Relative Acidity and Basicity of Amines in Tetrahydrofuran and the Influence of these Factors on the Carbonylation of Lithium Amides

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The equilibrium constants for the ion-pair formation between 2,4-dinitrophenol and the following amines: pyrrolidine, piperidine, dibutylamine, di-isopropylamine, cyclohexylisopropylamine, dicyclohexylamine, morpholine, and diethylamine, in tetrahydrofuran (THF) have been measured. The relative acidities of the same amines (except diethylamine) have been also determined, as well as the pK_a-values for di-isopropylamine, cyclohexylisopropylamine, and dicyclohexylamine in THF. The results show the importance of acid–base equilibria in determining the product distribution in the carbonylation of lithium amides in THF. They also explain the role of the [amine]:[amide] ratio in determining the reaction products.

The role of relative acidities and basicities in determining reactivity and selectivity of organolithium compounds is being recognized[1,2] and knowledge of those properties in aprotic solvents is of practical importance in organic synthesis.

We have recently investigated the carbonylation of lithium dialkylamides under several reaction conditions, and succeeded in finding the variables that control the reaction.[3,4] The relative yields are highly dependent on the solvent and mainly on the ratio [amide]:[amine], which made us suspect the importance of proton-transfer equilibria among the several intermediates and the reagent. It would have been desirable to have acidity and basicity data for the series of amines in the solvents used, but literature data are still scarce in spite of the recent interest in this area.[1,2,5–7]

The present paper describes ion-pair basicity measurements for the following amines in THF: pyrrolidine (**1a**), piperidine (**1b**), dibutylamine (**1c**), di-isopropylamine (**1d**), cyclohexylisopropylamine (**1e**), dicyclohexylamine (**1f**), morpholine (**1g**), and diethylamine (**1h**). It also includes measurements of the relative acidities of the lithium amide–amine pairs of compounds (**1a-g**) and (**2a–g**).

Results and Discussion

Basicity Measurements.—In view of the structures of the intermediates usually proposed for the carbonylation of organic compounds,[8] ion-pair formation represents a good model for correlation of reactivity with basicity. We chose the method recently used by Frenna *et al.*[1] for the determination of amine basicities in benzene, which is based on the ion-pair formation between amines and 2,4-dinitrophenol.

The ion-pair constants, *K*, were determined spectrophotometrically. At 400 nm the absorbance of 2,4-dinitrophenol in THF is practically nil and the molar extinction coefficient, ε, of the amine–2,4-dinitrophenol ion pair depends on the amine structure. The value of ε was determined by iterative application of equation (1) where *A* is the absorbance and [AH] and

$$[\mathrm{AH}] + [\mathrm{R^1R^2NH}] - A/\varepsilon = \varepsilon[\mathrm{AH}][\mathrm{R^1R^2NH}]/A - K^{-1} \quad (1)$$

[R^{1}R^{2}NH], the initial concentrations of 2,4-dinitrophenol and amine. Figure 1 shows some representative runs for the determination of molar extinction coefficients of the pairs for amines (**1c**), (**1f**), and (**1g**). Similarly, Figure 2 shows the plot of equation (2) for the same amines. The constants for ion-pair

$$[\mathrm{AH}]/A = \{([\mathrm{R^1R^2NH}] - A/\varepsilon)\varepsilon K\}^{-1} + \varepsilon^{-1} \quad (2)$$

formation in THF at 25 °C for all the amines studied are collected in Table 1.

