In the absence of ammonium ions addition of MeCN speeds reaction of 2,4-DNPP dianion, and the decrease of k_ψ in solutions of **2a** on addition of MeCN is typical of reactions mediated by micelles[5a,12] or hydrophobic ammonium ions.[8] For nonionic substrates the adverse solvent effect can be ascribed to an increase in solubility of the substrate in the bulk, aqueous phase, as well as to a breaking up of micelles or similar aggregates by disruption of the water structure. Substrate solubility should not be a factor for reactions of 2,4-DNPP, so the main effect of MeCN appears to be the breaking up of the aggregates.

Tri-*n*-octylammonium salts are surface active but they do not micellize; for example, they do not show a critical micelle concentration.[6] Nonetheless they bind nonionic and ionic hydrophobic solutes and, like micelles, they can change rate and equilibrium constants.[6,8] The overall rate enhancements of bimolecular reactions are often larger than those observed with micelles, but this is a consequence of high local concentration of reactants in small aggregates and for reactions in both functional and nonfunctional aggregates of **1** and **2**, for example, second-order rates *in* the aggregate are very similar to those in a micelle.[7,8]

The aryl group of 2,4-DNPP dianion is not attacked by alkoxide ion derived from a hydroxyethyl functionalized micelle, which behaves in that respect like **2a**.[3c] Nucleophilic primary and secondary amines attack the aryl group in water and in aqueous micelles,[3c] but tertiary amines weakly catalyze hydrolysis of 2,4-DNPP dianion in both water and aqueous cationic micelles, by forming a phosphoramidate,[13,15] and the small rate enhancement by 2,6-lutidine (Fig. 1) may have a similar origin.

Addition of aryloxide ion to CTABr decreases the micellar rate enhancement of hydrolyses of dinitrophenyl phosphate dianions by competing for the micelle,[3a] and the small rate decrease on addition of 2,4-dinitrophenoxide ion (Figure 1) may be due to competition. However, this explanation is suspect because mesylate ion does not inhibit reaction.

Micelles have well-defined structures which are not markedly perturbed by addition of small amounts of solutes,[5,14] but structures of small aggregates of **1** or **2** are probably very sensitive to even low concentrations of solutes which may bind to them.

The rate enhancements by the hydrophobic ammonium salts (Figure 1 and Tables II and III) are larger than found with micelles of cetyltrimethylammonium bromide or (2-hydroxyethyl)hexadecyldimethylammonium bromide where rates are increased by factors of ca. 25- and 35-fold, respectively,[3] but the rate enhancement by micellized cetylpyridinium chloride is by a factor of 50[15] and is similar to that by **1**. The highest values of k_ψ for hydrolysis in solutions of the ammonium salts **1** and **2** may not correspond to complete binding of substrate (Figure 1 and Tables II and III) but rate enhancement by **2** in 95% H_2O is more than twice that given by cationic micelles in water.[3]

The transition state for hydrolysis of dianionic 2,4-DNPP has considerable aryloxide character[1-3] and it should be stabilized by interaction with the head groups of cationic micelles or hydrophobic ammonium salts. There is extensive charge neutralization by micellar-bound counterions, and the fractional micellar charge is typically in the range 0.2–0.4,[16] but this neutralization seems to be much less important with nonmicellizing ammonium ions,[7] which should therefore be more able to stabilize an aryloxide-like transition state. The strong interactions between hydrophobic ammonium ions and charge-delocalized organic anions (Table I and ref 6 and 7) are consistent with this explanation of the rate enhancement.

Acknowledgment. Support of this work by the U.S. Army Office of Research is gratefully acknowledged.

Registry No. **1**, 79054-30-1; **2a**, 92642-02-9; **2b**, 92642-00-7; 2,4-dinitrophenyl phosphate dianion, 18962-96-4.

