Table I. Positional Incorporation of ^{18}O into Diastereomeric 2-Benzyloxy-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes

compd	^{18}O enrichment measd on molecular ion, %	distribution of ^{18}O in positions: equatorial, %	axial, %
11	76.0	94.8[a]	5.2
12	75.8	97.0	3.0[a]
13	78.7	3.9	96.1[a]
14	78.8	3.6[a]	96.4

[a] Measured on the $(M - C_7H_6O)^+$ ion.

a similar procedure, diastereomerically pure **10** was converted into a mixture of **13** and **14**, which was then separated into pure triesters (**13**, $\delta_{^{31}P(CHCl_3)}$ − 7.45 ppm; **14**, $\delta_{^{31}P(CHCl_3)}$ − 5.44 ppm). Electron impact mass spectra showed that the ^{18}O enrichment of compounds **11–14** was lower than that of **5** (see Table I).

The analysis of the mass spectra of *trans*- and *cis*-2-benzyloxy-2-oxo-4-methyl-1,3,2-dioxaphosphorinanes ([^{16}O]-**11** and [^{16}O]-**12**) clearly shows that, in addition to the molecular ions (*m/e* 242), the fragments corresponding to the loss of benzaldehyde $(M - C_7H_6O)^+$ are fairly abundant (*m/e* 136, 31.2% for [^{16}O]-**11**; *m/e* 136, 25.5% for [^{16}O]-**12**).

Since the spatial orientations of the benzyloxy groups in [^{16}O]-**11** and [^{16}O]-**12** have been assigned[14] and since the benzyloxy group is lost after one hydrogen transfer during the mass spectrum fragmentation process, we have been able to assign the distribution of ^{18}O in the axial and equatorial positions of triesters **11–14** on the basis of their mass spectra. The results are collected in Table I. An inspection of Table I clearly shows that the conversion of P-N → P-^{18}O proceeded with nearly complete retention of configuration at the phosphorus atom.[18] Thus, the S_p absolute configuration can be assigned to **3**.

The lack of complete stereospecificity in the P-N → P-^{18}O conversion is intriguing and must be answered. However, our results allow us to claim that the diastereomeric purity of **3** is at least 94.8% and demonstrate the further applicability of amidodiesters to the preparation of chiral phosphorus compounds. Conversion of deoxyadenosine cyclic 3′,5′-(R_p)- and -(S_p)-phosphoranilidates[19] into [^{18}O]-cdAMP with retention of configuration by means of NaH-C$^{18}O_2$ is described in the accompanying communication.[20]

Acknowledgment. This project was financially assisted by the Polish Academy of Sciences, Grant No. MR-I-12. The authors are indebted to Professor David Gorenstein for his early suggestion of the preparation of [^{18}O]-cAMP.

