the order of a diffusion-limited process, this and the above value of $K$ are in agreement with the rapid equilibrium situation, which can be expressed, as has been done by Birks:[7]

$$k_{TX}[Q] \text{ and } k_{XT} \gg k_{GT}, k_{PT}, k_{GX}$$

Saltiel et al.[8] have utilized the same concept to present evidence of singlet exciplex formation. They have studied the fluorescence quenching of several aromatic hydrocarbons as a function of quencher concentration in degassed and air-saturated solutions. An increase of the quenching parameter in the presence of $O_2$ is proposed as evidence of an exciplex intermediate.[9] A related, but less general argument, using a triplet quencher, has been presented by other authors[10] as evidence of a triplet exciplex intermediate in a photochemical reaction. By monitoring the molecular triplet state directly, our experiments provide a method for identifying an exciplex intermediate without the need of a stable reaction product.

We conclude that singlet and triplet exciplex mechanisms for the heavy-atom interactions are consistent with our data and that the reactions cannot proceed solely via simple collisions mechanisms. Also, the use of a second quencher is proposed as a general method for studying short-lived, nonemissive exciplexes in the triplet as well as in the singlet state.

**Acknowledgment.** Support of this research by the National Science Foundation is gratefully acknowledged.

**Registry No.** A, 120-12-7; EI, 75-03-6; ferrocine, 102-54-5.

(7) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; pp 309–311.

(8) Charlton, J. L.; Townsend, D. E.; Watson, B. D.; Shannon, P.; Kowalewska, J.; Saltiel, J. *J. Am. Chem. Soc.* **1977**, *99*, 5992 and references therein.

(9) Our studies of the fluorescence quenching of A by EI in degassed and in air-saturated solutions have yielded the relationship $k_{deg} < k_{air}$, consistent with an exciplex mechanism in the singlet state. These results will be discussed in a later publication.

(10) See, for example: Gupta, A.; Hammond, G. S. *J. Am Chem. Soc.* **1976**, *98*, 1219. Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. R. L. *J. Am. Chem. Soc.* **1975**, *97*, 3697.

## Stereocontrolled Synthesis of D-Pentitols, 2-Amino-2-deoxy-D-pentitols, and 2-Deoxy-D-pentitols from D-Glyceraldehyde Acetonide

Norio Minami, Soo Sung Ko, and Yoshito Kishi*

*Department of Chemistry Harvard University Cambridge, Massachusetts 02138*

*Received October 13, 1981*

In connection with our interest in the marine natural product, palytoxin,[1] it has become necessary to develop a method to transform selectively RCH(OH)CHO into every diastereomer possible for RCH(OH)CH(OH)CH(X)$CH_2$OH. By using the syntheses of D-pentitols, 2-amino-2-deoxy-D-pentitols, and 2-deoxy-D-pentitols from D-glyceraldehyde acetonide as examples, we would like to present a solution to this problem.

D-Glyceraldehyde acetonide (**1**)[2] was converted to the *trans*-allylic alcohol **2**[3] ($[\alpha]_D$ +33.9° ($CHCl_3$, *c* 3.63)) in two steps [(1) $(i\text{-PrO})_2P(O)CH_2CO_2Et/t\text{-BuOK/THF/}-78$ °C and (2) DIBAL/hexane/−78 °C] in 63% overall yield. The stereoselectivity of the modified Wittig reaction was at least 120:1, favoring the trans ester.[4] It was confirmed that loss of optical purity of **1** in this transformation was less than 2%, if any.[5] Sharpless asymmetric epoxidation reaction[6] using (−)-diethyl D-tartrate [*t*-BuOOH/Ti(*i*-PrO)$_4$/(−)-DET/$CH_2Cl_2$/−23 °C/2 days] yielded a 40:1 mixture[7,8] of the epoxides **4**[3] ($[\alpha]_D$ +38.6° ($CHCl_3$, *c* 1.45)) and **5**[3] ($[\alpha]_D$ −21.5° ($CHCl_3$, *c* 0.77)) in 77% yield. On the contrary, asymmetric epoxidation reaction using (+)-diethyl L-tartrate [*t*-BuOOH/Ti(*i*-PrO)$_4$/(+)-DET/$CH_2Cl_2$/−23 °C/2 days] yielded a 1:14 mixture[7,8] of the epoxides **4** and **5** in 74% yield. On the basis of observations made by Sharpless,[6] the stereochemistry of the epoxides **4** and **5** was tentatively assigned as indicated and was later confirmed by their successful transformation to pentaacetate of adonitol and pentaacetate of arabitol, respectively (vide infra).