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Acidity Measurements on Pyridines in Tetrahydrofuran Using Lithiated Silylamines

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Received January 25, 1985

We have recently reported the measurement of acidities of a variety of carbon acids in tetrahydrofuran using lithiated diisopropylamine (LDA) and lithiated 2,2,6,6-tetramethylpiperidine (LTMP) as the strong bases.[1,2] In addition several new lithiated amides have been synthesized which showed enhanced basicity when the nitrogen was more hindered and lesser basicity when silicon replaced the carbon attached to nitrogen.[3] For example, in comparison with diisopropylamine (DA) pK = 35.7, the acidities of isopropyl(trimethylsilyl)amine and bis(trimethylsilyl)amine (BTSA) were reported to be 31.4 and 29.5, respectively. In the present paper we wish to describe acidity measurements on alkylated pyridines using these amines. These studies have revealed an error[4] in the reported pK value for BTSA. The true value is actually much lower at 25.8 pK units. Fortunately, this greater acidity of BTSA now allows the measurement of pK's as low as 24 or less. Two such measurements on fluorene are described. The measurement of the acidity of *N*-isopropyl cyclohexylimine (pK = 31.3) adds to the THF scale 15 imines whose relative pK's were reported earlier.[5]

Method of pK Measurement. As in our earlier studies we have used ^{13}C NMR to measure the relative concentrations of all four species in the equilibrium, (1). By use

$$R_3CH + LiNR'_2 \rightleftharpoons R_3CLi + HNR'_2 \qquad (1)$$

of the value for K in (1), the determination of acidities of α-, β-, and γ-picoline was readily accomplished.[6] However, for the three benzylpyridines (2BP, 3BP, and 4BP) a new problem arose in that no suitable amine was available for the measurement of pK in the range 27–29. (Our initial report of a pK of 29.5 for BTSA, based on an erroneous peak assignment, had led us to conclude that BTSA was partly deprotonated by lithiated isopropyl(trimethylsilyl)amine.[3] The error emerged when we subsequently observed complete deprotonation of BTSA by the less basic lithiated *n*-propyl(trimethylsilyl)amine, pK = 30.9.) To serve as a reference in this region, we first found benzhydryl phenyl sulfide to be suitable, having a pK of 28.7 vs. 3BP. Since the equilibrium measurement used to obtain this pK involved two-carbon acids while all previous pK's have been derived from measurements involving a carbon and a nitrogen acid, the question arises as to the influence of differential solvation or aggregation effects in the two methods. To probe this question we examined this acidity of 3BP vs. xanthene and the acidity of each carbon acid as measured against isopropyl(trimethylsilyl)amine. As the data in Table I show, the value for the pK of 3BP vs. xanthene agrees well with their values as determined against the amine, indicating the absence of a "partner"

(1) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620.
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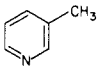
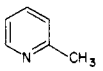
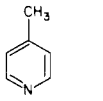
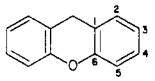
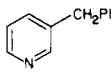
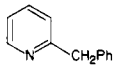
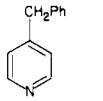
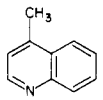
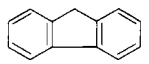
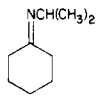
(3) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 3442.
(4) Fraser, R. R.; Mansour, T. S. *J. Org. Chem.* **1984**, *49*, 5284.
(5) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729.
(6) For the most recent comprehensive review, see: Streitweiser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier-North Holland: Amsterdam, 1980; Part A, p 323.

0022-3263/85/1950-3232$01.50/0

Table I

acid$_1$	ref acid$_2$ (pK_2)	K_{eq}	−log K	pK_1	lit. data
	TMP (37.3)	0.4	0.4	37.7	
	DA (35.7)	50	−1.7	34	34[1]
	$(CH_3)_3CNHSi(CH_3)_3$ (33.6)	25	−1.4	32.2	
	$(CH_3)_2CHNHSi(CH_3)_3$ (31.4)	0.9	+0.03	31.4	
	$(CH_3)_2CHNHSi(CH_3)_3$ (31.4)	18	−1.3	30.1	30.1[8]
	xanthene (31.4)	17	−1.2	30.2	
Ph_2CHSPh	3BP (30.2)	32	−1.5	28.7	26.7[11]
	Ph_2CHSPh (28.7)	2.8	−0.4	28.3	28.2[8]
	3BP (30.2)	59	−1.8	28.4	
	$[(CH_3)_3Si]_2NH$ (25.8)	6.4	−0.8	25.0	26.7[8]
	2BP	1400	−3.1	25.3	
	$[(CH_3)_3Si]NH$ (25.8)	0.02	+1.7	27.5	
$[(CH_3)_3Si]_2NH$	2BP (28.4)	406	−2.6	25.8	
	$[(CH_3)_3Si]_2NH$ (25.8)	27	−1.4	24.4	22.6[10]
	4BP (25.0)	4.5	−0.7	24.3	
	$(CH_3)_2CHNHSi(CH_3)_3$ (31.4)	1.2	−0.1	31.3	see ref 5

