10. W. Kabsch, *Acta Cryst.*, **A32**, 922 (1976), and **A34**, 827 (1978).
11. S. J. Weiner, P. A. Kollman, D. Case, P. Weiner, *J. Am. Chem. Soc.*, **106**, 765 (1984); (b) P. Weiner, P. A. Kollman, *J. Comput. Chem.*, **2**, 287 (1981).
12. A. Perry, *Int. J. Computer Math, Sec.* **B6**, 327 (1978).
13. U. Burkert, N. L. Allinger, "Molecular Mechanics", ACS Monograph, **177**, 21 (1982).
14. A. J. Irwin, J. B. Jones, *J. Am. Chem. Soc.*, **98**, 8476 (1976).
15. J. R. Miller, J. V. Beitz, R. K. Huddleston, *J. Am. Chem. Soc.*, **106**, 5057 (1984).
16. F. M. Menger, F. F. Chow, H. Kaiserman, P. C. Vesquez, *J. Am. Chem. Soc.*, **105**, 4996 (1983).
17. (a) G. Wipff, A. Dearing, P. K. Weiner, J. M. Blaney, P.A. Kollman, *J. Am. Chem. Soc.*, **105**, 997 (1983); (b) P. Kollman, *Acc. Chem. Res.*, **18**, 105 (1985).
18. M. W. Makinen, W. Maret, M. B. Yim, *Proc. Natl. Acad. Sci. USA.* **80**, 2584 (1983).

Direct Transformation of Carboxylic Acids into Aldehydes through Acyloxy-9-borabicyclo[3.3.1]nonane[1]

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New methods for the direct reduction of carboxylic acids to aldehydes through the treatments of B-acyloxy-9-borabicyclo [3.3.1]nonane (acyloxy-9-BBN) with *tert*-butyllithium and 9-borabicyclo[3.3.1]nonane or with lithium 9-boratabicyclo[3.3.1] nonane (Li 9-BBNH) are described. Both these systems provide the corresponding aldehydes from various carboxylic acids in high yields. A mechanism for the reduction through stepwise treatment of acyloxy-9-BBN with *tert*-butyllithium and 9-BBN, which seems to involve the hydride migration through 9-BBN, is proposed and discussed in connection with the reduction through treatment of acyloxy-9-BBN with Li 9-BBNH.

Introduction

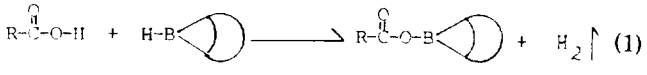
Direct transformation of carboxylic acids into the corresponding aldehydes is of great importance in organic syntheses because of their abundance in nature. A number of methods for the preparation of aldehydes from carboxylic acid derivatives have been developed[2], however, only a few methods are available to get aldehydes directly from carboxylic acids[3,4]. Among them, thexylchloroborane-methyl sulfide[3-a,b] and thexylbromoborane-methyl sulfide[3-c,d] have appeared to be the most promising reducing agents for such direct transformation. Furthermore, the convenient and practical methods for isolation of aldehyde products have been established[3-b]. Although these reagents have their own excellence, these reagents should be prepared by users themselves under the present situation. Consequently, we have centered our efforts to utilize the commercially available 9-borabicyclo[3.3.1]nonane(9-BBN) for such direct conversion.

In this paper, we describe details of such new facile methods for the direct syntheses of aldehydes from carboxylic acids using 9-BBN, which have already reported in form of communications[5], including the mechanistic considerations.

Results and Discussion

Reduction through Treatment of Acyloxy-9-BBN with 9-BBN. It is well known that the reduction of carboxylic acids with boranes(*i.e.*, BH_3-THF[6], BH_3-SMe_2[7], or alkylboranes[8]) proceeds *via* acyloxyboranes formed with evolution of equivalent hydrogen, followed by the hydride transfer to acyloxy group, which indicates that the acyloxyboranes are reactive intermediates for reduction. In this respect, we utilized a commercially available 9-BBN in order to make an acyloxyborane, in the hope of being a reactive intermediate with an adequate structural feature for its acyloxy group being converted to the aldehyde stage.

