in 50 mL of 1 N sodium deuteroxide in D_2O was heated at reflux for 1 h. The solution was cooled to 25 °C, extracted with methylene chloride, dried over anhydrous sodium sulfate, and filtered through a layer of anhydrous magnesium sulfate. The solvent was evaporated and the residue vacuum distilled to give 3.43 g (64%) of **12**: bp 37–38 °C (0.3 mmHg); NMR ($CDCl_3$) δ 3.34 (s, 3 H), 5.51 (s, 2 H); IR (film) 2940, 2825, 2240, 2190, 2110, 1454, 1386, 1345, 1235, 1090, 920, 822, 700 cm^{-1}; MS, *m/z* (relative intensity) 108 (M^+ + 1, 0.3), 107 (M^+ 3), 106 (0.5), 88 (2.1), 84 (19), 76 (8.6), 51 (17), 49 (50.6), 48 (7), 47 (12), 46 (39), 45 (100), 44 (28).

Methyl-d_3-amine Hydrochloride (14). A solution of 653 mg (6.1 mmol) of **12** in 12 mL of methanol at 0 °C was saturated with hydrogen chloride. The ice bath was removed, and the solution was refluxed for 2 h and then evaporated to dryness under vacuum. The residue was taken up in methanol, treated with charcoal, and filtered through Celite. Evaporation of the solvent followed by recrystallization of the residue from ethanol–acetone gave 381 mg (88%) of **14**, mp 215–220 °C. Further characterization was carried out on the *p*-toluenesulfonamide derivative: mp 74–75 °C; NMR ($CDCl_3$) δ 2.42 (s, 3 H), 4.45 (br, 1 H), 7.52 (q, 4 H); IR (solid film) 3280, 3061, 2980, 2340, 2080, 1930, 1820, 1598, 1495, 150, 1410, 1318, 1160 cm^{-1}.

Conversion of *N*-Nitroso-*N*-methylmethoxymethylamine (10) to Methylamine Hydrochloride. A solution of 615 mg (5.9 mmol) of **10** in 12 mL of methanol at 0 °C was saturated with hydrogen chloride. The solution was heated at reflux for 2 h and then evaporated to dryness on a rotary evaporator. The residue was taken up in 20% aqueous sodium hydroxide and the resulting solution distilled into a receiver containing 1 mL of 12 N hydrochloric acid. Evaporation of the solvent under vacuum gave 397 mg (97%) of methylamine hydrochloride, mp 225–227 °C (lit.[17d] 227–228 °C).

Conversion of *N*-Nitroso-*N*-ethylmethoxymethylamine (13) to Ethylamine Hydrochloride. A methanolic solution of 441 mg (3.3 mmol) of **13** was treated with hydrogen chloride as described above to give 264 mg (98%) of ethylamine hydrochloride: benzamide, mp 68–70 °C (lit.[16] benzamide mp 71 °C).

Reduction of 1 with Aluminum–Nickel Alloy. Adapting the method of Lunn et al.[13] to this type of compound, a partial solution of 122 mg (1.03 mmol) of **1** in 10 mL of 0.5 N aqueous potassium hydroxide was treated with 500 mg of aluminum–nickel catalyst and stirred at 25 °C. Aliquots of 1 μL were analyzed by direct injection into a gas–liquid chromatograph fitted with a 10% Carbowax 20M + 2% KOH column at 50 °C and a flow rate of 20 mL/min. The starting nitrosamine had completely disappeared after 1 h at 25 °C. A known amount of 1-butanol was added as an internal standard for the quantification of the flame-ionization detector peaks. The GLC analysis indicated a 91% yield of methylethylamine. The aqueous solution was distilled and the amine trapped in a receiver containing 1 mL of hydrochloric acid, giving 87 mg (89%) of methylethylamine hydrochloride: NMR (D_2O) δ 1.28 (t, 3 H), 2.26 (d, 3 H), 3.09 (q, 2 H).

Reduction of 3 with Aluminum–Nickel Alloy. This reaction was carried out on 100 mg (0.76 mmol) of **3** as described above. GLC analysis gave a quantitative yield of diethylamine. The amine was isolated as the hydrochloride in 86% yield: mp 220–225 °C (lit.[17e] mp 223.5 °C); NMR (D_2O) δ 1.3 (t), 3.09 (q).

Acknowledgment. This work was supported by Contract No. NO1-CO-23909 with the National Cancer Institute, NIH, Bethesda, MD. The low- and high-resolution mass spectra were recorded by M. Shorter and Dr. Y. Tondeur, respectively.

Registry No. **1**, 61738-05-4; **2**, 4549-40-0; **3**, 61738-03-2; **4**, 85894-35-5; **5a**, 85894-36-6; **5b**, 85894-37-7; **6**, 85894-38-8; **7**, 85894-39-9; **8**, 85894-40-2; **9**, 85894-41-3; **10**, 39885-14-8; **11a**, 85894-42-4; **11b**, 85894-43-5; **12**, 85894-44-6; **13**, 61738-04-3; **14**, 7436-22-8; **14** *p*-toluenesulfonamide derivative, 85894-45-7; MeI, 74-88-4; MeCHO, 75-07-0; $(Me)_2CO$, 67-64-1; BzBr, 100-39-0; EtI, 75-03-6; *n*-PrI, 107-08-4; $EtNH_2$·HCl, 557-66-4; $(Me)_2CHNH_2$·HCl, 15572-56-2; $MeCHOHCH_2NH_2$·HCl, 7780-04-3; $(Me)_2COHCH_2NH_2$·HCl, 30533-50-7; $Ph(CH_2)_2NH_2$, 64-04-0; $Me(CH_2)_2NH_2$·HCl, 556-53-6; $Me(CH_2)_3NH_2$·HCl, 660-68-4; $MeNH_2$, 74-89-5; MeOH, 67-56-1; MeNHEt·HCl, 624-60-2.

Photostimulated Reactions of 2-Bromopyridine and 2-Chloroquinoline with Nitrile-Stabilized Carbanions and Certain Other Nucleophiles[1a]

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Potassiophenylacetonitrile (**2**) reacts with 2-bromopyridine (**1**) and 2-chloroquinoline (**4**) via the $S_{RN}1$ mechanism when the reactants are exposed to near-UV light in liquid NH_3. Potassioacetonitrile (**6**) reacts similarly with **1** and **4** upon photostimulation; however, the photo-$S_{RN}1$ reaction with **1** is accompanied by S_NAr2 amination which becomes the major reaction in the dark or in the presence of di-*tert*-butyl nitroxide. Substrate **4** undergoes competing S_NAr2 amination with amide ion to form 2-aminoquinoline (**10**) and S_N(ANRORC) reactions with both amide ion and carbanion **6** to form 3-methylquinazoline (**11**) and 2-methyl-3-cyanoquinoline (**12**), respectively. Formation of **12** becomes the major pathway in reactions between **4** and **6** carried out in the dark. 4-Picolylpotassium (**14**) reacts with **1**, **4**, and 4-bromopyridinium chloride (**16**) under photostimulation to form the appropriate dihetarylmethanes, along with the corresponding amino heterocycles. Amination of **1**, **4**, and **16** predominates when these reactions are carried out in the dark. Ammonium thiophenoxide (**20**) undergoes a slow photo-$S_{RN}1$ reaction with **1** but fails to produce the expected 2-quinolyl phenyl sulfide with **4** after 2 h of irradiation. Potassium salts of acetylene, phenylacetylene, and phthalimide do not react with **1** or **4** after 2 h of exposure to near-UV light.