effect. We also measured the pK of 2BP against 3BP and against benzhydryl phenyl thioether, again observing excellent agreement between the two values. Since the acidity of 2BP turned out to be in the same region as the thioether, it could have served to bridge the initial gap in acidities. Nevertheless the duplicate measurements reinforce the consistency of the results. From 2BP, in equilibrium with BTSA, we then found the correct value of 25.8 for the pK_a of this disilylamine.

Using BTSA we then determined the acidities of two still more acidic hydrocarbons, 4BP having a pK of 25.1, and fluorene, having a value of 24.3.

One other carbon acid, *N*-isopropylcyclohexylimine, was studied in order to place our previous relative acidity measurements on aldimines and ketimines[5] onto the present THF scale.

Discussion of Results

The variation in the acidity of a methyl group as a function of its position on the pyridine ring is substantial. While the weaker acidity of 3-picoline is expected on the basis of its relative inertness to base-catalyzed condensations[7] it is surprising that 4-picoline is significantly more acidic than the 2-isomer. The difference could be the result of a repulsive dipolar interaction between the lithiomethyl group and the lone pair on nitrogen or may simply result from differential aggregation or solvation effects. There is a significant practical consequence of these observations on the picolines' acidities. Obviously LTMP is a sufficiently strong base to completely deprotonate 2- or 4-picoline. It should then be the base of choice to generate either of the derived carbanions, a fact not previously recognized in the literature. The isomeric benzylpyridines and 4-lepidine all show acidities which exceed the picoline pK values by 6–7 units. Thus for synthetic purposes LDA would achieve complete deprotonation of these compounds.

Our results in THF are very close to the earlier values reported by Bordwell[8] for the benzylpyridines in Me_2SO. Similar acidities in Me_2SO and ethereal solvents, according to earlier observations of Bordwell,[9] seem to be characteristic of highly delocalized anions. Fluorene, however, behaves slightly differently, being less acidic in THF than in either Me_2SO or cyclohexylamine, pK = 22.6 and 23.[10] A comparable behavior is seen for benzhydryl phenyl thioether, it too being less acidic by 2 pK units in THF relative to Me_2SO.[11]

There are a few compounds in the table whose acidities may also be compared to the early data of Conant and Wheland.[12] Their studies, based on equilibria between two carbon acids and their potassium salts in diethyl ether, provided a pK for fluorene of 24 and a pK for xanthene of 29. While the fluorene value is the same in both solvent systems, our xanthene value is slightly different at 31.3.

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(8) Bordwell, F. G., private communication.
(9) Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1216.
(10) Reference 6, p 337.
(11) Reference 6, p 338.
(12) Conant, J. B.; Wheland, G. W. *J. Am. Chem. Soc.* **1932**, *54*, 1212.

In general, our experience in the present work as well as for work in progress[13] would indicate most acidities in THF usually correspond reasonably well with those reported in Me_2SO. Perhaps the most important contribution of the data in THF is that when differences do occur it is the THF data that have direct application to synthetic problems.

The last compound in Table I, *N*-isopropylcyclohexanone imine, was found to have a p*K* of 31.3. Thus, for other imines whose p*K*'s have been previously measured relative to this imine[5] the values range from 28.9 for the benzylimine of acetone to 33.1 for the isopropyl imine of 3-pentanone. These data and the known effects of α-alkyl groups on decreasing acidity[5] would suggest that ketimines derived from branched ketones require LTMP to ensure complete deprotonation in a synthetic operation.

