Electrophilic Aromatic Substitution Reactions of Arsabenzene

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Arsabenzene undergoes electrophilic substitution at the 2- and 4-positions. Proton–deuterium exchange takes place in trifluoroacetic acid-*d*. Friedel–Crafts acetylation and nitration give mixtures of 2- and 4-substituted products. 2- and 4-(trimethylsilyl)arsabenzenes are protodesilylated in trifluoroacetic acid.

The aromatic character of arsabenzene has been amply demonstrated by spectroscopic and structural studies.[1] For example, arsabenzene possesses a planar ring with normal aromatic C–C bond distances of 1.395 Å.[2] Its proton NMR spectrum shows low-field signals which indicate an appreciable diamagnetic ring current.[3] The UV photoelectron[4] and electron transmission spectra[5] are consistent with aromatic bonding of arsabenzene.

On the other hand, the chemical exploration of this aromaticity has been more limited. Märkl has reported that substituted arsabenzenes undergo several aromatic-type rearrangements,[6] while we made a preliminary report on the Friedel–Crafts acylation of the parent system.[7] The present paper summarizes our work on the most characteristic aromatic reaction, electrophilic substitution.

Results and Discussion

Deuterium Exchange. Acid-catalyzed proton isotopic exchange is the simplest and one of the better studied electrophilic aromatic substitution reactions.[8] A large number of data is available for the exchange of benzocyclic compounds in trifluoroacetic acid.[9] For reasons of compound stability, we have chosen to examine the deuterium exchange of arsabenzene in 1:1 v/v mixtures of methylene chloride–trifluoroacetic acid-*d*. At 100 °C, arsabenzene shows mono- and dideuteration on the basis of mass spectral analysis at *m/e* 140 (d_0), 141 (d_1), and 142 (d_2) (see Table I). After 3 days modest amounts of trideuteration (*m/e* 143) were found. Heating to 130 °C for 4 days gave approximately 40% trideuteration while no higher deuterated products could be detected.

Initial deuteration takes place in the α position. The ^{1}H NMR spectrum of reisolated arsabenzene shows diminished intensity at the well-separated α-proton resonance frequency (δ 9.7).[3] Since it is statistically required that the first-order[10] rate constant for dideuteration be exactly half that for monodeuteration, the amount of dideuteration may be accurately calculated from the amount of monodeuterated product (Table I). The slower trideuteration takes place at the unique γ-position (eq 1). If the third exchange were occurring at the β-position, the rate constant for the fourth exchange would have been exactly half that for the third exchange. This would require the concentration of arsabenzene-d_4 (*m/e* 144) to be at least 50 times greater than that observed. Thus, at 130 °C the rate of γ exchange is greater than 50 times that of β exchange.

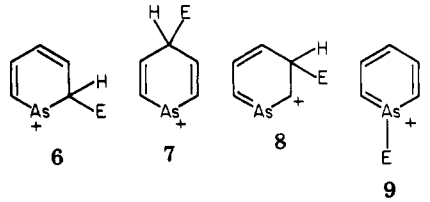
The relative reactivity of the α- and γ-positions may be compared approximately by competition experiments with benzocyclic aromatics. At 100 °C, α-arsabenzene exchange occurs 2.9 times slower than that for *m*-xylene and 6.3 times fater than that for *p*-xylene, while γ-arsabenzene exchange occurs 2.1 times slower than for toluene. With the plausible if imprecise assumption that the relative rates in the CF_3CO_2D/CH_2Cl_2 mixture at 100 °C are approxi-

Table I. Measured Relative Concentrations (Percent) of Deuterioarsabenzenes for Different Deuteration Conditions

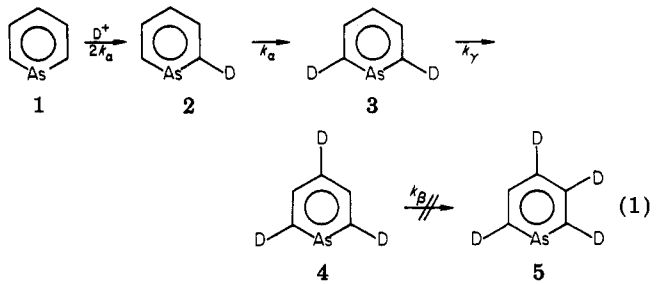
conditions	d_0	d_1	d_2	d_3	d_4
initial	100				
100 °C, 20 h	39.0	46.2 (46.9[a])	14.7	0.2	
100 °C, 3 days	11.0	41.5 (44.3[a])	46.3	1.0	
130 °C, 4 days			59.3	40.6	0.1 (5.3[a])

[a] Calculated concentration assuming $k_1 = 2k_2$ ($d_0 \xrightarrow{k_1} d_1 \xrightarrow{k_2} d_2$). [b] Calculated concentration assuming $k_3 = 2k_4$ ($d_2 \xrightarrow{k_3} d_3 \xrightarrow{k_4} d_4$).

