Acknowledgement. This work was supported by the Korea Science and Engineering Foundation through the Organic Chemistry Research Center. We also acknowledge Mr. Chi Hyo Park of Lucky Ltd., for GC-MS and NMR spectra.

References

1. (a) Tanis, S. P. *Tetrahedron Lett.* **1982**, *23*, 3115. (b) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833.
2. Walker, R. P.; Faulkner, D. J. *J. Org. Chem.* **1981**, *46*, 1098.
3. Ferrari, M.; Pelizzoni, F.; Ferrari, G. *Phytochemistry*, **1974**, *13*, 208.
4. (a) Nasipuri, D.; Das, G. *J. Chem. Soc. Perkin Trans 1*, **1979**, 2776. (b) Matsumoto, T.; Usui, *S. Chem. Lett.* **1978**, 105.
5. Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630.
6. (a) Schulte, G.; Scheuer, P. J.; McConnell, O. J. *Helv. Chim. Acta.* **1980**, *63*, 2159. (b) Tañis, S. P.; Herrinton, P. M. *J. Org. Chem.* **1985**, *50*, 3988.
7. (a) Sherman, E.; Amstutz, E. D. *J. Am. Chem. Soc.* **1950**, *72*, 2195. (b) Parker, K. A.; Johnson, W. S. *Tetrahedron Lett.* **1969**, 1329.
8. (a) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659. (b) Munzel, N.; Schweig, A. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 471.
9. (a) Lee, G. C. M.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Org. Chem.* **1992**, *57*, 3126. (b) Kataoka, Y.; Tezuka, M.; Takai, K.; Utimoto, *K. Tetrahedron*, **1992**, *48*, 3495, and references therein.
10. Cormier, R. A.; Grosshans, C. A.; Skibbe, S. L. *Synth. Commun.* **1988**, *18*, 677, and references therein.
11. An alternative synthesis of 2-acetonyloxiranes from the palladium-catalized reaction of α-haloketones with acetonyltin reagents was reported; Pri-bar, I.; Pearlman, P. S.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4629.
12. (a) Maurer, R. A.; Hauser, A. *Tetrahedron Lett.* **1984**, *25*, 1061. (b) Hegde, S. G.; Wolinsky, J. *J. Org. Chem.* **1982**, *47*, 3148.
13. (a) Kang, K.-T.; Lee, J. C.; U. J. S. *Tetrahedron Lett.* **1992**, *33*, 4953. (b) Kang, K.-T.; U. J. S. *Synth. Commun.* **1994**, *24*, 1507.
14. Lewis acid-mediated reactions of **1** with aldehydes have been conveniently empolyed in the synthesis of methylenetetrahydrofurans and methylenebutyrolactones, D' Aniello, F.; Taddei, M. *Synlett.* **1993**, 119.

Conversion of Nitriles into Aldehydes by Diisobutylaluminum Hydride-Dimethyl Sulfide Complex

Jin Soon Cha*, Oh Oun Kwon, Min Kyu Jeoung, and Eun Ju Kim

Department of Chemistry, Yeungnam University, Kyongsan 712-749, Korea

Received August 11, 1994

The conversion of nitriles into aldehydes is one of the most desirable means in organic synthesis. Numerous useful methods have been proposed to achieve such purposes.[1] Especially noteworthy is that some reagents, such as potassium 9-*sec*-amyl-9-borarabicyclo[3.3.1]nonane (K-9-*sec*-Am-9-BBNH),[2] lithium tris(dihexylamino)aluminum hydride (LTDHA)[3] and sodium tris(dihexylamino)aluminum hydride (STDHA)[4], nicely achieved the chemoselective reduction of aromatic nitriles to the corresponding aldehydes in which aliphatic nitriles remain intact.

