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Preparation of 2-Substituted Arsabenzenes[1,2]

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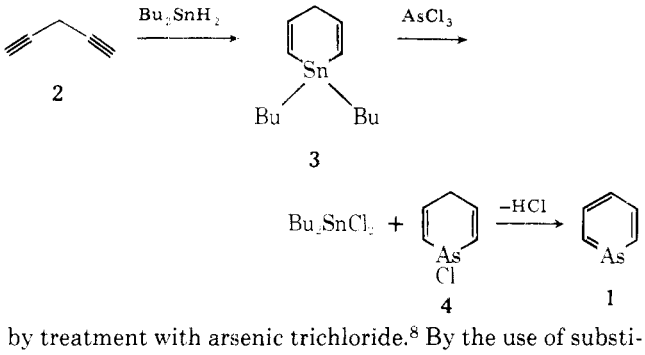
Received August 8, 1978

A variety of 1,4-diynes react with dibutyltin hydride to give predominately 2-alkyl-1,1-dibutyl-1,4-dihydrostannabenzenes. These may be readily converted to 2-alkylarsabenzenes by treatment with arsenic trichloride. In this manner, 6-acetoxy-1,4-hexadiyne has been converted to 2-arsabenzyl acetate and hence to a number of 2-functionalized arsabenzenes.

Spectroscopic studies of arsabenzene (arsenin, **1**) clearly show that this new heterocycle closely resembles its more familiar benzocyclic relatives.[3] For example, arsabenzene has a planar ring with normal aromatic C–C bond distances of 1.395 Å.[4] Its proton NMR spectrum shows low field signals indicative of a diamagnetic ring current.[5] Similarly, UV photoelectron spectral studies supported by several MO calculations further demonstrate this aromaticity.[6]

On the other hand, exploration of the chemistry of arsabenzene has been more modest. To some extent these chemical studies have been hampered by the lack of general methods for placing substituents on the arsabenzene ring. However, the parent system is easily prepared by a two-step synthesis. Thus, 1,4-pentadiyne (**2**) may be hydrostannated with dibutyltin dihydride to give 1,4-dihydro-1,1-dibutylstannabenzene (**3**),[7] which is readily converted to arsabenzene



by treatment with arsenic trichloride.[8] By the use of substituted 1,4-diynes in place of **2**, this synthesis appears to offer potential for the preparation of substituted arsabenzenes. In fact, this approach has been used to prepare several 4-functionalized arsabenzenes.[9,10] We now wish to report further on our synthesis of arsabenzene and its extension to the synthesis of 2-substituted arsabenzenes.

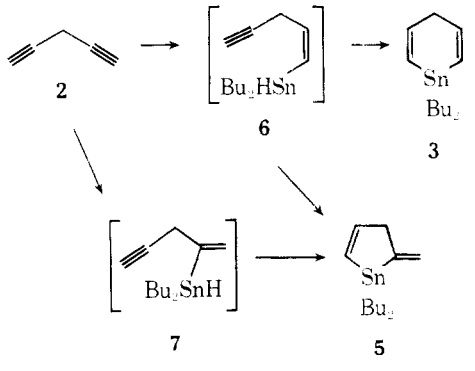
Results and Discussion

While the reactions of most diacetylenes with tin dihydrides give largely oligomeric products,[11] the hydrostannation of 1,4-pentadiyne with an equivalent of dibutyltin dihydride in refluxing heptane affords a 42% yield of 1,4-dihydro-1,1-dibutylstannabenzene (**3**). This 1:1 adduct is easily distilled from the apparently polymeric viscous residue. The characteristic AB pattern in the vinyl region of the ^{1}H NMR spectrum suggests structure **3** (Table I). A careful examination of the product revealed a minor isomer (5%) in addition to **3**. This material could be separated by GLC. Its IR spectrum showed bands assigned to a terminal methylene [905 cm^{-1} $(CS)_2$], while the ^{1}H NMR spectrum was consistent with formulation **5** (Table II). It might be noted that the five-membered ring has a characteristically smaller value for the coupling constants for vicinal vinyl ring protons, while the β-vinyl ring proton showed a lower field signal than those for **2**.

This structural assignment can be made ironclad by the use of the facile and stereospecific cleavage of vinylstannanes by acetic acid.[12] Both isomers give 1,4-pentadiene and dibutyltin acetate in near quantitative yield. However, the reaction of **3** with acetic-d_1 acid gave *cis,cis*-1,4-pentadiene-*1,5*-d_2 while **5** gave 1,4-pentadiene-*1,4*-d_2.

The presence of small quantities of the five-membered ring isomer in **3** is preparatively unimportant. Compound **3** is readily converted to arsabenzene by the exchange reaction with arsenic trihalide followed by gentle warming and treatment with base to remove hydrogen halide from intermediate **4**. Although air-sensitive, arsabenzene is a stable distillable liquid, easily handled under an inert atmosphere.