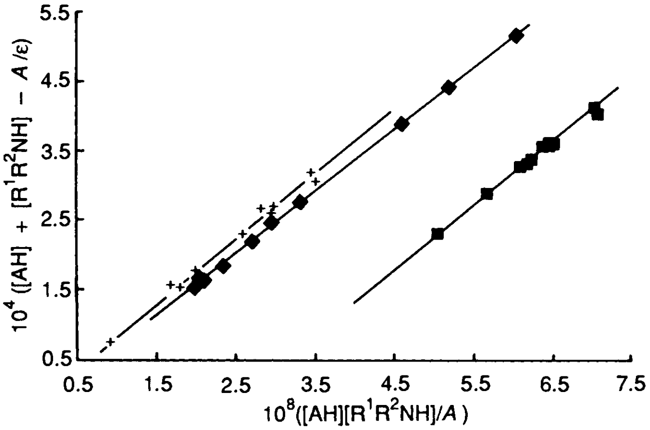


Figure 1. Determination of the extinction coefficient (λ_{max} 400 nm) for the ion pair of: + dibutylamine, ◆ dicyclohexylamine, and ■ morpholine in THF at 25 °C.

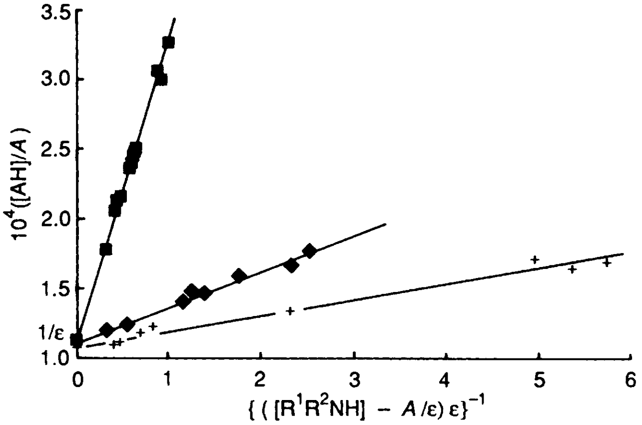


Figure 2. Determination of the equilibrium constant for the ion pair between 2,4-dinitrophenol and: ■ morpholine, ◆ dicyclohexylamine, and + dibutylamine in THF at 25 °C.

Table 1. Equilibrium constants for the reaction between secondary amines and 2,4-dinitrophenol (AH) in THF at 25 °C.

$$R^1R^2NH + AH \overset{K}{\rightleftharpoons} R^1R^2NH_2{}^+A^-$$

R^1R^2NH ($\varepsilon_{400\,nm}$/dm^3 mol^{-1} cm^{-1})	10^{-4} K/dm^3 mol^{-1}
(1a) Pyrrolidine (9 200)	42.0
(1b) Piperidine (9 370)	37.8
(1c) Dibutylamine (9 300)	8.9
(1d) Di-isopropylamine (9 650)	5.7
(1h) Diethylamine (9 700)	4.9
(1e) Cyclohexylisopropylamine (9 000)	4.2
(1f) Dicyclohexylamine (9 000)	3.9
(1g) Morpholine (8 800)	0.48

The basicity order can be interpreted by taking into account electronic as well as steric and strain effects. Prediction of pK_a-values for organic acids and bases in water is mostly concerned with electronic effects[9] but the importance of steric and strain effects on amine basicities have recently been emphasized.[10]

Table 1 shows that the basicity of the secondary cyclic amines in THF decreases with increasing ring size (**a** *vs.* **b**) as has been previously observed in benzene.[1] The introduction of a second heteroatom in the six-membered ring, such as oxygen in **(1g)**, causes a spectacular reduction in the amine basicity which can be rationalized in terms of the electron-withdrawing character of this substituent (field effect or inductive effect). The influence of *F*-strain is clear in the large pK_a-drop going from secondary cyclic amines **(1a)** or **(1b)** to secondary amines, while with hindered amines such as **(1e)** and **(1f)** the additional *B*-strain causes another small decrease in basicity. The relative basicities between secondary aliphatic amines **(1c)**, **(1d)**, and **(1h)** are easily rationalized in terms of the known electronic (field and inductive effects) and steric effects. Diphenylamine (not shown) exhibits such a low basicity in THF (likely due to the added effects of the electron-withdrawing phenyl groups and the strong *B*-strain in the cation) that the ion-pair constant could not be evaluated with a reasonable confidence level.

