Chemical Effects of Steric Strains. 25. Steric Effects as a Factor in the Stability of Addition Compounds of Borinane with Amines

Herbert C. Brown* and Ganesh G. Pai

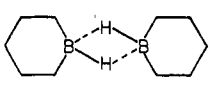
Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

Received June 24, 1981

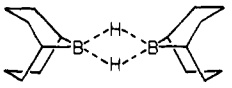
The infrared technique developed earlier to study the reaction of 9-borabicyclo[3.3.1]nonane (9-BBN) was utilized to establish the equilibria involved in the reactions between borinane (dimer) and representative amines at 25 °C in cyclohexane (in certain special cases, hexane or tetrahydrofuran was used): $(borinane)_2 + 2$ amine $\rightleftharpoons$ 2(borinane·amine). Except for very hindered cases, the complexation is complete for most tertiary amines. Thus, *N,N*-diethylmethylamine complexes fully, but the extent of coordination progressively decreases with triethylamine and *N,N*-diethylisopropylamine, becoming zero with the highly hindered *N,N*-diisopropylethylamine. A similar effect is seen in the pyridine series where the complexation is 100% with pyridine, 2-methyl-, and 2-ethylpyridines, 90% with 2-isopropylpyridine, but zero with 2-*tert*-butylpyridine. With the difunctional *N,N,N',N'*-tetramethylethylenediamine (TMED), both mono- and bisadducts are formed in tetrahydrofuran (THF) solution, but only the bisadduct is formed in hexane solution. With unhindered secondary amines, the study of equilibrium is not possible by the infrared technique due to a rapid side reaction involving liberation of hydrogen, leading to aminoborane formation: $(CH_2)_5BH + R(H)R'NH \rightarrow (CH_2)_5B{-}NR(H)R' + H_2\uparrow$. But with more hindered secondary amines, such as diisopropylamine, liberation of hydrogen is considerably slower (no reaction for ~1 h at 25 °C) and study of the equilibrium by IR is possible. With the highly hindered 2,2,6,6-tetramethylpiperidine, neither complexation nor aminoborane formation occurs. Because of a similar side reaction with primary amines, no quantitative study is possible. The results reiterate the importance of steric effects on the stability of these molecular addition compounds and establish that the steric requirements of borinane must be less than that of 9-BBN. Hence, borinane is a significantly stronger Lewis acid than 9-BBN.

The original studies[1] of molecular addition compounds of amines with boron trifluoride[2] and trimethylborane[3] convincingly established the importance of steric effects on the stabilities of the addition compounds. These early qualitative studies were followed by more definitive quantitative measurements of the heats of dissociation of trimethylborane–amine complexes in the gas phase[4] and calorimetric measurement of the heats of reaction of pyridine bases with boron trifluoride, trimethylborane, and borane in solution.[5] More recently, the equilibria in solution between 9-BBN and representative amines was studied by an infrared technique.[6,7]

Recently, another boracyclane, viz., borinane (1), has

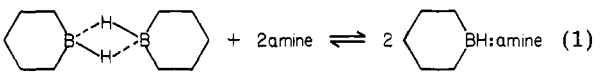


1



2

become readily available.[8] Borinane is a thermally stable (below 100 °C), low-melting solid and, like 9-BBN (2), exists as a dimer in solution. The dimer has a strong infrared absorption at 1560 cm^{-1}, which makes it readily amenable to the study of equilibria with amines (eq 1) by



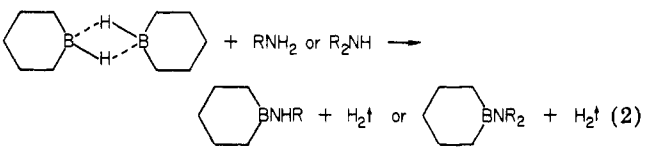
(1)

the IR technique.[6,7] In view of the similar earlier studies with 9-BBN,[6,7] we undertook to examine the borinane system for comparison with the behavior of 9-BBN. A special objective was to find one or more amines that would complex preferentially with either borinane or 9-BBN to permit a facile separation of the two reagents.

Results and Discussion

The experiments were conducted by adding a stoichiometric amount of amine to a solution of borinane (0.175 M in dimer) in cyclohexane (THF in the case of TMED), at 25 ± 0.05 °C, under a nitrogen atmosphere, monitoring the disappearance of the dimer by IR. Unlike 9-BBN, the attainment of the equilibrium was rapid, complete within 15 min in almost every case. In Table I the results are summarized and compared with the earlier results realized with 9-BBN. For reactions that proceed to completion, the concentration of the molecular addition compound was ~0.35 M.

