by Birch reduction of the corresponding reactants. 13[13] and 14[14] were identified by comparing their NMR and IR to published spectra. The products 2 and 4 were sensitive and rearomatized with time or when submitted to TLC or GC analysis. In these cases the yields (Table IV) were determined by NMR. Other yields quoted are for isolated products. The composition of reaction mixtures of less than 100% conversion was determined by NMR. Cyclohexane, δ 1.40 (s, 12 H), was used as an internal standard for the reaction mixtures of 1. For all others 1,1,2,2-tetrachloroethane, δ 5.90 (s, 2 H), was used. Integration was repeated several times and results were averaged.

Control Experiments. Each set of electrolysis conditions was accompanied by a blank experiment in which the substrate was exposed to all electrolysis conditions but no charge was transferred. The resulting mixture was worked up by the same procedure as described for preparative electrolysis. The isolated product was weighed compared to the original reactant and identified when different. Starting compounds were quantitatively recovered from control experiments with 1, 3, 5, and 7.

Solubility of Methoxybenzene (1) in Water and 1.0 M TBA,OH. A 25 mL volumetric flask was charged with 4.1433 g (0.03831 mol) of 1 in 25 mL of distilled water. This was thoroughly mixed and the layers allowed to separate. Then 1 mL of the aqueous layer was diluted to 10 mL. Examination of this solution by UV at 269 nm (by using UV spectrum [λ_{max} 269 (ϵ 1480)][19]) showed the concentration of 1 to be 0.013 M. In a similar manner the concentration of 1 in 1.0 M aqueous TBA,OH was measured to be 0.196 M.

Acknowledgment. Support of this work by the National Science Foundation and the Graduate School, University of Minnesota, is gratefully acknowledged.

Registry No. 1, 100-66-3; 2, 2886-59-1; 3, 1730-48-9; 4, 3469-31-6; 5, 1035-77-4; 6, 1091-93-6; 7, 17550-03-7; 8, 1042-57-5; 9, 72-33-3; 10, 1624-62-0; 11, 57-63-6; 12, 53-16-7; 13, 4350-64-5; 14, 7678-95-7; β-estradiol, 50-28-2.

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Relative Reactivities of Hetaryl Radicals in Hydrogen Atom Abstraction and Nucleophilic Addition Reactions

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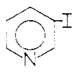
Received May 23, 1983

The 3-pyridyl, 4-isoquinolyl and 3-quinolyl σ radicals were generated photochemically from their corresponding halides in the presence of sodium methoxide and thiophenoxide in methanol. Each radical in competition abstracts a hydrogen atom from either methoxide ion or methanol or adds thiophenoxide ion. The corresponding reduction to substitution product ratios give rate constant ratios which are similar for the three hetaryl radicals, showing only a small influence of radical structure on relative reactivity. The thiolate ion is 2–5 times more reactive than methoxide ion; methoxide on the average is 39 times more reactive than methanol.

Little is known about the factors which influence the rates of addition of nucleophiles to aryl or hetaryl σ radicals. Some nucleophiles add with rates at or near the diffusion-controlled limit while many others simply do not react at all.[1-8]

We report the results of quantitative experiments in which a thiolate ion adds to three related hetaryl radicals, two being benzologues of the first (see below). This addition competes with hydrogen atom abstraction by the radicals from the solvent. The much better understood hydrogen atom transfer reaction serves as a convenient reference for the addition reaction.



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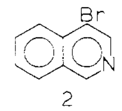

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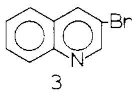

3

Results

Although our main focus is the competition between reduction and substitution, the reduction process also was studied exclusively with one substrate in order to learn how dehalogenation changes in the presence of a thiolate ion nucleophile and how photochemically initiated reduction compares with our earlier observations dealing with thermally induced reduction.[9]

Reductive Dehalogenation. 3-Iodopyridine (1) is rapidly reduced to pyridine when irradiated with Pyrex-filtered light in methanolic sodium methoxide. Observations indicate that (a) methoxide ion is required but that further addition in excess of about 1 equiv has little influence on the rate, (b) removal of dissolved oxygen produces a rate acceleration, and (c) reduction can be inhibited by 2-methyl-2-nitrosopropane.

When solutions of 1 without added methoxide ion are irradiated, the rate is very slow (Table I, run 1; hereafter references to table entries are designated as, for example, I-1). But in the presence of 2.2 M $NaOCH_3$ conversion to pyridine is rapid and complete (run I-2).

