Preparative gc on the same column afforded the 4- and 2-chloro-1,5-naphthyridines as pure compounds, mp 102–103° (lit.[1] 102–103°), mp 114–116° (lit.[1] 114–116°), respectively.

The 3-chloro-1,5-naphthyridine was obtained pure by the following procedure. A suspension of 1.9 g of the reaction mixture from this reaction in 40 ml of 12% NaOH was heated under reflux for 3 hr, and the resulting solution was continuously extracted with $CHCl_3$. The dried (anhydrous $MgSO_4$) extracts were evaporated to dryness to yield 0.19 g of a white crystalline residue. This material was shown (tlc, gc) to contain 3-chloro-, 4-chloro-, and parent 1,5-naphthyridine. The 4-chloro-1,5-naphthyridine was removed by heating the reaction mixture in methanolic CH_3ONa (50 ml, 1.00 g of CH_3ONa) for 4 hr. After removal of the solvent, the residue was dissolved in 20 ml of water and the solution was continuously extracted with $CHCl_3$. The contents of the $CHCl_3$ extracts were then placed on an alumina column (neutral grade III, 30 g) and the 3-chloro-1,5-naphthyridine (**3**) was eluted with 12% ether–hexane. In this manner, 53 mg of compound **3** (mp 90.5–91°) was obtained. This compound is identical with the 3-chloro-1,5-naphthyridine obtained by the Eisch procedure (*vide infra*). The per cent yields of compounds **4**, **3**, **2**, and 1,5-naphthyridine are 42.8, 2.6, 33.8, and 0.04%, respectively. The relative percentages of the four compounds obtained are listed in Table I. Essentially the same amounts of all of these compounds are also obtained when Brown's procedure, utilizing PCl_5–$POCl_3$, is employed.

Meisenheimer Reaction of 1,6-Naphthyridine 1-Oxide (5).—The 1-oxide **5** was prepared by the method described in ref 3 except that the excess H_2O_2 was decomposed as described in our preparation of 1,5-naphthyridine 1-oxide. When 1,6-naphthyridine 1-oxide (100 mg, 0.77 mm) was treated with $POCl_3$ for 2 hr and the reaction mixture was worked up as described for the 1,5-naphthyridine 1-oxide reaction, 96 mg of reaction products was obtained.

Tlc and gc (same conditions as described above) showed the presence of 1,6-naphthyridine, 3-chloro- (**7**), 4-chloro- (**8**), and 2-chloro-1,6-naphthyridine (**6**) in the relative percentages listed in Table I. The retention times on gc and the melting points of the compounds in the order mentioned are 11.9 min, 16.7 min (103–103.5°), 17.6 min [90° (lit.[9] 90°)], and 19.4 min [88–89° (lit.[3] 88°)]. The per cent yields of the compounds, in the order parent, **7**, **8**, and **6**, are 1.9, 9.1, 15.2, and 50.2%, respectively.

Formation of 2- (9) and 4-Methoxy-1,6-naphthyridine (10).—In order to ascertain that hydrolysis of neither the 2- nor the 4-chloro-1,6-naphthyridine takes place during the work-up, the procedure was modified in one experiment by "decomposing" the reaction products with methanol in place of water. The resulting methanolic solution was then refluxed in the presence of 500 mg of CH_3ONa for 4 hr. Evaporation of the reaction mixture afforded a solid residue. This residue was dissolved in 20 ml of water and the resulting solution was continuously extracted with $CHCl_3$. The dried (anhydrous $MgSO_4$) extracts were evaporated to dryness to afford 80 mg of products. An nmr spectrum of a $CDCl_3$ solution of this mixture was a composite of 4-methoxy-, 2-methoxy-, and 3-chloro-1,6-naphthyridine, along with traces of the parent compound. This composite spectrum was analyzed by comparison with suitable authentic samples.[9] The relative proportions of the component thus obtained are listed in Table I.

