10-HETEROSUBSTITUTED ARSAANTHRACENES

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Derivatives of arsabenzene^{1,2} and of arsaanthracene³⁻⁵ have been known for several years. However, only recently the group of Märkl reported the synthesis of arsabenzenes bearing functional groups as substituents⁶⁻⁸. The synthesis of arsaanthracenes with functional groups on the meso position seemed of interest in connection with the question as to which factors contribute to the stabilization of the areaanthracene system. It had been found that 10-phenylarsaanthracene⁵ is considerably more stable than the parent compound^{3,4} or its 10-methyl and 10-ethyl derivative⁹; however it was not clear whether steric or electronic factors were mainly responsible for this difference. It was expected that an investigation of 10-chloro-, 10-bromo- and 10-methoxyarsaanthracene (I, II and III respectively) would contribute to clarify this point.



The synthetic approach to these systems was greatly facilitated by the discovery of an oxidoreduction of the easily accessible arsinic acid IV^{10} . Treatment of IV with an excess of thionyl chloride (room temperature) or thionyl bromide (refluxing) yielded the 5,10--dihalo-5,10-dihydroarsaanthracenes Va^{11} [63% yield; m.p. 167 - 170°; NMR¹² (CDCl₃): 8.15 - 7.70 (m, 2, aryl protons), 7.70 - 7.15 (m, 6, aryl protons), 6.07 (s, 1, methine proton)] and Vb^{11} [46% yield; m.p. 179 - 181°; NMR (CDCl₃): 8.24 - 7.84 (m, 2, aryl protons), 7.67 - 7.15 (m, 6, aryl protons), 6.30 (s, 1, methine proton)], respectively.



The mechanism of this interesting novel reaction is not yet clear. As it does not occur with the corresponding phosphinic acid (which gives the expected phosphinic acid chloride), it is tempting to speculate on an intramolecular hydride shift in an intermediate such as VI. The reaction is further being studied.



The structures of Va and Vb were further corroborated by their conversion on boiling with dry methanol to VIIa¹¹ [91% yield; m.p. 120 - 122°; NMR (CDCl₃): 8.14 - 7.80 (m, 2, aryl protons), 7.60 - 7.20 (m, 6, aryl protons), 5.28 (s, 1, methine proton), 3.10 (s, 3, CH₃0)] and to VIIb¹¹ [70% yield; m.p. 116 - 118°; NMR (CDCl₃): 8.25 - 7.88 (m, 2, aryl protons), 7.64 - 7.17 (m, 6, aryl protons), 5.29 (s, 1, methine proton), 3.10 (s, 3, CH₃0)], respectively. The structure of VIIa was further confirmed by its oxydation to the 10-methoxy derivative of IV (m,p. 229 - 232° dec).

Treatment of Va, Vb, VIIa or VIIb with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in THF in a high vacuum sealed vessel resulted in elimination of hydrogen halide and gave the aromatic compounds I, II and III, respectively. In the case of Va, VIIa and VIIb the reaction was performed at room temperature. Similar conditions lead to the complete decomposition of Vb, so that the reaction had to be performed at - 60° ; at this temperature, formation of II was rapid, but the UV spectrum measured at room temperature began to diminish after one minute. The UV spectral data are presented in Table 1.

Table 1

	UV spectra (THF) in nm (log ε)			
I	390 (2.81)	410 (3.21)	434 (3.53)	461 (3.65)
II		414	439	468
111	378 (3.04)	400 (3.41)	440 (3.84)	463 (3.87)

The hydrogen halide elimination of VIIa and VIIb was followed by UV measurements. Both reactions were of second order, the reaction of VIIb being about one order of magnitude faster than that of VIIa.

Attempts to isolate the substituted arseanthracenes had no succes due to the instability of the compounds. II was the least stable, decomposition in solution (possibly dimerisation⁹) occuring at room temperature within one minute. I was stable in solution for two days, but decomposed after evaporation of the solvent (mass spectrum of the residue showed m/e = 548). III was stable in solution but decomposed also after evaporation of the colvent. Therefore I and III were further characterized by their Diels-Alder adducts^{3,9} after reaction with maleic enhydride: VIII¹¹ [74% yield; m.p. 255 - 256°; NMR (D₆-DMSO): 8.35 - 7.17 (m, 8, aryl protons), 4.06 (s, 2, methine protons)] and IX¹¹ [79% yield; m.p. 252 - 254°; NMR (D₆-DMSO): 8.04 - 7.14 (m, 8, aryl protons), 4.27 - 4.12 (AB spectrum, J_{AB} = 9.3 Hz, 2, methine protons), 4.00 (s, 3, CH₃O)], respectively.



The longest wavelength maxima of I, II and III show approximately the same bathochromic shifts relative to arsaanthracene as do 9-chloro-¹³, 9-bromo-¹⁴ and 9-methoxyanthracene¹⁵ as compared to anthracene. As is generally the case in these systems, the conclusion seems justified that the electronic structure of the anthracene and arsaanthracene series is similar^{16,17} as is the electronic influence (-I and +M) of the substituents. In spite of the obvious electronic effects of C1, Br and OCH₃, the arsaanthracene system does not

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appear to be substantially stabilized; this strongly suggests that the observed stabilization by a 10-phenyl substituent is predominantly steric and not electronic of nature. The definitive answer to this problem may be expected from a study of 10-t-butylarsaanthracene, the synthesis of which is being investigated.

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