(20) J. M. Norbeck and G. A. Gallup, *J. Amer. Chem. Soc.*, **95**, 4460 (1973).
(21) Obtained from the Quantum Chemistry Program Exchange, Indiana University.
(22) The most unstable conformation is 90° out of plane in both **7** and **8**.
(23) While values calculated by INDO theory could be greater than barriers determined experimentally, the trends are clear. Such barriers should be strictly compared within a related series of optimized structures.
(24) This is the barrier for the rotation of a single NH_2 group while the other three remain in the plane.
(25) Tables of the MO energy levels for species **3–8** are available on request from the authors. Configuration interaction was not used in calculations of the above transitions.

Mesitylation and Phenylation of Picolyl Anions by the SRN1 Mechanism[1]

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The 2- and 4-picolyl anions are arylated, to form arylmethylpyridines, by chlorobenzene, phenyltrimethylammonium ion, and 2-bromomesitylene under stimulation by potassium metal or near-ultraviolet light. These reactions are believed to occur by the SRN1 mechanism. The 2- and 4-picolyl anions are also phenylated in reactions with bromo- and iodobenzene that probably occur in part by the benzyne and in part by the SRN1 mechanism.

The arylation of ketone enolate ions,[3] α-cyanoalkyl anions,[4] and anions derived from several hydrocarbons[3c] *via* the recently discovered SRN1 mechanism[5-7] has been described.

This mechanism,[6] which is sketched in Scheme I for reaction of a carbanion with an aromatic substrate, is initiated by electron transfer (step 1) to the substrate, forming a radical anion. If the electron donor is a solvated electron, the residue is merely solvent. If the electron is donated by an anion, under thermal[5a] or photostimulation,[3b] the residue is a radical. In step 2, the radical anion of the substrate ejects a nucleofugic substituent, and an aryl radical is formed. This radical, in step 3, combines with the carbanion to form a new radical anion, which is usually not a particularly stable species. One of the ways in which it can gain stabilization is to transfer its excess electron to another substrate molecule (step 4). One product of that step is the radical anion which is a reactant in step 2, and thus steps 2, 3, and 4 constitute the propagation cycle of a chain mechanism. There are, of course, also termination steps.

Scheme I

$$\text{electron donor} + \text{ArX} \longrightarrow [\text{ArX}]\cdot^- + \text{residue} \quad (1)$$

$$[\text{ArX}]\cdot^- \longrightarrow \text{Ar}\cdot + \text{X}^- \quad (2)$$

$$\text{Ar}\cdot + \text{R}:^- \longrightarrow [\text{ArR}]\cdot^- \quad (3)$$

$$[\text{ArR}]\cdot^- + \text{ArX} \longrightarrow \text{ArR} + [\text{ArX}]\cdot^- \quad (4)$$

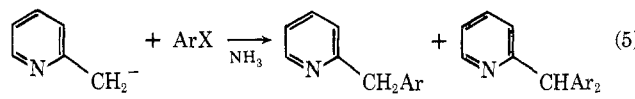
It is noteworthy that, although steps 2, 3, and 4 involve radical and radical anion intermediates, the net input is substrate ArX plus anion R:$^-$ and the net output substitution product ArR with by-product X$^-$; thus, in effect, the reaction is a nucleophilic substitution.

The present research extends studies of aromatic SRN1 reactions to include picolyl anion nucleophiles. The 2- and 4-picolyl anions are obtained by the action of KNH_2 on 2- and 4-picoline, respectively, in liquid ammonia solution.[8]

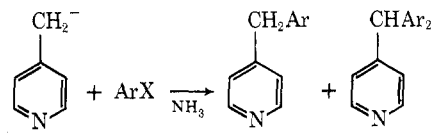
Results

We find that the 2- and 4-picolyl anions are arylated under conditions conducive to the SRN1 mechanism, according to the general pattern of eq 5 and 6. Our experiments are summarized in Table I.

Runs 1, 5, 7, and 9 were conducted either in the dark (in a flask wrapped with aluminum foil) or with exposure to the usual diffuse illumination of the laboratory, without stimulation by solvated electrons. Under these conditions, bromobenzene and the 2-picolyl anion (run 5) reacted to form arylation products in a total yield of 69%, conforming to the general pattern of eq 5. Iodobenzene and the 4-picolyl anion (run 1) formed 14% of 4-benzylpyridine in a much shorter reaction time and at a much lower temperature. However, chlorobenzene (run 7) and phenyltrimethylammonium ion (run 9) were essentially unreactive with the 2-picolyl anion.