Experimental Section

The preparation of samples for ^{13}C NMR was the same as given in the following example except those few cases in which a second carbon acid rather than an amine was used as the reference acid.

Each sample was prepared in a 10-mm septum-capped NMR tube (Wilmad Glass, Buena, NJ) fitted with an argon inlet and outlet. To a solution of 1.5 mequiv of amine in 2 mL of freshly distilled THF at 0 °C was added 1.5 mequiv of methyllithium in ether. After 15 min, a solution of 1.5 mequiv of hydrocarbon in 1 mL of THF was added at 0 °C. The cap was wrapped in parafilm and the tube then warmed and transferred to the probe of a Varian FT-80 NMR spectrometer operating at 27 °C. Spectra were accumulated using a small pulse angle (30°) and a 2-s repetition rate. That differential relaxation times were unimportant was shown by extending repetition rate to 3 s without affecting integral ratios. Other factors of quantitative influence, such as differential NOE's, were eliminated by using an empirically derived correction factor. For example, this factor applied to the methylene signals of TMP and LTMP was arried at by measuring the integral for TMP prior to then after the addition of 0.5 equiv of methyllithium, as well as that of the LTMP produced (both relative to naphthalene present as an internal standard). We estimate the accuracy of all *K*'s to be ±30%, leading to an uncertainty in ΔpK of ±0.2 p*K* units or less.

Metalation of each hydrocarbon was shown to occur without decomposition or rearrangement by quenching the anion and recovering pure starting material as established by NMR and GC analysis. The site of metalation was, in each instance, clearly indicated by comparison of the ^{13}C shifts for each lithiated compound with its starting material. This ^{13}C shift data appear below. Some of the assignments for the lithio derivatives should be considered as tentative. They have been made on the basis of previously reported lithiation shifts for 2- and 4-picolyl anions[14] as well as by assuming the phenyl substituent effect in diphenylmethane vs. toluene[15] would be similar in the picolines. The less certain assignments are presented in square brackets.

^{13}C Chemical Shifts (in ppm from Me_4Si, Using the α-Carbon of THF 69.0 ppm). 4-Picoline: 151.0 (C_2), 126.2 (C_3) 149.3 (C_4), 20.2 (CH_3). Lithio derivative: 144.6 (C_2), 110.8 (C_3), 149.2 (C_4), 69.0 (CH_2). 3-Picoline: 151.9 (C_2), 134.4 (C_3), 137.4 (C_4), 124.5 (C_5), 148.6 (C_6), 19.2 (CH_3). Lithio derivative: 140.9 (C_2), [138.2] (C_3), 94.2 (C_4) [139.0] (C_5) 102.4 (C_6), 45.2 (CH_2). 2-Picoline: 160.0 (C_2), 124.2 (C_3), 137.2 (C_4), 121.7 (C_5), 150.8 (C_6), 20.2 (CH_3). Lithio derivative: 165.5 (C_2), 116.8 (C_3), 132.4 (C_4), 98.3 (C_5), 149.3 (C_6), 57.3 (CH_2). 4BP: 151.6 (C_2), 125.5 (C_3), 151.6 (C_4), 42.4 (CH_2), 140.1, 130.6, 130.1, 128.0, (phenyl group). Lithio derivative: 144.5, 147.2 (C_2 and C_6 nonequivalent), 116.2, 115.9 (C_3 and C_5), 144.8 (C_4), 88.6 (CH), 146.9, 128.7, 123.3, 107.4 (phenyl group). 3BP: 151.9 (C_2), 138.2 (C_3), 137.2 (C_4), 124.7 (C_5), 149.2 (C_6), 40.4 (CH_2), 142.1, 130.4, 130.1, 127.8 (phenyl group). Lithio derivative: 143.0 (C_2), 125.5 (C_4), 123.5 (C_5), 80.8 (CH), 147.4, 128.8, 120.2, 111.6 (phenyl group). 2BP: 162.6 (C_2), 124.1 (C_3), 137.4 (C_4), 122.3 (C_5), 150.7 (C_6), 46.1 (CH_2), 141.4, 130.4, 129.7, 127.4 (phenyl group). Lithio derivative: 159.4 (C_2), 114.7 (C_3, 134.0 (C_4), 101.4 (C_5) 149.3 (C_6), 86.3 (CH), 147.0, 129.2, 121.5, (phenyl group). Xanthene (see Table I for numbering): 124.5 (C_1), 129.1 (C_2), 122.3 (C_3), 130.5 (C_4), 117.8 (C_5), 153.7 (C_6), 29.1 (CH_2). Lithio derivative: 151.4 (C_1), 111.9 (C_2), 125.1 (C_3), 110.4 (C_4), 113.2 (C_5), 143.2 (C_6), 63.2 (CH). Benzhydryl phenyl sulfide: 143.1, 129.9, 130.3, 128.6 (benzhydryl), 58.7 (CH), 138.7, 130.1, 131.9, 127.9 (phenyl). Lithio derivative: 150.9, 121.4, 128.2, 112.2 (benzhydryl), 63.1 (quaternary), 128.6, 125.7, 122.5 (phenyl). The shifts for fluorenyllithium and for the lithiated ketimines have been reported previously.[16,17]

