the *N*-aminopyridinium salt. Acid-catalyzed trimerization of benzonitrile to **17** is known.[13a]

$$R{-}C{\equiv}N + BF_3 \rightleftharpoons R{-}C{=}N{-}BF_3 \xrightarrow{H_2NR^1} \mathbf{16}$$

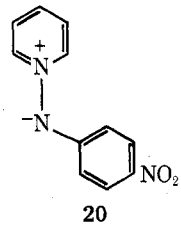
Treatment of the salts **14** with base such as sodium methoxide gave the ylide **19** (Table VI) which was converted back to **14** on acidification. The conjugate acid of **19** was also formed on treatment of **19** with aqueous silver nitrate, or dimethyl sulfate in benzene, or acetyl chloride in benzene.



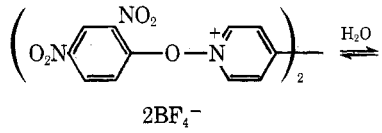
19

The reaction of diazonium tetrafluoroborates with *N*-aminopyridinium tetrafluoroborate was attempted in dioxane to avoid the participation of nitrile solvents. None of the desired product could be obtained. In order to make the substrate more nucleophilic so that it could compete more effectively with acetonitrile solvent for the electrophilic reagent the *N*-iminopyridinium ylide (from the *N*-amino compound and sodium carbonate or sodium hydride) in acetonitrile was treated with diazonium tetrafluoroborate. The only product formed was the corresponding aryl azide (25–52%) and starting aminopyridinium salt was recovered (75–15%). Similar behavior has been reported[13b] for reactions in aqueous medium.

Since an *N*-arylaminopyridinium salt could not be obtained in this way, a modification of Okamoto's method[12] was used to prepare pyridine-*N*-(4-nitrophenyl)imine (**20**). Pyridine 1-oxide is known to give the corresponding α anion with sodium hydride.[14] When **20** was heated with sodium hydride in acetonitrile the solution turned from red to black, but the black solid did not yield any of the desired amine (**13**, R =

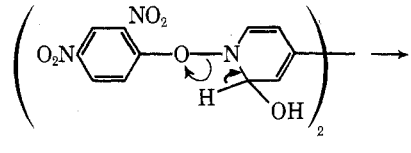


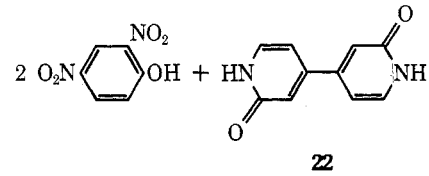
20



$2BF_4^-$

21





22

4-NO_2), only **20** being recovered (47%). Compound **20** was also recovered quantitatively on heating with lithium diethylamide. Thus, the base-catalyzed rearrangement of **20** to **13** has not been achieved yet.

1,1′-Di(2,4-dinitrophenoxy)-4,4′-dipyridylium ditetrafluoroborate (**21**) did not give the corresponding *o*-hydroxyarylpyridine with base. Heating in boiling water led to the elimination of 2,4-dinitrophenol and the formation of 4,4′-*di*(2-pyridone) (**22**). Treatment of **21** with triethylamine in nitromethane gave only 2,4-dinitrophenol (31.5%) and unidentified tarry material.

Experimental Section

Melting points are uncorrected. NMR spectra were recorded on a Varian Associates Model HA-100 or Perkin-Elmer Model R-20B spectrometer. Mass spectra were determined on a C. E. C. Model 21-104 spectrometer at an ionizing voltage of 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 257 instrument.

Reagents and Solvents. Acetonitrile was dried and distilled over calcium hydride. Sulfolane was distilled under vacuum just prior to use. Pyridine 1-oxides were purified by vacuum distillation or recrystallization and kept in a desiccator. Aryldiazonium tetrafluoroborates were prepared according to the standard procedure.[15]

O-Arylations. The general procedures used for the O-arylations using acetonitrile or sulfolane as the solvent are illustrated using specific examples. The products (**3**) so obtained are listed in Table I, as are the analytical data for new compounds.