The hydrostannation of nonpolar substituted acetylenes is known to be a homolytic addition reaction.[13,14] To some extent the relatively larger yield of **3** vs. **5** rests on the known preference of stannyl radicals for terminal addition to acetylenes.[15] Thus, production of **3** must involve two terminal additions (**2** → **6** → **3**) while a single nonterminal addition (**2** → **7** → **5** or **2** → **6** → **5**) can only give the five-membered ring adduct.



We had feared that the regioselectivity which led to the desired six-membered ring might be compromised by the use of substituted acetylenes. Unfortunately, this proved to be the case as 2,5-heptadiyne (**8a**) reacted with dibutyltin dihydride to give a 58% yield of two adducts in a ratio of 3:1. Acetic acid cleavage afforded only *trans,trans*-2,5-heptadiene. The two

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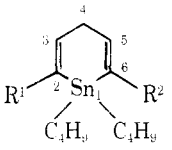
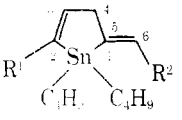
Table I. ^{1}H NMR Spectra (δ) of the 1,1-Dibutyl-1,4-dihydrostannabenzenes [a]



compd	R^2	H_5	H_4	H_3	R^1
3, R^1, R^2 = H	6.1 (dt, J = 14, 2 Hz)	6.6 (dt, J = 14, 4 Hz)	3.1 (m)		
10a, R^1, R^2 = CH_3	1.9 (s)	6.1 (m)	3.0 (m)		
10b, R^1 = CH_3, R^2 = H	6.0 (m)	6.6 (dt, J = 13, 4 Hz)	3.1 (m)	6.0 (m)	1.9 (d, J = 2 Hz)
10c, R^1 = C_2H_5, R^2 = H	6.2 (d, J = 14 Hz)	6.7 (dt, J = 14, 4 Hz)	3.1 (m)	6.2 (m)	2.3 (t, J = 6 Hz) [b]
10d, R^1 = $C(CH_3)_3$, R^2 = H	6.2 (d, J = 14 Hz)	6.5 (dt, J = 14, 3 Hz)	3.1 (m)	6.2 (m)	9.0 (s)
15a, R^1 = CH_2OCH_3, R^2 = H	6.0 (m)	6.5 (dt, J = 14, 4 Hz)	3.0 (m)	6.0 (m)	3.9 (m, CH_2); 3.2 (s, CH_3)
15b, R^1 = CH_2OTHP, R^2 = H	6.1 (m)	6.6 (dt, J = 13, 3 Hz)	3.1 (m)	6.1 (m)	4.7 (m, CH_2); 4.6, 3.9–3.5, 1.9 (m, OTHP)
15c, R^1 = CH_2OCOCH_3, R^2 = H	6.2 (m)	6.6 (dt, J = 13, 3 Hz)	3.1 (m)	6.2 (m)	4.7 (br m, CH_2); 2.3 (s, CH_3)

[a] In all cases, the normal butyl peaks occurred as multiplets at δ 1.6–0.7. [b] The methyl signal was obscured by the butyl peaks.

Table II. ^{1}H NMR Spectra (δ) of the 1,1-Dibutyl-5-methylenestannacyclopent-2-enes [a]



compd	R^1	H_3	H_4	H_6	R^2
5, R^1, R^2 = H	6.6 (d, J = 11 Hz)	6.9 (dt, J = 11, 3 Hz)	3.2 (m)	5.8 (br s)	5.4 (d, J = 2 Hz)
9a, R^1, R^2 = CH_3	2.0 (m)	6.3 (m)	3.1 (m)	6.2 (qt, J = 6, 2 Hz)	1.8 (dt, J = 6, 2 Hz)
9b, R^1 = H, R^2 = CH_3	6.4 (dt, J = 10, 2 Hz)	6.9 (dt, J = 10, 3 Hz)	3.2 (m)	6.2 (q, J = 6 Hz)	1.8 (d, J = 6 Hz)
9c, R^1 = H, R^2 = C_2H_5	6.4 (d, J = 11 Hz)	6.9 (dt, J = 11, 3 Hz)	3.2 (m)	6.2 (br t, J = 6 Hz)	2.0 (m, CH_2) [b]
9d, R^1 = H, R^2 = $C(CH_3)_3$	6.4 (d, J = 10 Hz)	6.9 (dt, J = 10, 3 Hz)	3.2 (m)	6.3 (br s)	1.0 (s)
9e, R^1 = H, R^2 = C_6H_5	6.4 (dt, J = 10, 2.5 Hz)	6.9 (dt, J = 10, 3 Hz)	3.3 (m)	7.2 (m)	7.2 (m)

[a] In all cases, the normal butyl peaks occurred as multiplets at δ 1.6–0.7. [b] The methyl signal was obscured by the normal butyl signals.

isomers could be separated by GLC, and ^{1}H NMR spectra allowed structural assignment of the major isomer as **9a**. In particular, it showed two nonequivalent allylic methyl peaks, one of which was split into a doublet (J = 6 Hz) by an adjacent hydrogen. The spectrum of the minor isomer was consistent with **10a**. Isomers **9a** and **10a** are not easily separated, while heating the mixture of **9a** and **10a** with $AsCl_3$ in CCl_4 gave a low yield of 2,6-dimethylarsabenzene (**11a**) as the only volatile arsenic-containing product. Unfortunately, the low overall conversion makes this method preparatively unattractive, and we have not further explored the route for the preparation of 2,6-disubstituted heterobenzenes.