The reaction of carboxylic acids and 9-BBN provides readily the corresponding acyloxy-9-BBN(**1**) with evolution of 1 equiv of hydrogen (eq 1)[8-c].



1

(H-B ≡ 9-borabicyclo[3.3.1]nonane ≡ 9-BBN)

We attempted to carry out the partial reduction of the acyloxy moiety of **1** to the aldehyde stage with another equiv of 9-BBN. However, the yields of the expected aldehydes were low (Table 1). Shortly, we realized that 9-BBN itself is too weak to attack the carbonyl carbon of acyloxy group.

Reduction through Treatment of Acyloxy-9-BBN with *tert*-Butyllithium. As described above, 9-BBN itself cannot attack the acyloxy group of **1** efficiently. Therefore, we turn-

Table 1. Yields of Aldehydes in the Reduction of Caproic and Benzoic Acids as Representative Aliphatic and Aromatic Carboxylic Acids through Treatment of Acyloxy-9-borabicyclo [3.3.1]nonane[a] with 9-Borabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature

Acid	Reaction time (h)	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)
caproic	1	31
	3	24
benzoic	3	24
	6	30

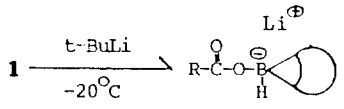
[a] From the reaction of equivalents of carboxylic acid and 9-borabicyclo[3.3.1]nonane.

Table 2. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids through Treatment of Acyloxy-9-borabicyclo[3.3.1]nonanes with *tert*-Butyllithium in Tetrahydrofuran at Room Temperature.[a]

Acid	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)[c]
hexanoic	75
decanoic	32
stearic	86
diphenylacetic	55
cyclohexanecarboxylic	39
chloroacetic	25
adipic	25
benzoic	82[b]
p-methylbenzoic	42
p-chlorobenzoic	73
p-aminobenzoic	64
p-nitrobenzoic	42
terephthalic	85[b]

[a] 1.1 Equiv of *tert*-butyllithium was added to acyloxy-9-BBN at -20°C and the mixture was stirred for 10 min at the temperature, and followed by the additional stirring for 3 h with aliphatic and for 12 h with aromatic carboxylic acids, both at room temperature. [b] 2.2 Equiv of *tert*-butyllithium per 1 equiv of the compound (2 equiv of each 9-BBN and acyloxy moieties). [c] Analysis with 2,4-dinitrophenylhydrazine.

ed to the formation of lithium 9-acyloxy-9-boratabicyclo[3.3.1]nonanes(Li 9-acyloxy-9-BBNHs, **2**) by treatment of **1** with *tert*-butyllithium (eq 2)[9], which are much stronger in hydride-donating ability than 9-BBN[10]



(2)

2

Initially, we expected that **2** readily undergoes the reduction of its acyloxy group intermolecularly or/and intramolecularly, followed by hydrolysis to give the corresponding aldehyde, the results of which are summarized in Table 2. However, acyloxyborohydride(**2**) itself, as shown in Table 2,

Table 3. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids through Treatment of Acyloxy-9-borabicyclo [3.3.1] nonanes with *tert*-Butyllithium and 9-Borabicyclo [3.3.1] nonane (9-BBN) in Tetrahydrofuran at Room Temperature[a]

