Reactions of Hydroxypyridines with 1-Chloro-2,4,6-trinitrobenzene − Product Structure, Kinetics, and Tautomerism

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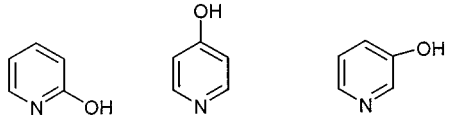
Reactions between 1-chloro-2,4,6-trinitrobenzene and 2-hydroxypyridine, 3-hydroxypyridine, and 4-hydroxypyridine are reported. 4-Hydroxypyridine produces the product of attack at the nitrogen atom, while 3-hydroxypyridine reacts at the oxygen atom. 2-Hydroxypyridine reacts as an ambidentate nucleophile, providing a mixture of products arising from attack at both the oxygen and the nitrogen atom. Reactions between X-substituted-3-hydroxypyridines (X = H, 5-Cl, 6-CH_3) and 1-chloro-2,4,6-trinitrobenzene provided 3-pyridinyl 2,4,6-trinitrophenyl ethers, analysed by ^1H and ^{13}C NMR spectra and by X-ray diffraction. Moderate heating of methanolic solutions of 3-pyridinyl 2,4,6-trinitrophenyl ether and of 6-methyl-3-pyridinyl 2,4,6-trinitrophenyl ether caused a methylation reaction of the pyridine nitrogen ring through trinitroanisole, providing 3-hydroxy-1-methylpyridinium picrate and 1,2-dimethyl-5-hydroxypyridinium picrate. Kinetic data are compared and discussed.

Introduction

The tautomerism of hydroxypyridines[1] receives constant attention in both the theoretical[2−6] and experimental[7−9] fields, with particular regard being paid to the solvent effect. It is interesting to note that hydroxypyridines may be simple models for investigating mechanisms of some enzymatic reactions[10] or for discerning the behaviour of the bases of nucleic acids in connection with mutation due to base mispairing or other mistaken helices.[11] Tautomerism and the presence of association by hydrogen bonds[12] are relevant to the structure, properties and replication characteristics of nucleic acids.[13]

While 2-hydroxypyridine (**1**) and 4-hydroxypyridine (**2**) have been the subject of much theoretical and experimental investigation, 3-hydroxypyridine (**3**) has been less extensively studied (Scheme 1). Derivatives of 3-hydroxypyridine are potential biocides.[14] In principle, polynitro derivatives may be of interest as rodenticides.



1 **2** **3**

Scheme 1. Hydroxypyridines

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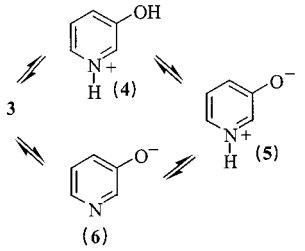
3-Hydroxypyridine and its derivatives display an interesting form of tautomerism[1,15] (the tautomer is a betaine form), which is shown in Scheme 2. Cationic and anionic forms **4** and **6**[16] are clearly possible intermediates on the tautomeric pathway. It is possible to depict **5** in a formally neutral oxo form.[17]



Scheme 2. Tautomerism of 3-hydroxypyridine

In previous papers, we investigated the kinetic behaviour of 2-hydroxypyridine as a nucleophilic reagent[18] towards 1-halo-2,4,6-trinitrobenzenes and as a catalyst (together with some related compounds such as δ-valerolactam, benzamides) in the S_NAr reaction[19−21] of nitro-activated substrates and amines, in apolar solvents. When 2-hydroxypyridine reacts with nitro-activated halobenzenes it is an ambidentate nucleophile, acting through both the oxygen and the nitrogen atom.

To obtain more information on the kinetic behaviour of hydroxy pyridines as nucleophiles in S_NAr reactions, and in particular to investigate the nucleophilic power of the different nucleophilic centres of hydroxypyridines, we report data on reactions between 1-chloro-2,4,6-trinitrobenzene ("picryl chloride", **9**) and the three isomers 2-hydroxypyridine (**1**), 4-hydroxypyridine (**2**), and 3-hydroxypyridine (**3**), as well as 5-chloro-3-hydroxypyridine (**7**) and 3-hydroxy-6-methylpyridine (**8**).

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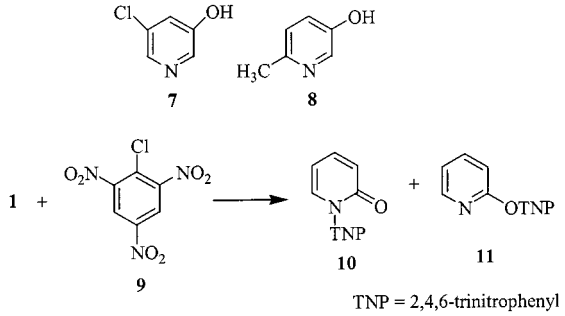
Results

Reactions of 2-Hydroxypyridine

In agreement with our previous findings,[18] reactions, in THF and in CH_3CN, between **1** and 1-chloro-2,4,6-trinitrobenzene (**9**) provided both isomers **10** and **11**, as shown in Scheme 3. Under our experimental conditions, no isomerization from **10** to **11** (or vice versa) was observed.