Results with monoalkyl-substituted 1,4-diacetylenes were more encouraging. 1,4-Hexadiyne (**8b**) reacted with dibutyltin dihydride to give two adducts in a ratio of 1:5. After separation by GLC, structural assignment could be made from the ^{1}H NMR spectra (Tables I and II). The major isomer was the desired six-membered ring compound **10b**. Heating the unseparated mixture with $AsBr_3$ in tetraglyme gave 43% of 2-methylarsabenzene. Similarly, 1,4-heptadiyne (**8c**) gave the corresponding adducts **10c**/**9c** in a ratio of 87:13, while 6,6-dimethyl-1,4-heptadiyne (**8d**) gave isomers **10d**/**9d** in a ratio of 93:7. In all cases, heating the unseparated mixture of adducts with $AsBr_3$ gave satisfactory yields of the corresponding

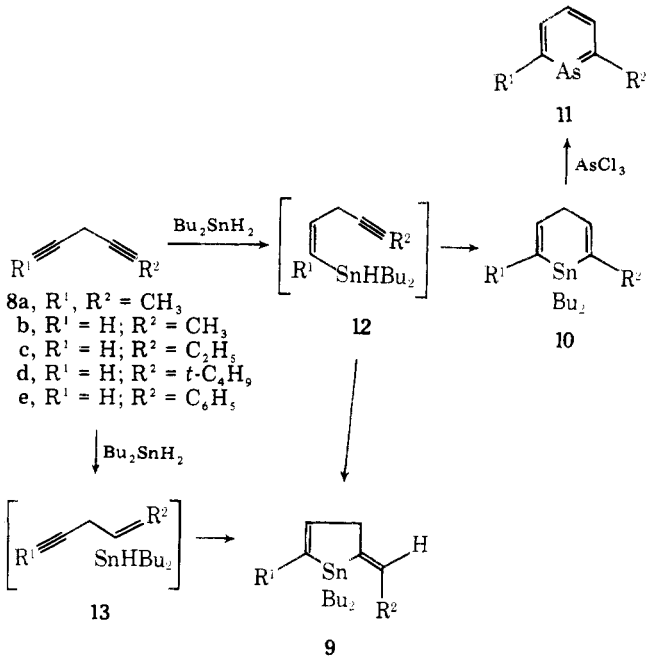
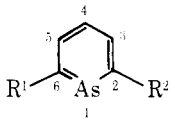


Table III. H NMR Spectral Data of the Arsabenzenes



compd	R^1	H_3, H_4, H_5	R^2
1, R^1, R^2 = H	9.7 (d, J = 10 Hz)	7.8–7.5	9.7 (d, J = 10 Hz)
11a, R^1, R^2 = CH_3	2.7 (s)	7.4 (s)	2.7 (s)
11b, R^2 = CH_3, R^1 = H	9.6 (d, J = 10 Hz)	7.3–7.7 (m)	2.7 (s)
11c, R^2 = C_2H_5, R^1 = H	9.7 (d, J = 10 Hz)	7.5–7.8 (m)	3.1 (q, J = 7 Hz, CH_2); 1.4 (t, J = 7 Hz, CH_3)
11d, R^2 = $C(CH_3)_3$, R^1 = H	9.7 (d, J = 10 Hz)	7.5–8.0 (m)	1.5 (s)
16a, R^2 = CH_2OCH_3 R^1 = H	9.6 (d, J = 10 Hz)	7.2–7.8 (m)	4.6 (s, CH_2); 3.3 (s, CH_3)
17, R^2 = CH_2OH, R^1 = H	9.6 (d, J = 10 Hz)	7.3–7.8 (m)	4.8 (s, CH_2); 3.9 (s, OH)
16c, R^2 = CH_2OAc, R^1 = H	9.8 (d, J = 10 Hz)	7.5–8.0 (m)	5.5 (s, CH_2); 2.1 (s, CH_3)
18, R^2 = CHO, R^1 = H	9.9 (d, J = 10 Hz)	8.4 (d, J = 8 Hz, H_3); 7.5–8.2 (m, H_4, H_5)	1.01 (p)
19, R^2 = $CH{=}CHCO_2C_2H_5$, R^1 = H	9.8 (d, J = 10 Hz)	7.5–7.9 (m)	8.0 (d, J = 16 Hz, CH); 6.7 (d, J = 16 Hz, CH); 4.3 (q, J = 7 Hz, CH_2); 1.3 (t, J = 7 Hz, CH_3)

2-alkylarsabenzenes **11** (see Table III). Interestingly, **10d** gave 15% arsabenzene itself in addition to the expected 2-*tert*-butylarsabenzene (**11d**). Apparently, the 2-*tert*-butylarsabenzene is protodealkylated by the HCl produced in the reaction.[16]