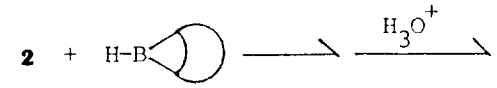
Acid	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)[e]
butyric	92
hexanoic	93 (79)[b]
decanoic	91
stearic	99 (91)[c]
isobutyric	98
isopentanoic	96
pivalic	92[d]
cyclopropanecarboxylic	84
cyclohexanecarboxylic	88
diphenylacetic	95
triphenylacetic	93
6-bromohexanoic	87
1,10-decanedicarboxylic	99 (93)[c]
benzoic	81
α-naphthoic	79
p-methoxybenzoic	72
p-chlorobenzoic	78
p-aminobenzoic	82
p-nitrobenzoic	83
terephthalic	98

[a] Reacted with 5% excess 9-BBN (1.05 equiv for monocarboxylic and 2.1 equiv for dicarboxylic acid) for 1 h with aliphatic and for 6 h with aromatic carboxylic acids, both at room temperature, after addition 10% excess *tert*-butyllithium at -20°C. [b] An yield of distilled product after hydrolysis. [c] Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde[3]. [d] Reacted for 6 h; 88% for 3 h. [e] Analysis with 2,4-dinitrophenylhydrazine.

appeared not to be general, providing the variable yields of aldehydes with the structure of acyloxy group, even though the yields of aldehydes are high in some cases.

Reduction through Stepwise Treatment of Acyloxy-9-BBN with *tert*-Butyllithium and 9-BBN. The ingenerality of **2** toward the partial reduction of their acyloxy group led us to believe that the system is unfavorable for attacking the acyloxy moiety intermolecularly or/and intramolecularly. Therefore, we added 1 equiv of 9-BBN to the solution of **2** in hopes that 9-BBN serves as a bridge to transfer the hydride of **2** to the acyloxy group.

In fact, the system achieved a nice conversion of the various acyloxy moieties of both aliphatic and aromatic carboxylic acids to the aldehyde stage (eq 3), showing the very high yields of aldehydes as summarized in Table 3.



(3)

As shown in Table 3, the system reduces aliphatic carboxylic acids to aldehydes in approximately 1 h at room tempera-

Table 4. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids through Treatment of Acyloxy-9-borabicyclo[3.3.1]nonanes with Lithium 9-Boratabicyclo[3.3.1]nonane(Li 9-BBNH) in Tetrahydrofuran at Room Temperature[a]

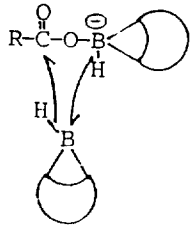
Acid	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)
butyric	90
hexanoic	92 (80)[b]
decanoic	92
stearic	99 (92)[c]
isobutyric	94
isopentanoic	89
pivalic	85[d]
cyclopropanecarboxylic	85
cyclohexanecarboxylic	88
diphenylacetic	96
triphenylacetic	94
6-bromohexanoic	87
1,10-decanedicarboxylic	99 (92)[c]
benzoic	78
α-naphthoic	80
p-methoxybenzoic	79
p-chlorobenzoic	76
p-aminobenzoic	79
p-nitrobenzoic	80
terephthalic	92

[a] Reacted with 5% excess Li 9-BBNH (1.05 equiv for monocarboxylic and 2.1 equiv for dicarboxylic acid) for 1 h with aliphatic and for 6 h with aromatic carboxylic acids, both at room temperature. [b] An isolated yield on distillation of the generated product after hydrolysis. [c] Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde[2-b,c]. [d] Reacted for 6 h.

ture in yields of 90-99%. Alicyclic derivatives undergo the reaction well in yields of 84-88%. Derivatives such as diphenylacetic and triphenylacetic acids work equally well to provide the corresponding aldehydes in yields of 93-95%. Diacids, such as 1,10-decanedicarboxylic acid, are converted to the dialdehydes almost quantitatively.

The reduction of aromatic carboxylic acids by this system requires 6 h for the complete reaction at room temperature. The yields of aldehydes are somewhat lower than those in aliphatic acids, but still high (*ca.* 80%). However, aromatic diacid such as terephthalic acid provides the corresponding dialdehyde essentially quantitative.