Scheme 3. Reactions between 2-hydroxypyridine (**1**) and 1-chloro-2,4,6-trinitrobenzene (**9**)

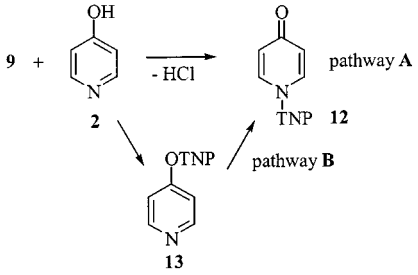
In principle, hydroxypyridines may also act as C-nucleophiles,[21,22] but we did not observe the presence of products of C-attack in the reaction mixtures. Picryl chloride is also a potentially ambidentate electrophile. Attack at C-3/C-5 of **9** is often found to be kinetically preferred,[22] but does not lead to a stable product and hence we did not detect it in this study. Kinetic constants of formation of **10** and **11**, k^N_{obs} and k^O_{obs}, respectively (in s^{-1} mol^{-1} dm^3), were obtained separately (see Exp. Sect.), and these data are shown in Table 1.

Even if **1** is considered to be strongly associated,[23–27] under the reported experimental conditions both reactions show regular kinetic behaviour: Both processes follow a second-order kinetic law, and the k_{obs} (k^N_{obs} and k^O_{obs}) values are unaffected by any change in the initial concentration value of **1**.

The values of the [**10**]/[**11**] ratios of the two final products calculated at "infinite" time (at about 100% of conversion) are 2.4 and 4.0 in THF and in CH_3CN, respectively. The ratios obtained at the end of the reactions were also the same at every percentage of conversion.

Reactions of 4-Hydroxypyridine

The reaction between **9** and **2** (in acetonitrile) provides, in almost quantitative yield, the picramide derivative **12**, as shown in Scheme 4. Recently,[28] *N*-(4-nitrophenyl)-4-pyridone has been obtained not only from the direct attack of the nitrogen atom of **2** onto 1-bromo-4-nitrobenzene, but also (at high temperatures and in the presence of a base) from the isomeric 4-nitrophenyl 4-pyridinyl ether. It is possible that **12** arises from 4-pyridinyl 2,4,6-trinitrophenyl ether (**13**) by means of a rearrangement, as indicated by pathway B of Scheme 4. This pathway B, under the experimental conditions reported here (at low temperatures and without a base in an inert solvent) is improbable. Furthermore, **12** was obtained in almost quantitative yields: in the reaction mixtures, from low percentages of conversion right up to high percentages of conversion, no evidence of the presence of other isomers of **12** was obtained by TLC analysis, by ^1H NMR spectroscopic analysis of the crude reaction product, or by UV/Vis spectroscopic analysis. The k^N value related to the reaction of Scheme 4 is reported in Table 1.



Scheme 4. Reaction pathways to compound 12

Reactions of 3-Hydroxypyridines

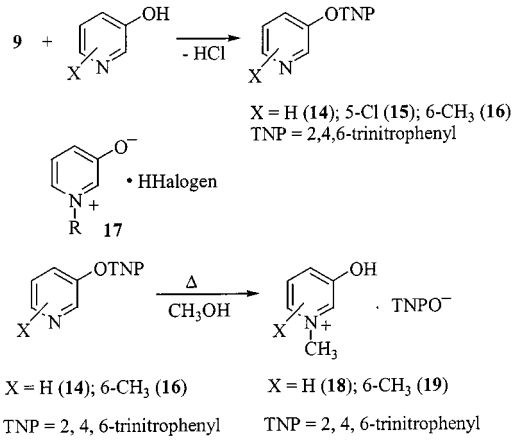
Table 1 reports data concerning the reactions, in THF, of 3-hydroxypyridine (**3**) and 3-hydroxy-6-methylpyridine (**8**) with **9** according to Scheme 5, with attack of the oxygen atom on the substrate. Both nucleophilic centres, oxygen and nitrogen, could react with **9**. In principle, **3** may also act as a C-nucleophile, although in practice this has not been observed.

Alkylation of **3** with alkyl halides in CH_3CN provides betaines **17**.[29] In the cases of 3-hydroxypyridine and 3-hydroxy-6-methylpyridine, the products of the attack on the oxygen atom (**14**, **16**) are unstable and react on simple heating of their methanolic solutions (see Scheme 5) to give **18** and **19** in almost quantitative yields. All attempts to crystallize **14** and **16** from methanol provided **18** and **19**. Attempts to crystallize **14** and **16** from other solvents failed (see Exp. Sect.).

Table 1. Reactions between hydroxypyridines and 1-chloro-2,4,6-trinitrobenzene (**9**)

Isomer	Solvent	$[9]_0$[a]	$10^4 \times k^O{}_{obs}$[b]	$10^4 \times k^N{}_{obs}$[b]	n[c]	$10^4 \times k^O$[d]	k^N [d]
1[e]	THF	4.0	3.55 ± 0.2	3.15 ± 0.1	11	3.9	0.41
1[f]	CH_3CN	2.1	0.74 ± 0.02	1.34 ± 0.06	4	0.75	2.0
3[g]	THF	1.2	1.33 ± 0.08	–	5	(1.3)	
8[g]	THF	1.0	7.30 ± 1	–	3	(7.3)	
2[h]	CH_3CN	1.0	≤ 5	541 ± 10	5	≤ 0.06	30