3-Chloro-1,5- and -1,6-naphthyridine (3 and 7).—Into an efficiently stirred solution of 130 mg (1 mmol) of the appropriate naphthyridine in 30 ml of CCl_4 cooled to 5° was bubbled Cl_2 gas for 15 min. The resulting mixture containing a white precipitate was heated to reflux and 180 mg of pyridine dissolved in 5 ml of CCl_4 was added over a 15-min period. After heating for an additional 24 hr, the cooled reaction mixture was filtered and the collected solid was digested with 10% sodium hydroxide (25 ml) for 1 hr. The solution was then extracted with CH_2Cl_2 and the extract was combined with the $CHCl_3$ filtrate. The combined solutions were evaporated *in vacuo* affording a tan solid.

Gas chromatographic separation under the conditions described for the separation of the Meisenheimer reaction products afforded the following compounds.

3-Chloro-1,5-naphthyridine: 16 mg, 10% yield, mp 90.5–91°. *Anal.* Calcd for $C_8H_5N_2Cl$: C, 58.37; H, 3.06; N, 17.02. Found: C, 58.49; H, 3.20; N, 17.22.

3,7-Dichloro-1,5-naphthyridine: 8 mg, 4% yield, mp 150–52°. *Anal.* Calcd for $C_8H_4N_2Cl_2$: C, 48.03; H, 2.01; N, 14.01. Found: C, 47.89; H, 2.11; N, 14.20.

3-Chloro-1,6-naphthyridine: 24 mg, 15% yield, mp 103–103.6°. *Anal.* Calcd for $C_8H_5N_2Cl$: C, 58.37; H, 3.06; N, 17.02. Found: C, 58.26; H, 2.89; N, 16.93.

No attempt was made at this point to isolate two other chloro-1,6-naphthyridines, presumably the 8-chloro and the 3,8-dichloro derivatives. Detailed studies of the Eisch chlorination procedure on numerous naphthridines along with analyses of their pmr spectra will be the subject of a forthcoming publication.

Registry No.—**1**, 27305-48-2; **3**, 7689-63-6; **5**, 23616-39-9; **7**, 28795-77-9; 3,7-dichloro-1,5-naphthyridine, 28795-78-0.

Piperidinodechlorination of Chloronitronaphthalenes. A Further Comparison between Nitro-Group and Aza-Group Activation[1]

GABRIELLO ILLUMINATI,* GIANCARLO SLEITER,* AND MAURIZIO SPERANZA

Department of Chemistry, The University of Rome, 00185 Rome, Italy, and Centro C.N.R. dei Meccanismi di Reazione, Rome, Italy

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The importance of specific solvation (H bonding) in the nucleophilic reactions of N-heteroaromatic substrates has been stressed in recent studies[2–5] and was suggested[3,5] to be a major differential feature between aza- and nitro-group activation, on the basis of the solvent effects observed in the reaction of 2- and 4-chloroquinoline with piperidine. The most appropriate comparison with the latter reaction requires the investigation of the nitronaphthalene analogs, which is the object of the present note.

The kinetics of the piperidinodechlorination of 2- and 4-chloro-1-nitronaphthalene have been studied in toluene, ethyl acetate, piperidine, methanol, and dimethyl sulfoxide. The reactions in ethyl acetate were followed as long as the piperidinolysis of the solvent[3,6] remained kinetically unimportant. Possible solvolysis in methanol solution[7] could be excluded either by product analysis or by an indirect method.[8] The reactions of the compounds investigated yielded the expected products and followed regular second-order or pseudo-first-order kinetics, in agreement with previous studies.[9] With the reaction of 4-chloro-1-nitronaphthalene in toluene, initially linear kinetic plots eventually became erratic after some 50–60% reaction, probably because thermal decomposition of the substrate occurred.[10] The second-order rate constants at varying temperatures and the activation parameters for 2- and 4-chloro-1-nitronaphthalene are collected in Table I.