Chart I[a]



[a] a, E = D; b, E = H; c, E = $COCH_3$; d, E = NO_2; e, E = $Si(CH_3)_3$.



(1) Ashe, A. J., III *Acc. Chem. Res.* **1978**, *11*, 153.
(2) Wong, T. C.; Bartell, L. S. *J. Mol. Struct.* **1978**, *44*, 169.
(3) Ashe, A. J., III; Sharp, R. R.; Tolan, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 5451.
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(5) Burrow, P. D.; Ashe, A. J., III; Bellville, D. J.; Jourdan, K. D., unpublished results.
(6) Märkl, G.; Rampal, J. B. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 690. Märkl, G.; Liebl, R. *Ibid.* **1977**, *16*, 637.
(7) Ashe, A. J., III; Chan, W.-T.; Smith, T. W. *Tetrahedron Lett.* **1978**, 2537.
(8) Taylor, R. *Int. Rev. Sci.: Org. Chem., Ser. One* **1973**, *3*, 1; *Int. Rev. Sci: Org. Chem., Ser. Two* **1976**, *3*, 25.
(9) Richards, K. E.; Wilkinson, A. L.; Wright, G. J. *Aust. J. Chem.* **1972**, *25*, 2369.
(10) In excess acid, rates of exchange are first order in aromatic hydrocarbon.[9]

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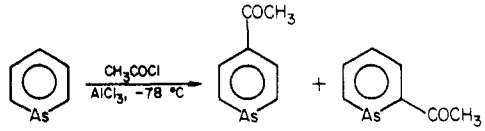
mately the same as those in trifluoroacetic acid at 70 °C, the relative order of reactivity is [4-H]-*m*-xylene (7.3×10^4) > [α-H]-arsabenzene (2.5×10^3) > [2-H]-*p*-xylene (1500) > [4-H]-toluene (410) ≈ [γ-H]-arsabenzene (400) > [β-H]-arsabenzene (<8); [1-H]-benzene (1).[11,12]

These data indicate that arsabenzene is a considerably stronger base than benzene in agreement with our previous gas-phase acidity study.[13] The gas-phase proton affinity of arsabenzene is 192.7 kcal/mol, while that of benzene is 186.1 kcal/mol. Although the exact site of the gas-phase protonation was undetermined, the fact that deuterium exchange was observed required that arsabenzene be protonated on carbon. At present there is no evidence for protonation of the arsenic atom (formation of **9b**, Chart I). We have discussed the reason for this low heteroatom basicity elsewhere.[1,13,14]

Structure **6b** (Chart I) is implicated as the most stable conjugate acid of arsabenzene, while **7b** is lower in energy than **8b**. We assume that protonation occurs only at the α- and γ-positions because only **6b** and **7b** in contrast to **8b** allow efficient electronic interaction of the positive charge with the electropositive arsenic atom. If the largest portion of the positive charge in intermediates **6b** and **7b** does reside on the electropositive arsenic atom, the greater stability of **6b** over **7b** may be due to greater stability of the terminally conjugated diene of **6b** over the cross-conjugated diene of **7b**.

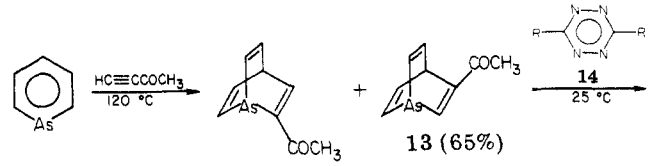
Acetylation. Acetylation of arsabenzene at −78 °C in methylene chloride using the Perrier complex (1:1 acetyl chloride–aluminum chloride) followed by warming to 25 °C prior to hydrolytic workup affords a good yield of 4-acetylarsabenzene (**10**, eq 2). However, if the reaction is



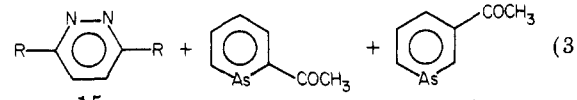
10 11 (2)

carried out and worked up at −78 °C, the product is a mixture of monoacetylarsabenzenes. Although this mixture was homogeneous on all GLC columns available to us, the ^{1}H NMR spectrum clearly revealed two acyl methyl signals at δ (C_6D_6) 2.13 and 2.37 in the ratio of 4:1. The major isomer remained 4-acetylarsabenzene, while the ^{1}H NMR spectrum of the mixture suggested that the minor compound was 2-acetylarsabenzene (**11**).