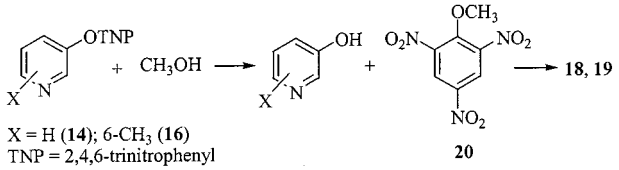
[a] $\times 10^4$ (in mol dm^{-3}). – [b] In $s^{-1}mol^{-1}$ dm^3; error is standard deviation. – [c] Number of determinations. – [d] In $s^{-1}mol^{-1}$ dm^3; calculated from Equations (1) and (2). – [e] $[1]_0$ from $8\cdot10^{-4}$ to $5\cdot10^{-2}$ [mol dm^{-3}]. – [f] $[1]_0$ from $7\cdot10^{-4}$ to $3\cdot10^{-3}$ [mol dm^{-3}]. – [g] $[3]_0$ and $[8]_0$ from $5\cdot10^{-4}$ to $1\cdot10^{-3}$ [mol dm^{-3}]. – [h] $[2]_0$ from $5\cdot10^{-4}$ to $1.0\cdot10^{-3}$ [mol dm^{-3}].



Scheme 5. Reactions between 3-hydroxypyridines and **9** and transformation of **14** and **16** in methanol

The structures of **14**, **16**, **18**, and **19** were assigned on the basis of ^1H and ^{13}C NMR spectral data.[30] The structures of **18** and **19** agree with those found in ^1H-^1H NOE experiments and shows considerable enhancement of both the 2-H and 6-H (18% and 14%) signals of **18**, and of 2-H (23%) and 6-CH_3 (6%) of **19**. These values were obtained by irradiating the N−CH_3 signal of **18** and **19**. An oil showing the same ^1H and ^{13}C NMR spectral characteristics as **14** was obtained from the treatment of the sodium salt of **3** with **9** (see Exp. Sect.).

During attempts to crystallize **14** and **16** from methanol, it was interesting to note that when the isomerization reaction was halted at about 50% of conversion, the presence of a large quantity of 2,4,6-trinitroanisole (**20**) (ca. 20%) was observed in the methanolic solutions. Compound **20** was present in small amounts (< 2%) at the end of the transformations of **14** into **18** and of **16** into **19** (see Scheme 6).



Scheme 6. Mechanism of the reaction between **14** (and **16**) and methanol

In separate experiments, we observed that trinitroanisole (**20**) (obtained as described in the literature[31]) reacts with **3** and **8**, providing **18** and **19**, respectively. These findings suggest a two-step mechanism, the first step being the attack of the methanol onto **14** or **16**, yielding **3** or **8** and trinitroanisole (**20**), and the second step being the attack of **3** or **8** on **20**. The formation of **18** and **19** may be explained by the attack of the aza nitrogen atom of **3** or **8** on the sp^3 carbon atom of **20**, causing a demethylation reaction of **20**, as in an S_N2 reaction.[32]

In conclusion, the intervention of methanol produces the trinitroanisole intermediate, which is demethylated by **3** or **8**. It is a reaction different to a simple shift from O to N, such as in the case of alkyl group migration derivatives of 2-alkoxypyridines under acid catalysis or on heating in solution.[33] Probably, for moieties sterically less hindered than the trinitrophenyl group, a pathway similar to that in Scheme 6 may explain the apparent migration from O to N of alkyl or aryl groups of derivatives of hydroxypyridines. The structure of **15** was ascertained by single-crystal X-ray analysis (Figure 1).

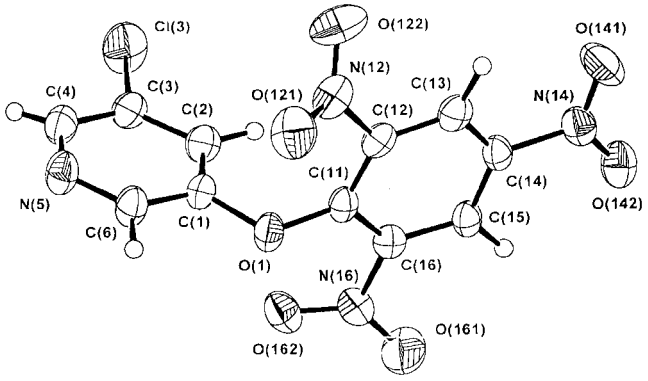
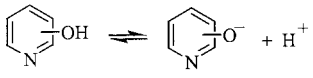


Figure 1. Perspective view and atom labelling of compound **15**; displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small circles of arbitrary radii

In solution, **15** is only moderately stable. This explains the low yield (60%). In THF, in DMSO and in methanol, **15** does not show any particular trinitrophenyl group reaction. On heating **15** to 50−60 °C in THF or in DMSO, considerable amounts of picric acid and of **7** are obtained. In **7**, the presence of the chlorine atom in position 5 probably depresses (through the electron-withdrawing effect) the nucleophilic power of the aza nitrogen atom and compounds corresponding to **18** or **19** cannot be formed.

Discussion

In principle, one possible nucleophilic centre may be the negative oxygen atom of the anion of hydroxypyridines, arising from the equilibrium in Scheme 7, which may also permit attack through ring carbon atoms. It is known that the oxygen anion is a more powerful nucleophile than the dicoordinated oxygen atom.[34] With the equilibrium in Scheme 7 in operation, and the nucleophile being the phenoxide ion, a strong autoinhibition of the substitution reaction was observed.[35] Because of the absence of a kinetic effect from the released acid, as the reaction progresses, the reactions of **1**, **2**, **3**, and **8** cannot be attributed to the anionic (or zwitterionic) form of the nucleophile. They may, however, be attributed to the undissociated nucleophiles.[35] HCl released during the reactions probably protonates the hydroxypyridines.