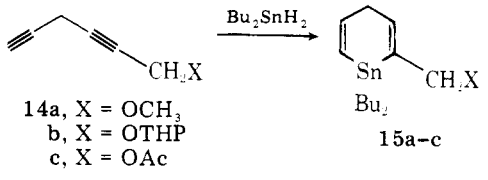
Attempted extension to aryl-1,4-pentadiynes was less satisfactory. 1-Phenyl-1,4-pentadiyne reacts with dibutyltin dihydride to give largely a single 1:1 adduct, from which acetic acid cleavage afforded *trans*-1-phenyl-1,4-pentadiene. The low field β-vinyl proton signal and the small value of vinyl J_{AB} in the ^1H NMR spectrum suggest assignment as the five-membered ring adduct **9a.** This assignment is confirmed by the reaction of **9e** with acetic-d_1 acid, which produces only *trans,trans*-1-phenyl-1,4-pentadiene-2,5-d_2.

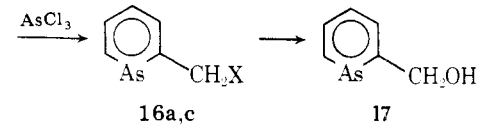
In the case of the alkylpentadiynes, we presume that the initial attack of tin hydride occurs predominately at the terminal acetylene to give **12,** from which ring closure occurs preferentially to give the six-membered ring adducts **10.** Presumably, there is only a small electronic difference between the two closure routes open to **12.** Thus, the observed preference may reflect steric factors favoring six-membered ring closure. In similar homolytic ring closure reactions involving alkyl radicals, five-membered ring products usually predominate.[17] We might note that the greater size of stannyl radical appears to allow a closer approach at C_6.[18]

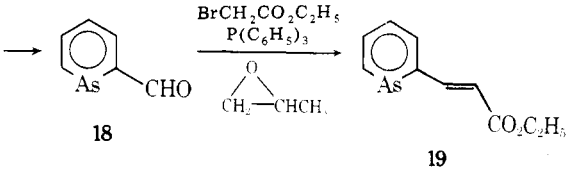
There is a modest increase in the relative yield of the six-membered ring products as the size of the alkyl group increases. It may be that the steric effects of the large alkyl group are more demanding for closure to the five-membered ring than for the six. Since stannyl radical additions to alkynes are trans additions,[19] the alkyl group must approach the bulky stannyl function to form cis product **9.** On the other hand, in attack to give **10** the alkyl group and the tin group must move away from each other.

In the case of 1-phenyl-1,4-pentadiyne, the phenyl group is likely to direct initial attack of the stannyl radical β to give **13e,** from which closure can only give the observed five-membered ring adduct **9e.** Any **12e** formed is also likely to be directed to close to **9e.** That the position β to the phenyl is more reactive can be demonstrated independently. Thus, treating an excess of 1-phenyl-1,4-pentadiyne with tributyltin hydride followed by acetic acid cleavage results in preferential reduction of the acetylene unit adjacent to the phenyl ring, producing *trans*-1-phenyl-1-penten-5-yne.

We had hoped to extend our synthesis to arsabenzenes with manipulatively useful functional groups. However, the above results suggest that the hydrostannation of 1,4-diynes bearing radical-stabilizing substituents would give largely five-membered ring adducts useless for conversion to arsabenzenes.[14] On the other hand, 6-substituted 1,4-hexadiynes appeared to be attractive precursors for 2-functionalized arsabenzenes. Thus, we have converted oxygen-substituted diynes **14a–c** to the corresponding six-membered ring adducts **15a–c.** ^1H NMR spectral parameters are consistent with the







indicated formulations (Table I). In no case did we attempt to separate the minor isomers.

Methyl ether **15a** was easily converted to the corresponding arsabenzene **16a.** Although we had hoped that this benzyl-like ether might be easily cleaved by Lewis acids, treatment with a variety of reagents (BBr_3, etc) leads to destruction of the ring system.[1] On the other hand, the more labile THP ether **15b** is itself destroyed by $AsCl_3$ and gives no arsabenzene products.[1] A satisfactory balance between robustness to reaction conditions and ease of removal of the protecting group is found by using acetate **15c.** This acetate is readily converted to arsabenzyl acetate **15c,** which can be converted to arsabenzenemethanol **17** with sodium methoxide in methanol.

While benzyl alcohol is easily oxidized to benzaldehyde without hazard to the phenyl ring, the arsabenzene ring is considerably more fragile. Oppenauer oxidation, Jones oxidation, and treatment with manganese dioxide or 1-chlorobenzotriazole all destroyed alcohol **17,** yielding intractable material.[1] Fortunately, milder oxidative methods are more satisfactory. A methylene chloride solution of arsabenzyl alcohol can be oxidized by silver carbonate impregnated on

Celite. Arsabenzaldehyde **18** is isolated in 50% yield.

Spectroscopically, 2-arsabenzaldehyde appears to be a normal electron-rich aromatic aldehyde. The CHO IR-stretching frequency at 1685 cm^{-1} is slightly lower than that of benzaldehyde (1700 cm^{-1}) but almost identical with the 1679 cm^{-1} reported for 2-thiophenecarboxaldehyde.[20] Synthetically, 2-arsabenzaldehyde shows normal aldehyde reactivity. Thus, the Wittig condensation with ethyl bromoacetate and triphenylphosphine gave a 70% yield of **19**, the arsabenzene analogue of ethyl cinnamate.