Acetonitrile Solvent. 1-(4-Cyanophenoxy)pyridinium Tetrafluoroborate. *p*-Cyanobenzenediazonium tetrafluoroborate (2.17 g, 0.01 mol) was added portionwise to an ice-cold solution of pyridine 1-oxide (1.14 g, 0.012 mol) in dry acetonitrile (30 ml) with vigorous stirring. Rapid gas evolution accompanied the slightly exothermic reaction. The mixture turned dark red on stirring for 24 h at room temperature (or on heating under reflux for 4 h). The solvent was evaporated and the residue was recrystallized from methanol to give the salt (1.98 g, 70%): mp 214–215 °C; ir (KBr) 2240 (C≡N), 1130–1030 cm^{-1} (BF_4^-); NMR (Me_2SO-d_6) δ 9.96 (d, 2 H, $J_{\alpha\beta}$ = 7 Hz, H_α), 9.13 (t, 1 H, $J_{\beta\gamma}$ = 7 Hz, H_γ), 8.71 (t, 2 H, $J_{\alpha\beta} = J_{\beta\gamma}$ = 7 Hz, H_β), 8.32 (d, 2 H, $J_{o,m}$ = 9 Hz, H_o), and 7.67 (d, 2 H, $J_{o,m}$ = 9 Hz, H_m); mass spectrum *m/e* 244 ($M\cdot^+$ − 2HF, 12), 196 ($M\cdot^+$ − HBF_4, 9), 119 ($CNC_6H_4OH\cdot^+$, 57), 79 ($C_5H_5N\cdot^+$, 100), 52 (65), 49 (54).

Sulfolane Solvent. 1,1′-Di(2,4-dinitrophenoxy)-4,4′-dipyridylium Ditetrafluoroborate (21). To a suspension of 4,4′-dipyridyl 1,1′-dioxide (1.88 g, 0.01 mol) in sulfolane (8 ml) at 40–45 °C was added 2,4-dinitrobenzenediazonium tetrafluoroborate (5.92 g, 0.021 mol) slowly with stirring over 30 min. Stirring at 40–45 °C was continued for a further 1 h while nitrogen was evolved. Trituration with benzene–ether (1:3 v/v, 30 ml) and then with warm methanol (15 ml) gave a yellow solid (6.80 g, 97.8%) which, on recrystallization from nitromethane–acetic acid (4:1 v/v), gave the salt (5.38 g, 77.8%): mp 217–218.5° dec; ir (KBr) 1535, 1335 (NO_2), 1100–1000 cm^{-1} (BF_4^-); NMR (CH_3NO_2) δ 9.51 (d, 4 H, $J_{\alpha,\beta}$ = 7 Hz, H_α), 9.10 (d, 2 H, J_{AB} = 2.5 Hz, H_A), 8.86 (d, 4 H, $J_{\alpha,\beta}$ = 7 Hz, H_β), 8.61 (dd, 2 H, J_{BC} = 9, J_{AB} = 2.5 Hz, H_B), and 7.39 (d, 2 H, J_{BC} = 9 Hz, H_C); mass spectrum *m/e* 183 ($C_6H_3N_2O_5^+$, 80), 156 ($C_{10}H_8N_2\cdot^+$, 100).

2-(*p*-Cyanoanilino)-4-nitropyridine. A solution of 4-nitropyridine 1-oxide (1.40 g) and *p*-cyanobenzenediazonium tetrafluoroborate (2.17 g) in acetonitrile (20 ml) was boiled under reflux for 1 h. The solvent was evaporated to dryness to give a tarry residue which solidified on standing overnight. The solid was dissolved in methanol (45 ml), the insoluble tars were filtered, and the filtrate was kept in the refrigerator when **2-(*p*-cyanoanilino)-4-nitropyridine** (0.445 g, 29%) separated: mp 222–224 °C (from methanol); ir (KBr) 3360, 2220, 1520, 1390 cm^{-1}; NMR (Me_2SO-d_6) δ 9.53 (s, 1 H, NH, exchangeable), 7.93 (d, 1 H, $J_{5,6}$ = 6 Hz, H_6), 7.30 (d, 2 H, $J_{o,m}$ = 9 Hz, H_o), 7.12 (d, 2 H, $J_{o,m}$ = 9 Hz, H_m), 7.01 (d, 1 H, $J_{3,5}$ = 2 Hz, H_5); mass spectrum *m/e* 240 ($M\cdot^+$, 15.5), 239 ($M\cdot^+$ − H, 100), 238 ($M\cdot^+$ − 2H, 95.5), 208 ($M\cdot^+$ − NO − 2H, 35.5), 193, 192, 166, 139, and 101.

Other 2-anilinopyridines obtained similarly are listed in Table II.

2-(*p*-Cyanoanilino)-4-ethoxypyridine. 2-(*p*-Cyanoanilino)-4-nitropyridine (0.360 g) was added to sodium ethoxide solution [from sodium (0.25 g) and ethanol (10 ml)]. The purple solution was stirred and heated under reflux for 3 h, diluted with boiling ethanol (70 ml), and filtered. The filtrate was evaporated and the residue was chromatographed on a column of silica gel. Elution with benzene gave **2-(*p*-cyanoanilino)-4-ethoxypyridine** (0.054 g, 15.1%): mp 138–139 °C (methanol); ir (KBr) 3340, 2220 cm^{-1}; mass spectrum *m/e* 239 ($M\cdot^+$, 72), 238 ($M\cdot^+$ − H, 69), 210 ($M\cdot^+$ − C_2H_5, 100).

Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.26; H, 5.49. Found: C, 70.17; H, 5.48.

Reaction of 4-Chloropyridine 1-Oxide with *p*-Nitrobenzenediazonium Tetrafluoroborate. A. 4-Chloro-2-(*p*-nitroanilino)pyridine. A solution of 4-chloropyridine 1-oxide (1.30 g) and *p*-nitrobenzenediazonium tetrafluoroborate (2.37 g) in acetonitrile (40 ml) was stirred at 0 °C for 1 h, then at room temperature overnight. The solvent was evaporated and the residue was crystallized from methanol (10 ml) to give an orange-yellow solid (2.076 g), mp 136–139 °C. Further recrystallization from methanol (20 ml) (charcoal) gave colorless crystals (1.226 g), mp 160–162 °C, which, after one more recrystallization from methanol, gave the analytically pure **4-methoxy-1-(4-nitrophenoxy)pyridinium tetrafluoroborate:** mp 152–153 °C; ir (KBr) 1510, 1345 (NO_2), 1110–1030 cm^{-1} (BF_4^-); NMR (CF_3CO_2H) δ 8.92 (d, 2 H, $J_{\alpha,\beta}$ = 7.5 Hz, H_α), 8.50 (d, 2 H, $J_{o,m}$ = 9.5 Hz, H_o), 7.77 (d, 2 H, $J_{\alpha,\beta}$ = 7.5 Hz, H_β), 7.24 (d, 2 H, $J_{o,m}$ = 9.5 Hz, H_m), and 4.37 (s, 3 H, OCH_3); mass spectrum *m/e* 294 ($M\cdot^+$ − 2HF, 50), 264 ($M\cdot^+$ − 2HF − NO, 40), 246 ($M\cdot^+$ − HBF_4, 100), 139 ($HOC_6H_4NO_2$, 45).

The mother liquor from the first recrystallization was evaporated and the residue was chromatographed on a column of silica gel (23 × 2.4 cm). Elution with $CHCl_3$ gave **4-chloro-2-(*p*-nitroanilino)pyridine** (0.175 g, 7%) (MeOH): mp 201–204 °C; ir (KBr) 3330, 1565, 1300 cm^{-1}; mass spectrum *m/e* 250 [$M\cdot^+$ (^{37}Cl) − 1, 7], 249 [$M\cdot^+$ (^{35}Cl), 10], 248 ($M\cdot^+$ − H, 22), 204 (55), 203 (10), 202 (14), 43 (100).

4-Chloro-2-(*p*-cyanoanilino)pyridine was obtained (15%) similarly from the reaction of *p*-cyanobenzenediazonium tetrafluoroborate and 4-chloropyridine 1-oxide in acetonitrile.

B. 4-Chloro-1-(4-nitrophenoxy)pyridinium Tetrafluoroborate. A mixture of 4-chloropyridine 1-oxide (1.30 g) and *p*-nitrobenzenediazonium tetrafluoroborate (2.37 g) in acetonitrile (30 ml) was stirred at room temperature overnight and then heated under reflux for 6 h. The solvent was evaporated in vacuo and the residue was triturated with benzene (20 ml) to give the 4-chloro salt (1.89 g, 56.2%) (from acetonitrile–ether, 1:3 v/v): mp 170 °C; ir (KBr) 1535, 1355, 1100–1030 cm^{-1}; NMR (CF_3CO_2H) δ 9.2 (d, 2 H, $J_{\alpha,\beta}$ = 6.5 Hz, H_α), 8.45 (m, 4 H, H_β and H_o), 7.34 (d, 2 H, $J_{o,m}$ = 9 Hz, H_m); mass spectrum *m/e* 300 [$M\cdot^+$ (^{37}Cl) − 2HF, 15], 298 [$M\cdot^+$ (^{35}Cl) − 2HF, 45], 270 (13), 268 (39), 252 (25), 250 (75), 206 (15), 204 (45), 139 ($HOC_6H_4NO_2\cdot^+$, 100). Recrystallization from methanol gave 4-methoxy-1-(4-nitrophenoxy)pyridinium tetrafluoroborate, mp 151.5–153 °C, identical with the sample obtained above.

Base-Catalyzed Rearrangement of Aryloxypyridinium Salts. The general procedure used will be illustrated by means of two examples. The products formed and analytical data for new compounds are given in Table III.

