Journal of Organometallic Chemistry, 67 (1974) 389—394

THE EQUILIBRIUM ACIDITY OF A 9,10-DIHYDROSILAANTHRACENE

ON THE DEGREE OF AROMATICITY OF A SYSTEM WITH TETRACOORDINATE SILICON

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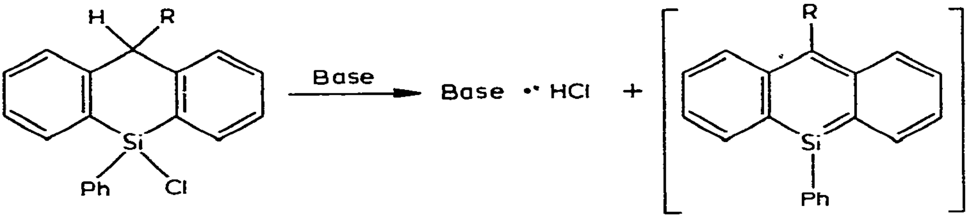
(Received August 1st, 1973)

Summary

The equilibrium acidity of 9,10-dihydro-9,9-dimethyl-10-phenyl-9-silaanthracene is determined with caesium cyclohexylamide in cyclohexylamine; the p*K* has the value of 27.4. From the fact that its acidity is only p*K* 0.6 stronger than that of its carbon analogue it is concluded that aromatic "through-conjugation" does not play an important role in this system. This conclusion is discussed in the context of current ideas and evidence on d_π—p_π bonding at silicon.

Introduction

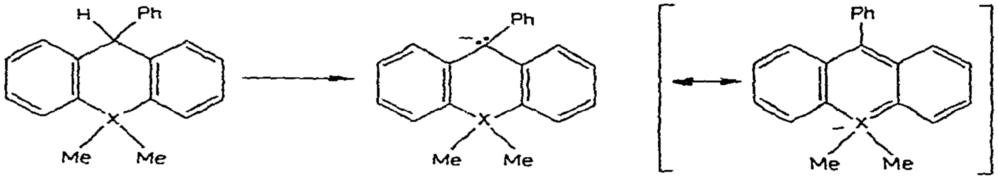
In spite of considerable efforts in recent years, aromatic systems with p_π hybridized tricoordinate silicon have not yet been prepared. For instance, the base induced hydrogen halide elimination from (Ia) did not furnish monomeric (IIa), although the hydrochloride of the base was obtained readily and in good yield [1,2].



(Ia) R = H
(Ib) R = Ph

(IIa) R = H
(IIb) R = Ph

In an attempt to prepare the presumably more stabilized (IIb) we found that the proton at C-10 in (Ib) was unexpectedly resistant towards abstraction, even with strong bases such as organolithium compounds [3]. We therefore decided to investigate proton abstraction and acidity of the stable model compound 9,10-dihydro-9,9-dimethyl-10-phenyl-9-silaanthracene (IIIa) and to compare it with its carbon analogue (IIIb).



(IIIa) X = Si
(IIIb) X = C

(IVa) X = Si
(IVb) X = C

(Va) X = Si

Results

Preliminary experiments indicated that (IIIa), like (Ib), was rather difficult to metallate. Reaction with n-butyllithium in hexane for several hours, even after addition of a small amount of THF, gave on deuterolysis only partially deuterated (IIIa), as did 3 hours at room temperature in diethyl ether. After refluxing with n-butyllithium in diethyl ether (6 hours) complete metallation was established.

For the determination of the equilibrium acidity cyclohexylamine was used as solvent. Streitwieser and coworkers [4] used it for this purpose, and as a consequence this system is well understood with regard to relative acidities and ion pair formation. For determination of the anion spectra from (IIIa) (Table 1) both lithium cyclohexylamide (LiCHA) and caesium cyclohexylamide (CsCHA) were used as base; for comparison (IIIb) [4] was investigated with CsCHA. In all cases Beer's law was obeyed. The spectra of (IVa) showed the well known hypsochromic shift on going from the predominantly solvent-separated ion pair (LiCHA, λ_{max} 453 nm) to the contact ion pair (CsCHA, λ_{max} 444 nm) [8,9]; both spectra have two small shoulders above 500 nm, which are more pronounced in the lithium derivative. Whereas the solution of the lithium derivative of (IVa) was stable for several days, the caesium derivative (in the presence of excess base) slowly decomposed under formation of a

