fraction 1, bp 60–70° (14 mm), 0.2 g; fraction 2, bp 85–89° (14 mm), 1.1 g; fraction 3, bp 120–150° (14 mm), 0.4 g.

The infrared spectrum of the main fraction (fraction 2) showed absorption bands at 3115 (=CH), 2860 (OCH_3), 2260 (CN), 1635 (C=C), 1175, 1145, 1100, 1060, and 1045 cm^{-1} (COCOC); mol wt (mass spectrum), 153. *Anal.* Calcd for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.78; H, 7.30; N, 9.06. The nmr spectrum of this fraction (100 MHz, 10% in CCl_4) suggested that this material was a 2:1 isomeric mixture of *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrofuran (I_c and I_t). The yield was 20% (based on 2,5-dimethylfuran used; current efficiency, 61%). Each isomer was then separated in pure form by preparative vpc, the column packing being PEG 6000. The cis isomer had a shorter retention time. The melting points were 31.5–32.5°, cis, and 49.5–50.5°, trans. The proton chemical shifts τ of these isomers are listed in Table III.

Fraction 1 was mainly a 1:1 mixture of 2-cyano-5-methoxy-2,5-dimethyldihydrofuran (I_c and I_t) and 2,5-dimethoxy-2,5-dimethyldihydrofuran (II_c and II_t), with trace quantities of 2-methoxymethyl-5-methylfuran (III) and 2,5-bis(methoxymethyl)furan (IV). Fraction 3 was a clear, viscous liquid. No attempt was made to identify it.

Nonpotentiostatic Oxidations.—Preparative-scale electrolysis was carried out in a two-compartment H-type cell with glass frit separating the compartments fitted with platinum foil electrodes (20 × 30 mm²). The anolyte was made up of 15.4 g (0.16 mol) of 2,5-dimethylfuran, 7.8 g (0.16 mol) of sodium cyanide, and 200 ml of methanol. The catholyte was a methanolic solution of sodium cyanide. The electrolysis was carried out under a nitrogen atmosphere for 18 hr at 35 V until 18,900 C had passed through the electrolyte. During the electrolysis, the solution was kept stirred magnetically and cooled externally with ice (2–5°).

TABLE III

PROTON CHEMICAL SHIFTS (τ VALUES) IN *cis*- AND *trans*-2-CYANO-5-METHOXY-2,5-DIMETHYLDIHYDROFURAN[a,b]

Compd	Vinyl proton	Methoxy proton	Methyl proton
I_c	3.92 (1 H, d, J = 5.6 cps)	6.81 (3 H, s)	8.38 (3 H, s)
	4.18 (1 H, d, J = 5.6 cps)		8.55 (3 H, s)
I_t	3.99 (1 H, d, J = 5.8 cps)	6.92 (3 H, s)	8.34 (3 H, s)
	4.13 (1 H, d, J = 5.8 cps)		8.49 (3 H, s)

[a] Measured at 100 MHz in CCl_4. [b] Abbreviations: d, doublet; s, singlet.

The electrolyzed mixture was treated as usual. Vacuum distillation afforded 7.4 g of I (30% yield based on 2,5-dimethylfuran used; current efficiency, 49%; cis/trans = 2.0) and 0.8 g of II (3% yield; current efficiency, 5%; cis/trans ≃ 1), with traces of III and IV. When the electrolysis was conducted in a undivided cell, the yield of I decreased considerably.

Registry No.—I_c, 28463-58-3; I_t, 28463-59-4; 2,5-dimethylfuran, 625-86-5.

Homolytic Arylation of Pyridine and Pyridine *N*-Oxide and the Effect of Localization Energy and Temperature on Arylation Patterns

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Pyridine and pyridine *N*-oxide have been phenylated by electrolytic reduction of benzenediazonium tetrafluoroborate in aprotic media giving high yields of phenylated products. Nonelectrolytic reduction systems were also investigated, leading to a new mechanism for diazonium salt–pyridine reactions. Partial rate factors and total rate ratios for pyridine *N*-oxide are reported for the first time. Experimental results are related to theoretical values calculated from molecular orbital theory by Brown and Barnes.

Previously this laboratory reported the polarographic reduction in aprotic solvents of substituted benzenediazonium tetrafluoroborates in which the most positive wave is produced by a reversible one-electron step.[1a] The phenyl radical formed in this system has been used to phenylate benzene, toluene, anisole, benzonitrile, nitrobenzene, bromobenzene, and naphthalene with most encouraging results.[1b]

Therefore, it seemed of interest to examine the electrochemical arylation of heteroaromatic nitrogen compounds. Pyridine was chosen because the abundant available data concerning the homolytic arylation of pyridine would provide a way to evaluate our method. Pyridine *N*-oxide was chosen for precisely the opposite reason: the few and conflicting data might be elucidated by our study.

