Transformation of Carboxylic Acids and Their Derivatives into Aldehydes by Lithium Tris(dialkylamino)aluminum Hydrides

Jin Soon Cha

Department of Chemistry, Yeungnam University, Kyongsan 712-749. *Received July 13, 1992*

A systematic study of the partial reduction of carboxylic acids and their derivatives to the corresponding aldehydes with lithium tris(dialkylamino)aluminum hydrides under practical conditions has been carried out. The diethylamino-substituted derivative of lithium aluminum hydride, lithium tris(diethylamino)aluminum hydride (LTDEA), shows quite general applicability in the conversion of carboxylic acids, carboxylic esters, and primary carboxamides to the corresponding aldehydes. Lithium tripiperidinoaluminum hydride (LTPDA) also appears to be a reagent of choice for such partial transformation of primary carboxamides. In additioin, both LTDEA and LTPDA reduce tertiary carboxyamides to aldehydes in high yields. Finally, lithium tris(dihexylamino)aluminum hydride (LTDHA) is capable of achieving the chemoselective reduction of aromatic nitriles to aldehydes in the presence of aliphatic nitriles under practical conditions.

Introduction

During the past some 70 years, numerous efforts have been paid to find simple and general synthetic routes to aldehydes from carboxylic acid derivatives.[1] Among them, the discovery of lithium aluminum hydride opened an era for the preparation of aldehydes by simple reduction of carboxylic acid derivatives.[2] Thus, modified reagents of lithium aluminum hydride such as lithium di- and triethoxyaluminum hydride or lithium tri-*tert*-butoxyaluminum hydride prepared from the addition of 2 or 3 equiv of alcohols to the parent compound appeared to be useful reagents for the synthesis of aldehydes from carboxylic esters or lactones,[3] tertiary carboxamides,[4] acid chlorides,[5] or even nitriles.[6]

Recently we have synthesized a new class of reducing agents, dialkylamino-substituted derivatives of lithium aluminum hydride, from the addition of 3 equiv of dialkylamines to the parent compound (Eq. 1).

$$LiAlH_4 + 3R_2NH \xrightarrow[0^0C]{THF} Li(R_2N)_3AlH + 3H_2\uparrow \quad (1)$$

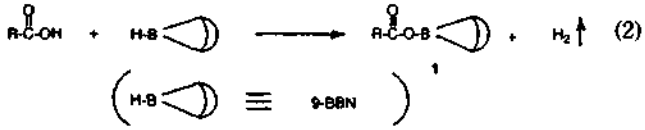
LTDEA (R=Et)
LTDBA(R=Bu)
LTDHA(R=Hex)
LTPDA(R_2N=N◯)

The approximate rates and stoichiometry of the reaction of these hydride reagents with selected organic compounds containing representative functional group under standardized conditions (tetrahydrofuran, 0℃) have been studied[7]. Each reagent possesses its own unique reducing characteristics. Especially, these reagents appeared to be very useful for the preparation of aldehydes from carboxylic acid derivatives. Consequently, we have examined the possibility of achieving such transformation systematically.

In this paper, details of the transformation of carboxylic acid derivatives into aldehydes by utilizing these dialkylamino-substituted derivatives are described, a part of which have already been reported in the form of communications.[8]

Results and Discussion

Reduction of Carboxylic Acids through Treatment of Acyloxy-9-BBN with LTDEA. Recently we reported that the commercially available 9-borabicyclo[3.3.1]nonane (9-BBN) provides a convenient route to aldehydes from carboxylic acids. The acyloxy moiety of acyloxy-9-BBNs (**1**), readily prepared from carboxylic acids and 9-BBN with evolution of 1 equiv of hydrogen (Eq. 2), is readily converted to the aldehyde through treatment with lithium 9-boratabicyclo[3.3.1]nonane (Li 9-BBNH) or *tert*-butyllithium and 9-



BBN.[9] The acyloxy group of **1** is also readily reduced by lithium aluminum hydride in the presence of pyridine to produce aldehyde.[10]

Similary, the acyloxy group of **1** is reduced by LTDEA to the aldehyde in fair yields (Table 1). However, in the presence of 2 equiv of pyridine the reductioin stops at the aldehyde stage and hydrolysis affords very high yields of the aldehydes (Eq. 3). This system reduces aliphatic carboxylic acids to aldehydes in approximately 0.5 h at 0℃ in yields of more than 90%. Alicyclic derivatives, such as cyclopro-

$$1 \xrightarrow{\text{(2 equiv) pyridine}} \xrightarrow{\text{LTDEA}} \xrightarrow{H_3O^+} RCHO \quad (3)$$

pane- and cyclohexanecarboxylic acids, give yields of 90%. α-Substituted acids and bromoacetic acid also readily undergo the reaction to the aldehyde in 87% yield. Diacids, such as succinic, adipic, 1,10-decanedicarboxylic, and maleic, are converted to the corresponding dialdehydes in yields of 91-95%.