The discovery that ketone enolates displace halide from 2-chloroquinoline (**4**)[2,3] and halopyridines[4] by the $S_{RN}1$ mechanism[5] when liquid NH_3 solutions of the reactants are exposed to near-UV light prompted us to examine the

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Table I. Reactions of 1 and 4 with Carbanion 2

expt	reactant	time, min	conditions[a]	product	yield,[b] %
1	1	15	dark	3	nil[d]
2	1	15	UV	3	88
3	1	4	UV	3	66
4	1	4	UV[c]	3	18
5	4	15	dark	5	<10[e]
6	4	15	UV	5	88[f]
7	4	15	UV[c]	5	<10[g]

[a] Photostimulated reactions are designated as UV. [b] Unless noted otherwise, yields were determined by GC analysis, and only unreacted starting materials were present along with the observed substitution product. [c] Reaction inhibited by 10 mol % (based on reactant) of DTBN. [d] Substrate 1 was recovered in 98% yield. [e] Substrate 4 was recovered in 90% yield. [f] Isolated yield. [g] Substrate 4 was recovered in 78% yield.

Table II. Reactions of 1 with Carbanion 6

expt[g]	condition[a,b]	product ratio (7/8)[c,d]
8	UV	4.7
9	UV[e]	2.05
10	UV[f]	0.49
11	dark	0.025
12	dark[f]	0.01

[a] All reactions were carried out by using 20 mmol of 1, 75 mmol of KNH_2, and 75 mmol of acetonitrile in 300 mL of liquid NH_3. [b] Photostimulated reactions are designated as UV. [c] Determined by GC analysis. [d] In all experiments 1 was completely consumed to form only 7 and 8. [e] Only one of four reactor lamps was used. [f] DTBN (10 mol % based on 1) was present in the reaction mixtures. [g] The time was 15 min in all cases.

possible participation of nitrile-stabilized carbanions and several other types of nucleophiles in photostimulated $S_{RN}1$ reactions with 2-bromopyridine (1) and 4. Earlier reports[6] concerning reactions of 1 and 4 with carbanions derived from nitriles either contained no discussion of mechanism or implied that displacement takes place by a biomolecular addition–elimination (S_NAr2) mechanism. More recently, Rossi and co-workers reported that potassioacetonitrile (6) undergoes photostimulated reaction with 2-chloropyridine to form (2-pyridyl)acetonitrile (7) via the $S_{RN}1$ mechanism.[7] Reactions of carbanion 6 with 1- or 2-chloronaphthalene, 4-chlorobiphenyl, and 4-bromobenzophenone also proceed in a straightforward manner by the same mechanism.[7] However, halobenzenes, phenyl diethyl phosphate, and phenyltrimethylammonium ion react with nitrile carbanions under $S_{RN}1$ conditions to give mixtures

Table III. Reactions of 4 with Carbanion 6

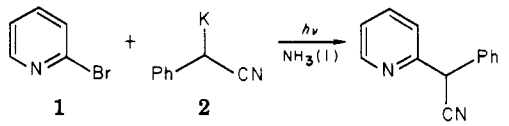
expt	conditions[a-c]	product composition,[d] % 9	10	11	12
13	UV, 1:3.75:3.75	50	e	1	2
14	UV, 1:3.75:7.50	19	e	e	5
15	UV, 1:3.75:11.25	15	e	e	e
16	dark, 1:3.75:3.75	d	e	e	37
17	dark, 1:4:5	4	e	e	18
18	dark, 1:4:7.5	3	e	e	9
19	UV, THF, KH[f]	31	e	e	9[g]

[a] All reactions were conducted in liquid NH_3 for 15 min unless noted otherwise. [b] Photostimulated reactions are designated as UV. [c] The molar ratio of 4/KNH_2/acetonitrile is given. [d] Yields determined by GC analysis. [e] Trace amounts detected by GC but not analyzed quantitatively. [f] The molar ratio ratio of 2/6 was 1.5. [g] Product 13 was isolated in 16% yield along with 32% of recovered 4.

consisting of α-phenylated nitriles, alkylbenzenes, and products arising through coupling of benzylic radicals derived from decyanation of intermediate radical anions.[5a,8,9]

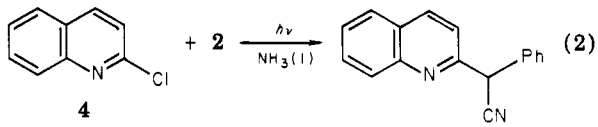
Results

Exposure of substrates 1 or 4 to 3.75 mol equiv of potassiophenylacetonitrile (2) in liquid NH_3 for 15 min afforded mainly recovered starting materials when the reaction mixture was protected from light (Table I, expts 1 and 5). When a similar reaction involving 1 and 2 (eq 1)



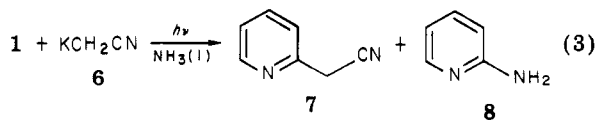
1 2 3 (1)

was carried out under irradiation at 350 nm, nitrile 3 was produced in yields of 88% and 66% after irradiation for 15 and 4 min, respectively (expts 2 and 3). Addition of the radical scavenger di-*tert*-butyl nitroxide (DTBN)[10] inhibited the photostimulated reaction to the extent that only 18% of 3 was formed after 4 min (expt 4). Photostimulation of a reaction mixture containing substrate 4 and carbanion 2 (eq 2) afforded nitrile 5 in 88% yield after 15 min (expt 6). Inhibition of this reaction with DTBN resulted in 78% recovery of 4 (expt 7).



4 5 (2)

Photostimulated reaction of 1 with potassioacetonitrile (6), prepared from equimolar amounts of KNH_2 and acetonitrile in liquid NH_3, produced 7 (eq 3) in 75% yield,



6 7 8 (3)

(1) (a) Supported by the National Science Foundation Grants CHE 77-13317 and CHE 80-22538. (b) Abstracted in part from the PhD dissertation of M. P. Moon, Virginia, Polytechnic Institute and State University, Dec 1978.

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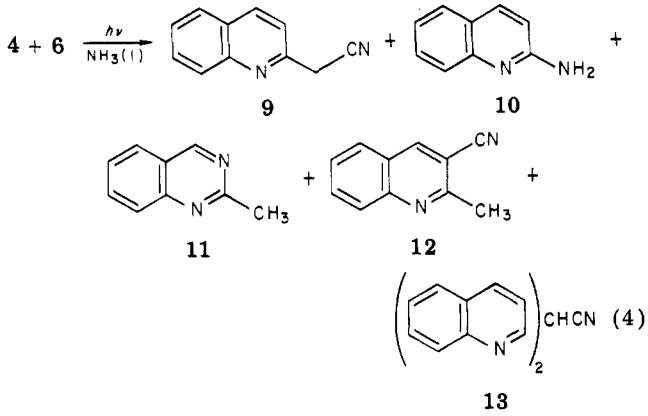
Table IV. Photostimulated Reactions of Carbanion 14 with Substrates 1, 4, and 16

expt	substrate	molar ratios[a]	products (% yield)
20	1	1:4:5	15 (24), 8 (67)
21	1	1:3.75:3.75	15 (37), 8 (53)
22	1	1:5:4	15 (47), 8 (46)
23	16	1:5:5	17 (78), 8 (<1)
24	4	1:5:4	19 (24),[c] 10 (49)[c]

