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AROMATIC REACTIVITY

LX*. THE CLEAVAGE OF 9-TRIMETHYLSILYLANTHRACENE BY ACID AND BY BASE

COLIN EABORN**, RUDOLF EIDENSCHINK and DAVID R.M. WALTON

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)

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Summary

9-Trimethylsilylanthracene has been found to be cleaved by aqueous methanolic perchloric acid ca. 100 times, and by base in aqueous dimethyl sulphoxide ca. 4 times, as readily as expected on electronic grounds. The high reactivity in the acid cleavage is attributed to relief of steric strain on going from the reactants to the transition state.

Introduction

Relative rates of reaction have been determined for both acid- and base-catalysed cleavage of $ArSiMe_3$ bonds (desilylation) in which the aryl group is derived from a polynuclear hydrocarbon [2,3]. In each case the reactivities in the desilylation run parallel to those in the analogous acid- or base-catalysed hydrogen-exchange in the corresponding hydrocarbon ArH, and the variations can be satisfactorily interpreted in terms of the proposed mechanisms of the reactions. We describe below, however, results for 9-trimethylsilylanthracene, which show that it has an abnormally high reactivity in both the acid- and base-catalysed processes, the abnormality being exceptionally large for the former.

Results and discussion

9-Trimethylsilylanthracene was surprisingly difficult to make. Attempts were made some years ago to prepare it from 9-bromoanthracene by treatment with (*a*) chlorotrimethylsilane and sodium in boiling toluene, (*b*) n-butyllithium in

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[*] For Part LIX, see ref. 1.

[**] To whom correspondence should be addressed.

ether, followed by chlorotrimethylsilane, and (*c*) magnesium in ether with ethylene dibromide entrainment, followed by chlorotrimethylsilane [4]. In each case the main product was anthracene, along with unchanged 9-bromoanthracene, and none of the required trimethylsilylanthracene was isolated. We have now made it by treatment of highly purified 9-bromoanthracene with n-butyllithium in tetrahydrofuran followed by coupling with chlorotrimethylsilane at low temperature and non-hydrolytic work-up.

The rate of acid cleavage was measured at 30° and 50°C in aqueous methanolic perchloric acid; the rate constant at 50°C was 71 times as large as that determined at the same time under identical conditions for *p*-methoxyphenyltrimethylsilane, and since for the latter k_{rel}, the rate relative to that for phenyltrimethylsilane in this medium, is ca. 1510 [5] the value of k_{rel} for 9-trimethylsilylanthracene is ca. 107000. The activation energy is approximately 16 kcal mol^{-1}.

The rate of base cleavage was measured at 48° and 70°C in a mixture of aqueous potassium hydroxide (1 vol) and dimethyl sulphoxide (6 vol), the medium used for other polynuclear aryltrimethylsilanes [3], and the corresponding rate for phenyltrimethylsilane was measured under comparable conditions. The value of k'_{rel} at 70 °C is 1000, and the activation energy is ca. 14.7 kcal mol^{-1}.

Table 1 shows the values of the relative rates k_{rel} and k'_{rel} along with those for some other polynuclear aryltrimethylsilanes, $ArSiMe_3$, and also the corresponding relative rates, *f* and *f'* respectively, of hydrogen-exchange at the relevant positions of the parent hydrocarbons, ArH, in trifluoroacetic acid [6] and in cyclohexylamine containing lithium cyclohexylamide [7]. It is apparent that the reactivity of 9-trimethylsilylanthracene is abnormally high in both acid and base cleavage, but especially so in the acid cleavage. For a good range of polynuclear and heterocyclic aromatic ring systems, the points in a plot of log k_{rel} for the acid-catalysed desilylation against log *f* for the hydrogen-exchange in trifluoro-

TABLE 1

RELATIVE RATES IN DESILYLATION AND HYDROGEN-EXCHANGE

Aromatic system and position of reaction	Relative rates			
	Acid-catalysis		Base-catalysis	
	Desilylation[a] k_{rel}	Exchange[b] f	Desilylation[c] k'_{rel}	Exchange[d] f'
Benzene, 1-	1.0	1.0	1.0	1.0
Naphthalene, 1-	8.1	1165	12.5	7.3
Naphthalene, 2-	2.2	150	4.7	4.7
Phenanthrene, 9-	4.5	1610	51	21
Pyrene, 1-	220	8.1×10^5	71	33
Anthracene, 9-	1.1×10^5	1.5×10^7	1.0×10^3	75

[a] In a mixture of methanol (5 vol) and aqueous perchloric acid (2 vol) at 50 °C; see ref. [2].
[b] In CF_3CO_2H at 70 °C; the values are taken from ref. [6], except for that for the 9-position of anthracene, which was personally communicated by Dr. R. Taylor.
[c] In a mixture of DMSO (6 vol) and 1.0 *M* aqueous KOH (1 vol) at 70°C; see ref. [3].
[d] In $C_6H_{11}NH_2/C_6H_{11}NHLi$; see ref. [7].

acetic acid lie reasonably well about a straight line [2], but the point for the 9-position of anthracene lies above this line by about 2 units, i.e., the reactivity in desilylation is 100 times greater than expected on electronic grounds. For the base-catalysed reactions, use of the points for the 1- and 2-positions of naphthalene, the 9-position of phenanthrene, and the 1-position of pyrene to establish a rough linear free energy correlation suggests that 9-trimethylsilylanthracene is ca. 4 times as reactive as would be expected on electronic grounds.