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Table I. Effect of Methoxide Ion Concentration and Additives on the Rate and Extent of the Photoinitiated Reductive Dehalogenation of 0.31 M 3-Iodopyridine (1) in Methanol

run	[$NaOCH_3$], M	time, min	mol % iodo	mol % pyridine	no. of lamps[a]
1	0	2207	99	trace	1
2	2.2	96	0	100	1
3	0.046[c]	10	65	18	2
4	0.23[c]	10	30	70	2
5	0.23[c]	20	28	66	2
6	2.3	10	20	80	2
7	0.43	3	87	11	1
8	0.43	3	69 ± 3[b]	27 ± 2[b]	1 (degassed)
9	0.31	10	90[d]	trace	1
10	0.31	10	5[d]	95	1 (degassed)
11	0.31	9	100[d,e]	trace	1 (degassed)

[a] Distance between lamp(s) and sample is 42 mm except in runs 9–11, where it is 165 mm. [b] Average of three. [c] Methoxide ion is the limiting reagent. [d] Initial concentration, 0.014 M. [e] Contains 0.08 M 2-methyl-2-nitrosopropane.

Table II. Product Distributions from the Photoinitiated Reactions of 0.30 M 3-Iodopyridine (1) with Sodium Methoxide and Thiophenoxide in Methanol[a]

run	[$NaOCH_3$], M	[$NaSC_6H_5$], M	time, min	mol % 3-halide	mol % pyridine	mol % 3-sulfide
1	0	0.49	100	35	17	34
2	0.45	0.48	20	56 ± 8[b]	18 ± 3	22 ± 4
3	0.45	0.48	31	40	21	27
4	0.45	0.48	40	28	27	34
5	0.45	0.48	60	16[c]	36	40
6	0.45	0.48	60	20 ± 6[d]	31 ± 4	37 ± 3
7	0.45	0.48	129	18	30	39
8	0.48	0.46	64	21	27	32
9	0.26	1.5	261	0	17	63
10	0.58	0.98	380	0[e]	30	53
11	1.1	0.47	120	0	53	32
12	1.1	0.47	380	0	53	35
13	0.45	0.49	768	[f,g]	[g,h]	[g,h]
14	0.45	0.49	811	[g,i]	[g,j]	[g,j]
15	1.4	0.67	60	64[k]	11	11
16	1.8	0.33	60	38[k]	33	11

[a] Irradiated with two lamps each at 42 mm from the sample. [b] Average of four runs; degassed. [c] Blanket of oxygen added. [d] Average of six runs. [e] 2% benzene detected. [f] 3-Bromopyridine. [g] Concentrations not determined. [h] Ratio of pyridine to 3-(phenylthio)pyridine is 0.77. [i] 3-Chloropyridine. [j] Ratio of pyridine to 3-(phenylthio)pyridine is 0.83. [k] Thermal, not photochemical, reaction. Contains 0.2 M azobis[isobutyronitrile] initiator.

Experiments I-3 to I-5 demonstrate that dehalogenation essentially ceases after methoxide ion has been consumed. For example, in I-4 the observed 70% yield of pyridine agrees closely with the predicted conversion of 74% which would be produced by consumption of all the base (0.23 M/0.31 M = 0.74). Doubling the irradiation time (I-4 vs. I-5) does not change the yield significantly; time must not be the primary limiting factor when a deficiency of methoxide is present. However, the time of irradiation is the limitaton in I-6 since more than 7 equiv of base was present initially, and reduction was incomplete. The average mass balance is nearly quantitative in these runs.

Dissolved oxygen slows reduction; compare I-7 and I-8 where sample degassing produces a higher conversion during the same time. A dramatic acceleration is found in I-9 and I-10 where the amount of 1 is 22 times less than usual. When the ratio of dissolved oxygen to substrate is high as in I-9, the inhibitory effect is magnified.

Dehalogenation was inhibited by the presence of 2-methyl-2-nitrosopropane (I-10 vs. I-11). The nitroso compound weakly absorbs light (methanol, λ_{max} 289 nm, ϵ 160) and therefore cannot be acting simply as a filter. The influence of oxygen and the nitrosopropane point to a radical-chain process. The 2-pyridyl radical is known to be trappable by the nitroso compound.[10]

Earlier we demonstrated that the thermal conversion of 1 to pyridine and to 3-methoxypyridine was a radical-chain reaction.[9] The present photochemical study was carried out a much lower temperature (71 vs. 165 °C), showing the beneficial effect of the light on the rate and on the product composition. The methoxypyridine formed at high temperature probably arose by an ionic S_NAr mechanism since it is not present in significant amounts in the photochemical conversion. In both the thermal[9] and photochemical processes formate ion (NMR detection) is a product of methanol oxidation.