Homolytic arylation of pyridine has been achieved using benzoyl peroxide, lead tetrabenzoate, phenyl iodobenzoate, and electrolysis of benzoic acid as sources of the free radical.[2–6] Abramovitch and coworkers,[7,8] using an equimolar mixture of pyridine and benzenediazonium tetrafluoroborate, reported production of phenyl radicals, but no results for the phenylation of pyridine were given.

Data on homolytic phenylation of pyridine *N*-oxide are scarce. Dyall and Pausaker[9] treated pyridine *N*-oxide with phenyl radical generated from diazoaminobenzene and succeeded in separating the three phenylpyridine *N*-oxides. The isomer ratio they observed agrees qualitatively with ratios predicted by Barnes[10] from molecular orbital theory. The actual ratios differed from one run to the next and no total rate ratio was measured. On the other hand, Abramovitch and Koleoso,[8] phenylating pyridine *N*-oxide at room temperature to 60°, with an equimolar mixture of benzenediazonium tetrafluoroborate and pyridine, obtained 0.9% of isomeric phenylated oxides and 6% of phenylated pyridines with isomer ratios qualitatively similar to theory, but no attempt was made to obtain the total rate ratio ${}^{\mathrm{N-O}}_{\mathrm{C-H}}K$ or partial rate factors. Since the total rate ratio we obtained is high, we have pursued

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(1) (a) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, **34**, 854 (1969); (b) F. F. Gadallah and R. M. Elofson, *ibid.*, **34**, 3335 (1969).

(2) R. O. C. Norman and G. K. Radda, *Advan. Heterocycl. Chem.*, **2**, 131 (1963).

(3) R. A. Abramovitch and J. G. Saha, *ibid.*, **6**, 229 (1966).

(4) G. H. Williams, "Homolytic Aromatic Substitution," Pergammon Press, London, 1960.

(5) D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

(6) P. J. Bunyan and D. H. Hey, *ibid.*, 3787 (1960).

(7) R. A. Abramovitch and J. G. Saha, *Tetrahedron*, **21**, 3297 (1965).

(8) R. A. Abramovitch and O. A. Koleoso, *J. Chem. Soc. B*, 1292 (1968).

(9) L. K. Dyall and K. H. Pausaker, *ibid.*, 18 (1961).

(10) R. A. Barnes, *J. Amer. Chem. Soc.*, **81**, 1935 (1959).

TABLE I

PHENYLATION OF PYRIDINE BY DIFFERENT METHODS[a]

Reaction	Radical source	Temp, °C	Yield, %	r	Isomer ratio %	$^{X}_{H}K$[b]	Fr[c]	Other products	Ref
1	Elect. redn of PhN_2BF_4			α	56		1.93		
	in $C_5H_5N + CH_3CN$	0	35	β	27	1.15	0.93	1.2% biphenyl	
				γ	17		1.17		
				α	54		1.7		
2	$(PhCO_2)_2$	105	62	β	32	1.04	1	PhCOOH	4,5
				γ	14		0.87		
				α	52				
3	$(PhCO_2)_4Pb$	105	42	β	32.5			PhCOOH	5
				γ	15.5				
				α	56				
4	Electrolysis of	10–20		β	35				6
	PhCOOH in C_5H_5N			γ	9				
5	Elect. redn of			α	57				
	PhN_2BF_4 in C_5H_5N only	0	81	β	24			0.7% biphenyl	
				γ	19				
6	PhN_2BF_4 in C_5H_5N			α	54				
	over Hg pool	15	87	β	28			0.7% biphenyl	
				γ	18				
7	PhN_2BF_4 in C_5H_5N only			α	57				
		15	92	β	27			0.7% biphenyl	
				γ	16				
8	Calcd from exptl			α	52		1.62		
	data of eq 1	105		β	30	1.04	0.95		
				γ	18		1.12		

[a] Experimental isomer ratios, total rate ratios, partial rate factors, yields, and calculated rates and isomer ratios. [b] $^{X}_{H}K$ = total rate ratio of pyridine relative to benzene (ref 4). [c] Fr = partial rate factor for position r (α, β, or γ) compared to any position in benzene (ref 4).

theoretical calculations to show quantitative correlations as described below.

Results

Electrolytic Reductions.—The method developed in our laboratory[1] of producing phenyl radical by the electrolytic reduction of benzenediazonium tetrafluoroborate was applied to the phenylation of pyridine in the presence of acetonitrile to give 35% (based on the diazonium salt) and in the absence of acetonitrile to give 81% yields (Table I). Both of these reactions consume for completion much less than the stoichiometric amount of current calculated for one-electron reduction of benzenediazonium tetrafluoroborate.