Scheme 7. Dissociation of hydroxypyridines

Reactions of 2-Hydroxypyridine

It has been reported that the use of **1** in S_NAr reactions produces a particular kinetic effect in two main ways. The

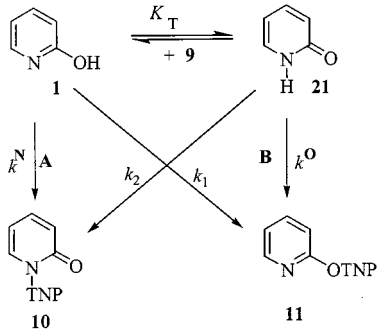
observed kinetic effect depends on the kind of solvent used.

i) Compound **1** is the nucleophile. Reactions between 1-fluoro-2,4,6-trinitrobenzene and **1**, in solvents less polar than those used here, show[18] (for the attack of the nitrogen atom, i.e. for formation of **10** alone) autocatalytic behaviour: k_{obs} (in s^{-1} mol^{-1} dm^3) increases as $[\mathbf{1}]_o$ values increase, without reaching a constant value (as in "saturation" phenomena). We attribute this kinetic behaviour to the presence of molecular complexes between the substrate and 2-hydroxypyridine on the reaction pathway.[18] ^1H NMR investigations show that these complexes mainly involve hydrogen bonding interactions.[36,37] In the more polar THF, no evidence for autocatalysis is observed.

ii) Compound **1** is the catalyst. S_NAr reactions between 1-fluoro-2,4-dinitrobenzene and amines (in apolar solvents) are catalysed by **1** (**1** is a well-known[38] "polyfunctional catalyst"): k_{obs} values increase as the concentration of the catalyst increases, until a constant value is reached. The plot of k_{obs} vs. $[\mathbf{1}]_o$ shows a saturation plateau. Some authors explain[39,40] the saturation by self association of 2-hydroxypyridine. However, our previous evidence (obtained using 2-hydroxypyridine and related compounds) strongly indicates[20] that the catalytic kinetic behaviour may be explained by the presence of an equilibrium involving all the reagents (substrate and amine) and the catalyst. The levelling off of k_{obs} values mainly arises from the obvious interaction (resembling acid−base interaction) between **1** and amines.[20]

The kinetic feature reported here (in poorly associating solvents THF and CH_3CN) agrees (as well as the reactions of **2**, **3**, and **8**) with the conclusions discussed above. The reactions of Scheme 2 to Scheme 4 are free of complications and they follow the simple second-order kinetic law. In the solvents used here, dimerization is probably low and virtually negligible.[41] No kinetic effects arising from association between **9** and hydroxypyridines are observed, probably because the chloro derivatives are less prone to associate with hydroxypyridines than the fluoro derivatives are.[36]

Of the isomers considered, only 2-hydroxypyridine behaves as a bidentate nucleophile; the possible reactions are shown in Scheme 8. No evidence for isomerization from **10** to **11** (or vice versa) was obtained. It is known that the migration of alkyl groups of 2-alkoxypyridines occurs through acid catalysis.[42]



Scheme 8. Reaction pathways of 2-hydroxypyridine with **9**

The reaction indicated by k_1 is not very significant, because in **1** the nucleophilic power of the dicoordinated oxygen atom is weak.[34,35] The electron-withdrawing effect of the aza group depresses the nucleophilic power of the dicoordinated oxygen atom of the OH group. Compound **21** is an amido form; its most nucleophilic centre should be the oxygen atom (protonation also occurs at the oxygen atom), and reaction k_2 is unlikely. Consequently, pathways **A** and **B** of Scheme 8 should be the preferred reaction pathways. This conclusion is in accord with the literature concerning alkylation of **1**.[43] From Scheme 8, assuming that **10** and **11** are from tautomers **1** and **21** respectively, if the tautomeric constant K_T is known, then k^N and k^O may be calculated by Equation (1) and Equation (2).[44]

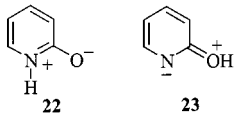
$$k^O = k^O_{obs}\,(1 + K_T)/K_T \quad (1)$$

$$k^N = k^N_{obs}\,(1 + K_T) \quad (2)$$

The K_T value of 2-hydroxypyridine in acetonitrile is 150,[43,45] and in THF (see Exp. Sect.) it is 12. Similar equations can be obtained for reactions of **2**; in CH_3CN, K_T = 4.6.[45] The k^N and k^O values are reported in Table 1.

