in addition to a broadened singlet within this doublet. At 9.61 ppm a clear doublet was evident (4 Hz). These signals are consistent with the presence of both $(C_6H_5)_3SiCHDCHO$ (10a) and $(C_6H_5)_3SiCH_2CDO$ (10b) in ca. equal amounts.

Registry No.—1a, 18666-68-7; 1b, 59231-24-2; 1c, 59231-25-3; 2a, 18666-55-2; 2b, 59231-26-4; 2c, 59231-27-5; 4a, 791-31-1; 5a, 56920-26-4; 5b, 56920-25-3; 9, 59231-28-6; 11, 59231-29-7; (E)-trimethyl(β-styryl)silane, 19372-00-0; (Z)-trimethyl(β-styryl)silane, 19319-11-0; ethynyl(triphenyl)silane, 6229-00-1; diisobutylaluminum deuteride, 59231-30-0; α-deuteriovinyl chloride, 4984-12-7; phenyllithium, 591-51-5; tetraphenylsilane, 1048-08-4; diisobutylaluminum hydride, 1191-15-7; hydrogen chloride, 7647-01-0; chlorotriphenylsilane, 76-86-8; benzylamine, 100-46-9.

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N. Newman [*J. Organomet. Chem.*, **3**, 1 (1965)] have detected complexes between lithium ethoxide and ethyllithium having varying stoichiometries by cryoscopic means. (c) L. M. Seitz and T. L. Brown [*J. Am. Chem. Soc.*, **88**, 2174 (1966)] have offered NMR exchange evidence that the presence of lithium ethoxide impedes the dissociation of such complexes, Li_4R_3X (where X = OC_2H_5), into dimeric or monomeric lithium alkyls. Thus, it seems reasonable that lithium alkoxide, halide [W. Glaze and R. West, *J. Am. Chem. Soc.*, **82**, 4437 (1960)], or oxide would retard the rate of reaction of lithium alkyls toward substrates which behave as electrophiles.
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(18) (a) J. K. Crandall and L.-H. C. Liu, *J. Am. Chem. Soc.*, **89**, 4527 (1967), have proposed the formation of such epoxide anions and carbenoids to explain the behavior of *tert*-butyllithium toward epoxides. (b) Ongoing studies in this laboratory have shown that the reaction of lithium alkyls with epoxyethyl(triphenyl)silane can, in certain solvents, pursue largely a different course: in ethyl ether or tetrahydrofuran the principal product is 1-hexen-2-yl(triphenyl)silane (>70% yield in THF), while in hexane the formation of *n*-butyl(triphenyl)silane is in accord with the pathway followed by phenyllithium (eq 15). Analogously, others have observed that epoxyethyl(trimethyl)silane and *tert*-butyllithium in THF yielded 3,3-dimethyl-2-butenyl(trimethyl)silane.[10] The action of Grignard reagents on these epoxides, as reported by these same workers to yield 1-trimethylsilyl-2-alkanols,[10] obviously involves magnesium bromide catalyzed isomerizations of these epoxides to the 2-silylacetaldehydes, as depicted in eq 11 for epoxyethyl(triphenyl)silane. As would be expected, magnesium halide free dialkylmagnesium reagents open such epoxides without rearrangement,[10] in the same manner as that of organocuprate reagents.[10]
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Demethylations of Quaternary Pyridinium Salts by a Soft Nucleophile, Triphenylphosphine. Electronic and Steric Accelerations[1]

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N-Methyl quaternary pyridinium salts are easily demethylated by PPh_3 in DMF. The relative rate constants are determined by NMR with a competition technique for 18 compounds. The range of reactivity is 10^3. The reaction is accelerated with electron-withdrawing substituents on the pyridine ring. The Hammett and Bronsted equation constants are $\rho = +2.34$; $\alpha = +0.387$. Ortho substituents increase the rate constants by strain release (a factor of 103 for the 2-*t*-Bu). The correlation with the opposite quaternization reactions is excellent (correlation coefficient R = 0.994). Linear free-energy relationships are obtained both with electronic and steric parameters, and give further insight into the structure of the transition state of these reactions.

Compared to the number of mechanistic and structural studies on the quaternization of pyridines,[3] no quantitative results have yet been reported for dequaternization of pyridinium salts.