The reduction of aromatic carboxylic acids, except for nitrobenzoic and naphthoic, are readily converted to aldehydes in essentially quantitative yields. Alkyl, alkoxy, and halogeno groups on the benzene ring are readily accommodated to yield more than 90%. However, the yields for nitrobenzoic acids are somewhat lower (about 80%), possibly due to reduction of the nitro group itself. Dicarboxylic aromatic acids, such as phthalic and terephthalic, are also readily reduced

Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids Through Treatment of Acyloxy-9-BBN with Lithium Tris(diethylamino)aluminum Hydride in the Presence of Pyridine in Tetrahydrofuran at 0℃

Acid	Yield(%)[b]	Acid	Yield(%)[b]
Acetic	92	Maleic	91
Butyric	93	Benzoic	96(81)[c](85)[d]
Caproic	91(70)[c](80)[d]	*o*-Toluic	92
Decanoic	90	*m*-Toluic	90
Pentadecanoic	93	*p*-Toluic	94(98)[c]
Palmitic	92	*o*-Anisic	92
Stearic	90(49)[c]	*m*-Anisic	91
Isobutyric	90(49)[c]	*p*-Anisic	98(80)[c]
Isopentanoic	90	*o*-Chlorobenzoic	92
Cyclopropanecarboxylic	90	*m*-Chlorobenzoic	94
Cyclohexanecarboxylic	91(78)[d]	*p*-Chlorobenzoic	96(81)[c](88)[d]
Phenylacetic	93	*o*-Nitrobenzoic	81
Diphenylacetic	94(81)[c]	*m*-Nitrobenzoic	80
Triphenylacetic	96	*p*-Nitrobenzoic	85(58)[c]
Bromoacetic	90	α-Naphthoic	97
6-Bromohexanoic	87	β-Naphthoic	98
Succinic	92	Phthalic	90
Adipic	94	Terephthalic	93
1,10-Decanedicarboxylic	95		

[a]2 equivalents of pyridine were added to 1 which was then treated with 1 equiv of LTDEA for 0.5 h. [b]Yields based on 2,4-dinitrophenylhydrazones. [c]No pyridine added. [d]Yields based on the analytically pure aldehydes isolated by the sodium bisulfite procedure.[11]

to the dialdehydes in greater than 90% yields.

The presence of pyridine in the reduction with LTDEA provides significant yield enhancement, as in the case of reduction with lithium aluminum hydride.[10] At present, the role of pyridine in this reduction is not clear, but we believe that it coordinates to the boron atom of **1** resulting in a boron-pyridine complex which inhibits hydride transfer from LTDEA to the boron atom.

LTDEA appears to be much milder and, hence, more selective for the reduction of functional groups than the parent compound itself. Therefore, this reagent is of use, particularly in the synthesis of aldehydes from carboxylic acids bearing other readily reducible groups in a molecule.

Reduction of Carboxylic Esters with LTDEA. Many useful reducing agents for the transformation of carboxylic esters in the corresponding aldehydes have been reported, *e.g.*, lithium tri-*tert*-butoxyaluminum hydride,[12] diisobutylaluminum hydride,[13] sodium diisobutylaluminohydride,[14] and bis (4-methyl-piperazinyl)aluminum hydride.[15] In addition, LTDEA also effects such transformation in good yields at −78 ℃ (Eq. 4).

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR' \xrightarrow{LTDEA} \xrightarrow{H_3O^+} RCHO \qquad (4)$$

The reagent reduces aliphatic carboxylic esters to aldehydes in yields of 55-80%. Diethyl adipate is converted to the corresponding dialdehyde with 2.2 equiv of LTDEA in a yield of 70%. α, β-Unsaturated esters such as ethyl crotonate and ethyl cinnamate also undergo the reduction to afford the corresponding olefinic aldehydes in yields of 60-80%. The reduction of aromatic esters by this reagent provides the corresponding aldehydes in 65-99% yields. The unsubstituted benzoates with a variety of alcohol portions are reduced to benzaldehyde in yields of 70-80%, showing no significant difference in the yields. Methyl-substituted benzoates such as ethyl 3- and 4-methylbenzoates afford the corresponding aldehydes in 73-75% yields. Finally, chloro and nitro groups on the benzene ring are readily accommodated and give aldehyde in better than 95% yield.

Table 2. Yields of Aldehydes in the Reduction of Representative Carboxylic Esteres with Lithium Tris(diethylamino)aluminum Hydride in Tetrahydrofuran at −78℃[a]

Eater	Reaction time, h	Yield of aldehyde(%)[b]
Isopropenyl acetate	1	79
Ethyl butyrate	3	56,54[c]
Ethyl isobutyrate	3	60
Ethyl isovalerate	3	76(64)[c]
Ethyl caproate	1	67,64[c]
Ethyl caprylate	1	76(63)[c]
Diethyl adipate[d]	1	70
Ethyl crotonate	1	68
Ethyl cinnamate	3	60
Methyl benzoate	3	70
Ethyl benzoate	3	79,70[d]
Butyl benzoate	3	70
Phenyl benzoate	3	76
Ethyl 3-methylbenzoate	3	73
Ethyl 4-methylbenzoate	3	75,72[d]
Methyl 3-chlorobenzoate	3	95,90[d]
Methyl 4-chlorobenzoate	3	99,94[d](90)[e]
Ethyl 4-nitrobenzoate	3	95

[a]Treated with 1 equiv of reagent for aliphatic and 1.1 equiv for aromatic esters. [b]analysis with 2,4-dinitrophenylhydrazine. [c]1 equiv of reagent was added. [d]1.1 equiv of reagent was added. [e]Isolated yield. [f]2.2 equiv of reagent was added.