For unambiguous identification authentic samples of 2- and 3-acetylarsabenzene were prepared by an independent synthesis. The Diels–Alder addition of 3-butyn-2-one to arsabenzene afforded 1:1 adducts **12** and **13** (eq 3) in the ratio of 35:65. Small quantities of pure **12** and **13** were separated by GLC, and structures were assigned from their ^{1}H NMR spectra. Treating the unseparated mixture with 3,6-bis(α-pyridyl)-1,2,4,5-tetrazine (**14**,[15] R = α-pyridyl) at 25 °C in methylene chloride gave 3,6-bis(α-pyridyl)-1,2-



12 (35%) 13 (65%)

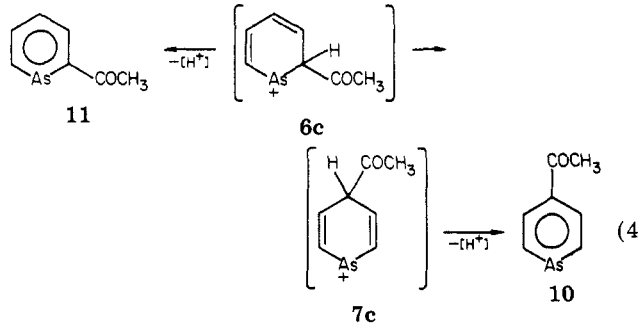


15 11 16 (3)

diazine (**15**, R = α-pyridyl) and the desired 2- and 3-acetylarsabenzenes **11** and **16** in the ratio of 30:70. The isomers were separated by GLC. The 2-acetylarsabenzene showed a ^{1}H NMR spectrum identical with signals observed for the minor component in the low-temperature acetylation mixture. 3-Acetylarsabenzene was not present in the Friedel–Crafts acetylation products down to an estimated level of detection of 0.5%. Thus, at −78 °C the rates for acetylation of the different positions of arsabenzene are in a α:β:γ ratio of 40:(<1):300.

When the most reactive 4-position is blocked, substitution takes place in lower yield at the 2-position. 4-Methylarsabenzene (**17**) gave a 50% yield of 2-acetyl-4-methylarsabenzene (**18**). However, in this case there was also a nonaromatic, very air-sensitive, arsenic-containing product, which rapidly formed an intractable tar. We have been unable to characterize this labile material.

The temperature variation in the ratio of γ/α products suggests that the 4-acetylarsabenzene may be the thermodynamically controlled product. However, all three acetylarsabenzenes are stable to the Friedel–Crafts reaction conditions. Thus, the exclusive formation of 4-acetylarsabenzene at higher temperature can only result from interconversion of intermediates, probably the conversion of σ-complex **6c** to **7c**[16a] (eq 4).



11 6c 7c 10 (4)

In contrast to **6b** and **7b**, the cross conjugated **7c** appears to be more stable than **6c**. Cation **6c** is likely to be strongly destabilized by the electrostatic repulsion between the proximate carbonyl group and the positively charged arsenic atom.

Competitive acetylation of arsabenzene and mesitylene at −78 °C showed that mesitylene is acetylated half as fast as arsabenzene. Thus, arsabenzene is approximately 10^3–10^4 times more reactive than benzene.[16] Arsabenzene behaves like a moderately activated ortho–para-directing substituted benzene toward electrophilic attack. Presumably, the electrophile attacks only at the α- or γ-positions because only these positions allow efficient resonance in-

(11) Ansell, H. V.; Taylor, R., unpublished work mentioned in: "Aromatic and Heteroaromatic Chemistry"; The Chemical Society: London, 1974; Vol. 2, p 225. Baker, R.; Eaborn, C.; Taylor, R. *J. Chem. Soc.* **1961**, 4927.

(12) The relative rates of different positions are taken from ref 9 and 11. Rates are corrected for statistical differences. Under our conditions [4H]-*m*-xylene was 29.4 times more reactive than [2H]-*p*-xylene while at 70 °C in pure trifluoroacetic acid the relative reactivity factor was 49.

(13) Hodges, R. V.; Beauchamp, J. L.; Ashe, A. J., III; Chan, W.-T. *J. Am. Chem. Soc.*, in press.

(14) Ashe, A. J., III; Bahl, M. K.; Bomben, K. D.; Chan, W.-T.; Grimzewski, J. K.; Sitton, P. G.; Tomas, T. D. *J. Am. Chem. Soc.* **1979**, *101*, 1764.

(15) Warrener, R. N. *J. Am. Chem. Soc.* **1971**, *93*, 2346.

(16) (a) The proposal that **6c** is converted to **7c** requires that proton elimination be the rate-determining step in the acetylation of arsabenzene. This is very plausible since proton elimination is kinetically significant in the Friedel-Crafts acetylation of benzene, toluene, and mesitylene. Olah, G. A.; Kuhn, S. J.; Flood, S. H.; Hardie, B. A. *J. Am. Chem. Soc.* **1964**, *86*, 2203. (b) Marino, G.; Brown, H. C. *Ibid.* **1959**, *81*, 5929.