Until recently no general method existed for N-dealkylation of quaternary salts of heteroaromatic amines. The techniques applied to ammonium salts are inadequate: they use hard nucleophiles and (or) high temperatures,[4–15] so that sensitive

Table I. Relative Rate Constants for Demethylation of Pyridinium Iodides by PPh_3 in Boiling DMF (153 °C)

| Compd	Substituent on pyridine ring	k/k_H	pK_a of the pyridinium salt[22]	σ constants[23]
1	H	1	5.19	0
2	3,4-di-Me	0.255	6.48	-0.239^a
3	3-NH₂	0.263	6.04	-0.16
4	3,5-di-Me	0.279	6.15	-0.138
5	4-Me	0.566	6.00	-0.170
6	3-Me	0.619	5.70	-0.069
7	2-Me	1.00	5.96	
8	2-Et	1.49	5.89	
9	3-CONH₂	2.37	3.35	0.28
10	2-*i*-Pr	2.88	5.83	
11	2-Ph	8.40	4.77	
12	3-Br	9.76	2.85	0.391
13	2-PhO	10.9		
14	3-Cl	6.68	2.81	0.373
15	2-*t*-Bu	50.2	5.76	
16	2-Cl	70.4	0.49	
17	2-CHO	74.2	3.77	
18	2-CN	163	-0.26	

^{a} σ constants of di-Me are considered as additive.

functions[4-6,8] as well as the heteroaromatic ring can be affected.[16] Recently soft nucleophiles (PPh_3, NH_2CSNH_2)[17] or DMF[18] were reported to give clean dealkylations.

We wish to report that the use of a soft nucleophile in an aprotic solvent permits the easy dealkylation of pyridinium salts. This study allowed us to determine the role of substitution on the behavior of these dealkylation reactions.

Results and Discussion

In Table I are reported the relative rate constants for the demethylation of 18 quaternary pyridinium iodides, including nine ortho-substituted compounds, by reaction with PPh_3 in DMF (Scheme I).

Scheme I
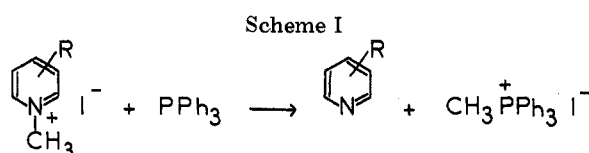
There is only evidence for a nucleophilic substitution by PPh_3 on the carbon atom of the methyl group, with displacement of the substituted pyridine.[19] Comparable yields of recovered amines are obtained with a reflux period much shorter than with DMF alone.[18]

The relative rate constants of demethylation have been measured by a competition technique[21] using the intensities of the N–Me NMR signals of each compounds and of a suitable standard. In the series studied there is a range of reactivity of 10^3. The relative values agree with preliminary reports which indicate an acceleration of the reaction with electron-withdrawing substituents.[18] However, the rate ratio of compounds **7** and **15** is good evidence that steric effects are also involved with ortho substituents.

With **3**, **4**, and **5** substituents there is a correct Hammett relation $\log k/k_H = \rho\sigma$ with a correlation coefficient $R = 0.971$ (Figure 1). The sign and magnitude of $\rho = +2.34$ is consistent with the direct displacement by PPh_3 of the substituted pyridine, since the positive charge of the nitrogen atom is released in part in the transition state.[24,37] Moreover, in the transition state of an S_N2 process the C–N bond should be
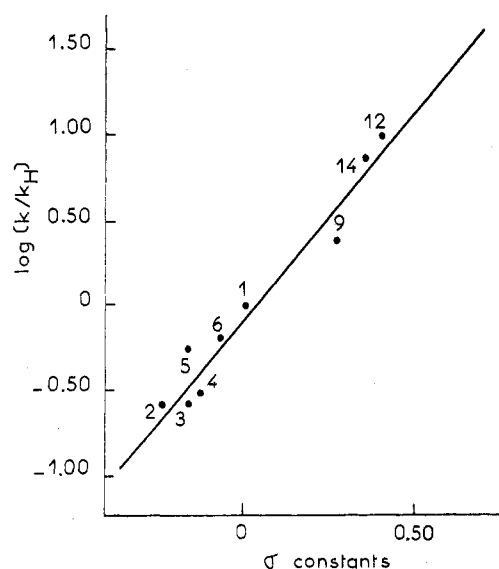