2-(2-Hydroxy-5-nitrophenyl)pyridine. A solution of 1-(4-nitrophenoxy)pyridinium tetrafluoroborate (1.52 g, 0.005 mol) and potassium phenoxide (0.79 g, 0.006 mol) in acetonitrile (20 ml) was heated under reflux for 1 h. The solvent was evaporated and the residue was treated with 2 *N* HCL (20 ml). Extraction with ether (3 × 30 ml) and evaporation of the dried ($MgSO_4$) extract gave the phenol (0.703 g, 65%): mp 216–217 °C (ethanol); ir (KBr) 2600 (–N^+H=), 1480, 1330 cm^{-1} (NO_2); λ_{max} (CH_3CN) 248, 287, 315 nm; NMR (CF_3CO_2H) δ 8.93–8.67 (m, 5 H), 8.00 (t, 1 H, *J* = 7 Hz), 7.37 (d, 1 H, *J* = 10 Hz); mass spectrum *m/e* 216 ($M\cdot^+$, 100), 200 ($M\cdot^+$ − O), 186 ($M\cdot^+$ − NO), 170 ($M\cdot^+$ − NO_2), 142 ($M\cdot^+$ − NO_2 − CO).

2-(2-Hydroxy-5-nitrophenyl)-4-methylpyridine. Triethylamine (0.46 g, 0.0045 mol) was added to a solution of 4-methyl-1-(4-nitrophenoxy)pyridinium tetrafluoroborate (0.954 g, 0.003 mol) in acetonitrile (20 ml) and the solution was heated under reflux for 1 h. The solvent was evaporated, the residue was extracted with hot ether (4 × 40 ml), the ether extract was evaporated, and the residue was chromatographed on a column of silica gel. Elution with benzene (300 ml) gave *p*-nitrophenol (0.207 g, 49.7%), mp 113–114 °C. Elution with benzene–chloroform (80:20 v/v, 400 ml) gave **2-(2-hydroxy-5-nitrophenyl)-4-methylpyridine** (66 mg, 9.6%): mp 204–205.5 °C (EtOH); ir (KBr) 2600 cm^{-1}; NMR ($CDCl_3$ + 3 drops of CF_3CO_2H) δ 8.9–8.6 (m, 2 H, H_α and H_6), 8.5–8.2 (m, 2 H, H_β and H_4), 7.85 (dd, $J_{\alpha\beta}$ = 5.5, $J_{\beta\beta'}$ = 1.2 Hz, $H_{\beta'}$), 7.30 (d, 1 H, $J_{3,4}$ = 9 Hz, H_3), 2.62 (s, 3 H, CH_3); mass spectrum *m/e* 230 ($M\cdot^+$, 100), 214 (15), 200 (20), 184 (28).

Authentic 2-(2-Hydroxy-5-nitrophenyl)pyridine. 2-(2-Methoxy-5-nitrophenyl)pyridine[9] (0.83 g) was heated in hydrobromic acid (48%, 16 ml) for 7 h. The mixture was adjusted to pH 3 and extracted with ether to give the phenol (0.146 g, 13%): mp 213–214° (EtOH), identical in all respects with the sample obtained above.

2-(2-Hydroxy-4-nitrophenyl)pyridine (7). 2-(2-Methoxy-4-nitrophenyl)pyridine (0.41 g) [obtained in low (6%) yield from Gomberg–Hey arylation of pyridine with 2-methoxy-4-nitroben-

zenediazonium chloride followed by chromatography on silica gel and elution with chloroform] was heated with 48% HBr as above, and the mixture adjusted to pH 8 and extracted with chloroform to give 7 (0.33 g, 85%), mp 186–187 °C (MeOH), identical with the sample obtained by base-catalyzed rearrangement of 1-(3-nitrophenoxy)pyridinium tetrafluoroborate.

The nitro compound was reduced with sodium polysulfide[16] in methanol to give 2-(4-amino-2-hydroxyphenyl)pyridine (**9**, 16%): mp 107–108 °C (benzene); ir (KBr) 3450, 3360, 2500 cm^{-1}; NMR (Me_2SO-d_6) δ 8.84 (d, 1 H, $J_{5,6}$ = 5 Hz, H_6), 8.28 (t, 2 H, $J_{3,4} = J_{4,5}$ = 5 Hz, H_3, H_4), 8.07 (d, 1 H, $J_{\beta\gamma}$ = 9 Hz, H_γ), 7.58 (dt, 1 H, $J_{5,6} = J_{4,5}$ = 5, $J_{3,5}$ = 2 Hz, H_5), 6.66 (dd, $J_{\beta\gamma}$ = 9, $J_{\alpha\beta}$ = 2 Hz, H_β), 6.57 (d, 1 H, $J_{\alpha\beta}$ = 2 Hz, H_α), 5.99 (s, 2 H, exchangeable with D_2O, NH_2); mass spectrum *m/e* 186 ($M^{\cdot+}$, 100), 185 (40.5), 79 (26.5).

