Communications to the Editor

 Table 2. Characteristic <sup>1</sup>H NMR data of U-BSPs, la-ld and their precursors, 2, 3 & 4 in the region of 2.5-6.5 ppm (in CDCl<sub>3</sub>)

Compound	methylene (=CH <sub>2</sub> )	N-Me (FB)	N-M α	e (SP)۴ / ω	vinyl a	(H-3') <sup>μ</sup> / ω	ratio <sup>0</sup>
2 (AFB)	3.73	2.96					
3 (BFB)	3.80	2.99					
4a (SP <sup>H</sup> -FB)	3.83	3.01		2.69		5.65	
4b (SPMe-FB)	3.82	2.98	2.67		5.62		
la			2.69	2.70	5.67	5.85	1:1
1b			2.63	2.69	5.66	5.71	1:1
lc			2.70	4.05	5.82	6.54 <sup>c</sup>	1:1
1d			2.61	2.64	5.56	5.76	1:1

<sup>a</sup>The  $\alpha$  &  $\omega$  denote the corresponding peak of  $\alpha$ - &  $\omega$ -ring of U-BSPs. <sup>b</sup>Integration ratios of the corresponding peak of  $\alpha$ - &  $\omega$ -ring. <sup>c</sup>The values are of the opened MC form of 1c.

Table 3. Electron-Spray (ES) mass spectral data\* of U-BSPs, la-ld

C	Mari	Molecular Ion			
Compound	MW	(m/z)	rel. int. (%)		
	795.96	796.24	25		
16	1002.76	1003.40	43		
Ic	840.96	841.21	32		
1d	809.96	810.10	12		

\*ES mass spectra was recorded on a VG Quattro mass spectrometer at Queen's University.

Electron Spray (ES) mass spectral data of the synthesized U-BSPs are summerized in Table 3. Unlikely to the symmetrical bis-spiropyrans,<sup>7</sup> relative intensities of U-BSPs were quiet low.

Investigations on the intra- and intermolecular SP-MC aggregation behaviors are currently underway.

Acknowledgment. This work was supported partly by research fund from the Korea Science and Engineering Foundation (941-0300-006-2) and partly from the Korean Ministry of Education of the Republic of Korea under the Basic Research Program (BSRI-94-3406).

## References

- (a) Brown, G. H., editor, Photochromism, in Techniques of Chemistry, Wiley, New York, 1971; Vol. 3. (b) Durr, H.; Bouas-Laurent, H. editors in Photochromism, Molecules and Systems; Elsevier, 1992.
- (a) Levy, D.; Avnir, D. J. Phys. Chem. 1988, 92, 4734; (b) Tamaki, T; Chimura, K. J. Chem. Soc. Chem. Commun. 1989, 1477. (c) Durr, H. Angew. Chem. Int. Ed. Engl. 1989, 28, 413. (d) Inouye, M.; Kim, K.; Kitao, T. J. Am. Chem. Soc. 1992, 114, 778. (e) Miyata, A.; Unuma, Y.; Higashigaki, Y. Bull. Chem. Soc. Japn. 1993, 66, 993.
- Williams, D. J. in Nonlinear Optical Properties of Organic and Polymeric Materials; ACS Symposium Series, 1983, 233, pp. 135-151.

- (a) Keum, S. R.; Hur, M. S.; Kazmair, P. M.; Buncel, E. Can. J. Chem. 1991, 69, 1940. (b) Keum, S. R.; Lee, K. B.; Kazmair, P. M.; Buncel, E. Magn. Res. Chem. 1992, 30, 1128. (c) Keum, S. R.; Yun, J. H.; Lee, K. W. Bull. Kor. Chem. Soc. 1992, 13, 351. (d) Keum, S. R.; Lee, K. W. Bull. Kor. Chem. Soc. 1993, 14. (e) Keum, S. R.; Lee, K. B.; Kazmair, P. M.; Buncel, E. Tet. Lett. 1994, 35, 1015. (f) Keum, S. R.; Lee, M. J.; Yun I. K. J. Sci. Tech. 1995, in press.
- (a) Wyn-Jones, E.; Gormally, J. in Aggregation Processes in Solution; editor Elsevier, 1983, Chapter 10-12. (b) Miyata, A.; Unuma, Y.; Higashigaki, Y. Bull. Chem. Soc. Japn. 1993, 66, 993.
- Krongauz, V. A.; Shartsman, F. P. J. Phys. Chem. 1984, 88, 6448.
- (a) Keum, S. R.; Lee, J. H.; Seok, M. K.; Yoon, C. M. Bull. Kor. Chem. Soc. 1994, 15, 275. (b) Keum, S. R.; Lee, J. H.; Seok, M. K. Dyes and Pigments, 1994, 25, 21. (c) Keum, S. R.; Lim, S. S.; Min, B. H.; Kazmaier, P. M.; Buncel E. Dyes and Pigments, 1995, in press.
- Gale, D. J.; Whilshire, J. F. J. Soc. Dyeyers Colour, 1974, 90, 97.