The infrared technique fails with primary and unhindered secondary amines. In these cases the complexation reaction is accompanied by hydrogen evolution and concurrent aminoborane formation reaction (eq 2). (It is



(2)

probable that the initially formed addition compound is transformed into the aminoborane by an elimination of hydrogen. However, we did not attempt to investigate the precise mechanism of this reaction.) Since both of these reactions remove dimer from the solution, it is not possible to ascertain the amount of dimer involved in the complexation reaction. In such cases, a qualitative estimation of the equilibrium can be made by ^{11}B NMR. The dialkylborane, the amine complex, and the aminoborane possess different chemical shifts. By peak integration, it is possible to obtain a rough estimate of these species present in solution. Unfortunately, this is not strictly quantitative, since the peaks are not quantitatively related

(1) For a summary of data and conclusion, see Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; Chapters 5–8.
(2) Brown, H. C.; Schlesinger, H. I.; Cardon, S. Z. *J. Am. Chem. Soc.* **1942**, *64*, 325.
(3) Brown, H. C. *J. Am. Chem. Soc.* **1945**, *67*, 378, 1452. Brown, H. C.; Pearsall, H. *Ibid.* **1945**, *67*, 1765.
(4) Brown, H. C.; Bartholomay, H., Jr.; Taylor, M. D. *J. Am. Chem. Soc.* **1944**, *66*, 435. Brown, H. C.; Taylor, M. D. *Ibid.* **1947**, *69*, 1332. Brown, H. C.; Sujishi, S. *Ibid.* **1948**, *70*, 2878. Brown, H. C.; Gorstein, M. *Ibid.* **1950**, *72*, 2926. Brown, H. C.; Taylor, M. D.; Sujishi, S. *Ibid.* **1951**, *73*, 2464. Brown, H. C.; Barbaras, G. K. *Ibid.* **1953**, *75*, 6.
(5) Brown, H. C.; Horowitz, R. H. *J. Am. Chem. Soc.* **1955**, *77*, 1733. Brown, H. C.; Gintis, D.; Podall, H. *Ibid.* **1956**, *78*, 5378. Brown, H. C.; Domash, L. *Ibid.* **1956**, *78*, 5384.
(6) Brown, H. C.; Kulkarni, S. U. *Inorg. Chem.* **1977**, *16*, 3090.
(7) Brown, H. C.; Wang, K. K. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 117.
(8) Brown, H. C.; Negishi, E. *J. Organomet. Chem.* **1971**, *26*, C67.

0022-3263/81/1946-4713$01.25/0

Table I. Stability of Addition Compounds of Amines with Borinane

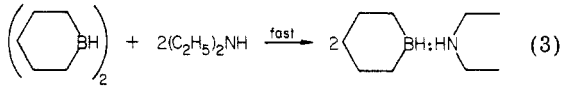
entry	amine	assoc with borinane,[a,c] %	assoc with 9-BBN,[b,c] %
1	*tert*-butylamine	100[d,e]	100
2	diethylamine	100[d,e]	100
3	pyrrolidine	100[d,e]	
4	piperidine	100[d,e]	
5	2,6-dimethylpiperidine	100[d,e]	45
6	diisopropylamine	58[f]	36
7	2,2,6,6-tetramethylpiperidine	0	0
8	trimethylamine	100	100[j]
9	*N,N*-diethylmethylamine	100	
10	triethylamine	81	0
11	*N,N*-diethylisopropylamine	10 ± 5[g]	
12	*N,N*-diisopropylmethylamine	0	
13	*N,N*-diisopropylethylamine	0	
14	pyridine	100	100
15	2-methylpyridine	100	91
16	2-ethylpyridine	100	59
17	2-isopropylpyridine	90	26
18	2-*tert*-butylpyridine	0	0
19	2,6-dimethylpyridine	0	0
20	1,4-diazabicyclo[2.2.2]octane (TED)	100[h,i]	100
21	*N,N,N',N'*-tetramethylethylenediamine (TMED)	100[h,i]	100[j]
22	*N,N,N',N'*-tetraethylethylenediamine	100	

[a] Concentrations of amine and of borinane monomer were ~0.35 M each. [b] Concentrations of amine and of 9-BBN monomer were 0.15 M each. Reference 7. [c] Equilibria were measured in cyclohexane solution unless indicated otherwise. [d] By ^{11}B NMR. [e] Concurrent aminobornae formation takes place. [f] Hexane solution. [g] Uncertainty in the result is due to the small decrease in the concentration of borinane dimer. [h] THF solution. [i] Both with 1 and 0.5 equiv amine. [j] Reference 6.