(5)



(6)

It is probable that, in runs 1 and 5, reaction occurred by the benzyne mechanism.[9,10] The 2- and 4-picolyl anions have pK_a's of approximately 31 and 29, respectively, not far from pK_a = 33.2 for amide ion.[8] It is therefore not unreasonable that the picolyl anions or amide ion in equilibrium with them should bring about benzyne formation on reaction with iodo- and bromobenzene, which are particularly prone to form benzyne on reaction with strong bases.[9] On the other hand, chlorobenzene has a lesser and phenyltrimethylammonium ion a much lesser tendency to form benzyne on reaction with amide ion in ammonia.[9,14]

Because of the considerable reactivity of iodo- and bromobenzene with the picolyl anions in unstimulated reactions, the mechanisms of their reactions stimulated by potassium metal (runs 2 and 3) or irradiation (run 6) are uncertain. A mixture of benzyne and SRN1 mechanisms seems probable.

On the other hand, for reasons mentioned it is likely that the potassium metal stimulated reaction of chlorobenzene (run 8) and the photostimulated reaction of phenyltrimethylammonium ion (run 10), both with the 2-picolyl anion, occur largely or entirely by the SRN1 mechanism. These runs formed 2-benzylpyridine in yields of 48 and 66%, respectively. Very similar is the photostimulated phenylation of the 4-picolyl anion by phenyltrimethylammonium ion (run 4), which gave 88% of 4-benzylpyridine.

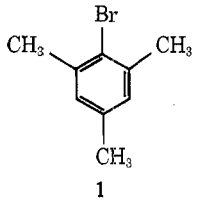
As a means of avoiding absolutely the possibility of the benzyne mechanism as a complication, we turned our attention to arylation with 2-bromomesitylene (1), which

Table I
Arylation of 2- or 4-Picolyl Anion in Liquid Ammonia under N_2

Run no.	Picolyl anion isomer	$[C_5H_4NCH_2^-]$, M	ArX[a]	[ArX], M	Stimulant[b]	Temp, °C	Reaction time, min	Product yields, % Recovered ArX	C_5H_4N-CH_2Ar[c]	C_5H_4N-$CHAr_2$[c]	Other products (yield, %)
1	4	0.98	PhI	0.35	Nil[d]	−77	8	*e*	14		
2	4	0.26	PhI	0.80	K (0.98)[b]	−77	*f*	*g*	44[h]	27[h]	C_6H_6[g]
3	4	1.39	PhI	0.47	K (1.4)[b]	−77	*f*		51	12	C_6H_6 (12)
4	4	0.50	$PhNMe_3^+I^-$	0.042	*hν*	−33	60		88	3[h]	
5	2	0.33	PhBr	0.10	Dark	−33	60	0	57	*i*	
6	2	0.42	PhBr	0.13	*hν*	−33	60	0	73	*i*	
7	2	0.93	PhCl	0.31	Nil[d]	−77	8	100			
8	2	1.02	PhCl	0.33	K (0.36)[b]	−77	*f*	7	48		C_6H_6 (14)
9	2	0.26	$PhNMe_3^+I^-$	0.10	Dark	−33	60		<2		$C_6H_5NMe_2$ (21) 2-Ethylpyridine (20[h])
10	2	0.28	$PhNMe_3^+I^-$	0.11	*hν*	−33	60		66	*i*	$C_6H_5NMe_2$ (9)
11	4	1.21	MesBr[a]	0.22	*hν*	−33	120	38	55		Mesitylene (3[h])
12	2	0.50	MesBr[a]	0.05	Dark	−33	60	92			
13	2	0.50	MesBr[a]	0.05	*hν*	−33	60		87		Mesitylene (4)

[a] Ph stands for phenyl, Mes for mesityl. [b] For potassium metal stimulated runs, mol of K/mol of ArX is given in parentheses. [c] Same orientation as in the starting picoline. [d] Reaction was exposed only to ordinary illumination of the laboratory. [e] Most of the C_6H_5I was recovered. [f] See Experimental Section for procedure. [g] Identified but not quantified. [h] Approximate yield. [i] A few per cent (2–12%) of a substance of longer glpc retention time, probably 2-benzhydrylpyridine, was observed.