Very recently, we prepared diisobutylaluminum hydride-dimethyl sulfide (DIBAH-SMe_2) complex by a simple addition of dimethyl sulfide to the solution of diisobutylaluminum hydride (DIBAH)[5] (Eq. 1).

$$(i\text{-Bu})_2\text{AlH} + \text{SMe}_2 \xrightarrow{\text{toluene}} \underset{\text{DIBAH-SMe}_2}{(i\text{-Bu})_2\text{AlH-SMe}_2} \qquad (1)$$

The complex, DIBAH-SMe_2, is very stable and possesses unique reducing characteristics. Accordingly, we have examined the reducing characteristics of the complex systematically in order to enlarge the scope of applicability as a reducing agent.[5] In the course of this systematic study, we found that DIBAH-SMe_2 converted both benzonitrile and capronitrile into the corresponding aldehydes in higher yields than those obtained by DIBAH itselt. Consequently, we decided to investigate a full scope of such transformations. This paper reports the results for the reduction of nitriles by utilizing DIBAH-SMe_2 in a limiting amount at 0 ℃, along with the results obtained previously by DIBAH itself[6] for comparison.

In general, as shown in Table 1, the yields of aldehydes by DIBAH-SMe_2 are better than those by DIBAH itself which is well known as a superior reagent for synthesis of aldehydes from nitriles.

DIBAH-SMe_2 in toluene reduced unsubstituted aromatic nitriles, such as benzonitrile and naphthonitrile, to the corresponding aldehydes in yields of 90-91% in 3 h at 0 ℃. Dinitriles, such as phthalonitrile and terephthalonitrile, were reduced to dialdehydes in yields of 92-99%. Ring substituted derivatives are readily accommodated. Thus, chloro-and dichlorobenzonitriles were converted into the corresponding aldehydes in yields better than 90%. Tolunitriles, regardless of the position of the methyl substituent, were also readily reduced to give the aldehydes in better than 92% yields.

The reagent also reduced aliphatic nitriles to aldehydes in yields of 71-99% in 3h at 0 ℃. Alicyclic derivatives, such as cyclopropanecarbonitrile, worked equally well. α,β-Unsaturated nitriles, such as crotononitrile, provided the corresponding aldehydes in a yield of 97%. Finally, it is also possi-

Table 1. Yields of Aldehydes in the Reduction of Nitriles with Diisobutylaluminum Hydride-Dimethyl Sulfide Complex in Toluene at 0 ℃[a]

Compound	Time	Yield of aldehyde, %[b]	
	hr	DIBAH-SMe_2	DIBAH[c]
benzonitrile	1	88, 87,[d] 80,[e] 72[d,e]	–
	3	90, 89,[d] 84,[e] 80[d,e]	86
1-naphthalonitrile	3	91	87
phthalonitrile	6	92	–
terephthalonitrile	3	99 (96)	90
p-chlorobenzonitrile	3	93	–
2,6-dichlorobenzonitrile	3	90	85
o-methoxybenzonitrile	6	91	–
o-tolunitrile	3	92	82
m-tolunitrile	3	93	84
p-tolunitrile	3	92	–
butyronitrile	3	94	62
capronitrile	3	89 (79)	87
caprylonitrile	3	86	–
decanenitrile	3	99	75
isobutyronitrile	3	85	–
isovaleronitrile	3	71	–
pivalonitrile	3	72	–
cyclopropanecarbonitrile	3	75	–
crotononitrile	3	97	–
decanedinitrile[f]	3	76	–

[a]Reacted with 1.1 equiv of DIBAH-SMe_2. [b]Analysis with 2,4-dinitrophenylhydrazine. Figures in parenthesis are isolated yields. [c]Data taken from ref. 6. [d]At room temperature. [e]In THF. [f]Reacted with 2.2 equiv of the reagent.

ble to reduce aliphatic dinitrile, such as decanedinitrile, to the corresponding dialdehyde in a yield of 76%.

In conclusion, a simple adition of dimethyl sulfide to a solution of diisobutlyaluminum hydride in toluene provides a stable complex of DIBAH-SMe_2, which reduces aromatic and aliphatic nitriles of various structure to the corresponding aldehydes in yields better than those by DIBAH itself. The systematic study of DIBAH-SMe_2, showes that the reducing power of the reagent is weaker and, hence, more selective than that of DIBAH itself. Therefore, this study adds an advantage to DIBAH and enlarges its applicability in organic synthesis.

