

ORGANOSILICON COMPOUNDS XXXIX*. EFFECTS OF VARYING R ON THE RATE OF ACID CLEAVAGE OF p -MeOC₆H₄SiR₃ COMPOUNDS

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INTRODUCTION

Extensive studies have been made of the effects of substituents, X, in the rate of acid cleavage of R₃SiC₆H₄X compounds^{2,3}, but investigations⁴⁻⁶ of the effects of the R groups have been limited in scope. In one of these⁴, Benkeser and his co-workers showed that the relative rates of cleavage of R₃SiC₆H₅ compounds by p -toluenesulphonic acid in aqueous acetic acid were: (R =) Me, 1000; Et, 480; iso-Pr, 60. They attributed the rate decrease in this series to increasing steric hindrance.

In order to make some analysis of the relative importance of steric and electronic effects, we have examined the cleavage by aqueous-methanolic perchloric acid of some Aryl₃SiC₆H₄OMe- p and Alkyl₃SiC₆H₄OMe- p compounds. As expected from the known high reactivity of the p -MeOC₆H₄-Si bonds², there was no detectable interference from cleavage of the other bonds to silicon.

DISCUSSION

The results are shown in Table 1 as observed (pseudo) first-order rate constants, k_1 at the (added) acid concentrations specified, and as rates at 50°, k_{rel} relative to that of the trimethyl compound, Me₃SiC₆H₄OMe- p , expressed as 1000, it being assumed that the relative reactivities are independent of the acid concentration. The important features of the results are as follows:

(i) Electron release from the substituent Y in (YC₆H₄)₃SiC₆H₄OMe- p compounds facilitates and electron withdrawal hinders reaction. These electronic effects are fairly small; for example, when Y = p -Me, the three methyl groups together cause little over a 2-fold rate increase, whereas the change from the compound Me₃SiC₆H₅ to Me₃SiC₆H₄Me- p is accompanied by a 21-fold rate increase².

(ii) The compound (o -MeC₆H₄)₃SiC₆H₄OMe- p is some 500 times less reactive than its tri- p -tolyl analogue, and some 200 times less reactive than the corresponding triphenyl compound. Since electronic effects of o - and p -Me groups are very similar, the low reactivity of the tri- o -tolyl compound must arise from steric hindrance.

(iii) The reactivities of the trialkylsilyl compounds fall in order (R =) Me >

* Part XXXVIII see ref. 1.

TABLE 1

RATES OF CLEAVAGE OF p - $R_3SiC_6H_4OMe$ COMPOUNDS

In a mixture of methanol (5 vol) and aqueous perchloric acid (2 vol).

R_3	$[HClO_4]^a$ (M)	10^3k , 40.0° (min ⁻¹)	10^3k , 50.0° (min ⁻¹)	E_{Act} (kcal/mole)	k_{rel}
Me_3	3.68	40	108	19.9	1000
	4.58	67	170	18.8	
Et_3	3.68	19.2	52	20.2	490
	4.58	33	83	18.5	
Pr_3	3.68	17.1	45	19.5	420
	4.58	27.8	71	18.9	
iso - Pr_3	9.14	48	122	18.9	55
Me_2Ph	4.58		56		330
	6.37		153		
$MePh_2$	6.37		34.5		74
	9.14		165		
Ph_3	9.14	12.9	35.5	20.1	16
	11.96		171		
$(p$ - MeC_6H_4) ₃	9.14		79		36
$(p$ - ClC_6H_4) ₃	11.96		57.5		5.4
$(o$ - MeC_6H_4) ₃	11.96		$\sim 0.8 \pm 0.1$		~ 0.075

^a Concn. of aqueous acid, 2 vol of which was mixed with 5 vol of methanolic organosilane.