The K_T value of 2-hydroxypyridine in THF indicates that both tautomers are present (in THF) at the same time. The K_T values reported here agree with those reported in the literature.[8,9,45] In particular, the tautomeric forms of 5-chloro-2-hydroxypyridine are present in approximately equal amounts in dioxane,[46] and both tautomers should be detectable. In $[D_8]$THF, however, low-temperature ^1H NMR unfortunately does not provide evidence for the simultaneous presence of both tautomers.[27]

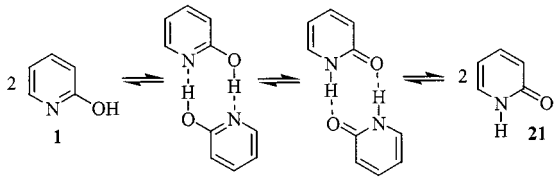
In the solvent used here, the rate of formation of **10** is close to that of **11**, in agreement with the [**11**]/[**10**] ratios reported in the Results Section. The dicoordinated oxygen atom displays nucleophilicity similar to that of the neutral nitrogen atom. However, the k^N/k^O ratios − of 11 in THF and 267 in CH_3CN − favour the nitrogen atom, as is to be expected, considering the difference in basicity and nucleophilicity of the two neutral heteroatoms. Probably, the reactivity at the oxygen atom of **21** arises from the structure **22**, with charge separation as conventionally accepted for the amido group (see Scheme 9).



Scheme 9. Charge separation of 2-hydroxypyridine

The reactivity at the nitrogen atom of **1** may arise from the mesomeric effect of the hydroxy group, as depicted in **23**. In position 2 of the pyridine ring, this mesomeric electronic effect is strongly balanced by the electron-withdrawing inductive effect.[47] When the hydroxy group is far from the aza nitrogen atom (**2**), the mesomeric electron-donating effect of the OH group produces a reactivity at the nitrogen atom higher than that in **1** (k_2^N/k_1^N = 15). Reaction through the O centre of **2** is not competitive with N-attack, and so no product of O-reaction is found. In ap-

rotic, poorly polar solvents, the mechanism for the tautomeric equilibrium of **1** involves the dimeric form of **1**, which may be the intermediate for both tautomers as in Scheme 10.[8,25,48] The current data show that the rate of the studied reactions is unaffected by the presence of self association.

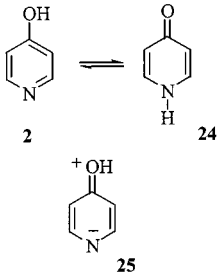


Scheme 10. Tautomerism of 2-hydroxypyridine by dimer formation

4-Hydroxypyridine

For **2**, it is possible to draw a scheme similar to Scheme 8 for **1**. However, **12** is the only product recovered, even if the more populated form of **2** is the oxo form **24**.[49]

The high reactivity of **2** may be explained by considering that the nitrogen atom of **2**, of the four nucleophilic centres of the tautomers of Scheme 11, is clearly the centre most prone to make the nucleophilic attack, because of the strongly electron-donating mesomeric effect of the OH group (without the electron-withdrawing inductive effect present in isomer **1**).



Scheme 11. Tautomerism of 4-hydroxypyridine

In conclusion, tautomer **2** is the form of 4-hydroxypyridine reactive towards **9**. This is an example of the possibility that the product can arise from the less prevalent tautomer **2**, in agreement with the Curtin−Hammett principle.

3-Hydroxypyridines

In principle, the ethers **14**, **15**, and **16**, may arise from attack on picryl chloride either by the neutral oxygen atom of **3**, or from the charged oxygen atom of forms **5** and **6**. When the charged oxygen atom of the sodium salt of **3** is the reacting centre, the reaction is very fast (see Exp. Sect.). Thus, **5** should also be more reactive than **3**. The fact that the HCl generation did not affect the reaction rate as the reaction progressed clearly indicates that very basic centres are not involved in the reaction pathway. These reactions may be associated with the formally neutral hydroxypyridines without intervention of the other forms of Scheme 1. This conclusion agrees with those of von Philipsborn[30] and of Albert and Phillips[50] regarding the phenolic form of **3** in apolar solvents. As a consequence, k^O is identical with k^O_{obs} for **3** in Table 1. In **8** the nucleophilicity of the oxygen atom is enhanced by the electron-releasing effect of the methyl group in position 6: $k^O_8/k^O_3 = 5.5$.

Conclusion

In conclusion, while 2-hydroxypyridine is found to react as an ambidentate nucleophile, 3-hydroxypyridines react essentially as oxygen nucleophiles and 4-hydroxypyridine as a nitrogen nucleophile. In agreement with literature reports,[47] the ratio $k^O_1/k^O_3 = 3$ confirms that the electronic interaction between the endocyclic nitrogen atom and the hydroxy group in position 2 is mainly inductive in character. There is a moderate superposition of the conjugative electron-releasing effect of the OH group in position 2, which is less relevant in position 3. Probably, in **2** structure **25** is so dominant that the oxygen atom cannot act as nucleophilic centre.

In agreement with our previous findings,[18,20] these data show that the rates of the studied reactions are unaffected by the presence or otherwise of self association of **1** or of other hydroxypyridines. A tentative explanation may be the possibility that the monomer and the dimer (which may be also in a linear, noncyclic form) of **1** react with **9** at the same rate. An alternative explanation is that the self association and homoconjugation in solvents used here are not important.[41,51]

Finally, attack by the nitrogen atom of hydroxypyridines **1** and **2** is faster than attack by the oxygen atom, as expected on the basis of the difference in nucleophilicity. The k^N/k^O ratios arise from electronic interaction between the aza nitrogen atom and the hydroxy group. The electronic interaction is relevant to the rate of reactions, and to the regioselectivity of the reactions.