We anticipate that arsabenzyl alcohol and arsabenzaldehyde may be converted to a variety of 2-functionalized arsabenzenes by application of the well-honed methods of organic chemistry. Thus, their easy preparation should greatly facilitate further exploration of the chemistry of the novel arsabenzene system.

Experimental Section

The NMR spectra were recorded using either a JEOL JNM-PS 100 PFT or a Varian T60A spectrometer. Chemical shifts are reported to the nearest 0.1 ppm, while coupling constants are to the nearest 1.0 Hz. Mass spectral data were obtained using an AEI MS 902 instrument operating at an ionizing voltage of 70 eV. IR spectra were recorded using a Perkin-Elmer Model 457 spectrometer calibrated with polystyrene. C, H combustion analyses were obtained on all new compounds by Spang Microanalytical Laboratory, Eagle Harbor, Mich. In all cases, analyses agreed with calculated values (±0.3%). GLC analyses and separations were performed using a Varian 90P chromatograph equipped with a thermal conductivity detector. No corrections were made for the possible different thermal conductivities of isomers. The following columns were used: column A (a 4 ft × 0.25 in. column containing 20% Apiezon L on Chromosorb W), column B (a 5 ft × 0.25 in. column containing 10% Carbowax 20M on Chromosorb W), and column C (a 10 ft × 0.25 in. column containing 20% SE 30 on Chromosorb W).

1,4-Diynes. 1,4-Pentadiyne, 1,4-hexadiyne, and 1,4-heptadiyne are commercially available.[21] 6,6-Dimethyl-1,4-heptadiyne,[22] 1-phenyl-1,4-pentadiyne,[23] and 2,5-heptadiyne[24] were prepared from the cuprous chloride catalyzed coupling reaction of the alkynylmagnesium bromide with the appropriate propargyl bromide. Properties were consistent with those reported in the original literature.[22-24]

2,5-Hexadiyn-1-yl 2-Tetrahydropyranyl Ether (14b). To a solution of ethylmagnesium bromide prepared from 27 g (1.1 g-atom) of magnesium and 109 g (1 mol) of ethyl bromide in 700 mL of tetrahydrofuran was added a solution of 130 g (0.93 mol) of propargyl 2-tetrahydropyranyl ether[25] in 150 mL of tetrahydrofuran. The solution was heated to 60 °C for half an hour and then cooled in a cold water bath. A 0.5-g sample of cuprous chloride was added followed by 119 g (1 mol) of propargyl bromide in 100 mL of tetrahydrofuran. In 15 min, the solution became a very viscous liquid with a yellow suspension. The mixture was stirred for a total of 2 h and quenched with 150 mL of saturated ammonium chloride solution. After dilution with 500 mL of water, followed by extraction with pentane (2 × 200 mL), the combined organic phase was washed with water and dried over Na_2SO_4. Distillation afforded 96 g (54%) of product: bp 75 °C (0.5 torr); H NMR ($CDCl_3$) δ 1.6 (m, 6 H), 2.0 (q, J = 2 Hz, 1 H), 3.1 (q, J = 2 Hz, 2 H), 3.6 (m, 2 H), 4.1 (t, J = 2 Hz, 2 H), 4.6 (m, 1 H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.98; H, 7.94.

2,5-Hexadiyn-1-yl Methyl Ether (14a). To a solution of ethylmagnesium bromide prepared from 27 g (1.1 g-atom) of magnesium and 109 g (1 mol) of ethyl bromide in 700 mL of tetrahydrofuran was added portionwise a solution of 60 g (0.85 mol) of methyl propargyl ether in 50 mL of tetrahydrofuran over a period of 1 h. The reaction was warmed with a water bath at 50 °C for 30 min and then cooled in a cold water bath. A 2-g sample of cuprous chloride was added followed by 100 g (0.84 mol) of propargyl bromide in 100 mL of tetrahydrofuran. After being stirred for 90 min, the reaction was quenched with 125 mL of saturated ammonium chloride solution and diluted with 500 mL of water. After filtration, the aqueous phase was extracted with ether (2 × 100 mL). The combined organic phase was washed with water and then with saturated sodium chloride solution. After drying over Na_2SO_4, distillation afforded 58 g (65%) of product: bp 42 °C (2 torr); ^1H NMR ($CDCl_3$) δ 2.0 (t, J = 2 Hz, 1 H), 3.2 (q, J = 2 Hz, 2 H), 3.3 (s, 3 H), 4.0 (t, J = 2 Hz, 2 H). Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.77; H, 7.32.