Hydrolysis of 1,1'-Di(2,4-dinitrophenoxy)-4,4'-dipyridylium Ditetrafluoroborate (21). A. A suspension of the salt (1.74 g) in water (40 ml) was boiled under reflux for 15 min and then concentrated down to 10 ml. A yellow precipitate separated on cooling and was extracted with hot chloroform (50 ml). Evaporation of the extract gave 2,4-dinitrophenol (0.68 g, 74%): mp 111 °C, identical with an authentic sample. The chloroform-insoluble portion was recrystallized from water to give **4,4'-di(2-pyridone) (22,** 0.34 g, 72%): mp >300 °C; ir (KBr) 3250–2600 (bonded NH), 1700–1600 cm^{-1} (bonded C=O); NMR (CF_3CO_2H) δ 8.33 (d, 2 H, $J_{5,6}$ = 6 Hz, H_6), 7.6 (m, 6 H, H_3, H_5, and NH); mass spectrum *m/e* 188 ($M^{\cdot+}$, 100), 187 (30), 160 (10), 159 (16), 132 ($M^{\cdot+}$ – 2CO, 22), 104 (20).

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.83; H, 4.26; N, 14.89. Found: C, 63.64; H, 4.30; N, 14.86.

B. The salt (3.78 g) and triethylamine (0.61 g) in nitromethane (150 ml) were heated under reflux for 2 h. The only product isolated from the oil obtained was 2,4-dinitrophenol (0.58 g, 31.5%), mp 111–112 °C.

2-(3-Bromo-5-cyano-2-hydroxyphenyl)pyridine. Bromine (0.75 g) in acetic acid (6 ml) was added at room temperature with stirring to 2-(5-cyano-2-hydroxyphenyl)pyridine (0.39 g) in acetic acid (6 ml). The stirred solution was heated at 100 °C for 3 h, the solvent was evaporated, and the residue was recrystallized from methanol to give the bromo compound (0.39 g, 72%): mp 175–178°; ir (KBr) 2220 cm^{-1}; NMR (CF_3CO_2H) δ 8.87 (dd, 1 H, $J_{5,6} = J_{4,6}$ = 2 Hz, H_6), 8.71 (dt, 1 H, $J_{4,6}$ = 2, $J_{4,5} = J_{3,4}$ = 8 Hz, H_4), 8.37 (d, 1 H, $J_{3,4}$ = 8 Hz, H_3), 8.16 (s, 2 H, H_o and H_p), 8.08 (dd, 1 H, $J_{4,5}$ = 8, $J_{5,6}$ = 6 Hz, H_5); mass spectrum *m/e* 276 (93), 274 (100).

Anal. Calcd for $C_{12}H_7BrN_2O$: C, 52.39; H, 2.57. Found: C, 52.42; H, 2.66.

A similar bromination of 2-(2-hydroxy-3-nitrophenyl)pyridine afforded **2-(5-bromo-2-hydroxy-3-nitrophenyl)pyridine** (17%), mp 163–164 °C (MeOH).

Anal. Calcd for $C_{11}H_7BrN_2O_3$: C, 44.76, H, 2.40. Found: C, 44.95; H, 2.45.

Reaction of 1-Aminopyridinium Tetrafluoroborates with Aryldiazonium Tetrafluoroborates in Nitrile Solvents. This will be illustrated by means of a few typical examples. The properties of compounds so prepared are given in Tables IV–VI.

1-[(*N*-*p*-Cyanophenylacetimidoyl)amino]pyridinium Tetrafluoroborate. A solution of 1-aminopyridinium tetrafluoroborate (0.91 g) and *p*-cyanobenzenediazonium tetrafluoroborate (1.09 g) in acetonitrile (25 ml) was stirred at room temperature for 6 h and then boiled under reflux for 1.5 h. The brown tarry residue left on evaporation of the solvent was recrystallized from methanol to give the acetimidoylamino salt (0.88 g, 54%): mp 282–283 °C; ir (KBr) 3360, 3240 (NH), 2220 (CN), 1620 (C=N), 1140–1000 cm^{-1} (BF_4^-); NMR (Me_2SO-d_6) δ 10.82 (s, 1 H, NH), 9.48 (d, 2 H, $J_{\alpha,\beta}$ = 6 Hz, H_α), 9.03 (t, 1 H, $J_{\beta,\gamma}$ = 7 Hz, H_γ), 8.68 (m, 2 H, H_β), 8.38 (t, 4 H, phenyl hydrogens), 2.73 (s, 3 H, CH_3); mass spectrum *m/e* 236 ($M^{\cdot+}$ – HBF_4, 24), 235 ($M^{\cdot+}$ – H – HBF_4, 100), 195 (9), 79 (77), 52 (62), 49 (95).