References and Notes

(1) Stec, W. J.; Okruszek, A.; Lesiak, K.; Uznanski, B.; Michalski, J. *J. Org. Chem.* **1976**, *41*, 227.
(2) Lesiak, K.; Lesnikowski, Z. J.; Stec, W. J.; Zielinska, B. *Pol. J. Chem.* **1979**, *53*, 2041.
(3) Zielinski, W. S.; Lesnikowski, Z. J.; Stec, W. J. *J. Chem. Soc., Chem. Commun.* **1976**, 772. See also ref 4 therein.
(4) Lesiak, K.; Stec, W. J. *Z. Naturforsch., B* **1978**, *33*, 782.
(5) Baraniak, J.; Lesiak, K.; Stec, W. J. *Pol. J. Chem.* **1979**, *53*, 1387.
(6) Baraniak, J.; Kinas, R. W.; Lesiak, K.; Stec, W. J. *J. Chem. Soc., Chem. Commun.* **1979**, 940.
(7) Cullis, P. M.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1978**, 512.
(8) Abbot, S. J.; Jones, S. R.; Weinman, S. A.; Knowles, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 2558.
(9) Compound **5** (86.5% enriched in ^{18}O) has been obtained by hydrolysis of benzylideneaniline in 98% $H_2{}^{16}O$.
(10) Schaller, H.; Weinmann, G.; Lerch, B.; Khorana, H. G. *J. Am. Chem. Soc.* **1963**, *83*, 3821.
(11) Lesiak K.; Stec, W. J., poster presented at the IUPAC International Symposium on Phosphorus Chemistry Directed Towards Biology, Sept. 25–28, 1979; Burzenin, Poland, Abstract Book, p 66.
(12) Stec, W. J.; Lopusinski, A. *Tetrahedron* **1973**, *29*, 547.
(13) Brown, D. M.; Magrath, D. I.; Todd, A. R. *J. Chem. Soc.* **1955**, 4396
(14) Negative chemical shift values are assigned to compounds absorbing at higher field than H_3PO_4. The assignment of the spatial orientations of the benzyloxy groups in **11** and **12** was achieved by means of a chemical shift criterion[15] and independently by means of the stereospecific (retention) oxidation[16] of *cis*-2-benzyloxy-2-selenono-4-methyl-1,3,2-dioxaphosphorinane [$\delta_{^{31}P(C_6H_6)}$ + 64.9 ppm ($^1J_{^{31}P-^{77}Se}$ = 1006 Hz)] to [^{16}O]-**11** and of the *trans*-2-selenono isomer [$\delta_{^{31}P(C_6H_6)}$ + 68.4 ppm ($^1J_{^{31}P-^{77}Se}$ = 965 Hz)] to [^{16}O]-**12**.[17]
(15) Engels, J.; Schlaeger, E.-J. *J. Med. Chem.* **1977**, *20*, 907.
(16) Stec, W. J.; Okruszek, A.; Michalski, J. *J. Org. Chem.* **1976**, *41*, 233.
(17) Stec, W. J. Z. Naturforsch., *B* **1974**, *29*, 109.
(18) The same stereospecificity was observed in a separate set of experiments performed with benzaldehyde containing 46.9% [^{16}O].
(19) Lesnikowski, Z. J.; Stec, W. J.; Zielinski, W. S. *Nucleic Acids Res., Spec. Publ.* **1978**, *4*, S49.
(20) Gerlt, J. A.; Coderre, J. A. *J. Am. Chem. Soc.*, preceding paper in this issue.

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Received March 14, 1980

A Method for the Preparation of Unesterified Acyl Phosphates via Stannyl Phosphate Intermediates

Sir:

Acyl phosphates are of importance since the compounds such as acetyl phosphate,[1] adenosine 5′-aminoacyl phosphates,[2] and luciferyladenosine 5′-phosphate[3] are known to be biologically significant. Acyl phosphates belong to a class of mixed anhydrides consisting of carboxylic and phosphoric acids. However, little[4] is known concerning a general method for the synthesis of analytically pure acyl phosphates because of their instability.

We now report a general and practically useful method for the synthesis of unesterified acyl phosphates employing stannyl phosphates via the silyl phosphate intermediates.

Stannyl phosphates were found to react smoothly and stoichiometrically with acyl chlorides.

When diethyl tri-*n*-butylstannyl phosphate (**1**)[5] was treated with 1 equiv of acyl chlorides in dry carbon tetrachloride, the corresponding acyl diethyl phosphates (**2**) were obtained in almost quantitative yields. The reaction proceeded smoothly

$$\underset{}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl} + \underset{(1)}{Bu_3Sn\text{-}O\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2} \xrightarrow[\text{in } CCl_4]{-\,Bu_3SnCl} \underset{(2)}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{P}}(OEt)_2}$$

at room temperature and the complete conversion was monitored by its ^1H NMR spectra; in the case of acetyl diethyl phosphate [NMR (CCl_4, 60 MHz) δ 1.90 (d, 3 H, J_{HP} = 2 Hz, $CH_3C(O)$)] and also in the case of diethyl pivaloyl phosphate [NMR (CCl_4, 60 MHz) δ 1.25 (s, 9 H, $(CH_3)_3CC(O)$)]. Both compounds are not stable during the distillation and partially decomposed. They were isolated in 45 and 66% yields, respectively.

Similarly, aroyl diethyl phosphates such as benzoyl (92%), 4-chlorobenzoyl (86%), toluoyl (89%), 2-methylbenzoyl (83%), and anisoyl (88%) derivatives could be obtained and isolated by means of silica gel column chromatography using a mixture of *n*-hexane and ether (4:1–1:1 v/v). The mixed anhydride structure was confirmed by their IR spectrum ($\nu_{C=O}$ 1750 cm^{-1}, benzoyl).