Reduction of Primary Carboxamides with LTDEA and LTPDA. Every method for the transformation of carboxamides into aldehydes has involved the reduction of N,N-disubstituted amides, such as 1-acylaziridines,[16a] 1-acylcarbazoles,[16b] N-methylanilides,[16c-g] 1-acyl-3,5-dimethylpyrazoles,[16h,i] 1-acylimidazoles,[16j] N-methoxy-N-methylamides,[16k] N-acylsaccharines,[16l-m] 3-acylthiazolidine-2-thione,[16n-p] and N,N-dimethylamides,[16q-t] with lithium aluminum hydride or substituted aluminum hydrides. However, these has been no report to utilize primary carboxamide itself for such purpose.

Excess LTDEA reduces both aliphatic and aromatic primary carboxamides slowly, requiring 12 h at room temperature, with concurrent evolution of less than 1 equiv hydrogen (Eq. 5). LTDEA reduces aliphatic primary carboxamides examined to aldehydes in 12 h at room temperature in yields

Table 3. Yields of Aldehydes in the Reduction of Representative Primary Carboxamides with Lithium Tris(diethylamino)aluminum Hydride (LTDEA)[a] and Lithium Tripiperidinoaluminum Hydride (LTPDA)[b] in Tetrahydrofuran at Room Temperature

Amide	Yield of aldehyde (%)[c]	
	LTDEA	LTPDA
Acetamide	51	37
2-Chloroacetamide	53	20
Trimethylacetamide	72	72
n-Butyramide	59	42
Isobutyramide	73	73
Methacrylamide	–	24
Caproamide	62(40)[d](61)[e]	66(57)[e]
Octadecanamide	83(68)[e]	84
Cyclohexanecarboxamide	62	60
Benzamide	91(53)[d](88)[e]	92(81)[d](88)[e]
o-Toluamide	86(75)[e]	89
4-Methoxybenzamide	84	94(82)[e]
2-Ethoxybenzamide	83	82
2-Chlorobenzamide	68	83
2-Nitrobenzamide	26	34
Nicotinamide	53	53

[a] Ratio of reagent to compound is 2 : 1. Reacted for 12 h for aliphatic and 6-12 h for aromatic. [b] Ratios of reagent to compound are 2 : 1 for aliphatic and 3 : 1 for aromatic. Reacted for 24-48 h for aliphatic and 24 h for aromatic. [c] Analyzed with 2,4-dinitrophenylhydrazine. [d] At 0℃. [e] At 50℃. [f] Yields based on the analytically pure aldehydes isolated sodium bisulfite procedure.[11]

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[\text{or LTPDA}]{\text{excess LTDEA}} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}N\langle^{H}_{Al^-\leq} + H_2\uparrow \longrightarrow \xrightarrow{H_3O^+} RCHO \quad (5)$$

of 50-85%. Alicyclic derivatives, such as cyclohexanecarboxamide, undergo the reaction in moderate yields. The reduction of aromatic primary carboxamides requires shorter reaction time and affords the corresponding aldehydes in higher yields than those of aliphatic series. Thus, benzamide is readily reduced to benzaldehyde in 6 h in a yield of 91%. Derivatives containing substituents, such as alkyl, alkoyl, and halogeno groups on benzene ring, are readily accommodated to yield more than 70%. However, the yield for nitrobenzamide is poor, possibly due to the reduction of nitro group itself by this reagent. Finally, nicotinamide undergoes the reaction in a yield of 53%.

The raction with excess LTPDA also undergoes reduction slowly to require 24 or 48 h at room temperature, with concurrent evolution of hydrogen (1 equiv for aliphatics and 2 equiv for aromatics) (Eq. 5).

In general, the yields from aliphatic carboxamides examined are varying with the structure, showing yields in the range of 50-80%, except for acetamide and methacrylamide. Reduction of acetamide and methacrylamide affords only poor yields of the corresponding aldehydes. However, the reagent readily converts aromatic primary carboxamides into the corresponding aldehydes in yields of 80-95%, with the exception of nitrobenzamides. The nitro group itself appears to be reduced readily by this reagent under the reaction conditions. Derivatives bearing alkyl, alkoxy, or halogeno groups are readily accommodated. Nicotinamides is also reduced to the corresponding aldehyde in a moderate yield.

Table 4. Yields of Aldehydes in the Reduction of Representative Tertiary Carboxamides with Lithium Tris(diethylamino)aluminum Hydride (LTDEA) and Lithium Tripiperidinoaluminum Hydride (LTPDA) in Tetrahydrofuran[a]

N,N-Dimethylamide	Temp.(℃)	Yield of aldehyde (%)[b]	
		LTDEA	LTPDA
Benzamide	0	96	97
	25	92	98
p-Toluamide	0	93	–
	25	–	94
o-Toluamide	25	82	89
p-Methoxybenzamide	25	92	98
Caproamide	0	85	86
Isobutyramide	0	74	79
Trimethylacetamide	0	72	81

[a] Ratios of reagent to compound are 1.1 : 1. Reacted for 3 h at 0℃ and 1 h at 25℃. [b] Analyzed with 2,4-dinitrophenylhydrazine.

Reduction of Tertiary Carboxamides with LTDEA and LTPDA. Both LTDEA and LTPDA also reduce N,N-dimethylcarboxamides to aldehydes in goodd yields (Eq. 6). The reduction of aromatic amides affords the corresponding

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NME_2 \xrightarrow[\text{or LTPDA}]{\text{LTDEA}} \xrightarrow{H_3O^+} RCHO \quad (6)$$

aldehydes in more than 90% both at 0℃ and 25℃. However, the yields from aliphatic amides are somewhat lower (about 80%).