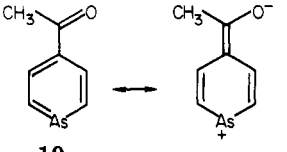
Table II. γ_{CO} for Various Para-Substituted Acetophenones and Acetylarsabenzenes

compd	γ_{CO}, cm^{-1}
p-aminoacetophenone	1667
p-methylacetophenone	1682
acetophenone	1686
p-nitroacetophenone	1696
2-acetylarsabenzene (11)	1683
3-acetylarsabenzene (16)	1692
4-acetylarsabenzene (10)	1673

teraction with the electropositive arsenic in intermediates 6 and 7.

Unfortunately, there is little independent evidence for the electron availability of the various positions of arsabenzene. Hammett substituent constants of the 2-, 3-, and 4-positions of arsabenzene are 0.3, 0.4, and 0.1.[17] These positive values indicate that all of the carbon atoms of arsabenzene are electron deficient with respect to benzene. However, Hammett substituent constants for para positions do not correlate with the relative rates of aromatic substitution reactions.[18] Presumably the resonance stabilization of the intermediate benzenonium cations by para substituents is different than the substituent effects on the ionization of benzoic acids used to define the σ values. For the same reason the σ constants for the 2- and 4-positions of arsabenzene are unlikely to correlate with the rates of aromatic substitution, while the more appropriate σ^+ values[18] are not presently available.

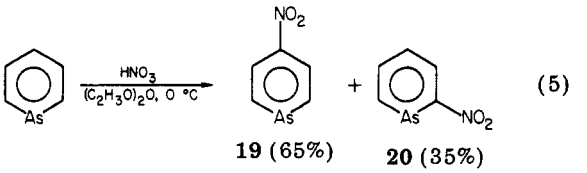
Nonetheless, we feel that a crude measure of the degree of electronic interaction of the arsenic atom with α-, β-, and γ-positions can be obtained by examining the three acetylarsabenzenes in hand. Thus, the IR carbonyl stretching frequencies of para-substituted acetophenones correlate with the electron donor–acceptor ability (σ^+) of the substituents in electrophilic substitution.[19] Ortho–para-directing substituents lower the γ_{CO} of the acetophenone, while deactivating substituents raise the γ_{CO} (see Table II). The γ_{CO} of 2- and 4-acetylarsabenzenes is below that of acetophenone, while 3-acetylarsabenzene has a higher stretching frequency. The carbonyl double bond of 10 (and 11) must be weakened by electron donation from



10 10′

arsenic (resonance structure 10′) in a manner similar to the stabilization of 7. Presumably, the strengthening of the carbonyl double bond of 16 implies that the arsenic withdraws electron density from the β-position. This suggests that the β-position of arsabenzene is deactivated toward electrophilic substitution.

Nitration. The usual conditions for sulfonation and halogenation of benzene led to the formation of intractable products when applied to arsabenzene. Attempted nitration with mixtures of nitric and sulfuric acids was similarly unsuccessful. However, the cautious nitration with nitric acid in acetic anhydride at 0 °C gave a 20% yield of nitroarsabenzenes along with a large quantity of tarlike material. Separation by GLC showed 4-nitroarsabenzene (19) and 2-nitroarsabenzene (20) (eq 5) in the ratio of 2:1.



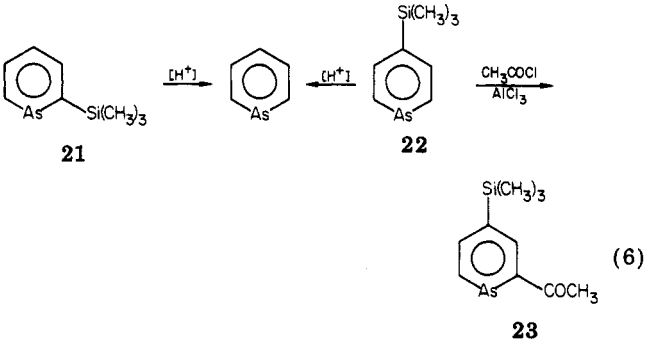
(5)

19 (65%) 20 (35%)

Structures were assigned from analysis of their simple ^{1}H NMR spectra. In addition, 4-nitroarsabenzene could be reduced with iron in acetic acid to 4-aminoarsabenzene which had previously been prepared independently by Märkl.[20]

Desilylation. From a synthetic standpoint only the acylation of arsabenzene takes place in preparatively satisfactory yield. Desilylation of (trimethylsilyl)benzocyclic aromatics has proved to be a mild and useful method for introducing electrophilic substituents.[21] Since we had hoped that desilylation of arsabenzenes might overcome some of the limitations of direct substitution, we have explored the desilylation reactions of (trimethylsilyl)arsabenzenes. 2- and 4-(trimethylsilyl)arsabenzenes (21 and 22)[22] can be readily prepared by treating the corresponding stannacyclohexadienes with arsenic tribromide. Unfortunately, we have no route to prepare 3-(trimethylsilyl)arsabenzene.[23]

Acetylation of (trimethylsilyl)benzene takes place readily with desilylation to give acetophenone.[24] However, 4-(trimethylsilyl)arsabenzene does not desilylate under acetylation conditions, since acetylation affords only 2-acetyl-4-(trimethylsilyl)arsabenzene (23, eq 6).



