(q, 4 H, $N(CH_2CH_3)_2$), 4.22 (q, 2 H), 4.48 (q, 2 H).

Anal. Calcd for $C_{12}H_{20}N_2O_5S$: C, 47.35; H, 6.62; N, 9.21. Found: C, 47.26; H, 6.63; N, 9.20.

3-Ethoxy-5-(ethoxycarbonyl)-4-(methylamino)isothiazole 1,1-Dioxide (7c). To a solution of compound **6b** (1.61 g, 6.0 mmol) in 10 mL of CH_2Cl_2 was added dropwise a solution of methylamine in THF (5.77 mL, 2.6 M, 15 mmol) at such a rate that the temperature remained at 30–35 °C. After stirring for 30 min, the mixture was filtered and the filtrate concentrated in vacuo. Chromatography of the residue on Merck silica gel, eluting with CH_2Cl_2, gave 110 mg (7%) of recovered **6b**. Elution with 1% EtOH, followed by 2%, and then 5% EtOH in CH_2Cl_2 gave 930 mg (59%) of crude 7c. Recrystallization from EtOAc gave analytically pure material, mp 183–185 °C; ^1H NMR (Varian T-60, $CDCl_3$) δ 1.38 (t, 3 H), 1.5 (t, 3 H), 3.35 (d, 3 H), 4.40 (q, 2 H), 4.70 (q, 2 H), 7.95 (br s, 1 H).

Anal. Calcd for $C_9H_{14}N_2O_5S$: C, 41.21; H, 5.38; N, 10.68. Found: C, 40.91; H, 5.41; N, 10.67.

3,4-Diamino-5-(ethoxycarbonyl)isothiazole 1,1-Dioxide (8a). The 3,4-diethoxy compound **6c** (1.0 g, 3.6 mmol) dissolved in 60 mL of dry THF was stirred in an ice bath while a solution containing NH_3 in THF (7.7 mL, 0.465 M, 3.6 mmol) was added. A TLC (silica GF, 95:5 $CHCl_3$–EtOH) inspection of the reaction solution after 30 min at 0 °C showed that all of **6c** had reacted to give compound **7a**, with a trace of a second, more polar product. Addition of a second equivalent (7.7 mL, 0.465 M, 3.6 mmol) of NH_3 resulted in formation of a white precipitate after 30 min at ambient temperature. TLC showed the reaction mixture to contain only the lower R_f material seen previously as a minor spot. The white solid was collected by filtration and washed with ether to give **8a**, 560 mg (71%), mp 259–265 °C dec. This material analyzed correctly without further purification. ^1H NMR (Me_2SO-d_6) δ 1.27 (t, 3 H), 4.25 (q, 2 H), 8.20 (br s, 4 H exchanged with D_2O). A potentiometric titration in 30% aqueous EtOH with NaOH gave pK_a = 9.60 (proton lost).

Anal. Calcd for $C_6H_9N_3O_4S$: C, 32.88; H, 4.14; N, 19.17. Found: C, 32.99; H, 4.25; N, 19.01.

3-Amino-4-(diethylamino)-5-(ethoxycarbonyl)isothiazole 1,1-Dioxide (8b). To a solution of compound **7b** (300 mg, 1 mmol) in 10 mL of dry THF was added NH_3 in THF (4.3 mL, 0.465 M, 2 mmol). The solution was stirred at room temperature overnight. TLC (silica GF, 9:1 $CHCl_3$–EtOH) revealed two products at R_f 0.48 (major) and R_f 0.30 (minor). Evaporation of the solvent followed by trituration with absolute EtOH gave 180 mg (65%) of a yellow solid that contained the two components indicated previously. The minor component, at R_f 0.30, was shown to have the same R_f and was not separable from a mixture with the 3,4-diamino compound **8a**. Flash chromatography of the crude solid (Merck silica gel, 230–400 mesh), eluting with a 9:1 $CHCl_3$–EtOH mixture, afforded TLC pure **8b** (140 mg). Recrystallization from THF-ether gave analytically pure material, mp 175–177 °C dec; ^1H NMR ($CDCl_3$) δ 1.1–1.45 (m, 9 H), 3.48 (q, 4 H), 4.37 (q, 2 H), 6.70 (br s, 2 H). A potentiometric titration in water with NaOH gave pK_a = 9.15 (proton lost).

Anal. Calcd for $C_{10}H_{17}N_3O_4S$: C, 43.62; H, 6.22; N, 15.26. Found: C, 43.78; H, 6.54; N, 15.20.

Acknowledgment. We thank Dr. W. C. Randall for least-squares regression analysis of the ^{13}C CNDO data and generation of computer plots, Ms. Joan Murphy for ^1H NMR spectra, Mr. Yung Lee for potentiometric titrations, Mr. John Moreau for elemental analysis, and Ms. Thelma Brunner for manuscript preparation.