Acidity Measurements.—For the determination of the relative acidities the method designed by Fraser *et al.*[7] was used. The method is based on ^{13}C NMR determinations of the relative concentrations of all four species in equilibrium, equation (3).*

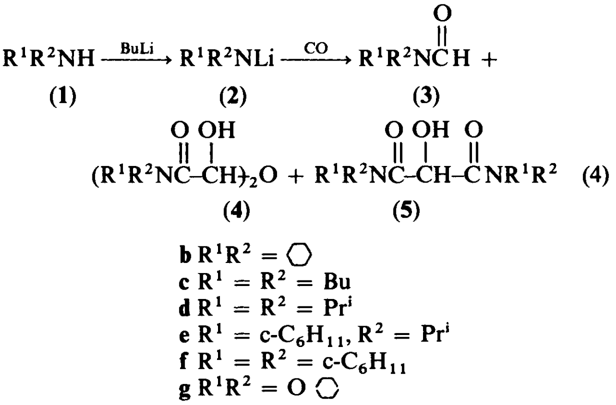
$$HA^1 + LiA^2 \rightleftharpoons LiA^1 + HA^2 \qquad (3)$$

In the present case, it was not always possible to observe the four species, therefore the relative acidities were evaluated directly from the ^{13}C NMR shifts which are shown in Table 2. The observed acidity order is: **g** > **a** > **b** > **c** > **d** > **e** > **f**.

This order is understandable in terms of the already discussed electronic and steric and strain effects. The strong acidity of morpholine is worthy of remark: steric effects are negligible and the electron-withdrawing effect of the oxygen stabilizes the anion; the effect is so strong that this amine is the only one in the series that exhibits the weakest basicity and the strongest acidity. In the case of the more unstable lithium amides, the role of steric effects is clear in the H–Li exchange rate determined from equation (3), and also in the formation of lithium amides by reaction of the amine with butyl-lithium. Thus, while lithium morpholide is formed instantaneously, the lithium piperidide takes 20 s and the lithium dicyclohexylamide takes about 1 min to appear. The H–Li exchange depicted in equation (3) can be interpreted as occurring through the formation of a tetracentric transition state which should be retarded by enhanced *F*-strain. As can be deduced from Table 2, the acidities of amines **(1d–f)** are close enough for the four species of equation (3) to co-exist in equilibrium in the pairs: **d–e** and **e–f**. This allows determination of the respective pK_a-values which are 35.7, 35.9, and 36.1 for species **d**, **e**, and **f**, respectively.

The observed order of basicities and acidities in THF would have not been easy to predict, since the relative importance of electronic and steric and strain effects in determining those properties, as well as in the role of aggregates, were unknown in this solvent. Their influence in the carbonylation reaction of the respective lithium amides is shown below.

Mechanism/s of Carbonylation of Lithium Amides.—The reaction of lithium amides, **(2)**, with carbon monoxide leads to the production of three main products: dialkylformamides, **(3)**, dialkylglyoxylamides, **(4)**, or tetralkyltartronamides, **(5)**[3,4] [equation (4)].



$$\underset{(1)}{R^1R^2NH} \xrightarrow{BuLi} \underset{(2)}{R^1R^2NLi} \xrightarrow{CO} \underset{(3)}{R^1R^2N\overset{O}{\overset{\|}{C}}H} + \underset{(4)}{(R^1R^2N\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H})_2O} + \underset{(5)}{R^1R^2N\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}NR^1R^2} \qquad (4)$$