Reduction of Nitriles with LTDEA, LTDBA, and LTDHA. Numerous useful methods have been proposed to achieve the conversion of nitriles to aldehydes;[17] however, only one example, using potassium 9-*sec*-amyl-9-boratabicyclo [3.3.1]nonane (K 9-*sec*-Am-9-BBNH), for the chemoselective reduction of aromatic nitriles of the corresponding aldehydes has appeared in which aliphatic nitriles remain intact.[18]

In this systematic study, LTDEA, LTDBA, and LTDHA have been applied for the conversion on nitriles into aldehydes in order to probe the structural features of dialkylamino-substituents in such transformation.

In general, as shown in Table 6, the yields of aldehydes in the reduction of aromatic nitriles are in order of LTDEA<LTDBA<LTDHA. The alkyl group evidently plays a role in obtaining high yields of aldehydes. Thus, as the length of alkyl-chain increases the yields become higher. LTDEA seems to be too reactive to stop at the aldehyde stage. LTDBA is also good enough to convert aromatic nitriles into aldehydes. However, LTDHA reduces various nitriles, except for nitrobenzonitrile, to aldehydes in essentially quantitative yields. The yield from nitrobenzonitrile is significantly low (62%), due to the reduction of nitro group itself by this reagent. Dinitriles, such as phthalonitrile and terephthalonitrile,

Table 5. Yields of Aldehydes in the Reduction of Nitriles with Lithium Tris(dialkylamino)aluninum Hydrides in Tetrahydrofuran at 0℃

Niriile	Temp (℃)	Time h	Ratio of H to cpd	Yield of aldehyde (%)[a]		
				LTDEA[b]	LTDBA[c]	LTDHA[d]
Benzonitrile	0	1.0	1.0	60	68	99(96)[e](81)[f]
			1.1	71	83	86
	25	0.5	1.0	93	98	99
o-Tolunitrile	0	1.0	1.0	–	–	98
			1.1	–	83	–
	25	0.5	1.1	64	–	–
m-Tolunitrile	0	1.0	1.0	–	–	99(95)[f]
			1.1	70	83	–
	25	0.5	1.1	74	–	–
p-Methoxyhenzonitrile	0	1.0	1.0	–	95	97
	25	0.5	1.1	86	–	–
p-Chlorobenzonitrile	0	1.0	1.0	–	90	98(833)[f]
	25	0.5	1.0	92	–	–
2,6-Dichlorobenzonitrile	0	1.0	1.0	52	88	96
	25	0.5	1.0	60	–	–
p-Nitrobenzonitrile	0	1.0	1.0	69	68	62
Phthalonitrile	0	1.0	2.0	18	63	76
Terephthalonitrile	0	1.0	2.0	90	98	97(99)[f]
3-Cyanopyridine	0	1.0	1.0	–	30	62
			1.1	–	32	75
		3.0	1.0	30	42	98
	25	0.5	1.0	36	–	–
4-Cyanopyridine	0	1.0	1.1	32	36	97
		3.0	1.0	30	42	98
	25	0.5	1.0	36	–	–
Hexanenitrile	0	1.0	1.0	21	6	0[g]
Decanenitrile	0	1.0	1.0	26	11	0[g]

[a] Analysis with (2,4-dinitrophenyl)hydrazine. [b] Lithium tris(diethylamino)aluminum hydride. [c] Lithium tris(dibutylamino)aluminum hydride. [d] Lithium tris(dihexylamino)aluminum hydride. [e] Analysis with GC. [f] Isolated yield on distillation. [g] Unreacted starting materials are recovered (>90%).

Table 6. Selective Reduction of Aromatic Nitrile in the Presence of Aliphatic Nitrile with Lithium Tris(dihexylamino)aluminum Hydride in Tetrahydrofuran at 0℃[a,b]

Compound	Product	Mol %[c]
Benzonitrile	Benzaldehyde	92
	+	
+	Benzonitrile	2
	+	
Capronitrile	Caproaldehyde	0
	+	
	Capronitrile	99
Terephthalonitrile[d]	Terephthaloaldehyde	95
	+	
+	Terephthalonitrile	0
	+	
Decanenitrile	Decanenitrile	98

[a] 1.0 equiv of the reagent per mixture of 1 equiv in each of the compounds was utilized. [b] Reacted for 1 h at 0℃. [c] Determined by GC analysis with an internal standard and authentic samples. [d] 2.0 equiv of the reagent was used.

are reduced to aldehydes in yields of 76-97%. LTDHA also converts cyanopyridines into the corresponding aldehydes in essentially quantitative yields. As a result, this reagent appears to be superior to K 9-*sec*-Am-9-BBNH in the conversion of aromatic nitrile function into aldehyde stage.