Experimental

Materials. DIBAH was purchased from Aldrich Chemical Co. as a neat and diluted with freshly-distilled toluene and standardized by hydrolyzing a known aliquot of the solution with methanol and measuring the hydrogen evolved. Most of the organic compounds utilized were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. All glassware was dried thoroughly in a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solution.

Preparation of DIBAH-SMe_2 in Toluene. An oven-dried, 1-L flask with a sidearm equipped with a magnetic stirring bar and a stopcock leading to a mercury bubbler was flushed with dry nitrogen. To this flask was added *ca.* 70 mL of toluene and the flask was cooled to 0 ℃ with use of an ice-water bath. The DIBAH stored in cylinder was transferred to the volume of 50 mL (*ca.* 250 mmol) in a graduated cylinder. To this was added 20 mL (*ca.* 275 mmol) of dimethyl sulfide with stirring. The resulting DIBAH-SMe_2 solution in toluene was found to be 2.0 M.

Partial Reduction of Nitriles. The following reduction of terephthalonitrile is representative. An oven-dried, 50-mL flask fitted with a septum inlet and a magnetic stirring bar, and connected to a mercury bubbler was charged with 0.64 g (5 mmol) of terephthalonitrile and 5 mL of toluene. The solution was immersed in an ice-water bath and 5.5 mL of a precooled 2.0 M solution of DIBAH-SMe_2 (11 mmol) in toluene was injected slowly with stirring. The reaction mixture was stirred for 3h at 0 ℃ and analysis with 2,4-dinitrophenylhydrazine. The yield was 99%: mp of the hydrazone 115-117° (lit.[7] mp. 116°).

Preparative Reduction of Nitriles. The following procedure for the reduction of capronitrile to caproaldehyde is representative. To the flask, typically equipped as above, 4.86 g (50 mmol) of capronitrile in 20 mL of toluene was introduced and the solution was cooled to 0 ℃. To this was added 27.5 mL of a precooled 2.0 M solution of DIBAH-SMe_2 (55 mmol) in toluene was injected slowly with vigorous stirring. The reaction was mixture was stirred for 3 h and then 10 mL of toluene-methanol (1 : 1) solution was added slowly, followed by 20 mL of 2.0 M hydrochloric acid solution. The resulting mixture was stirred for 0.5 h at 0 ℃ and the soluion was separated from the solid aluminum salts *via* a gas dispersion tube. The organic layer was separated and the aqueous layer was extracted twice with 20 mL portions of ether, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvents were evaporated and a careful distillation of the residue afforded 3.96 g (79%) of caproaldehyde : bp. 130-132 ℃. GC analysis showed 98% purity and ^1H NMR spectrum agreed with that of an authentic sample.

Acknowledgment. The work supported by the Organic Chemistry Research Center-KOSEF.

References

1. (a) Stannous chloride: Stephen, E. *J. Chem. Soc.* **1925**, *127*, 1874. (b) Sodium triethoxyaluminohydride: Hesse, G.; Schrodel, R. *Angew. Chem.* **1956**, *68*, 438; *Ann.* **1957**, *607*, 24. (c) Lithium triethoxyaluminohydride: Brown, H. C.; Schoaf, C. J.; Garg, C. P. *Tetrahedron Lett.* **1959**, 9; Brown, H. C. *J. Chem. Educ.* **1961**, *38*, 173; Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* **1964**, *86*, 1079, 1085; de Peretti, D.; Strzalko-Bottin, T.; Seydenpenne, *J. Bull. Soc. Chim. Fr.* **1974**, 2925. (d) Diisobutylaluminum hydride: Zakharkin, L. I.; Khorlina, I. M. *Dokl. Akad. Nauk SSSR* **1957**, *116*, 422; Minato, H.; Nagasaki, T. *J. Chem. Soc.* [*c*] **1966**, 1866; Haeck, H. H.; Kralt, T. *Rec. Trav. Chim. Pays-Bas* **1966**, *85*, 343; Miller, A. E. G.; Bliss, J. W.; Schwartzman, L. H. *J. Org. Chem.* **1959**, *24*, 627; Teisseire, P.; Plattier, M.; Corbier, B. *Recherches* **1964**, *14*, 44; Marshall, J. A.; Andersen, N. H.; Johnson, P. C. *J. Org. Chem.* **1970**, *35*, 186; Stevens, R. V.; Dupree, Jr., L. E.; Loewenstein, P. L. *J. Org. Chem.* **1972**, *37*, 977; Caton, M. P. L.; Coffee,