2,5-Hexadiyn-1-yl Acetate (14c). In a 250-mL round-bottom flask was placed 47 g (0.5 mol) of 2,5-hexadiynol[26] and 90 mL of freshly distilled acetic anhydride. A catalytic amount of concentrated hydrochloric acid was added, and the mixture was stirred at room temperature for 16 h. Distillation under reduced pressure removed all of the acetic acid and excess acetic anhydride. 2,5-Hexadiyn-1-yl acetate, 55 g (83%), was collected at 65 °C (0.5 torr) as a colorless, viscous oil: ^1H NMR ($CDCl_3$) δ 2.1 (m, 4 H), 3.2 (q, J = 2 Hz, 2 H), 4.7 (t, J = 2 Hz, 2 H); mass spectrum, m/e 136 (M^+). Anal. Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.71; H, 6.08.

Reaction of 1,4-Pentadiyne with Dibuyltin Hydride. A mixture of 72 g (1.1 mol) of 1,4-pentadiyne[21] in 700 mL of heptane was allowed to reflux with 278 g (1.2 mol) of dibutyltin hydride for 16 h. The course of the reaction may be conveniently monitored by following the decrease of intensity of IR spectral bands at 1825 (SnH) and 3300 (≡CH) cm^{-1}. Alternatively, GLC (column C at 50 °C) may be used to follow the disappearance of diyne. The solvent was then distilled off, and the residue was subjected to vacuum distillation, giving 150 g (43%) of product, bp 105 °C (0.3 torr). A large quantity of viscous apparently polymeric material remained in the distillation pot. If the pot temperature was allowed to rise above 150 °C, this material underwent an exothermic reaction, yielding mossy tin and uninvestigated volatile products.

GLC analysis of the products (column A at 200 °C, 40 lb of He elution) showed **5** (retention time, 1.8 min) and **3** (retention time, 2.4 min) in a ratio of 5:95.

Reaction of Other 1,4-Diynes with Dibutyltin Hydride. In a similar manner, hydrostannation of the following diynes produced the indicated products.

1,4-Hexadiyne[21] (40 g, 0.5 mol) and dibutyltin dihydride (118 g, 0.5 mol) in 500 mL of heptane gave 106 g (65%) of product, bp 107 °C (0.7 torr). Separation by GLC (column A at 200 °C, 40 lb of He elution) gave **9b** (retention time, 2.4 min) and **10b** (retention time, 2.8 min) in a ratio of 1:4.

1,4-Heptadiyne[21] (12 g, 0.13 mol) and dibutyltin hydride (40 g, 0.17 mol) in 175 mL of heptane gave 22.5 g (53%) of product, bp 125–130 °C (2.0 torr). Separation by GLC (column A at 200 °C, 40 lb of He elution) gave **9c** (retention time, 3.0 min) and **10c** (retention time, 3.8 min) in a ratio of 13:87.

6,6-Dimethyl-1,4-heptadiyne[22] (3.8 g, 0.32 mol) and dibutyltin hydride (10 g, 0.44 mol) in 50 mL of heptane gave 6.4 g (56%) of product, bp 90–105 °C (0.5 torr). Separation by GLC (column A at 200 °C, 40 lb of He elution) gave **9d** (retention time, 4.5 min) and **10d** (retention time, 5.5 min) in a ratio of 7:93.

1-Phenyl-1,4-pentadiyne[23] (14 g, 0.1 mol) and dibutyltin hydride (24 g, 0.1 mol) in 150 mL of heptane gave 15.3 g (41%) of **9e**, bp 150 °C (0.3 torr).

2,5-Heptadiyne[24] (9.2 g, 0.1 mol) and dibutyltin hydride (23.4 g, 0.1 mol) gave 13.5 g (41%) of product, bp 100 °C (0.5 torr). Separation by GLC (column A at 200 °C, 40 lb of He elution) gave **9a** (retention time, 2.7 min) and **10a** (retention time, 3.1 min) in a ratio of 3:1.

2,5-Hexadiynyl methyl ether (31.5 g, 0.29 mol) and dibutyltin hydride (70 g, 0.3 mol) in 60 mL of heptane gave 56 g (55%) of product **14a**, bp 86 °C (0.001 torr).

2,5-Hexadiynyl 2-tetrahydropyranyl ether (8.9 g, 0.05 mol) and dibutyltin hydride (11.7 g, 0.05 mol) in 10 mL of heptane gave 12.1 g (59%) of product **14b**, bp 96 °C (0.001 torr).

2,5-Hexadiynyl acetate (132 g, 1 mol), dibutyltin hydride (235 g, 1 mol), and azobis(2-methylpropionitrile) (250 mg) in 500 mL of heptane gave, after recovery of 60 g of unreacted acetate, 75 g (39%) of product **14c**, bp 115 °C (0.001 torr).

Reaction of the Vinyltin Heterocycles with Acetic Acid. The vinyltin compound (2 g) was mixed with excess acetic acid (6 mL) and heated in a small distillation apparatus until approximately half of the liquid had distilled. On addition of excess water to the distillates of the volatile olefins, the oil which separated was collected and dried over anhydrous sodium carbonate. In the case of higher molecular weight olefins, the pot residue itself was subjected to vacuum distillation to obtain the product. The olefins were identified by comparison with authentic samples or by obvious assignments from their ^1H NMR spectra. Compounds **3** and **5** were shown to give 1,4-pentadiene.[27] The mixture of **9b** and **10b** gave *trans*-1,4-hexadiene,[27] while **9e** gave *trans*-1-phenyl-1,4-pentadiene.[28] The mixture of **9a** and **10a** gave *trans,trans*-2,5-heptadiene:[29] IR (CS_2) 960 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (m, 6 H), 2.67 (m, 2 H), 5.41 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 17.9 (CH_3), 35.7 (CH_2), 125.3, 129.9 (CH).