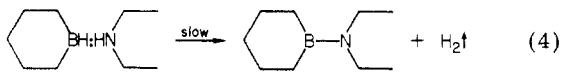
to the concentrations. With more hindered secondary amines, such as diisopropylamine, the side reaction involving aminoborane formation is much slower at 25 °C. (After 1 h, ^{11}B NMR shows only a trace of aminoborane.) But complexation is rapid and equilibrium is attained within 5 min. Thus, a quantitative study of the equilibrium was possible in this case.

As already mentioned, no quantitative study was possible with primary amines, such as *n*-butylamine. However, no unreacted borinane was observed in the ^{11}B NMR spectrum immediately following the addition of a stoichiometric amount of amine. Since 9-BBN associates 100% with even the relatively hindered *tert*-butylamine, it is reasonable to conclude that borinane also complexes completely with *n*-butylamine and similar primary amines.

In the case of diethylamine, both complexation and hydrogen evolution proceed concurrently (eq 3 and 4), but

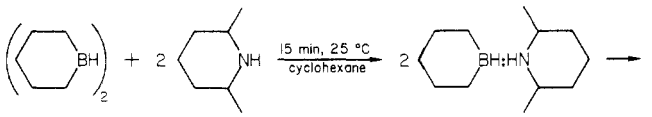


(3)

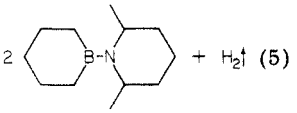


(4)

the latter reaction is slower. A similar reaction occurs with pyrrolidine and piperidine. With the more hindered 2,6-dimethylpiperidine, the extent of aminoborane formation in the time required to attain equilibrium is much less (eq 5). With increased steric crowding in 2,2,6,6-tetramethylpiperidine, neither complexation nor aminoborane formation occurs (eq 6). Even after 24 h at room temperature, no reaction is detected. The behavior of diisopropylamine comes somewhere between these two cases. With this amine, complexation is rapid but proceeds to only 58% at equilibrium, with subsequent hydrogen evolution very slow (eq 7).

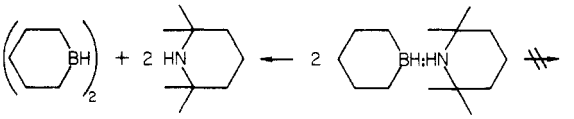


~95%

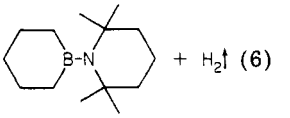


(5)

~5%

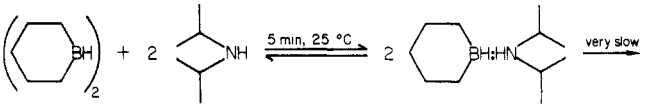


0%

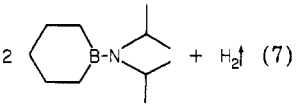


(6)

0%



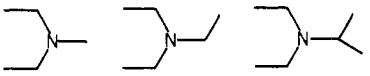
58%



(7)

0%

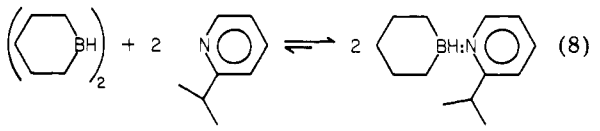
No such complications are encountered with tertiary amines. Consequently, these amines were explored in much greater detail. The effect of increasing steric crowding in the amine is strikingly demonstrated in the aliphatic series, *N,N*-diethylmethylamine (3), triethylamine (4), *N,N*-diethylisopropylamine (5) (entries 9–11 in Table I). It may be noted that the highly hindered triethylamine fails to complex with 9-BBN. The fact that the equilibrium between the triethylamine and borinane is far toward the right shows that the borinane is sterically much less



3 (100%) 4 (81%) 5 (0%)

demanding than 9-BBN. This property was exploited in selectively complexing borinane in an admixture with 9-BBN, effecting their separation.[9]