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TABLE I

SOLVENT EFFECTS ON THE PIPERIDINODECHLORINATION REACTION AT 90°

Substrate	Solvent	10^5k[a]	E_{act}[b]	$-\Delta S^{\ddagger}$[c]
2-Chloro-1-nitronaphthalene[d]	Toluene	25.7	13.9	39
	Ethyl acetate	38.0	12.0	44
	Methanol	16.0	18.1	29
	Piperidine	46.6[e]	11.8	43
	Dimethyl sulfoxide	345[e]	10.8	42
4-Chloro-1-nitronaphthalene[f]	Toluene	0.265[e]	13.7	49
	Ethyl acetate	5.55[e]	9.95	53
	Methanol	27.4	14.4	38
	Piperidine	7.73[e]	9.08	54
	Dimethyl sulfoxide	1550[e]	10.0	41

[a] k = rate constants in l. mol^{-1} sec^{-1}. [b] In kcal/mol. [c] In eu. [d] Additional 10^5 k values (temp, °C): in toluene, 4.48 (60.0), 8.34 (70.0), 14.5 (80.0); in ethyl acetate, 22.4 (80.0), 55.5 (100.0), 87.5 (110.0); in methanol, 3.74 (70.0), 7.73 (80.0), 30.7 (100.0); in piperidine, 0.211 (0.0), 0.461 (10.0), 0.744 (17.0), 1.27 (25.0), 3.44 (40.0); in DMSO, 9.62 (20.0), 18.0 (30.0), 32.5 (40.0), 53.0 (50.0). [e] Calculated from Arrhenius parameters. [f] Additional 10^5 k values (temp, °C): in toluene, 2.57 (140.0), 3.37 (150.0), 5.42 (160.0), 11.0 (180.0); in ethyl acetate, 15.9 (120.0), 21.8 (130.0), 29.6 (140.0), 38.7 (150.0); in methanol, 15.5 (80.0), 47.7 (100.0), 76.2 (110.0); in piperidine, 0.382 (20.0), 0.661 (30.0), 1.06 (40.0), 1.63 (50.0); in DMSO, 56.0 (20.0), 103 (30.0), 163 (40.0), 280 (50.0).

TABLE II

DIFFERENTIAL SOLVENT EFFECTS IN THE NITRONAPHTHALENE AND AZANAPHTHALENE SYSTEMS

	Toluene (T)	Ethyl acetate (EA) k_{EA}/k_T	Piperidine (P) k_P/k_T	Methanol (M) k_M/k_T	Dimethyl sulfoxide (DMSO) k_{DMSO}/k_T
	Solvent Effects Relative to Toluene				
2-Chloro-1-nitronaphthalene (I)[a]	1	1.48	1.81	0.62	13.0
2-Chloroquinoline (II)[b]	1	2.47	7.68	6.02	54.8
4-Chloro-1-nitronaphthalene (III)[a]	1	21.8	29.1	103	5850
4-Chloroquinoline (IV)[b]	1	11.3	16.9	458	1700
	Relative Activating Power				
I *vs.* II, k_{NO_2}/k_{aza}[c]	63	38	15	6.5	15
III *vs.* IV, k_{NO_2}/k_{aza}[c]	51	94	88	11	176

[a] At 90.0°. [b] Values at 86.5°, taken from ref 3. [c] Evaluated from the rate constants at 86.5°; values for the quinolines were taken from ref 3.

A comparison of 2- and 4-chloro-1-nitronaphthalene with 2- and 4-chloroquinoline, respectively, with regard to solvent effects on reactivity, is reported in Table II. As expected, with both types of substrates the reactivities in the diverse solvents are less broadly spaced in the 2-chloro than in the 4-chloro isomer, as a result of a "built-in" solvation effect.[11] This effect is particulary strong with 2-chloro-1-nitronaphthalene [in fact, it is stronger than with either 2-chloroquinoline (α-aza effect) or 2-chloro-1-nitrobenzene[12]] and is most evident when comparing solvents of markedly different polarity (see, for example, the k_{DMSO}/k_T values in Table II).