Registry No. 4 (R = CO_2Et), 55897-04-6; **5a**, 84538-31-8; **5b**, 84538-32-9; **6b**, 84538-33-0; **6c**, 84538-34-1; **7a**, 84538-35-2; **7b**, 84538-36-3; **7c**, 84538-37-4; **8a**, 84538-38-5; **8b**, 84538-39-6; ethyl oxalyl chloride, 4755-77-5; ethyl *N*-(methylsulfonyl)oxamate, 84538-30-7; (ethoxycarbonyl)methanesulfonyl chloride, 55896-93-0; methanesulfonamide, 3144-09-0; diethyl oxalate, 95-92-1.

Supplementary Material Available: Tables II–IV containing atomic coordinates, thermal parameters, bond lengths and bond angles (3 pages). Ordering information is given on any current masthead page.

Preparation of 4-Substituted Arsabenzenes[1]

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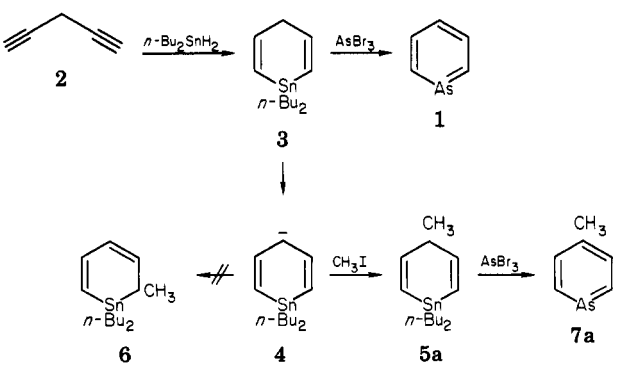
Alkylation of lithium 1,1-dibutylstannacyclohexadienide with primary alkyl halides gives the corresponding 4-alkyl-1,1-dibutylstannacyclohexa-2,5-dienes, which on treatment with arsenic tribromide afford 4-substituted arsabenzenes.

In 1971 we reported the synthesis of the new heteroaromatic arsabenzene.[2] Work in the past decade has indicated that arsabenzene is electronically, structurally, and chemically very similar to carbocyclic aromatics.[3] Thus, it is not unreasonable to hope that suitable derivatives of arsabenzene might display some of the biological activity of the corresponding carbocyclic aromatics. In order to explore this possibility, we sought to prepare arsabenzenes substituted with manipulatively useful functional groups. We now report on a general synthesis of 4-substituted arsabenzenes and its application to the preparation of arsabenzene analogues of β-phenethylamines.

Scheme I



Arsabenzene (1) itself is easily prepared by a two-step synthesis.[2] 1,4-Pentadiyne (2) may be hydrostannated with

(1) Based in part on the Ph.D. Thesis of S. T. A.-O., The University of Michigan, 1982.

(2) Ashe, A. J., III. *J. Am. Chem. Soc.* **1971**, *93*, 3293.

(3) For reviews of the chemistry of arsabenzene, see: (a) Märkl, G. *Phosphorus Sulfur* **1977**, *3*, 77. (b) Jongsma, C.; Bickelhaupt, F. *Top. NonBenzenoid Aromat. Chem.* **1977**, *2*, 139. (c) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232. (d) Ashe, A. J., III. *Acc. Chem. Res.* **1978**, *11*, 153. (e) Tzschach, A.; Heinicke, J. "Arsenheterocyclen"; VEB Deutscher Verlag für Grundstoffindustrie: Leipzig, 1978; pp 124–130, 135–138. (f) Ashe, A. J., III. *Top. Curr. Chem.* **1982**, *105*, 125.

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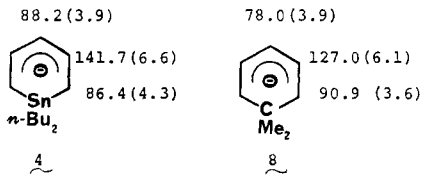


4 8

Figure 1. ^{13}C NMR and H NMR (in parentheses) chemical shift values for the ring carbon and hydrogen atoms of **4** and **8** (after ref 13).

dibutyltin dihydride to give 1,1-dibutylstannacyclohexa-2,5-diene (**3**)[4] which is readily converted to arsabenzene by treatment with arsenic trihalides (Scheme I). By use of substituted 1,4-diynes in place of **2**, 2- and 4-functionalized arsabenzenes have been prepared.[5-7]

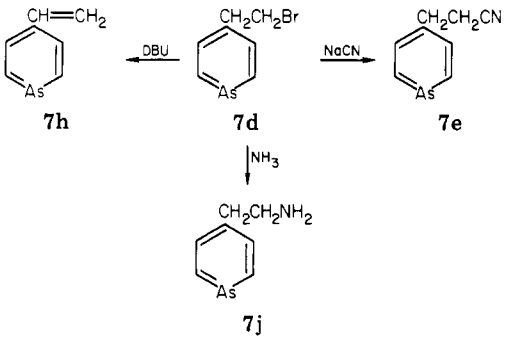
4-Alkylarsabenzenes have also been prepared by direct functionalization of **3**.[8,9] Thus, treating **3** with lithium diisopropylamide in THF gives a red solution of the lithium stannacyclohexadienide **4**. The reaction of **4** with methyl iodide affords a 65% yield of 1,1-dibutyl-4-methylstannacyclohexa-2,5-diene (**5a**) uncontaminated with its 2-methyl regioisomer **6**.[8,10] Stannacyclohexadiene **5a** is readily converted to the corresponding 4-methylarsabenzene (**7a**).[6a] In view of the number of available alkylating agents, this method offers the potential to prepare a large variety of substituted arsabenzenes.