Figure 1. Plot of log (k/k_H) vs. Hammett substituent constants for the demethylation of 3- and 4-substituted pyridinium iodides by PPh_3. The numbers in the graph correspond to those in Table I.
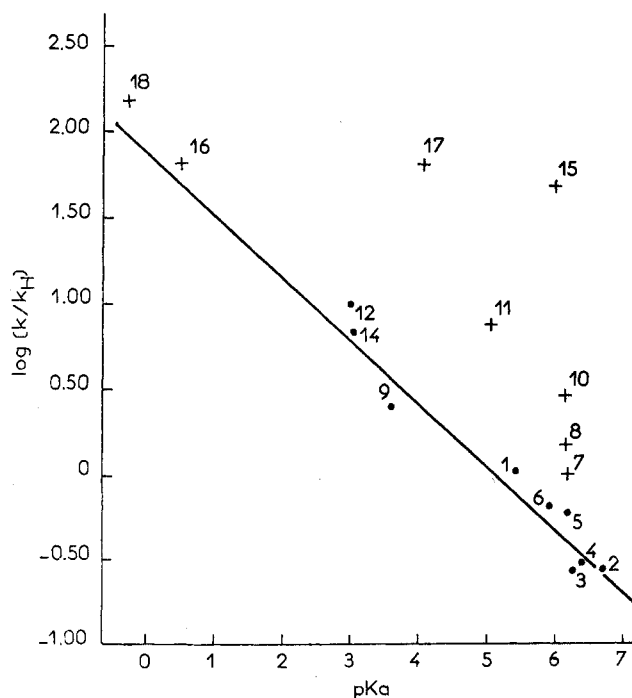

Figure 2. Plot of log (k/k_H) for demethylation of pyridinium iodides by PPh_3 vs. pK_a of the corresponding pyridinium ions. The numbers in the graph correspond to those of compounds in table I. Pyridinium salts are substituted in 2 position (+) or in 3, 4, or 5 position (●).

weakened and thus steric interactions of an ortho substituent with the methyl group be released in part (Scheme II).

Scheme II
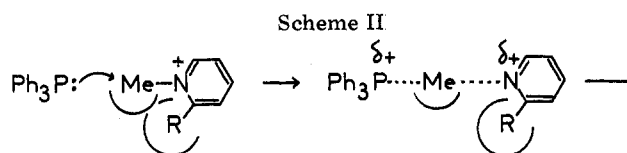
The Bronsted relation (Figure 2) shows a good correlation ($R = 0.971$) with the 3 and 4 substituents. The slope $\alpha = 0.387$ corresponds to a lower reactivity for the more basic amines (the lower the pK_a, the better is the free base as leaving group).

Table II. Demethylation of Pyridinium Iodides vs. Methylation of Pyridines

Compd	Substituent on pyridine ring	Registry no.	Demethylation[a] k/k_H	Demethylation[a] log (k/k_H)	Methylation[b,c] k/k_H	Methylation[b,c] log (k/k_H)
1	H	110-86-1	1	0	1	0
2	3,4-di-Me	583-58-4	0.255	−0.593	4.23	0.626
3	3-NH$_2$	462-08-8	0.263	−0.580	4.01	0.603
4	3,5-di-Me	591-22-0	0.279	−0.554	3.97	0.599
5	4-Me	108-89-4	0.566	−0.247	2.22	0.346
6	3-Me	108-99-6	0.619	−0.208	2.08	0.318
9	3-CONH$_2$	98-92-0	2.37	0.376	0.375	−0.426
12	3-Br	626-55-1	9.76	0.989	0.100	−1.00
14	3-Cl	626-60-8	6.68	0.824	0.090	−1.05

[a] Of the N-methylpyridinium iodides by PPh$_3$ in boiling DMF (153 °C). [b] Of the corresponding pyridines by ICH$_3$ in CH$_3$CN at 30 °C. [c] The relative rates of methylation are very little solvent dependent in polar aprotic solvents.[31]

Table III. Demethylation vs. Methylation of Ortho- Substituted Pyridines

2 substituent	Demethylation[a] k/k_{Me}	Demethylation[a] log (k/k_{Me})	Methylation[b] k/k_{Me}	Methylation[b] log (k/k_{Me})
Me	1.00	0	1.00	0
Et	1.49	0.163	0.63	−0.20
i-Pr	2.88	0.459	0.13	−0.88
t-Bu	50.20	1.70	0.00068	−3.16

[a] Of the pyridinium iodide by PPh$_3$ in DMF at 153 °C. [b] Of the corresponding pyridine with ICH$_3$ in NO$_2$Ph at 30 °C.[27]

However, there is a reactivity higher than expected from the pure basicity for the 2 substituents. The steric accelerations by strain release of the ortho substituents can be evaluated from the deviations above the Bronsted plot and give the following values: Me = 2.4, Et = 3.4, i-Pr = 6.3, t-Bu = 103, Ph = 7.1, CHO = 26, Cl = 1.3, CN = 1.6.