Several reports have recently appeared employing tri-*n*-butylstannyl group as a leaving group in organic synthesis.[6] In the field of the organophosphorus chemistry, the stannyl groups can be also employed for the synthesis of phosphate esters.

It was found that diethyl tri-*n*-butylstannyl phosphate (**1**) can be converted with trimethylsilyl chloride into diethyl trimethylsilyl phosphate (**3**) almost quantitatively. The conversion of **1** into **3** was ascertained by its ^1H NMR spectra (CCl_4),

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Table I. Yields and Physical Properties of Unesterified Acyl Phosphates (7)

R	yield, %	mp, °C	formula (mol wt)	spectral properties
CH_3	80	93-94[a]	$C_8H_{12}NO_5P$[c] (233.2)	^1H NMR[d] 2.00 (d, 3 H, J_{HP} = 2 Hz, $CH_3C(O)$), 7.35 (s, 5 H, aromatic); IR[f] 1750 (C=O), 1255 (P=O)
CH_3CH_2	54	107-108[b]	$C_{10}H_{16}NO_5P$[c] (261.2)	^1H NMR[e] 0.97 (t, 3 H, J = 7 Hz, CH_3C), 2.05 (s, 3 H, CH_3 aromatic), 6.97 (m, 5 H, aromatic), 7.76 (s, 3 H, HN); IR[f] 1745 (C=O), 1255 (P=O)
$CH_3(CH_2)_6$	49	103-104[b]	$C_{15}H_{26}NO_5P$[c] (331.4)	^1H NMR[e] 0.50-1.90 (m, 13 H, n-$C_6H_{13}C$), 2.13 (s, 3 H, CH_3 aromatic), 6.87 (m, 5 H, aromatic), 8.60 (s, 3 H, HN); IR[f] 1750 (C=O), 1240 (P=O)
$(CH_3)_3C$	54	110-112[b]	$C_{12}H_{20}NO_5P$[c] (289.3)	^1H NMR[e] 1.17 (s, 9 H, $(CH_3)_3C$), 2.12 (s, 3H, CH_3 aromatic), 5.18 (s, 3 H, HN), 6.87 (m, 5 H, aromatic); IR[f] 1745 (C=O), 1245 (P=O)

[a] The value indicates the monoanilinium salt. Literature values reported by R. Bentley [*J. Am. Chem. Soc.*, **70**, 2183 (1948)] are 104-105 °C as the dianilinium salt and 128-130 °C as the diammonium salt. [b] The value shows the mono *o*-toluidinium salt. [c] Data of elemental analyses agree well with the corresponding theoretical values. [d] ^1H NMR data in δ units [D_2O-Me_2SO-d_6 (1:1 v/v) as solvent and Me_4Si as standard]. [e] ^1H NMR data in δ units (Me_2SO-d_6 as solvent and Me_4Si as standard). [f] IR data in cm^{-1} (solid as KBr pellet).

by the change of the chemical shift of trimethylsilyl protons: δ 0.10 (s, 9 H, $(CH_3)_3Si$). From the above facts, it would seem

$$\underset{(1)}{Bu_3Sn\text{-}O\text{-}\overset{\overset{O}{\|}}{P}(OEt)_2} + Me_3SiCl \longrightarrow \underset{(3)}{Me_3Si\text{-}O\text{-}\overset{\overset{O}{\|}}{P}(OEt)_2} + Bu_3SnCl$$

possible to convert stannyl esters into the unesterified acyl phosphates via the silyl ester intermediates since the silyl esters can be smoothly transformed to the corresponding unesterified phosphate derivatives. Consequently, tris(tri-*n*-butylstannyl) phosphate (**4**), reported by Church,[7] was chosen as a starting material for the synthesis of unesterified acyl phosphates via the silyl phosphate intermediates.

Compound **4** was obtained in 99% yield as follows. To a solution of bis(tri-*n*-butyltin) oxide (43.52 g, 73 mmol) in methanol (200 mL) was added dropwise 85% H_3PO_4 (3.9 mL, 57 mmol) with continuous stirring and the mixture was kept at room temperature overnight. After removal of solvent the residue was dissolved in CH_2Cl_2 (300 mL). It was washed with three portions of 5% sodium bicarbonate (3 × 100 mL) to complete the removal of H_3PO_4. The organic layer was dried over Na_2SO_4 and concentrated to dryness. That the highly viscous oil obtained was a pure sample of **4** was confirmed by its ^{31}P NMR spectrum: δ 4.3 (85% H_3PO_4). It was used in further reactions without any purification.