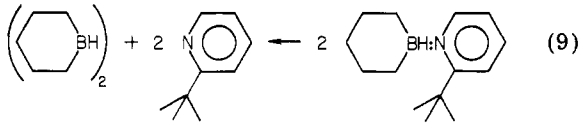
A similar difference between the Lewis acidities of borinane and 9-BBN is revealed by their complexes with pyridine bases. Unsubstituted pyridine reacts completely with both dialkylboranes. As the steric requirements of the 2-alkyl substituent in the pyridine base are increased, a regular decrease in the extent of association is observed in the case of 9-BBN. Borinane, on the other hand, is much less sensitive to this change. For example, borinane is fully associated with 2-ethylpyridine, whereas 9-BBN is coordinated only to the extent of 59% with this base. Moreover, as the steric bulk of the 2-alkyl substituent becomes significant, as in the case of 2-isopropylpyridine, borinane exhibits a minor amount of dissociation at equilibrium (10%; eq 8), whereas the 9-BBN derivative



(8)

90%

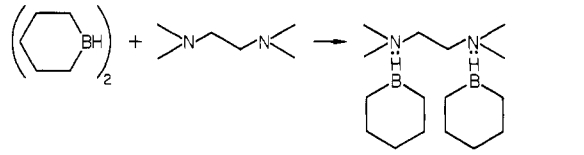
is highly dissociated (74%). The steric bulk of the 2-*tert*-butyl group is too demanding for even borinane. With this base, no complexation takes place, either with borinane (eq 9) or with 9-BBN (Table I).



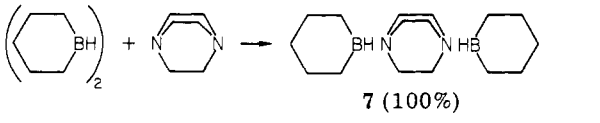
(9)

0%

Borinane forms bisadducts with difunctional Lewis bases, such as TMED and triethylenediamine, TED (eq 10). Thus, on mixing 0.5 or 1.0 equiv of either TMED or

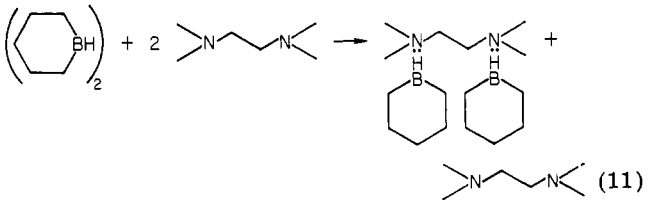


6 (100%) (10)



7 (100%)

TED, the dimer absorption disappears completely. However, the IR spectrum does not establish whether or not a monoadduct is formed in the presence of 1 molar equiv of amine. In this case, it would be possible that only bisadduct formation takes place, with 50% of the amine remaining unreacted (eq 11). Comparable behavior has been observed for boron trifluoride, borane, and alane, with such amines varying with the solvent.[10] To remove this ambiguity, we isolated the actual complex and established its constitution by ^1H NMR and ^{13}C NMR spectroscopy.



(11)

(See Experimental Section for more details.) It was established that the nature of the complex between TMED and borinane varies with the reaction solvent. In hexane, even in the presence of excess TMED, only the bisadduct is formed. In THF and chloroform, both the bis- and monoadducts are formed, according to the amount of TMED present. A similar result was anticipated for TED. However, with this amine, borinane forms both the bis- and monoadducts in hexane. 9-BBN also forms stable complexes with TMED and TED in THF solution (100% associated). However, in the case of 9-BBN, the complexation proceeds very slowly. In contrast, the bisadduct of TMED or TED with borinane forms practically instantaneously. The bisadduct (**6**) is sparingly soluble in hexane (85% precipitates from a 1 M solution at 0 °C). Both the low solubility and the fast formation of the adduct proved useful in separating borinane from 9-BBN. Similarly, the bisadduct of TED (**7**) is practically insoluble in hexane. One can also make use of the much faster reaction between borinane and TED to precipitate borinane almost quantitatively in the presence of 9-BBN.

With the more hindered *N,N,N′,N′*-tetraethylethylenediamine, only monoadduct formation takes place.