cannot form an aryne on reaction with a strong base.[9] As anticipated, it was unreactive with the 2-picolyl anion when denied stimulation by light or potassium metal (run 12). On the other hand, it underwent photostimulated reaction with the 4-picolyl anion in the manner of eq 6 to form a monoarylation product (2) in 55% yield, with 38%



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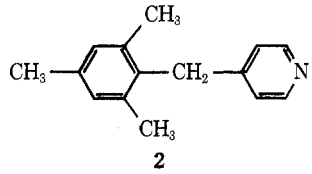

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of the 2-bromomesitylene remaining unreacted (run 11). The photostimulated mesitylation of the 2-picolyl anion (run 13) was even better, forming a monoarylation product in 87% yield. The formation of small amounts of mesitylene as a by-product in runs 11 and 13 is consistent with the intermediacy of mesityl radicals, and constitutes incidental support of the SRN1 mechanism of Scheme I.

Discussion

Our results (Table I) indicate that the 2- and 4-picolyl anions may be arylated under conditions conductive to the SRN1 mechanism.

Worthy of note is our observation of the mesitylation of nucleophiles in good yield (runs 11 and 13). We have found in the literature only one prior report of the mesitylation of carbanions. Beringer and Galton[15] obtained, from reaction of dimesityliodonium chloride with the anion of 2-phenylindan-1,3-dione in *tert*-butyl alcohol, a 23% yield of the anticipated C-mesitylation product. Mesitylation of the anion of indan-1,3-dione under similar conditions was less rewarding. They proposed a nonchain, electron transfer, radical mechanism having some resemblance to that of Scheme I.

Our observations of mesitylation, together with the fact that 2-iodo-1,3-xylene undergoes potassium metal stimulated reaction with KNH_2 to form the corresponding amino compound in 64% yield,[5b] suggest that the reactivity of the phenyl radical toward nucleophiles is not seriously impaired by ortho methyl groups.

Experimental Section

General Procedure. Experiments were conducted in liquid ammonia solution, for the most part as previously described.[3b,c] Potassium amide was formed by reaction of potassium metal with ammonia, catalyzed by a little ferric nitrate. 2- or 4-picoline was then added, in molar amount equal to that of KNH_2 (runs 1, 2, 3, 7, and 8) or in slight excess (0.5% in run 6, 2% in runs 4, 11, 12, and 13, 4% in run 10, 5% in run 5, 7% in run 9). For runs 2, 3, and 8, the halobenzene and bits of potassium metal were added alternately in small portions, and the concentration of halobenzene stated in Table I is that which would have prevailed at completion of addition had there been no reaction while addition was in progress. Runs at −33° were conducted at reflux, and runs at −77° with the reaction flask partially immersed in a slush of solid carbon dioxide in isopropyl alcohol. For runs 5, 9, and 12, the reaction flask was wrapped in aluminum foil to exclude light. Runs 4, 6, 10, 11, and 13 were performed in a Rayonet photochemical reactor equipped with 350-nm lamps.

Runs 3 and 8 were quenched by addition of sodium benzoate and then NH_4Cl, the others just by addition of NH_4Cl. Reaction mixtures were processed by standard procedures in preparation for analysis by glpc (column of 5% SE-30 silicone rubber on Chromosorb P). Biphenyl or, in suitable cases, bromobenzene was employed as internal standard. The yields stated in Table I are by glpc analysis. Portions of several reaction product mixtures were submitted to distillation *in vacuo;* substantial samples of 2- and 4-benzylpyridines and 2- and 4-mesitylmethylpyridines were thereby obtained for examination of physical properties, etc.

Product Identification. 2-Benzylpyridine, bp 109° (1.5 Torr), and 4-benzylpyridine, bp 113° (1.5 Torr), were identified by the match of their infrared spectra to those of authentic samples, as well as by their mass spectra. Mesitylene was recognized by the identity of its glpc retention time with that of an authentic sample. 4-Benzhydrylpyridine, which appeared on glpc at longer retention times, was identified from its mass spectrum: *m/e* (rel intensity) 245 (41), 244 (27), 169 (21), 168 (34), 167 (100), 166 (26), 165 (43), 152 (15), 139 (16), 115 (20), 91 (16), 65 (14), 63 (19); the parent peak at *m/e* 245 and the prominent fragment at *m/e* 167 (appropriate to benzhydryl cation) indicate the assigned structure.