## Selective Reduction of $\alpha,\beta$ -Unsaturated Aldehydes and Ketones to Allylic Alcohols with Diisobutylchloroalane

Jin Soon Cha\*, Oh Oun Kwon, and Sang Yong Kwon

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

Received July 21, 1995

Diisobutylaluminum hydride (DIBAL-H) and triisobutylaluminum (TIBAL) have secured their place as reducing agents in organic synthesis.<sup>12</sup> As may be expected, aldehydes and ketones are easily reduced to the corresponding alcohols on treatment with either of the reducing agents.<sup>1+3</sup> Although the reaction of carbonyl compounds with the reagents affords the same reduction products, the modes of reduction are different. Thus, the reduction with DIBAL-H involves hydride shift from the aluminum4; the reduction with TIBAL involves hydride shift from the  $\beta$ -carbon atom and thus proves to be very similar to a Meerwein-Ponndorf-Verley reduction process.<sup>4,5</sup> In general, TIBAL is a mild reducing agent, and hence most organic functional groups, except aldehydes and ketones, are compatible with the reagent<sup>1,2</sup>; on the other hand, DIBAL-H is a strong one, and hence most organic functional groups are reactive with the reagent even at low temperature.<sup>3</sup> These differences led us to extend the use of diisobutylchloroalane (DIBAL-Cl) as a reducing agent, up to now the systematic study on the reagent has been scarcely appeared.<sup>6</sup> Based on these considerations, we have therefore undertaken an investigation of the reactivity of DIBAL-Cl towards general organic functionalities. In the course of this 1010 Bull. Korean Chem. Soc. 1995, Vol. 16, No. 11

Table 1. Reduction of  $\alpha,\beta$ -Unsaturated Aldehydes and Ketones with Diisobutylchloroalane in Diethyl Ether at Room Temperature<sup>4</sup>

C	Time	Product ratio <sup>b</sup>	Yield* (%)	
Compound	(h)	1,2 : 1,4		
Crotonaldehyde	1	100 : 0	94	
	3	100 : 0	>99.9	
2-Hexenal	1	100 : 0	90	
	3	100 : 0	99	
	6	100 : 0	>99.9	
Cinnamaldehyde	12	100 : 0	80	
	24	100 : 0	>99.9	
3-Penten-2-one	1	100 : 0	92	
	3	100 : 0	95	
	6	100 : 0	99.9	
Benzalacetone	1	100 : 0	12	
	3	100 : 0	25	
	6	100 : 0	40	
	12	100 : 0	75	
	24'	100 : 0	<b>99.</b> 9	
Chalcone	1	100 : 0	50	
	6	100 : 0	67	
	12	100 : 0	75	
	24	100 : 0	80	
	48	100 : 0	98	
	72	100 : 0	99.9	
2-Cyclohexen-1-one	1	100 : 0	75	
-	3	100 : 0	90	
	6	100 : 0	99.9	
2-Cyclopenten-1-one	1	100 : 0	15	
- <b>-</b>	3	100 : 0	40	
	6	100 : 0	82	
	12	100 : 0	99.9	
Isophorone'	1	100 : 0	<del>98</del>	
-	3	100 : 0	99	
	6	100 : 0	100	

•Reaction mixture were cz. 1 M in substrates. A 1.1:1 ratio for reagent: compound was utilized, except where otherwise indicated. •Normalized ratio and yield determined by GC with appropriate internal standard. •A 2:1 ratio for reagent: compound was utilized.

investigation, we found that DIBAL-C! readily reduces  $\alpha$ ,  $\beta$ -unsaturated aldehydes and ketones to the corresponding allylic alcohols at room temperature without any detectable 1,4-reduction product. Herein we report the application of this reagent for the selective reduction of enals and enones. The reagent was conveniently prepared by a simple reaction between DIBAL-H and hydrogen chloride in diethyl ether<sup>7</sup> (eq. 1).