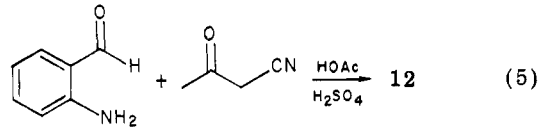
[a] Molar ratio of substrate/4-picoline/KNH_2. [b] Determined by GC analysis unless otherwise indicated. [c] Isolated yield.

along with 16% of 2-aminopyridine (8) (Table II, expt 8). The ratio of 7/8 was reduced from 4.7 in this initial experiment to 2.05 when the reaction mixture was irradiated at lower light intensity (expt 9). In expt 10, DTBN inhibition of a fully illuminated reaction afforded a 7/8 ratio of 0.49. When the reaction was conducted in total darkness, the ratio 7/8 declined to 0.025 (expt 11). A 15-min dark reaction in the presence of DTBN gave a 7/8 ratio of 0.01 (expt 12). It is clear from these experiments that low light intensity and/or DTBN unequivocally favor production of 8 at the expense of 7.

Photostimulated reaction of 4 with carbanion 6 (eq 4)

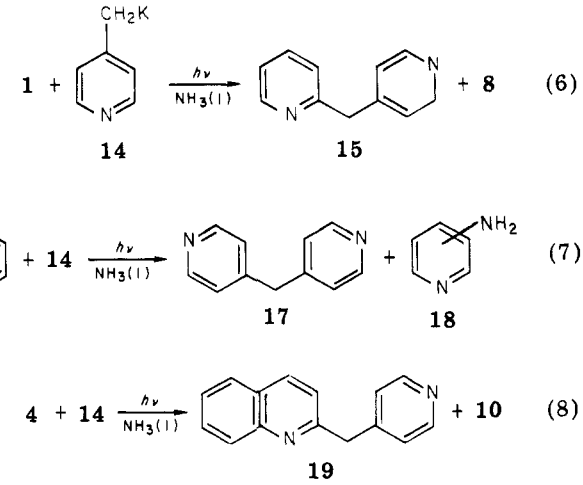


afforded 50% of the expected (2-quinolyl)acetonitrile (9), traces of 2-aminoquinoline (10), 1% of 2-methylquinazoline (11), 2% of 3-cyano-2-methylquinoline (12), bis(2-quinolyl)acetonitride (13), and polymeric material containing cyano groups (Table III, expt 13). In the absence of photostimulation the major characterizable product was 12 (eq 5; expts 16–18). The identity of this unexpected



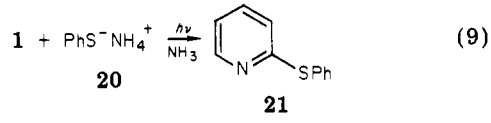
product was confirmed by comparison of its spectral properties with an authentic sample synthesized from *o*-aminobenzaldehyde and cyanoacetone. Attempts to increase the equilibrium concentration of carbanion 6 by using higher acetonitrile/KNH_2 ratios resulted in lower yields of tractable products in both photostimulated and dark reactions (expts 14, 15, 17, 18). When 6 was prepared from acetonitrile by means of potassium hydride in THF and then allowed to react with 4 in this solvent, a less complex array of products and a better material balance was obtained. Thus, irradiation for 1 h afforded 31% of 9, 9% of 12, 16% of 13, and 32% of unreacted 4 (expt 19).

We next turned our attention to reactions of 1, 4, and 4-bromopyridinium chloride (16) with 4-picolylpotassium (14) in liquid NH_3. Treatment of these substrates with 14 under maximum irradiation for 15 min resulted in their complete consumption to afford mixtures of the expected dihetarylmethanes 15, 17, and 19 (see eq 6–8), along with



the corresponding amino derivatives 8, 10, and 18 (Table IV, expts 20–24). Reactions conducted in the dark or with full illumination in the presence of DTBN gave predominately amines 8, 10, and 18. The yield of 15 obtained in photoassisted reactions improved, while the yield of 8 decreased when the ratio of 4-picoline/KNH_2 was increased (expts 20–22). The best yield (78%) of dihetarylmethane obtained in this series of reactions was observed with substrate 16 (expt 23).

Exposure of 1 to excess ammonium thiophenoxide (20) in the dark returned only starting material. The photostimulated reaction of 1 with 20 was more sluggish than those observed with nitrile and picolyl carbanions, giving 21% of 2-pyridyl phenyl sulfide (21) after 90 min of irradiation (eq 9). Treatment of 4 with excess 20 lead to an



83% recovery of 4 after 90 min of irradiation; 2-quinolyl phenyl sulfide could not be detected.

Attempted reaction of 1 with dimsylpotassium[11] in liquid NH_3 afforded none of the anticipated $S_{RN}1$ product. Instead, 1 was consumed within 15 min in both dark and illuminated reactions to give 8 (eq 10) and a minor, unidentified product.

$$1 + CH_3SOCH_2K \xrightarrow[NH_3(l)]{h\nu} 8 \qquad (10)$$

Attempted photostimulated reactions of 1 and 4 with the potassium salts of acetylene, phenylacetylene, and phthalimide in liquid NH_3 all failed to yield the expected substitution products. In each case 1 was recovered in good yield after 120 min of irrdiation.

Discussion

The response to near-UV light and the inhibitory action of DTBN provide strong support for operation of the $S_{RN}1$ mechanism in successful reactions of substrates 1, 4, and 16 with nucleophiles 2, 6, 14, and 20. The general features of this radical-chain process are illustrated in Scheme I,

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Scheme I

$$\text{Het-X} + \text{N}^- \rightarrow [\text{Het-X}]^{-}\cdot + \text{N}\cdot \quad (11)$$

$$[\text{Het-X}]^{-}\cdot \rightarrow \text{Het}\cdot + \text{X}^- \quad (12)$$

$$\text{Het}\cdot + \text{N}^- \rightarrow [\text{Het-N}]^{-}\cdot \quad (13)$$

$$[\text{Het-N}]^{-}\cdot + \text{Het-X} \rightarrow \text{Het-N} + [\text{Het-X}]^{-}\cdot \quad (14)$$

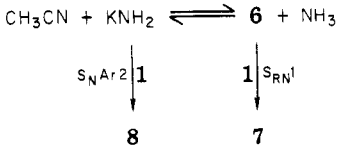
where Het-X and N^- represent the appropriate substrate and nucleophile, respectively. It is assumed that initiation (eq 11) is effected by photoassisted electron transfer from the nucleophilic reactant to the substrate, perhaps via a charge-transfer complex.[5b,12] Equations 12–14 constitute a propagation cycle, for which there is ample precedent.[5]