Results and Discussion

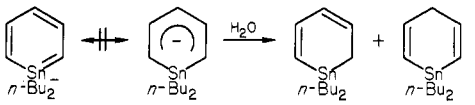
Initially we felt it prudent to examine the properties of lithium stannacyclohexadienide **4**. Treating a cold THF-d_8 solution of **3** with either *tert*-butyllithium in pentane or LDA in hexane/THF immediately afforded an orange-green solution of anion **4**. Signals for the ring protons and carbon atoms of **4** were easily observed in the ^1H and ^{13}C NMR spectra, although the upfield signals for the *n*-butyl groups were obscured by excess alkane. Chemical shift data are summarized in Figure 1.

The chemical shift values of the ring protons and carbon atoms of **4** are rather typical of those shown by pentadienyl anions.[11] That is, the uncharged carbons (C_3, C_5) and the attached protons show chemical shifts which are nearly the same as those in the precursor olefin **3**[12] while C_2, C_4, C_6, and their attached protons are shifted substantially upfield. In fact, the NMR spectra of **4** are very similar to those reported for the corresponding lithium 6,6-dimethylcyclohexadienide (**8**).[13] This strongly suggests a similar electronic structure for both anions. Hypervalent resonance structures analogous to **9** which have been suggested for silacyclohexadienide anions[14,15] are not likely to be important resonance contributions to **4**.

Scheme II



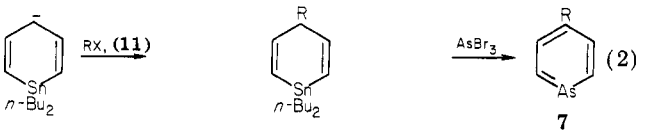
Quenching anion **4** with water affords a 1:4 mixture of **3** with its conjugated isomer **10** (eq 1) in poor yield. In all



(1)

cases we have examined, reaction of **4** with alkyl halides affords exclusively isomer **5**. Most likely the two pendant butyl groups stericly block alkylation at the 2-position.[16]

Stannacyclohexadienide **4** may be alkylated with a variety of primary alkyl halides bearing pendant functionality. For example, quenching the anion with excess ethyl bromoacetate (**11b**) gave a 78% yield of 4-[(ethoxycarbonyl)methyl]-1,1-dibutylstannacyclohexa-2,5-diene (**5b**, eq 2), which on treatment with arsenic tribromide in



(2)

5b, R = $CH_2CO_2C_2H_5$
c, R = CH_2CN
d, R = CH_2CH_2Br
e, R = CH_2CH_2CN
f, R = $CH_2CH_2CO_2C_2H_5$
g, R = $CH_2CHBrCH_3$

THF afforded 68% of 4-[(ethoxycarbonyl)methyl]arsabenzene **7b**. In the same manner, halides **11c–g** gave the corresponding 4-substituted arsabenzenes **7** with an average yield of 50%. As had previously been noted for other 4-substituted heterobenzenes, these compounds are considerably less labile than the parent compound.[10]

The pendant functionality of **7d–g** could be manipulated by standard methods of organic chemistry. Bromide **7d** readily underwent substitution and elimination reactions. In situ treatment of **5d** with arsenic tribromide followed by DBU afforded a good yield of 4-vinylarsabenzene (**7h**, Scheme II). Reaction of **7d** with sodium cyanide gave **7e** which on hydrolysis and esterification gave **7f**. Bromide **7d** reacted with ammonia in methanol to afford the 4-arsabenzene analogue of β-phenethylamine (**7j**). However, the similar reaction of bromide **7g** gave only the elimination product.

We had hoped to convert ester **7f** to amino acid derivative **15** via bromide **13**. The synthesis of **13** appeared to offer difficulties since the arsabenzene ring is destroyed under electrophilic brominating conditions[17] and is sen-