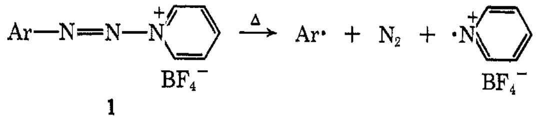
Using electrolytic reduction of benzenediazonium tetrafluoroborate in acetonitrile to phenylate pyridine *N*-oxide at 0°, relatively high yields of phenylated pyridine *N*-oxides (*ca.* 35%) have been obtained. Competitive reactions at 0° have resulted in total and partial rates close to the theoretically predicted values discussed below (Tables II and III).

Nonelectrolytic Reductions.—When it was found that fewer coulombs than calculated were required to complete the electrolysis of pyridine reactions, several nonelectrolytic systems were investigated. Benzenediazonium tetrafluoroborate in pyridine over mercury with stirring but without current and at 15° resulted in a vigorous reaction which was complete in about 15 min. About 0.7% biphenyl and 87% phenylpyridines were obtained. When mercury was absent, about 60 min was required for completion and 0.7% biphenyl and 92% phenylpyridines were obtained. The isomer ratios in nonelectrolytic and electrolytic reactions were virtually the same. Near-quantitative yields were obtained in all reactions in the absence of acetonitrile (Table I).

Since our isomer ratios at 0° were different from those obtained by Dyall and Pausaker[9] for pyridine *N*-oxide at 131°, we repeated their work. Another set of reactions was performed to obtain the total rate ratio at 131°. Anisole was chosen as the reference compound because of its high boiling point.

Discussion

Abramovitch and coworkers[7,8] have suggested that aromatic diazonium tetrafluoroborates couple with pyridine giving complex 1 which decomposes on heating (eq 1). However, our decompositions of diazonium salts were performed at temperatures less than or equal to 15°. The yields were high and the isomer ratios very like those observed in benzoyl peroxide reactions. Therefore, if complex 1 is a significant intermediate, it must be rapidly formed and decomposed at one low temperature, which seems unlikely. Furthermore, when we phenylated pyridine *N*-oxide using benzenediazonium tetrafluoroborate and pyridine (100:2:4 molar ratio) at 20°, the predicted isomer ratios (Table II, f_1 and f_2), accompanied by traces of phenylpyridines, were obtained.



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(1)

It seems reasonable to suggest the system used by Abramovitch and Koleoso[8] (1:1:1 molar ratio) produced high yields of polysubstituted phenylpyridine

TABLE II

PHENYLATION OF PYRIDINE *N*-OXIDE BY DIFFERENT METHODS[a]

	Reaction conditions	Temp, °C	Yield, %	r	Isomer ratio %	${}^{\text{N-O}}_{\text{C-H}}K$[b]	Fr[c]	Other products and comments	Ref
a	Elect. redn of PhN_2BF_4 in $PyN\rightarrow O + CH_3CN$ (+PhH)	0	35	α	89	52	139	From isomer ratio and competitive reactions	
				β	<1		1.5		
				γ	10		31.2		
b	$PhNHN_2Ph + PyN\rightarrow O$ (+$PhOCH_3$)	131	45	α	82	20.6	50.7	From isomer ratio and competitive reactions; ${}^{\text{OCH}_3}_{\text{H}}K$ 1.43 calculated at 131° from 1.96 at 0°	
				β	4		2.5		
				γ	14		17.3		
c	$PhNHN_2Ph + PyN\rightarrow O$ (+$PhOCH_3$)	131	45	α	82	16.2	39.85	As in b but ${}^{\text{OCH}_3}_{\text{H}}K$ found experimentally at 131°	
				β	4		1.95		
				γ	14		13.6		
d	$PhNHN_2Ph + PyN\rightarrow O$	131	27	α	76.2			Average of three runs	9
				β	7.8				
				γ	16				
e	$PhNHN_2Ph + PyN\rightarrow O$	181	28	α	79			~6% phenylpyridines	9
				β	7.7				
				γ	13.3				
f_1	$PhN_2BF_4 + C_5H_5N + PyN\rightarrow O$ (0.02:0.04:1.0 mol) in CH_3CN	20	23	α	87			<1% of phenylpyridines	
				β	<1				
				γ	12				
f_2	$PhN_2BF_4 + C_5H_5N + PyN\rightarrow O$ (0.02:0.04:1.0) on Hg pool in CH_3CN	20	20	α	87			<1% of phenylpyridines	
				β	<1				
				γ	12				
g	$PhN_2BF_4 + C_5H_5N + PyN\rightarrow O$ (equimolar) + CH_3CN	rt-60	0.9	α	66.2			65.5 Phenylpyridines in 6%	8
				β	2.5			11.8	
				γ	31.3			22.7	

[a] Experimental isomer ratios, total rate ratios, partial rate factors, yields and isomer ratios. [b] ${}^{\text{N-O}}_{\text{C-H}}K$ = total rate ratio of pyridine *N*-oxide relative to benzene. [c] In a, b, and c, Fr calculated from isomer ratios and ${}^{\text{N-O}}_{\text{C-H}}K$.