*i*-Bu<sub>2</sub>AlH+HCl(in Et<sub>2</sub>O) 
$$\xrightarrow{\text{Et2O}} i$$
-Bu<sub>2</sub>AlCl+H<sub>2</sub>  $\uparrow$  (1)  
(DIBAL-H) (DIBAL-Cl)

The reduction was carried out by the addition of 10% or 100% excess DIBAL-Cl in diethyl ether to the aldehyde or ketone in diethyl ether at room temperature. The reduction was traced by GC analysis at appropriate time intervals. The data are collected in Table 1.

In all the cases investigated, no conjugate reduction or conjugate addition<sup>8</sup> to the  $\alpha,\beta$ -unsaturated system occurred. Thus, reduction of simple conjugated aldehydes, such as crotonaldehyde, 2-hexenal and cinnamaldehyde, afforded exclusively corresponding allylic alcohols, resulting only from 1,2-reduction. Acyclic enones, such as 3-penten-2-one, benzal-acetone and chalcone, were also selectively reduced to the corresponding allylic alcohols in essentially quantitative yields at room temperature. Excess reagent (two equivalents) did not affect the selectivity but accelerated the reduction rate. 2-Cyclohexen-1-one was converted to 2-cyclohexenol in a quantitative yield. Even 2-cyclopenten-1-one, known for its susceptibility to undergo conjugate reduction, was converted to the desired 2-cyclopentenol cleanly. Similarly, isophorone was readily reduced to 3,3,5-trimethyl-2-cyclohexen-1-ol.

Selective 1,2-reduction of a, \beta-unsaturated aldehydes and ketones with metal hydride reducing agents is often difficult to achieve in organic synthesis due to competing 1,2- vs. 1,4-attack by hydride.<sup>9</sup> Among the various reducing systems which have been devised for this purpose, diisobutylaluminum hydride (DIBAL-H),10 triisobutylaluminum (TIBAL),11 lithium aluminum hydride (LAH),11 9-borabicyclo[3.3.1]nonane (9-BBN),12 lithium n-butylborohydride,13 and sodium borohydride in aqueous methanol containing rare earth metal chloride<sup>14</sup> are generally the most efficient and convenient.<sup>15</sup> However, these can by no means be adapted as a very general procedure.<sup>16</sup> Results summarized in Table 1 clearly reveal that the reagent is really an ideal reducing agent for the selective reduction of  $\alpha,\beta$ -unsaturated aldehydes and ketones to the corresponding allylic alcohols. The selectivity is essentially 100%. Furthermore, DIBAL-Cl is extremely mild. Even acid chloride, the most reducible functional group, is compatible.17 In this context, DIBAL-Cl is comparable to diisopinocampheylchloroborane (Ipc<sub>2</sub>BCl),<sup>18</sup> another mild, selective reducing agent for such purpose.

The following procedure for the reduction of crotonaldehyde to crotyl alcohol is representative. An oven-dried 25mL flask equipped with a side arm fitted a rubber stopple and a reflux condenser connected to a mercury bubbler was cooled down to room temperature under a stream of nitrogen. The flask was charged with 2.5 mL of a 2 M crotonaldehyde solution (5 mmol) in diethyl ether and tridecane as an internal standard. To this solution was added 2.75 mL of a 2 M DIBAL-Cl solution (5.5 mmol) in diethyl ether<sup>19</sup> with stirring, and the reaction mixture was stirred for 3 h at room temperature. Then the reaction mixture was hydrolyzed with 3 N HCl aqueous solution. The aqueous layer was saturated with potassium carbonate and the dry ether layer was subjected to GC analysis on a 15% Carbowarx 20 M column, 12 ft×0.125 in., indicating the presence of crotyl alcohol as a sole product in >99.9% yield.

Acknowledgment. This work was financially supported by Ministry of Education (BSRI-94-3420) and Organic Chemistry Research Center-KOSEF.

## References

therein.