Benzoyl chloride (1 equiv) in CCl_4 was added dropwise carefully to **4** at room temperature and the mixture was refluxed for 2 h to afford a mixture of benzoyl bis(tri-*n*-butylstannyl) phosphate (**5**) and tri-*n*-butyltin chloride, which, without isolation of **5**, was transformed by treatment with trimethylsilyl chloride into benzoyl bis(trimethylsilyl) phosphate (**6**) which was in turn alcoholyzed (with 2 equiv of ethanol) in the presence of aniline (1 equiv) in dry ether. The

$$\underset{(4)}{(Bu_3SnO)_3P{=}O} + R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \longrightarrow \underset{(5)}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{P}(OSnBu_3)_2} + Bu_3SnCl$$

$$5 \xrightarrow{Me_3SiCl} \underset{(6)}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{P}(OSiMe_3)_2}$$

$$6 \xrightarrow[\text{in ether}]{PhNH_2/EtOH} \underset{(7)}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}\text{-}O^- \; H_3\overset{+}{N}Ph}$$

5a, 6a, 7a R = Ph
5b, 6b, 7b R = CH_3

monoanilinium salt of unesterified benzoyl phosphate (**7a**) was precipitated from the ethereal solution and collected by centrifuge. It was dried over P_4O_{10} (56% yield). However, acetyl bis(tri-*n*-butylstannyl) phosphate (**7b**) could not be obtained selectively with acetyl chloride in the manner described. After several experiments, tri-*n*-butylstannyl bis(trimethylsilyl) phosphate (**8**) was chosen as the most suitable starting material for this purpose.

Compound **8** was prepared as follows. To a solution of tris(trimethylsilyl) phosphate[8] (2.045 g, 6.5 mmol) in dry CCl_4 (20 mL) was added dropwise tri-*n*-butyltin methoxide (2.087 g, 6.5 mmol) at room temperature under an argon atmosphere. After 1 h, the solvent was removed completely in vacuo. That the residual sticky oil was a pure sample of **8** was confirmed by its ^{31}P NMR spectrum: δ 25.1 (85% H_3PO_4). It was used in further reactions without any purification.

For example, when **8** (3.455 g, 6.5 mmol) was treated with acetyl chloride (0.536 g, 6.83 mmol) in CCl_4 (20 mL) under reflux for 1 h and the mixture was further treated with a mixed solution of aniline (0.65 mL, 7.1 mmol) and ethanol (0.84 mL, 14.4 mmol) in dry ether (20 mL) at room temperature, the monoanilinium salt of acetyl phosphate (**7b**) was precipitated and collected (80% yield) as a white powder. In this experiment, acetanilide was not detected during the addition of aniline-containing ethanol.

$$\underset{(8)}{Bu_3SnO\text{-}\overset{\overset{O}{\|}}{P}(OSiMe_3)_2} + R\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl \xrightarrow{-Bu_3SnCl} \underset{(6)}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{P}(OSiMe_3)_2}$$

$$\xrightarrow{EtOH + ArNH_2} \underset{(7)}{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}\text{-}O^- \; H_3\overset{+}{N}Ar}$$

The unesterified acyl phosphates were obtained similarly. Yields and physical properties are given in Table I.

It is noteworthy that tri-*n*-butylstannyl bis(trimethylsilyl) phosphate is a new useful synthetic intermediate in phosphate chemistry and the present method provides analytically pure samples of unesterified acyl phosphates, possessing melting points which were not given in previous reports.[4] The method may be widely applicable to the synthesis of unesterified acyl phosphates.