TABLE III

PHENYLATION OF PYRIDINE *N*-OXIDE[a]

		Temp, °C	r	Isomer ratio %	${}^{\text{N-O}}_{\text{C-H}}K$	Fr[b]	Comments
h	Calcd values from L.E.[c] at 0° taking β = 0.95	0	α	92.0	48.5	134	Calcd from Dickerman[21]
			β	1		1.2	
			γ	7.2		19.7	
i	Calcd from h	131	α	84.6	10.8	27.4	
			β	3.5		1.13	
			γ	11.6		7.49	
j	Calcd from exptl, 0° (a), eq 3	131	α	84	12.6	28.06	
			β	3.4		1.3	
			γ	13.6		10.23	

[a] Calculated isomer ratios, total rate ratios, and partial rate factors. [b] In h, i, and j, Fr was calculated first considering no change in Lr or ΔH with temperature; then ${}^{\text{N-O}}_{\text{C-H}}K$ was calculated from ${}^{\text{N-O}}_{\text{C-H}}K = (2F\alpha + 2F\beta + 2F\gamma)/6$; then the isomer ratio was calculated from % r = Fr/3K for α and β and = Fr/6K for γ. [c] L.E., localization energy.

N-oxides (not isolated) owing to the high reactivity of pyridine *N*-oxide. The reaction might have been further complicated by side reactions which occurred during heating in an acetonitrile solution and during reductions involving thiourea.

We suggest pyridine forms a coordination complex **2** analogous to the pyridine complex of positive iodine.[11] A one-electron reversible half-wave potential was obtained ($E_{1/2}$ = −0.16 V *vs.* sce).[12] We suggest −0.16 V is the value for reduction of complex **2**. A redox reaction could then follow in nonelectrolytic arylation in which the diazonium cation accepts one electron from pyridine giving a diazo radical and a pyridyl radical according to Scheme I.[13] Pyridyl radical then abstracts hydrogen atoms from σ complex **3** giving pyridinium tetrafluoroborate; Hg^0 apparently exerts a catalytic effect by facilitating the one-electron transfer from the nitrogen lone pair.[17] Hence the rate of decomposition is increased when mercury is present.

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[11] (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley, New York, N. Y., 1966, p 680; (b) N. W. Alcock and T. C. Waddington, *J. Chem. Soc.*, 2510, (1962).

[12] Polarography of benzenediazonium tetrafluoroborate. As described previously[1b] the polarogram was run for a solution of 6.0 × 10^{-4} *M* benzenediazonium tetrafluoroborate, 6 × 10^{-3} *M* pyridine, and 0.1 *M* Bu_4NClO_4 in acetonitrile at 0°.

[13] This reaction is similar to the one between iodide ion and diazonium cation.[14-16]

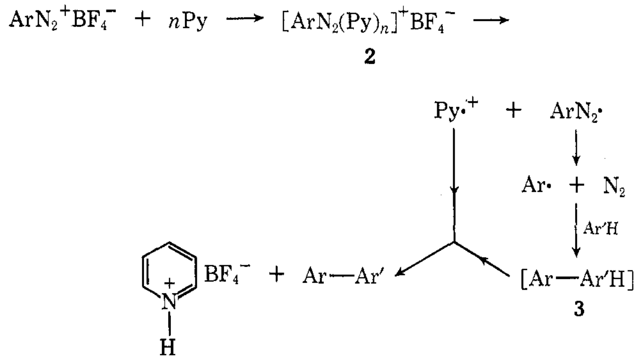
[14] B. Chauncy and E. Gullert, *Aust. J. Chem.*, **22**, 993 (1969).

[15] R. M. Elofson and F. F. Gadallah, unpublished results.

[16] D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Commun.*, 1375 (1969).

[17] Clearly the role of mercury as a catalyst in our reactions is more like the role of Cu_2Cl_2 in Meerwein reactions than that of zinc in related reactions. Hg^0 may be oxidized by diazonium cations ($E^0_{(-N_2\cdot \rightarrow -N_2^+)}$ = −0.541)[1a] to produce Hg^+. Hg^+ ($E^0_{(Hg^0\rightarrow Hg^+)}$ = −0.789) facilitates oxidation of the σ complex to produce $Hg^0 + H^+$ and the reaction mixtures become acidic. As shown by Waters [*J. Chem. Soc.*, 864 (1939)], Zn^0 can reduce diazonium salts to produce free radicals. But the resulting Zn^{2+} cannot oxidize the σ complex, the oxidizing potential is low ($E^0_{(Zn^0\rightarrow Zn^{2+})}$ = + 0.763), and zinc lacks an intermediate valence state to catalyze the necessary one-electron transfer. Therefore, Zn^0 must be used in stoichiometric amounts.