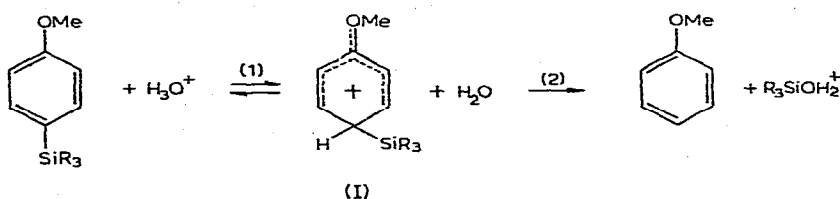
$Et > Pr > iso$ - Pr . (The relative rates are remarkably, and presumably coincidentally, similar to those obtained by Benkeser *et al.* with $R_3SiC_6H_5$ compounds in acetic acid containing water and p -toluenesulphonic acid⁴.) The observed order is the opposite of that expected for facilitation of reaction by the increasing inductive electron release of the alkyl groups, and must be attributed to increasing steric hindrance, as previously suggested^{4,7}.

(iv) The $Ph_3SiC_6H_4OMe$ - p compound is some 60 times less reactive than the $Me_3SiC_6H_4OMe$ - p compound. Probably greater steric hindrance and greater electron withdrawal by the phenyl group contribute to this low reactivity⁷. The fact that the replacement by a phenyl group of the second and third methyl group in the series ($R_3Si=$) Me_3Si , Me_2PhSi , $MePh_2Si$, and Ph_3Si causes only a slightly larger rate reduction than the replacement of the first methyl group suggests that the steric effect is not large, and thus that the electronic effect is dominant. (The Ph_3Si group is known to be electron-withdrawing in circumstances in which the Me_3Si group is electron releasing⁸).

(v) Values of the activation energy, E_{Act} , are based on measurements at two temperatures only 10° apart, and so are not very accurate. There is no significant variation in E_{Act} for the compounds with $R =$ Alkyl or Ph. Values of $\log A$, calculated from the pseudo-first rate constant in sec⁻¹ are all about 10¹². These cannot be accurately transformed into values derived from the second order rate constants because the oxonium ion activity is not known in the media concerned, but since acid concentrations are in the 1 M region the transformation would not greatly alter the values of $\log A$, which are a little below the range of "normal" values for bimolecular reaction.

The results are consistent with the view⁹ that the rate-determining step in the

cleavage is the initial proton transfer from the oxonium ion (H_3O^+ or MeH_2O^+) to the aromatic ring, to give the intermediate (I), which then gives the products in a fast step (which, for simplicity, we show as giving initially the compound $\text{R}_3\text{SiOH}_2^+$, but there are other possibilities):



The transition state of the slow step (1) will have some of the character of the positively-charged intermediate (I), and thus will be stabilized by electron-release from the R groups. The origins of the observed steric effects are not so obvious, but it should first be noted that although the tri-*o*-tolyl is 500 times less reactive than the tri-*p*-tolyl compound, this difference corresponds to only about 4 kcal/mole in free energy of activation. Inspection of a model of (I) (with the ring assumed to remain a planar regular hexagon) reveals that when $\text{R} = o\text{-tolyl}$, the *o*-tolyl groups approach rather close to the *p*-methoxyphenyl ring (intruding on the π -electron cloud), and effectively cover one side of it. There will, then, be not only compression strain in the transition state but also steric hindrance to solvation of the forming positive charge which is spread over the methoxyl-substituted ring. Related but smaller effects would be expected for some of the other R_3Si compounds, more particularly the triisopropyl compound, and must be assumed to be responsible, for example, for the decrease in reactivity from the trimethyl to the triethyl compound.

This picture of steric hindrance is consistent with the observation by Benkeser and Clark⁵ that the activating effect of a *meta*-alkyl group, X, on the ease of acid cleavage of $\text{XC}_6\text{H}_4\text{SiR}_3$ compounds increases as R is varied from Me to Et to iso-Pr. Not only with the proton-transfer to the ring have progressed further with the most hindered, least reactive compound, to give a larger charge on the ring in the transition state⁵, but hindrance to solvation leaves a greater portion of the charge to be stabilized by interaction with the *meta*-alkyl substituent.