b R^1R^2 =

c $R^1 = R^2 = Bu$

d $R^1 = R^2 = Pr^i$

e $R^1 = c\text{-}C_6H_{11}, R^2 = Pr^i$

f $R^1 = R^2 = c\text{-}C_6H_{11}$

g R^1R^2 = O

The relative yields of products are very sensitive to reaction conditions. Conditions were found which led to the production of compounds **(3)–(5)** in satisfactory yields for organic synthesis.[3,4] One of the variables that influences the product yield is the [amine]:[amide] ratio, as shown in Table 3. Some points in the Table in connection with the present discussion on relative acidities and basicities are worthy of remark. (*a*) Morpholine and piperidine give only products **(3)**. (*b*) In all cases the yield of formamides **(3)** is the same as that of recovered amine **(1)**. (*c*) For amines **(1c)** and **(1f)** the yield of compounds **(3)** is low, the yield of compounds **(4)** is high at relatively high [**(1)**]:[**(2)**] ratio, while the yield of compounds **(5)** increases at low [**(1)**]:[**(2)**]. From a study of the reaction at several [**(1)**]:[**(2)**] ratios, a total interdependence between yields of compounds **(4)** and **(5)** was observed (see Figure 1 in ref. 3).

Alkylformamides **(3)** were assumed[14] to arise from hydrolysis of the carbamoyl anion **(6)** [equation (5) in Scheme 1],† but oxidation studies performed with some secondary amines **(1d–f)** showed that the dilithium tetralkylurea dianion, **(7)**, is the real precursor of formamides **(3)** in these cases [equation (6)], since tetralkylureas **(8d–f)** were obtained after work-up.[4] Nevertheless, when the same oxidation procedure was applied to the reaction of amide **(2g)** with CO, no dimorpholinourea was obtained but the same 50% conversion into the formamide **(3g)** was observed. In the case of amide **(2b)**, the yields after

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* Although lithium amides are usually drawn as monomers (and so will be used hitherto) it has been shown that they exist mainly as dimers,[6,8,11–13] also as trimers[12a] and even tetramers[12b] in solution.

† Although the carbamoyl anion is usually drawn as structure **(6)** we have evidence that could suggest some carbenoid character.[3,15] X-Ray diffraction studies of dihaptocarbamoyls of U and Th are also consistent with oxycarbenoid structures.[16]

Table 2. ^{13}C NMR shifts (δ_C/ppm) of the carbon α to the nitrogen of the secondary amines and lithium amides in THF.

$$\mathrm{R^1R^2NH + R^3R^4NLi \rightleftharpoons R^1R^2NLi + R^3R^4NH}$$

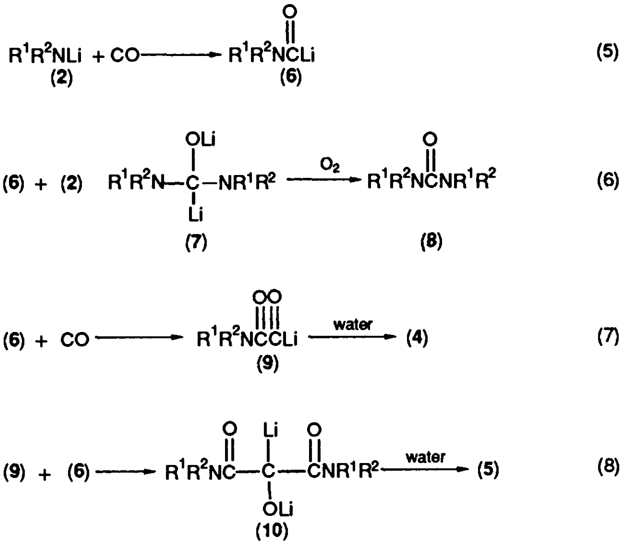
	g	a	b	c	d	e	f
R^1R^2NH	48.5	48.7	49.1	51.5	46.8	54.9–46.3	54.5
R^1R^2NLi	53.5	55.9	55.1	57.5	53.0	63.3–53.1	63.5
Pairs[a]							
g–b	53.5		49.5				
b–c			53.8	52.8			
c–f				57.4			54.6
g–a	50.9	49.3					
a–b		52.5	50.2				
b–f			55.1				54.9
c–e				56.2		54.9–46.3	
e–f						63.2–53.2 54.9–46.6	63.5 54.5
c–d				57.5	46.8		
d–e					53.0 46.8	54.9–46.3 63.3–53.1	

[a] Signal observed once the above amine-amide equilibrium is attained.

