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Preliminary communication

THE BASE CLEAVAGE OF 1-BENZOCYCLOPROPENYLTRIMETHYLSILANE. THE ACIDITY OF BENZOCYCLOPROPENE*

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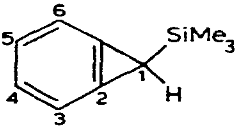
Summary

1-Benzocyclopropenyltrimethylsilane is cleaved approximately 64 times as rapidly as benzyltrimethylsilane by sodium hydroxide in 5 : 1 V/V $MeOH/H_2O$ at 50°C, implying that benzocyclopropene is more acidic than toluene, probably having a pK_a of ca. 36.

There is much theoretical interest in the acidity of highly strained cyclic hydrocarbons, and especially of cyclopropane and cyclopropene derivatives. Cyclopropene itself appears to have an extremely low acidity at the methylene position [1]; this is thought to be due to the anti-aromaticity of the cyclopropenyl carbanion [1, 2], which greatly outweighs the acid-strengthening effect associated with the enhanced *s*-character of the C-orbital of the C—H bond arising from the small C—C—C angle [3]. The value of $J(^{13}CH)$ for the 1-position of benzocyclobutene is 178 cps [4], suggesting that in the absence of delocalisation effects the acidity would be a little greater than that of ethylene. Simple Hückel MO theory (which takes no account of the considerable distortion of the aromatic ring) [5] indicates that the benzocyclopropenyl anion has a slightly lower total π-energy than the benzyl anion [6], and so in this sense may not be anti-aromatic.



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The ease of base cleavage of Me_3SiR bonds is related mainly to the stability of the carbanion R^-, and thus to the acidity of the carbon acid RH. Indeed, in the absence of exceptional steric effects, for a range of R groups of the aralkyl type, there is an excellent linear relationship between the pK_a of the acids RH and the logarithms of the rate constants for the cleavages relative to that for $R = PhCH_2$ [7]. Thus to provide information on the stability of the benzocyclopropenyl anion and the pK_a of benzocyclopropene we have determined the rate of cleavage of 1-benzocyclopropenyltrimethylsilane (I) by sodium hydroxide in 5:1 V/V $MeOH/H_2O$ at 50°C, a medium used previously to cleave a range of benzylsilanes [8]. We find I to be more reactive than benzyltrimethylsilane by a factor of 64, which implies [7] a pK_a of ca. 36 for benzocyclopropene compared with 41 for toluene.

The conclusion that benzocyclopropene has a relatively high acidity is in keeping with the ease of its metallation at low temperature (see below). This behaviour contrasts with that of benzocyclobutene, which is metallated by n-butyllithium only slowly in refluxing ether [9]; consistently, 1-benzocyclobutenyltrimethylsilane is cleaved more slowly than benzyltrimethylsilane by base [10].

Experimental

A solution of benzocyclopropene [11] (2.00 mmol) in tetrahydrofuran (6 ml) was cooled to −78°C under nitrogen, and n-butyllithium (2.50 mmol) in hexane (1.20 ml) was added slowly with stirring. After 1 h the temperature was raised to −55°C, and kept there for 1.5 h. The deep-orange solution was cooled to −78°C and chlorotrimethylsilane (2.50 mmol) in tetrahydrofuran (2.5 ml) was added with stirring. The mixture was allowed to warm slightly, and after 1 h aqueous sodium bicarbonate (5 ml) was added, followed by ether (10 ml). Separation, drying, and rapid fractionation of the ethereal layer gave I (0.71 mmol, 35%), b.p. 40°C/ca. 1 mmHg; NMR ($CDCl_3$, TMS): δ 7.15 (s, 4H), 3.02 (s, 1H), 0.13 ppm (s, 9H); IR (neat): 1688 cm^{-1} (C=C in aromatic ring [4, 12]); UV (MeOH) λ (nm) (log ϵ): 286.5 (3.26), 280 (3.37), 273(sh) (3.30). The mass spectrum showed the expected peak at m/e 147 ($P - 15$).

For the rate measurements, 5.00 M aqueous (1 ml) was added to a solution of I (ca. 40 μl) in freshly distilled methanol (5 ml) and the reaction was followed spectrophotometrically at 287 nm. Good first order kinetics were observed, and the UV spectrum of the solution at the end of the reaction was identical with that of benzocyclopropene. The observed first-order rate constant was $1.93 \times 10^{-5}\ s^{-1}$ corresponding with a specific rate constant (see ref. 8) of 2.25×10^{-5} l $mole^{-1}\ s^{-1}$. This compares with a value of 3.5×10^{-7} l $mole^{-1}\ s^{-1}$ for benzyltrimethylsilane at a comparable base concentration [8].

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