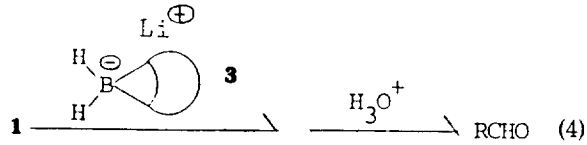
The reaction seems to proceed *via* the consecutive hydride-transfer pathway in which the hydride from **2** migrates



Scheme 1

to 9-BBN (*i.e.*, formation of 9-boratabicyclo[3.3.1]nonane, 9-BBNH) and then again the hydride from 9-BBNH species attacks the carbonyl carbon of acyloxy moiety, as illustrated in Scheme 1.

Reduction through Treatment of Acyloxy-9-BBN with Lithium 9-Boratabicyclo[3.3.1]nonane(Li 9-BBNH)[11]. If the suggested mechanism as illustrated in Scheme 1 is correct, we might obtain similar results when treated the acyloxy-9-BBN(**1**) with 9-BBNH itself instead of addition of 9-BBN to the solution of **2**. We examined this possibility. Thus, we added 1 equiv of Li 9-BBNH(**3**) to the solution of **1** (eq 4). Finally, we found that this system equally achieves a nice conversion of the various acyloxy moieties of **1** to the aldehyde stage and the results are summarized in Table 4.



(4)

As shown in Table 4, the results are essentially same as the case of reduction of carboxylic acids through stepwise treatment of **1** with *tert*-butyllithium and 9-BBN, as listed in Table 3, which indicates strongly that our suggestion for reaction mechanism is correct.

Isolation of Aldehyde Products. Aldehydes are notoriously unstable, and hence it is desirable to find the convenient isolation method from the reaction mixture to obtain the aldehyde in pure form.

Recently, the sodium bisulfite procedure[3] have been appeared to be broadly applicable. We examined this procedure and the results are listed in Table 3 and 4. As shown in the Tables, the sodium bisulfite procedure provides a convenient and practical means for such purpose, especially useful for the aldehydes of relatively high boiling point (more than 200°C). However, in the case of products of lower boiling point the distillation after stirring the reaction mixture over excess anhydrous magnesium sulfate overnight gives the quite reasonable yield of aldehyde products.[3-c]

Conclusion

The treatments of acyloxy-9-BBN with *tert*-butyllithium and 9-BBN or with Li 9-BBNH provide the corresponding aldehydes in high yields. These systems utilize the commercially available 9-BBN and its derivative, Li 9-BBNH. 9-BBN is an acid-type reducing agent[8-c], while Li 9-BBNH is a base -type.[10] Therefore, these two systems are complements each of the other on the basis of their reducing characteristics toward organic functionalities, which provides an useful judging tool to select a proper system to the practical reduction of carboxylic acid bearing organic functions in a molecule. In addition, because the practical procedures for isolation of aldehyde products have been established, these systems should find useful applications in organic synthesis.

Experimental Section

All glassware used was dried throughly 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. Further special experimental techniques are described elsewhere[12].

All chemicals were commercially products of the highest purity which were carefully purified by standard methods before use. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl.

The yields reported in all cases are of analytically pure compounds unless otherwise mentioned.

GLC analyses were carried out using a Varian Model 1400 FID chromatograph equipped with a Hewlett-Packard 3390 A Integrator/Plotter.

Preparation of Li 9-BBNH(3)[11]. An oven-dried 500-m*l* flask equipped with a side-arm and a stopcock leading to a mercury bubbler was added 200 m*l* of 9-BBN-THF solution (0.5 M, 100 mmol) and the content was cooled to -20°C with a cooling bath. At this temperature, 58 m*l* of *tert*-butyllithium-pentane solution (1.9 M, 110 mmol, 10% excess) was injected slowly with constant stirring. After stirring for another 10 min, the reaction mixture was allowed to room temperature. The concentration of the resulting standard solution was measured gasometrically to indicate 0.38 M in Li 9-BBNH(**3**).