TABLE 1

ANION SPECTRA AND pK VALUES IN CYCLOHEXYLAMINE

Compound	Base	λ (nm)	ε	K^a	pK
(IIIa)	LiCHA	453	27250	20.4 ± 5.4	27.7
		530(sh)	4800		
		570(sh)	2300		
(IIIa)	CsCHA	444	35750	6.5 ± 1.5	27.4
		510(sh)	5300		
		540(sh)	2300		
(IIIb)	CsCHA	444	33300	24 ± 2	28.0
		445^b	33600	28 ± 2	28.0^c

^{a}K is the equilibrium constant relative to 1,1,3-triphenylpropene (LiCHA: pK 26.4 [6]; CsCHA: pK 26.59 [7]). ^{b}Ref. 5. ^{c}Ref.4.

shoulder near 500 nm. However, in the equilibrium measurements the caesium system gave acceptable values for *K* over longer periods than the lithium system, in agreement with the observations of Streitwieser [6,7].

Since we expected an appreciable resonance stabilization of (IVa) by the contribution of structure (Va) [10] we first tried to relate the acidity of (IIIa) to that of fluorene (p*K* 22.74 [7]), but no (IVa) was formed in this system. Comparison with 1,1,3-triphenylpropene worked satisfactorily (Table 1).

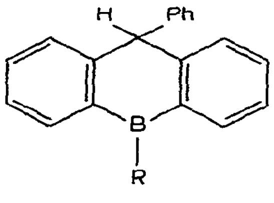
Discussion

In the first place our results answer the initially posed question as to the cause of the difficult metallation of the tertiary position in compounds of type (Ib) and (IIIa); it is kinetic (and presumably steric) rather than thermodynamic in nature.

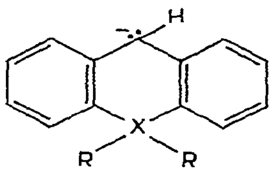
Of greater importance is the result that (for the caesium derivatives) the p*K* value of the silicon heterocycle (IIIa) is only 0.6 less than its carbon analogue (IIIb). This permits an estimate to be made of the degree of cyclic delocalization and aromaticity in the anion (IVa).

On the basis of an inductive effect alone one would predict (IVa) to be less stable than (IVb) relative to their corresponding carbon acids. In order to explain the reverse order of acidity one has to invoke the well documented effect which enables silicon to accept electrons from neighbouring atoms or bonds [11]; it has recently again been shown to overcompensate the inductive effect [12]. Whereas in general the involvement of d_π—p_π bonding in this effect is agreed upon [11,13], the participation of *d* orbitals in through-conjugation at silicon is much more controversial [11]. Spectroscopic [14] and theoretical [15] evidence seems to indicate that through-conjugation at silicon is possible but weak, and that it is unlikely to reach the level of aromaticity.

In agreement with this evidence our results point to a relatively low degree of stabilization if one takes Δp*K* as a measure for the relative thermodynamic stability of the anions (IVa) and (IVb) [16]. This is contrasted by the substantially lowered p*K* of 9-phenylfluorene [7] and of the structurally similar boron heterocycle (VI) [17]. Furthermore, geometrical and conformational differences between (IVa) and (IVb), due to the different size of silicon and carbon, might contribute to the observed effect.



(VI) R = mesityl



(VIIa) X = Si, R = Me
(VIIb) X = C, R = Me
(VIIc) X = C, R = H

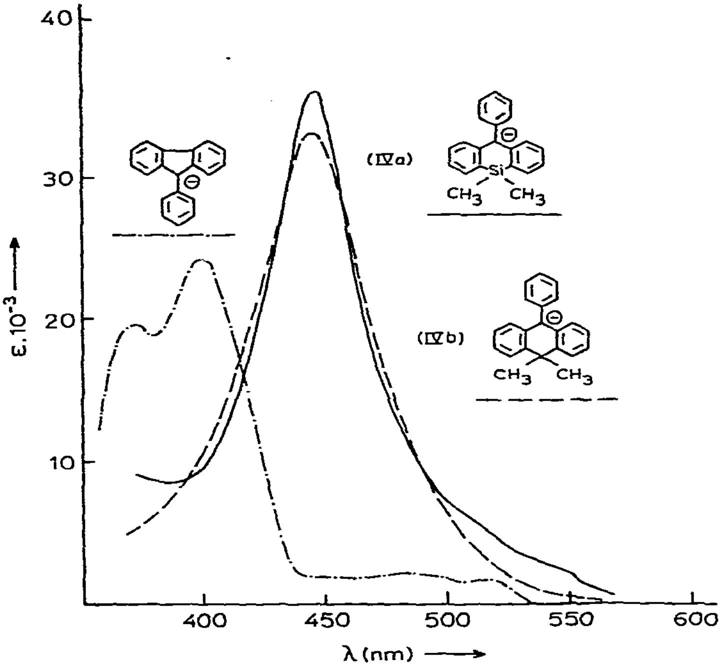


Fig. 1. Spectra of (IVa), (IVb) and 9-phenylfluorenyl anion in cyclohexylamine with Cs $^+$ as counterion.

