# Cleavage of Furan-2-yl, 2-Thienyl-, Benzo[*b*]furan-2-yl-, and Benzo[*b*]thiophen-2-yl-methyl(trimethyl)silanes ($RCH_2SiMe_3$) by Methanolic Sodium Methoxide; Acidities of the Corresponding $RCH_3$ Species

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Rates of cleavage of $RCH_2SiMe_3$ by 2.00M-NaOMe in MeOH or MeOD at 50 °C have been determined for R = furan-2-yl, 2-thienyl, benzo[*b*]furan-2-yl, and benzo[*b*]thiophen-2-yl; the values of $10^5k_s$ in MeOH and (in parentheses) in MeOD, where $k_s$ is the specific second order rate constant, are, respectively: 0.070 (0.167), 0.26 (0.52), 165 (310), and 70 (130) $dm^3 mol^{-1} s^{-1}$. The values of the ratios of $k_s$ in MeOH to that in MeOD are in the range 0.42—0.54, consistent with rate-determining separation of the carbanion $RCH_2^-$. [In contrast, for 2-thienylmethyl(trimethyl)stannane, for which $10^5 k_s$ is 1.57 (1.55), the ratio is 1.01, consistent with electrophilic assistance by proton transfer from the solvent to the separating carbon centre.] The results are discussed in the light of the deprotonation energies calculated (STO-3G) for the corresponding carbon acids $RCH_3$, and approximate $pK_a$ values are derived for the latter, *viz.* (R =) furan-2-yl, 40.6; 2-thienyl, 39.7; benzo[*b*]furan-2-yl, 35.2; benzo[*b*]thiophen-2-yl, 35.8.

Cleavage of R–$SiMe_3$ bonds, where R is a carbon-centred organic ligand, by NaOMe–MeOH is known normally to involve rate-determining formation of the carbanion $R^-$;[1] thus the rate of reaction provides a measure of the stability of $R^-$, and hence of the acidity of the carbon acid RH.[2] (In contrast, the corresponding cleavages of R–$SnMe_3$ bonds usually involve attachment of a proton from the solvent to the R group as the R–Sn bond breaks.[3,4]). We present here the results of measurement of the rates of cleavage of $RCH_2SiMe_3$ with R = furan-2-yl, 2-thienyl, benzo[*b*]furan-2-yl, and benzo[*b*]thiophen-2-yl, derive approximate $pK_a$ values for the corresponding $RCH_3$ species, and compare the relative acidities with those calculated by a simple *ab initio* MO method. Cleavage of the tin compound $RCH_2SnMe_3$ with R = 2-thienyl was also studied, in order to see whether the normally observed differences in behaviour between the silicon and tin compounds apply in this series.

## Results and Discussion

The various compounds $RCH_2SiMe_3$ were made by treatment of the appropriate RLi species with $Me_3SiCH_2Br$. The compound $RCH_2SnMe_3$ with R = 2-thienyl was made from 2-thienylmethylmagnesium bromide and $Me_3SnCl$.

The values of the specific second-order rate constants, $k_s$ (given by dividing the observed first-order rate constant by the concentration of NaOMe) determined with 2.00M-NaOMe in MeOH or MeOD at 50 °C, are shown in Table 1, which also lists the values of: (*a*) the ratio, $k_{rel}$, of $k_s$ for each compound relative to that for $PhCH_2SiMe_3$; (*b*) the rate isotope effect (r.i.e.), given by the ratio of $k_s$ in MeOH to that in MeOD; (*c*) the known[5] or derived $pK_a$ value for the corresponding $RCH_3$ species; and (*d*) the calculated difference in energy, $\Delta E$, between $RCH_3$ and $RCH_2^-$. Some data for cleavage of the tin compound $RCH_2SnMe_3$ with R = 2-thienyl are given in a footnote to the Table.

The features of the results are as follows.

(i) The r.i.e. values, 0.42—0.54, for the silicon compounds are in the usual range, and consistent with rate-determining separation of the carbanion $RCH_2^-$ with no electrophilic assistance from the solvent. In contrast the value for the tin compound studied is 1.01, consistent with such assistance, involving proton transfer from the solvent to the separating carbon centre. The thienylmethyl-tin compound is *ca.* 6 times as reactive as the corresponding silicon compound in MeOH (the factor is only 3 in MeOD); this is to be compared with a factor of 16 for cleavage of the compounds $PhCH_2MMe_3$ in MeOH.[4]

(ii) The sequence of reactivity of the $RCH_2SiMe_3$ compounds, *viz.* R = benzo[*b*]furan-2-yl > benzo[*b*]thiophen-2-yl > 2-thienyl > furan-2-yl, is the same as that observed for hydrogen exchange of the parent compounds $RCH_3$ in EtOK–EtOD at 180 °C.[6] The spread of rates is greater in the hydrogen exchange.

