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10-MESITYL-9-ARSAANTHRACENE

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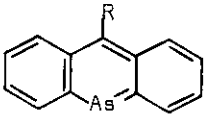
The highly sterically hindered, 10-mesityl-9-arsaanthracene (1c) has been prepared by pyrolysis of the dihydro-precursor 3. Due to steric hindrance at the 10-position, 1c is the most stable of all known derivatives of arsaanthracene; even the Diels-Alder reaction with maleic anhydride is slow and reversible at ambient temperatures, leading to the 9,10-adduct 4. At higher temperatures, an alternative Diels-Alder reaction yields the 1,4-adduct 5, the first known derivative of arsanaphthalene. The carbon analog 6 of 1c gives the corresponding 1,4-adduct 7.

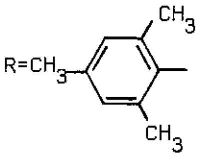
It has been shown that substitution in the 10-position generally increases the stability of the 9-arsaanthracene system (1)[1] towards dimerization and polymerization[2,3]. More in particular, it has been observed that substituents with a broad range of electronic effects (1, R=H[4], CH_3[2], C_2H_5[2], OCH_3[5], Cl[5], Br[5]) do not confer sufficient stability on 1 to make it isolable at room temperature, whereas R=aryl (1, R=C_6H_5(1b)[6], p-$CH_3C_6H_4$[7], p-$CH_3OC_6H_4$[7]) does so in spite of the fact that the UV-spectra clearly indicate that the aryl groups are nearly perpendicular to the tricyclic system; the conclusion has been drawn that steric factors are predominant in determining the stability of 1[1].



1

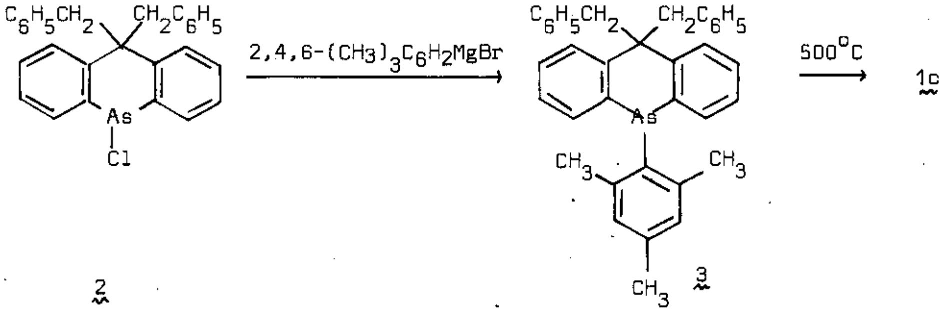
R=H : 1a

R=C_6H_5 : 1b



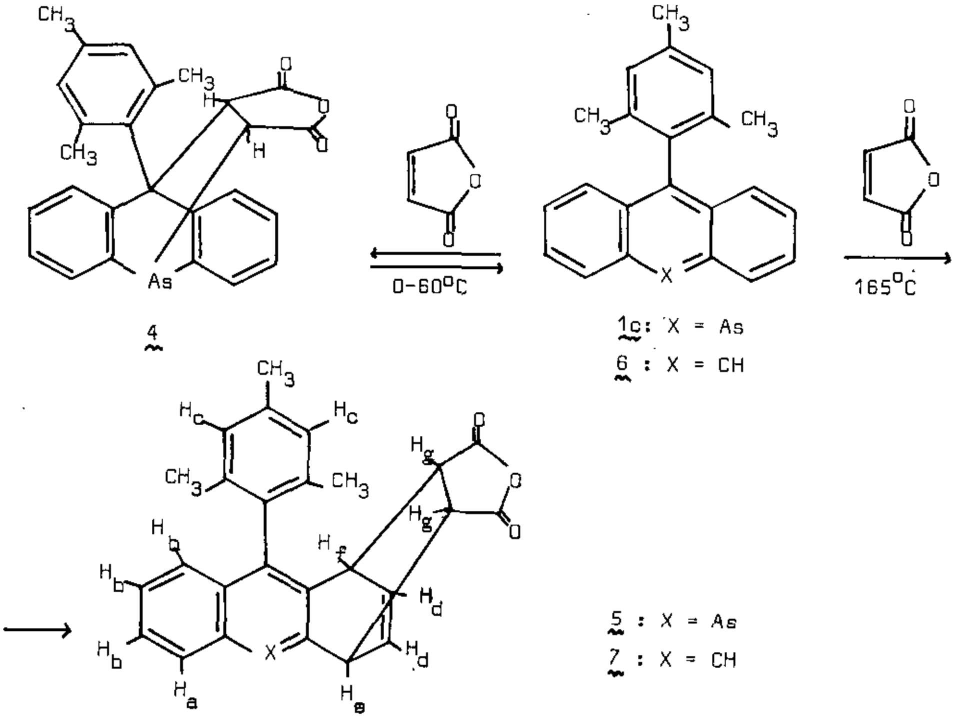
1c

In order to corroborate this hypothesis and thereby to obtain even more stable derivatives of 1, it was desirable to introduce still bulkier groups R in the 10-position of 1. As attempts to synthesize 10-t-butyl-9-arsaanthracene (1, R=t-C_4H_9) have failed so far[8], we undertook the synthesis of 10-mesityl-9-arsaanthracene (1c).