SCHEME I[a]



[a] n = number of pyridine molecules (presently under investigation) associated with a diazonium cation. This reaction is similar to the reaction between iodide ion and diazonium cation.[14-16]

The properties of this coordination complex **2** will be the subject of a subsequent paper.

If the diazonium cation is in fact reduced by pyridine, and the σ complex oxidized by pyridyl radical, it would most certainly occur during electrochemical reductions, hence making the short time and less than expected current required readily explicable.

Phenylation of pyridine *N*-oxide with benzenediazonium tetrafluoroborate at 0° produced a distribution of products quite different from that obtained by Dyall and Pausaker using diazoaminobenzene at 131°; so we were prompted to repeat their work. Good agreement was found with a single run (no. 3; α:β:γ as 80.9:5.6:13.5, respectively) of Pausaker's work,[9] especially considering Dyall and Pausaker used infrared spectral analysis, and in the work reported here glc and mass spectra analysis were used.

Moreover, the total rate factor proved to be remarkably large and was lower at 131° than at 0° (16.2 and 52, respectively). Coupled to the obvious shift in isomer ratio with the temperature change, this development alerted us to the necessity as well as the opportunity to compare the partial and total rates observed at two temperatures with the theory of rate processess, and also to compare these relative rates at any temperature with molecular orbital calculations by Barnes.[10]

Brown,[18] among others,[19,20] showed how this could be done. Rates of attack by trichloromethyl radical on several aromatic hydrocarbons at 91° were compared with atom localization energies according to eq 2,

$$2.303RT \log k_1/k_2 = a(L_2 - L_1) \qquad (2)$$

where a is a constant characteristic of the attacking species, and L_1 and L_2 are the calculated localization energies of pairs of aromatic positions. By plotting $RT \log k_1/k_2$ *vs.* localization energy differences, he obtained a good linear plot for this reaction expressed in β units, where β is the standard resonance integral for the C–C bond in benzene.

Brown[18] concluded that a similar value for a could be used for phenylation. Using experimental localization energies calculated from the experimental partial rates ($k_1/k_2 = Fr$) for pyridine at 80° using eq 2, he was able to perform molecular orbital calculations for pyridine to obtain satisfactory values for the parameters h (=0.5) and k (=1) for the coulomb integral $\alpha_N = \alpha_C + h\beta$ and the resonance integral $\beta_{C-N} = k\beta$. More recently Dickerman, *et al.*,[21] found a value of 17.8 for phenylation of naphthalene and anthracene. This value is used in our calculations.

Subsequently Barnes[10] calculated a series of localization energies for pyridine *N*-oxide wherein β_{N-O} was taken to be 0.5β, 1.0β, and 1.5β. From these and experimental results, he found β_{N-O} for electrophilic reactions to be greater than 0.5β and for nucleophilic reactions to be approximately 0.8β. No experimental data for free-radical reactions were available at the time. By interpolation of Barnes' calculations at 0.5β, 1.0β, and 1.5β, we obtained from experimental data for the phenylation of pyridine *N*-oxide at 0° the best fit value of $\beta_{N-O} = 0.95\beta$ (see item h, Table III). Assuming, reasonably, that localization energies do not change with temperature and that they are the sole factor in controlling isomer ratios, calculations were made to obtain theoretical values for 131° (item i, Table III). A third set of values were obtained from eq 3,[4] where ΔS^* accounts for differences in the sta-

$$2.303 \log \frac{k_1}{k_2} = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad (3)$$

tistical weights of reactive positions and ΔH^* is the difference in activation energies here designated as differences in localization energies. This third set was designed to transform experimental results obtained at 0° to values for 131° (item j, Table III).

The agreement between calculated values for 131° (10.8; Table III, i), experimental results (16.2; Table II, c), and calculated values for 131° based on experimental 0° (12.6; Table III, j) is very close.[22] The total rate factor at 0° is clearly large and is considered accurate within the limits of the glc method. At 0° only substitution in the α and γ positions contributes significantly to the total rate. Because of its very low value, which made accurate experimental determination rather difficult, the isomer ratio for phenylation at the β position in pyridine *N*-oxide at 0° should be considered semiquantitative. At 131° all experimental values fall within the range permitting accurate estimation of isomer ratios.