Table 3. Reaction of lithium amides with carbon monoxide in THF at 0 °C.

R^1R^2NH	$[R^1R^2NH]/[R^1R^2NLi]$	Yield (%) of products[a] (3)	(4)	(5)	(1)
(**1g**)	1[b]	50			50
(**1b**)	1[b]	50			50
(**1c**)	0.8	13	69	5	13
(**1c**)	0.2		15	85	
(**1f**)	0.8	24	43	9	24
(**1f**)	0.2		10	90	

[a] Products: dialkylformamide (**3**), dialkylglyoxylamide (**4**), tetralkyltartronamide (**5**), amine (**1**). The numbers represent conversion yields. [b] Lithium morpholide and lithium piperidide crystallize as 1:1 complexes with their respective amine.



$$\underset{(2)}{\mathrm{R^1R^2NLi}} + \mathrm{CO} \longrightarrow \underset{(6)}{\mathrm{R^1R^2N\overset{\overset{\displaystyle O}{\|}}{C}Li}} \qquad (5)$$

$$(6) + (2)\quad \underset{(7)}{\mathrm{R^1R^2N{-}\overset{\overset{\displaystyle OLi}{|}}{\underset{\underset{\displaystyle Li}{|}}{C}}{-}NR^1R^2}} \xrightarrow{O_2} \underset{(8)}{\mathrm{R^1R^2N\overset{\overset{\displaystyle O}{\|}}{C}NR^1R^2}} \qquad (6)$$

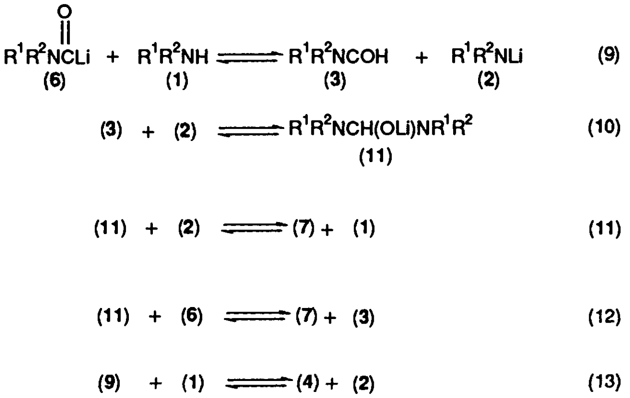
$$(6) + \mathrm{CO} \longrightarrow \underset{(9)}{\mathrm{R^1R^2N\overset{\overset{\displaystyle O}{\|}}{C}\overset{\overset{\displaystyle O}{\|}}{C}Li}} \xrightarrow{\text{water}} (4) \qquad (7)$$

$$(9) + (6) \longrightarrow \underset{(10)}{\mathrm{R^1R^2N\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle Li}{|}}{\underset{\underset{\displaystyle OLi}{|}}{C}}{-}\overset{\overset{\displaystyle O}{\|}}{C}NR^1R^2}} \xrightarrow{\text{water}} (5) \qquad (8)$$

Scheme 1.

the oxidation treatment were: 30% for (**3b**) and 24% for tripiperidinomethanol.