Reduction of Carboxylic Acids through Treatment of 1 with 9-BBN. In the usual setup, 0.35g of caproic acid (3 mmol) was added. 6 m*l* of a 0.5M 9-BBN solution in THF (3 mmol) was injected slowly and the reaction mixture was stirred at room temperature until hydrogen was no longer evolved. After the complete hydrogen evolution, THF was evaporated. And then was added 6 m*l* of 9-BBN-THF solution and the mixture was stirred for 1 h or 3 h at room temperature. Analysis with 2,4-dinitrophenylhydrazine yielded 31% and 24% of the corresponding aldehyde for 1 h and 3 h reactions, respectively. The results including benzoic acid are summarized in Table 1.

Reduction of Carboxylic Acids through Treatment of 1 with *tert*-Butyllithium. The following procedure for the reaction of caproic acid is representative. In the usual setup, 0.35g of caproic acid (3 mmol) and 6 m*l* of a 0.5 M 9-BBN -THF solution (3 mmol) were added successively. After the complete hydrogen evolution, the mixture was cooled to -20°C. At this temperature, 1.9 m*l* of *tert*-butyllithium-pentane solution (1.9 M, 3.6 mmol, 20% excess) was added dropwise and the mixture was stirred for 10 min. The reaction mixture was then warmed to room temperature and stirred for another 3 h. Analysis with 2,4-dinitrophenyhydrazine indicated the yield of 75% of the corresponding aldehyde (Table 2).

Reduction of Carboxylic Acids through Stepwise Treatment of 1 with *tert*-Butyllithium and 9-BBN. The following procedure for the reduction of stearic acid is illustrative. In the usual setup, 6.47g (53 mmol) of 9-BBN and 15.08g (53 mmol) of stearic acid were added. To this mixture was injected 10 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 -20°C with a cold bath and 29 m*l* of 2.0 M *tert*-butyllithium (10% excess) in pentane was injected into the well-stirred mixture. After stirring for 10 min at -20°C, 112 m*l* of 0.5 M solution of 9-BBN (65 mmol, 5% excess) in THF was added and the mixture was warmed to room temperature and stirred for 1 h at the temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded 99% of the corresponding aldehyde.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 30 m*l* of 2 N HCl for 1 h at room temperature. The mixture was then saturated with sodium chloride and the separated organic layer was subjected to the sodium bisulfite isolation procedure[3-a,b]. Thus, the separated organic layer was poured into 75 m*l* of a saturated aqueous sodium bisulfite 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 and washed with 3 × 25 m*l* of pentane and dried. The solid adduct was placed in 40 m*l* of water and then 50 m*l* of THF and 8 m*l* of a 37% formaldehyde solution were added. The mixture was heated to 90-95°C for 1 h with stirring. The solid disappeared. The mixture was cooled to room temperature and saturated magnesium sulfate heptahydrate. The organic layer was separated, dried, and on removal of the solvent, analytically pure stearaldehyde (12.22g, 91%) was obtained: mp 37-38°C (Table 3).

Reduction of Carboxylic Acids through Treatment of 1 with 3. The following procedure for the reduction of hexanoic acid is representative. In the assembly previously described, 6.47g (53 mmol) of 9-BBN and 6.16g (53 mmol) of hexanoic acid were charged. To this mixture was added 10 m*l* of THF and the slurry was stirred at room temperature until hydrogen evolution ceased. After completing the hydrogen evolution, 111 m*l* of a 0.5 M solution of Li 9-BBNH (**3**, 55.6 mmol, 5% excess) in THF was injected *via* a double-ended needle and the reaction mixture was stirred for 1 h at room temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded 92% of hexanal.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 20 m*l* of water for 1 h at room temperature. The mixture was then saturated with sodium chloride and the organic layer was separated. The separated organic layer was stirred over anhydrous magnesium sulfate overnight and subjected to fractional distillation: 4.0g of hexanal (80%): bp 131-132 °C (Table 4).