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(7) Märkl, G.; Kneidl, F. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 931; **1974**, *13*, 667, 668. Märkl, G.; Kellerer, H.; Kneidl, F. *Tetrahedron Lett.* **1975**, 2411; Märkl, G.; Kellerer, H. *Ibid.* **1976**, 665. Märkl, G.; Advena, J.; Hauptmann, H. *Ibid.* **1974**, 203.
(8) Smith, T. W. Ph.D. Thesis, The University of Michigan, 1977.
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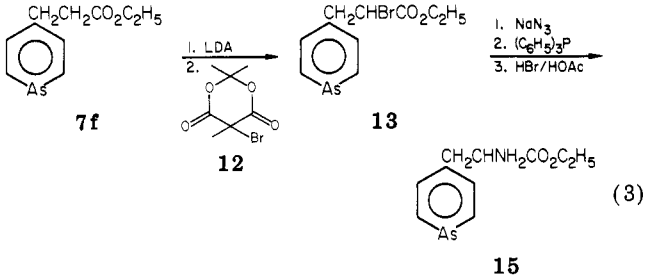
(10) Ashe, A. J., III; Diephouse, T. W.; El-Sheikh, M. Y. *J. Am. Chem. Soc.* **1982**, *104*, 5693.
(11) Olah, G. A.; Asensio, G.; Mayr, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 4347.
(12) Compound **2** shows the following: ^1H NMR δ 6.10 (H_2), 6.60 (H_3); ^{13}C NMR δ 125.9 (C_2), 144.9 (C_3).
(13) Bates, R. B.; Brenner, S.; Cole, C. M.; Davidson, E. W.; Forsythe, G. D.; McCombs, D. A.; Roth, A. S. *J. Am. Chem. Soc.* **1973**, *95*, 926. Bates, R. G.; Gosselink, D. W.; Kaczynski, J. A. *Tetrahedron Lett.* **1967**, 205.
(14) Jutzi, P. *J. Organomet. Chem.* **1970**, *22*, 297.
(15) However, see: Bickelhaupt, F.; Van Mourik, G. L. *J. Organomet. Chem.* **1974**, *67*, 389.
(16) It could also be argued that C_2-alkylated products were formed but did not survive the workup.
(17) Ashe, A. J., III; Chan, W.-T.; Smith, T. W.; Taba, K. M. *J. Org. Chem.* **1981**, *46*, 881.

sitive to strong bases.[18,19] However, the reaction of **7b** with lithium diisopropylamide followed by quenching with Meldrum's acid derivative **12**[20] gave **13** in 55% yield.

Bromo ester **13** did not readily react with ammonia in CCl_4. An indirect procedure based on a modification of Horner's phenylalanine preparation was more satisfactory.[21] The reaction of **13** with sodium azide in ethanol afforded the corresponding azide, which on treatment with triphenylphosphine followed by hydrolysis with HBr in acetic acid gave ethyl ester **15** (eq 3). The nonaromatic



(3)

portion of the ^1H NMR spectrum of **15** was virtually identical with that of phenylalanine ethyl ester **16**, while the mass spectral fragmentations of **15** and **16** were very similar.

In summary, chemical transformations of the functionality of substituted arsabenzenes can take place without disrupting the arsabenzene ring. This observation emphasizes the robustness of this new aromatic system.

Experimental Section

The NMR spectra were recorded by using either a Varian T60A, a JOEL JNMPS 100 PFT, or a Bruker WH-360 spectrometer. Chemical shifts are reported to the nearest 0.1 ppm for routine T60A spectra and to 0.01 ppm for higher field spectra. Coupling constants are reported to the nearest 0.5 Hz. Mass spectra data were obtained by using a Finnigan 4021 GC/MS instrument operating at an ionizing voltage of 70 eV. C and H combustion analyses were obtained on new compounds by Spang Microanalytical Laboratory or Galbraith Laboratories. In all cases analyses agreed with calculated values (±0.4%). Infrared spectra (IR) were obtained with a Beckman 4240 spectrometer and were calibrated by using the 1601.4-cm^{-1} absorption of polystyrene. GLC analyses and separations were performed by using a Varian 90P or an Antek 300 chromatograph equipped with thermal-conductivity detectors. No corrections were made for the different thermal conductivities of different compounds. All operations were performed under argon or nitrogen.

Alkylation Reactions of 1,1-Dibutylstannacyclohexa-2,5-diene. A solution of lithium diisopropylamide was prepared by treating 3.0 g (30 mmol) of diisopropylamine in 50 mL of tetrahydrofuran with 7.4 mL (17 mmol) of 2.3 N butyllithium in hexane. This solution was added dropwise at −78 °C to a solution of 5.0 g (16.7 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene[4] in 150 mL of tetrahydrofuran. On addition, the solution turned dark orange and then green. After warming to 0 °C, the solution of lithium 1,1-dibutylstannacyclohexadienide was added to a solution of an excess of the appropriate alkyl halide in 50 mL of tetrahydrofuran. The reaction mixture was allowed to warm to 25 °C with stirring for 1 h, after which it was added to 300 mL of water. The organic layer was separated, while the aqueous layer was exracted with 100 mL of hexane. The combined organic fractions were washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent and excess base, the residue was distilled.

(a) In this manner chloroacetonitrile gave 3.3 g (59%) of 1,1-dibutyl-4-(cyanomethyl)stannacyclohexa-2,5-diene (**5c**): bp 115–120 °C (0.001 torr); ^1H NMR ($CDCl_3$) δ 0.85–1.65 (m, 18 H), 2.50 (d, J = 6 Hz, 2 H), 3.30 (m, 1 H), 5.6–6.70 (m, 4 H); IR (CCl_4) 2260 cm^{-1}; MS (70 eV), m/e 339 (M^+ for $C_{15}H_{25}N^{120}Sn$). Anal. Calcd for $C_{15}H_{25}NSn$: C, 53.29; H, 7.45; N, 4.14. Found: C, 53.17; H, 7.42; N, 4.03.