In the aprotic solvents, the reactivity is in the order DMSO > ethyl acetate > toluene, as expected[13] from the polarity of the medium. This order is analogous to the one observed with the quinoline compounds. Despite its basic character, piperidine is only a slightly "faster" solvent than ethyl acetate of the same polarity. This observation suggests that the basic properties of DMSO[14] are probably not a major factor in the rate-enhancing effect of this solvent, which is likely to solvate ionic transition states.[15] It should be noted that the reaction of the 4-chloro isomer in this solvent is accompanied by a relatively high entropy of activation.

In contrast, an important difference between the two types of substrates is observed in methanol. Whereas the reactivity in the aprotic solvents *relative* to toluene is greater for 4-chloro-1-nitronaphthalene than for 4-chloroquinoline (Table II), in methanol solution the reverse is true. This confirms the different importance of the hydroxylic solvent in the two types of substrates, as suggested in a previous comparison.[3] We attribute this difference to a greater rate-enhancing H-bonding solvent–substrate interaction in the case of the quinoline compound. In the nitro-activated compounds such an interaction is so much weaker as to become overshadowed in the 2-chloro isomer by other factors; in this case, the reaction rate in methanol is lower than in toluene solution (k_M/k_T = 0.62). An inverted order of this kind has been noted previously under similar conditions,[16] but is not found with 2-chloroquinoline, where the influence of the solvent may still include appreciable specific solvation with the heterocyclic nitrogen. A major opposing factor tending to lower the overall reactivity in methanol solution is the reduced effective nucleophilic power of piperidine due to H-bonding solvent–nucleophile interaction.[17] This effect may be responsible for the observed changes in the activation parameters, *i.e.*, higher energies and entro-

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pies of activation for the reactions in methanol solution relative to other solvents.

In the light of the reactivity pattern displayed in methanol solution, the similar behavior of piperidine to that of ethyl acetate, as noted above, indicates that the former solvent is not sufficiently protic to promote any appreciable specific solvent–substrate interaction.

Since the reaction rates are different functions of the solvent depending on both the activating group and its position relative to the reaction site, the activating power of the nitro group relative to that of the aza group also depends on the solvent, as shown by the k_{NO_2}/k_{aza} ratios reported in Table II, which display variations of more than one order of magnitude. In particular, the lowest values were obtained for the reactions in methanol solution, where a major contribution to this effect comes from the greater H-bonding interaction observed with the N-heteroaromatic substrates. It is of interest to note that, on comparing the reactivity of the nitrobenzene with that of the pyridine series in methanol, the k_{NO_2}/k_{aza} ratio is greater at the ortho than at the para positions,[18] but the reverse is true for the corresponding fused-ring systems considered here.

Experimental Section

Materials.—2-Chloro-1-nitronaphthalene, mp 95.5–96.5° (lit.[16] mp 99°), and its 4-chloro-1-nitro isomer, mp 84.5–85.5° (lit.[19] mp 87°), were prepared from the appropriate nitronaphthylamines by the methods of Hodgson and Walker[20] and of Bassilios and Shawky,[21] respectively. The products expected from the reactions under kinetic investigation were prepared by refluxing the chloronitronaphthalenes in neat piperidine for about 2 hr: 4-nitro-1-piperidinonaphthalene, mp 75–76° (lit.[22] mp 76°), and 1-nitro-2-piperidinonaphthalene, mp 63.5–64° (red needles from methanol).

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.3; H, 6.3; N, 10.9. Found: C, 70.5; H, 6.4; N, 11.0.

Dimethyl sulfoxide (Erba-RP) was purified by allowing it to percolate slowly in the dark through a 1-m column filled with molecular sieve "Bayer T10" (Schuchardt), water content *ca.* 30 ppm. Methanol,[23] piperidine,[24] toluene,[25] and ethyl acetate[26] were purified as in the given references.

