additions to norbornene[5d] and for the development of molecular mechanics force fields for the study of regioselectivity.[5c] It would be desirable to ascertain if the MP2 geometries give significantly different results.

We also investigated a new structure **3** for the complex of borane and ethylene, in which the unique B–H is perpendicular rather than parallel to the C–C double bond (Figure 2). Indeed, **3** is the only minimum for the complex at the RHF level (the B–H parallel form, studied by earlier investigators,[5,6] is a transition structure at RHF; see Figure 3). However, **3** is a transition structure when optimized at MP2. The imaginary vibration corresponds to rotation of the BH_3 unit; the reaction path then leads directly to ethylborane.[6] Hence, complex **3** represents the transition structure for degenerate rearrangement of ethylborane, $H_2BCH_2CH_3 \rightleftarrows$ **3** $\rightleftarrows CH_3CH_2BH_2$. The three-center bonding in transition structure **3** is characterized by a substantial π-donation, 0.252 e, from ethylene to boron and by C–B and C–C bond indexes comparable to those found in the transition structure for addition, **2b** (Table III). Such intramolecular boron migrations occur stereospecifically, as was found experimentally, e.g., with cyclic substrates under mild reaction conditions.[11] At higher temperatures, mixtures are obtained, as expected from Brown's alternative dehydroboration/hydroboration mechanism.[2] Our results agree nicely. We calculate the migration barrier (ΔE_a) in ethylborane to be 23 kcal/mol (MP4SDTQ/6-31G**//MP2/6-31G**), whereas dissociation into ethylene and borane requires 31.5 kcal/mol. The latter process, however, is favored by entropy. For this model reaction, we calculate the free energies of activation to be nearly equal at 300 K, 22.5 kcal/mol. The dissociation mechanism prevails at higher temperatures, while intramolecular rearrangement is favored below this temperature.

Note Added in Proof. After this note was submitted, we located the TS for reaction of borane and ethylene at the RQCISD/6-31G** level, which also exhibits three-center character. The activation barrier, relative to the π-complex, is 0.05 kcal/mol at RQCISD(T)/6-311+G**//RQCISD/6-31G**.

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Facile One-Pot Amidation of Carboxylic Acids by Amines Catalyzed by Triphenylstibine Oxide/Tetraphosphorus Decasulfide (Ph_3SbO/P_4S_{10})

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Although thiocarboxylic acids are useful acylating reagents for the synthesis of amides and peptides,[1,2] their popularity is markedly lower than that of acyl chlorides, anhydrides, and such active esters as thiol esters.[3] This has much to do with their limited availability,[4] higher susceptibility to autoxidation,[5] and unpleasant odor. In our continuing studies on the utilization of organoantimony compounds in organic synthesis, triphenylstibine oxide (Ph_3SbO) was found to catalyze several condensation reactions,[6] including the aminolysis of thiocarboxylic acids by amines to give amides.[2] It was also found that, in the presence of tetraphosphorus decasulfide (P_4S_{10}), Ph_3SbO accelerated the thiolation of carboxylic acids to the corresponding thiocarboxylic acids **4**.[7] Thus, we deduced that

Scheme I

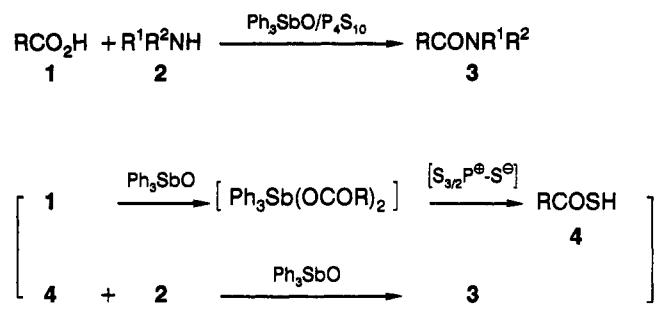

Table I. Ph_3SbO/P_4S_{10}-Catalyzed Amidation of Carboxylic Acids[a]