References and Notes

1. A part of this work was presented at the 192nd American Chemical Society National Meeting, Anaheim, CA, U.S.A., September 7-12, 1986.
2. (a) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley, New York, 1971, Vol. 1; 1974, Vol. 2; 1977, Vol. 3; (b) E. Mosettig, *Org. Reac.*, **8**, 218 (1954); (c) K. W. Rosenmund, *Ber.*, **51**, 585 (1918); (d) E. Mosettig, *Org. Reac.*, **4**, 362 (1948); (e) J. A. Peters and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas.*, **90**, 1323 (1971); (f) J. A. Peters and H. van Bekkum, *ibid.*, **100**, 21 (1981); (g) J. D. Citron, *J. Org. Chem.*, **34**, 1977 (1969); (h) S. P. Dent, C. Eaborn and A. Pidcock, *Chem. Commun.*, 1703 (1970); (i) H. Stephen, *J. Chem. Soc.*, 1874 (1925); (j) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947); (k) H. C. Brown, *Tetrahedron*, **35**, 567 (1979); (l) F. Weygand and G. Eberhardt, *Angew, Chem.*, **64**, 458 (1952); (m) H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 4549 (1961); (n) L. I. Zakharkin and I. M. Khorlina, *Tetrahedron Lett.*, 619 (1962); (o) P. M. Weissman and H. C. Brown, *J. Org. Chem.*, **31**, 283 (1966); (p) H. C. Brown and A. Tsukamoto, *J.*

Am. Chem. Soc., **86**, 1089 (1964); (q) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958); (r) H. C. Brown, C. J. Shoaf, and C. P. Garg, *Tetrahedron Lett.*, 9 (1959); (s) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964); (t) T. Izawa and T. Mukaiyama, *Bull Chem. Soc. Jpn.*, **52**, 555 (1979); (u) I. D. Entwistle, P. Boehm, R. A. W. Johnstone, and R. P. Telford, *J. Chem. Soc., Perkin Trans*, **1**, 27 (1980); (v) M. Mukai and Mukaiyama, *Chem. Lett.*, 215 (1975); (w) R. O. Hutchins and M. Markowitz, *Tetrahedron Lett.*, 813 (1980); (x) J. H. Babler and B. J. Invergo, *ibid.*, 11 (1981); (y) L. I. Zakharkin, V. V. Gavrilenko, D. N. Maslin, and I. M. Khorlina, *ibid.*, 2087 (1963); (z) T. E. Cole and R. Petit, *ibid.*, 781 (1977).