EXPERIMENTAL

Compounds used

(*p*-Methoxyphenyl)triisopropylsilane. A mixture of fluorotriisopropylsilane (21.5 g) and a 4-fold excess of *p*-methoxyphenyllithium in ether (200 ml) was refluxed for 40 h, then treated with dilute aqueous acid. The usual working-up and fractionation gave a solid, which was recrystallised from methanol, to give the required compound, m.p. 36.5°, in 80% yield. (Found: C, 72.5; H, 10.7. $\text{C}_{16}\text{H}_{28}\text{OSi}$ calcd.: C, 72.6; H, 10.7%.)

Trialkyl(*p*-methoxyphenyl)silanes. Coupling of the appropriate trialkylsilyl chloride with *p*-methoxyphenyllithium in ether, followed by the usual working up and fractionation gave trimethyl-, b.p. 222°, n_D^{20} 1.5043; triethyl-, b.p. 180°/8 mm, n_D^{20} 1.5130; and tripropyl(*p*-methoxyphenyl)silane, b.p. 308°, n_D^{20} 1.5018.

(*p*-Methoxyphenyl)tri-*o*-tolylsilane. Fluorotri-*o*-tolylsilane was refluxed with

a 4-fold excess of *p*-methoxyphenyllithium in ether for 40 h, and the usual hydrolysis followed by washing, drying, and evaporation of the ether layer left a solid which was recrystallised from light petroleum (b.p. 60–80°) to give (*p*-methoxyphenyl)tri-*o*-tolylsilane¹⁰, m.p. 183°, in 51% yield.

(*p*-Methoxyphenyl)triphenylsilane. Chlorotriphenylsilane was stirred with a 2-fold excess of *p*-methoxyphenyllithium in ether for 2 h. Hydrolysis, followed by washing, drying, and concentration of the ethereal layer gave a solid which was recrystallised from ethyl acetate and then from a large volume of ether to give (*p*-methoxyphenyl)triphenylsilane, m.p. 167°, in 80% yield. (Found: C, 81.8, H, 5.9. $C_{25}H_{22}OSi$ calcd.: C, 81.95; H, 6.0%.)

Other compounds. The following $R_3SiC_6H_4OMe$ -*p* compounds were supplied by Dr. R. C. Moore¹¹. ($R_3=$) (*p*-tolyl)₃, m.p. 194°; (*p*-ClC₆H₄)₃, m.p. 161°; Me₂Ph, b.p. 186°/30 mm; MePh₂, m.p. 77.5°.

Rate studies

The general spectrophotometric technique has been described². The medium consisted of a mixture of a methanolic solution (5 vol) of the organosilane (*ca.* 0.25 g/l) and aqueous perchloric acid (2 vol) of the strength shown in Table 1. With the tri-*o*-tolyl compound, reaction samples were kept in sealed tubes in a thermostat and transferred to absorption cells at appropriate times, but with the other compounds the reaction samples were kept in 1 cm stoppered cells in a thermostatted block in the spectrophotometer². "Infinity" values of the optical density were obtained from samples kept in sealed tubes for 10 half-lives if this exceeded 20 h. The absorption at 281 mμ was used in all cases.

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SUMMARY

The rates of cleavage have been measured of some $R_3SiC_6H_4OMe$ -*p* compounds in aqueous methanolic perchloric acid at 50°. The relative reactivities of the compounds in which $R = p\text{-MeC}_6\text{H}_4$, C_6H_5 , and $p\text{-ClC}_6\text{H}_4$ indicates that electron release from *R* facilitates reaction. The low reactivity of the compound with $R = o\text{-MeC}_6\text{H}_4$, which is approximately 500 times less reactive than that with $R = p\text{-MeC}_6\text{H}_4$, is attributed to steric hindrance. The results are consistent with a mechanism involving rate-determining proton transfer to the carbon atom of the *p*-MeOC₆H₄-Si bond.

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