E. C. J.; Watkins, G. L. *Tetrahedron Lett.* **1974**, 585. (e) Sodium diethylaluminohydride in the presence of 2,6-di-*t*-butylphenoxydiethylaluminum: Yoon, N. M.; Kim, S. K.; Gyong, Y. S. *Bull. Korean Chem. Soc.* **1986**, *7*, 323. (f) Hydrogenation: Peitra, S.; Trinchera, C. *Gazz. Chim. Ital.* **1955**, *85*, 1705; Gaiffe, A.; Pallaud, R. *Compt. Rend.* **1961**, *252*, 1339, **1962**, *254*, 486; Plieninger, H.; Werst, G. *Angew. Chem.* **1955**, *67*, 156; *Chem. Ber.* **1955**, *88*, 1965; Coker, J. N.; Kohlhase, W. L.; Fields, M.; Rogers. A. O.; Stevens, M. A. *J. Org. Chem.* **1962**, *27*, 850; Staskun, B.; Backeberg, O. G. *J. Chem. Soc.* **1964**, 5880; van Es, T.; Staskun, B. *J. Chem. Soc.* **1965**, 5775; *Org. Syn.* **1971**, *51*, 20. (g) Organosilicon hydride: Fry, J. L. *Chem. Comm.* **1974**, 45; Fry, J. L.; Ott, R. A. *J. Org. Chem.* **1981**, *46*, 602. (h) Thexylbromoborane-dimethyl sulfide: Cha, J. S.; Oh, S. Y.; Kim, J. E. *Bull. Korean Chem. Soc.* **1987**, *8*, 301.
2. Cha, J. S.; Yoon, M. S. *Tetrahedron Lett.* **1989**, *30*, 3677.
3. (a) Cha, J. S.; Lee, S. E.; Lee, H. S. *Org. Prep. Proced. Int.* **1992**, *24*, 331. (b) Cha, J. S. *Bull. Korean Chem. Soc.* **1992**, *13*, 670.
4. Cha, J. S.; Jeoung, M. K.; Kim, J. M.; Kwon, O. O.; Lee, J. C. *Org. Prep. Proced. Int.* **1994**, *26*, 552.
5. Cha, J. S.; Jeoung, M. K.; Kwon, O. O.; Lee, K. D. Lee, H. S. *Bull. Korean Chem. Soc.* **1994**, *15*, 873.
6. Yoon, N. M.; Gyoung, Y. S. *J. Org. Chem.* **1985**, *50*, 2443.
7. *CRC Handbook of Tables for Organic Compound Identification*; 3rd ed.; CRC Press, Inc.: Cleveland, 1967.