In contrast to reactions of 1 and 4 with ketone enolates, where straight forward $S_{RN}1$ reactions occur upon irradiation and starting materials are recovered in good yields from dark and DTBN-inhibited experiments, the present nucleophiles lead to more complicated results. The nature of several of the reactions reported in this study is markedly influenced by the acidity of the carbon acid used as precursor to the respective carbanion nucleophile[13–16]. For example, the most acidic carbanion progenitor, phenylacetonitrile, is apparently completely converted to its conjugate base, **2**, by KNH_2 in NH_3. As a result, there is not amide ion present in equilibrium with **2** to react with substrates 1 or 4 even when the $S_{RN}1$ reactions are suppressed by lack of irradiation or by DTBN. It is apparant from the results summarized in Table II that acetonitrile is not completely ionized to form carbanion **6** and that 2-aminopyridine (**8**) is produced via an S_NAr_2 reaction of 1 with amide ion in equilibrium with **6**, while (2-pyridyl)acetonitrile (**7**) arises from a photostimulated $S_{RN}1$ reaction of 1 with **6** (Scheme II). Thus, **7** is the major product obtained under conditions which favor the $S_{RN}1$ process. Formation of **8** in the presence of DTBN or under low-intensity illumination establishes the S_NAr2 pathway for the amination of 1.[17]

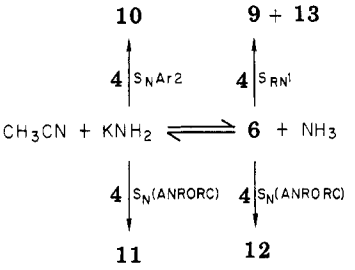
The aminations of 1 and **16**, which accompany $S_{RN}1$ reactions of these substrates with carbanion **14**, and the formation of **8** in attempted $S_{RN}1$ reaction of 1 with dimsylpotassium can be rationalized by similar equilibria.[13]

In reactions of 4 with carbanion **6**, $S_{RN}1$ formation of **9** and **13**, as well as S_NAr2 formation of **10**,[18] is accompanied by ring transformations involving both amide ion[18] and **6**,

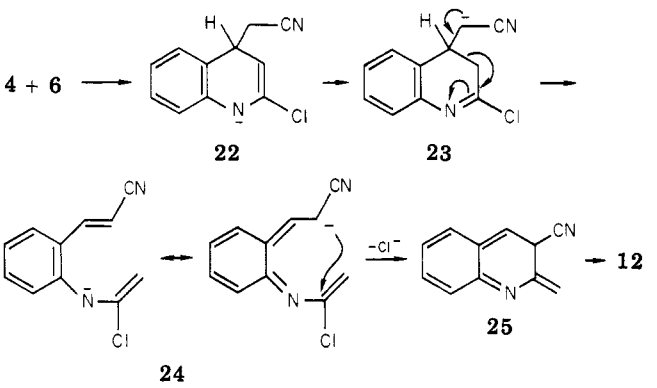
Scheme II



Scheme III



Scheme IV



along with undefined reactions leading to intractable material (Scheme III). On the basis of the fact that dark reactions of KNH_2 in liquid NH_3 with 2-bromoquinoline[18] or 4 form nearly identical mixtures consisting exclusively of **10** and **11** (see Experimental Section), it is clear that generation of these two products in photostimulated reactions occurs by action of residual amide ion on 4. Formation of **11** has been proposed[18] to take place via an $S_N(ANRORC)$[19] mechanism involving initial addition of amide ion to C_4 of the 2-haloquinoline. With this as a model, formation of 1-methyl-3-cyanoquinoline (**12**) can be rationalized by envoking an $S_N(ANRORC)$ pathway involving carbanion **6** as shown in Scheme IV. In this proposed sequence of reactions, **6** attacks C_4 of 4 to form adduct **22**, which can undergo prototropic rearrangement to give **23**. Cleavage of the C_3–C_4 bond of **23**, via what can be regarded as a retro-Michael-type reaction, gives the acyclic intermediate **24**. Ring closure of **24** may then occur by attack of the carbanion center adjacent to the nitrile function on what was formerly C_2 of the quinoline ring. Loss of chloride ion, either concomitantly with carbanion attack or by an addition–elimination process, would produce **25**. A final prototropic shift converts **25** into **12**. Attempts to isolate one or more of the proposed intermediates in its protonated form were unsuccessful, owing to the labile nature of the components of reaction mixtures quenched quickly after addition of 4 to liquid NH_3 solutions of **6**. Such experiments did demonstrate, however, that in typical dark or photostimulated reactions, substrate 4 is no longer present within 1 min of its addition to the carbanion solution. In photoinduced reactions of this

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(13) Although pK_a values for phenylacetonitrile, acetonitrile, and dimethyl sulfoxide (Me_2SO) in NH_3 are not known, the values in Me_2SO obtained by Bordwell and co-workers[14] (21.9, 31.3, and 35.1, respectively) appear on the basis of the results obtained in the present study to be reasonable values for NH_3 solutions. The pK_a of 4-picoline in NH_3 is 29,[15] and the pK_a of NH_3 in NH_3 is 32.5.[16]

(14) See: (a) Matthews, W. S.; Bares, J. E.; Bartmess, K. E.; Bordwell, F. G.; Cornforth, P. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCallum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bardwell, F. G.; Bartmess, J. E.; Drucker, G. E.; Margolin, A.; Matthews, W. S. *Ibid.* **1975**, *97*, 3226. (c) Algrim, D.; Bares, J. E.; Branca, J. C.; Bardwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024. (d) Bardwell, F. G.; Fried, H. F. *Ibid.* **1981**, *46*, 4327.

(15) Zoltewicz, J. A.; Helmick, L. S. *J. Org. Chem.* **1973**, *34*, 658.

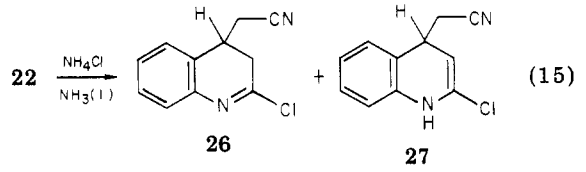
(16) Coulter, L. V.; Sinclair, J. R.; Cole, A. G.; Raper, G. C. *J. Am. Chem. Soc.* **1959**, *81*, 2986.

(17) It should be noted that amination of 2-chloropyridine to form **8** was not observed in photostimulated reactions carried out by Rossi under conditions similar to ours.[7] This could result from the use of more efficient illumination in their experiments or from a lower susceptibility of 2-chloropyridine vs. 1 toward S_NAr2 amination.

(18) den Hertog, H. J.; Buurman, D. J. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 187. It is possible that acetylenic intermediates such as proposed in this reference may also be generated from intermediates **22** or **24** of Scheme IV.

(19) For a recent review of this mechanism, see: van der Plas, H. C. *Acc. Chem. Res.* **1978**, *11*, 462.

duration, the major component of quenched reaction mixtures is the $S_{RN}1$ product **9** as shown by ^1H NMR analysis. No products of substitution or ring transformation could be detected after reaction periods of 1–6 min in the dark. Instead, the ^1H NMR spectrum of the quenched reaction mixture, after removal of NH_3, contained a symmetrical A_2B_2 pattern in the region δ 7.2–7.35 and a strong doublet at δ 2.6. In addition, there was complex aliphatic proton absorption at δ 2.0–3.5 with no recognizable patterns. The absence of absorption for the easily recognizable methylene protons of **9** (δ 4.03) and the methyl protons of **11** (δ 9.22) and **12** (δ 8.42) indicated that these products were not present. These data suggest an initial, rapid attack of carbanion **6** at C_4 of **4** leading to **22**. When the reaction is quenched, **22** could yield a mixture of **26** and **27** (eq 15), which may be responsible for the observed ^1H NMR characteristics.