Conclusion

The present study once again demonstrates the importance of steric effects in the stability of molecular addition compounds and establishes borinane as a Lewis acid of considerably lower steric requirements than those of 9-BBN. Both the extent of complexation with selected amines and the vast difference in the rates of complexation of borinane and 9-BBN with these amines can be utilized to effect separation of the borane reagents from mixtures.

Experimental Section

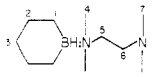
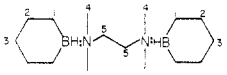
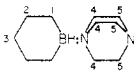
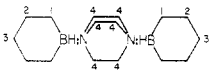
Materials. All commercially available amines were distilled from calcium hydride under nitrogen and stored over molecular sieves. *N,N*-Diisopropylmethylamine and *N,N*-diethylmethylamine were prepared by adapting the general methods of synthesis.[11] *N,N*-Diethylisopropylamine was prepared by reducing the corresponding amide with $BH_3{\cdot}SMe_2$[12] and an improved method developed in our laboratory.[13] The solvents were purified as described elsewhere.[14] The concentration of borinane is reported as the dimer.

Instruments. ^1H NMR spectra were scanned on a Varian T-60 NMR spectrometer. ^{11}B and ^{13}C NMR spectra were scanned on a Varian FT-80A spectrometer. A Mirian-1A variable-filter infrared spectrometer from the Wilks Scientific Corp. was used to monitor the dimer absorption at 1560 cm^{-1}. The reaction mixture was pumped at 4 mL/min through a 0.11-mm Wilks flow-through NaCl cell mounted on a stainless steel holder. The absorbance was recorded on a Hewlett-Packard 71274 strip-chart recorder.

Method. An oven-dried, 50-mL, round-bottom flask with a side arm was cooled to room temperature in a stream of dry nitrogen. The flask was charged with 14.3 mL of a 0.175 M (2.5 mmol) of borinane solution in a suitable solvent. The flask was immersed in a constant temperature bath kept at 25 ± 0.05 °C and allowed to equilibrate for 0.5 h. The solution was then

(9) Brown, H. C.; Pai, G. G., *Heterocycles*, in press (issue dedicated to Prof. K. Tsuda).
(10) Brown, H. C.; Singaram, B. *Inorg. Chem.* **1980**, *19*, 455.
(11) Puterbaugh, W. H.; Hauser, C. R. *J. Org. Chem.* **1959**, *24*, 416.
(12) Lane, C. F. *Aldrichimica Acta* **1975**, *8*, 20.
(13) Brown, H. C.; Choi, Y. M.; Narasimhan, S. *Synthesis* **1981**, 941.
(14) Brown, H. C. "Organic Syntheses via Boranes"; Wiley-Interscience: New York, 1975; Chapter 9.

Table II. ^{13}C NMR Chemical Shift Data (ppm) for the Bis- and Monoadducts of Borinane with TMED and TED

compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7
	17-19	27.7	30.3	46.7	57.7	53.2	45.6
	17-19	27.8	30.5	47.5	54.4		
	17.1-17.6	27.5	30.3	47.9	45.4		
	17.2	27.2	30.2	46.9			

pumped through the IR cell to determine the initial absorbance. The reaction was initiated by the addition of 0.395 g (0.4 mL, 5 mmol) of pyridine and the disappearance of dimer absorption at 1560 cm^{-1} monitored. At the end of the reaction, a flat line across the chart paper was obtained. A blank experiment was run to determine the absorption due to pyridine: % association = $[a - (b - c)]/a \times 100$, where a is the initial absorbance, b is the absorbance at equilibrium, and c is the blank value.

In these equilibrium studies, the concentration of amine and of borinane (as monomer) were ~0.35 M each.

Stoichiometry of the Reaction between TMED and Borinane. a. In Hexane. An oven-dried, 50-mL centrifuge vial was cooled under dry nitrogen and charged with 0.581 g (0.77 mL, 5.0 mmol) of TMED and 0.385 g (0.54 mL, 3 mmol) of *n*-nonane (GLC internal standard). Five milliliters of *n*-hexane was added to the vial and the amount of TMED estimated by GLC analysis on 6 ft × 0.25 in. 10% SE-30 Chromosorb W (50–120 °C, 5 °C/min; injection port temperature, 40 °C). Five milliliters of 0.5 M borinane solution (2.5 mmol) was added to the vial. After 15 min, the vial was centrifuged and the amount of TMED in supernatant solution determined. Exactly 2.5 mmol of TMED remained in solution. The supernatant solution was decanted with a double-ended needle, and the precipitate was washed with dry *n*-pentane and dried by vacuum: 0.595 g (85%), mp 142–144 °C (recrystallized from THF); ^1H NMR ($CDCl_3$) δ 3.0 (s, 4 H), 2.5 (s, 12 H), 2.2–0.4 (complex, 20 H); ^{11}B NMR ($CDCl_3$) δ −5 (br); ^{13}C ($CDCl_3$) proton decoupled (see Table II).