D-Glyceraldehyde acetonide (**1**) was also stereospecifically converted to the *cis*-allylic alcohol **3**[3] ($[\alpha]_D$ +14.0° ($CHCl_3$, *c* 4.52)) in four steps [(1) $C_6H_5HgCCl_2Br/(C_6H_5)_3P/C_6H_6$/reflux,[9] (2) *n*-BuLi/THF/−78 °C followed by MeOCOCl/THF/−78 °C, (3) $H_2$ (1 atm)/Pd–$CaCO_3$/hexane/room temperature, and (4) DIBAL/hexane/−78 °C] in 46% overall yield.[10] The optical purity of **3** was shown to be 98.1%.[5] Sharpless asymmetric epoxidation of **3** using (+)-diethyl L-tartrate proceeded very slowly [*t*-BuOH/Ti(*i*-PrO)$_4$/(+)-DET/$CH_2Cl_2$/−23 °C/11 days] but yielded a 12:1 mixture[7] of the epoxides **6**[3] ($[\alpha]_D$ −15.6° ($CHCl_3$, *c* 1.03)) and **7**[3] ($[\alpha]_D$ + 11.0° ($CHCl_3$, *c* 1.12)) in 57% yield. On the basis of observations made by Sharpless,[6] the stereochemistry of the epoxides **6** and **7** was tentatively assigned as indicated and was confirmed later from the epoxide ring-opening experiment (vide infra). Asymmetric epoxidation of **3** using (−)-diethyl D-tartrate [*t*-BuOOH/Ti(*i*-PrO)$_4$/(−)-DET/$CH_2Cl_2$/−23 °C/11 days] yielded a 3:2 mixture[7] of the epoxides **6** and **7** with the unexpected epoxide **6** as the major product. The observed result does not seem to be exceptional for cases of sterically crowded *cis*-allylic alcohols.[11]

The cooperative effect recognized in *m*-chloroperbenzoic acid (MCPBA) epoxidation of a similar system[12] seemed to have po-

(1) Uemura, D.; Hirata, Y.; Naoki, H.; Iwashita, T. *Tetrahedron Lett.* **1981**, 2781. Moore, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491 and references cited therein.

(2) D-Glyceraldehyde acetonide (**1**) was prepared according to the method reported by H. O. L. Fischer and E. Baer (*Helv. Chim. Acta* **1934**, *17*, 622). If necessary, L-glyceraldehyde acetonide is available; for example, see: M. E. Jung and T. J. Shaw, *J. Am. Chem. Soc.* **1980**, *102*, 6304.

(3) Satisfactory spectroscopic data were obtained for this substance. Spectroscopic data including a copy of the $^1H$ NMR spectrum are included in the supplementary material.

(4) In studies on the synthesis of monensin, we have recognized that the ratio of cis and trans esters in the Horner–Emmons modification of Wittig reaction is sensitive to the structure of phosphonate reagents. In general, a phosphonate reagent with a large phosphonate ester group yields predominantly a trans-$\alpha,\beta$-unsaturated ester. Examples are given in footnote 7 of ref 11.

(5) Optical purity of this substance was determined by HPLC analysis [$\mu$-Porasil; ethyl acetate–hexane (1:10)] of the MTPA derivative prepared in four steps [(1) $C_6H_5CH_2Br$/NaH/DMF/0 °C, (2) 60% aqueous AcOH/room temperature, (3) $(Me)_3CCOCl$/Py/room temperature, and (4) (−)-$C_6H_5C(OMe)(CF_3)COCl$/Py/room temperature]. No enantiomeric discrimination was observed under the conditions used for this derivatization.

(6) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. The most recent contribution to this method from the Sharpless laboratory is found in: Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237; we thank Professor Sharpless for a preprint of this paper.