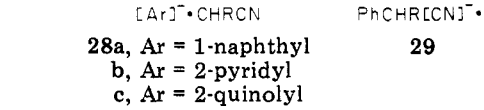


26 **27** (15)

In a recent study of electrochemically induced aromatic nucleophilic substitution in liquid NH_3, Saveant[20] reported that carbanion **6** reacts spontaneously with **4**. However, no cyclic voltammetric data were given for this combination of reactants, and no products were identified. Consequently, it is not clear what the product distribution was under these conditions.

Comparison of the present $S_{RN}1$ reactions of heteroaromatic substrates **1**, **4**, and **16** with analogous reactions involving carboaromatic halides reveals certain similarities, as well as some striking differences. In terms of similar features, nucleophiles **2**, **6**, **14**, and **20** all participate in photo-$S_{RN}1$ reactions with phenyl and/or naphthyl halides.[5a,7-9,21,22] However, liquid NH_3 solutions of **6** and **14** afford little amination product in reactions with halobenzenes, even in the dark or with an inhibitor present. This is apparently due to the failure of carboaromatic halides to undergo S_NAr2 or benzyne reactions with the rather low equilibrium concentrations of amide ion present in these reactions at rates which are competitive with those of the respective $S_{RN}1$ reactions.

The tendency for naphthyl, pyridyl, and 2-quinolyl halides to undergo simple, ipso $S_{RN}1$ substitution with nitrile-stabilized carbanions such as **2**, rather than the more complex decyanation and radical coupling reactions observed with phenyl halides, has been ascribed to the fact that radical anions such as **28a–c** are more stable than the



28a, Ar = 1-naphthyl
b, Ar = 2-pyridyl
c, Ar = 2-quinolyl

29

corresponding phenyl substituted radical anion **29**.[23] This increased stability and the accompanying reluctance of **28a–c** to undergo loss of cyanide ion have been attributed to localization of the extra electron in the LUMO of the Ar moiety of these radical anions, rather than in the CN function, as is the case with **29**.

Ring transformations such as that observed with **4** and nitrile carbanion **6** are unprecedented with carboaromatic systems.

The sluggish reactions of substrates **1** and **4** with thiophenoxide ion (**20**) were surprising since **1** and **4** tend to show greater reactivity than phenyl halides toward ketone enolates,[4] and carboaromatic halides have been found to react smoothly with **20**.[5b] This apparent inconsistency can be explained by considering the steps outlined in Scheme I. Since **1** and **4** should have more positive reduction potentials than phenyl or naphthyl halides,[24] the $S_{RN}1$ sequence should be initiated more rapidly for the heterocyclic substrates. Also, the rate of halide loss from the intermediate halogen-containing radical anions (step 2) and the rate of combination of the resulting radicals with **20** (step 3) should be comparable.[20] Therefore, the difference in overall rates of substitution between **1** and **4** and the more reactive carboaromatic halides must result from differences in rates of electron transfer from the respective radical anion intermediates (**30**) to the original substrate **31** (eq 16). When the Ar moiety of **30** and **31** is 2-pyridyl

$$\underset{\mathbf{30}}{[ArSPh]^{-}\cdot} + \underset{\mathbf{31}}{ArX} \rightarrow ArSPh + [ArX]^{-}\cdot \qquad (16)$$

or 2-quinolyl, the standard reduction potential of the $ArX/ArX^{-}\cdot$ couple is only slightly positive relative to that of the $ArSPh/ArSPh^{-}\cdot$ couple, and electron transfer is relatively slow.[20,25a,26,27] However, when Ar is phenyl or 1-naphthyl, the $ArX/ArX^{-}\cdot$ couple is significantly more positive than the $ArSPh/ArSPh^{-}\cdot$ couple. Consequently, electron transfer is more rapid than with the heteroaromatic analogues, and the overall substitution process is accelerated.[28]

Finally, it should be noted that the photostimulated reaction of anion **14** with **16** provides a convenient new synthesis of **17**.[24] Previous attempts to prepare **17** by reaction of 4-chloropyridine with 4-picolylsodium in liquid NH_3 gave erratic results because the $S_{RN}1$ character of this reaction was not recognized, and no attempts were made to effect photostimulation.[29,30]

Experimental Section

All $S_{RN}1$ reactions were conducted under nitrogen. Photostimulated reactions were carried out in a Rayonet RPR-204 photochemical reactor[31] equipped with four 12.5-W bulbs emitting maximally at 350 nm. Matheson anhydrous NH_3 was used directly from the tank. Dark reactions were conducted in a darkened laboratory by using standard Pyrex glassware enclosed in a black shroud or aluminum foil. Inhibited experiments were carried out by mixing DTBN (10 mol % based on the substrate) with the heteroaromatic halide before it was added to the anion solution. Unless indicated otherwise, the molar ratio of substrate to nucleophile was 1:3.75.

Gas chromatographic (GC) analyses and separations were accomplished on Varian Associates 90-P or 1200 instruments by using columns of 10% SE-30, 1.5% SE-52, or 1.5% Carbowax 20M on Chromosorb W, AW/DMCS, or, 5% Carbowax 20M on

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(24) Wiberg, K. B.; Lewis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154.
(25) (a) For example, the standard reduction potential of 2-(phenylthio)quinoline is −1.48 V in liquid NH_3, whereas the standard potential for **4** in the same solvent is ca. −1.3 V as estimated from cyclic voltamograms.[20] (b) The reduction potential of diphenyl sulfide in DMF vs. $Ag^+/AgCl$ is −2.549 V,[26] and the reduction potential of iodobenzene in DMF is −1.21 V.[27]
(26) Gerdill, R. *J. Chem. Soc. B* **1966**, 1071.
(27) Sease, J. W.; Bunton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595.
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(29) Gaus, P. L.; Hain, A.; Johnson, F. *J. Org. Chem.* **1977**, *42*, 564.
(30) Jampolsky, L. M.; Baum. M.; Kaiser, S. Sternbach, L. H.; Goldberg, M. W. *J. Am. Chem. Soc.* **1952**, *74*, 5222.
(31) Manufactured by Southern New England Ultra Violet Co., Middleton, CT.

Chromosorb G-HP. Methyl benzoate, dimethyl phthalate, benzyl benzoate, 4-methylquinoline, and acenaphthene were employed as internal standards for yield determinations. ^{1}H NMR spectra were determined on a JEOL JMN-PS-100 spectrometer at 100 MHz with tetramethylsilane as an internal standard. Mass spectra were determined by Jorge Bedia and Douglas S. Shearer on a Hitachi Perkin-Elmer RMU 6E mass spectrometer. Infrared spectra were produced on a Beckman IR-10A-X spectrophotometer. Microanalyses were determined in this department on a Perkin-Elmer 240 elemental analyzer and by Galbraith Laboratories, Knoxville, TN. Melting points were observed in a Thomas-Hoover apparatus and are uncorrected.

Tetrahydrofuran (THF) was refluxed over lithium aluminum hydride several hours prior to distillation and was stored in bottles under argon and over molecular sieves. 2-Bromopyridine (1) was distilled from barium oxide, and 2-chloroquinoline (4) was fractionated at reduced pressure. 4-Picoline was fractionated, acetonitrile was distilled from P_2O_5, and both were stored in bottles over molecular sieves. 2-Aminoquinoline[32] (10), 2-methylquinazoline (11),[18] and (2-quinolyl)acetonitrile[33] (9) were prepared as described elsewhere. 4-Bromopyridinium chloride (16) and all other reagents were commercial grade and were used without further purification.