References and Notes

(1) (a) F. Lipmann, *J. Biol. Chem.*, **155**, 55 (1944); (b) I. A. Rose, M. G-Manago, S. R. Korey, and S. Ochoa, *ibid.*, **211**, 737 (1954); (c) E. R. Stadman, *ibid.*, **196**, 535 (1952); (d) E. R. Stadman, G. D. Novelli, and F. Lipmann, *ibid.*, **191**, 365 (1951).
(2) (a) M. B. Hoagland, *Biochim. Biophys. Acta*, **16**, 288 (1955); (b) P. Berg, *J.*

Biol. Chem., **222**, 1025 (1956); (c) J. A. DeMoss, S. M. Genuth, and G. D. Novelli, *Proc. Natl. Acad. Sci. U.S.A.*, **42**, 325 (1956); (d) P. Casrelfraco, K. Moldave, and A. Meister, *J. Am. Chem. Soc.*, **80**, 2335 (1958).
(3) (a) R. Airth, W. Rhodes, and W. D. McElroy, *Biochim. Biophys. Acta*, **27**, 519 (1958); (b) W. D. McElroy and A. Green, *Arch. Biochem. Biophys.*, **64**, 257 (1956).
(4) Methods for the synthesis of acetyl phosphate were proposed and examined after the first report described by Lipmann appeared: (a) F. Lipmann, *Chem. Ber.*, **73**, 367 (1940). Recently, Whitesides and his co-workers proposed a practical method for the synthesis of acetyl phosphate: (b) G. M. Whitesides, M. Siegel, and P. Garrett, *J. Org. Chem.*, **40**, 2516 (1975); (c) G. M. Whitesides, J. M. Lewis, and S. L. Haynie, *ibid.*, **44**, 864 (1979).
(5) Diethyl tri-*n*-butylstannyl phosphate is known compound: H. Kubo, *Agr. Biol. Chem.*, **29**, 43 (1965). An improved procedure was established by the reaction of diethyl phosphate and tri-*n*-butyltin methoxide in methylene chloride at room temperature. The compound is a colorless sticky oil and could be purified by distillation. Therefore, it was used without any purification procedure after complete removal of methanol: ^{31}P NMR δ 9.45 (85% H_3PO_4).
(6) (a) J. Volade and M. Pereyre, *C.R. Acad. Sci.*, **254**, 3693 (1962); (b) M. Kosugi, Y. Shimizu, and T. Migita, *Chem. Lett.*, 1423 (1977); (c) D. N. Harpp, T. Aida, and T. H. Chan, *Tetrahedron Lett.*, 2853 (1979); (d) V. K. Srivastava and C. Schuerch, *ibid.*, 3269 (1979); (e) G. Himbert, *Angew. Chem., Int. Ed. Engl.*, **18**, 405 (1979); (f) A. Shazer, *Tetrahedron Lett.*, **21**, 221 (1980); (g) D. Waguer, J. P. H. Verheyden, and J. G. Moffatt, *J. Org. Chem.*, **39**, 24 (1974).
(7) Tris(tri-*n*-butylstannyl) phosphate was reported by Church: J. M. Church, U.S. Patent 2 630 436; *Chem. Abstr.*, **48**, 1420*e* (1954); The compound was prepared from the reaction of phosphorus oxychloride with 3 equiv of tri-*n*-butyltin hydroxide. In the present experiment it was prepared from the reaction of bis(tri-*n*-butyltin) oxide (3 mol) with phosphoric acid (2 mol) in methanol in 99% yield: ^{31}P NMR δ 4.96 (85% H_3PO_4).
(8) Tri(trimethylsilyl) phosphate was prepared by a modification of the literature procedures: (a) M. Schmidt, H. Schmidbaur, and A. Binger, *Chem. Ber.*, **93**, 872 (1960); (b) M. G. Voronkov and V. N. Zgonnik, *Zh. Obshch. Khim.*, **27**, 1483 (1957) [*Chem. Abstr.*, **52**, 3569 (1958)].

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Reaction Mechanism of Hydroboration. Ab Initio MO Study on the $C_2H_4 + BH_3$ Reaction

Sir:

Despite its great synthetic usefulness and applicability, the detailed mechanism of the hydroboration reaction[1] has been a matter of a considerable dispute. Brown[2] originally proposed a simple four-center transition-state mechanism. On stereochemical grounds, Seyferth[3] and Streitwieser et al.[4] have suggested an intermediate triangular π complex prior to a three-center-like transition state. These possible mechanisms have been argued by Pasto and Kang[5] on the basis of kinetic isotope effects.