(b) In the same manner ethyl bromoacetate gave 4.6 g (78%) of 1,1-dibutyl-4-(carbethoxymethyl)-1-stannacyclohexa-2,5-diene (**5b**): bp 115–123 °C (0.001 torr); IR (CCl_4) 1735 cm^{-1}; MS (70 eV), m/e 329 ($M^+ - C_4H_9$). Anal. Calcd for $C_{17}H_{30}O_2Sn$: C, 53.02; H, 7.85. Found: C, 53.25; H, 7.71.

(c) In the same manner 1,2-dibromoethane gave 2.8 g (41%) of 1,1-dibutyl-4-(β-bromoethyl)-1-stannacyclohexa-2,5-diene (**7d**). This material showed an identical ^1H NMR spectrum with that reported by Jutzi and Baumgärtner.[9]

(d) In the same manner 3-bromopropionitrile gave 2.8 g (48%) of 1,1-dibutyl-4-(β-cyanoethyl)stannacyclohexa-2,5-diene (**5e**): bp 125–132 °C (0.001 torr); ^1H NMR ($CDCl_3$) δ 0.85–1.60 (m, 18 H), 1.80–2.40 (m, 4 H), 3.20 (m, 1 H), 5.60–6.60 (m, 4 H); IR (CCl_4) 2260 cm^{-1}; MS (70 eV), m/e 296 ($M^+ - C_4H_9$). Anal. Calcd for $C_{16}H_{27}NSn$: C, 54.58; H, 7.73; N, 3.98. Found: C, 54.52; H, 7.72; N, 3.86.

(e) In the same manner ethyl 3-bromopropionate gave 2.5 g (38%) of 1,1-dibutyl-4-(β-carbethoxyethyl)stannacyclohexa-2,5-diene (**5f**): bp 120–130 °C (0.001 torr); ^1H NMR ($CDCl_3$) δ 0.8–2.30 (m, 25 H), 3.20 (m, 1 H), 4.30 (q, J = 7 Hz, 2 H), 5.95–6.70 (m, 4 H); IR (CCl_4) 1740 cm^{-1}; MS (70 eV), m/e 343 ($M^+ - C_4H_9$). Anal. Calcd for $C_{18}H_{32}O_2Sn$: C, 54.16; H, 8.08. Found: C, 53.89; H, 8.13.

(f) In the same manner 1,2-dibromopropane gave 5.0 g (71%) of 1,1-dibutyl-4-(β-bromopropyl)stannacyclohexa-2,5-diene (**5g**). This product decomposed on attempted distillation at 140 °C: ^1H NMR ($CDCl_3$) δ 0.8–2.0 (m, 24 H), 3.20 (m, 1 H), 6.0–7.0 (m, 4 H); MS (70 eV), m/e 283 (M^+ − HBr, C_4H_9). Anal. Calcd for $C_{16}H_{29}BrSn$: C, 45.75; H, 6.96; Br, 19.03. Found: C, 45.31; H, 7.06; Br, 18.68.

Reaction of Lithium 1,1-Dibutylstannacyclohexadienide with Water. To a solution of lithium 1,1-dibutylstannacyclohexadienide prepared in the usual manner from 3.0 g (10 mmol) of 1,1-dibutylstannacyclohexa-2,5-diene was added 1 mL of water. The mixture was then added to excess water and extracted with pentane. The extracts were dried over anhydrous magnesium sulfate and distilled, yielding 1.0 g (33%) of product, bp 100–105 °C (1 torr). GLC analysis of the product (on a 5 ft × 0.25 in. column containing 20% Apiezon L on Chromosorb W at 200 °C; 40 lb of He pressure for elution) showed **3** (retention time 2.0 min) and **10** (retention time 3.0 min) in the ratio of 1:4. 1,1-Dibutylstannacyclohexa-2,4-diene (**10**) showed the following: ^1H NMR ($CDCl_3$) δ 0.85–1.58 (m, 18 H), 1.72 (dm, J = 6.4 Hz, 2 H), 5.75 (m, 1 H), 5.93 (m, 1 H), 6.40 (d, J = 13.5 Hz, 1 H), 6.64 (dd, J = 13.5, 6.3 Hz, 1 H); MS (70 eV), m/e 300 (M^+ for $C_{13}H_{24}{}^{120}Sn$), 243 ($M^+ - C_4H_9$). Anal. Calcd for $C_{13}H_{24}Sn$: C, 52.22; H, 8.09. Found: C, 52.11; H, 7.97.