amides	method[c]	T (°C)	t (h)	yields[b] (%)
AcNH-*n*-Hex[d]	A	40	5	90
	A[e]	80	12	0
	A[f]	80	12	0
	A[g]	80	24	0
AcNH-*t*-Bu	A	40	6	80
$AcNEt_2$	A	60	12	75
AcNHPh	A	60	5	69
$AcNHCH_2CH_2OH$	B	50	1	95[h]
$AcNHCH_2CH{=}CH_2$	B	40	0.5	90[h]
$Cl_2CHCONHPr$	A[i]	60	8	96
$CH_2{=}CHCONH$-*i*-Pr	A	50	6	56
t-BuCONH-*t*-Bu	B	80	12	88[h]
t-BuCONHPh	A	80	5	87
$(CH_2CH_2CO)_2(NHPr)_2$	A	80	6	65
BzNH-*t*-Bu	A	80	24	65
BzNHPh	A	80	5	75
Z-Gly-Gly-OEt	C	30	0.5	83
Z-Phe-Leu-OEt	C	30	2	75
Z-Leu-Phe-OMe	C	30	2	73
Z-Ser-Gly-OEt	C	30	2	71
Z-Tyr-Gly-OEt	C	30	2	79

[a] Reaction conditions: $1/2/Ph_3SbO/P_4S_{10}$ = 5/5/0.25/0.75; 20 mL of solvent. [b] Isolated yield. [c] Details of methods A, B, and C are given in the Experimental Section. [d] *n*-Hex denotes *n*-C_6H_{13}. [e] No P_4S_{10} was present. [f] No Ph_3SbO was present. [g] Neither Ph_3SbO nor P_4S_{10} was present. [h] Yield based on 1. [i] $CHCl_3$ was the solvent.

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the use of a combination of the two catalysts would permit the one-pot amidation of carboxylic acids (Scheme I), thereby obviating the previously mentioned disadvantages of thiocarboxylic acids.

Results and Discussion

The Ph_3SbO/P_4S_{10}-catalyzed amidation of acetic acid by hexylamine at 40 °C for 5 h gave hexylacetamide in almost quantitative yield. In contrast, no amidation occurred in the absence of either Ph_3SbO, P_4S_{10}, or a combination of the two below 80 °C, even after prolonged reaction time. Thus, it was apparent that Ph_3SbO and P_4S_{10} synergistically promoted the amidation under mild conditions. Amidation was also attempted using dibutyltin oxide or bis(tributyltin) oxide in place of Ph_3SbO. However, neither promoted the reaction at 40 °C.

Several amides **3** were prepared by the Ph_3SbO/P_4S_{10}-catalyzed reaction of carboxylic acids **1** and amines **2**. Typical results are summarized in Table I. Simple aliphatic and aromatic amides were obtained in good yield under mild conditions. With an increase in steric congestion at both the C- and N-terminals of **3**, severe conditions were required to obtain good yields. For example, a higher reaction temperature (80 °C) and the use of a large excess of **2** were necessary to prepare *t*-BuCONH-*t*-Bu. Amidation by ethanolamine or allylamine was achieved by using an excess of **2**. The corresponding **3** were obtained in quantitative yields and without any O-acylation (in the case of ethanolamine) or addition to the C=C (in the case of allylamine). In contrast, the acylation of ethanolamine by acyl chlorides sometimes gave both N- and O-acylated products. These results indicated that the reactivities of the thiol carboxylic acids prepared in situ were perhaps lower than those of acyl chlorides and about equal to those of anhydrides. The catalyst also strongly promoted the coupling of N-protected amino acids with amino acid esters. Dipeptides possessing only alkyl side chains, like Z-Gly-Gly-OEt, Z-Phe-Leu-OEt, and Z-Leu-Phe-OMe, were readily obtained without racemization in CH_2Cl_2 solution at 30 °C. Furthermore, the catalyst displayed efficiency sufficient to amidate hydroxylated dipeptides like Z-Ser-Gly-OEt and Z-Tyr-Gly-OEt. It should be noted that the catalyst could also be applied to the preparation of diamides of adipic acid.

The Ph_3SbO/P_4S_{10}-catalyzed amidation apparently involves two successive reactions: (1) the Ph_3SbO-catalyzed thiolation of **1** by P_4S_{10}[7a] and (2) the aminolysis of **4**[7b] thus generated in situ. ^{13}C and ^{31}P NMR analysis of the reaction of acetic acid and hexylamine in C_6D_6 supported this interpretation. As the reaction proceeded, the ^{13}C NMR spectrum showed a gradual increase in the intensity of the signal due to thiolacetic acid (δ $^{13}COSH$ = 194.5 ppm) that was accompanied by a decrease in that of the signal due to acetic acid (δ $^{13}COOH$ = 175.5 ppm). Then, the signal due to thiolacetic acid gradually disappeared as the signal due to the amide (δ $^{13}CONH-$ = 171.6 ppm) gradually appeared. In the ^{31}P NMR spectrum, as the reaction progressed, the signal due to $^{31}P_4S_{10}$ (δ 57.6[8] relative to 85% D_2PO_4 in D_2O) disappeared as new broad signals appeared at δ 0, 3, and −10. The latter signals could be due to phosphoric acid and partially sulfurated phosphoric acids, resulting from decomposition of P_4S_{10} in the thiolation step.

