of the absorption band of flavin. We carried out the oxidation of Cr_{red} and 1,4-butanedithiol by 3-methyllumiflavin (λ_{max} 445 nm) in water–ethanol (20:80, v/v) at 30 °C. The pseudo-first-order rate constants (k_1) are plotted as a function of the template (cesium tosylate) concentration in Figure 1. Interestingly, the k_1 values for the oxidation of Cr_{red} increased with increasing cesium tosylate concentration. In contrast, the k_1 values for the oxidation of 1,4-butanedithiol decreased gradually. The rate decrease is probably attributed either to the effect of ionic strength or to the formation of tight ion pairs. The data in Figure 1 imply, therefore, that the "kinetic" template effect is also operative on the ring-formation step in eq 3.

In conclusion, the present study established that the redox reaction between dithiol and disulfide is useful to give a switch function to crown ether analogues and that the ring-formation step is significantly subjected to the template effect. Although the "reversibility" and "response speed" of the present redox-switched crown ethers should be further improved, we believe that the concept is applicable more fruitfully to ion extraction, ion transport, selective metal recognition, etc. The investigations are currently underway in this laboratory.

Acknowledgment. Support of this research by the Ministry of Education of Japan is gratefully acknowledged.

Registry No. Cr_{red}, 91295-69-1; Cr_{ox}, 91295-70-4; Cr, 67950-78-1; K^+ANS, 76402-43-2; Rb^+ANS, 91295-71-5; Cs^+ANS, 91295-72-6; 1,4-butanedithiol, 1191-08-8; 3-methyllumiflavin, 18636-32-3.

Seiji Shinkai,* Kenichi Inuzuka
Osamu Miyazaki, Osamu Manabe*
Department of Industrial Chemistry
Faculty of Engineering
Nagasaki University
Nagasaki 852, Japan

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Acidity Measurements with Lithiated Amines: Steric Reduction and Electronic Enhancement of Acidity

Summary: A study of 15 secondary amines having either two alkyl, or an alkyl and a silyl, or two silyl substituents of differing bulk reveals acidities which vary by more than 10 p*K* units. Use of their lithio derivatives permits measurement of acidities in tetrahydrofuran in the p*K* range of 27–43. The most hindered amines show potentially useful selectivity in their preference for methyl proton abstraction.

Sir: More than 10 years have elapsed since Olofson and Dougherty[1] described the superior properties of lithium tetramethylpiperidide (LTMP) as a proton-specific base, as indicated by a comparison of yields for the conversion of benzyl chloride to phenylcarbene and conversion of *o*-chloroanisole to its benzyne using a variety of bases. Its proton selectivity, coupled with its ready availability, suggested the preferential use of LTMP for the lithiation of weak carbon acids. As a result, LTMP has become widely used in organic reactions as has lithium bis(trimethylsilyl)amide and perhaps most frequently, lithium diisopropylamide (LDA). Another very potent "superbase", the potassium salt of 1,3-diaminopropane[2] (KAPA) has also proven useful and appears to possess a basicity comparable to that of LDA.[3]

We have recently undertaken the measurement of acidities of weak carbon acids in tetrahydrofuran (THF) using ^{13}C NMR[4,5] to determine the position of the equilibrium [1]. The classes studied have included aromatic,

$$R_3CH + LiNR_2 \rightleftharpoons R_3CLi + HNR_2 \qquad [1]$$

heterocyclic,[5] and heteroallylic[6] and, most recently, a series of monosubstituted benzenes.[7] The number of compounds amenable to study has been restricted by the lack of bases having significantly different p*K*'s, yet adequate proton specificity.[8] Thus, the p*K* values for diisopropylamine and tetramethylpiperidine, 35.7 and 37.3, respectively, confines the measurements to the p*K* range of 33 to 40 units. We now describe the synthesis of a variety of dialkylamines and alkylsilylamines whose acidities vary over a range of almost 11 p*K* units. Use of their lithiated derivatives significantly enhances our ability to measure acidities in THF. In addition, the most basic of these new lithiated amines show considerable regioselectivity in abstracting only very unhindered protons.[9]

All new amines have been prepared by standard methods.[10] Their p*K* values have been determined as described previously, by measurement of the equilibrium analogous to [1] vs. LDA or another suitable standard.[12] The p*K* values are reported relative to diisopropylamine previously determined to be 35.7 relative to 2-methyl-1,3-dithiane.[5] As seen in Table I, there is a consistent correlation between the size of the alkyl substituents on the nitrogen and the acidity of the amine.