1-[(*N*-*p*-Nitrophenylcyanoacetimidoyl)amino]pyridinium Tetrafluoborate (15, R^2 = $CNCH_2$; X = 4-NO_2; R^1 = H). A solution of 1-aminopyridinium tetrafluoroborate (0.546 g) and *p*-nitrobenzenediazonium tetrafluoroborate (0.771 g) in malononitrile (5 g) was stirred for 6 h at 90 °C. The mixture was chromatographed on a column of silica gel (40 g). Elution with chloroform (1000 ml) gave malononitrile. Further elution with $CHCl_3$ gave *ω*-cyano-*p*-nitroacetanilide (55 mg, 9%): mp 221–222 °C (lit.[17] mp 198–202 °C); ir (KBr) 3290, 2270, 1710, 1620, 1560, 1330 cm^{-1}; mass spectrum *m/e* 206 ($M^{\cdot+}$ + 1, 13), 205 ($M^{\cdot+}$, 100), 165 ($M^{\cdot+}$ – CH_2CN, 25), 159 ($M^{\cdot+}$ – NO_2, 5), 138 ($NO_2C_6H_4NH_2^+$, 55), 108 (71), 92 (41). Further elution with $CHCl_3$–MeOH gave **1-[(*N*-*p*-nitrophenylcyanoacetimidoyl)amino]pyridinium tetrafluoroborate** (0.636 g, 57%): mp 187–188 °C (MeOH); ir (KBr) 3320, 2260, 1635, 1620, 1550, 1335, 1100–1000 cm^{-1}; NMR (Me_2SO-d_6) δ 10.90 (s, 1 H, NH), 9.10 (d, 2 H, $J_{\alpha,\beta}$ = 6 Hz, H_α), 8.61 (t, 1 H, $J_{\beta,\gamma}$ = 6.8 Hz, H_γ), 8.33 (d, 2 H, $J_{o,m}$ = 9 Hz, H_o), 8.25 (dd, 2 H, $J_{\alpha,\beta}$ = 6 Hz, H_β), 7.98 (d, 2 H, $J_{o,m}$ = 9 Hz, H_m), 4.00 (s, 2 H, CH_2); mass spectrum *m/e* 280 ($M^{\cdot+}$ – H – HBF_4, 6), 279 (50), 249 (16), 79 (93), 52 (64), 49 (100).

1-(*N*-Butyrimidoylamino)iminopyridinium Tetrafluoroborate (16, R = $CH_3CH_2CH_2$; R^1 = H). A solution of 1-aminopyridinium tetrafluoroborate (0.91 g) and *p*-trifluoromethylbenzenediazonium tetrafluoroborate (1.35 g) in butyronitrile (20 ml) was stirred and boiled under reflux for 2 h. The solvent was evaporated in vacuo and the residue was chromatographed on a column of silica gel. Elution with chloroform–ethanol (10:1 v/v) gave **1-(*N*-butyrimidoylamino)iminopyridinium tetrafluoroborate** (0.34 g, 28%): mp 159–160 °C (MeOH); ir (KBr) 3440, 3370, 3280, 1660, 1640, 1170–1000 cm^{-1}, NMR (Me_2SO-d_6) δ 8.75 (dd, 2 H, $J_{\alpha,\beta}$ = 4/5= $J_{\alpha,\gamma}$ = 1.5 Hz, H_α), 8.45 (m, 1 H, H_γ), 8.08 (dd, 2 H, $J_{\alpha,\beta}$ = 4.5, $J_{\beta,\gamma}$ = 7.5 Hz, H_β), 7.3 (br s, 2 H, D_2O exchange, NH_2), 2.31 (t, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 1.58 (sextuplet, 2 H, J = 7.5 Hz, $CH_2CH_2CH_3$), 1.01 (t, 3 H, J = 7.5 Hz, CH_3); mass spectrum *m/e* 164 ($M^{\cdot+}$, 19), 133 ($M^{\cdot+}$ – CH_3 – NH_2, 25), 121 ($M^{\cdot+}$ – C_3H_7, 100), 79 (C_5H_5N, 68).

1-[(*N*-*p*-Cyanophenylacetimidoyl)imino]pyridinium Ylide (19, R = H; X = *p*-CN). 1-[(*N*-*p*-Cyanophenylacetimidoyl)amino]pyridinium tetrafluoroborate (1.30 g) and sodium methoxide (0.54 g) in acetonitrile (30 ml) were heated for 3 h. The solvent was evaporated to dryness and the residue was extracted with boiling benzene (600 ml). The extracts were evaporated to give the ylide (0.633 g, 67%): mp 159–160 °C (from ethyl acetate); ir (KBr) 2220 cm^{-1}; NMR (Me_2SO-d_6) δ 9.12 (d, 2 H, $J_{\alpha,\beta}$ = 6 Hz, H_α), 8.39 (t, 1 H, $J_{\beta,\gamma}$ = 7 Hz, H_γ), 8.13 (br t, 2 H, J = 7 Hz, H_β), 7.8 (d, 2H, $J_{o,m}$ = 8 Hz, H_o), 7.04 (d, 2 H, $J_{o,m}$ = 8 Hz, H_m), 2.24 (s, 3 H, CH_3); mass spectrum *m/e* 236 ($M^{\cdot+}$, 16), 235 ($M^{\cdot+}$ – H, 59), 194 (9), 121 (17), 118 (17), 102 (20), 81 (33), 79 (100).