Reaction of 2[7] with mesitylmagnesium bromide in ether/benzene gave 3 (94% yield; m.p. 209-211°C; NMR ($CDCl_3$, 20°C): 7.50-6.50 (m, 20, aryl-H), 3.95 (s, 2, CH_2), 3.11 (s, 2, CH_2), 2.31 (s, 3, p-CH_3), 3-1 p.p.m. (bs, 6, o-CH_3); at -20°C tha latter signal was split in two: 3.0 (s, 3, o-CH_3) and 1.32 p.p.m. (s, 3, o-CH_3); coalescence at 0°C with a rotation barrier of 13.8 kcal/mol). When 3 was pyrolized in a flow system[7] at 500°C in vacuo 1c was obtained in surprisingly good yield (56%; m.p. 150-152°C; UV (THF), λ_{max} (log ε): 386 sh (2.93), 406 (3.61), 429 (3.95), 455 nm (4.08); NMR ($CDCl_3$): 8.65-8.50 (m, 2, aryl-H), 7.85-7.67 (m, 2, aryl-H), 7.42-7.22 (m, 4, aryl-H), 7.05 (s, 2H, mesityl-H), 2.47 (s, 3, p-CH_3), 1.67 p.p.m. (s, 6, o-CH_3); mass spectrum m/e: found 358.0690, $C_{22}H_{19}As^{+\cdot}$ calcd. 358.0703). The longest wavelength absorption of 1c is 4 nm more hypsochromic than that of 1b[6], indicating even further reduced conjugation between the mesityl group and the tricyclic ring system; apparently, the two ortho methyl groups enforce a practically perpendicular position. The ^1H NMR absorption of the ortho methyl groups is strongly shifted upfield due to the shielding effect of the arsaanthracene system; a similar effect has been observed for the recently prepared[9] carbon analog 6 of 1c. In accordance with the above-mentioned prediction, 1c proved to more stable than 1b; in a high vacuum system the UV spectrum of a solution of 1c in THF remained absolutely stable for weeks, whereas that of 1b irreversibly diminished after a few days. The reaction of 1c with oxygen (air), however, is instantaneous and not noticeably slower than that of other 1; this permits the conclusion that oxidation of arsaaromatic compounds is initiated by attack of oxygen at the arsenic atom.

As a further illustration of steric hindrance as the major cause of the high stability of 1c, its reactivity in the Diels-Alder reaction with maleic anhydride is remarkably reduced. While all other known derivatives of 1 add maleic anhydride at positions 9 and 10 in a reaction which at room temperature is complete and more or less instantaneous, the analogous reaction of 1c to 4 is reversible and slow; the kinetic and thermodynamic parameters of this equilibrium are under investigation. As dissociation is favoured at higher temperatures, 4 is air-sensitive because of the formation of 1c; for both reasons we did not yet succeed in the purification of 4 by recrystallization or sublimation; it was obtained in quite pure form by heating in vacuo to 50°C, in order to remove excess of maleic anhydride (m.p. 124-126°C (IR(KBr)): 1845,1770 cm^{-1}; NMR ($CDCl_3$): 7.91-7.60 (m, 2, aryl-H), 7.42-6.67 (m, 8, aryl-H), 5.06 and 3.34 (AB, J_{AB}= 9 Hz, 2, ≡CH), 2.73 (s, 3, CH_3), 2.37 (s, 3, CH_3), 1.12 p.p.m. (s, 3, CH_3)).



4

1c: X = As
6 : X = CH

5 : X = As
7 : X = CH

Above 165°C, 1c and maleic anhydride react in an alternative Diels-Alder fashion at positions 1 and 4 of 1c under formation of 5; at higher temperatures, this reaction is reversible. For this reason, we have not yet obtained 5 completely free of 1c, and the air-sensitivity of both compounds has thwarted attempts for further purification. However, the structure of **5** follows unambiguously *from its NMR spectrum ($CDCl_3$; compare also the NMR spectrum of* **7**): 8.49-8.31 (m, 1, H_a), 7.82-7.20 (m, 3, H_b), 7.07 (s, 2, H_c), 6.78-6.53 (m, 2, H_d), 5.38-5.22 (m, 1, probably H_e), 4.42-4.24 (m, 1, probably H_f), 3.44, 3.14 (AB part of ABXY, J_{AB} = 9 Hz, $J_{AX} \approx J_{BY}$ = 3.5 Hz, 2, H_g), 2.43 (s, 3, CH_3), 1.79 (s, 3, CH_3), 1.67 p.p.m. (s, 3, CH_3). To our knowledge, **5** is the first known derivative of 1-arsanaphthalene.

In the anthracene system, 1,4-addition is seldom and restricted to cases with steric crowding in the meso-position[10]. It was therefore of interest to compare the behaviour of **1c** with that of its carbon analog **6**. As the Diels-Alder reaction of anthracenes occurs at higher temperatures than that of **1**, the step of 9,10-addition between **6** and maleic anhydride to form the carbon analog of **4** was apparently by-passed; at 165°C, **7** was formed (m.p. 187-188°C; IR (KBr): 1860, 1780 cm^{-1}; UV (C_2H_5OH), λ_{max} (log ε): 291 (3.84), 279 (3.97), 269 (3.93), 254 nm (4.01); NMR ($CDCl_3$): 7.90-7.70 (m, 2, aryl-H), 7.50-7.10 (m, 3, aryl-H), 7.04 (s, 2, H_c), 6.80-6.57 (m, 2, H_d), 4.78-4.58 (m, 1, H_e?), 4.33-4.11 (m, 1, H_f?), 3.47, 3.22 (AB part of ABXY, J_{AB} = 9 Hz, $J_{AX} \approx J_{BY}$ = 3.5 Hz , 2, H_g), 2.42 (s, 3, CH_3), 1.83 (s, 3, CH_3), 1.69 (s, 3, CH_3); on heating above its melting point, **7** was reconverted to **6**.

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