Experimental Section

General: The ^1H and ^{13}C NMR spectra were recorded at 200 or 300 MHz and 50.3 or 75.46 MHz, respectively, using Gemini 200 and 300 instruments. Chemical shifts were measured in δ (ppm) with reference to TMS or to the solvent ([D_6]DMSO: δ = 2.6 and 39.5 for ^1H and ^{13}C spectra, respectively). − Melting points were measured with a Büchi apparatus and are uncorrected. − UV/Vis spectra were recorded with Perkin−Elmer Lambda 5 and Lambda 12 spectrophotometers.

Materials: Hydroxypyridines were commercial samples (Fluka) purified by conventional procedures.[30] 1-Chloro-2,4,6-trinitrobenzene (**9**) was a commercial sample (Carlo Erba), purified by crystallization from chloroform, m.p. 82−83 °C. THF (Carlo Erba) was dried with sodium, distilled, and then redistilled from $LiAlH_4$ under nitrogen immediately before use.[52] Trinitroanisole (**20**) was prepared as described in the literature.[31]

General Procedure: A solution of 1 mmol of **9** was added to a solution of 2 mmol of the hydroxypyridine in THF (or CH_3CN), with vigorous stirring. After the disappearance of **9** (TLC, silica gel, eluent dichloromethane), the solvent was removed under vacuum (12 mm/Hg) and the reaction product was separated using a chromatographic column (silica gel, eluent dichloromethane). The ^1H

NMR spectra of crude products resulting from reactions between all of the hydroxypyridines and **9** are identical to those of the eluted products. However, the spectral data of **14**, **15**, and **16** are different from those of the solid product crystallized from methanol or from a THF/methanol mixture. All attempts to crystallize **14**, **15**, and **16** from a number of solvents (dichloromethane, diethyl ether, tetrahydrofuran, acetonitrile, light petroleum) failed. − The ^{1}H NMR and MS spectra of compounds **10** and **11** are as previously reported.[18] The yield of **12** was 95%. − The structures of **12**, **14**, **15**, **16**, **18**, and **19** were assigned on the basis of ^{1}H and ^{13}C NMR spectral data and by comparison with the data by von Philipsborn.[30] The spectrum of the crude reaction product of **2** is identical to that of the eluted product and to that after crystallization from MeOH. − Under the experimental conditions used, compounds **10**, **11**, and **12** are stable. In particular, no conversion of **10** into **11** (or of **11** into **10**) was observed, even after long reaction times, either in the absence or in the presence of **1**.

Reaction between the Sodium Salt of 3 and 9: NaH (0.060 g, 2.5 mmol) was added to a vigorously stirred solution of **3** (0.183 g, 1.9 mmol) in 10 mL of anhydrous THF. After 10 min, compound **9** (0.504 g, 1.9 mmol) was slowly added. After 10 min, the solvent was removed under vacuum and after column chromatography an oil was obtained. Addition of this oil to a solution of **14** did not change its ^{1}H NMR spectrum.

Kinetics: The choice of solvents was determined by the low solubility of hydroxypyridines in a number of solvents. − The reaction at $[\mathbf{9}]_o = 10^{-4}$ mol dm^{-3} was carried out by monitoring the appearance of the reaction products using UV/Vis spectrophotometry. In the case of reactions of **1**, the reactions were monitored at 3 different λ values to determine the quantities of **9**, **10**, and **11** and to check the analytical data, taking into account that [**9**] + [**10**] + [**11**] = $[\mathbf{9}]_o$. − λ values used in the spectrophotometric determinations are as follows:

λ = 360, ε = 300, 1000, 700 for **9**, **10**, and **11**, respectively;

λ = 380, ε = 130, 1000, 230 for **9**, **10**, and **11**, respectively;

λ = 400, ε = 30, 850, 70 for **9**, **10**, and **11**, respectively;

λ = 360, ε = 13.000 for **12**.

From the analytical data, k_{obs} values were calculated, as an initial rate, by using conventional procedures. Table 2 reports some selected experimental data.

Table 2. Reactions between 1-chloro-2,4,6-trinitrobenzene (**9**) and hydroxypyridines at 30 °C

$[\mathbf{2P}]_o \times 10^3$ [mol dm^{-3}][a]	0.841	1.12	1.40	1.73	2.37	3.15
$k^N_{obs} \times 10^4$ [s^{-1} mol dm^{-3}]	3.00	3.21	3.28	3.30	3.10	3.02
$k^O_{obs} \times 10^4$ [s^{-1} mol dm^{-3}]	3.60	3.25	3.37	3.72	3.40	3.68
$[\mathbf{2P}]_o \times 10^3$ [mol dm^{-3}][a]	5.05	6.31	7.15	26.1	52.2	
$k^N_{obs} \times 10^4$ [s^{-1} mol dm^{-3}]	3.02	3.00	3.24	3.20	3.35	
$k^O_{obs} \times 10^4$ [s^{-1} mol dm^{-3}]	3.58	3.77	3.68	3.41	3.54	

[a] Solvent = tetrahydrofuran; $[\mathbf{9}]_o = 4.0 \cdot 10^{-4}$ [mol dm^{-3}].

The K_T value related to **1**, in THF, was calculated by described procedures.[45,48] Values of [**1**] ranged from $7 \cdot 10^{-4}$ to $1 \cdot 10^{-5}$ mol dm^{-3}. Compound **1**: λ_{max} = 306 (ε = $4.0 \cdot 10^3$); 2-methoxypyridine: λ = 306 (ε = 1); 1-methyl-2-pyridone: λ_{max} = 306 (ε = $4.45 \cdot 10^3$).