Treatment of the ylide with a solution of tetrafluoroboric acid regenerated the starting salt.

Treatment of the ylide with acetyl chloride in benzene gave **1-[(*N*-*p*-cyanophenylacetimidoyl)amino]pyridinium chloride** (56%); mp 304–306 °C (methanol–ethyl acetate); ir (KBr) 3280, 2220, 1640 cm^{-1}; NMR (D_2O) δ 8.78 (d, 2 H, $J_{\alpha,\beta}$ = 6 Hz, H_α), 8.60 (t, 1 H, $J_{\beta,\gamma}$ = 7.5 Hz, H_γ), 8.18 (dd, 2 H, $J_{\alpha,\beta}$ = 6, $J_{\beta,\gamma}$ = 7.5 Hz, H_β), 7.88 (s, 4 H, phenyl hydrogens), 2.13 (s, 3 H, CH_3); mass spectrum *m/e* 236 ($M^{\cdot+}$ – Cl, 26), 235 ($M^{\cdot+}$ – HCl, 100), 188 ($CNC_6H_4NH_2^{\cdot+}$, 43).

Anal. Calcd for $C_{14}H_{13}ClN_4$: C, 60.53; H, 4.72. Found: C, 60.64; H, 4.77.

Attempted Rearrangement of Ylide 19 (R = H; X = *p*-CN) with Sodium Hydride. A mixture of the ylide (128 mg) and sodium hydride (26 mg) in acetonitrile (20 ml) was stirred overnight at room temperature and then heated under reflux for 12 h. Water (5 ml) was added. Workup of the mixture gave starting ylide (104 mg, 81%).

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Registry No.—**1** (R^2 = 4-NO_2; R^3 = H), 456-27-9; **1** (R^2 = 4-CN; R^3 = H), 2252-32-6; **1** (R^2 = 4-CF_3; R^3 = H), 36407-40-6; **1** (R^2 = 3-NO_2; R^3 = H), 586-36-7; **1** (R^2 = 2-NO_2; R^3 = H), 365-33-3; **1** (R^2 = 2-CF_3; R^3 = H), 447-59-6; **1** (R^2 = 2-CN; R^3 = H), 55165-45-2; **1** (R^2 = 2-NO_2; R^3 = 4-NO_2), 345-12-0; **1** (R^2 = 3-NO_2; R^3 = 5-NO_2), 369-20-0; **1** (R^2 = 3-Cl; R^3 = H), 456-39-3; **1** (R^2 = R^3 = H), 369-57-3; **1** (R^2 = 4-Cl; R^3 = H), 673-41-6; **2** (R^1 = H), 694-59-7; **2** (R^1 = 4-CH_3), 1003-67-4; **2** (R^1 = 4-C_6H_4), 1131-61-9; **2** (R^1 = 4-OCH_3), 22346-75-4; **2** (R^1 = 4-OC_6H_5), 33399-53-0; **2** (R^1 = 4-Cl), 1121-76-2; **2** (R^1 = 4-CN), 14906-59-3; **2** (R^1 = 2-OCH_3), 10242-36-1; **2** [R^1 = 4-(4-pyridyl 1-oxide], 24573-15-7; **2** (R^1 = 4-NO_2), 1124-33-0; **8**, 58425-96-0; **9**, 58425-97-1; **10** (R = 4-CN), 58673-26-0; **10** (R = 2-CH_3), 58425-99-3; **10** (R = 3,5-Me_2), 58426-01-0; **10** (R = 2,6-Me_2), 58426-02-1; **22**, 58426-03-2; 2-(3-bromo-5-cyano-2-hydroxyphenyl)pyridine, 58426-04-3; 2-(5-bromo-2-hydroxy-3-nitrophenyl)pyridine, 58448-77-4; 1-[(*N*-*p*-cyanophenylacetimidoyl)amino]pyridinium chloride, 58426-05-4; 2-(*p*-cyanoanilino)-4-ethoxypyridine, 58426-06-5.