The actual value of total rate ratio for pyridine *N*-oxide at 131° (${}^{\text{N-O}}_{\text{C-H}}K$) was estimated experimentally against anisole. The total rate ratio for anisole was calculated to be 1.43 at 131° from the experimental result 1.96 obtained at 0°,[1b] which gave a value of 20.6 for ${}^{\text{N-O}}_{\text{C-H}}K$. However, ${}^{\text{OCH}_3}_{\text{H}}K$ was determined experimentally at 131° to be 1.13, giving a value of 16.2 for ${}^{\text{N-O}}_{\text{C-H}}K$. The latter value was considered more accurate.

The effect of temperature on phenylation of pyridine at 105° (K = 1.04) agrees well with the value calculated from results at 0° (K = 1.15). However, the difference is probably too small (~0.1) to be experimentally significant.

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(18) R. D. Brown, *J. Chem. Soc.*, 272 (1956).

(19) D. A. Brown and M. J. S. Dewar, *ibid.*, 2406 (1953).

(20) J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.*, **84**, 3539, 3541, 3546, 3548 (1962).

(21) S. C. Dickerman, N. Milstein, and J. F. W. McOmie, *ibid.*, **87**, 5522 (1965).

(22) The overall difference between the calculated value of 12.6 and the observed value of 16.2 amounts to a total discrepancy in apparent energy of activation of about 200 cal for the total rate ratio of pyridine *N*-oxide or a discrepancy in the frequency factor of $<10^{0.11}$.

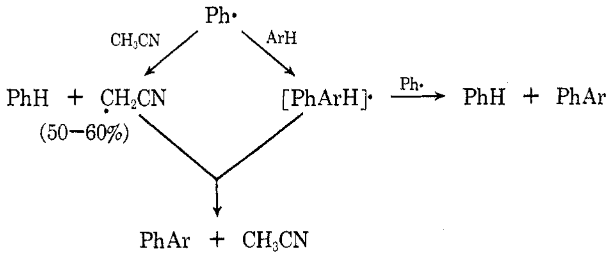
Clearly, our calculations are somewhat naive. Their validity is obviously limited by the assumption that either localization energies do not change with temperature or that the frequency factor is independent of temperature. Nevertheless, they do indicate trends quite satisfactorily.

For naphthalene, the only other highly active substance which has been intensively investigated, given $K = 16.6$ at 0°,[1b] the calculated value at 80° is 9.1. Experimental results from benzoyl peroxide reaction at 80° give $K = 10$, in excellent agreement with calculations. The results presented in Table II demonstrate unequivocally that for pyridine oxide isomer distributions total rate ratios and partial rate factors can be related to localization energies as conceived by Wheland[23] and calculated by Barnes.[10]

Total rate ratios and partial rate factors do change with temperature. This was pointed out by Inukai, Kobayashi, and Simamura[24] regarding high values obtained for the phenylation of nitrobenzene at 20° ($K = 5$),[25] compared with those found at 80° ($K = 2.9$). However, nitrobenzene is not particularly satisfactory as an aromatic substrate compound because of the high yields of tars at high temperatures.

One of the difficulties recognized in determining the validity of partial rate factors is the possible effect of side reactions on the course of the reaction. In the case of reactions of benzoyl peroxide, the problem has been summarized and discussed by Hey.[25] The phenylation technique developed in our laboratory[1b] gives little, if any, dimerization or disproportionation products except, possibly, during reactions with nitrobenzene.[26] Acetonitrile in these reactions (at low temperatures) appears to behave similarly to oxygen or nitrobenzenes in the benzoyl peroxide reaction (Scheme II).[25] Hence total rate ratios and partial rate factors calculated from these reactions should be relatively free of the effect of side reactions. Furthermore, because our results agree generally with the results obtained using benzoyl peroxide,[1b] it is reasonable to agree with Morrison[27] that "side reactions have no significant effect on isomer distribution or relative reactivities as measured by product analysis."

SCHEME II



Finally, the results demonstrate that total and partial rates are subject to the laws of the theory of rate processes. Thus kinetic information not otherwise obtainable can be estimated by competitive reactions with a known standard at a single temperature. However, experimentally, temperature effects are probably not significant unless the total rate ratio at 0° is >10 and/or temperature differences are >100°.