The abnormally high reactivity of 9-trimethylsilylanthracene can reasonably be associated with the large degree of steric strain which must be present in this compound because of interaction between the Me_3Si group and the 1- and 8-hydrogen atoms. In the acid cleavage the strain will be relieved as the proton attaches to the 9-position and the Me_3Si group moves out of the plane of the ring system; this type of steric acceleration occurs, though to a much smaller extent, with, for example, (2,6-dimethylphenyl)- and (1-naphthyl)-trimethylsilane [8].

The situation is not so clear for base cleavage. If the 9-anthranyl carbanion separates, there could be some small relief of strain as the C—$SiMe_3$ bond lengthens even though the bond stays in the plane of the ring system, but we should expect this to be outweighed by the increase in strain as the Me_3Si flattens upon attachment of the hydroxide ion, If, as seems possible [10], there is some proton transfer from the solvent to the 9-carbon atom as it separates, then the slightly enhanced reactivity even in the base cleavage may be a reflection of the great ease of electrophilic attack at the 9-carbon atom.

It should be noted that a much smaller k_{rel} value viz., 4.1, was previously recorded for the acid cleavage of 9-trimethylsilylanthracene [4] and has been cited in influential reviews [9]. It is now clear that the trimethylsilylanthracene used in the earlier study [4] must have been the 1- or the 2-isomer.

Experimental

Preparation of 9-trimethylsilylanthracene

A solution of highly purified 9-bromoanthracene (2.57 g; 10 mmol) in tetrahydrofuran (50 ml) under nitrogen was cooled to —78 °C,and a hexane solution of n-butyllithium (4.9 ml of a 2.04 *M* solution; 10 mmol) was added dropwise with stirring. The solution was allowed to warm to 0 °C, the colour changing from pale yellow to orange, and kept at that temperature for 30 min. It was then cooled to —78 °C, and chlorotrimethylsilane (0.86 g; 8 mmol) in tetrahydrofuran (4 ml) was added dropwise. The mixture was allowed to warm to 0 °C and the solvent evaporated off under reduced pressure at this temperature. The residue was extracted with a boiling mixture of n-hexane (9 ml) and benzene (1 ml), and evaporation of the solvent from the extract left an oil (2.40 g), 0.40 g of which was subjected to preparative GLC (SE 50 on Chromosorb A at 270 °C) to give 84 mg of 9-trimethylsilylanthracene, m.p. 51°C. (Found: C, 82.2; H, 7.2 $C_{17}H_{18}Si$ calcd.: 81.6; H, 7.2%). ^1H NMR: τ (CCl_4, 100 MHz) 9.28s (9H, Me_3Si), 3.64 m (4H 2-, 3-, 6-, 7-H), 3.18 m (2H, 5- and 4-H), 2.81 m (3H, 1-, 8-, and 10-H). ^{13}C NMR: (ppm rel. to TMS, in $CDCl_3$) 137.0, 135.6, 131.3, 129.9, 129.5, 128.6, 124.7, 124.5, 4.6; mol. ion in mass spectrum at *m/e* 250, with a slightly larger peak at *m/e* 235.

The amount of pure compound isolated from part of the product mixture corresponds with a total yield of 27%.

Rate measurements

The usual spectrophotometric technique [2,3,5] had to be modified to take account of the high rates of reaction of the 9-trimethylsilylanthracene under the conditions used. For the acid cleavage, the appropriate very small volume (<0.3 μl) of the pure *p*-methoxyphenyltrimethylsilane or of a saturated solution of the 9-trimethylsilylanthracene in methanol was injected into a mixture of methanol (5 vol) and aqueous 1.0 *M* perchloric acid (2 vol) which had been brought to equilibrium in the thermostatted cell compartment of a Unicam SP 1700 spectrophotometer; the mixture was quickly stirred and optical densities were recorded automatically, a wavelength of 386.5 nm being used for the anthracene compound and one of 281 nm for the *p*-methoxyphenyl compound. The absorption spectrum at the completion of the reaction for the 9-trimethylsilylanthracene was identical with that of anthracene. First-order rate constants of 0.125 and 0.61 min^{-1} were obtained for the anthracene compound at 30.3° and 50.0 °C respectively, and a rate constant of 0.86×10^{-2} min^{-1} for the *p*-methoxyphenyl compound at 50.0 °C.

For the base cleavage, a small volume (<3 μl) of a saturated solution in benzene was similarly injected into a pre-heated mixture of dimethyl sulphoxide (6 vol) and 0.100 *M* aqueous potassium hydroxide (1 vol) and optical density measurements made as before at 386 nm; first order rate constants of 0.290 and 1.16 min^{-1} were obtained at 47.9° and 70.0 °C respectively. (The spectrum after the completion of the reaction was identical with that of anthracene; the volume of benzene introduced was too small to have any significant influence on the measurements.) The rate constant for phenyltrimethylsilane in a mixture of dimethyl sulphoxide (6 vol) and 1.00 *M* aqueous potassium hydroxide (1 vol) was 1.29×10^{-2} min^{-1} at 70.0 °C. (Optical density measurements at 270.5 nm.) Allowing for the rate factor of 11 associated with the 10-fold increase in base concentration [10], the value of k_{rel} for the 9-trimethylsilylanthracene is 1000.

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