Reduction and Substitution. Irradiation of 1 in the presence of sodium methoxide and thiophenoxide leads to the formation of pyridine and the substitution product 3-(phenylthio)pyridine. On extended irradiation small amounts of benzene were detected, probably arising from the degradation of the (phenylthio)pyridine.

Entry II-1 (Table II) shows that methoxide ion need not be added in order to have reduction and substitution take place, in contrast to reduction alone. However, some methoxide ion is formed by a solvolysis reaction with the moderately basic thiophenoxide ion,[11] and so the mixture is basic. Runs II-2 to II-7 in which the initial concentrations of methoxide and thiophenoxide ions are the same demonstrate that the product ratio is not significantly dependent on time, being about 0.82 ± 0.04. The two reacting ions are not present in large excess over 1, and their concentrations do vary with time. But the ratio of methoxide to thiophenoxide ions changes by less than 10% in these and other runs in Table II. These competition

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(10) Ledwith, A.; Russell, P. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 582.

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Table III. Product Distributions from the Photoinitiated Reactions of 0.30 M 4-Bromoisoquinoline (2) or 0.30 M 3-Bromoquinoline (3) with Sodium Methoxide and Thiophenoxide in Methanol[a]

run	compd	[$NaOCH_3$], M	[$NaSC_6H_5$], M	mol % reduction	mol % sulfide
1	2[b]	0.025	0.97	14	48
2	2	0.45	0.48	41 ± 1[c]	52 ± 2[c]
3	2	0.60	0.97	29	65
4	2	1.1	0.48	56 ± 2	39 ± 1
5	2[d]	0.45	0.49	10	14
6	2[d]	1.1	0.49	27	20
7	3[e]	0.45	0.49	27	51
8	3	0.45	0.48	23 ± 1[c]	48 ± 1[c]
9	3	0.60	0.97	21 ± 1[c]	78 ± 9[c]
10	3	1.1	0.48	43	51
11	3	1.1	0.47	32 ± 1	43 ± 4

[a] Irradiated for 234 min with two lamps 42 mm from the sample. [b] 1375-min irradiation; contains 23% of 2. [c] Average of two. [d] Thermal reaction of 0.059 M 2 initiated by AIBN at 100 °C for 50 min. [e] 177-min irradiation.

experiments therefore are suitable for the derivation of competition constants given in the Discussion.

The reduction to substitution product ratios do vary with large changes in the relative amounts of the two anions, ranging from a low of 0.50 in II-1 to a high of 1.66 in II-11. More product arises as the appropriate reactant ion concentration increases. Mass balances are at least 80%, but the analysis of 1 by GLC showed poor reproducibility.

The presence or absence of oxygen (II-5 vs. II-6) had no real bearing on the product ratio. Apparently, there are no significant competing radical and ionic pathways.

A control was carried out to determine the stability of the pyridyl sulfide. Thus, by use of the same configuration of lamps employed for 1 in Table II, a 0.17 M solution of the sulfide in 0.61 M $NaOCH_3$ was irradiated for 61 and 310 min. No loss of sulfide was detected in the shorter run while 86% remained after longer irradiation. Neither benzene nor pyridine was detected. These conditions are not entirely similar to those employed with 1 when sulfide is being formed; other reactions are not taking place, but the results do suggest that the sulfide is not highly labile.

3-Bromo- (II-13) and 3-chloropyridine (II-14) were examined in place of 1. Again, pyridine and 3-(phenylthio)pyridine were produced but only on extended irradiation. Reactions were considerably slower than in the case of 1; even after extended irradiation much starting material remained. Although concentrations were not obtained, product ratios were measured. Comparison of these data with runs II-2 to II-7 having similar concentrations of methoxide and thiophenoxide ions reveals that all three halides give a reduction to substitution product ratio of 0.8. The halide ion leaving group has no influence on product distribution. Substitution and reduction products must arise from a common intermediate.

An important control reaction suggests the identity of the precursor to pyridine. The reaction medium was CH_3OD instead of CH_3OH. Analysis of two different reaction mixtures having different ratios of methoxide and thiophenoxide ions by GLC–mass spectrometry demonstrated that the pyridine formed in the photolysis of 1 contained less than 2% deuterium. The 3-pyridyl anion cannot be the precursor of pyridine because had it been present, it would have reacted with the OD portion of the solvent to incorporate deuterium.[12] Therefore, pyridine is likely to be formed by hydrogen atom abstraction from the CH group of methanol and methoxide ion by the 3-pyridyl radical.[13] Reduction of the 3-pyridyl radical to the corresponding anion was insignificant.