This result is at variance with the conclusion of Jutzi [10] who, with some reservations, favours a delocalized structure for e.g. (VIIa) on the basis of UV, IR and NMR evidence. While we do not feel competent to discuss the IR evidence, in our opinion the electronic spectra agree perfectly with a localized rather than with a delocalized structure. For this purpose one should compare the spectrum of the silicon anion (VIIa) with its carbon analogue (VIIb) and not with the fluorenyl anion [10]; Fig. 1 illustrates this point for our corresponding phenyl derivatives. The low field shift of the NMR signal of the *meso* proton on going from the corresponding carbon acid to the anion (VIIa) of 0.3 - 0.8 ppm [10] is, although at first sight admittedly surprising, no convincing argument for a paramagnetic ring current of the central ring*. It is also found in the not aromatically delocalized (VIIc) [19] and even in the diphenylmethyl anion [20]. It has been explained as a consequence of the sp^2 hybridization of the anions [20]; possibly a movement of the proton to a more strongly deshielded region [21] of the adjacent benzene rings might also play a role.

We therefore conclude that the contribution of a resonance structure such as (Va) to the anion (IVa) is very small and certainly does not lead to an "aromatic" system as defined by Häfelinger [15].

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* A much larger ring current shift of approximately 3 ppm has been observed in the substantially delocalized fluorenyllithium [18].

Experimental

Ultraviolet spectra were recorded on a Perkin—Elmer 137 spectrophotometer.

Preparation of 9,10-dihydro-9,9-dimethyl-10-phenyl-9-silaanthracene (IIIa)

A mixture of 2,2′-dibromotriphenylmethane [22] (0.536 g, 0.00133 mol) in diethyl ether (20 ml) and n-butyllithium (0.0226 mol) in hexane (1.5 ml) was stirred for 4 hours under nitrogen at room temperature. It was then added dropwise during one hour to dimethyldichlorosilane (0.188 g, 0.00146 mol) in refluxing diethyl ether (15 ml). After refluxing for one hour the mixture was filtered through glass wool. The filtrate was evaporated and yielded 400 mg of crude (IIIa); this was purified by sublimation to yield (IIIa) (300 mg, 75% yield), m.p. 79.5 - 82.5°. (Found: C, 83.95; H, 6.90; $C_{21}H_{20}Si$ calcd.: C, 83.94; H, 6.71%.) The ^1H NMR spectrum (CCl_4) showed the following resonances: δ 6.5 - 7.7 (multiplet, 13H, aromatic protons), 5.28 (singlet, 1H, proton at C-10), 0.45 (singlet, 3H, CH_3), — 0.18 ppm (singlet, 3H, CH_3). The mass spectrum showed the molecular ion at *m/e* 300.1318 ($C_{21}H_{20}{}^{28}Si$ calcd.: 300.1334). For the acidity measurements (IIIa) was subjected to preparative GLC (10% SE 30, 1.5 m, 200°) and resublimed.

Determination of the extinction coefficients

All experiments were repeated several times; details are given for one determination: 5 ml of a solution of (IIIa) (36.6 mg) in n-hexane (100 ml) was pipetted into a flame dried vessel with two cuvets as described by Streitwieser et al. [6]. The solution was evaporated in vacuo to dryness and cyclohexylamine (19.6 ml) was distilled on the residue from LiCHA in a stock vessel. Under spectral quality nitrogen n-butyllithium (0.5 ml, 2 *M* in hexane) was added to the frozen contents (— 196°); the vessel was evacuated, nitrogen supplied, the contents were melted and the vessel closed and removed from the nitrogen line. Dilutions for the check on Beer's law were obtained by distilling cyclohexylamine on the vacuum line.

Determination of the equilibrium constants

Small amounts of both (IIIa) and 1,1,3-triphenylpropene* were dissolved in the aforementioned vessel in cyclohexylamine and sufficient LiCHA or CsCHA was injected to permit observation of both anions. Scans were made as long as the stability of the anions permitted (usually 4 - 10 times) and average *K* values calculated; the experiments were repeated until reproducible *K* values were found.

Acknowledgement

We thank Mr. E.A.I.M. Evers for measuring the mass spectra.

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* 1,1,3-Triphenylpropene was prepared from 1,1,3-triphenylpropanol [23] by a dehydration procedure analogous to that used by Streitwieser et al. for 1,3,3-triphenylpropene [6].

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