The question remains of the scatter of the points for the 3 and 4 substituents in the Bronsted and Hammett relations; this scatter is of common occurrence, and appears when kinetic (k) and thermodynamic (σ, pK_a) data are compared.[25] It may be due, in part, to the fact that Hammett σ constants do not apply very well to pyridines.[26] The direct (N-methylations) and reverse (N-demethylations) reactions in the pyridine series should afford better relations since this is a comparison of two sets of kinetic data.

The results of quaternization by ICH$_3$ of 3- and 4-substituted pyridines are reported in Table II. There is an excellent relation (correlation coefficient R = 0.994) with the demethylation reactions by PPh$_3$ of the corresponding pyridinium iodides. The slope δ = −0.89 indicates a sensitivity to electronic effects of the same magnitude but of opposite sign (Figure 3).

The steric acceleration evidenced in Figure 2 may also be treated quantitatively through a linear free-energy relationship with ortho substituents of different size which bring almost no change to the basicity of the amine (e.g., the α series of Ingold: Me, Et, i-Pr, t-Bu). The results of demethylation vs. methylation of 2-alkylpyridines are reported in Table III. The excellent correlation observed (correlation coefficient R = 0.999) has a slope δ = −0.53, which means that the reactivity of ortho-substituted pyridines is decreased in quaternization reactions and increased in dequaternization reactions (Figure 4). The nonbonded interactions between the ortho-substituted pyridine and the methyl group lead to a steric compression (front strain)[28] in methylation reactions and to a steric decompression (relief of front strain)[29] in demethylations. The
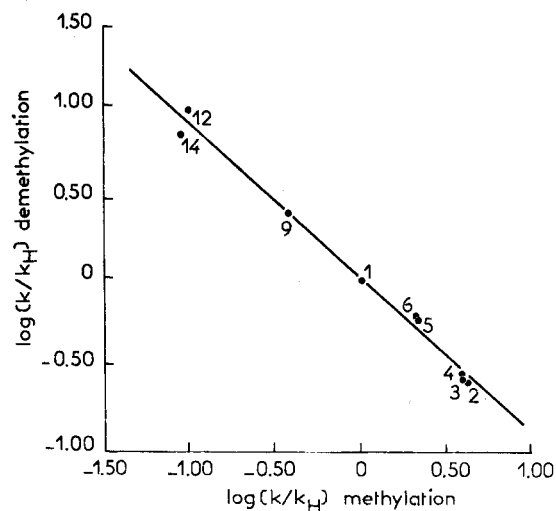

Figure 3. Plot of log (k/k_H) for demethylation of pyridinium iodides by PPh$_3$ vs. log (k/k_H) for methylation of the corresponding pyridines by ICH$_3$. The numbers in the graph correspond to those of compounds in Table III.
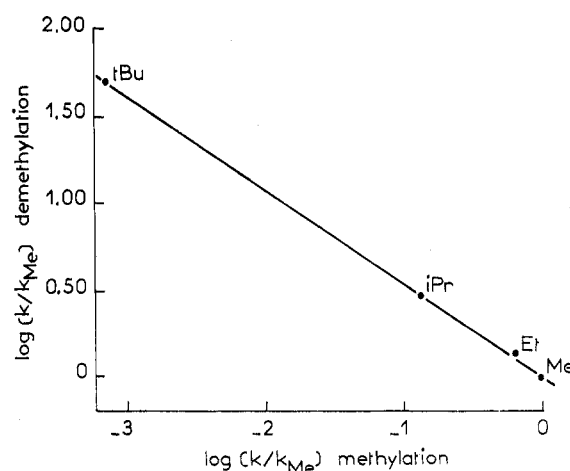

Figure 4. Plot of log (k/k_{Me}) for demethylation of 2-alkylpyridinium iodides by PPh$_3$ vs. log (k/k_{Me}) for methylation of the corresponding pyridines by ICH$_3$.

sensitivity to steric effects is twice as important in methylations as in demethylations.