***N*-(2,4,6-Trinitrophenyl)-2-pyridone (10):**[18] M.p. 194−195 °C (from methanol). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 107.5, 120.3, 124.6, 131.5, 136.9, 142.8, 147.0, 147.2, 160.3.

2-Pyridinyl 2,4,6-Trinitrophenyl Ether (11):[18] M.p. 129−130 °C (from methanol). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 111.2, 121.2, 125.1, 141.9, 143.5, 143.8, 144.2, 147.0, 160.6; (CDCl$_3$): δ = 111.3, 120.8, 124.3, 141.0, 143.1, 144.9, 145.4, 146.8, 160.7.

***N*-(2,4,6-Trinitrophenyl)-4-pyridone (12):** M.p 174−176 °C (from methanol). − ^{1}H NMR (300 MHz, [D$_6$]acetone): δ = 6.47 (d, *J* = 7.9 Hz, 2 H), 7.90 (d, *J* = 7.9 Hz, 2 H), 9.51 (s, 2 H, Ph). − ^{13}C NMR (75.46 MHz, [D$_6$]acetone): δ = 119.9, 126.0, 135.2, 140.9, 149.1, 149.2, 178.7. − MS (EI); *m*/*z* (%): 306 [M$^+$] (1), 229 (5), 172 (54),144 (88), 117 (26), 90 (14), 78 (48), 51 (100).

3-Pyridinyl 2,4,6-Trinitrophenyl Ether (14): Oil. − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.58 (dd, *J* = 4.3 Hz, *J* = 4.9 Hz, 1 H, 5-H), 7.70−7.85 (m, 1 H, 4-H), 8.45−8.60 (m, 2 H, 2-H and 6-H), 9.38 (s, 2 H, Ph). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 123.0, 124.7, 125.7, 137.8, 143.8, 144.3, 145.5 (2 signals overlap), 153.5. − MS (EI); *m*/*z* (%): 306 [M$^+$], 229 (100), 199 (10), 95 (31).

5-Chloro-3-pyridinyl 2,4,6-Trinitrophenyl Ether (15): M.p. 145−146 °C (from methanol). − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.99−8.02 (m, 1 H, 4-H), 8.58−8.61 (m, 2 H, 2-H, 6-H), 9.40 (s, 2 H, Ph). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 107.37, 123.3, 126.3, 131.8, 136.9, 144.1, 144.2, 144.5, 154.0. − MS (EI); *m*/*z* (%): 342 (3), 340 (9), 139 (8), 128 (5), 112 (11), 102 (29), 100 (100). − HRMS for $C_{11}H_5ClN_4O_7$: calcd. 339.9847; found 339.9853.

6-Methyl-3-pyridinyl 2,4,6-Trinitrophenyl Ether (16): M.p. 126−128 °C (crude product). − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.55 (s, 3 H, Me), 7.39 (d, *J* = 8.6 Hz, 1 H, 5-H), 7.57 (dd, *J* = 8.6 Hz, *J* = 3.3 Hz, 1 H, 4-H), 8.39 (d, *J* =3.3 Hz, 1 H, 2-H), 9.36 (s, 2 H, Ph). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 23.1, 123.6, 124.1, 125.7, 136.7, 143.6, 143.8, 144.6, 151.7, 154.0. − MS (EI); *m*/*z* (%): 320 (5) [M$^+$], 229 (8), 109 (42), 108 (12), 91 (14), 80 (100). − HRMS for $C_{12}H_8N_4O_7$: calcd. 320.0393; found 320.0387.

3-Hydroxypyridinium Picrate: M.p. 202−203 °C. This product was made by mixing a saturated (methanol) solution of picric acid with a solution of 3-hydroxypyridine. − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.90−8.10 (m, 2 H, 4-H and 5-H), 8.40−8.55 (m, 2 H, 2-H and 6-H), 8.70 (s, 2 H, Ph), 11.40−11.70 (br. s, 2 H, O*H* and N*H*).

3-Hydroxy-1-methylpyridinium Picrate (18): M.p. 197−199 °C (from methanol) ref.[53] 202−203. − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.38 (s, 3 H, N−CH$_3$), 7.90−8.10 (m, 2 H, 4-H and 5-H), 8.45−8.60 (m, 2 H, 2-H and 6-H), 8.68 (s, 2 H, Ph), 11.00−12.00 (br. s, 1 H, OH). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 47.8, 124.1, 125.1, 128.2, 130.8, 133.7, 136.4, 141.8, 156.6, 160.8. − $C_{12}H_{10}N_4O_8$ (338.2): calcd. C 42.61, H 2.98, N 16.56; found C 42.55, H 3.02, N 16.50. − λ = 360, ε = 13.000.

5-Hydroxy-1,2-dimethylpyridinium Picrate (19): M.p. 190 °C (from methanol). − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.65 (s, 3 H, C−CH$_3$), 4.25 (s, 3 H, N−CH$_3$), 7.85−7.96 (m, 2 H, 3-H and 4-H), 8.55−8.60 (m, 1 H, 6-H), 8.69 (s, 2 H, Ph), 11.45−11.65 (br. s, 1 H, OH). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 18.5, 45.5, 124.1, 125.1, 129.4, 131.7, 133.6, 141.8, 146.0, 154.6, 160.7. − $C_{13}H_{12}N_4O_8$ (352.3): calcd. C 44.33, H 3.43, N 15.90; found C 44.45, H 3.47, N 15.80.