(7) This ratio was determined by HPLC analysis [$\mu$-Porasil; ether–hexane (1:5)] of the corresponding carbobenzyloxy derivative, prepared by treatment with $C_6H_5CH_2OCOCl$/Py/THF/−23 °C → room temperature. No diastereomeric discrimination was observed under the conditions used for this transformation.

(8) The difference in the degree of stereoselectivity observed between the cases using (−)-diethyl D-tartrate (unnatural) and (+)-diethyl L-tartrate (natural) might be attributed to the optical purity of the diethyl tartrates themselves or to the effect of the acetonide group existing in the substrate; the $[\alpha]_D$ value of unnatural diethyl tartrate, purchased from Aldrich Chemical, was −8.5° (neat), whereas that of the natural, purchased from Aldrich Chemical, was +7.9° (neat).

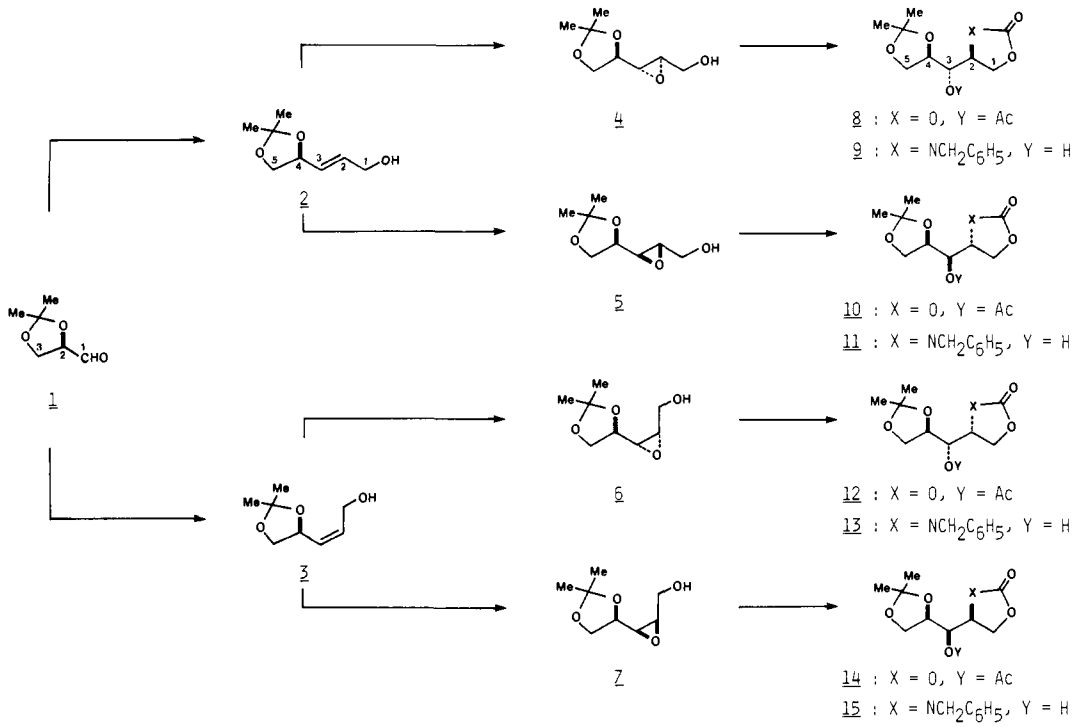
(9) Seyferth, D.; Simmons, H. D. Jr.; Singh, G. *J. Organomet. Chem.* **1965**, *3*, 337. Seyferth, D.; Heeren, J. K.; Singh, G.; Grim, S. O.; Hughes, W. B. *J. Organomet. Chem.* **1966**, *5*, 267.

(10) Wittig reaction of D-glyceraldehyde acetonide (**1**) with $(C_6H_5)_3P{=}CHCO_2Me$ in methanol at room temperature gave a 7:1 mixture of cis- and trans-unsaturated esters. The optical purity ($[\alpha]_D$ +129° ($CHCl_3$, *c* 2.63)) of the cis ester obtained by this method was as good as that ($[\alpha]_D$ +127° ($CHCl_3$, *c* 2.38)) obtained from the acetylenic route. Thus, this Wittig reaction provided a short, practical synthesis of **3**: Mitra, A.; Kishi, Y., unpublished results.