Reaction of the Vinyltin Heterocycles with Acetic-d_1 Acid. As needed acetic-d_1 acid was prepared by heating an equivalent of acetic anhydride with deuterium oxide until the mixture became homogeneous. In the same manner as above, **3** gave *cis,cis*-1,4-pentadiene-*1,5-d*$_2$ [^1H NMR (CCl_4) δ 5.8–5.5 (m, 2 H, H_2, H_4), 4.9 (d, J = 11 Hz, 2 H, cis H_1, H_5), 2.7 (t, J = 6 Hz, 2 H, H_3)], **5** gave 1,4-pen-

tadiene-*1,4,-d*$_2$ [^{1}H NMR ($CDCl_3$) δ 5.8–5.5 (m, 1 H, H_2), 4.9 (m, 3 H, H_1, H_5), 2.7 (br d, J = 6 Hz, 2 H, H_3)], and **9e** gave 1-phenyl-1,4-pentadiene-*2,5-d*$_2$ [^{1}H NMR (CCl_4) δ 7.1 (m, 5 H, C_6H_5), 6.3 (br s, 1 H, H_1), 5.7 (m, 1 H, H_4), 5.0 (d, J = 10 Hz, 1 H, cis H_5), 2.9 (d, J = 6 Hz, 2 H, H_3)].

Reaction of 1-Phenyl-1,4-pentadiyne with Tributyltin Hydride. 1-Phenyl-1,4-pentadiyne (6 g, 0.04 mol) and tributyltin hydride (6 g, 0.025 mol) in 50 mL of heptane were heated to reflux for 7 h. On vacuum distillation 2.5 g of 1-phenyl-1,4-pentadiyne was recovered, while 5.0 g of product, bp 165 °C (0.05 torr), was obtained. This material was heated to reflux with 7 mL of acetic acid. Distillation gave 1 mL of product, bp 65 °C (0.05 torr). Analysis by GLC (column B, 160 °C, 30 lb of He elution) showed 1-phenyl-4-penten-1-yne[30] (retention time, 1.6 min) and *trans*-1-phenyl-1-penten-4-yne (retention time, 2.6 min) in a ratio of 3:7. *trans*-1-Phenyl-1-penten-4-yne showed ^{1}H NMR ($CDCl_3$) δ 7.1 (s, 5 H, C_6H_5), 6.5 (d, J = 16 Hz, 1 H, H_1), 6.2 (dt, J = 16, 5 Hz, 1 H, H_2), 3.0 (m, 2 H, H_3), and 1.8 (d, J = 2 Hz, 1 H, H_5). Anal. Calcd for $C_{11}H_{10}$: C, 92.91; H, 7.09. Found: C, 93.04; H, 7.16.

Arsabenzene (1). A solution of 10 g (33 mmol) of 1,4-dihydro-1,1-dibutylstannabenzene (**3**)[31] and 10.4 g (33 mmol) of arsenic tribromide in 20 mL of tetraglyme [bis[2-(2-methoxyethoxy)ethyl] ether] was allowed to stir for 1 h at room temperature and then for 2 h at 80 °C. Excess (8 mL) 1,5-diazabicyclo[5.4.0]undecene (DBU) was added, and the mixture was stirred at 80 °C for another 0.5 h. Vacuum distillation gave 1.8 g (40%) product: bp <25 °C (0.1 torr); mp −54 °C. Analytical samples were obtained by preparative GLC (column C at 140 °C, 10 lb of He elution).

2-Methylarsabenzene (11b). In a similar manner, **10b**[31] (10 g, 32 mmol) and arsenic tribromide (10 g, 32 mmol) in 20 mL of tetraglyme gave 1.7 g (35%) of product, bp <25 °C (0.1 torr).

2-Ethylarsabenzene (11c). In a similar manner, **10c**[31] (3 g, 9 mmol) and arsenic tribromide (2.9 g, 9 mmol) in 10 mL of tetraglyme gave 0.6 g (48%) of product, bp <25 °C (0.1 torr).

2-*tert*-Butylarsabenzene (11d). In a similar manner, **10b**[31] (3 g, 8.5 mmol) and arsenic tribromide (2.7 g, 8.5 mmol) in 10 mL of tetraglyme gave 0.5 g (42%) of product, bp 33 °C (0.1 torr). A forerum of arsabenzene (0.12 g) was also obtained.

2,6-Dimethylarsabenzene (11a). A carbon tetrachloride solution (5 mL) containing 5 g (16 mmol) of the unseparated mixture of tin heterocycles **9a** and **10a** (3:1) and 1.9 g (11 mmol) of arsenic trichloride was heated to reflux for 18 h. The solvent was then partially removed (about 3 mL) by distillation under nitrogen, and vacuum distillation of the residue, bp <25 °C (0.1 torr), gave a light yellow liquid containing the product in a dilute carbon tetrachloride solution. Preparative GLC separation (column C at 140 °C, 10 lb of He elution) gave 150 mg (9%) of pure product.