However, dialkylamines having a p*K* below 35 are not suitable for p*K* measurements. For example, the ^{13}C signals for *N*-2-butyl-*N*-1-propylamine in the presence of its lithium salt are quite broad as a result of the diminished hindrance to Li–H exchange. Still less bulky amines have more rapid exchange, giving only time averaged signals at room temperature.[4] Fortuitously, we have found that alkyl(trimethylsilyl)amines maintain the slow Li–H interchange yet possess appreciably greater acidity (4–6 p*K* units) than dialkylamines,[13] thereby providing the capa-

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(1) Olofson, R. A.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 582.

(2) Brown, C. A. *J. Chem. Soc., Chem. Commun.* **1975**, 222.

(3) Arnett, E. M.; Venkatasubramaniam, K. G. *Tetrahedron Lett.* **1981**, 987; *J. Org. Chem.* **1983**, *48*, 1569.

(4) Fraser, R. R.; Baignée, A.; Bresse, M.; Hata, K. *Tetrahedron Lett.* **1982**, 4195.

(5) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Chem. Soc., Chem. Commun.* **1983**, 620.

(6) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729.

(7) Fraser, R. R.; Bresse, M.; Mansour, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 7790.

(8) Streitwieser's group has recently reported "Cesium Ion Pair Acidities" of several delocalized aromatic hydrocarbons. With use of the UV method, to measure the equilibrium between two carbon acids, p*K*'s as low as 20 have been determined: Streitwieser, A., Jr.; Sors, D. A.; Kaufman, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1394.

(9) In two very recent papers, Corey and Gross describe the synthesis of a new hindered base *tert*-octyl-*tert*-butylamine whose lithio derivative exhibits enhanced selectivity in the formation of *E* vs. *Z* enolates; Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 491, 495.

(10) Those dialkylamines not previously reported in the literature have been prepared by addition of *n*- or *tert*-butyllithium to the appropriate aldimine. The neopentyl(trimethylsilyl)amine was prepared by reacting bis(trimethylsilyl)amine with 2 equiv of neopentylamine.[11] A detailed description of their preparation and properties is given in the supplementary material section.

(11) Fessenden, R.; Fessenden, J. *Chem. Rev.* **1961**, 361.

(12) All equilibrium measurements have been made as described previously[7] using ^{13}C NMR. Each amine's acidity was confirmed by determination vs. a second standard. In all cases agreement was within experimental error (±0.2 p*K* unit). The more accurate value, derived from the *K* closer to unity, appears in Table I.

(13) The increase in acidity of an amine upon replacement of a carbon by a silicon atom is consistent with the known ability of silicon to stabilize an adjacent carbanion; see: Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981; Chapter 2.

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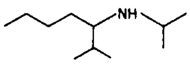
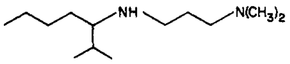
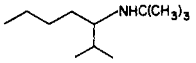
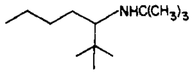
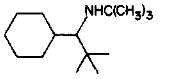
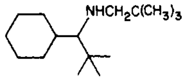
Table I. pK_a Values for Secondary Amines in THF

amine	reference acid	K_{eq}	pK_a
$(CH_3)_3SiNHSi(CH_3)_3$ (**1**)	**2**	0.0125	29.5
$(CH_3)_2CHNHSi(CH_3)_3$ (**2**)	thiophene[17]	0.028	31.4
$(CH_3)_3CCH_2NHSi(CH_3)_3$ (**3**)	**4**	0.44	33.2
$(CH_3)_3CNHSi(CH_3)_3$ (**4**)	**7**	0.008	33.6
$C_2H_5CH(CH_3)NHCH_2CH_2CH_3$ (**5**)	**7**	0.2	35.0
cis-2,6-dimethylpiperidine (**6**)	**7**	0.34	35.2
$(CH_3)_2CHNHCH(CH_3)_2$ (**7**)	**9**	0.025	35.7
dicyclohexylamine (**8**)	**7**	1	35.7
2,2,6,6-tetramethylpiperidine (**9**)	*a*	0.30	37.3
 10	$C_6H_5SCH_3$	0.30	37.6
 11	$C_6H_5SCH_3$	0.60	37.9
 12	$C_6H_5SCH_3$	1.6	38.3
 13	$C_6H_5SCH_3$	9.9	39.1
 14	$C_6H_5SCH_3$	27.6	39.5
 15	$C_6H_5SCH_3$	79	40.0

[a] We have previously measured a pK of 37.3 for TMP relative to the arbitrary standard 2-methyl-1,3-dithiane.[5]

bility to measure pK values well below 30. The most acidic of these is the bis(trimethylsilyl)amine (pK_a 29.5). For the other end of the scale, we have prepared amines more hindered than TMP, which exhibit still less acidity, as anticipated. Because of their reduced rates of transmetalation, their acidities have been measured by using thioanisole as the standard.[5,14] As seen in the table, these dialkylamines having two very bulky substituents possess pK's up to 40.[15] This total complement of amines having pK's of 29.5–40 extends the range of accessible pK measurements to 27–43 pK units.