21 22

(6)

23

On the other hand, both (trimethylsilyl)arsabenzenes will undergo protodesilylation to arsabenzene on treatment with trifluoroacetic acid. Competition experiments at 25 °C showed that 2-(trimethylsilyl)arsabenzene is protodesilylated 2.15 times faster than (trimethylsilyl)benzene, while 4-(trimethylsilyl)arsabenzene reacts 1.65 times as fast. Under identical conditions, 4-(trimethylsilyl)toluene reacts 15.7 times as fast as (trimethylsilyl)benzene.[25] This relative reactivity contrasts with acetylation and deuterium exchange of arsabenzene since it was more reactive than toluene.

(Trimethylsilyl)benzene undergoes protonation approximately 10^4 times faster than benzene.[26] This en-

(17) Ashe, A. J., III; Chan, W.-T. *J. Org. Chem.* **1980**, *45*, 2016.
(18) Stock, L. M.; Brown, H. C. *Adv. Phys. Org. Chem.* **1963**, *1*, 35.
(19) Rossetti, G. P.; Susz, B. P. *Helv. Chim. Acta* **1964**, *47*, 299.
(20) Märkl, G.; Rampal, J. B. *Tetrahedron Lett.* **1978**, 1175.
(21) Eaborn, C. *Pure Appl. Chem.* **1969**, *19*, 375.
(22) Jutzi, P.; Baumgärtner, J. *J. Organomet. Chem.* **1978**, *148*, 247.
(23) We have been unable to use the Diels-Alder method which allowed successful preparation of 11, since the addition of (trimethylsilyl)acetylene to arsabenzene afforded only 2-(trimethylsilyl)-1-arsabicyclo[2.2.2]octa-2,5,7-triene. Ashe, A. J., III; Abu-Orabi, S.; Chan, W.-T., unpublished results.
(24) Dey, K. *J. Indian Chem. Soc.* **1972**, *49*, 375.
(25) 4-(Trimethylsilyl)toluene undergoes protodesilylation 18–21 times faster than does (trimethylsilyl)benzene at 50 °C under different acid conditions. A great deal of data is available for substitution effects on this reaction. See: Eaborn, C.; Bott, R. W. In MacDiarmid, A. G., Ed. "Organometallic Compounds of the Group IV Elements"; Marcel Dekker: New York, 1968; Vol. 1, Part I, pp 408–417.

hanced rate is usually associated with the hyperconjugative stabilization of the trimethylsilyl group for the positive charge of the intermediate benzenonium cation.[25,27] Evidently the hyperconjugative stabilization is relatively less efficient in (trimethylsilyl)arsabenzenes. Since these results suggest that desilylation of **21** and **23** by other electrophiles would be unsuccessful, we have not pursued the reactions further.

Conclusions

Although the arsabenzene ring system is more sensitive to oxidation than are normal benzocyclics, it undergoes a variety of electrophilic substitution reactions. Qualitatively, the effect of the electropositive heteroatom of arsabenzene appears to be comparable to that of an activating ortho–para-directing group on a benzene ring. Both deuterium exchange and protodesilylation take place faster in the α- than in the γ-position. Presumably, the terminally conjugated intermediates **6b,e** are more stable than the cross-conjugated intermediates **7b,e**. On the other hand, both nitration and acetylation show a preference for substitution in the γ-position. In these cases, we suggest that electrostatic repulsion between the electropositive electrophile and the positively charged arsenic atom destabilizes intermediates **6c,d** relative to **7c,d**. Finally, we have been unable to detect electrophilic substitution in the β-position. It is suggested that intermediate **8** is a high-energy species.

Experimental Section

The NMR spectra were recorded by 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 spectra data were obtained by using a Finnigan 4021 GC–MS instrument operating at an ionizing voltage of 70 eV. IR spectra were recorded by using a Perkin-Elmer Model 457 spectrometer calibrated with polystyrene. C and H combustion analyses were obtained on all new compounds by Spang Microanalytical Laboratory or Galbraith Laboratories. In all cases, except as noted for compound **20**, analyses agreed with calculated values (±0.4%). GLC analyses and separations were performed by using a Varian 90P or 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.