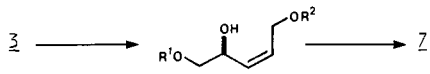
(11) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873.

(12) Johnson, M. R.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4347. Hasan, I.; Kishi, Y. *Ibid.* **1980**, 4229.

0002-7863/82/1504-1109$01.25/0 




tential for a stereocontrolled route to the epoxide **7**. Thus, the *cis*-allylic alcohol **3** was converted to the secondary alcohol **16**[3] ($[\alpha]_D$ +19.3° ($CHCl_3$, *c* 1.54)) in three steps [(1) $(C_6H_5)_2$(*t*-Bu)SiCl/Py/0 °C → room temperature, (2) 0.1 N HCl/AcOH/0 °C → room temperature, and (3) $(Me)_3CCOCl$/Py/room temperature] in 63% overall yield. MCPBA epoxidation of **16** (MCPBA/$CH_2Cl_2$/−23 °C/3 weeks) yielded a 7.3:1 mixture[13,14] of the two possible epoxides in 83% yield. The major epoxide was converted to the epoxide **7** in 3 steps [(1) 0.1 N NaOH/MeOH/room temperature (2) camphorsulfonic acid (CSA)/$MeC(OMe)_2Me$/acetone/room temperature, and (3) (*n*-Bu)$_4$NF/THF/room temperature] in 72% yield.




**16**

$R^1 = (Me)_3CCO$, $R^2 = (C_6H_5)_2(t\text{-}Bu)Si$

Regio- and stereospecific transformation of the epoxides **4–7** into all the stereoisomers possible for D-pentitols, 2-amino-2-deoxy-D-pentitols, and 2-deoxy-D-pentitols was achieved by using three different types of epoxide ring-opening reactions.

First, synthesis of D-pentitols from **4–7** was planned via carbonates **17**.[15] Among several carbonates examined,[16] the benzyl carbonate **17a**[3] was chosen because of the ease and cleanness of the ring-opening step. Lewis acids [$AlCl_3$, $TiCl_4$, $EtAlCl_2$, $(Me)_2AlCl$, $BF_3{\cdot}Et_2O$] were found effective to enforce the ring opening, but *p*-TSA was ineffective; among Lewis acids examined, $AlCl_3$, $TiCl_4$, or $EtAlCl_2$ generally gave the best results.[17] Thus, the epoxide **4** was cleanly converted in two steps [(1) $C_6H_5CH_2OCOCl$/Py/THF/−23 °C → room temperature and (2) $AlCl_3/Et_2O$/−23 °C] to the carbonate **18**, which was isolated (72% overall yield from **4**) and characterized as its acetate **8**[3,18] ($[\alpha]_D$ −20.8° ($CHCl_3$, *c* 1.40)). The structure of carbonate **8** was concluded from the following evidence. The presence of a five-membered carbonate ring rather than a six-membered ring was evident from its IR spectrum ($\nu_{max}^{neat}$ 1810 $cm^{-1}$). The stereochemistry of the three asymmetric centers of **8** was unambiguously established by the fact that acid hydrolysis (TFA/$H_2O$/room temperature), base hydrolysis (NaOH/$H_2O$/MeOH/room temperature), and then acetylation ($Ac_2O$/Py/room temperature) of **8** yielded pentaacetate of adonitol in 81% overall yield. Thus, it was clear that this epoxide ring-opening reaction took place selectively at the 2 position[19] with inversion of its stereochemistry. Similarly, the epoxides **5**, **6**, and **7** were regio- and stereospecifically converted to the carbonates **10**[3,18] (84% overall yield; $[\alpha]_D$ +36.4° ($CHCl_3$, *c* 1.30)), **12**[3,18] (74% overall yield; $[\alpha]_D$ −1.59° ($CHCl_3$, *c* 1.32)) and **14**[3,18,20] (76% overall yield; $[\alpha]_D$ +16.5° ($CHCl_3$, *c* 0.94)), respectively. Acid hydrolysis, base hydrolysis, and acetylation of **10** and **12** yielded D-arabitol pentaacetate, and the same treatment of **14** yielded xylitol pentaacetate.