Reactions of 2-Bromopyridine (1) with Potassiophenylacetonitrile (2). (A) Irradiated. Potassium metal (2.93 g, 75 mmol) was added to 300 mL of NH_3 followed by 50–100 mg of $Fe(NO_3)_3{\cdot}9H_2O$ to catalyze amide formation. After the potassium amide had formed (gray suspension), phenylacetonitrile (8.79 g, 75 mmol) was added and rinsed into the vessel with anhydrous ether. When the solution of anion 2 had been stirred for 10 min, 2-bromopyridine (1) (3.16 g, 20 mmol) was added under irradiation and rinsed into the vessel with 50 mL of ether. After the mixture had been irradiated for 15 min, it was poured onto excess solid ammonium chloride contained in a 1.5-L beaker. Ether (300 mL) was added while the ammonia was evaporated with the aid of a warm water bath. The ethereal suspension was filtered, and the residual salts were triturated with ether (4 × 50 mL). The combined ethereal washes and extracts were concentrated, and a portion was analyzed by GC to show no 1 and 88% of 3. The crude product was distilled under vacuum to remove the excess phenylacetonitrile. The residual solid was recrystallized from ethanol–hexane (carbon) to give white crystals of α-(2-pyridyl)-phenylacetonitrile (3): 88% yield; mp 88–89 °C (lit.[6] mp 87–88 °C); ^{1}H NMR ($CDCl_3$) δ 5.31 (s, 1 H, CH), 7.03–7.68 (m, 8 H, aromatic), 8.46–8.56 (m, 1 H, aromatic).

A similar reaction mixture irradiated for 4 min gave 3 in 66% yield (Table I, expt 3).

(B) Irradiated and Inhibited. An inhibited reaction was carried out under conditions identical with those of procedure A except that 10 mol % of DTBN (288 mg, 2 mmol) was mixed with 1 prior to addition to the anion solution. The solution was irradiated for 4 min (expt 4).

(C) Dark. A dark reaction was conducted for 15 min with the same quantities as in A, except that a foil-wrapped flask replaced the cylindrical vessel (expt 1).

Reactions of 2-Chloroquinoline (4) with 2. (A) Irradiated. Phenylacetonitrile (8.79 g, 75 mmol) was added dropwise to a potassium amide solution prepared from 2.93 g (75 mmol) of potassium and 300 mL of NH_3. After the mixture had been stirred for 10 min, irradiation was begun, and 4 (3.27 g, 20 mmol) dissolved in ether was added dropwise and rinsed in with an additional 50 mL of ether. After the mixture had been irradiated for 15 min, it was poured onto excess solid ammonium chloride in a beaker. Ether (300 mL) was added while the ammonia was evaporated with the aid of a warm water bath. The ethereal solution was filtered, and the residual salts were triturated repeatedly (until white) with warm ether. After the combined ethereal extracts had been concentrated, GC analysis showed no 4 remaining. The excess phenylacetonitrile was distilled at 90 °C under vacuum to give 5.28 g of crude product. Recrystallization from ethanol/hexane (carbon) gave 4.29 g (88%) of α-(2-quinolyl)-phenylacetonitrile (5) as pale yellow needles: mp 95–96 °C (lit.[34] mp 92–93 °C); IR (KBr) 2240 cm^{-1} (CN); ^{1}H NMR ($CDCl_3$) δ 5.43 (s, 1 H, CH), 7.1–8.1 (m, 11 H, aromatic).

(B) Dark. A dark reaction was carried out by using the same quantities as in procedure A. The reaction was quenched after 15 min, and the ethereal solution resulting after the workup was concentrated. A portion (1/25) was analyzed by GC to show 90% of unreacted 4. The remaining part (24/25) of the crude reaction mixture was distilled to remove most of the excess phenylacetonitrile, and the residue was triturated several times with small portions of hexane to remove any remaining 4. After vacuum drying and recrystallization there was obtained 0.4 g (8%) of 5, which was spectroscopically identical with 5 obtained from the irradiated reaction.

A similar reaction was quenched after 30 min and showed 71% of unreacted 4 by GC analysis.

(C) Inhibited. An inhibited reaction was carried out under conditions identical with procedure A except that 10 mol % of DTBN (288 mg, 2 mmol) was mixed with 4 prior to its addition to the anion solution. The reaction was quenched after 30 min to yield 78% of recovered 4 (expt 7).

Reactions of 1 with Potassioacetonitrile (6). (A) Irradiated. Dry acetonitrile (3.08 g, 75 mmol) was added to a potassium amide solution prepared from 2.93 g (75 mmol) of potassium in 300 mL of NH_3 and rinsed in with anhydrous ether. After the acetonitrile anion solution had been stirred for 10 min, irradiation was begun and 1 (3.16 g, 20 mmol) was added and rinsed into the vessel with 50 mL of ether. After the mixture had been irradiated for 15 min, it was quenched on excess solid ammonium chloride. Ether (300 mL) was added while the ammonia was evaporated. The ether was filtered, and the residual salts were triturated with ether (4 × 50 mL). The combined ethereal extracts were concentrated and analyzed by GC, which showed no 1, 16% of 2-aminopyridine (8) (spectroscopically identical with an authentic sample), and 75% of (2-pyridyl)acetonitrile (7). For nitrile 7: ^{1}H NMR (CCl_4) δ 3.87 (s, 2 H, CH_2), 7.03–7.34 (m, 2 H, aromatic), 7.47–7.69 (m, 1 H, aromatic), 8.35–8.45 (m, 1 H, aromatic) (Table II, expt 8). Anal. Calcd for $C_7H_6N_2$: C, 71.16; H, 5.12. Found: C, 71.00; H, 5.06.

(B) Low Intensity Irradiation. A reaction mixture identical with that in procedure A was irradiated for 15 min with only one lamp. The light intensity was further reduced by a cardboard collar around the lower half of the ammonia solution (expt 9).

(C) Irradiated and Inhibited. An inhibited reaction was carried out under conditions identical with those of procedure A except that DTBN (288 mg, 2 mmol) was mixed with 1 prior to addition (expt 10).

(D) Dark. A dark reaction was conducted for 15 min with the same quantities as in procedure A, except that a foil-wrapped flask replaced the cylindrical vessel (expt 11).

(E) Dark and Inhibited. This involved a dark reaction similar to **D**, except that DTBN (288 mg, 2 mmol) was mixed with 1 prior to its addition.

(F) Potassium Amide Only. 2-Bromopyridine (1; 3.16 g, 20 mmol) was added to a potassium amide solution prepared from 2.93 g (75 mmol) of potassium in 300 mL of NH_3 in a foil-wrapped flask. The mixture was quenched after 15 min and worked up as in A. GC analysis of the crude product (95% yield) showed only 8.

Reactions of 4 with Carbanion 6. These reactions are summarized in Table III.

(A) Irradiated. Acetonitrile (3.08 g, 75 mmol) was added to a potassium amide solution prepared from 2.93 g (75 mmol) of potassium in 300 mL of NH_3 and was rinsed in with anhydrous ether. After the mixture was stirred for 15 min, irradiation was begun, and 4 (3.27 g, 20 mmol) dissolved in ether was added to the mixture. The resulting mixture was irradiated for 15 min and then quenched on excess solid ammonium chloride. THF was added as the ammonia was evaporated. The residual salts were washed with THF. The combined extracts were concentrated, whereupon a small amount of solid of unknown composition (polymeric) precipitated from the solution. The soluble portion was analyzed by GC, which showed no 4, 50% of (2-quinolyl)-acetonitrile (9), 2% of 3-cyano-2-methylquinoline (12), 1% of

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2-methylquinazoline (11), and an unmeasurable amount of 2-aminoquinoline (10) (expt 13). All products were found to be spectroscopically identical with authentic samples. Nitrile 9 showed the following: IR (KBr) 2240 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 4.03 (s, 2 H, CH_2), 7.40–8.04 (m, 6 H, aromatic).

