

10-HETEROSUBSTITUTED ARSAANTHRACENES

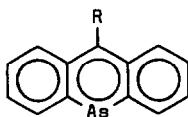
R.J.M. Weustink, C. Jongema and F. Bickelhaupt

Scheikundig Laboratorium der Vrije Universiteit,

De Lairesestraat 174, Amsterdam-Z, The Netherlands

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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 arsabenzene 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 arsaanthracene 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.



I R = Cl

II R = Br

III R = OCH₃

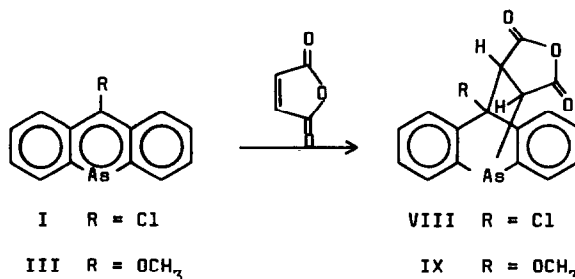
The synthetic approach to these systems was greatly facilitated by the discovery of an oxidoreduction of the easily accessible arsenic acid IV¹⁰. Treatment of IV with an excess of thionyl chloride (room temperature) or thionyl bromide (refluxing) yielded the 5,10-dihalo-5,10-dihydroarsaanthracenes Va¹¹ [63% yield; m.p. 167 - 170^o; 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 Vb¹¹ [46% yield; m.p. 179 - 181^o; 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.

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
III	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 arsaanthracenes had no success due to the instability of the compounds. II was the least stable, decomposition in solution (possibly dimerisation⁹) occurring 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 solvent. Therefore I and III were further characterized by their Diels-Alder adducts^{3,9} after reaction with maleic anhydride: VIII¹¹ [74% yield; m.p. 255 - 256^o; NMR (D_6 -DMSO): 8.35 - 7.17 (m, 8, aryl protons), 4.06 (s, 2, methine protons)] and IX¹¹ [79% yield; m.p. 252 - 254^o; NMR (D_6 -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, CH_3O)], 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 Cl, Br and OCH₃, the arsaanthracene system does not

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-butylarsa-anthracene, the synthesis of which is being investigated.

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