It had been earlier recognized by Olofson and Dougherty that di-*tert*-butylamine and other very hindered amines offered additional potential but lacked availability. The work herein and that reported by Corey[9] now provide simple synthetic access to very hindered amines. During this investigation we have even encountered an overly hindered amine. Reduction of 2,6-di-*tert*-butylpyridine produced the corresponding piperidine,[16] an amine so hindered that it is inert to methyllithium, *n*-or *tert*-butyllithium in THF, with or without TMEDA or diethylamine as catalyst. Clearly, there is little scope for further increase in amine pK via increase in steric hindrance. There is, in contrast, a strong likelihood that the most highly hindered bases possess useful regioselectivities. For example, we have observed appreciably different rates of deprotonation of anisole, at the ortho position, and thioanisole at the methyl group. Although thioanisole is more acidic by a factor of 2,[18] its half-life for methyl group deprotonation is less than one sixth that for ring deprotonation of anisole.

We are now using the amines **1**–**15** in extending our measurements of acidity. For example, measurement of the metalation of thiophene in the presence of **4** has established its pK, previously unattainable in THF, as 33.3[17] (per hydrogen, compared to the value of 38.2 in cyclohexylamine[14]). Examination of the metalation of *p*-methylbiphenyl with **14** revealed appreciable lithiation, thereby providing a value of 40.4 (per hydrogen, compared to the value of 39.0 in cyclohexylamine[14]).

Supplementary Material Available: Procedures for the synthesis of all new amines along with their physical and spectral properties (5 pages). Ordering information is given on any current masthead page.

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[14] Streitwieser, A., Jr.; Guibé, F. *J. Am. Chem. Soc.* **1978**, *100* 4532.

[15] Since, in general, alkyl groups increase acidity in the gas phase and decrease it in solution, the observed effects in our trends in amine acidities most likely reflect steric hindrance to solvation and aggregation (see Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry"; Harper and Row: New York, 1981; Chapter 3).

[16] Day, J. C. *J. Org. Chem.* **1978**, *43*, 3646.

[17] Its pK of 33.3, per hydrogen, determined in equilibrium with **4** was confirmed by a second measurement vs. **1**. Its pK per molecule is 33.0.

[18] The acidities per hydrogen, in pK units are 39.0 and 38.6 for anisole and thioanisole, respectively (values revised slightly from the initial report[5]).

Robert R. Fraser,* Tarek S. Mansour
Ottawa-Carleton Institute for Research
and Graduate Studies in Chemistry
University of Ottawa, Ottawa, Canada K1N 9B4

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Stable and Explosive Alkali Metal-Anion Radical-Ammonia Complexes

Summary: Solid crystalline Rb and Cs salts with the composition $M^+{}_2(NH_3)(\text{naphthalene}^{-}\cdot)_2$ have been generated and are found to hold the ammonia molecule endothermically, and similar salts involving alkaline earth metals or alkali metals with other anion radicals detonate upon crystallization due to the exothermic release of ammonia.

Sir: Relatively little importance has been given to the coordination chemistry of alkali metal cations due to the fact that the complexing ability of these cations is much weaker than those of the transition-metal ions, and the complexes of the alkali metals are thought to be simple and understandable in terms of the ionic model.[1,2] However, salts of the small cations possess the ability to hold various types of solvents in the crystal lattice.[1] This is especially true of the hydrogen-bonding solvents, which can interact strongly with the anion of a salt. For example, $Na_2SO_4\cdot 10H_2O$ is a common solvent complex wherein the cation is within the $Na(H_2O)_6$ octhedron.[3] We have made use of the strong affinity of the lone pair of electrons for alkali metals and the hydrogen bond that forms between ammonia and organic anion radicals[4] to generate a novel series of compounds containing two alkali metal cations, two naphthalene anion radicals, and one molecule of ammonia.

When 1 mol of naphthalene (NP) is reacted with 1 mol of K, Rb, or Cs in very dry liquid ammonia and the solvent (NH_3) is removed under reduced pressure, a solid is left that has the formula $M_2(NH_3)(NP)_2$. When a similar

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