Journal of Organometallic Chemistry, 82 (1974) 13–15

AROMATIC REACTIVITY

LVIII*. BASE-CLEAVAGE OF BONDS BETWEEN TRIMETHYLSILYL GROUPS AND POLYNUCLEAR AROMATIC RINGS

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(Received June 24th, 1974)

Summary

The relative rates of cleavage of aryl—$SiMe_3$ compounds in a mixture of 1.0 *M* potassium hydroxide (1 vol) and DMSO (6 vol) at 70° have been found to be as follows: (aryl =) Ph, 1.0; 1-naphthyl, 12.5; 2-naphthyl, 4.7; 9-phenanthryl, 51; 1-pyrenyl, 71. The order of reactivity is the same as that observed for hydrogen-exchange of the corresponding hydrocarbons in cyclohexylamine containing lithium cyclohexylamide, and it seems that the stability of the aryl carbanion is the dominant influence in both cases.

Introduction

The relative rates of acid-cleavage of aryl—$SiMe_3$ bonds are known for a range of cases in which the aryl group is polynuclear [2], but base-cleavage of such bonds has not previously been quantitatively studied. We have now measured the rates of base-cleavage of a small representative range of such aryl—$SiMe_3$ compounds.

Results and discussion

Rates of cleavage were measured spectrophotometrically at 50.0 and 70.2° in a mixture of 1.0 *M* potassium hydroxide (1 vol) and DMSO (6 vol). The results are shown in Table 1 as observed first order rate constants, k, and as relative rates, k_{rel}, at 70°. Approximate values of the activation energy, E, are

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* For part LVII see ref. 1.

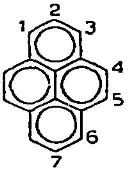
TABLE 1

CLEAVAGE OF TRIMETHYLSILYL-SUBSTITUTED POLYNUCLEAR AROMATIC COMPOUNDS, $RSiMe_3$ IN A MIXTURE OF 1.0 *M* AQUEOUS POTASSIUM HYDROXIDE (1 VOL) AND DIMETHYL SULPHOXIDE (6 VOL)

No.	R	λ [a] (nm)	10^4k, 50.0° (s^{-1})	10^4k, 70.2° (s^{-1})	k_{rel} (70°)	E [b] (kcal mol^{-1})	H-exchange [c] rel. rates
1	Phenyl	270.5		2.1	1.0		1.0
2	1-Naphthyl	297	4.1	25.8	12.5	20	7.3
3	2-Naphthyl	292	1.80	9.8	4.7	18	4.7
4	9-Phenanthryl	304.5	13.2	105	51	22	21
5	1-Pyrenyl	345	257	147	71	19	33

[a] Wave-length used to follow progress of reaction. [b] Rough value of activation energy (± 2 kcal mol^{-1}).
[c] Rel. rates of hydrogen-exchange at the relevant positions of the corresponding hydrocarbons, RH, in cyclohexylamine containing lithium cyclohexylamide [3].

also listed, but the variations are within the limits of error. For comparison, the relative rates of hydrogen-exchange, *f*, at 50° for the corresponding aryl—H compounds in cyclohexylamine containing lithium cyclohexylamide [3] are also listed*.



(I)

It will be seen that the sequence of reactivity in the desilylation is the same as that in the hydrogen-exchange, viz. 1-pyrenyl > 9-phenanthryl > 1-naphthyl > 2-naphthyl > phenyl. Indeed, a plot of log *f* against log k_{rel} is reasonably linear (Fig. 1). The relative rates of hydrogen-exchange have been satisfactorily interpreted in terms of the stabilization of the relevant carbanions by electrostatic interaction between the lone pair and the other carbon nuclei in the ring systems [3], and it seems likely that in the desilylation, also, the carbanion stabilities exert the dominant influence on the rates, even though it is believed that the carbanions probably are never free in this reaction, proton transfer from the solvent to the separating carbon assisting the cleavage of the aryl—$SiMe_3$ bond [6]. Because of this electrophilic assistance, an exact linear free energy correlation between the two reactions could not necessarily be expected, since such assistance could make a different contribution or be entirely absent in the hydrogen-exchange.

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* Somewhat different values of the relative rates have been derived from the same data [4], but use of these values would not affect the discussion. The numbering of the pyrene ring is shown in I because an older numbering system has sometimes been used previously in connection with rates of acid-cleavage [5].

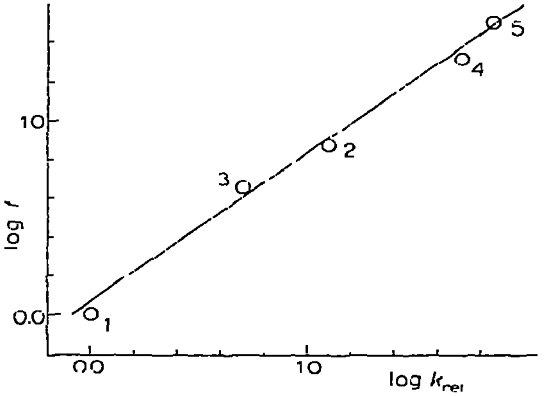

Fig. 1. A plot of log f for base-catalysed hydrogen-exchange of polynuclear aromatic hydrocarbons against log k_{rel} for the base-catalysed cleavage of the corresponding aryltrimethylsilanes. (For numbering of points see Table 1).

Experimental

Aryltrimethylsilanes. These were made by known methods, and the physical constants agreed with the published values [2].

Rate measurements. The spectrophotometric method used has been described previously [6]. The wave-lengths used in each case are shown in Table 1. Good first order plots were obtained, and the UV spectra of the solutions after 10 half-lives were identical with those of the expected hydrocarbons.

The medium consisted of a mixture of 1 vol of 1.0 *M* aqueous potassium hydroxide with 6 vol of dimethyl sulphoxide.

Acknowledgements

We thank the Royal Norwegian Council for Scientific and Industrial Research for the award of a Research Fellowship to B.B., and Dow Corning Ltd. for a gift of chemicals.

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