2-Mesitylmethylpyridine, alternatively named as 2,4,6-trimethyl-2′-azadiphenylmethane, had bp 108° (0.25–0.3 Torr); $n^{23}D$ 1.5699; nmr (CCl_4) δ 2.19 (s, 6 H of *o*-CH_3′ s), 2.23 (s, 3 H of *p*-

CH_3), 4.13 (s, 2 H of CH_2), 6.80 (s, 2 H of mesitylene moiety), 6.67 ("d," H_e, J_{ef} = 7.5 Hz), 6.93 ("d," H_g, $J \cong 7$ Hz), 7.32 (m, H_f, $J \cong 7.5$ and 2 Hz), 8.42 ("d," H_h) (H_e, H_f, H_g, and H_h are presumed to be at positions 6′, 5′, 4′, and 3′ of the pyridine ring, respectively); ir (neat) 3080–2850, 1610, 1580, 1565, 1465, 1430, 1370, 1200, 1145, 1090, 1048, 1030, 990, 850, 750 cm^{-1}; mass spectrum *m/e* (rel intensity) 212 (6), 211 (32), 196 (100), 181 (34), 119 (25), 91 (25), 77 (21), 51 (32), 39 (37), m* 182 (211 → 196), 167.2 (196 → 181), doubly charged 105.5, 104.5, 97.5, 96.5, 90.5, 89.5.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found:[16] C, 85.13; H, 8.27; N, 6.71.

4-Mesitylmethylpyridine (2), alternatively named as 2,4,6-trimethyl-4′-azadiphenylmethane, had bp 138–139° (0.75 Torr); mp 40–41° (from ether); nmr (CCl_4) δ 2.10 (s, 6 H of *o*-CH_3's), 2.22 (s, 3 H of *p*-CH_3), 3.88 (s, 2 H of CH_2), *ca.* 6.8 (s, 2 H of mesitylene moiety), *ca.* 6.82 (d, 2 H), 8.28 (d, 2 H, J = 6 Hz); ir (neat) 3080–2860, 1601, 1480, 1440, 1410, 1370, 1215, 1068, 1028, 993, 882, 853, 780, 722, 603 cm^{-1}; mass spectrum *m/e* (rel intensity) 212 (16), 211 (100), 196 (78), 181 (27), 133 (67), 119 (37), 91 (16), 77 (14), m* 182 (211 → 196), 167.2 (196 → 181), doubly charged 105.5, 104.5, 103.5, 97.5, 96.5, 90.5, 89.5, 83.5, 82.5.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found:[16] C, 85.23; H, 8.19; N, 6.80.

Registry No. 2, 43136-90-9; 2-picolyl anion, 18860-16-7; 4-picolyl anion, 18860-18-9; 2-benzylpyridine, 101-82-6; 4-benzylpyridine, 2116-65-6; 4-benzhydrylpyridine, 3678-72-6; 2-mesitylmethylpyridine, 43136-96-5.