The reduction of aliphatic nitriles with these reagents appears to be unuseful. In addition, sequence for yielding aldehydes is in the reverse order. Examination of the reaction mixture of LTDHA reveals that almost all the starting nitriles are unreacted. This remarkable feature in the rate of reaction suggests the possibility of achieving the chemoselective reduction of aromatic nitriles to aldehydes in the presence of aliphatic nitriles. Indeed, as shown in Table 6, we achieved up to 92-95% conversion of aromatic nitriles into aldehydes in mixtures with aliphatic nitriles, with only minor reduction of the aliphatic nitriles, with a limiting amount of reagent (Eq. 7).

$$ArC\equiv N + RC\equiv N \xrightarrow{LTDHA} \xrightarrow{H_3O^+} ArCHO + RC\equiv N \quad (7)$$

Conclusion

From this systematic study, the dialkylamino-substituted

derivatives of lithium aluminum hydride appear to be very useful for the synthesis of aldehydes from carboxylic acids and their derivatives under practical condition in very good yields. Moreover, it is possible to reduce selectively aromatic nitriles to aldehydes in the presence of aliphatic nitriles. The mild reducing ability of these modified reagents adds an additional advantage, especially in the synthesis of aldehydes bearing other readily reducible groups in molecule.

Experimental Section

All glassware used was dried thoroughly in a drying oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out under a dry nitrogen atmosphere.

All chemicals were commerical products of the highest purity, which were carefully purified by standard methods before use. The carboxylic acids were commercial products and were purified either by distillation or by recrystallization. N,N-dimethylcarboxamides were synthesized from the reaction of dimethylamine and the corresponding carboxamides by the standard procedure[10]. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl and all other solvents (*n*-pentane and diethyl ether) were thoroughly dried over molecular sieves and distilled. 9-Borabicyclo[3.3.1]nonane (9-BBN) and lithium aluminum hydride (LAH) were used directly as received from Aldrich.

All of the compounds prepared have been fully characterized by ^{1}H and ^{27}Al-NMR spectra. Yields reported in all cases are of analytically pure compounds unless otherwise specified. Melting points and boiling points reported are uncorrected. ^{1}H-NMR spectra were recorded on a Varian EM-360A instrument. ^{27}Al-NMR spectra were recorded on a Bruker WP 85SY spectrometer. ^{27}Al-NMR chemical shifts are with reference to $Al(H_2O)_6^{6+}$. GC analyses were carried out using a Hewlett-Packard Model 5790A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter.

Preparation of Lithium Tris(dialkylamino)aluminum Hydrides in THF. The following procedure for the preparation of lithium tris(diethylamino)aluminum hydride (LTDEA) is representative. To an oven-dried, 500 m*l* flask fitted with a side arm and a stopcock leading to mercury bubbler was added 100 m*l* of a 2 M solution of LAH in THF and the solution was cooled to 0℃. To this solution was added 46 g of diethylamine (630 mmol, 5% excess) dropwise with vigorous stirring. The reaction mixture was stirred for 3 h at 0℃ until the evolution of hydrogen was complete. The resulting LTDEA solution in THF was diluted with THF to be 1.0 M. The ^{27}Al-NMR spectrum of the solution showed a broad singlet at δ 120.

Similarly, lithium tris(dibutylamino)aluminium hydride (LTDBA), lithium tris(dihexylamino)aluminum hydride (LTDHA), and lithium tripiperidinoaluminum hydride (LTPDA) were prepared by adding 3 equiv of the corresponding dialkylamino to LAH solution at 0℃. The ^{27}Al-NMR spectra of the solution of LTDBA, LTDHA, and LTPDAS showed broad singlet at δ 128, 129.5, and 123.5 ppm, respectively.

Reduction of Carboxylic Acids. The following reduction is typical of the procedure utilized for the quantitative analysis with 2,4-dinitrophenylhydrazine. Benzoic acid (6.47 g, 53 mmol) and 9-BBN (12.93 g, 53 mmol) were placed in an oven-dried, 200 m*l* flask fitted with a side arm and a bent adapter, which was connected to a mercury bubbler. To this mixture was added 50 m*l* of THF and the slurry was stirred at room temperature until hydrogen was no longer evolved. The reaction mixture was then cooled to 0℃ and 8.56 g (106 mmol) of pyridine and 53 m*l* of LTDEA (1.0 M, 53 mmol) in THF were injected in sequence at 0℃. The reaction mixture was withdrawn and subjected to analysis with 2,4-dinitrophenylhydrazine, showing a yield of 96%: mp. of hydrazone 235-236° (lit. mp. 237°). The rest of the reaction mixture (50 mmol) was further tested for isolating the aldehyde. In a small-scale (3 mmol) blank experiment without addition of pyridine, the analysis with 2,4-dinitrophenylhydrazine showed a yield of 81%.

Sodium Bisulfite Adduct Formation and Regeneration of Aldehydes. The procedure for the product formation and regeneration of benzaldehyde in the reaction mixture is representative. After reaction of benzoyloxy-9-BBN (53 mmol) with the reagent for 0.5 h at 0℃ (*vide ante*), an aliquot of the reaction mixture was withdrawn for analysis with 2,4-dinitrophenylhydrazine. Then the remaining reaction mixture was hydrolyzed with 70 m*l* of 3 N HCl at room temperature. The mixture was saturated with NaCl, and the organic layer was separated, and poured into 75 m*l* of a saturated aqueous $NaHSO_3$ solution. The mixture was stirred for 1 h and cooled in an ice-water bath to ensure complete crystallization of the bisulfite adduct, which was then collected by filtration, washed with pentane, and dried. The solid adduct was placed in 50 m*l* of a saturated aqueous $MgSO_4$ solution, and then 50 m*l* of pentane and 8 m*l* of a 37% formaldehyde solution were added. The mixture was stirred for 1 h. The pentane layer was separated and dried with anhydrous $MgSO_4$. Evaporation of all volatile materials gave an 85% yield (4.5 g) of analytically pure benzaldehyde. GC analysis showed >99% purity and the ^{1}H-NMR spectrum agreed with that of an authentic sample.