Additional evidence for a radical route to reduction and substitution products comes from thermolysis experiments using the radical initiator azobis[isobutyronitrile] (AIBN) at 100 °C in the absence of light. In the presence of methoxide and thiophenoxide ions and 1 the thermolysis mixture gave pyridine and 3-(phenylthio)pyridine (II-15 and II-16). The ratio of products is not unlike those from photolysis reactions.

Similar but less extensive experiments were performed with two other substrates. 4-Bromoisoquinoline (**2**) gave isoquinoline and 4-(phenylthio)isoquinoline. 3-Bromoquinoline (**3**) yielded quinoline and 3-(phenylthio)quinoline. Photoinduced reductive dehalogenation of **2** and **3** has been reported[14] but not photosubstitution with thiophenoxide ion.

Little **2** or **3** remained in the photolysis experiments except in III-1 (Table III) where methoxide ion is the limiting reagent. As with **1**, product ratios depend on the relative concentrations of the two ionic reactants; either product can predominate, depending on the conditions. With **2** AIBN served as an initiator in thermal, dark reactions, giving the expected reduction and sulfide products; conversions increased with increasing methoxide ion concentrations (compare III-5 and III-6). Yields are low due to poor conversions. No attempt was made to use AIBN with **3**. Mass balances are lower from **3** than from **2**; the lowest was 75% in III-11.

Product ratios from **1**–**3** may be compared under similar conditions: 0.45 M sodium methoxide and 0.48 M sodium thiophenoxide, runs II-2, III-2, and III-8. The reduction to substitution ratios are 0.79, 0.82, and 0.48, respectively. Only the quinoline substrate differs somewhat.

Photolysis experiments also were carried out with iodobenzene. Thus, 0.31 M iodobenzene, 0.46 M $NaOCH_3$, and 0.48 M $NaSC_6H_5$ gave 86% benzene, 2% diphenyl sulfide, and 2% biphenyl. No starting material remained. Sulfides are known to degrade under the $S_{RN}1$ conditions in which they are formed,[15,16] and aryl radicals in methanol–benzene do give biphenyls.[13] Therefore, product ratios may be an unreliable indication of reduction and substitution due to sulfide decomposition.

Irradiation of 0.30 M 1-bromonaphthalene in 0.47 M $NaOCH_3$ and 0.47 M $NaSC_6H_5$ gave 27% starting material, 48% naphthalene, and 8% 1-(phenylthio)naphthalene. Other experiments with longer times showed that the sulfide cleaves to give benzene as one product. Therefore, our product ratio may not be reliable. Naphthyl sulfides are reported to be more stable than phenyl sulfides in ammonia under $S_{RN}1$ conditions.[16,17]

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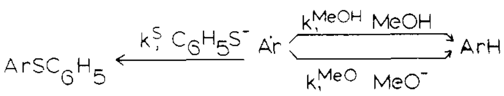
Scheme I

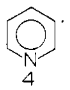


Qualitatively, the distribution of reduction and substitution products from halogenated benzene and naphthalene are not dissimilar to those from **1**–**3**, but reduction does appear to be more favorable.

In all the experiments reduction is an important competing reaction which detracts from substitution as a useful synthetic method. Selection of a less reducing solvent would improve the yield of substitution product.

Discussion

Reductive dehalogenation and nucleophilic substitution of **1**–**3** must involve a common radical intermediate. Support comes from the observations that (a) reactions are promoted by light and by the radical initiator AIBN, (b) reduction is inhibited by the presence of the election- and radical-trapping agents oxygen and 2-methyl-2-nitrosopropane, and (c) the pyridine formed from **1** in CH_3OD reflects reaction at H and not D. The precursor of both reduction and substitution products must not contain the nucleofugic group because essentially the same product ratio is observed from 3-chloro-, 3-bromo- or 3-iodopyridine. The likely common intermediates are the 3-pyridyl radical (**4**), the 4-isoquinolyl radical (**5**), and the 3-quinolyl radical (**6**). All are expected to be σ radicals.[18] The same meta relationship between the annular heteroatom and the singly occupied orbital occurs in all.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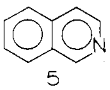
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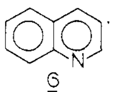
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Reduction product is expected to arise by hydrogen atom abstraction from both methanol and methoxide ion in a chain reaction.[19] The likely chain carriers are the resultant radical $\cdot CH_2OH$ and radical anion $\cdot CH_2O^-$.[13] The latter, a stronger reducing agent,[19] also forms by deprotonation of $\cdot CH_2OH$ by methoxide ion[20] and may account for the faster reduction in the presence of this base.[13]