The accelerative effect of Ph_3SbO on the thiolation step is attributed to the high reactivity of the triphenylantimony dicarboxylate that was generated in situ by the spontaneous condensation of Ph_3SbO with the carboxylic acid[6a,9] toward nucleophilic attack by $S_{3/2}P^+-S^-$.[7a] Although P_4S_{10} is known to be a particularly effective agent for the sulfuration of carbonyl compounds,[10] its low reactivity at low temperatures has prevented its wide application in organic synthesis. For example, the reaction of carboxylic acids with amines in the presence of P_4S_{10}, but in the absence of Ph_3SbO, must be performed above 100 °C. Only thioamides are produced.[11a] This indicates that thionation predominates at such high temperatures. Lawesson's reagent as well gives mainly thionated products.[12] Consequently, it is the high catalytic activity displayed by Ph_3SbO in the thiolation of carboxylic acids by P_4S_{10} that is responsible for the success of this simple one-pot amidation process, which occurs without thionation.

Experimental Section

General Procedures. Melting and boiling points are uncorrected. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with a Hitachi R90H FT spectrometer. IR spectra were recorded with a Hitachi 260-30 spectrophotometer. Mass spectra were recorded with a JEOL JMS-DX303 (Faculty of Engineering, Osaka University). Optical rotations were measured with a JASCO DIP-181 digital polarimeter. Triphenylstibine oxide (Ph_3SbO) was prepared by H_2O_2 oxidation of triphenylstibine[13] (Sankyo Synthetic Chemicals Co., Ltd., Tokyo). Tetraphosphorus decasulfide (P_4S_{10}) (Wako, extra pure grade) was purified further by Soxhlet extraction with CS_2.[14] Other reagents and solvents were used after distillation or recrystallization. All the amides and dipeptides that were prepared gave satisfactory mass spectra and elemental analyses.

Ph_3SbO-Catalyzed Reaction of Thioacetic Acid with Diethylamine. *N,N*-Diethylacetamide ($AcNEt_2$). Thioacetic acid (5 mmol, 381 mg) was added drop-by-drop to an ice-cooled mixture of Et_2NH (5 mmol, 366 mg), Ph_3SbO (0.1 mmol, 37 mg), and benzene (5 mL). The mixture was stirred at 20 °C for 8 h. After the reaction was complete, the solid Ph_3SbO and the sulfur that was produced were removed by filtration. Evaporation of the solvent from the filtrate gave a colorless oil. Vacuum distillation gave the pure amide (yield 432 mg, 75%). When the reaction was performed in the absence of Ph_3SbO, after 24 h a 34% yield of the amide was obtained: colorless liquid; bp 94 °C (4 kPa) [lit.[15] bp 90.1–91 °C (4 kPa)].

Amidation Method A. *n*-Hexylacetamide (AcNHHex). A mixture of HOAc (5 mmol, 300 mg), Ph_3SbO (0.25 mmol, 92 mg), P_4S_{10} (0.75 mmol, 333 mg), and benzene (20 mL) was stirred at 40 °C for 1 h, during which time the solid Ph_3SbO dissolved. *n*-Hexylamine (5 mmol, 506 mg) was then slowly added with cooling. The mixture was stirred at 40 °C for 5 h. During the reaction, the solid P_4S_{10} gradually turned into a yellowish gummy solid. After the residual P_4S_{10} was removed by filtration, the filtrate was evaporated in vacuo to yield a yellowish oil. Kugelrohr vacuum distillation gave a colorless oil (yield 645 mg, 90%): bp