Four molecular orbital studies,[6-9] at the semiempirical and the ab initio minimal basis set levels, have appeared within the last year to elucidate the mechanism of a prototype reaction of C_2H_4 with BH_3. The results, however, are very divergent. A CNDO/2 result of Dasgupta et al.[6] preferred a three-center transition state. In a MNDO study, Dewar and McKee[7] have found that a loose π complex is formed with an energy barrier of 7.6 kcal/mol, this being the rate-determining step for the overall reaction. In contrast to this, an ab initio study with a very limited geometry optimization with the minimal basis set by Clark and Schleyer[8] has found that the formation of the π complex, located at a late stage of reaction, requires no energy barrier. The resultant three-center π complex transforms into the final products through a transition state which resembles the π complex closely in structure and in energy, the reaction proceeding without an overall energy barrier. Finally, Lipscomb et al.[9] very recently have reported a PRDDO study which mostly concurs with that of Clark and Schleyer, though there seem to be some differences in transition-state geometries.

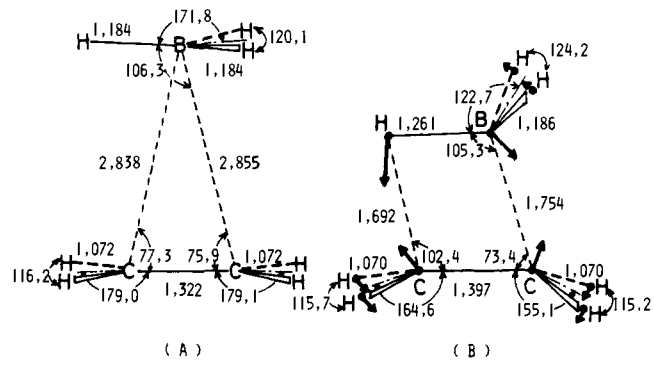

Figure 1. Optimized geometries (in angströms and degrees) for the intermediate π complex (A) and the transition state (B) at the 4-31G SCF level. The arrows in B indicate the displacement vector of the reaction coordinate (the normal coordinate with an imaginary frequency) at the transition state.

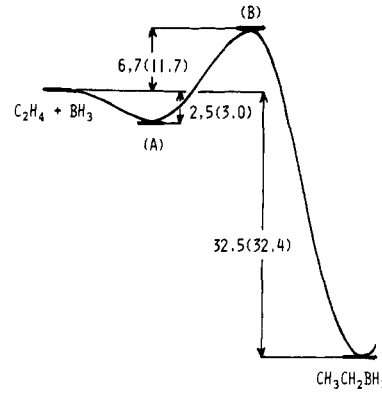

Figure 2. The energy profile (kilocalories/mole) for the reaction of C_2H_4 with BH_3 at the 4-31G (in parentheses) and 6-31G** SCF levels. Geometries used are optimized at the 4-31G SCF level. A and B are the π complex and the transition state, respectively.

To resolve the discrepancies and to determine the reaction mechanism, we have searched carefully for the stationary points on the potential energy surface of the title reaction with the ab initio SCF energy gradient method[10] at the split-valence 4-31G level.[11] The stationary points were identified as the equilibrium or the saddle point by examining the calculated normal vibrational frequencies. At the 4-31G SCF optimized stationary points, energies were also calculated with the 6-31G** basis set[12] which includes polarization functions needed for a better estimate of the energy differences involved. The barrier height for the reaction was further refined with the direct configuration interaction (CI) method.[13]

Upon going from the reactant, $C_2H_4 + BH_3$, to the final product, ethylborane, with a C_s symmetry constraint, we found two stationary points, an intermediate π complex and a transition state (saddle point), as shown in Figure 1. The π complex is in a fairly early stage of reaction and is held together by a three-center bond. The transition state, having *a four-center-like structure*, involves the concerted formation of the C—H and the C—B bond and cleavage of the B—H and the C=C bond, as shown by the reaction coordinate vector in Figure 1.

The energy profile at the SCF level is given in Figure 2. There exists no energy barrier to the formation of the π complex. The predicted exothermicities of 32.4 (4-31G) and 32.5 (6-31G**) kcal/mol agree well with an estimated value[14] of ~33 kcal/mol, while the previous studies provided 38.8 (MNDO),[6] 63.1 (STO-3G),[7] and 70.7 (PRDDO)[8] kcal/mol, respectively. Interestingly the polarization functions have little effect on the exothermicity.

An important point to notice in Figure 2 is that the π com-

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