Substitution probably takes place by an $S_{RN}1$[1] mechanism in which a hetaryl radical reacts with thiolate ion to give the radical anion of the substitution product. Transfer of an election to the starting halide continues the chain-propagation sequence. We have provided evidence for a thermally initiated radical chain reduction of **1** and **2**[9] and for an $S_{RN}1$ path for **2** and thiophenoxide ion,[21] all in methanol with methoxide ion.

The formation of reduction and substitution products by competitive trapping of a radical intermediate is given by Scheme I and resultant eq 1 where Ar· denotes one of

$$\frac{\%\,\mathrm{ArH}}{\%\,\mathrm{ArSC_6H_5}} = \frac{k^{\mathrm{MeOH}}[\mathrm{MeOH}] + k^{\mathrm{MeO}}[\mathrm{MeO^-}]}{k^{\mathrm{S}}[\mathrm{C_6H_5S^-}]} \tag{1}$$

the radical intermediates **4**–**6** and rate constants k^{MeOH}, k^{MeO}, and k^{S} pertain to reduction by reaction with methanol or methoxide ion and to substitution, respectively. Equation 1 may be linearized by cross multiplying by $[C_6H_5S^-]$. Reduction–substitution product ratios were correlated using the linearized equation. On application of the data from Table II to a least-squares linear regression, the average value of several runs at the same concentration was entered as a single data point. Thus, the data for **4** generate an eight-point regression (correlation coefficient $r = 0.952$) which includes values for iodo, bromo, and chloro substrates. Three rate constant ratios (Table IV) may be derived from the correlation. They compare the abilities of thiophenoxide and methoxide ions ($k^{\mathrm{S}}/k^{\mathrm{MeO}}$), thiophenoxide ion and methanol ($k^{\mathrm{S}}/k^{\mathrm{MeOH}}$), and methoxide ion and methanol ($k^{\mathrm{MeO}}/k^{\mathrm{MeOH}}$) to trap **4**.

Table IV. Rate Constant Ratios Comparing Methoxide Ion, Methanol, and Thiophenoxide Ion as Hetaryl Radical Trapping Agents[a]

compd	$k^{\mathrm{S}}/k^{\mathrm{MeO}}$	$k^{\mathrm{S}}/k^{\mathrm{MeOH}}$	$k^{\mathrm{MeO}}/k^{\mathrm{MeOH}}$ [b]
1	2.2	102	46
2	2.4	101	42
3	4.7	168	35

[a] No statistical corrections applied to reflect the three equivalent hydrogen atoms of the methyl group. [b] Using 22 M as the concentration of methanol at 70 °C. Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1, p 303. A 5% correction for substrate dilution was applied.

Data from AIBN-initiated reactions were not included in the construction of the correlation line for **4**. The value from II-15 fits poorly while that from II-16 agrees well. Perhaps the low conversions in II-15 and associated quantitation errors are the cause. Meerly increasing the yield of pyridine from the observed 11% to 14% would place the resultant point on the correlation line, for example. In view of this outcome with AIBN it seems likely that the products form in the "dark" rather than in photochemically excited states.[22]

Similar linear regressions applied to the data from **5** ($r = 0.973$) and from **6** ($r = 0.961$) give the correlations listed in Table IV.

Our analysis is strengthened by the close agreement of $k^{\mathrm{MeO}}/k^{\mathrm{MeOH}}$ (39 ± 3) for the three hetaryl radicals and provides an independent check of the value 45 ± 10 obtained by Bunnett and Boyle for the reduction of the 4-nitrophenyl radical by methoxide ion and methanol.[23] This high selectivity also demonstrates that hydrogen atom transfer is not diffusion controlled for both donors.

Before consideration of the ratios in Table IV, it is pertinent to first examine reported information about hydrogen atom transfer to hetaryl and to aryl σ radicals. Thus, the 2-quinolyl radical abstracts a hydrogen atom from ethoxide ion in liquid ammonia at −40 °C with a rate constant of $1.2 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$, very rapid but substantially below the diffusion-limited value.[24] Benzo fusion does have a modest influence on the ease of atom transfer. 1-Naphthyl is 12 times more reactive toward dimethyl sulfoxide than is 9-anthracyl.[25]

Variations in the rate constants for hydrogen atom transfer to **4**–**6** can reasonably be assumed to be small. Hence, the 2–5-fold variation in the addition of thiophenoxide ion to **4**–**6** relative to hydrogen atom abstraction ($k^{\mathrm{S}}/k^{\mathrm{MeO}}$) does signify only a small influence of radical structure on the addition step. But it is not yet apparent how close the trapping rates are to the limit imposed by

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diffusion and whether the small changes reflect this limit.