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106 °C (0.7 kPa) [lit.[16] bp 156 °C (2.1 kPa)]. Similarly, the following eight amides and *N,N*-diethylacetamide were obtained from the reactions of the corresponding carboxylic acids and amines. Solid amides were recrystallized from EtOAc/hexane. **N-Propyldichloroacetamide ($Cl_2CHCONHPr$)**: bp 67 °C (0.8 kPa); IR (KRS-5) 1700 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (br, 1 H, N*H*), 4.60 (s, 1 H, CCl_2H), 4.03 (t, 2 H, J = 6.0 Hz, NCH_2), 1.80 (sextet, 2 H, CH_2), 0.91 (t, 3 H, J = 6.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 185.3 (s, *C*=O), 68.7 (d, CCl_2H), 47.7 (t, NCH_2), 20.7 (t, CH_2), 11.2 (q, CH_3); MS m/z 169 (M^+, ^{35}Cl). Anal. Calcd for $C_5H_9Cl_2NO$: C, 35.32; H, 5.33; Cl, 41.70; N, 8.24. Found: C, 35.02; H, 5.43; Cl, 42.01; N, 8.23. **N-tert-Butylacetamide (AcNH-*t*-Bu)**: mp 95–96 °C (lit.[17] mp 97–98 °C). **Acetanilide (AcNHPh)**: mp 115 °C (lit.[18] mp 115 °C). **N-Isopropylacrylamide (CH_2=CHCONH-*i*-Pr)**: mp 63–64 °C [lit.[19] mp 110–115 °C (2.0 kPa)]; IR (KBr) 1650 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.07 (d, 2 H, J = 6.4 Hz, $=CH_2$), 5.53 (t, 1 H, C*H*=), 5.20 (br, 1 H, N*H*), 3.26 (septet, 1 H, C*H*), 1.21 (d, 6 H, J = 6.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 172.3 (s, *C*=O), 134.1 (t, $=CH_2$), 128.6 (d, =*C*H), 43.4 (d, *C*H), 20.8 (q, CH_3); MS m/z 113 (M^+). Anal. Calcd for $C_6H_{11}NO$: C, 63.69; H, 9.80; N, 12.38. Found: C, 63.72; H, 9.82; N, 12.44. **N,N'-Dipropyladipoamide ($(CH_2CH_2CO)_2(NHPr)_2$)**: mp 164 °C (lit.[20] mp 164 °C). **N-tert-Butylbenzamide (BzNH-*t*-Bu)**: mp 133–134 °C; IR (KBr) 1630 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–7.7 (m, 5 H, aromatic *H*), 5.9 (br, 1 H, N*H*), 1.46 (s, 9 H, CH_3); ^{13} NMR ($CDCl_3$) δ 166.4 (s, *C*=O), 135.1 (s, ipso), 131.0 (d), 128.3 (d), 126.7 (d), 51.6 (s), 28.9 (q); MS m/z 177 (M^+). Anal. Calcd for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found C, 74.49; H, 8.52; N, 7.90. **N-Phenyltrimethylacetamide (*t*-BuCONHPh)**: mp 130–131 °C (lit.[21] mp 132.5–133 °C). **Benzanilide (BzNHPh)**: mp 159–161 °C (lit.[22] mp 164–165 °C).

Amidation Method B. N-(2-Hydroxyethyl)acetamide ($AcNHCH_2CH_2OH$). To a mixture of Ph_3SbO (0.25 mmol), P_4S_{10} (0.75 mmol), and ethanolamine (20 mmol, 1.22 g) was added acetic acid (5 mmol) drop-by-drop with stirring and cooling. The mixture was then stirred at 50 °C for 1 h. After evaporation of excess ethanolamine in vacuo, workup similar to that described previously gave a slightly yellow viscous oil (yield 450 mg, 95%): bp 151 °C (0.7 kPa); IR (KRS-5) 1622 (amide C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.86 (s, 1 H, N*H*), 3.85 (br, 1 H, O*H*), 3.69 (t, 2 H, J = 5.2 Hz, CH_2OH), 3.39 (t, 2 *H*, CH_2NH), 2.01 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 171.1 (s, *C*=O), 60.5 (t, *C*H_2OH), 41.8 (t, *C*H_2NH), 22.4 (q, CH_3); MS m/z 103 (M^+). Anal. Calcd for $C_4H_9NO_2$: C, 46.59; H, 8.80; N, 13.58. Found: C, 46.60; H, 8.80; N, 13.57. **N-Propenylacetamide ($AcNHCH_2CH$=CH_2)**: bp 90 °C (0.7 kPa) [lit.[23] bp 130–131 °C (2.1 kPa)]. **N-tert-Butyltrimethylacetamide (*t*-BuCONH-*t*-Bu)**: bp 117–118 °C (0.7 kPa); IR (KBr) 1640 (amide (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.4 (br, 1 H, N*H*), 1.34 (s, 9 H, CH_3), 1.15 (s, 9 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 177.5 (s, *C*=O), 50.6 (s, $(CH_3)_3CN$), 38.9 (s, $(CH_3)_3CC$), 28.7 (q, $(CH_3)_3CN$), 27.7 (q, $(CH_3)_3CC$); MS m/z 157 (M^+). Anal. Calcd for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.68; H, 12.20; N, 8.89.