These otherwise surprising results are understandable in the light of the preceding acid–base studies. Owing to the high acidity of morpholine (**1g**), once anion (**6g**) is formed it is rapidly converted into the formamide (**3g**) [equation (9) in Scheme 2] and no further reaction occurs. Amide (**2b**), with an intermediate pK_a-value, only partly converts anion (**6b**) into the formamide (**3b**). The rest of the amines are not acidic enough for equilibrium (**9**) to be relevant and the reaction continues to give further addition of remaining anion (**2**) to amide anion (**6**) [equation (6)], or even proceeds to a second carbonylation to give intermediates (**9**) which produces glyoxylamides (**4**) on hydrolysis [equation (7)]. Although double carbonylation had been assumed to be thermodynamically unfavourable,[17,18] we have recently shown by MNDO calculations[15] that the reaction is possible if the solvent effect is taken into account. The double carbonylated intermediates (**9**) may add to carbamoyl anions (**6**), producing the dilithium intermediates (**10**), precursors to tartronamides (**5**) [equation (8)]. Reactions (7) and (8) are competitive depending on the [(**1**)]:[(**2**)] ratio [see equation (13)], and the results of Tables 1 and 2 make clear the rationale behind this fact. A sequence of proton-transfer equilibria [equations (9)–(13) in Scheme 2] may take place between the different intermediates depending on their relative acid–base properties.



$$\underset{(6)}{\mathrm{R^1R^2N\overset{\overset{\displaystyle O}{\|}}{C}Li}} + \underset{(1)}{\mathrm{R^1R^2NH}} \rightleftharpoons \underset{(3)}{\mathrm{R^1R^2NCOH}} + \underset{(2)}{\mathrm{R^1R^2NLi}} \qquad (9)$$

$$(3) + (2) \rightleftharpoons \underset{(11)}{\mathrm{R^1R^2NCH(OLi)NR^1R^2}} \qquad (10)$$

$$(11) + (2) \rightleftharpoons (7) + (1) \qquad (11)$$

$$(11) + (6) \rightleftharpoons (7) + (3) \qquad (12)$$

$$(9) + (1) \rightleftharpoons (4) + (2) \qquad (13)$$

Scheme 2.

It was already shown that equilibrium (9) lies well to the right in the case of morpholine (**1g**), partly to the right for piperidine (**1b**), and well to the left for the rest of the amines, in accord with the relative acidities shown by Table 2. If the nucleophilicity of species (**2**) and (**6**) is correlated with basicity, it is observed that morpholine is so weak (as shown by Table 1) that reactions shown by equation (6)–(8) and (10) do not take place under our reaction conditions with this amine.

For piperidine (**1b**), its intermediate basicity determines that equation (10) can be observed as shown by experiments with deuteriated anion (**2b**).[19] For amines of lower acidity reactions (6)–(8) take place. In the presence of a relatively high amine content, proton transfer to compound (**9**) occurs, the equilibrium (13) lies well to the right, and the yield of compounds (**4**) is high. The reverse situation occurs at low [amine], giving rise to a high conversion into tartronamides (**5**). The proton transfer to anions (**9**) is confirmed by deuteriation studies.[19]

Conclusions.—The present paper reports orders of basicity and acidity for several amines in THF which show the importance of electronic as well as steric and strain effects in determining those properties. It also describes how these values can be used to interpret results obtained in the carbonylation of lithium amides, and how the proton-transfer equilibria govern reactivity and formation of alternative products.

Experimental

All reactions involving organolithium reagents were carried out by using standard techniques for the manipulation of air- and water-sensitive compounds.[20] Spectrophotometric measurements were recorded on a Gilford 250 mod. and/or on a diode-array Hewlett–Packard spectrophotometer. NMR spectra were recorded on a Varian 100 MHz spectrometer.

Solvents and Reagents.—THF was first passed through a column of alumina, then stirred over sodium hydroxide pellets for several days, then refluxed over sodium benzophenone ketyl until dark blue solutions were obtained, and was then distilled. It was redistilled from dark blue solutions of sodium benzophenone ketyl under nitrogen immediately prior to use.

Amines.—Commercial dialkylamines were left over sodium string for several days, then refluxed and distilled over sodium immediately prior to use.