4-(Cyanomethyl)arsabenzene (7c). A solution of 2.0 g (5.9 mmol) of 1,1-dibutyl-4-(cyanomethyl)stannacyclohexa-2,5-diene in 20 mL of tetrahydrofuran was added to 2.0 g (6.3 mmol) of arsenic tribromide in 30 mL of tetrahydrofuran. The reaction mixture was allowed to stir for 1 h at 25 °C and was then heated to 80 °C for 3 h. After removal of the solvent, the product was distilled at 70 °C (0.5 torr), yeilding 0.9 g (85%) of **7c**: ^1H NMR ($CDCl_3$) δ 3.65 (s, 2 H), 7.70 (d, J = 11 Hz, 2 H), 9.60 (d, J = 11 Hz, 2 H); IR (CCl_4) 2260 cm^{-1}; MS (70 eV), m/e 179 (M^+ for C_7H_6AsN). Anal. Calcd for C_7H_6AsN: C, 46.95; H, 3.38; N, 7.82. Found: C, 47.08; H, 3.43; N, 7.67.

4-[(Ethoxycarbonyl)methyl]arsabenzene (7b). In the same manner 2.0 g (5.2 mmol) of 1,1-dibutyl-4-[(ethoxycarbonyl)-methyl]stannacyclohexa-2,5-diene and 1.70 g (5.3 mmol) of arsenic tribromide in 50 mL of tetrahydrofuran gave 0.8 g (68%) of **7b**: bp 78–82 °C (0.5 torr); ^1H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 3.50 (s, 2 H), 4.05 (q, J = 7 Hz, 2 H), 7.80 (d, J = 11 Hz, 2 H), 9.70 (d, J = 11 Hz, 2 H); IR (CCl_4) 1750 cm^{-1}; MS (70 eV), m/e 226 (M^+ for $C_9H_{11}AsO_2$). Anal. Calcd for $C_9H_{11}AsO_2$: C, 47.81; H, 4.90. Found: C, 47.94; H, 5.02.

4-(β-Bromoethyl)arsabenzene (7d). In the same manner 2.8 g (6.9 mmol) of 1,1-dibutyl-4-(β-bromoethyl)stannacyclohexa-2,5-diene and 2.3 g (7.3 mmol) of arsenic tribromide in 50 mL of tetrahydrofuran gave 1.4 g (82%) of **7d**: bp 65–70 °C (0.1 torr);

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^{1}H NMR ($CDCl_3$) δ 3.06–3.80 (m, 4 H), 7.80 (d, J = 11 Hz, 2 H), 9.70 (d, J = 11 Hz, 2 H); MS (70 eV), m/e 248 (M^+ for $C_7H_8{}^{81}BrAs$). Anal. Calcd for C_7H_8AsBr: C, 34.04; H, 3.27; Br, 32.36. Found: C, 34.27; H, 3.40; Br, 32.45.

4-(β-Cyanoethyl)arsabenzene (7e). In the same manner 6.0 g (17 mmol) of 1,1-dibutyl-4-(β-cyanoethyl)stannacyclohexa-2,5-diene and 5.5 g (17.5 mmol) of arsenic tribromide in 40 mL of tetrahydrofuran gave 2.5 g (76%) of 4-(β-cyanoethyl)arsabenzene, bp 70–75 °C (0.5 torr). This product was also obtained by the reaction of 150 mg (0.6 mmol) of 4-(β-bromoethyl)arsabenzene with 0.1 g of sodium cyanide with 0.1 g of benzyltrimethylammonium chloride in 15 mL of water. The mixture was heated to reflux for 20 h, after which the product was extracted with ether. After the extract was dried over anhydrous magnesium sulfate, removal of the solvent left 100 mg (85%) of **7e**: ^{1}H NMR ($CDCl_3$) δ 2.40–3.0 (m, 4 H), 7.60 (d, J = 11 Hz, 2 H), 9.60 (d, J = 11 Hz, 2 H); IR (CCl_4) 2260 cm^{-1}; MS (70 eV), m/e 193 (M^+ for C_8H_8AsN). Anal. Calcd for C_8H_8AsN: C, 49.76; H, 4.18; N, 7.26. Found: C, 49.83; H, 4.20; N, 7.15.

4-[(β-Ethoxycarbonyl)ethyl]arsabenzene (7f). In a similar manner 2.0 g (5 mmol) of 1,1-dibutyl-4-[(β-ethoxycarbonyl)-ethyl]stannacyclohexa-2,5-diene and 1.9 g (6 mmol) of arsenic tribromide in 60 mL of tetrahydrofuran gave an oil which was purified by column chromatography on activated alumina with dichloromethane–hexane as the eluent. The yield was 0.90 g (75%).

