

## Synthesis of 1-Arsanaphthalene

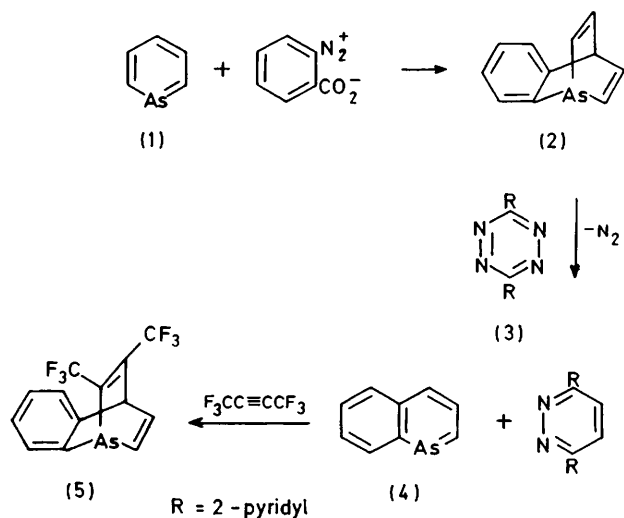
By ARTHUR J. ASHE, III,\* DENNIS J. BELLVILLE, and HOWARD S. FRIEDMAN

*(Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109)*

*Summary* The reaction of 1,4-etheno-1,4-dihydro-1-arsanaphthalene with 3,6-di-(2-pyridyl)-s-tetrazine has been used to generate arsanaphthalene for the first time.

THE aromaticity of arsabenzene, arsenin (**1**), is now well established.<sup>1</sup> While arsabenzene is a stable, easily handled compound, the dibenzannelated arsenin, 9-arsa-anthracene,

is so labile that it can only be obtained in dilute solution at low temperature.<sup>2,3</sup> The previously unknown monobenzenelated arsenin, 1-arsanaphthalene (**4**), might be expected to possess an intermediate reactivity and its synthesis seemed highly desirable for our continuing study of aromatic arsenic heterocycles.<sup>1</sup>



We now report the first synthesis of 1-arsanaphthalene. The reaction of arsenabenzene with benzenediazonium-2-carboxylate in  $\text{CH}_2\text{Cl}_2$  gave a 33% yield of 1,4-etheno-1,4-dihydro-1-arsanaphthalene (**2**), m.p.  $45^\circ\text{C}$ .† In our hands, the pyrolysis of (**2**) at  $300^\circ\text{C}$  gave only intractable material. Use of the low temperature acetylene abstraction agent, 3,6-di(2-pyridyl)-s-tetrazine (**3**),<sup>4</sup> was more satisfactory. A solution of equivalent quantities of (**2**) and (**3**) in  $\text{CDCl}_3$  slowly evolved  $\text{N}_2$ , while the  $^1\text{H}$  n.m.r. spectrum indicated the formation of 3,6-di-(2-pyridyl)pyridazine. In addition, a low field doublet at  $\delta$  10.22 ( $J$  9 Hz) appeared as expected for the C(2)-proton of 1-arsanaphthalene.<sup>5</sup> However, after several hours at  $25^\circ\text{C}$ , the  $\delta$  10.22 signal slowly decreased, indicating the destruction of (**4**).

1-Arsanaphthalene can be trapped with reactive dienophiles. When a mixture of (**2**) and (**3**) was treated with an excess of hexafluorobut-2-yne it gave the 1:1 adduct (**5**),† m.p.  $58.5^\circ\text{C}$ . Small quantities of 1-arsanaphthalene itself can be isolated from the mixture by g.l.c. This very air-sensitive yellow oil shows mass spectral peaks at  $m/e$  190 ( $M^+$ ) and 115 ( $M^+ - \text{As}$ ). The  $^1\text{H}$  n.m.r. spectrum shows the  $\delta$  10.22 doublet as well as a more complicated pattern in the normal aromatic region ( $\delta$  8.5–7.3).

We thank the National Science Foundation for partial support of this work.

(Received, 25th June 1979; Com. 665.)

† New compounds (**2**) and (**5**) are crystalline solids for which satisfactory elemental analyses and the usual range of spectroscopic data have been obtained.

<sup>1</sup> A. J. Ashe, III, *Accounts Chem. Res.*, 1978, **11**, 153.

<sup>2</sup> P. Jutzi and K. Deuchert, *Angew. Chem. Internat. Edn.*, 1969, **8**, 991; H. Vermeer and F. Bickelhaupt, *ibid.*, p. 992.

<sup>3</sup> However, 10-substituted arsa-anthracenes are more stable. See: H. Vermeer and F. Bickelhaupt, *Tetrahedron Letters*, 1970, 3255.

<sup>4</sup> R. N. Warren, *J. Amer. Chem. Soc.*, 1971, **93**, 2346; A. J. Ashe, III, W.-T. Chan, and T. W. Smith, *Tetrahedron Letters*, 1978, 2537

<sup>5</sup> A. J. Ashe, III, R. R. Sharp, and J. W. Tolan, *J. Amer. Chem. Soc.*, 1976, **98**, 5451.