Materials. Trifluoroacetic acid-*d* was prepared by mixing 1 equiv of deuterium oxide with trifluoroacetic anhydride. Arsabenzene,[28] 4-methylarsabenzene,[29] and 4-(trimethylsilyl)arsabenzene[22] were prepared by the reaction of arsenic tribromide with the appropriate 1,1-dibutylstannacyclohexa-2,5-dienes by using the standard procedure.[28] Properties were consistent with those reported in the original literature.[22,28,29]

1-(Trimethylsilyl)-1,4-pentadiyne. To a solution of ethynylmagnesium bromide prepared from 24 g (1.0 mol) of magnesium and 105 g (1.0 mol) of ethyl bromide in 1 L of tetrahydrofuran was added a solution of 77 g (0.8 mol) of (trimethylsilyl)acetylene[30] in 500 mL of tetrahydrofuran. The solution was heated to 60 °C for 30 min and then cooled in a cold water bath. A 2.0-g sample of cuprous chloride was added followed by 95 g (0.8 mol) of propargyl bromide. The mixture was heated to reflux for 90 min, during which it turned dark red. After being cooled, the mixture was quenched with excess dilute hydrogen chloride. The organic layer was separated, and the aqueous layer was extracted with pentane. The combined organic phase was washed with excess water and then dried over 3A molecular sieves. After removal of the solvent the product was distilled [bp 48–55 °C (40 torr)], yielding 60 g (55%) of product: ^{1}H NMR (neat) δ 0.0 (s, 9 H), 2.0 (t, J = 3 Hz, 1 H), 3.0 (d, J = 3 Hz, 2 H). Anal. Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 70.49; H, 8.94.

1,1-Dibutyl-2-(trimethylsilyl)stannacyclohexa-2,5-diene. A mixture of 46 g (0.3 mol) of 1-(trimethylsilyl)-1,4-pentadiyne and 78 g (0.3 mol) of dibutyltin dihydride in 200 mL of heptane was allowed to reflux for 16 h. Distillation gave 30 g (34%) of product: bp 120 °C (0.5 torr); ^{1}H NMR (neat) δ 0.1 (s, 9 H), 0.7–1.6 (m, 18 H), 3.1 (m, 2 H), 6.1 (d, J = 13 Hz, 1 H), 6.5 (dt, J = 13, 3 Hz, 1 H), 6.8 (t, J = 4 Hz, 1 H); mass spectrum, m/e 372 (M^+, $C_{16}H_{32}Si^{120}Sn$), 315 ($M^+ - C_4H_9$). Anal. Calcd for $C_{16}H_{32}SiSn$: C, 51.76; H, 8.69. Found: C, 51.60; H, 8.76.

2-(Trimethylsilyl)arsabenzene (21). A solution of 7.4 g (20 mmol) of 1,1-dibutyl-2-(trimethylsilyl)stannacyclohexa-2,5-diene and 2.4 g (13.3 mmol) of arsenic trichloride in 10 mL of carbon tetrachloride was stirred at 25 °C for 2 h and then heated to reflux for 16 h. After solvent removal the product was distilled, yielding 0.56 g (20%) of product: bp 30 °C (0.5 torr); ^{1}H NMR (CCl_4) δ 0.1 (s, 9 H), 7.0–7.8 (m, 3 H), 9.7 (d, J = 10 Hz, 1 H); mass spectrum, m/e 212 (M^+, $C_8H_{13}AsSi$). Anal. Calcd for $C_8H_{13}AsSi$: C, 45.32; H, 6.18. Found: C, 45.34; H, 6.20.

Deuteration of Arsabenzene. A solution was prepared from 5 mL of trifluoroacetic acid-*d*, 5 mL of methylene chloride, and 200 mg of arsabenzene. Aliquots (700 μL) were sealed under argon in each of several ampules. The ampules were placed in a heating bath and then removed at intervals. Some tar formation was noted. When the ampule was opened, the contents were added to an excess of saturated aqueous sodium carbonate. The organic layer was separated, dried, and subjected to analysis by gas chromatography–mass spectrometry. The intensities of peaks at m/e 140, 141, 142, etc. allowed determination of arsabenzene-d_0, -d_1, -d_2, etc. Correction was made for the ^{13}C contribution to the (M + 1) peaks, but no correction was needed for the small (<5%) M – 1 peak of arsabenzene.

The concentrations of arsabenzene-d_1 (B_t) could be calculated from those of arsabenzene-d_0 (A_t). It was assumed that the first-order rate constant for deuteration of arsabenzene-d_1 was half that for deuteration of arsabenzene-d_0 from the scheme given by eq 7–10.

$$A \xrightarrow{k} B \xrightarrow{k/2} C \tag{7}$$

$$A_t = A_0 e^{-kt} \tag{8}$$

$$B_t = 2A_0(e^{-kt/2} - e^{-kt}) \tag{9}$$

$$B_t = 2((A_0A_t)^{1/2} - A_t) \tag{10}$$

Calculated concentrations of arsabenzene-d_1 agreed well with observed values for low deuteration but showed a small drop-off at higher deuteration. This was associated with the buildup of CF_3CO_2H.