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Mesoionic Compounds. 38. The *anhydro*-2-Aryl-1,3-dithiolium Hydroxide System[1]

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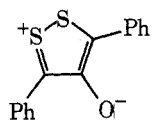
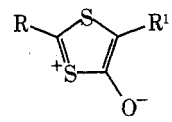
anhydro-4-Hydroxy-2-phenyl-1,3-dithiolium hydroxide has been prepared from thiobenzoylthioglycollic acid, acetic anhydride, and triethylamine at 0–10 °C and the product previously assigned this structure shown to be *anhydro*-4-hydroxy-2-phenyl-5-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium hydroxide. This mesoionic ring system undergoes ready cycloaddition of acetylenic dipolarophiles yielding substituted thiophenes with elimination of carbonyl sulfide. With olefinic dipolarophiles and azirines stable 1:1 adducts were formed.

Interest in the chemistry of five-membered ring systems containing sulfur has increased considerably over the past several years, particular attention being paid to those systems containing two sulfur atoms in the 1,2 positions[2] and in the 1,3 positions.[3] Cycloaddition reactions have played a prominent part in these studies,[4] and have resulted in several useful synthetic procedures. Mesoionic derivatives[5] of both the 1,2-dithiole and 1,3-dithiole ring systems can be devised and a study of their synthesis and properties was initiated as part of our interests in this area.

anhydro-3,5-Diphenyl-4-hydroxy-1,2-dithiolium hydroxide (**1**) has been synthesized[6] from 1,1,3,3-tetrabromo-1,3-diphenylacetone and potassium ethyl xanthate, or from 1,3-diphenylpropanetrione and H_2S–HCl, followed by Et_3N.[7] We have found this ring system to be completely unresponsive to a variety of dipolarophiles[8] whereas *anhydro*-4-hydroxy-2-phenyl-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = H) was an extremely reactive system whose reactions are described below.



1



2

3

The ring system **2** was described as being prepared from thiobenzoylthioglycollic acid (**3**, R = Ph; R^1 = H) and acetic anhydride–boron trifluoride.[9a] The corresponding exocyclic imino derivatives have also been prepared by cyclization of cyanomethyl dithiobenzoate with anhydrous HCl or acid chlorides,[9b] and an unstable ortho-protonated derivative of **2** (R = Ph; R^1 = H) was obtained by cyclization of carboxymethyl dithiobenzoate with perchloric acid,[9c] a convenient cyclization agent for the preparation of a variety of 1,3-dithioles.[3]

Repetition of the reported procedure[9a] gave a deep-red, crystalline product, mp 185–186 °C dec, as described previously when a reaction time of several minutes was used. Longer reaction times resulted in considerable polymer formation. This red product failed to undergo cycloadditions with several dipolarophiles and, on examination of its spectral characteristics, they were found to be incompatible with the assigned structure. The mass spectrum showed an ion at *m/e* 388 (5%), most likely a molecular ion which, in conjunction with analytical data, established the molecular formula as $C_{18}H_{12}O_2S_4$. The NMR data for this product indicated the presence of two phenyl groups [δ 7.48 (m, 10)] and two methylene protons which appeared as two AB doublets (J = 16.5 Hz) at δ 4.33–4.08 and 4.01–3.75, and the infrared spectrum showed two absorptions at 1690 and 1590 cm^{-1}, conceivably due to two carbonyl groups related to each other in such a way that an exocyclic negative charge was delocalized over both groups. These data are most satisfactorily accommodated by the structure *anhydro*-4-hydroxy-2-phenyl-5-(thiobenzoylthiomethylcarbonyl)-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = $COCH_2SCSPh$).

This "overacylation" of a mesoionic system under similar cyclodehydration conditions has been observed in the oxazole,[10] imidazole,[11] and thiazole[12] ring systems, and the spectral parameters of this present product are consistent with those of the comparable products in these ring systems. Indicative of a high degree of charge density at that position of the nucleus, it also indicates considerable potential in 1,3-dipolar cycloaddition reactions. However, these acylated products themselves often do not undergo cycloadditions owing to delocalization of the negative charge of the masked 1,3-dipole over the carbonyl groups.

The acylation can often be avoided by the use of Et_3N and low reaction temperatures.[12c] When the thiobenzoylthioglycollic acid (**3**, R = Ph; R^1 = H) was treated with a mixture of Et_3N–Ac_2O (1:3) at 0–10 °C for several minutes only, glistening scarlet needles, mp 113–115 °C dec, were obtained. That this product was the desired mesoionic system, *anhydro*-4-hydroxy-2-phenyl-1,3-dithiolium hydroxide (**2**, R = Ph; R^1 = H) was evident from the following considerations. Analytical and mass spectral data [$M^{\cdot+}$ 194 (40%)] showed the molecular formula to be $C_9H_6S_2O$ and, in addition to aromatic protons at δ 7.51 (5), the NMR spectrum showed only a sharp