Experimental Section

Reagents.—All liquid reagents and solvents were dried over anhydrous sodium sulfate, fractionally distilled, degassed by bubbling purified nitrogen through them, and stored in the dark in air-tight containers. Acetonitrile was treated as previously described.[1b] Solid reagents and reference compounds were recrystallized. Melting points agreed with literature values. Pyridine *N*-oxide was prepared from pyridine, glacial acetic acid, and hydrogen peroxide,[28] mp 65–66°. Benzenediazoniumtetrafluoroborate was prepared from the published method.[1a]

Reduction of Pyridine *N*-Oxides.—Reduction using thiourea[29] gave a tarry reaction mixture and low yields of deoxygenated products. A synthetic mixture of pyridine *N*-oxide and phenylpyridine *N*-oxide was added to 8 *N* hydrochloric acid. Zinc dust (100% molar excess) was added slowly over an hour and the mixture left for 16–24 hr with stirring. The mixture was filtered and made basic. After liquid–liquid extraction with benzene for 24 hr, the benzene extract was dried and concentrated to 10 ml for glc analysis. Yields of 96–98% of the corresponding deoxygenated compounds were consistently obtained. This technique was used to identify and estimate the products of pyridine *N*-oxide reactions.

Electrolytic Reductions.—Generally, the previously published method was used.[1b] All reactions were run under purified nitrogen. Control voltage *vs.* sce was 0.35 V for pyridine[13] and 0 V for pyridine *N*-oxide. In competitive reactions, the ratios of concentrations of aromatic substrates (*i.e.*, nitrogen compound: benzene or anisole) were 1:1 and 1:10 for pyridine and 1:10 and 1:20 for pyridine *N*-oxide. To avoid disubstituted products, diazonium salt concentration was kept not higher than $^1/_{50}$th (mol/mol) of that of the aromatic substrates.

Initial currents ranged from 80 to 200 mA. A reaction was considered complete when the current had fallen to less than 1 mA and the α-naphthol test for diazonium salt was negative. All reactions developed dark colors, but no attempt was made to identify the source.

Nonelectrolytic Reactions of Pyridine.—Benzenediazonium tetrafluoroborate (1.92 g, (0.01 mol) was added to dry pyridine (79 g, 1 mol) at 15 ± 1° under nitrogen. A reaction began at once which was complete in 60–70 min, at which time the α-naphthol test for diazonium salt was negative. Repeating the reaction over a mercury pool, a more vigorous reaction resulted which was complete in about 15 min. The reaction mixture was analyzed by glc.

Phenylation Using Diazoaminobenzene.—Diazoaminobenzene (1.97 g, 0.01 mol) was added to 95 g of pyridine *N*-oxide (1 mol) under nitrogen in an oil bath maintained at 131 ± 2°. After 24 hr the mixture was cooled to room temperature and sufficient benzene was added to bring the volume to 100 ml. A 20-ml aliquot was reduced with zinc and HCl as described above.

Phenylation of Pyridine *N*-Oxide Using Benzenediazonium Tetrafluoroborate and Pyridine.—Two systems were investigated, the only difference between them being that one contained a mercury pool and one did not. Pyridine *N*-oxide (9.5 g, 0.1 mol) and 0.316 g of pyridine (0.004 mol) were dissolved in 23 ml of CH_3CN at 20 ± 1°. Diazonium salt (0.384 g, 0.002 mol) was added to the clear, degassed solution. The solution was stirred under nitrogen and guarded with a drying tube.

Both reactions began immediately and darkened in color. The one with mercury was very vigorous and was complete in less than

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[26] The absence of significant quantities of disproportionation products, particularly dihydrobiphenyls was shown by the results of combined glc-mass spectra measurements. High yields of benzene (50–60%) and clear light-colored reaction mixtures indicated the absence of high molecular weight materials. That the σ complex is being efficiently oxidized is attested by the fact that electrolytic reductions in the presence of oxygen gave lower yields and dark-colored reaction mixtures, precisley opposite to results obtained in phenylations with benzoyl peroxide.[27] Presumably, oxygen interferes with the activity of $H_2\dot{C}CN$ and/or Hg,[17] resulting in high yields of dimerization, disproportionation, and polymerization products.

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2 hr. The reaction without mercury required *ca.* 10 hr for completion.

Half of each reaction mixture was taken to dryness under vacuum at room temperature, basified with 20 ml of 5% NaOH, and extracted with benzene. The dried benzene extract was concentrated and used for glc analysis. The other half of each mixture was reduced with zinc and HCl as described above.

Competitive Reactions at 131°. (a) Pyridine *N*-Oxide.—Diazoaminobenzene (3.94 g, 0.02 mol) was added to a mixture of 19 g of pyridine *N*-oxide (0.2 mol) and 216 g of anisole (2 mol) under nitrogen at 131 ± 2°. After 24 hr the mixture was cooled and evaporated under vacuum to 100 ml. Hydrochloric acid (50 ml, 0.5 *N*) was added to each of duplicated 10-ml aliquots of this solution, and the mixtures were extracted with ether. The ether extracts, containing methoxybiphenyls, were dried and concentrated for glc analysis. The aqueous phases, containing the phenylpyridines and phenylpyridine *N*-oxides, were reduced with zinc and HCl as above.