Competitive Deuterations. Competitive deuteration experiments were run in the same manner as above by using 200 mg of the appropriate benzocyclic aromatic. Analysis of the appropriate mass spectral m/e values was accomplished by comparison with those of arsabenzene. Where necessary, correction was made for large M – 1 hydrocarbon peaks.

Relative Rates of Protodesilylation. Solutions were prepared from 0.5 mmol of 1,2,3,5-tetramethylbenzene (internal standard), 0.5 mmol of (trimethylsilyl)benzene, and 0.5 mmol of **21**, **22**, or *p*-(trimethylsilyl)toluene in 2 mL of methylene chloride. The solutions were frozen at –78 °C, and then 1.35 g (12 mmol) of trifluoroacetic acid was added. The solutions were placed in a constant-temperature bath at 25 °C. At intervals 200-μL aliquots were removed and added to saturated aqueous sodium carbonate. The organic layer was separated and dried. The concentrations of trimethylsilyl aromatics were determined relative to the internal standard by GLC. Relative rate constants were determined by plotting the natural logarithm of concentration against time. Good linear plots were obtained. The relative rates were 1:1.65:2.06:15.7 for (trimethylsilyl)benzene/**21**/**22**/*p*-(trimethylsilyl)toluene.

Acetylation of Arsabenzene. Method a: At –78 °C. To a suspension of 1 g of aluminum chloride in 20 mL of methylene chloride at –78 °C was added 1 g of acetyl chloride followed by

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500 mg (3.6 mmol) of arsabenzene in 10 mL of methylene chloride. After the mixture was stirred at −78 °C for 2.5 h, 10 mL of 2-propanol was added followed by excess water. After the mixture was warmed, the organic layer was separated while the aqueous layer was extracted with 5 mL of methylene chloride. The combined organic phases were dried, and on distillation 560 mg (86%) of crude product was obtained. The material was homogeneous on a variety of GC columns. However, ^{1}H NMR (C_6D_6) showed signals for two acetyl methyl groups at δ 2.13 and 2.37 in the ratio of 4:1. The spectrum was consistent with a 4:1 mixture of **10** and **11**.

Method b. If the reaction was run in the same manner except that the temperature was allowed to warm to 25 °C for 30 min prior to quenching with 2-propanol, 500 mg (70%) of product was isolated. The product was pure 4-acetylarsabenzene (**10**): ^{1}H NMR (C_6D_6) δ 2.13 (s, 3 H), 8.22 (d, J = 10 Hz, 2 H), 9.38 (d, J = 10 Hz, 2 H); IR ($CDCl_3$) 1673 cm^{-1}; mass spectrum, m/e 182 (M^+, C_7H_7AsO). Anal. Calcd for C_7H_7AsO: C, 46.19; H, 3.87. Found: C, 46.35; H, 4.03.

2-Acetyl-4-methylarsabenzene (18). In a similar manner, acetylation of 320 mg (2 mmol) of 4-methylarsabenzene (**17**) gave 195 mg (50%) of 2-acetyl-4-methylarsabenzene: ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 2.7 (s, 3 H), 7.8 (d, J = 10 Hz, 1 H), 8.3 (s, 1 H), 9.7 (d, J = 10 Hz, 1 H); mass spectrum, m/e 196 (M^+, C_8H_9AsO). Anal. Calcd for C_8H_9AsO: C, 49.02; H, 4.63. Found: C, 49.41; H, 4.86.

2-Acetyl-4-(trimethylsilyl)arsabenzene (23). In a similar manner, 235 mg (0.1 mmol) of 4-(trimethylsilyl)arsabenzene gave 160 mg (57%) of 2-acetyl-4-(trimethylsilyl)arsabenzene as a red oil: ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 9 H), 2.7 (s, 3 H), 8.11 (d, J = 10 Hz, 1 H), 8.65 (s, 1 H), 9.8 (d, J = 10 Hz, 1 H).

2-Acetylarsabenzene (11) and 3-Acetylarsabenzene (16). A solution of 1 g of arsabenzene and 2 g of 3-butyn-2-one in 15 mL of mesitylene was heated at 110 °C for 3 h, after which the excess starting materials and solvent were removed by distillation, leaving a residual yellow oil. Analysis by GLC (6 ft × $^1/_4$ in. column packed with 20% SE-30 on Chromosorb W at 180 °C, 30 lb of He pressure) showed **13** (retention time 3 min) and **12** (retention time 4.5 min) in the ratio of 65:35. Small quantities of the isomers were collected for identification. Isomer **13**: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3 H), 6.04 (tq, J = 6, 2 Hz, 1 H), 6.98 (dd, J = 7, 2 Hz), 7.18 (t, J = 7 Hz, 2 H), 7.90 (d, J = 2 Hz, 1 H). Isomer **12**: ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 5.40 (qt, J = 6, 1.5 Hz, 1 H), 7.08 (dd, J = 7, 2 Hz, 2 H), 7.22 (t, J = 7 Hz, 2 H), 7.80 (d, J = 6 Hz, 1 H).