Brown et al. measured the steric strains in transition states of N-methylations of ortho alkylpyridines and evaluated the steric strain in pyridinium salts by considering homomor-

phous complexes of pyridines and Lewis acids; they estimated the strain in the transition state of N-methylation reactions to be $\frac{2}{3}$ of the strain of the final product.[30] Our present finding of a ratio of $\frac{1}{3}$ to $\frac{2}{3}$ in demethylation vs. methylation is in agreement with the above hypothesis.

The present study could also be applied to an evaluation of the position of the transition state, if one considers the dealkylation reaction as a reverse Menschutkin reaction. Indeed, recent results, obtained on quaternization of sterically crowded pyridines,[32] have shown that the position of the transition state could be estimated, in agreement with the Hammond postulate;[33] such an evaluation has also been possible, based on results of the Menschutkin reaction, by varying the nature of the leaving group of the alkylating agent.[34] Our present work on the dealkylation reaction could then be taken as a complement to these studies.[34,35]

In summary the use of a soft nucleophile PPh_3 allows the quantitative study of the dealkylation of pyridinium salts. With this method free-energy values can be obtained for the reversible process N-alkylation–N-dealkylation thus opening a new way for the quantitative study of the structure of the transition state in SN2 reactions.[36]

Experimental Section

Materials. The methiodides were prepared according to literature data.[21,28] The DMF was dried over sodium carbonate, fractionally distilled and stored over molecular sieves. Fluka triphenylphosphine was used without further purification.

Relative Rate Determinations. The relative rates of demethylations were obtained by a competitive method. Pairs of salts were allowed to react with an excess of triphenylphosphine in DMF at the boiling point of the solvent (153 °C). After 25–70% reaction the consumption of the salt was determined by NMR analysis of the N-methyl signals. The ring protons of mesitylene were used as integration standard. The rate constant ratio (k_1/k_2) was calculated from the knowledge of the initial and final concentrations of the salts by the use of the equation

$$k_1/k_2 = \frac{\log (salt_1)_0/(salt_1)_t}{\log (salt_2)_0/(salt_2)_t}$$

The rate constant ratio determined at various stages of the reaction (25–70%) agreed to ±10%. NMR spectra and GC indicated that the reactions were clean, in accordance with previous studies.[17,18] Two possible side reactions were considered (Scheme III).

Scheme III
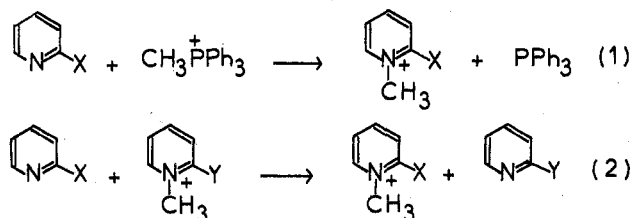
Path 1 is the reverse of the demethylation studied. Control experiments with the most reactive nucleophiles, pyridine and 2-methylpyridine, showed that no reaction of this type took place under the reaction conditions.

Path 2 was checked by treating the more nucleophilic pyridine with the easier demethylated salt of the pairs used in the demethylation experiments. Pairs on different level of the reactivity scale were studied. In all cases, except one, no cross methylation product was formed. When 1 mmol of 2-methylpyridine was allowed to react with 1 mmol of 1-methyl-2-isopropylpyridinium iodide in refluxing DMF and in the presence of triphenylphosphine, 90% of the salt was demethylated and ca. 4% of 1,2-dimethylpyridinium salt was indeed

formed. This side reaction introduces an error of the same size as the error of the rate measurements (ca. 10%) and was neglected in the calculations.

A typical procedure for a demethylation reaction is as follows: 1–1.5 mmol of each salt, ca. 0.7 mmol of mesitylene, and ca. 5 mmol of triphenylphosphine were weighed into a 5-ml flask; 2 ml of DMF was added and the solution refluxed for 2 min to 5 h depending upon the reactivity of the salts. The reaction mixture was directly analyzed by NMR. The rate data are mean values of two to four, usually three, experiments. The spectra were recorded using a Perkin-Elmer R-32, JEOL HM-100, or a Varian EM-360 spectrometer.

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