The preference shown by the radicals for reaction with the nucleophile instead of with methoxide ion does demonstrate that reduction by this ion is not yet diffusion limited. Moreover, nucleophilic addition to **4–6** is favored over hydrogen atom abstraction (Table IV), and such is not the case for the phenyl radical. The electron-stabilizing nitrogen atom and fused benzene ring lower the energy barrier for the formation of a radical anion and thereby promote nucleophilic addition over hydrogen atom transfer.

Worthwhile would be new competition experiments which would employ a nucleophile known to be more reactive than thiophenoxide ion toward other radicals.[5,6] If the new nucleophile proves to be more reactive toward **4–6** than the thiolate ion, then rates are not diffusion limited for the sulfide ion.

Our observations are consistent with reports that the phenyl radical is only 24 times less reactive than 2-quinolyl toward thiophenoxide ion in ammonia[5,6] and that this same anion in ammonia reacts only 1.6 times faster with 1-naphthyl than with 2-quinolyl.[26] The rate constant for the addition of this ion to 2-quinolyl in ammonia at −40 °C is 1.4×10^7 M^{-1} s^{-1}, a value which is only about 2000 times smaller than the diffusion limit. But addition of this same anion in acetonitrile at 20 °C to the 4-cyanophenyl radical is diffusion limited.[26]

Contrasting with these small variations in rates of addition of a nucleophile to aromatic σ radicals to give radical anions are the much larger rate changes for the formally reverse reactions, expulsion of an anion from a radical anion to give the aromatic radical.[3] For example, 1-naphthyl forms 1000 times faster than 9-anthracyl in dimethyl sulfoxide, both from the corresponding brominated radical anions.[27]

Much remains to be learned about the addition of nucleophiles to radicals, reactions which can be extraordinarily rapid. The competition method outlined here provides a convenient way to obtain such information.

Experimental Section

Instrumentation. Gas chromatographic analyses were performed with a Varian Aerograph Model 1440 instrument equipped with a flame-ionization detector. Chromatograms were obtained with a recorder equipped with a Disc integrator. Analyses by GLC/MS were performed with a linear programable gas chromatograph interfaced to an AEI MS-30 double-beam mass spectrometer. Periodic scanning and data handling for the GC/MS system was accomplished with a Data General Nova/4 computer.

Chemicals. Thiophenol was distilled from zinc turnings under reduced presssure. The concentration of sodium methoxide stock solutions was determined by the NMR shift method.[28,29] The methanol used was spectrograde. 3-(Phenylthio)pyridine[30] was prepared by a literature method.

3-(Phenylthio)quinoline. In a 150-mL Monel bomb were mixed 8.3 g (0.040 mol) of 3-bromoquinoline, 9.3 mL (9.9 g, 0.090 mol) of thiophenol, 4.0 g (0.030 mol) of anhydrous copper(II) chloride, and 90 mL of 2.3 M lithium methoxide (0.21 mol). The mixture was heated at about 165 °C for 7.5 h. The cooled mixture was filtered. Removal of the solvent provided a brown oil which solidified upon standing at room temperature. Recrystallization of the yellow solid from hexane afforded crystals: 1.7 g (0.0071 mol, 18%); mp 76–79.5 °C. A second recrystallization provided crystals: mp 78.5–80.8 °C; NMR ($CDCl_3$) δ 7.15–7.87 (m, 3), 7.35 (m, 5) 7.98–8.20 (m, 1), 8.06 (d, 1, J = 2.2 Hz), 8.82 (d, 1, J = 2.2 Hz). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.91; H, 4.68; N, 5.90. Found: C, 75.80; H, 4.69, N, 5.89.

Photolysis Procedures. For all photolyses, 275-W Sears sunlamps (catalog no. 7080, mercury vapor arc) were employed. Samples were irradiated in either sealed or tightly capped Pyrex NMR tubes. The number of lamps and the distance from the center of the surface of the lamp(s) to the center of the sample tube (in parentheses) for each set of conditions was either 2 (42 mm), 1 (42 mm), or 1 (165 mm).