Evidence for Coordination of Picoline N-oxides to Iron(III) Porphyrin Complexes

Koo Shin

Department of Chemistry, Sejong University, Seoul 133-747, Korea

Received September 22, 1994

Metalloporphyrins have been found as effective catalysts for the chemical oxidation of organic and inorganic compounds in the presence of oxygen donors.[1] As an oxygen donating reagent, iodosylbenzene, organic perbenzoic acid, hydrogen peroxide, sodium hypochlorite, potassium persulphate, molecular oxygen and amine N-oxide have been used.[2] Bruice and coworkers primarily showed the oxygen donation ability of N,N-dimethylaniline N-oxide to an iron(III) porphyrin catalyst.[3] Advantages of N-oxides over other chemical oxidants are their higher solubility in organic solvents, their monomeric nature, and their inability to oxidatively destroy the porphyrin ring. Hirobe and coworkers have also reported that iron(III) porphyrins serve to deoxygenate tertiary amine N-oxide compounds.[4] The high-spin six coordinate complex, $[(TPP)Fe(III)(PNO)_2]ClO_4$, (TPP=dianion of tetraphenyl porphyrin PNO=4-picoline N-oxide), has been prepared and purified by Reed, Scheidt, and coworkers.[5] They characterized this complex by infrared spectroscopy, magnetic susceptibility and elemental analysis, but not NMR spectroscopy. In this paper an evidence for coordination of PNO to the iron(III) porphyrins by ^1H NMR measurments is described.

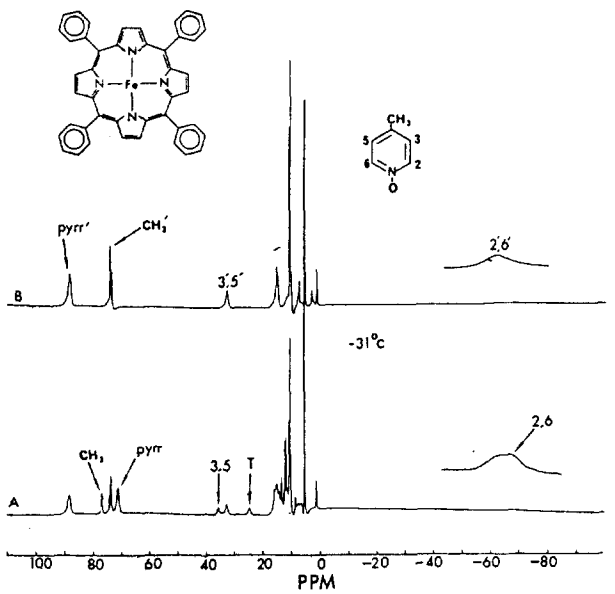

Figure 1. ^1H NMR Spectra of Titration of $(TPP)Fe(III)SO_3CF_3$ Both spectra were taken in CD_2Cl_2 at -31 ℃ : (A) in the presence of 2.0 equiv of PNO, (B) in the presence of 5.0 equiv of PNO. T represents a pyrrole resonance of the initial iron(III) triflate complex.

Experimental

PNO was purchased from Aldrich and recrystallized from acetone and diethyl ether. As reported previously, the triflate complex, $(TPP)Fe(III)SO_3CF_3$, was prepared by dissolving the $[(TPP)Fe(III)]_2O$ in CH_2CCl_2 and stirring with 1 M aqueous HSO_3CF_3 (Aldrich) for several hours.[6] ^1H NMR spectra were recorded on Bruker AC-200 Fourier transform spectrometer. All NMR signal positions were obtained through the use of the solvent as a reference. The solvent signal for CH_2Cl_2 ($CDHCl_2$) was assigned as 5.32 ppm *vs* TMS. NMR measurements were performed at 25 ℃ or -31 ℃.

Results and Discussion

Coordination of picoline N-oxide in CH_2CCl_2 solution to the iron(III) porphyrin containing a very weak ligand, (triflate anion $CF_3SO_3^-$), is evident by NMR spectroscopy. A pyrrole proton resonance of the iron(III) triflate porphyrin, $(TPP)Fe(III)SO_3CF_3$, in CD_2CCl_2 was observed at 39.6 ppm in the ^1H NMR spectrum at room temperature.[6] Titration of the triflate complex with PNO in a non-coordination solvent results in the following observation. Addition of 1.0 equiv of PNO gives a very broad pyrrole signal at -48.5 ppm at room temperature. This 48.5 ppm signal shifts further downfield to 60.1 and 68.4 ppm with addition of 2.0 and 5.0 equiv of PNO. The shift downfield and broadness of the pyrrole proton resonance in the ^1H NMR spectrum probably indicates a fast exchange process for the triflate ligand and PNO