- Downs, A. J. Chemistry of Aluminum, Gallium, Indium and Thallium; Blackie Academic & Professional: London, 1993; Chapter 7-8.
- (a) Yoon, N. M.; Gyoung, Y. S. J. Org. Chem. 1985, 50, 2443.
   (b) Cha, J. S.; Jeoung, M. K.; Kwon, O. O.; Lee, K. D.; Lee, H. S. Bull. Korean Chem. Soc. 1994, 15, 873.
- 4. Heinsohn, G. E.; Ashby, E. C. J. Org. Chem. 1973, 38, 4232.
- Ashby, E. C.; Yu, S. H.; Lardicci, L. Tetrahedron Lett. 1971, 4135.
- 6. Giacomelli, G.; Lardicci, L. J. Org. Chem. 1981, 46, 3116.
- 7. DIBAL-Cl can also be prepared by the redistribution of i-Bu<sub>3</sub>Al with finely crushed anhydrous AlCl<sub>3</sub> in diethyl ether at 0°.
- 8. In the reaction of  $\alpha,\beta$ -unsaturated ketones with TIBAL, the 1,2-addition of the isobutyl group bound to the aluminum atom is generally competitive with the reduction. See, ref (6).
- (a) House, H. O. Modern Synthetic Reactions, 2nd Ed.;
   W. A. Benzamin: Menlo Park, CA, 1972. (b) Ho, T.-L. Hard and Soft Acids-Bases Principles in Organic Chemistry.; Academic Press : New York, 1977.
- Wilson, K. E.; Seildner, R. T.; Masamune, S. J. J. Chem. Soc., Chem. Commun. 1970, 213.
- (a) Giacomelli, G.; Caporusso, A. M.; Lardicci, L. Tetrahedron Lett. 1981, 22, 3663. (b) Johnson, M. R.; Rickborn, B. J. Org. Chem. 1970, 35, 1041.
- (a) Krishnamurthy, S.; Brown, H. C. J. Org. Chem. 1975, 40, 1864. (b) Idem, *Ibid.* 1977, 42, 1197.
- Kim, S.; Moon, Y. C.; Ahn, K. H. J. Org. Chem. 1982, 47, 3311.
- 14. (a) Ganem, B. J. Org. Chem. 1975, 40, 146. (b) Ganem, B.; Fortunato, J. M. Ibid. 1976, 41, 2194.
- For Selective 1,2-reduction with other hydride reagents, see: (a) Mordenti, L.; Brunet, J. J.; Caubere, I. J. Org. Chem. 1979, 44, 2203. (b) Chaikin, S. W.; Brown, W. G. J. Am. Chem. Soc. 1949, 71, 122. (c) Cain, M. E. J. Chem. Soc. 1964, 47, 3532. (d) Brown, H. C.; Hess, H. M. J. Org. Chem. 1969, 34, 2206. (e) Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. Ibid. 1977, 42, 3180. (f) Gemal, A. L.; Luche, T. L. J. Am. Chem. Soc. 1981, 103, 5454. (g) Hutchins, R. O.; Kandasamy, D. J. Org. Chem. 1975, 40, 2530. (h) Corey, E. J.; Becker, K. B.; Varma, R. K. J. Am. Chem. Soc. 1972, 94, 8616. (i) Brown, H. C.; Mathew, C. P.; Pyun, C.; Son, J. C.; Yoon, N. M. J. Org. Chem. 1984, 49, 3091. (j) Sande, A. R.; Jagadale, M. H.; Mane, R. B.; Salunkhe, M. M. Tetrahedron Lett. 1984, 25, 3501.
- (a) Brown, H. C.; Krishnamurthy, S.; Yoon, N. M. J. Org. Chem. 1976, 41, 1778. (b) Delter, A.; Smith, K.; Brown, H. C. Borane Reagents; Academic Press: London, 1988.
- 17. Cha, J. S.; Kwon, O. O. Unpublished results.
- Cha, J. S.; Kim, E. J.; Kwon, O. O.; Kim, J. M. Bull. Korean Chem. Soc. 1994, 15, 1033.
- A solution of DIBAL-Cl in diethyl ether was prepared by the reaction of DIBAL-H with a stoichiometric amount of HCl in diethly ether at 0°.

