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NOTE

ADDITIONAL SUBSTITUENT EFFECTS OF TRIALKYLSILYL AND TRIALKYLSTANNYL GROUPS

C. EABORN, A. R. THOMPSON AND D. R. M. WALTON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

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To obtain additional information on the electronic influences of trialkylsilyl and -stannyl groups we have measured spectrophotometrically the rates of cleavage of $Me_3MC_6M_4C{\equiv}CSiMe_3$ and $Me_3MCH_2C_6H_4C{\equiv}CSiMe_3$ compounds in a 5/1 v/v mixture of methanol and aqueous sodium hydroxide at 29.6°. (Alkali cleavage of phenylalkynyl-$SiMe_3$ bonds is known to occur much more readily than that of benzyl–silicon and benzyl–tin bonds[1], and no interference from loss of Me_3M groups occurs during cleavage of the $Me_3MCH_2C_6H_4C{\equiv}CSiMe_3$ compounds.) The results are given in Table 1, which for each compound shows the wave-length, λ, used, the observed first-order rate constant, k, and the rate, k_{rel}, relative to that of the parent compound (phenylethynyl)trimethylsilane.

TABLE 1

CLEAVAGE OF $XC_6H_4C{\equiv}CSiMe_3$ COMPOUNDS IN A MIXTURE OF METHANOL (5 VOL.) AND 0.050 *M* AQUEOUS SODIUM HYDROXIDE (1 VOL.) AT 29.6°

X	λ (mμ)	10^3k_1 (min^{-1})	k_{rel}
p-$SiMe_3$	276	198	1.06
p-$SiEt_3$	272	190	1.02
H	273	187	1.00
p-$SnMe_3$	286	169	0.91
m-$SiMe_3$	270	160	0.86
m-$SnMe_3$	268	151	0.81
m-$SiEt_3$	268	144	0.77
p-Me_3SiCH_2	280	80.2	0.43
p-Me_3SnCH_2	285	69.0	0.37

The features of the results are as follows:

(*a*) The strongest deactivation is, as expected, by the Me_3MCH_2 groups, and the order of deactivation, $Me_3SnCH_2 > Me_3SiCH_2$ is consistent with the order of electron release by these groups as revealed in acid-catalysed aryl–tin cleavage in p-$Me_3MCH_2C_6H_4SnMe_3$ compounds[2] and in base-catalysed hydrogen exchange in $Me_3MCH_2C{\equiv}CH$ compounds[3]. The value [2] (*viz.* 4.4) of log k_{rel} for the compound m-$BrC_6H_4C{\equiv}CSiMe_3$ in the medium used corresponds to a value of 1.64

for the magnitude of ρ in the Hammett relation $\log k_{rel} = \rho\sigma$, and from this values of σ of -0.22 and -0.26 can be obtained for the p-Me_3SiCH_2 and p-Me_3SnCH_2 group, respectively. (Compare the literature value of -0.210 for σ for the p-Me_3SiCH_2 group derived[4] from the strengths of the acid p-$Me_3SiCH_2C_6H_4CO_2H$[5].)

(*b*) The Me_3Si and Et_3Si groups deactivate from the *meta*- but activate slightly from the *para*-position, in accord with the view that inductive electron release by the R_3Si group is counteracted by p_π–d_π bonding between the aryl group and the silicon atom[6]. For the p-R_3Si groups the π-bonding dominates to make the group (which is sometimes slightly electron-releasing[5]) electron-withdrawing overall in this reaction, but this effect cannot operate directly to the *meta*-position. The overall electron-withdrawal is slightly greater for the p-Me_3Si than for the p-Et_3Si group, which is consistent with a larger inductive electron-release by ethyl than by methyl groups, and the overall electron-release is correspondingly greater for the m-Et_3Si than for the m-Me_3Si group.

(*c*) The Me_3Sn group deactivates from both the *para*- and the *meta*-position, more so from the latter. The overall electron-releasing effect is greater than that of the Me_3Si group, but it cannot be decided at present how much this is attributable to a greater inductive release and how much to less effective p_π–d_π bonding to the tin atom.

EXPERIMENTAL

Preparations

The preparations of the nuclear-substituted (phenylethynyl)trimethylsilanes have been described previously[7].

Rate measurements

The spectrophotometric technique has been described elsewhere[1]. The medium used was a mixture of a methanolic solution of the organosilane (5 vol.) with 0.05 *M* aqueous alkali (1 vol.).

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