3. (a) H. C. Brown, J. S. Cha, B. Nazer, and N. M. Yoon, *J. Am. Chem. Soc.*, **106**, 8001 (1984); (b) H. C. Brown, J. S. Cha, N. M. Yoon, and B. Nazer, *J. Org. Chem.*, **52**, 54 (1987); (c) J. S. Cha, J. E. Kim, S. Y. Oh, J. C. Lee and K. W. Lee, *Tetrahedron Lett.*, **28**, 2389 (1987); (d) J. S. Cha, J. E. Kim and K. W. Lee, *J. Org. Chem.*, **52**, 5030 (1987).
4. For other efforts, see:
(a) A. O. Bedenbaugh, J. H. Bedenbaugh, W. A. Bergin, and J. D. Adkins, *J. Am. Chem. Soc.*, **92** 5774 (1970); (b) H. C. Brown, P. Heim, and N. M. Yoon, *J. Org. Chem.*, **37**, 2942 (1972); (c) M. Muraki and T. Mukaiyama, *Chem. Lett.*, 1447 (1974); (d) F. Sato, T. Jinbo, and M. Sato, *Synthesis*, 871 (1981); (e) T. Fujisawa, T. Mori, S. Tsuge, and T. Sato, *Tetrahedron Lett.*, 1543 (1983); (f) L. I. Zakharkin and I. M. Khorlina, *Zh. Obsch. Khim.*, **34**, 1029 (1964); (g) T. D. Hubert, D. P. Eyman, and D. F. Wiemer, *J. Org. Chem.*, **49**, 2279 (1984).
5. (a) J. S. Cha, J. E. Kim, S. Y. Oh, and J. D. Kim, *Tetrahedron Lett.*, **28**, 4575 (1987); (b) J. S. Cha, J. E. Kim, M. S. Yoon, and Y. S. Kim, *Tetrahedron Lett.* (1987), in press.
6. (a) H. C. Brown, P. Heim, and N. M. Yoon, *J. Am. Chem. Soc.*, **92**, 1637 (1970); (b) N. M. Yoon, C. S. Park, H. C. Brown, S. Krishnamurthy, and T. P. Stocky, *J. Org. Chem.*, **38**, 2786 (1973).
7. C. F. Lane, *Aldrichimica Acta*, **8**, 20 (1975), and references cited therein.
8. (a) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962); (b) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962); (c) H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41**, 1778 (1976).
9. E. J. Corey, S. M. Albonico, V. Koelliker, T. K. Schaaf, and R. K. Varma, *J. Am. Chem. Soc.*, **93**, 1491 (1971).
10. H. C. Brown, C. P. Mathew, C. Pyun, J. C. Son, and N. M. Yoon, *J. Org. Chem.*, **49**, 3091 (1984).
11. Li 9-BBNH is readily prepared by hydridating 9-BBN with lithium hydride or *tert*-butyllithium: See,
(a) ref. 9; (b) ref. 10; (c) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **41**, 3065 (1976); (d) S. Krishnamurthy, *Aldrichimia Acta*, **7**, 55 (1974).
12. H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, 1975, Chapter 9.

The Syntheses of *p*-Acylcalix[4]arenes

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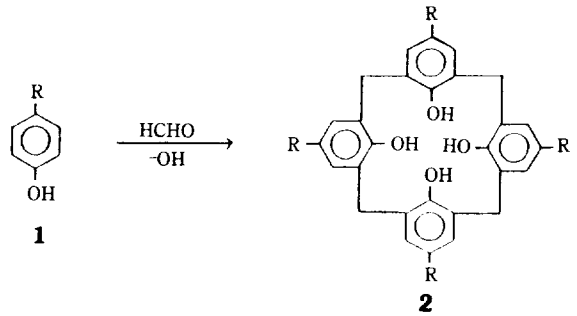
Starting with readily available *p-tert*-butylcalix[4]arene **3** *tert*-butyl groups are removed by $AlCl_3$-catalyzed de-alkylation reaction, and the calix[4]arene **4** formed is converted into the tetraacyl esters. These compounds undergo Fries rearrangement to yield *p*-acylcalix[4]arenes. *p*-Acetyl, *p*-propionyl, *p*-butyryl, and *p*-benzoylcalix[4]arene **10**, **11**, **12** and **14** are synthesized in 70-80% yields by treatment of the corresponding esters **5**, **6**, **7** and **9** with $AlCl_3$ in nitrobenzene. When the tetraisobutyryl ester **8** was treated with the same condition, only two isobutyryl groups were rearranged to the para-positions of calix[4]arene, and remaining two groups were simply cleaved.

Introduction

Since the interesting prospects for enzyme model building were proposed by Gutsche[1], various calixarenes have been tried to synthesize by the base-induced condensation reaction between *p*-alkylphenols and formaldehyde as shown on scheme 1[2]. As the results of the research work, the synthetic procedures and the cyclic structure of *p-tert*- butylcalixarenes and some other calixarenes are well established.

If calixarenes are to serve as enzyme mimics it is necessary that they carry various functional groups that can act as active catalystic sites or binding sites[3]. Because the carbonyl



Scheme 1