Two similar experiments (expts 14 and 15) were conducted in which the amounts of acetonitrile were increased to 6.16 g (150 mmol) and 9.24 g (225 mmol), respectively. In both cases the amount of uncharacterizable precipitate increased.

(B) Dark. A dark reaction (expt 16) was conducted for 15 min with the same quantities as in procedure A, except that a round-bottomed flask wrapped with a black shroud was used as the reaction vessel. Resinous material was also formed in this reaction. GC analysis of the soluble portion indicated 12 to be present in 37% yield. Extremely small amounts of 9–11 were observed. Preparative GC of this fraction afforded 12, which was spectroscopically identical with an authentic sample.

Two similar experiments were conducted. In expt 17, 3.13 g (80 mmol) of potassium metal and 4.11 g (100 mmol) of acetonitrile were used. Only the amount of acetonitrile (6.16 g, 150 mmol) was increased in expt 18.

(C) Potassium Amide Only. 2-Chloroquinoline (4; 6.54 g, 40 mmol) was added to a potassium amide solution prepared from potassium metal (5.86 g, 150 mmol) in 600 mL of NH_3 in a foil-wrapped flask. The mixture was quenched over solid ammonium chloride after 15 min. The NH_3 was replaced with ether and filtered. The residual salts were extracted with ether and filtered. The residual salts were extracted with ether several times, and the extracts were combined and concentrated. GC analysis of the crude product (5.1 g) showed no 4; only 10 and 11 were present.

(D) Irradiated Using THF as the Reaction Solvent. A 22% suspension of potassium hydride in mineral oil (9.11 g, 50 mmol) was washed with hexane and transferred to a cylindrical Pyrex vessel fitted with a cooling finger. The hexane was drafted from the settled solid and replaced with 250 mL of dry THF. The stirred solution was kept under a positive pressure of nitrogen as acetonitrile (2.05 g, 50 mmol) dissolved in THF was added to the vessel. Anion formation was allowed to proceed for 20 min before irradiation was begun. Addition of 4 (1.64 g, 10 mmol) dissolved in THF was followed by a reaction time of 1 h and quenching with water. The aqueous layer was removed and extracted several times with ether. These extracts were combined with the THF layer, dried with $MgSO_4$, filtered, and concentrated. GC analysis showed 36% of 4, 9% of 12, and 31% of 9. Spectral characteristics of these products agreed with those of authentic samples. Chromatography of the reaction mixture on silica gel (methylene chloride) afforded, in addition to the other products, 0.24 g (16%) of bis(2-quinolyl)acetonitrile (13) as a feathery orange solid: mp 280–282 °C (lit.[35] mp 281–283 °C); IR (KBr) 2200 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 7.15–7.95 (m, 12 H, aromatic); 17.1 (s, 1 H, CH); mass spectrum, m/e 295 (M^+), 147.5 (M^{2+}). Anal. Calcd for $C_{20}H_{13}N_3$: C, 81.34; H, 4.43; N, 14.23. Found: C, 81.11; H, 4.81; N, 14.11.

Synthesis of 3-Cyano-2-methylquinoline (12). An adaptation of Fehnel's procedure was followed.[36] Freshly prepared cyanoacetone[37] (1.66 g, 20 mmol) and *o*-aminobenzaldehyde[38] (2.42 g, 20 mmol) were placed into a three-necked round-bottomed flask fitted with a condenser. Glacial acetic acid (20 mL) was immediately added to the mixture. The mixture was stirred and heated for about 3 min, and then 0.2 mL of 18 M sulfuric acid was added. The resulting maroon solution was refluxed for 3 h and then quenched by adding the solution to a cold solution of 30 mL of 15 M ammonium hydroxide and 60 mL of water. The crude solid which formed was filtered and recrystallized from aqueous ethanol to afford 2.07 g (62%) of 12 as bright yellow needles: mp 132–133.5 °C; IR (KBr) 2230 cm^{-1} (CN); mass spectrum, m/e 168 (M^+); ^1H NMR ($CDCl_3$) δ 2.93 (s, 3 H, CH_3), 7.49–8.07 (m, 4 H, aromatic), 8.42 (s, 1 H, aromatic). Anal. Calcd for $C_{11}H_8N_2$: C, 78.56; H, 4.79; N, 16.34. Found: C, 78.27, H, 4.55; N, 16.34.

Photostimulated Rection of 1 with 4-Picolylpotassium (14). 4-Picoline (6.98 g, 75 mmol) was added to a potassium amide solution prepared from 2.93 (75 mmol) of potassium in 300 mL of NH_3 and was rinsed in with anhydrous ether. After the anion solution had been stirred for 20 min, irradiation was begun, and 1 (3.26 g, 20 mmol) dissolved in ether was added. The mixture was irradiated for 15 min and then quenched on excess, solid ammonium chloride. Ether was added as the ammonia was evaporated. The resulting solution was filtered, and the residual salts were rinsed with ether. After concentration of the combined extracts, GC analysis showed 37% of (2-pyridyl)(4-pyridyl)-methane (15) and 53% of 2-aminopyridine (8). Isolation of 15 by preparative GC afforded a colorless oil: ^1H NMR ($CDCl_3$) δ 4.09 (s, 2 H, CH_2), 7.01–7.16 (m, 4 H, aromatic), 7.40–7.62 (m, 1 H, aromatic), 8.32–8.52 (m, 3 H, aromatic). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.54; H, 6.05; N, 16.33.

Similar reactions were conducted in which the amounts of reagents were varied. Experiment 20 involved the reaction of 1 (1.58 g, 10 mmol) with an anion solution of 14 prepared from 1.95 g (50 mmol) of potassium in 150 mL of NH_3 followed by 4-picoline (3.72 g, 40 mmol). Potassium amide, prepared from 1.56 g (40 mmol) of potassium in 150 mL of NH_3 were used to make 14 from 4.65 g (50 mmol) of 4-picoline for reaction with 1 in expt 22.

Photostimulated Reaction of 4-Bromopyridinium Chloride (16) with 14. 4-Picoline (9.31 g, 100 mmol) was added to a potassium amide solution prepared from 3.91 g (100 mmol) of potassium and 300 mL of NH_3 in an *oversized* Pyrex cylindrical reaction vessel. After the anion solution had been stirred for 20 min, irradiation was begun, and solid 16 (3.89 g, 20 mmol) was quickly added. (**Caution**: The initial acid–base reaction is quite vigorous.) The solid adhering to the vessel walls was washed in with ether. The mixture was irradiated for 15 min and quenched on solid ammonium chloride. The NH_3 was evaporated and replaced with ether and THF. The resulting solution was filtered, concentrated, and analyzed by GC to show 78% of bis(4-pyridyl)methane (17),[29,30] <1% of 3- and 4-aminopyridines (18), and 6% of 1,2-bis(4-pyridyl)ethane. Isolation of 17 by prepartive GC afforded a pale yellow oil: ^1H NMR ($CDCl_3$) δ 3.95 (s, 2 H, CH_2), 7.07–7.12 (m, 4 H, aromatic), 8.47–8.56 (m, 4 H, aromatic). Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.51; H, 5.82; N, 16.13.