This product could also be obtained from 4-(β-cyanoethyl)-arsabenzene (**7c**). A mixture of **7e** (2.0 g, 10 mmol) with 0.6 g of potassium hydroxide in 20 mL of water was heated to reflux for 15 h. After cooling, the mixture was acidified with 10% hydrochloric acid, and the desired carboxylic acid was extracted with ether. On removal of the solvent, the residue (1.9 g) was added to 30 mL of ethanol and 3 mL of dilute hydrochloric acid. After the mixture was heated to reflux for 3 h, the solvent was removed and the residue extracted with ether. After drying over anhydrous magnesium sulfate, distillation gave 1.80 g (73%) of **7f**: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.80 (m, 4 H), 4.05 (q, J = 7 Hz, 2 H), 7.70 (d, J = 11 Hz, 2 H), 9.60 (d, J = 11 Hz, 2 H); IR (CCl_4) 1750 cm^{-1}; MS (70 eV), m/e 240 (M^+ for $C_{10}H_{13}AsO_2$). Anal. Calcd for $C_{10}H_{13}AsO_2$: C, 50.22; H, 5.46. Found: C, 49.99; H, 5.34.

4-(β-Bromopropyl)arsabenzene (7g). In a similar manner 2.0 g (4.8 mmol) of 1,1-dibutyl-4-(β-bromopropyl)stannacyclohexa-2,5-diene and 1.6 g (5 mmol) of arsenic tribromide in 40 mL of tetrahydrofuran gave 0.8 g (65%) of **7g**: bp 90–95 °C (0.2 torr); ^{1}H NMR ($CDCl_3$) δ 1.95 (d, J = 6 Hz, 3 H), 3.10 (dd, J = 3, 8 Hz, 2 H), 4.25 (m, 1 H), 7.75 (d, J = 11 Hz, 2 H), 9.50 (d, J = 11 Hz, 2 H); MS (70 eV), m/e 262 (M^+ for $C_8H_{10}{}^{81}BrAs$). Anal. Calcd for $C_8H_{10}AsBr$: C, 36.81; H, 3.86; Br, 30.62. Found: C, 36.80; H, 3.89; Br, 30.48.

4-Vinylarasabenzene (7h). 1,1-Dibutyl-4-(β-bromoethyl)-1-stannacyclohexa-2,5-diene (2.8 g, 6.9 mmol) in 20 mL of tetrahydrofuran was added to a solution of 2.3 g (7.3 mmol) of arsenic tribromide in 20 mL of tetrahydrofuran. The reaction mixture was allowed to reflux for 3 h. After the mixture cooled to 25 °C, 5 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene was added, and the mixture was allowed to stir at 25 °C for 1 h. The product was distilled at 40 °C (0.2 torr) to give 0.65 g (57%) of a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 5.30 (dd, J = 11, 2 Hz, 1 H), 5.80 (dd, J = 17, 2 Hz, 1 H), 6.70 (dd, J = 17, 11 Hz, 1 H), 7.80 (d, J = 11 Hz, 2 H); IR (CCl_4) 3100, 1015, 910 cm^{-1}; MS (70 eV) m/e 166 (M^+ for C_7H_7As). Anal. Calcd for C_7H_7As: C, 50.63; H, 4.25. Found: C, 50.47; H, 4.23.

4-(β-Aminoethyl)arsabenzene (7j). A mixture of 0.3 g of 4-(β-bromoethyl)arsabenzene in 3 mL of methanol and 3 mL of anhydrous liquid ammonia was sealed in a Carius tube and heated to 55 °C for 10 h. Removal of the solvent left 180 mg of an oil which was separated by GC (5 × 0.25 in. column packed with 20% SE-30 on Chromosorb W) into 30% **7h** and 70% **7j**: ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 2 H), 2.60–3.0 (m, 4 H), 7.70 (d, J = 11 Hz, 2 H), 9.50 (d, J = 11 Hz, 2 H); IR (CCl_4) 3400 cm^{-1}; MS (70 eV), m/e 183 (M^+ for $C_7H_{10}AsN$). Anal. Calcd for $C_7H_{10}AsN$: C, 45.92; H, 5.51; N, 7.65. Found: C, 46.08; H, 5.49; N, 7.59.

Attempted Preparation of 4-(β-Aminopropyl)arsabenzene. A mixture of 100 mg (0.38 mmol) of 4-(β-bromopropyl)arsabenzene in 2 mL of methanol and 2 mL of anhydrous liquid ammonia was sealed in a Carius tube and heated to 55 °C for 10 h. After removal of the solvent, 40 mg (53%) of a brown liquid was obtained. This compound was identified as 4-(1-propenyl)arsabenzene (**7i**): ^{1}H NMR ($CDCl_3$) δ 1.80 (d, J = 6 Hz, 3 H), 6.40 (m, 2 H), 7.80 (d, J = 11 Hz, 2 H), 9.60 (d, J = 11 Hz, 2 H); MS (70 eV), m/e 180 (M^+ for C_8H_9As). Anal. Calcd for C_8H_9As: C, 53.36; H, 5.04. Found: C, 53.15; H, 4.96.