References and Notes

(1) Financial support from the National Science Foundation is gratefully acknowledged.
(2) Grateful recipient of a fellowship, 1971–1972, from the Schweizerische Stiftung fur Stipendien auf dem Gebiete der Chemie.
(3) (a) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972); (b) *J. Org. Chem.*, **38**, 1407 (1973); (c) *ibid.*, **38**, 3020 (1973).
(4) J. F. Bunnett and B. F. Gloor, *J. Org. Chem.*, **38**, 4156 (1973).
(5) (a) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970); (b) *ibid.*, **92**, 7464 (1970).
(6) The mechanism designated $S_{RN}1$[5a] was discovered by Kornblum, Russell, and their coworkers[7] for certain nucleophilic substitution reactions at aliphatic sites. Later, Kim and Bunnett[5] recognized it as an aromatic substitution mechanism.
(7) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5662 (1966); N. Kornblum, *Proc. Int. Congr. Pure Appl. Chem., 23rd*, **4**, 81 (1971); G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966); **90**, 347 (1968); G. A. Russell, R. K. Norris, and E. J. Panek, *ibid.*, **93**, 5839 (1971).
(8) J. A. Zoltewicz and L. S. Helmick, *J. Org. Chem.*, **38**, 658 (1973).
(9) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).
(10) Phenylation of the anions of 1-picoline,[11] 2-methylquinoline,[12] 4-methylquinoline,[11] and 2-methylpyrazine[13] under conditions conducive to the benzyne mechanism has been described.
(11) P. H. Dirstine and F. W. Bergstrom, *J. Org. Chem.*, **11**, 55 (1946).
(12) R. E. Wright and F. W. Bergstrom, *J. Org. Chem.*, **1**, 179 (1936).
(13) J. D. Behun and R. Levine, *J. Org. Chem.*, **26**, 3379 (1961).
(14) Unstimulated reaction between the 2-picolyl and phenyltrimethylammonium ions (run 9) afforded appreciable amounts of 2-ethylpyridine and *N,N*-dimethylaniline, probably *via* the S_N2 mechanism.
(15) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3417 (1963).
(16) Analysis by Micro-Tech Laboratories, Skokie, Ill.

Thermolysis of Peresters. The Relative Stability of Allylic and Propargylic Radicals

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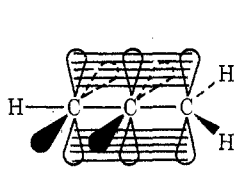
tert-Butyl peroxy-2,2-dimethylbutenoate (7) undergoes thermolysis in cumene with ΔH^* = 24.0 ± 0.3 kcal mol^{-1} and ΔS^* = −1.0 ± 1.0 eu while *tert*-butyl peroxy-2,2-dimethylbutynoate (8) shows activation parameters of ΔH^* = 27.1 ± 0.6 kcal mol^{-1} and ΔS^* = 4.7 ± 1.8 eu. The difference in activation enthalpies is interpreted in terms of polar effects and not on the basis of radical stabilities. Other evidence suggests that propargylic radicals are slightly less stable than allylic radicals, but the difference is too small to measure accurately by present techniques.

A propargyl radical (1) can be regarded as an allyl radical (2) with an additional π bond perpendicular to the plane of the orbital bearing the odd electron. In view of



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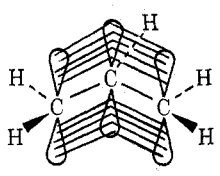

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the geometric change imposed by this extra bond, one might ask whether the two species differ in stability. A more stable radical will have a greater resonance energy (RE), which is defined for our purposes as the difference between the bond dissociation energy (BDE) of an appropriate saturated compound and that of the unsaturated one.

$$RE(allyl) = BDE(propyl\ H) - BDE(allyl\ H)$$

$$RE(propargyl) = BDE(propyl\ H) - BDE(propargyl\ H)$$

Bond dissociation energies and hence radical stabilities have been determined by such "physical" methods as mass spectroscopic appearance potentials,[2,3,13] iodine-catalyzed equilibration,[4,11,12] pyrolytic techniques,[7,14] and shock-tube studies.[9] In surveying some of the results for allylic and propargylic radicals (*cf.* Figure 1) two general trends can be observed: a lower resonance energy in the more recent measurements and slightly less stabilization for propargylic than for allylic radicals. However, the latter observation is tenuous in view of the experimental uncertainties involved.

Another general approach to the question of radical stabilities assumes that the activation energy for thermolysis of a radical precursor reflects the stability of the radical.[15] Two classes of organic molecules which exhibit such a trend are azo compounds and peresters; in fact, some information regarding the stability of allylic and propargylic radicals is available from studies of their thermolysis. In 1967, Martin and Sanders[16] reported that perester 3 decomposed with an activation enthalpy 4.0 kcal mol^{-1} less than that of the analagous propargylic perester 4 and concluded that "the 2-butenyl radical is about 4 kcal mol^{-1} more stable than the 2-butynyl radical." More recently, one of us[17] found that azo compounds 5 and 6 decomposed with nearly the same activation enthalpy and suggested that the resonance energy of the dimethylallyl radicals differed little from that of dimethyl-