2,4-*Dinitrophenol.*—The Eastman Kodak material was first recrystallized from water slightly acidified with hydrogen chloride and then from carbon tetrachloride, m.p. 106–108 °C.

n-Butyl-lithium.—Lithium wire (1.35 g, 193 mmol) was cut into small pieces and placed into a flask containing boiling hexane (80 cm^3) and the flask was capped with a septum stopper, and kept at 50 °C. Butyl chloride (10 cm^3, 96 mmol) was syringed in small aliquots into the flask during 3 h and the mixture was left to react for 1 h at 50 °C.[21]

Lithium Amides.—Cooled (0 °C) Bu^{n}Li (2.5 cm^3; 0.8 mol dm^{-3} in hexane) was syringed into a tube under nitrogen, and the freshly distilled amine (2 mmol) was added. The white lithium amide precipitate was worked up as previously described.[3a] In the case of lithium isopropylcyclohexyl- and di-isopropyl-amide, which are soluble in hexane, the solvent was distilled off at reduced pressure. The resulting syrup was dissolved in THF.

Determination of Constants for Ion-Pair Formation between Amines and 2,4-*Dinitrophenol.*—A solution of 2,4-dinitrophenol in THF, on treatment with an excess of different amines, gave UV and visible spectra with two characteristic maxima, at 360 and 400 nm. Since pure 2,4-dinitrophenol exhibits a negligible absorbance at 400 nm (ε 125), this wavelength was used for measurements.

Solutions containing various concentrations of 2,4-dinitrophenol (*ca.* 1 × 10^{-4} mol dm^{-3}) and various concentrations of the amine (5 × 10^{-5} to 5 × 10^{-4} mol dm^{-3}) were prepared in THF and their absorbances measured at 25 °C in thermostatted cells. Calculations of K were done by applying equations (1) and (2). A starting value for ε was assumed and a new one was obtained from the slope of the plot of the first member of equation (1) *vs.* $[\mathrm{AH}][\mathrm{R}^1\mathrm{R}^2\mathrm{NH}]/A$ (*e.g.*, Figure 1). The procedure was repeated until linearity and consistency were obtained. In most of the cases determination of K from the intercept was rather inaccurate because of the small value of its reciprocal. In those cases, the constants were calculated from the plots of $[\mathrm{A}]/A$ *vs.* $\{([\mathrm{R}^1\mathrm{R}^2\mathrm{NH}] - A/\varepsilon)\varepsilon\}^{-1}$ [equation (2)] which yielded straight lines (*e.g.*, Figure 2).

^{13}C *NMR Measurements.*—^{13}C NMR spectra of THF solutions (*ca.* 2 mol dm^{-3}) of all the amines and of the lithium amides were recorded. It was observed (Table 2) that lithiation causes a clear shift (range 5–9 ppm) in the signal of the carbon α to the nitrogen relative to the free amine.

For measurements of the relative acidities, an amine (2 mmol) was syringed into the same amount of the lithium 'salt' of another amine previously dissolved in THF (1 cm^3). An aliquot (0.4 cm^3) of that solution was then transferred under nitrogen to an evacuated NMR tube capped with a septum stopper, and the ^{13}C NMR spectrum of the mixture was recorded. In the cases of di-isopropylamine, cyclohexylisopropylamine, and dicyclohexylamine the spectra of the equilibrium mixture of amine-pairs gave rise to identifiable signals for all four species. Since the K_a-value for di-isopropylamine was known from the literature,[22] it was possible to calculate the K_a-value for the other amines from equation (14), where K_{eq} represents the constant for the equilibrium shown by equation (3), and was determined from the ^{13}C NMR measurements.

$$K_{eq} = \frac{K_{a\,(\mathrm{HA}_2)}}{K_{a\,(\mathrm{HA}_1)}} \qquad (14)$$

Reaction of Lithium Dialkylamide with Carbon Monoxide.—The general procedure previously reported was followed.[3a] Quantitative determination of the reagents was routinely carried out by the double-titration technique[21] and the product composition was determined by GLC.

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