Photostimulated Reaction of 4 with 14. 4-Picoline (4.66 g, 50 mmol) was added to a potassium amide solution prepared from 1.56 g (40 mmol) of potassium in 150 mL of NH_3 and was rinsed in with anhydrous ether. After the anion solution had been stirred for 20 min, irradiation was begun, and 4 (1.64 g, 10 mmol) in ether was added. The mixture was irradiated for 15 min and then quenched on excess solid ammonium chloride. A 50:50 mixture of ether and THF was used to replace the ammonia. The resulting solution was filtered, and the residual salts were washed with more ether–THF. After concentration of the combined extracts, GC analysis showed no 4. Chromatography on silica gel (ether) afforded 0.53 g (24%) of (2-quinolyl)(4-pyridyl)methane (19) as a brown oil and 0.7 g (49%) of 2-aminoquinoline (10) which was spectroscopically identical with an authentic sample. Compound 19 displayed the following: ^1H NMR ($CDCl_3$) δ 4.19 (s, 2 H, CH_2), 7.06–8.00 (m, 8 H, aromatic), 8.28–8.40 (m, 2 H, aromatic).

Reactions of 1 and 4 with Ammonium Thiophenoxide (20). Thiophenol (4.41 g, 40 mmol) was placed in the photolysis vessel followed by 300 mL of NH_3. After the thiophenoxide solution had been stirred for 10 min, 1 (3.16 g, 20 mmol) was added and rinsed into the vessel with 50 mL of anhydrous ether. After the mixture had been irradiated for 90 min, it was quenched on ammonium chloride, and the ammonia was evaporated. Ether was used to dissolve the products and wash the residual salts. The resulting solutions were combined, filtered, and concentrated. GC analysis showed, in addition to unreacted 1, 21% of 2-pyridyl phenyl sulfide (21), which was collected as a colorless oil: ^1H NMR (CCl_4) δ 6.73–6.90 (m, 2 H, aromatic), 7.20–7.56 (m, 6 H, aromatic), 8.18–8.28 (m, 1 H, aromatic). Anal. Calcd for $C_{11}H_9NS$: C, 70.55; H, 4.84. Found: C, 70.54; H, 4.79.

The procedure for the reaction of 4 with 20 followed that of 1 with 20 (above) except that 4 (3.27 g, 20 mmol) was used instead of 1. GC analysis of the concentrated reaction solution after 120

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min of irradiation showed only 4 (83%).

Reactions of 1 with Dimsyl Anion. Dimethyl sulfoxide (5.86 g, 75 mmol), freshly vacuum distilled from calcium hydride, was added to 75 mmol of potassium amide in 300 mL of NH_3 and stirred for 10 min. Irradiation was begun, and 1 (3.16 g, 20 mmol) was added and rinsed in with 50 mL of ether. After 15 min the mixture was quenched and worked up as usual. GC analysis showed mostly 2-aminopyridine (8) along with a trace of an unidentified pyridine-containing product.

A reaction similar to the above was conducted for 15 min in the dark and produced only 8.

Attempted Reactions of 1 with Other Anions. 2-Bromopyridine (1) or 2-chloroquinoline (4) (20 mmol) was added to solutions of 75 mmol of potassium acetylide, potassium phenylacetylide, and potassium phthalimide, each prepared from 75 mmol of potassium amide in 300 mL of NH_3. The reactions were irradiated for 120 min, quenched on ammonium chloride, and worked up as usual. GC analysis showed only unreacted 1 or 4.

Registry No. 1, 109-04-6; 2, 75782-32-0; 3, 5005-36-7; 4, 612-62-4; 5, 22297-12-7; 6, 59175-44-9; 6 carbanion, 21438-99-3; 7, 2739-97-1; 8, 504-29-0; 9, 14068-28-1; 12, 72248-92-1; 13, 22200-36-8; 14, 85736-21-6; 15, 78903-70-5; 16, 19524-06-2; 17, 60776-05-8; 19, 85736-22-7; 20, 54043-02-6; 21, 3111-54-4; NH_3, 7664-41-7; KNH_2, 17242-52-3; K, 7440-09-7; $Fe(NO_3)_3$, 10421-48-4; CH_3CN, 75-05-8; potassium phenylacetylene, 1122-79-8; potassium phthalimide, 107-82-4; potassium acetylene, 1111-63-3; di-*tert*-butyl nitroxide, 2406-25-9; phenylacetonitrile, 140-29-4; cyanoacetone, 2469-99-0; *o*-aminobenzaldehyde, 529-23-7; 4-picoline, 108-89-4; dimsyl anion, 13810-16-7; dimethyl sulfoxide, 67-68-5.

MINDO/3-Derived Geometries and Energies of Alkylpyridines and the Related *N*-Methylpyridinium Cations[1]

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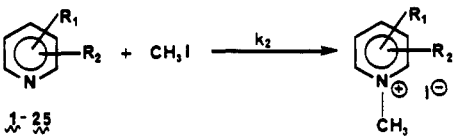
The structures of 25 alkyl-substituted pyridines and their corresponding *N*-methylpyridinium cations were calculated by using GEOMO/RV, utilizing semiempirical all-valence electron (MINDO/3) self-consistent-field procedures. The effects of substituents on the ring systems were examined with particular attention focused on the changes in the aromatic ring bond angles. The energy of methylation for these 25 pyridines was calculated by subtracting the total energy of each pyridine-free base from the total energy of the corresponding *N*-methylpyridinium cation. An excellent correlation was obtained between this calculated energy of methylation and Brown's experimental heats of trifluoroboronations for the same pyridines; implications of this correlation are discussed. Nonadditive structural parameters and energetic effects are calculated and evaluated.

During the past year we[2,3] have been investigating the Menschutkin reaction of alkylpyridines (Scheme I) with the help of the semiempirical MINDO/3 all-valence-electron theory.[4] For a series of 2-alkylpyridines, we have found that the nonadditive part of the second-order methylation rate constant was highly correlated with the molecular position of the 2-substituent.[2] This finding is of importance to the evaluation of structure–reactivity relationships in the Menschutkin reaction. In a subsequent study, we constructed model transition states for a series of 21 pyridines and used the MINDO/3 theory to estimate relative activation energies.[3] An excellent Arrhenius-type correlation was found between the logarithms of the relative methylation rate constants and the calculated relative activation energies for systems which span over four orders of magnitude in alkylation rate.

These two studies incorporated complete geometry optimization for the free bases and for the model transition states. A sizeable set of data was, therefore, generated relative to the effect of alkyl substituents on pyridine ring and substituent geometry. We decided to extend the study to also determine the geometries and relative energies of

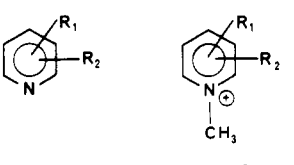
Scheme I



the series of product *N*-methylpyridinium ions. In so doing, we have searched for relationships between structure, molecular energy, and geometry. In the present paper, we present these results which are important since there is little systematic information regarding the effects of alkyl substituents on aromatic ring structure, bond angles, and bond lengths.[5]

Results and Discussion

The 25 pairs of compounds chosen for study (**1–25** and **1C–25C**; see Table I) incorporate both a wide range of



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