## New Cytotoxic Anthraquinones from the Crinoid *Ptilometra*: 1'-Deoxyrhodoptilometrin-6-Osulfate and Rhodoptilometrin-6-O-sulfate

Nam Kyung Lee\* and Yong Hae Kim<sup>†</sup>

Department of Chemistry, College of Natural Science, Duksung Women's University, Seoul 132-714, Korea <sup>†</sup>Department of Chemistry, Korea Advanced Institute of Science and Technology, Kusung Dong 373-1, Yusung Gu, Taejon 305-701, Korea

Received July 21, 1995

Anthraquinone pigments have been isolated from the various marine natural sources and extensively studied by the several groups.1 Crinoids, in contrast with the familar starfishes and sea urchins, are perhaps the little known and have been described from a restricted geographical area, the Indo-Pacific including the coast of Thailand.<sup>2</sup> Interests in crinoids chemistry are of the molecular structures and also spectacularly colorful appearance of the pigments. We have studied on the biologically active marine natural products.3 We wish to report two new anthraquinone derivatives along with a known compound. One is the known rhodoptilometrin 1 (3-(1'-hydroxypropyl)-1,6,8-trihydroxy-9,10-anthraguinone). The remaining two had not previously been isolated from a natural source : 1,8-Dihydroxy-3-propyl-9,10-anthraquinone-6-O-sulfate 2 and 1,8-dihydroxy-3-(1'-hydroxypropyl)-9,10-anthraquinone-6-O-sulfate 3. Specimens of Ptilometra were collected subtidally and intertidally in the Eastern coast of the Gulf of Thailand. The pooled Ptilometra were homogenized, extracted with methanol, and concentrated to give a sticky syrup (10 g). The residues were partitioned into methylene chloride and water. The methylene chloride extracts were concentrated and chromatographed on silica gel (200-400 µm. Merck, 4 cm $\times$ 50 cm) with a mixture of ethylacetate and nhexane (2:1). The active fractions were concentrated, and the residue (1.2 g) was further chromatographed on sephadex (LH-20) with methanol to give rhodoptilometrin (1, 10 mg, 0.2% from methanol ext.) and a mixture of 2 and 3, which were seperated by a high pressure liquid chromatography  $(C_{18}, MeOH: H_2O=1: 1, 2: 20 \text{ mg}, 0.2\%, 3: 100 \text{ mg}, 1.0\%)$ : 1; the specific rotation rerative to the sodium D line at 20 °C,  $[\alpha]_{\rho} = -8^{\circ}$  (c=0.5, MeOH), values of the wavelength at the maximun molar absorptivity, electron impact mass spectrometry, MS, m/z 314 M<sup>+</sup> (C<sub>17</sub>H<sub>14</sub>O<sub>6</sub>), UV  $\lambda_{max}$  (ε). MeOH (nm), 224 (12,000), 258 (8,000), 432 (5,000), IR v<sub>max</sub>, KBr (cm<sup>-1</sup>), 3345 (OH), 1598 (C=O), 1385, 1269 (Me); 2, C<sub>17</sub>H<sub>13</sub>O<sub>8</sub>S<sub>1</sub>Na<sub>1</sub>, ion spray mass spectrometry (negative). MS. m/z 376.9 M<sup>-</sup>, 296.9 [M-SO<sub>3</sub>]<sup>-</sup>, UV  $\lambda_{max}$  ( $\epsilon$ ), MeOH (nm), 224 (13,000), 258 (8,000), 432 (6,000), IR v<sub>sect</sub>, KBr (cm<sup>-1</sup>), 3402 (OH), 1610 (C=O), 1395 (Me), 1095, 1058 (- $SO_{3}$ -), 3,  $[\alpha]_D - 14^\circ$  (c=0.2, MeOH),  $C_{17}H_{13}O_9S_1Na_1$ , ion spray mass spectrometry (negative), MS, m/z 393.0 M<sup>-</sup>, 312.9 [M-SO<sub>3</sub>]<sup>-</sup>, UV  $\lambda_{max}$  (c), MeOH (nm), 224 (13,000), 258 (8,000), 432 (6,000), IR  $v_{max}$ , KBr (cm<sup>-1</sup>), 3350 (OH), 1624 (C=O), 1281 (Me), 1049 (-SO<sub>3</sub>-). The data of 'H nuclear magnetic resonance