2-Arsabenzenemethyl Methyl Ether (16a). A solution of 6.9 g (20 mmol) of **15a** and 3.6 g (20 mmol) of arsenic trichloride in 7 mL of tetrahydrofuran was heated to reflux for 16 h. Vacuum distillation gave 1 g (25%) of product, bp 45 °C (0.1 torr).

2-Arsabenzenemethyl Acetate (16c). A solution of 8.9 g (24 mmol) of **15c** and 7.8 g (24 mmol) of arsenic tribromide in 10 mL of tetrahydrofuran was stirred at room temperature for 16 h and then at 65 °C for 2 h. A solution of 3 mL of DBU in 5 mL of tetrahydrofuran was added, and the mixture was heated to reflux for 2 h. Vacuum distillation gave 2.8 g (56%) of product, bp 68 °C (0.10 torr).

2-Arsabenzenemethanol (17). A solution of 1.7 g (80 mmol) of 2-arsabenzenemethyl acetate (**16c**) and 100 mg of sodium methoxide in 20 mL of anhydrous methanol was heated to reflux for 4 h. Vacuum distillation gave 1.2 g (88%) of product, bp 78 °C (0.1 torr).

2-Arsabenzenecarboxaldehyde (18). Silver carbonate on Celite was prepared by using 8.5 g of silver nitrate, 3 g of sodium carbonate, and 10 g of Celite. The reagent was dried in a vacuum desiccator for 6 h. In a 100-mL flask was placed the silver carbonate and 50 mL of methylene chloride. A solution of 105 mg (0.88 mmol) of 2-arsabenzenemethanol (**17**) in 5 mL of methylene chloride was added through an addition funnel. The light green suspension turned black in ~10 min, after which the reaction was stirred for 16 h. The suspension was filtered over a bed of Celite, and the solvent was evaporated under vacuum. GLC separation (column B, 185 °C) of the remaining oil gave 60 mg (41%) of product: IR (CCl_4) 1685 cm^{-1}.

3-(2-Arsabenzene)-2-propenoic Acid Ethyl Ester (19). A solution of **18** (100 mg, 0.6 mmol), triphenylphosphine (157 mg, 0.6 mmol), ethyl bromoacetate (100 mg, 0.6 mmol), and propylene oxide (1 mL) in 5 mL of methylene chloride was stirred at room temperature for 16 h. All volatile material was then removed under vacuum, and molecular distillation (0.01 torr, pot temperature 150 °C) gave 100 mg (70%) of product: IR (CCl_4) 1710 cm^{-1}.

Acknowledgment. Support of our work by the National Institutes of Health (Grant No. R01-GM 20992) and the National Science Foundation (CHE 77-9740) is gratefully acknowledged.

Registry No.—**1**, 289-31-6; **2**, 24442-69-1; **3**, 31732-31-7; **5**, 69225-64-5; **8a**, 50428-63-2; **8b**, 10420-91-4; **8c**, 66084-38-6; **8d**, 18864-42-1; **8e**, 6088-96-6; **9a**, 69225-65-6; **9b**, 69225-66-7; **9c**, 69225-67-9; **9d**, 69225-68-9; **9e**, 69238-69-3; **10a**, 56578-03-1; **10b**, 56578-02-0; **10c**, 69225-60-1; **10d**, 69238-70-6; **11a**, 56578-01-9; **11b**, 56577-93-6; **11c**, 69225-69-0; **11d**, 69225-70-3; **14a**, 34498-27-6; **14b**, 40924-58-1; **14c**, 69225-76-9; **15a**, 69225-61-2; **15b**, 69225-62-3; **15c**, 69225-63-4; **16a**, 69225-71-4; **16c**, 69225-73-6; **17**, 69225-72-5; **18**, 69225-74-7; **19**, 69225-75-8; propargyl bromide, 106-96-7; propargyl 2-tetrahydropyranoyl ether, 6089-04-9; methyl propargyl ether, 627-41-8; 2,5-hexadiynol, 28255-99-4; dibutyltin hydride, 1002-53-5; *trans*-1,4-hexadiene, 7319-00-8; *trans*-1-phenyl-1,4-pentadiene, 55666-17-6; *trans,trans*-2,5-heptadiene, 39619-60-8; *cis,cis*-1,4-pentadiene-*1,5-d*$_2$, 69225-77-0; 1,4-pentadiene-*1,4-d*$_2$, 69225-78-1; *trans,trans*-1-phenyl-1,4-pentadiene-*2,5-d*$_2$, 69225-79-2; tributyltin hydride, 688-73-3; 1-phenyl-4-penten-1-yne, 4289-20-7; *trans*-1-phenyl-1-penten-4-yne, 69225-80-5; arsenic tribromide, 7784-33-0; arsenic trichloride, 7784-34-1; acetic acid, 64-19-7; acetic-d_1 acid, 758-12-3.

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