Control samples were irradiated to determine the temperatures attained during photolysis. They consisted of an NMR tube containing methanol into which an iron–constantan thermocouple wire was immersed. The thermocouple wire was sealed in the cap with epoxy cement. Temperature readings were taken with a potentiometer. When two lamps were employed at a sample to lamp distance of 42 mm, a temperature of 71 ± 2 °C was attained after approximately 1 min; for a single lamp at a distance of 42 mm, a temperature of 62 ± 2 °C was reached after 15 min of irradiation. For a single lamp at 165 mm the temperature was assumed to be 23 °C.

Preparation of Reaction Mixtures. Mixtures were prepared in volumetric flasks. Liquids were added by use of a microliter syringe. Aliquots of the appropriate stock solutions of substrate, standard, and sodium methoxide were followed by the addition of thiophenol which was generally determined by weight. Other reagents were either weighed into the volumetric flask or were added as stock solutions. Aliquots were then transfered to NMR tubes for photolysis.

AIBN was weighed into a 2-mL ampule, and the appropriate stock solution of substrate was added, followed by the sodium methoxide and thiophenol. Enough methanol was added to bring the final volume to 1 mL. Although small amounts of the AIBN were often initially insoluble, the undissolved solids were consumed during the reaction. Ampules were wrapped in foil and then heated in a steam cone.

Samples were degassed to remove dissolved oxygen by alternate freeze–thaw cycles (two or three times) under vacuum. Samples first were frozen by immersion into liquid nitrogen and then were evacuated (ca. 10^{-2} torr) for of 1–2 min.

Procedures for Gas–Liquid Chromatography. Three different types of $^1/_8$ in o.d. copper columns were employed. The solid support consisted of HMDS-treated, 60/80-mesh Chromosorb W. Column A was 2 m in length and consisted of a 17% loading of Carbowax 20M; column B was 1 m long with a mixed loading of 20% Versamid 900 and 10% sodium carbonate; column C was 4 m long with a 20% loading of UCON-LB-550. The rotating evaporator method was used to coat the Chromosorb W with the appropriate liquid phase.

About 0.5–2 μL of sample were injected for analysis. Calibration curves representing peak area relative to a standard vs. concentration were constructed. Plots were linear over the concentration range employed in the competition experiments. Anisole often served as an internal standard, but biphenyl was employed with 3-iodopyridine in AIBN experiments due to signal overlap with a product of AIBN degradation. Similarly, 7,8-benzoquinoline was used as a standard with 4-bromoisoquinoline in runs with AIBN. Column B was used for the quinoline and isoquinoline substrates and column C for the naphthalene. A control was first examined with AIBN; the mixture contained methoxide and thiophenoxide ions but no halide; the resultant chromatogram served to indicate peak overlap problems in subsequent runs containing halogenated substrate.

Experiments were carried out initially to determine whether the anisole standard is consumed during the photoinitiated reactions of 3-iodopyridine. 3-Iodopyridine was irradiated in methanolic methoxide containing thiophenoxide ion as usual except that anisole was added after and not before irradiation. The average mass balance for the five such runs is 89 ± 3%.

An additional experiment was undertaken to determine the extent of anisole degradation. A mixture of 0.13 mmol of anisole, 0.30 mmol of 3-iodopyridine, 0.49 mmol of thiophenoxide ion, and 0.43 mmol of methoxide ion was irradiated for 60 min with two

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lamps at a distance of 42 mm. After irradiation, a solution containing 4.8×10^{-2} mmol of biphenyl was added. Quantitation of anisole, using biphenyl as the standard, indicated that 3 ± 0% (duplicate analyses) of the anisole had degraded during sample irradiation.

The presence of 3-(phenylthio)pyridine in reaction mixtures also was confirmed by GLC/mass spectrometric analysis.

Search for Deuterated Pyridine during Reduction. Substitution of 3-Iodopyridine in Methanol-*d*. Two samples were prepared. The first consisted of 0.32 M 3-iodopyridine, 1.1 M CH_3ONa, and 0.47 M C_6H_5SNa, the second being 0.32, 0.62, and 0.48 M, respectively, all in CH_3OD. The first was irradiated for 60 min and the second for 131 min. Both NMR tubes were irradiated with two sunlamps, each at a distance of 42 mm. Analysis by GLC/mass spectrometry on a carbowax column showed the presence of pyridine and some benzene probably arising from the degradation of 3-(phenylthio)pyridine. Multiple scans of the pyridine peak gave ratios ranging from m/z 100/5.5 to 100/5.8 for m/z 79/80 for the first sample and m/z 100/5.5 to 100/6.9 for the second. Authentic pyridine under the same conditions gave m/z 100/5.0 to 100/5.3 for the same mass ratio. Using the mass 80 peak as a measure of the amout of pyridine-*d*, the maximum amount present is 6.9 − 5.0 = 1.9%.