Dipeptide Synthesis (Method C). Z-Glycylglycine Ethyl Ester (Z-Gly-Gly-OEt). To a solution of Z-glycine (5 mmol, 1.05 g) in CH_2Cl_2 (10 mL) were slowly added, in order, Ph_3SbO (0.25 mmol, 92 mg), P_4S_{10} (1 mmol, 444 mg), and a solution of glycine ethyl ester hydrochloride (5 mmol, 698 mg) and Et_3N (5 mmol, 506 mg) in CH_2Cl_2 (10 mL). The mixture was stirred at 30 °C for 0.5 h. Workup was done with the general ethyl acetate extraction followed by washing with aqueous citric acid and neutralization. The dipeptide was then recrystallized from EtOAc/hexane: mp 81 °C (lit.[24] mp 80–81 °C). **Z-Phenylalanylleucine ethyl ester (Z-Phe-Leu-OEt)**: mp 102–103 °C (lit.[25] mp 110–111 °C); $[\alpha]^{20}_D$ -23.9° (*c* 1.0, EtOH) (lit.[25] $[\alpha]^{20}_D$ -24.7° (*c* 1.0, EtOH)). **Z-Leucylphenylalanine methyl ester (Z-Leu-Phe-OMe)**: mp 79–90 °C (lit.[26] mp 79–80 °C); $[\alpha]^{20}_D$ -19.2° (*c* 2.0, MeOH) $[\alpha]^{20}_D$ -19.3° (*c* 2.0, MeOH)). **Z-Serylglycine ethyl ester (Z-Ser-Gly-OEt)**: mp 105–107 °C; (lit.[25] mp 106–107 °C); $[\alpha]^{20}_D$ -5.8° (*c* 1.0, EtOH) (lit.[25] $[\alpha]^{20}_D$ -5.9° (*c* 1.0 EtOH)). **Z-Tyrocylglycine ethyl ester (Z-Tyr-Gly-OEt)**: mp 168–170 °C (lit.[27] mp 168–170 °C); $[\alpha]^{20}_D$ -23.5° (*c* 5.0, DMF) (lit.[27] $[\alpha]^{20}_D$ -23.6° (*c* 5.0, DMF)).

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Synthesis of Strained Aromatic Polycyclic Compounds via the Reaction of Arynes with Enolates of Cyclic Ketones

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The synthesis and characterization of polyphenylene derivatives continue to be topics of interest.[1] However, new partially hydrogenated polyphenylenes are only infrequently described in the literature. The latter compounds would be expected to interact with DNA or RNA.[2] Knowledge of such behavior would be useful for the design of new antitumor or antiviral agents.[3]

As a continuation of a program directed toward the synthesis of polycyclic benzocyclobutene derivatives and the study of their chemical and biological properties,[4] we sought to develop a new route to benzocyclobutabiphenylenes. Here, we report a new and convenient synthesis of such compounds. We also report some of their chemical properties.

Results and Discussion

A series of hexahydrobenzocyclobutabiphenylenes was obtained by the pathways shown in Scheme I.

When the complex base $NaNH_2$/*t*-BuONa[5] was replaced by $NaNH_2$, the attempted condensation of benzyne and the enolate **6** was unsuccessful. As previously reported,[6] this failure was probably due to the fact that **6** is not a good activating agent[7] for $NaNH_2$. It should also be noted that only the thermodynamically more stable of the two possible enolates of **7** was formed. It was reported[8] that complex bases favor such enolization.

The assigned structures of **5** and **8** were consistent with their IR, UV, ^1H NMR, and ^{13}C NMR spectra. The stereochemistry of **8** (Z = H) was deduced from the

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