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AROMATIC REACTIVITY
LIV*. ACID CLEAVAGE OF (2,4,6-TRIMETHOXYPHENYL)-TRIMETHYLSILANE

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SUMMARY

(2,4,6-Trimethoxyphenyl)trimethylsilane has been shown to be cleaved by a mixture of aqueous perchloric acid (2 vol.) and methanol (5 vol.) at 50° about 2×10^8 times as rapidly as phenyltrimethylsilane. The reactivity is that which would be expected for additivity of the separate effects of two *o*-OMe and one *p*-OMe group.

INTRODUCTION

We recently had occasion to make (2,4,6-trimethoxyphenyl)trimethylsilane, and so decided to look briefly at the reactivity towards acid of this highly activated compound. We found that in a mixture of 8.5×10^{-4} *M* aqueous perchloric acid (2 vol.) and methanol (5 vol.), the first order rate constant, k, for the rate of cleavage of the aryl–silicon bond was 0.130 min^{-1} at 30°. A rate constant of 0.024 min^{-1} was previously recorded for mesityltrimethylsilane in a mixture of methanol with 0.106 *M* perchloric acid at 50°, and assuming that the rate constant is proportional to the concentration of acid, which is probably roughly true at these low concentrations, and allowing a factor of about 5 for the different temperatures of reaction (for a consideration of activation energies in this type of cleavage see ref. 2), it can be calculated that the trimethoxyphenyl compound is roughly 3350 times as reactive as the mesityl compound. Since the mesityl compound is about 53600 times as reactive as phenyltrimethylsilane[3], the trimethoxyphenyl compound must be roughly 1.8×10^8 times as reactive as phenyltrimethylsilane**. The value which would be expected assuming additivity of the effects of the three methoxy groups would be $1510 \times 335 \times 335$ (the separate activating effects of a *para*- and an *ortho*-methoxy group being 1510 and 335, respectively)[3], *i.e.* 1.7×10^8. The excellent agreement is fortuitous, of course, since our estimate of the actual reactivity could be in error by as much as a factor of 2, but it is clear that any departure from additivity of substituent effects must be relatively small. This is possibly somewhat surprising in view of the fact that the transition state for the trimethoxyphenyl compound must lie significantly closer to the initial state (*i.e.*

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*For Part LIII see ref. 1.

** A very similar figure is obtained if slightly different data[4] are used for the mesityl compound.

further from the Wheland intermediate) than does that for phenyltrimethylsilane and the (monomethoxyphenyl)trimethylsilanes.

The trimethoxyphenyl compound was also cleaved fairly readily by aqueous methanol in the absence of added acid; each reaction was first-order, but the rate constants varied between 2.5×10^{-3} and 5×10^{-3} min^{-1} (corresponding to half-lives in the region of 4 h) with different batches of solvent at 50°. The cleavage was completely inhibited by the presence of a little sodium bicarbonate, indicating that the effective electrophiles in the "neutral" medium were not water or methanol molecules but rather oxonium ions produced by autoprotolysis or by the presence of acidic impurities. From the rate at 30° in the mixture of methanol (5 vol.) with 8.5×10^{-4} *M* perchloric acid (2 vol.), in which the concentration of oxonium ion would be 2.4×10^{-4} *M*, it can be calculated that oxonium ion concentrations in the region of $1\text{–}2 \times 10^{-6}$ *M* would be needed to account for the observed rates in "neutral" aqueous methanol at 50°. Such a concentration, while it cannot be ruled out, seems rather high for autoprotolysis compared with the value of 10^{-7} *M* for water alone, and taken along with the variability of the rate constant in the "neutral" aqueous methanol suggests that some traces of some acidic impurity (*e.g.* carbon dioxide) were present.

EXPERIMENTAL

Preparation of (2,4,6-trimethoxyphenyl)trimethylsilane

A mixture of 1,3,5-trimethoxybenzene (16.8 g, 0.10 mole), n-butyllithium (0.15 mole of 1 *M* solution in hexane), and ether (100 ml) was made up at 0° and stirred at room temperature for 6 h. To the pale yellow emulsion chlorotrimethylsilane (13.0 g, 0.12 mole) in ether (200 ml) was added dropwise, and the mixture was stirred for 12 h. Solvent and volatile material was evaporated off, and organic material was extracted from the residue with light petroleum (b.p. 40–60°). The extract was fractionated to give (2,4,6-trimethoxyphenyl)trimethylsilane, b.p. 118°/ca. 0.35 mm, m.p. 78–79°. (Found: C, 60.3; H, 8.05. $C_{12}H_{20}O_3Si$ calcd.: C, 60.0; H, 8.3%.) The PMR spectrum had the expected integration pattern with τ values as follows: Me_3Si, 9.74 (s); *o*-OMe, 6.28(s); *p*-OMe, 6.22 (s); 3- and 5-H, 3.92(s).

Rate studies

For the rate measurements, either water (2 vol.) or 8.5×10^{-4} *M* aqueous perchloric acid was added to a methanolic solution of the organosilane. The progress of the reaction was followed spectrophotometrically, as previously described[2,3], at 245 nm. The water and methanol used for the "neutral" cleavages were boiled-out before use.

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