Registry No. **1**, 1120-90-7; **2**, 1532-97-4; **3**, 5332-24-1; sodium methoxide, 124-41-4; sodium thiophenoxide, 930-69-8; methanol, 67-56-1; 3-pyridyl, 29761-81-7; 4-isoquinolyl, 54978-42-6; 3-quinolyl, 54978-40-4; 3-bromopyridine, 626-55-1; 3-chloropyridine, 626-60-8; 1-bromonaphthalene, 90-11-9; iodobenzene, 591-50-4; 3-(phenylthio)quinoline, 87393-53-1.

The Effect of a Cyano Group on the Thermodynamic Ease of Electron Removal from Hydrazines

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Received October 5, 1982

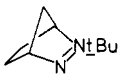
Formal oxidation potentials relative to SCE are reported for several cyano-substituted hydrazines and their analogues with the cyano group replaced by a methyl group. $\Delta E^{\circ\prime}$ was 0.83 V for 2-cyano- and 2-methyl-3-*tert*-butyl-2,3-diazabicycloheptane (1(CN) and 1(Me)), 0.35 V for trimethyl(cyanomethyl)hydrazine and ethyltrimethylhydrazine (**3**(CN) and **3**(Me)), and 0.23 V for (β-cyanoethyl)trimethylhydrazine and propyltrimethylhydrazine (4(CN) and 4(Me)). The ESR spectrum of 1(CN)-d_2 has nitrogen splittings of 17.2 and 7.7 G. The significance of these results is discussed.

Table I. Cyclic Voltammetry Data[a] for Some Tetraalkyl- and Trialkylcyanohydrazines

compd	$E^{\circ\prime}$, V	ΔE_p^{ox}, mV [electrode]
1(Me)	0.21	100 [Au]
1(CN)	ca. 1.04	210 [Pt]
2(Me)	0.11	62 [Au]
2(CN)	ca. 1.0	550 [Pt]
3(Me)	0.33	80 [Au]
3(CN)	0.64	80 [Pt]
4(Me)	0.32	88 [Au]
4(CN)[b]	ca. 0.55	240 [Au]

[a] Conditions: ca. 2 mM substrate in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate vs. SCE, 200 mV/s scan rate. [b] Data from ref 7.

In this work we compare the thermodynamic ease of electron removal from tetraalkylhydrazines with that for related compounds in which a methyl group is replaced by a cyano group. For the most interesting case, that in which the cyano group is directly attached to nitrogen, we chose examples in which α-deprotonation of the radical cation is kinetically inhibited by having the α CH bonds held near the nodal plane of the p orbital at the adjacent nitrogen. We hoped that then the thermodynamically destabilized radical cation would prove to be long-lived under cyclic voltammetry (CV) conditions, so that the thermodynamically significant formal potential for electron removal ($E^{\circ\prime}$) could be measured. Stable diazenium salts[1,2] $\mathbf{1^+BF_4^-}$ and $\mathbf{2^+BF_4^-}$ were treated with methyllithium–TMEDA[3] and potassium cyanide[4] to give the desired X = CH_3 and X = CN derivatives. Because a cation radical reduction wave as large as the oxidation wave was observed by CV, **1(CN)** gives a cation radical which is long-lived on the CV time scale. Cation decomposition could be detected in the CV of **2(CN)** at slow scan rates. Large oxidation, reduction peak separations (ΔE_p) were observed, however, showing that heterogeneous electron transfer is quite slow. One factor is that platinum had to be used for the working electrode because of the high $E^{\circ\prime}$ values for these cyanohydrazines. Tetraalkylhydrazines are already known to show slower electron transfer (larger ΔE_p values) at platinum than at gold.[5] It is nevertheless clear, especially for **2(CN)**, that heterogeneous electron transfer is significantly slower than for tetraalkylhydrazines. We suspect that conformational effects are important in causing the large ΔE_p values, but will not return to this interesting point here. For the present purpose, determination of the effect of cyano substitution on the thermodynamics of electron loss, the large ΔE_p values observed are a distinct disad-



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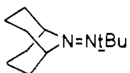

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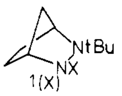

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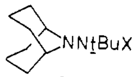

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