4-[2-Bromo-2-(ethoxycarbonyl)ethyl]arsabenzene (13). A solution of 480 mg (2 mmol) of **7f** in 50 mL of tetrahydrofuran was treated with 3 mmol of lithium diisopropylamide at −78 °C. After warming to 0 °C, the solution was added to 600 mg (2.4 mmol) of 5-bromo-2,2,5-trimethyl-1,3-dioxane-4,5-dione[16] in 30 mL of tetrahydrofuran. This reaction mixture was allowed to stir at 0 °C for 1 h and was then added to a mixture of 100 mL of hexane and 300 mL of water. The organic layer was separated, washed twice with 300 mL of water, and then dried over anhydrous magnesium sulfate. After removal of the solvent, the product was purified by column chromatography on activated alumina with dichloromethane as the eluent. The yield of **13** was 350 mg (55%): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 3.27 (dd, J = 14, 8 Hz, 1 H), 3.48 (dd, J = 14, 8 Hz, 1 H), 4.16 (q, J = 7 Hz, 2 H), 4.40 (t, J = 8 Hz, 1 H), 7.81 (d, J = 11 Hz, 2 H), 9.75 (d, J = 11 Hz, 2 H); IR (CCl_4) 1740 cm^{-1}; MS (70 eV), m/e (relative intensity) 320 (1, M^+ for $C_{10}H_{12}As^{81}BrO_2$), 239 (100, M^+ − Br). Anal. Calcd for $C_{10}H_{12}AsBrO_2$: C, 37.65; H, 3.79; Br, 25.05. Found: C, 37.81; H, 3.91; Br, 24.81.

4-[2-Amino-2-(ethoxycarbonyl)ethyl]arsabenzene (15). A solution of 200 mg (0.63 mmol) of **13** and 100 mg of sodium azide in 30 mL of ethanol was heated to reflux for 15 h. After the mixture cooled, ethanol was removed at reduced pressure, and the residue was added to 100 mL of diethyl ether and 100 mL of water. The organic layer was separated, washed twice with 100 mL of water, and dried over anhydrous magnesium sulfate. After removal of ether, 120 mg (68%) of 4-[2-azido-2-(ethoxycarbonyl)ethyl]arsabenzene was obtained as a viscous brown oil which was used without further purification: ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 3.20 (dd, J = 6, 8 Hz, 2 H), 4.0 (t, J = 8 Hz, 1 H), 4.20 (q, J = 7 Hz, 2 H), 7.80 (d, J = 11 Hz, 2 H), 9.65 (d, J = 11 Hz, 2 H); IR (CCl_4) 2130 cm^{-1}; MS (70 eV), m/e 281 (weak, M^+ for $C_{10}H_{12}AsN_3O_2$).

The azide in 15 mL of benzene and 120 mg of triphenylphosphine in 15 mL of benzene were simultaneously added together dropwise. After the mixture was stirred for 2 h at 25 °C, the benzene was removed to give a brown solid, which was added to a solution of 1 mL of 48% hydrobromic acid and 5 mL of acetic acid in 50 mL of water. The mixture was heated to reflux for 3 h. On cooling, the mixture was extracted with ether. The ether extracts were discarded after checking for starting material. The aqueous fraction was treated with a solution of sodium bicarbonate, and then the product was extracted with ether and dried over anhydrous magnesium sulfate. After removal of ether, 30 mg of the white solid **15** was obtained: ^{1}H NMR ($CDCl_3$) δ 1.15 (t, J = 7 Hz, 3 H), 1.55 (s, 2 H), 2.90 (dd, J = 6, 8 Hz, 2 H), 3.60 (dd, J = 6, 8 Hz, 1 H), 4.10 (q, J = 7 Hz, 2 H), 7.80 (d, J = 11 Hz, 2 H), 9.70 (d, J = 11 Hz, 2 H); IR (CCl_4) 3400, 1740, 1600, 1470 cm^{-1}; MS (70 eV) m/e (relative intensity 255 (1, M^+ for $C_{10}H_{14}AsNO_2$), 153 (3, $C_6H_7As^+$), 102 (100, M^+ − C_6H_7As). Anal. Calcd for $C_{10}H_{14}AsNO_2$: C, 47.07; H, 5.53. Found: C, 47.28; H, 5.74.

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Registry No. 5b, 84602-37-9; **5c**, 84602-38-0; **5d**, 66546-66-5; **5e**, 84602-39-1; **5f**, 84602-40-4; **5g**, 84602-41-5; **7b**, 84602-42-6; **7c**, 84602-43-7; **7d**, 84602-44-8; **7e**, 84602-45-9; **7f**, 84602-46-0; **7g**, 84602-47-1; **7h**, 84602-48-2; **7i**, 84602-49-3; **7j**, 84602-50-6; **10**, 84602-51-7; **13**, 84602-52-8; **15**, 84602-53-9; 4-[2-azido-2-(ethoxycarbonyl)ethyl]arsabenzene, 84602-54-0; 1,1-dibutylstannacychlohexa-2,5-diene, 31732-31-7; lithium 1,1-dibutylstannacyclohexa-2,5-dienide, 66531-48-4; chloroacetonitrile, 107-14-2; ethyl bromoacetate, 105-36-2; 1,2-dibromoethane, 106-93-4; 3-bromopropionitrile, 2417-90-5; ethyl 3-bromopropionate, 539-74-2; 1,2-dibromopropane, 78-75-1.