2,4,6-Trinitroanisole (20): M.p. 68 °C.[31] − ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 4.15 (s, 3 H, OCH$_3$), 9.18 (s, 2 H, Ph). − ^{13}C NMR (75.46 MHz, [D$_6$]DMSO): δ = 64.8, 124.6, 141.4, 143.8, 150.7.

Table 3. Selected bond lengths [Å], angles [°] and torsion angles [°] with e.s.d. values in brackets for compound **15**

C(1)−C(2)	1.388(6)	C(3)−C(4)	1.376(6)
C(1)−C(6)	1.364(6)	C(4)−N(5)	1.331(6)
C(1)−O(1)	1.393(4)	N(5)−C(6)	1.341(5)
C(2)−C(3)	1.380(5)	O(1)−C(11)	1.362(5)
C(3)−Cl(3)	1.724(5)		
O(1)−C(1)−C(6)	116.4(3)	C(3)−C(4)−N(5)	21.7(4)
O(1)−C(1)−C(2)	123.3(3)	C(4)−N(5)−C(6)	118.1(4)
C(2)−C(1)−C(6)	120.3(4)	C(1)−C(6)−N(5)	122.6(4)
C(1)−C(2)−C(3)	116.2(4)	C(1)−O(1)−C(11)	118.7(2)
C(2)C−C(3)−C(4)	121.1(3)		
C(2)−C(1)−O(1)−C(11)	21.8(5)	O(1)−C(1)−C(6)−N(5)	−178.2(4)
C(1)−O(1)−C(11)−C(12)	76.8(4)		

Molecular Geometry of 5-Chloro-3-pyridinyl 2,4,6-Trinitrophenyl Ether (15): Selected bond lengths, angles, and torsion angles are given in Table 3. The structure is shown in Figure 1. The intramolecular bond lengths and angles, in line with the hybridization expected for the atoms involved, are similar to those of analogous ethers reported in the literature.[54]

The out-of-plane distortion of the oxygen atom from the mean pyridine plane [0.040(3) Å] as well as the value of the O(1)−C(1)−C(6)−C(5) torsion angle [−178.2(4)°] and the dihedral angle between the two mean planes of the six-membered rings (87.9(1)°) are indicative of a possible conjugative interaction solely of the oxygen p orbitals in the direction of the pyridine ring. The nitro groups are not equivalently oriented with respect to the phenyl ring, the dihedral angles between the planes involving N(12), N(14), and N(16) and that of the benzene ring being 41.4(2), 5.6(2), and 25.5(3)°, respectively. − Packing is consistent with van der Waals interactions.

Crystal Structure of (5-Chloro-3-pyridinyl) 2,4,6-Trinitrophenyl Ether (15): Table 4 shows the experimental and crystallographic data for **15**. X-ray measurements were performed using a Siemens AED single-crystal diffractometer in the range $3° < \theta < 70°$ using Ni-filtered Cu-K_α radiation ($\lambda = 1.54178$ Å). The diffraction angle θ for every reflection was determined on the basis of the orientation matrix and the outline of the diffraction peak was collected in the ω-2θ step scanning mode, using a scan width from $(\theta - 0.60)°$ to $(\theta + 0.60 + \Delta\lambda/\lambda\tau\gamma\theta)°$. The intensities I_{hkl} were determined by analysing the reflection profiles using the Lehmann and Larsen[58] procedure. Corrections for Lorentz and polarization effects were performed. There were no corrections for absorption effects. The structure was solved by direct methods and refined with cycles of full-matrix, anisotropic least squares. All hydrogen atoms were located in the difference Fourier map and refined isotropically.

Atomic scattering factors were taken from the International Tables for X-ray Crystallography.[59] Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma, Italy. − Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-154937. Copies of the data can be obtained free of charge by writing to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Experimental data for the X-ray diffraction studies on crystalline compound **15**

Empirical formula	$C_{11}H_5ClN_4O_7$
Crystal habit	prism
Crystal colour	pale brown
Molecular mass	340.6
$F(000)$	688
Crystal system	monoclinic
Space group	$P2_1/c$
Cell parameters at 295 K[a]	
a [Å]	9.505(2)
b [Å]	13.029(3)
c [Å]	11.299(3)
β [°]	110.6(1)
V [Å^3]	1309.8(10)
Z	4
$d_{calcd.}$ [g cm^{-3}]	1.72
Crystal dimensions [mm]	0.32 × 0.25 × 0.45
Linear absoption coefficient [cm^{-1}]	30.7
hkl range	$\pm h,k,l$
Unique total data	272
Criterion of observation	$I > 2\sigma(I)$
Unique observed data (NO)	1577
Number of refined parameters (NV)	228
Overdetermination ratio (NO/NV)	6.9
R	0.056
R_w	0.062
GOF	0.840
Largest shift/esd	0.043
Largest peak [eÅ^{-3}]	0.39
Programs	[b]

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 30 carefully centred reflections chosen from various regions of the reciprocal space. − [b] SHELXS86,[55] SHELX76,[56] PARST,[57] $R = |DF|/|F_o|$, $R_w = [w(DF^2)^2/w(F_o^2)^2]^{1/2}$, GOF $= [w|DF|^2/(NO - NV)]^{1/2}$.

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