The major portion of the mixture of **12** and **13** was taken up in 20 mL of methylene chloride and then treated with 2 g of 3,6-bis(α-pyridyl)-1,2,4,5-tetrazine[15] for 12 h at 25 °C. After removal of solvent the residue was extracted with excess pentane, and the extracts were distilled at reduced pressure, giving 750 mg (58%) of product. Analysis by GLC (5 ft × $^1/_4$ in. column packed with 15% XF-1150 on Chromosorb W at 190 °C, 30 lb of He pressure) showed 70% 3-acetylarsabenzene (retention time 10 min) and 30% of 2-acetylarsabenzene (retention time 11.5 min).

3-Acetylarsabenzene: ^{1}H NMR (C_6D_6) δ 2.2 (s, 3 H), 7.4–8.1 (m, 2 H), 9.5 (d, J = 10 Hz, 1 H), 10.0 (s, 1 H); IR ($CDCl_3$) 1692 cm^{-1}; mass spectrum, m/e 182 (M^+, C_7H_7AsO). Anal. Calcd for C_7H_7AsO: C, 46.19; H, 3.87. Found: C, 46.43; H, 3.91.

2-Acetylarsabenzene: ^{1}H NMR (C_6D_6) δ 2.4 (s, 3 H), 7.2–7.7 (m, 2 H), 8.3 (d, J = 8 Hz, 1 H), 9.5 (d, J = 9 Hz, 1 H); IR ($CDCl_3$) 1683 cm^{-1}; mass spectrum, m/e 182 (M^+, C_7H_7AsO). Anal. Calcd for C_7H_7AsO: C, 46.19; H, 3.87. Found: C, 46.00; H, 3.67.

Nitration of Arsabenzene. A nitrating solution was prepared by cautious addition of 0.22 g (3.5 mmol) of nitric acid to 0.5 mL of acetic anhydride at 0 °C. This solution was added dropwise to a mixture of 200 mg (1.42 mmol) of arsabenzene in 1.5 mL of acetic anhydride at −10 °C. During the course of the addition the temperature did not rise above 0 °C. After being stirred an additional 15 min at 0 °C, the mixture was poured into 20 mL of ice–water, which was then extracted with ether. The extracts were dried over magnesium sulfate. Removal of solvent left 50 mg (20%) of a red oil. GLC analysis (8 ft × $^1/_4$ in. column packed with 20% SE-30 on Chromosorb W at 165 °C, 20 lb of He pressure) showed 65% 4-nitroarsabenzene (retention time 10.5 min), and 35% 2-nitroarsabenzene (retention time 12.5 min).

4-Nitroarsabenzene (**19**): ^{1}H NMR ($CDCl_3$) δ 8.8 (d, J = 12 Hz, 2 H), 9.9 (d, J = 12 Hz, 2 H); IR ($CDCl_3$) 1540, 1380 cm^{-1}; mass spectrum, m/e 185 (M^+ for $C_5H_4AsNO_2$). Anal. Calcd for $C_5H_4AsNO_2$: C, 32.43; H, 2.16. Found: C, 32.56; H, 2.17.

2-Nitroarsabenzene (**20**): ^{1}H NMR ($CDCl_3$) δ 7.9 (m, 2 H), 8.7 (d, J = 9 Hz, 1 H), 9.8 (d, J = 10 Hz, 1 H); IR ($CDCl_3$) 1540, 1380 cm^{-1}; mass spectrum, m/e 185 (M^+ for $C_5H_4AsNO_2$). Anal. Calcd for $C_5H_4AsNO_2$: C, 32.43; H, 2.16. Found: C, 33.02; H, 2.27.

4-Aminoarsabenzene. Iron powder (0.4 g, 7.1 mol) was added to a mixture of 4-nitroarsabenzene (100 mg, 0.54 mmol) and acetic acid (0.84 g, 14 mmol) in 5 mL of ethanol. The mixture was refluxed under nitrogen for 3 h. After cooling, this mixture was added to 20 mL of water, and then this was extracted successively with ether (2 × 20 mL) and chloroform (2 × 20 mL). After being washed with water, the combined extracts were dried over anhydrous magnesium sulfate. Removal of solvent left a red oil which was taken up in ether and then extracted with dilute hydrochloric acid. These extracts were added to excess aqueous sodium bicarbonate and then extracted with ether. After being dried, the solvent was removed to give 67 mg of a red oil, which showed an NMR spectrum identical with that reported for 4-aminoarsabenzene.[20]

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