Reduction of Carboxylic Esters. The following procedure for the reduction of 4-chlorobenzoate is illustrative. An oven-dried 25 m*l* flask, fitted with a side arm and a bent adapter connected to a mercury bubbler, was charged with 5 m*l* of 1 M methyl 4-chlorobenzoate solution in THF (0.85 g, 5 mmol). The flask was immersed into a Dry Ice-acetone bath. To this solution was added 5 m*l* of 1 M LTDEA solution in THF (5 mmol) dropwise with vigorous stirring, and the reaction mixture was stirred for 3 h at −78℃. Analysis with 2,4-dinitrophenylhydrazine indicated a yield of 99%.

The following procedure was used for a larger scale reaction. In the assembly described above, a solution of 8.53 g of methyl 4-chlorobenzoate (50 mmol) in 40 m*l* of THF solution was charged in the flask and the solution was cooled to −78℃. To this solution was injected 50 m*l* of 1 M LTDEA solution in THF (50 mmol) slowly with vigorous stirring and the mixture was stirred for 3 h at −78℃. THF was removed at reduced pressure, and then 50 m*l* of diethyl ether and 50 m*l* of 4 N HCl solution were added. The mixture was stirred overnight at room temperature, saturated with NaCl, and then filtered. The organic layer was washed with 2 N HCl solution three times and dried over $MgSO_4$. All the volatile materials were removed at reduced pressure to yield

6.3 g of analytically pure 4-chlorobenzaldehyde (90%), mp. 48-50°. The PMR spectrum agreed with that of an authentic sample.

Reduction of Primary Carboxamides. The following procedure for the reduction of benzamide is illustrative. An oven-dried, 200 m*l* flask, fitted with a side arm and a bent adapter leading to a mercury bubbler, was flushed with dry nitrogen and charged with 6.42 g (53 mmol) of benzamide and 120 m*l* of THF. To this mixture was added 106 m*l* of 1.5 M LTPDA (159 mmol) solution in THF slowly at room temperature and the mixture was stirred for 24 h at that temperature. An amount less than 2 equiv of hydrogen was evolved slowly. Analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded 92% of the corresponding aldehyde.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 3 N H_2SO_4 and then saturated with NaCl. The separated organic layer was subjected to the sodium bisulfite isolation procedure to provide an analytically pure benzaldehyde (81 %).

Reduction of Tertiary Carboxamides. The following reduction of N,N-dimethylbenzamide with LTDEA is representative. In a usual set-up, 5 m*l* of 1 M, N,N-dimethylbenzamide solutiuon in THF (0.75g, 5 mmol) was charged in the flask and the flask was immersed into an ice-bath. To this solution was added 5 m*l* of 1 M LTDEA solution in THF (5 mmol) dropwise with vigorous stirring, and the reaction mixture was stirred for 3 h. Analysis with 2,4-dinitrophenylhydrazine indicated a yield of 96%.

Reduction of Aromatic Nitriles. The following procedure for the reduction of benzonitrile is representative. An oven-dried 200 m*l* flask, equipped with a side arm, a condenser, and an adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 5.47 g (53 mmol) of benzonitrile and 20 m*l* of THF. The solution was cooled to 0℃ in an ice-water bath and 106 m*l* of 0.5 M solution of LTDHA (53 mmol) in THF was added solowly with stirring. The reaction mixture was stirred for 1 h at 0℃ and analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded 99% of the corresponding aldehyde. The rest of the reaction mixture (50 mmol) was further tested for isolating the aldehyde.

Isolation of Product Aldehydes. The rest of the reactioin mixture (50 mmol) was hydrolyzed with excess 3 N HCl and the mixture was then saturated with sodium chloride. The separated organic layer was treated with methanesulfonyl chloride. The supernatant solution was separated by filteration, dried with anhydrous magnesium sulfate, and subjected to a fractional distillation to provide 4.35 g of benzaldehyde (82%). GC analysis showed >99% purity and ^{1}H-NMR spectrum agreed with that of an authentic sample.

Competitive Reaction. The following procedure for the competitive reaction between benzonitrile and capronitrile is representative. In the usual setup, a 50 m*l* flask was charged with 0.41 g of benzonitrile (4 mmol), 0.39 g of capronitrile (4 mmol), and 1.5 m*l* of THF. The solution was cololed to 0℃ in an ice-water bath and 8.0 m*l* of 0.5 M LTDHA (4 mmol) in THF was added rapidly with vigorous stirring. The reaction mixture was stirred for 1 h at 0℃ and the reaction was then quenched with water. *n*-Dodecane as an internal standard and 4 m*l* of ether were added and a part of organic layer was analyzed by GC for nitriles. The rest of organic layer was subjected to GC analysis for aldehydes. The combined GC analysis indicated a 92% yield of benzaldehyde and 9% of unreacted capronitrile.

Acknowledgement. The support of this research by the Organic Chemistry Research Center-KOSEF, is gratefully acknowledged.