Second, stereo- and regiospecific transformation of the epoxides **4–7** to 2-amino-2-deoxy-D-pentitols was realized by a method similar to the one described above. Epoxide **4** was first converted to the benzylurethane **19a**[3] (mp 65–66 °C; $[\alpha]_D$ +34° ($CHCl_3$, *c* 0.76)) in 68% yield by standard procedures [$C_6H_5CH_2N{=}C{=}O$/(*i*-Pr)$_2$(Et)N/$C_6H_6$/50 °C]. On base treatment (*t*-BuOK/THF/−10 → 0 °C), the epoxide ring was opened to yield exclusively the cyclic urethane **9**[3] (mp 123–125 °C; $[\alpha]_D$ +28.6° ($CHCl_3$, *c* 0.38)) in 81% yield. No regio- or stereoisomer nor any

(13) This ratio was determined by HPLC analysis [μ-Porasil; ethyl acetate–hexane (1:9)].

(14) Besides the allylic alcohol **16**, two additional substrates were tested for the MCPBA epoxidation under the same conditions as those reported in the text. A 6.6:1.0 ratio was observed for the compound with $R^1 = R^2 = (C_6H_5)_2(t\text{-}Bu)Si$ in structure **16**, and a 4.5:1.0 ratio for the compound with $R^1 = C_6H_5CH_2$, $R^2 = (Me)_3CCO$. In both cases, the stereochemistry of the major epoxides correspond to that of **7**. Epoxidation of **16** under the Sharpless conditions [*t*-BuOOH/VO(acac)$_2$: *J. Am. Chem. Soc.* **1973**, *95*, 6136] yielded a 5.3:1.0 mixture of the two possible epoxides at room temperature in benzene and a 3.4:1.0 mixture at −23 °C in toluene. The stereochemistry of the major epoxide correponds to that of **7**.

(15) Epoxide ring opening of a system somewhat similar to this is known; for example, see: Corey, E. J.; Hopkins, P. B.; Munroe, A. M.; Hashimoto, S. *J. Am. Chem. Soc.* **1980**, *102*, 7986.

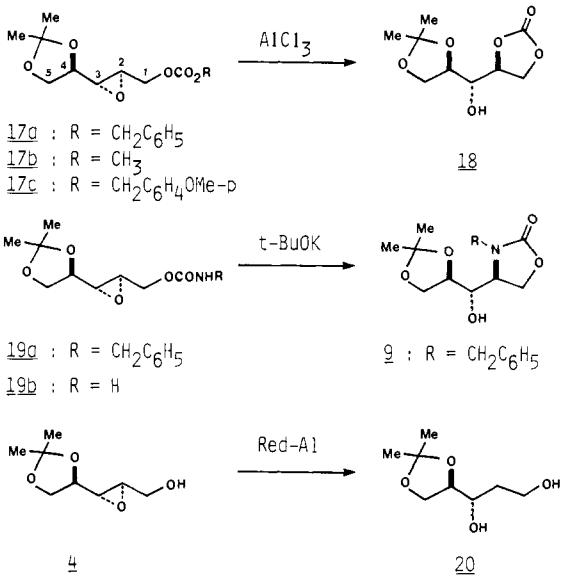
(16) For example, the ring opening of the carbonate **17b** under acidic conditions was sluggish. The ring-opening reaction of the carbonate **17c** seemed slightly faster than that of the carbonate **17a**, but the chemical yields were very similar.

(17) $AlCl_3$ was found best for the substrates given in this paper, but $TiCl_4$ or $EtAlCl_2$ worked better for some other substrates examined.

(18) It was also practical to isolate this carbonate as its 3,4,5-triacetate, prepared in two steps [(1) TFA/$H_2O$/room temperature and (2) $Ac_2O$/Py/room temperature].

(19) Numbering in this paper corresponds to that used in carbohydrate chemistry; see structures **1**, **2**, and **8**.