Product Analyses.—The mixtures from the kinetic measurements were analyzed by tlc. Single spots were found except in the high-temperature reactions of 4-chloro-1-nitronaphthalene in toluene solution after 57% reaction at 140°, 62% at 150°, 69% at 160°, and 84% at 180°. No further investigation on the by-products was made.

Kinetic Measurements.—The general procedure used has been described previously.[3,23,24] The reaction rates were followed by analyzing for the displaced chloride ion. Samples were quenched in 10 ml of 2 *N* nitric acid (3 *N* when piperidine was the solvent); sufficient acetone was added to dissolve any organic material; and the homogeneous solutions were titrated by the potentiometric method.[3,27] The rate constants were obtained graphically from second-order or pseudo-first-order plots. All the second-order rate constants were corrected for the thermal expansion of the solvent. Activation energies and entropies were calculated from the k values at four or five temperatures, using the least-squares method. Values of k are accurate to ±2.5% or better, energies of activation to ±0.4 kcal/mol, and values of $\Delta S^{\pm}$ to ±1 unit.

Registry No.—I, 4185-63-1; II, 612-62-4; III, 605-61-8; IV, 611-35-8; 1-nitro-2-piperidinonaphthalene, 7711-41-3.

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Reduction of Diazonium Fluoroborates in Dimethylformamide, Catalyzed by Rhodium Complexes

GERARD S. MARX

Department of Organic Chemistry, Hebrew University, Jerusalem, Israel

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I wish to report on a novel reduction of aromatic diazonium fluoroborates to arenes by DMF, a reaction which is catalyzed by $RhCl(CO)(PPh_3)_3$ (RCCP) and $RhCl(PPh_3)_3$ (RCTP) at room temperature and at 80°

$$ArN_2^+BF^{-4} \xrightarrow{\text{Rh complex, DMF}} ArH$$

Electron-attracting substituents appear to favor this reduction, whereas, in the one observed case of a strong electron-donating substituent (OMe), no reduced product was observed. Ortho substitution (NO_2, CO_2Et, Me) did not appear to affect significantly the yield of reduced product. In fact, in the case of the 2-methyl-4-nitrobenzenediazonium salt, the reduction competed successfully with the spontaneous cyclization to 6-nitroindazole.[1]

Addition of small amounts of water or formic acid to the DMF lowered the yields of the reduction products. Reduction was not observed in the absence of the Rh complex.

Only traces of fluorinated compounds were detected in the products by elemental analysis, vpc, or tlc, whether the reactions were carried out at room temperature or at 80°[2] (see Table I).

A few other solvents were tested, *viz.*, dimethylacetamide (DMA), acetonitrile, and, in one case, formamide. Only in formamide was the same reduction process observed. This points to the formyl hydrogen of DMF or formamide as the source of the hydrogen involved in the reduction.[3] An ir study of RCCP has shown that a hydrido–rhodium complex may be an intermediate in this reaction; a solution of RCCP in DMF develops, in addition to the C=O peak at 1970 cm^{-1},[4] a peak at 2100 cm^{-1}, which is transformed within 24 hr into a broad envelope with a maximum at 2150 cm^{-1}. On the other hand, a similar solution of RCCP in DMA showed only the initial peak at 1970

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(2) In experiments with the diazonium fluoroborate derived from ethyl-3-amino-2-naphthoate in DMF with RCCP for 2 days at room temperature, the product (30% yield) after work-up was a mixture of 17% 2-naphthoic acid and 13% 3-fluoro-2-naphthoic acid. This result agrees with a previous report from this laboratory [J. Blum, *Israel J. Chem.*, **4**, 158 (1966)] in which also *p*-tolyl- and 1-naphthyldiazonium fluoroborates reacted with RCTP in DMF to give *p*-fluorotoluene and 1-fluoronaphthalene. We are unable, at this time, to rationalize this divergence in results.
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