References

1. (a) I. T. Harrison and D. Harrison, "Compendium of Organic Synthetic Methods", Wiley, New York, Vol. 1, 1971; Vol. 2, 1974; Vol. 3, 1977; (b) E. Mosettig, *Org. React.* (N.Y.), **8**, 218 (1954); (c) J. Malek, *Org. React.*, **34**, 1 (1985); **36**, 249 (1988).
2. A. E. Finhalt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).
3. (a) L. I. Zakharkin and I. M. Khorlina, *Tetrahedron Lett.*, 619 (1962); (b) P. M. Weissman and H. C. Brown, *J. Org. Chem.*, **31**, 283 (1966); (c) R. Kanazawa and T. Tokoroyama, *Synthesis*, 526 (1975).
4. H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **86**, 1089 (1964).
5. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 537 (1958).
6. (a) H. C. Brown, C. J. Shoat, and C. P. Garg, *Tetradhedron Lett.*, **9** (1959); (b) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964).
7. (a) LTDBA; J. S. Cha, S. E. Lee, and H. S. Lee, *Bull. Korean Chem. Soc.*, **12**, 644 (1991); (b) The reducing characteristics of LTDEA, LTDHA, and LTPDA will be reported shortly.
8. (a) J. S. Cha, J. C. Lee, S. E. Lee, J. M. Kim, O. O. Kwon, H. S. Lee, and S. J. Min, *Tetrahedron Lett.*, **32**, 6903 (1991); (b) J. S. Cha, J. C. Lee, S. E. Lee, and H. S. Lee, *Bull. Korean Chem. Soc.*, **12**, 598 (1991); (c) J. S. Cha, J. C. Lee, and H. S. Lee, *Org. Prep. Proced. Int.*, **24**, 327 (1992); (d) J. S. Cha, S. E. Lee, and H. S. Lee, *Org. Prep. Proced. Int.*, **24**, 331 (1992); (e) J. S. Cha, S. E. Lee, H. S. Lee, J. C. Lee, J. M. Kim, O. O. Kwon, and S. J. Min, *Bull. Korean Chem. Soc.*, **13**, 338 (1992); (f) J. S. Cha, S. J. Min, J. C. Lee, S. E. Lee, and H. S. Lee, *Org. Prep. Proced. Int.*, **24**, 335 (1992).
9. (a) J. S. Cha, J. E. Kim, S. Y. Oh, and J. D. Kim, *Tetrahedron Lett.*, **28**, 4575 (1987); (b) J. S. Cha, S. Y. Oh, K. W. Lee, M. S. Yoon, J. C. Lee, and J. E. Kim, *Bull. Korean Chem. Soc.*, **9**, 48 (1988); (c) J. S. Cha, J. E. Kim, M. S. Yoon, and Y. S. Kim, *Tetrahedron Lett.*, **28**, 6231 (1987).
10. J. S. Cha, J. C. Lee, M. S. Yoon, J. B. Seo, and J. M. Kim, *Bull. Korean Chem. Soc.*, **11**, 76 (1987).
11. H. C. Brown, J. S. Cha, B. Nazer, and N. M. Yoon, *J. Org. Chem.*, **52**, 5400 (1987).
12. P. M. Weissman and H. C. Brown, *J. Org. Chem.*, **31**, 282 (1966).
13. L. I. Zakharkin and I. M. Khorlina, *Tetrahedron Lett.*, 619 (1962).
14. L. I. Zakharkin and I. M. Khorlina, *Iza. Akad. Nauk, SSSR, Ser. Khim*, 465 (1964).
15. M. Muraki and T. Mukaiyama, *Chemistry Lett.*, 215 (1975).
16. (a) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961); (b) G. Witting and P. Hornberger, *Ann.*,

577, 11 (1952); (c) F. Weygand and G. Eberhardt, *Angew. Chem.*, **64**, 458 (1952); (d) F. Weygand, G. Eberhardt, H. Linden, F. Schafter, and I. Eigen, *ibid.*, **65**, 525 (1953)l (e) F. Weygand and H. Linden, *ibid.*, **66**, 174 (1954); (f) F. Weygand and R. Mitgau, Ber., **88**, 301 (1955); (g) F. Weygand and J. Bestmann, *Chem. Ber.*, **92**, 528 (1959); (h) W. Ried and F. J. Konigstein, *Angew. Chem.*, **70**, 165 (1958); (i) W. Ried and P. Pfaeender, *Ann.*, **640**, 111 (1961). (j) H. A. Staab and H. Braunling, *ibid.*, **654**, 119 (1962); (k) J.-A. Fehrentz and B. Castro, *Synthesis*, 676 (1983); (l) V. Bazant, M. Capka, M. Cerny, V. Chavalosky, K. Kocholoefl, M. Krasus, and J. Malek, *Tetrahedron Lett.*, 3303 (1968); (m) N. S. Ramegowda, M. N. Modi, A. K. Koul, J. M. Bora, C. K. Narang, and N. K. Mathur, *Tetrahedron*, **29**, 3985 (1973); (n) Y. Nagao, K. Kwabata, K. Seno, and E. Fujita, *J. Chem. Soc. Perkin Transaction*, **1**, 2470 (1980); (o) T. Izawa and T. Mukaiyama, *Chemistry Lett.*, 1443 (1977); (p) T. Izawa and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **52**, 555 (1979); (q) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.* **86**, 1089 (1964); (r) *idem, ibid.*, **81**, 502 (1959); (s) L. I. Zakharkin, D. N. Maslin, and V. V. Gavrilenko, *Tetrahedron*, **25**, 5555 (1969); (t) M. Muraki and T. Mukaiyama, *Chemistry Lett.*, 875 (19 75).