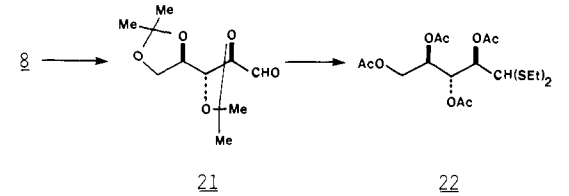
(20) Under acidic conditions, the originally produced 4,5-acetonide 1,2-carbonate, i.e., X = O, Y = H in **14**, partially isomerized to the 3,4-acetonide 1,2-carbonate.




product originating from the ring opening by the oxygen atom of the urethane moiety was detected in this reaction. It is interesting to add the observation that the urethane **19b**[3,21] was recovered unchanged under the same conditions. The gross structure of **9** was concluded on the basis of spectroscopic data, while its stereochemistry was assigned on the basis of analogy to the corresponding carbonate case and also on the fact that the cyclic urethanes **11**[3] (78% overall yield; mp 102–103 °C; $[\alpha]_D$ −12.9° ($CHCl_3$, *c* 0.31)), **13**[3] (65% overall yield; mp 106–108 °C; $[\alpha]_D$ +31.7° ($CHCl_3$), *c* 0.31)), and **15**[3] (78% overall yield; mp 112–113 °C; $[\alpha]_D$ −72.0° ($CHCl_3$, *c* 0.32)) were obtained from the epoxides **5–7**, respectively. Cyclic urethanes **9**, **11**, **13**, and **15** were transformed into the corresponding 2-amino-2-deoxy-D-pentitol 4,5-acetonide 1,2,3-triacetates[3] in three steps [(1) Li/liquid $NH_3$/−78 °C, (2) $LiOH/H_2O$/EtOH/reflux, and (3) $Ac_2O$/Py/room temperature] in excellent yield.

Third, reductive ring opening of the epoxide **4** was regiospecifically realized by using Red-Al [$NaAlH_2(OCH_2CH_2OCH_3)_2$/ThF/room temperature];[22] the product, 2-deoxy-D-arabitol 4,5-acetonide (**20**), was isolated and characterized as its diacetate[3] ($[\alpha]_D$ −23.2° ($CHCl_3$, *c* 0.63)) in 89% overall yield. The NMR and TLC analyses of the crude product showed practically no 3-deoxy-D-adonitol 4,5-acetonide 1,2-diacetate formed in this reduction. The same sequence of reactions on the epoxide **6** yielded 2-deoxy-D-arabitol 4,5-acetonide 1,2-diacetate, while these on the epoxides **5** and **7** gave 2-deoxy-D-xylitol 4,5-acetonide 1,2-acetate[3] ($[\alpha]_D$ +36.7° ($CHCl_3$, *c* 0.29)) in about 90% overall yield.

The unique pattern in the arrangement of the protecting groups of carbonates **8–15** allows achievement of further useful manipulations. For example, the carbonate **8** was transformed to the diacetonide aldehyde **21**[3] ($[\alpha]_D$ −11.8° ($CHCl_3$, *c* 0.97)) in five steps [(1) 1 N NaOH/MeOH/0 °C, (2) $(C_6H_5)_2(t\text{-Bu})SiCl$/Py/40 °C, (3) CSA/$MeC(OMe)_2Me$/acetone/room temperature, (4) $(n\text{-Bu})_4NF$/THF/room temperature, and (5) PCC/NaOAc/$CH_2Cl_2$/room temperature] in 67% overall yield. The aldehyde **21** was converted to D-ribose via the thioacetal **22**.[23] Alternatively, the aldehyde group of **21** could be utilized for the next chain extension.




(21) This substance was prepared from **2** in two steps, i.e., (1) $CCl_3CON{=}C{=}O/CH_2Cl_2$/0 °C and (2) $K_2CO_3/H_2O$/MeOH/0 °C → room temperature.

(22) The remarkable regiospecificity observed has been shown to be primarily due to the alcoholic group: Finan, J. M.; Kishi, Y.; manuscript in preparation.

(23) Jordaan, J. H.; Serfontein, W. J. *J. Org. Chem.* **1963**, *28*, 1395.

**Acknowledgment.** The support of the National Institutes of Health (NS-12108) and the National Science Foundation (CHE 78-06296) is gratefully acknowledged.