Registry No. 4BP, 2116-65-6; 4BP (lithio deriv), 81771-00-8; 3BP, 620-95-1; 3BP (lithio deriv), 97254-18-7; 2BP, 101-82-6; 2BP (lithio deriv), 56501-99-6; TMP, 768-66-1; TMP (lithio deriv), 38227-87-1; DA, 108-18-9; DA (lithio deriv), 4111-54-0; $[(CH_3)_3Si]_2NH$, 999-97-3; $[(CH_3)_3Si]_2NH$ (lithio deriv), 4039-32-1; $C_6H_8{=}NCH(CH_3)_2$, 13652-31-8; $C_6H_8{=}NCH(CH_3)_2$ (lithio deriv), 97254-20-1; *i*-Pr-NH-Pr-*i*, 5577-67-3; *i*-Pr-NH-Pr-*i* (lithio deriv), 18270-42-3; $(CH_3)_2CHNHSi(CH_3)_3$, 5577-65-1; $(CH_3)_2CHNHSi(CH_3)_3$ (lithio deriv), 42423-10-9; 4-picoline, 108-89-4; 4-picoline (lithio deriv), 26954-25-6; 3-picoline, 108-99-6; 3-picoline (lithio deriv), 26954-24-5; 2-picoline, 109-06-8; 2-picoline (lithio deriv), 1749-29-7; xanthene, 92-83-1; xanthene (lithio deriv), 40102-97-4; benzhydryl phenyl sulfide, 21122-20-3; benzhydryl phenyl sulfide (lithio deriv), 81771-01-9; 4-methylquinoline, 491-35-0; 4-methylquinoline (lithio deriv), 97254-19-8; fluorene, 86-73-7; fluorene (lithio deriv), 881-04-9.

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(15) Hunter, D. H.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2884.
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An Apparent, Deep-Seated, Carbonium-Ion-Mediated Sesquiterpene Rearrangement

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Received December 20, 1984

The bicyclic cation **1**, based on a himachalane-type carbon skeleton and readily derivable from *cis,trans*-farnesyl pyrophosphate **2**, has long been recognized as the biogenetic progenitor of a variety of bi- and tricyclic sesquiterpenoid carbon skeletons.[1] Among notable natural products derived from **1** are longifolene (**3**)[2], α-longipinene (**4**)[3], vulgarone (**5**)[4], and allohimachalol (**6**)[5] (Scheme I). The biomimetic cationic cylization of **1** or a derivative, therefore, presents interesting possibilities, but much effort in this direction has not been forthcoming, due perhaps, to the relative inaccessibility of **1** in its correct stereochemical form.[6] In this note, we delineate on the fate of a derivative of **1**, which after initially taking a biomimetic route to longipinene system (**4**), charters an unanticipated

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0022-3263/85/1950-3234$01.50/0