17. (a) Stannous chloride: E. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925); (b) Sodium triethoxyaluminohydride: G. Hesse and R. Schrodel, *Angew. Chem.*, **68**, 438 (1956). *Ann.*, **607**, 24 (1957); (c) Lithium Triethoxyaluminohydride.: H. C. Borwn, C. J. Schoaf, and C. P. Grag, *Tetrahedron Lett.*, 9 (1959); H. C. Brown, *J. Chem. Educ.*, **38**, 173 (1961); H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1079, 1985 (1964); D. de Peretti, T. Strzalko-Bottin, and J. Seydenpenne, *Bull. Soc. Chim. Fr.*, **12**, 2925 (1974); (d) Diisobutylaluminum Hydride: L. I. Zakharkin and L. M. Kohrlina, *Dokl. Akad. Nauk SSSR*, **116**, 422 (1957); J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Org. Chem.*, **35**, 186 (1970); R. V. Stevens, L. E. DuPree, Jr. and P. L. Loewenstein, *ibid.*, **37**, 977 (1972); M. P. L. Caton, E. C. J. Coffee, and G. L. Waktkins, *Tetrahedron Lett.*, 585 (1974); (e) Sodium diethylaluminohydride in the presence of 2,6-di-*t*-butylphenoxydiethylaluminum: N. M. Yoon, S. K. Kim, and Y. S. Gyong, *Bull. Korean Chem. Soc.*, **7**, 323 (1986); (f) Hydrogenation: S. Peitra and C. Trinchera, *Gazz. Chim. Ital.*, **85**, 1705 (1955); A. Gaiffe and R. Pallaud, *Compt. Rend.*, **252**, 1339 (1961), **254**, 486 (1962); H. Plieninger and G. Werst, *Angew. Chim.*, **67**, 156 (1955), *Chem. Ber.*, **88**, 1965 (1955); J. N. Coker, W. L. Kohlhase, M. Fields, A. O. Rogers, and M. A. Stevens, *J. Org. Chem.*, **27**, 850 (1962); B. Staskun and O. G. Backeberg, *J. Chem. Soc.*, 5880 (1964); T. van Es and B. Staskun, *ibid.* 5775 (1965). *Org. Syn.*, **51**, 20 (1971); (g) Organosilicon hydride: J. L. Fry, *Chem. Comm.*, 45 (1974); J. L. Fry and R. A. Ott, *J. Org. Chem.*, **46**, 602 (1981); (h) Thexylbromoborane-dimethyl sulfide: J. S. Cha, S. Y. Oh, and J. E. Kim, *Bull. Korean Chem. Soc.*, **8**, 301 (1987).

18. J. S. Cha and M. S. Yoon, *Tetrahedron Lett.*, **30**, 3677 (1989).

19. A. C. Cope andd E. Ciganek, "Organic Syntheses", John Wiley and Sons, Inc., Coll. Vol. 4, p. 339, 1963.

Photodecomposition of N-*t*-Butyl-N-chloro-ω-phenylalkanesulfonamides in the Presence of Oxygen

Jong Hun Lee and Kyongtae Kim*

Department of Chemistry, Seoul National University, Seoul 151-742. *Received July 15, 1992*

Irradiation of N-*t*-butyl-N-chloro-3-phenylpropanesulfonamide (**1a**) in benzene at 20℃ using 450 W high pressure mercury arc lamp in the presence of oxygen affored N-*t*-butyl-3-phenylpropanesulfonamide (**2**), N-*t*-butyl-3-chloro-3-phenylpropanesulfonamide (**3**), and N-*t*-butyl-3-oxo-3-phenylpropanesulfonamide (**4**). Similarly, N-*t*-butyl-4- (**5**), N-*t*-butyl-4-chloro-4- (**6**), and N-*t*-butyl-4-oxo-4-phenylbutanesulfonamides (**7**) were obtained from N-*t*-butyl-N-chloro-4-phenylbutanesulfonamide (**1b**). However, irradiation of N-*t*-butyl-N-chloro-5-phenylpentanesulfonamide (**1c**) under the same conditions gave complex mixtures. These results indicate that sulfonamidyl radical generated from each of **1a** and **1b** can abstract intramolecularly a hydrogen atom from the benzylic position only by forming six and seven-membered transition states, respectively.

Introduction

Photodecomposition of N-alkyl-N-haloalkanesulfonamides has recently received much attention owing to the chemistry of N-alkylalkanesulfonamidyl radicals formed by the homolysis of halogen-nitrogen bond of the N-alkyl-N-haloalkanesulfonamides.[1] Komori *et al.*[1c] studied photodecomposition of N-*t*-butyl-N-chloroalkanesulfonamides in benzene, aqueous acetic acid, aqueous t-butyl alcohol, and a mixture of acetic acid, water and sulfuric acid using 150 W high pressure mercury arc lamp at 28 to 30℃ under nitrogen atmosphere and isolated N-*t*-butylalkanesulfonamide, γ-, δ-, and ε-chloroalkanesulfonamides, of which yields were dependent on the reaction conditions. The formations of γ-, δ-chloroal-