**Registry No. 1**, 22323-80-4; **2**, 79060-23-4; **3**, 80532-35-0; **4**, 80532-36-1; **5**, 80581-19-7; **6**, 80581-20-0; **7**, 80581-21-1; **8**, 80532-37-2; **9**, 80532-38-3; **10**, 80581-22-2; **11**, 80581-23-3; **12**, 80581-24-4; **13**, 80581-25-5; **14**, 80581-26-6; **15**, 80581-27-7; **16**, 80532-39-4; **16** epoxide isomer 1, 80532-40-7; **16** epoxide isomer 2, 80581-28-8; **6** ($R^1$, $R^2$ = $(C_6H_5)_2(t\text{-Bu})Si$) isomer 1, 80532-41-8; **16** ($R^1$, $R^2$ = $(C_6H_5)_2(t\text{-Bu})Si$) isomer 2, 80581-29-9; **16** ($R^1$ = $C_6H_5CH_2$, $R^2$ = $(Me)_3CCO$) isomer 1, 80532-42-9; **16** ($R^1$ = $C_6H_5CH_2$, $R^2$ = $(Me)_3CCO$) isomer 2, 80581-30-2; **17a**, 80532-43-0; **18**, 80532-44-1; **19a**, 80532-45-2; **19b**, 80532-46-3; **20** diacetate, 80532-47-4; **21**, 50866-82-5; adonitol pentaacetate, 7208-42-6; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomerl, 80532-48-5; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 2, 80581-31-3; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 3, 80581-32-4; 2-amino-2-deoxy-D-penitol-4,5-acetonide 1,2,3-triacetate isomer 4, 80581-33-5; 2-deoxy-D-xylitol-4,5-acetonide 1,3-acetate, 80581-34-6; 2-deoxy-D-arabitol-4,5-acetonide 1,3-diacetate, 80532-47-4.

**Supplementary Material Available:** Spectroscopic data for new compounds described in this paper (63 pages). Ordering information is given on any current masthead page.

## Preparation and Characterization of $HFe_4(BH_2)(CO)_{12}$. A Hydrogenated Iron Boride Cluster

Kwai Sam Wong, W. Robert Scheidt, and Thomas P. Fehlner*

*Department of Chemistry, University of Notre Dame Notre Dame, Indiana 46556*

*Received November 5, 1981*

In a continuing effort to synthesize five-atom ferraboranes in order to experimentally define the relationship between boranes and small metal clusters,[1] we have prepared a tetrairon system, namely, $HFe_4(BH_2)(CO)_{12}$ (I). This compound, which is a $HFe_4(CO)_{12}$ "butterfly" with a $BH_2$ fragment bridging the wing tips, is a product of the reaction of $B_2H_6Fe_2(CO)_6$[2] with $Fe_2(CO)_9$. It is isoelectronic with $HFe_4(CH)(CO)_{12}$,[3] an iron cluster exhibiting a Fe–H–C interaction, and as such it is a member of a growing class of tetrairon butterfly complexes.[4-9] In addition, I is a structural analogue for $HFe_4(CH_2)(CO)_{12}^+$, a presumed intermediate in the conversion of $Fe_4(CO)_{13}^{2-}$ to methane by protonic acids.[5] In this paper, we describe the structural properties of this compound and present evidence indicating that I is properly

(1) See, for example: Haller, K. J.; Andersen, E. L.; Fehlner, T. P. *Inorg. Chem.* **1981**, *20*, 309. Andersen, E. L.; DeKock, R. L.; Fehlner, T. P. *Ibid.* **1981**, *20*, 3291.

(2) Andersen, E. L.; Fehlner, T. P. *J. Am. Chem. Soc.* **1978**, *100*, 4606.

(3) Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4540. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1980**, *102*, 4542. Beno, M. A.; Williams, J. M.; Tachikawa, M.; Muetterties, E. L. *Ibid.* **1981**, *103*, 1485.

(4) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

(5) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Organomet. Chem.* **1981**, *213*, 125.

(6) Bradley, J. S.; Anell, G. B.; Leonowicz, M. E.; Hill, E. W. *J. Am. Chem. Soc.* **1981**, *103*, 4968.

(7) Bradley, J. S.; Ansell, G. B.; Hill, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 7417.

(8) Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1981**, *20*, 3533.

(9) Davis, J. H.; Beno, M. A.; Williams, J. M.; Zimme, J.; Tachikawa, M.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 668.

0002-7863/82/1504-1111$01.25/0 