Two other 10-ml aliquots of the reaction mixture were acidified, washed with ether to remove methoxybiphenyls, basified, and extracted with benzene to give phenylpyridines in <1% yield. The isomer ratios were found to be between those for phenylation of pyridine and those found for phenylation of pyridine *N*-oxide. The authors therefore found it reasonable to overlook this insignificant amount in calculations.

(b) Anisole.—Diazoaminobenzene (3.94 g, 0.02 mol) was dissolved in a cold solution of 108 g of anisole (1 mol) and 78 g of benzene (1 mol) in a Carius tube. The solution was frozen in liquid nitrogen and the tube sealed. The tube and contents were allowed to come to room temperature and then agitated in an oil bath at 131° overnight. The tube was then frozen again; the contents were removed, concentrated to 25 ml and used directly for glc analysis.

Identification and Estimation of Products.—All reaction mixtures were analyzed by gas–liquid partition chromatography (glc). Phenylpyridines and biphenyls were identified by retention times and mass spectroscopy and were collected for verification from melting points and infrared spectra. After completion of reactions containing acetonitrile, the latter was distilled under vacuum at room temperature. In the pyridine reaction dry ether was added to precipitate tetrabutylammonium perchlorate. The ether solution was concentrated under vacuum and used directly for glc analysis. Yields, isomer ratios, total rate ratios, and partial rate factors are mean values of duplicate or triplicate runs.

Glc Columns Used and Retention Times.—It was found that any of the following stationary phases could be used for separation of biphenyl, methoxybiphenyls, and phenylpyridines: ethylene glycol adipate (10%), butanediol succinate (15%), Apiezon L (25%), and QF-1 (20%) [all weight/weight % on Chromosorb WNAW, 60–80 mesh].

QF-1, 6 ft × $^{3}/_{16}$ in., temperature programming from 70 to 160°, was used to separate phenylpyridines. The retention times for biphenyl and 2-, 3-, and 4-phenylpyridines were 6.5, 16, 17, and 17.5 min, respectively. Apiezon L, 8 ft × $^{3}/_{16}$ in., temperature programming from 70 to 250° and held at 250°, separated 2-, 3-, and 4-methoxybiphenyls with retention times 28, 30.5, and 31.5 min, respectively.

Registry No.—Pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7.

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The Radical-Induced Decomposition of Aryliodine Dicarboxylates

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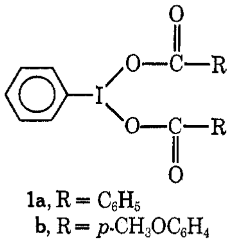
Benzoyl and substituted benzoyl peroxides induce the decomposition of phenyliodine dibenzoate or dianisate in C_6H_5Cl at 80°. The rate of decomposition of the peroxide is slightly diminished, and the yield of chlorobiphenyls from the peroxide is increased as compared to the values in the absence of the iodine compounds. The major products from the iodine compound are iodobenzene and the corresponding carboxylic acid. The product mixture from previously decomposed benzoyl peroxide also accelerates the decomposition of the iodine compound. It is suggested that phenylchlorocyclohexadienyl radicals induce the decomposition of the iodine compound. The catalytic effect of peroxide decomposition products is attributed to substituted tetrahydroquaterphenyls acting as chain-transfer agents.

The thermal decomposition of aryliodine dicarboxylates (**1**) is accelerated both by added radical initiators and by radical chain-transfer agents.[1,2]

The decomposition of phenyliodine dibenzoate[3] (**1a**, R = C_6H_5), accelerated by benzoyl peroxide, continues at an enhanced rate long after the peroxide concentration has been reduced to a negligible value, and indeed a chlorobenzene solution of benzoyl peroxide decomposition products also accelerates the decomposition.[1] Thus benzoyl peroxide not only produces radicals capable of attacking the dibenzoate, but also a chain-transfer agent that increases the effectiveness of the dibenzoate itself as initiator.



1a, R = C_6H_5
b, R = $p\text{-}CH_3OC_6H_4$

The chain-transfer agent is not benzoic acid, phenyl benzoate, biphenyl, iodobenzene, or any of the isomeric chlorobiphenyls, since these substances are produced in substantial amounts by the decomposition of the dibenzoate in the absence of added peroxide and the expected autocatalysis is not observed.

In the present paper we report the results of an investigation of the peroxide-accelerated decomposition of phenyliodine dibenzoate and dianisate in chlorobenzene at 80°. At this temperature the spontaneous decomposition of the phenyliodine dicarboxylate is extremely slow, and its decomposition products are almost exclusively those of the induced reaction.

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