b. In THF. An oven-dried, 50-mL flask with side arm was equipped with a connecting tube and cooled to room temperature under nitrogen. As before, the flask was charged with 5 mmol of TMED and 3 mmol of *n*-nonane and a solution in THF was prepared. The amount of TMED was estimated by GLC. Dimeric borinane (2.5 mmol) in THF solution was added, and after 5 min, an aliquot was analyzed by GLC. About 2.5 mmol of free TMED appeared to be present in solution, but the results varied by ~10% in different injections. The solvent and *n*-nonane were pumped off at 0.01-mm pressure at room temperature. A white semisolid was obtained: 0.951 g. It was dissolved in $CDCl_3$, and ^1H and ^{13}C NMR spectra were obtained: ^1H NMR δ 3.4–2.2 (unresolved with sharp peaks at 2.5 and 2.3, 16 H), 2.0–0.4 (complex, 10 H); ^{11}B NMR −0.3 (br); for ^{13}C NMR, see Table II. The spectral data and physical state of the complex clearly establish it as the monoadduct. It appears that the 1:1 complex decomposes during GLC analysis, even at an injection port temperature of 40 °C. Attempts to recrystallize the complex from THF, THF–ether, and chloroform failed. On attempted dissolution in hexane, the complex decomposed, giving the bis complex.

Stoichiometry of the Reaction between TED and Borinane. In Hexane. In a centrifuge vial, 0.560 g (5 mmol) of TED was suspended in hexane. Five milliliters of a 0.5 M borinane solution was added, and after the solution was stirred for 0.5 h, the complex was collected by centrifugation. It was washed with *n*-pentane several times and dried under vacuum. The white powder so obtained melted at 183–187 °C: 0.941 g, 97%; ^1H NMR (Me_2SO-d_6) δ 2.9 (br s, 2 H), 2.8 (br s, 8 H), 2.6 (br s, 2 H), 2.0–0.4 (complex, 10 H); ^{11}B NMR (Me_2SO-d_6) δ −2 (slightly resolved doublet); ^{13}C NMR (Me_2SO-d_6), see Table II.

A similar experiment with 2.5 mmol of TED and 2.5 mmol of borinane gave the corresponding bisadduct in ~100% yield: mp 232–234 °C; ^1H NMR (Me_2SO-d_6) δ 2.9 (s, 12 H), 2–0.3 (20 H); ^{11}B NMR (Me_2SO-d_6) δ −0.1 (s); ^{13}C NMR (Me_2SO-d_6), see Table II.

Acknowledgment. Financial assistance from the National Institutes of Health (GM 10937-19) is gratefully acknowledged.

Registry No. 1, 289-53-2; 1 *tert*-butylamine, 79069-72-0; 1 diethylamine, 79083-86-6; 1 pyrrolidine, 79069-73-1; 1 piperidine, 79069-74-2; 1 2,6-dimethylpiperidine, 79069-75-3; 1 diisopropylamine, 79069-76-4; 1 trimethylamine, 79069-77-5; 1 *N,N*-diethylmethylamine, 79069-78-6; 1 triethylamine, 79069-79-7; 1 *N,N*-diethylisopropylamine, 79069-80-0; 1 pyridine, 79069-81-1; 1 2-methylpyridine, 79069-82-2; 1 2-ethylpyridine, 79069-83-3; 1 2-isopropylpyridine, 79069-84-4; 1 TED, 79069-85-5; 1 TMED, 79069-86-6; 1 *N,N,N',N'*-tetraethylenediamine, 79069-87-7; 6, 79069-88-8; 7, 79069-89-9; 2,2,6,6-tetramethylpiperidine, 768-66-1; *N,N*-diisopropylmethylamine, 10342-97-9; *N,N*-diisopropylethylamine, 7087-68-5; 2-*tert*-butylpyridine, 5944-41-2; 2,6-dimethylpyridine, 108-48-5.