(iii) The acidity sequence for the $RCH_3$ compounds indicated by the rates differs from that suggested by the calculations of $\Delta E$ only in that the latter suggest that the furyl should be very slightly more acidic than the thienyl compound. The major effects evident in the $\Delta E$ values, namely the marked increase in the stabilities of the anions $RCH_2^-$ on fusion of a benzene ring, and the fact that this increase is significantly larger for the furan than for the thiophene system, are reflected in the cleavage and exchange data. It is noteworthy that the thienyl stabilizes the carbanion more than does the furyl group in $RCH_2^-$, whereas the opposite is the case (as indicated by the relevant cleavage rates) for $RPhCH^-$.[7]

(iv) Whereas the cleavages of the compounds $RCH_2SiMe_3$ proceed less readily than those for the corresponding compounds $RSiMe_3$ for R = 2-thienyl and furan-2-yl (and so, by implication, the acidities of $RCH_3$ are lower than those of RH), the opposite is the case for R = benzo[*b*]-thiophen-2-yl or -furan-2-yl, *i.e.* the benzene ring stabilizes $RCH_2^-$ more than $R^-$.

(v) The $k_{rel}$ values in Table 1 have been used along with the experimental $pK_a$ values available for $PhCH_3$ and some of the compounds RH to estimate the $pK_a$ values for the $RCH_3$ species shown in Table 1, a linear relationship between log $k_{rel}$ and $pK_a$ being assumed.

## Experimental

*Preparations of* $RCH_2SiMe_3$.—These were made from $Me_3SiCH_2Br$ and the appropriate RLi; the latter were made as previously described for R = 2-thienyl,[8] furan-2-yl,[9] and

**Table 1.** Cleavages of $R'SiMe_3$ by 2M-NaOMe in MeOH or MeOD at 50.0 °C and the acidities of the corresponding compounds R′H

| R′ | $10^5k_s/dm^3\ mol^{-1}\ s^{-1}$ [a] | R.i.e.[b] | $k_{rel}$[c] | $pK_a$[d] | $\Delta E/kJ\ mol^{-1}$[e] |
|---|---|---|---|---|---|
| Furan-2-yl-$CH_2$ | 0.070 (0.167) | 0.42 | 2.12 | (40.6) | 0.8007 |
| 2-Thienyl-$CH_2$[f] | 0.26 (0.52) | 0.50 | 7.9 | (39.7) | 0.8018 |
| Benzo[*b*]furan-2-yl-$CH_2$ | 165 (310) | 0.53 | $5.0 \times 10^3$ | (35.2) | 0.7778 |
| Benzo[*b*]thiophen-2-yl-$CH_2$ | 70 (130) | 0.54 | $2.13 \times 10^3$ | (35.8) | 0.7849 |
| Furan-2-yl | | | 13.3 | (39.3) | |
| 2-thienyl | | | 36.3 | 38.2 | |
| Benzo[*b*]furan-2-yl | | | 475 | 36.84 | |
| Benzo[*b*]thiophen-2-yl | | | 580 | 37.05 | |
| $PhCH_2$ | | | 1.0 | 41.2 | |

[a] Observed first-order rate constant divided by [NaOMe]; values in parentheses refer to reactions in MeOD. [b] Ratio of $k_s$ in MeOH to that in MeOD. [c] Rate relative to that for $PhCH_2SiMe_3$ at similar base concentration. [d] Experimental values for equilibrium ion-pair acidities in $C_6H_{11}NHCs$–$C_6H_{11}NH_2$,[3] or, in parentheses, values calculated by assuming log $k_{rel} \propto pK_a$. [e] Calculated values of the energy required to go from $R'CH_3$ to $R'CH_2^-$. [f] For the tin analogue, (2-thienyl)$CH_2SnMe_3$, the $10^5k_s$ values were 1.57 and (1.55) $dm^3\ mol^{-1}\ s^{-1}$, corresponding to an r.i.e. of 1.01.

**Table 2.** B.p.s and analytical data for $RCH_2SiMe_3$

| R′ | B.p. (°C/mmHg) | Found (%) | | Calc. (%) | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| Furan-2-yl | 150/760 | 62.4 | 9.1 | 62.3 | 9.15 |
| 2-Thienyl | 90/20 | 55.9 | 8.4 | 56.0 | 8.3 |
| Benzo[*b*]furan-2-yl | 88/2 | 71.2 | 8.0 | 70.5 | 7.9 |
| Benzo[*b*]thiophen-2-yl | 118/3[a] | 65.4 | 7.4 | 65.4 | 7.3 |

[a] M.p. 61 °C

benzo[*b*]thiophen-2-yl,[10] and the method used for the last compound was also used to make the reagent with R = benzo[*b*]furan-2-yl.

The stirred RLi solution was treated dropwise at −15 °C with an equimolar amount of $Me_3SiCH_2Br$ in tetrahydrofuran, and the mixture was allowed to warm to room temperature (*ca.* 2 h) then stirred for 10 h. The solvent was removed under reduced pressure and diethyl ether was added. The cooled mixture was treated with cold saturated aqueous $NH_4Cl$, and the ethereal layer was washed, dried ($Na_2SO_4$), and fractionally distilled. The b.p.s and analytical data are listed in Table 2.

*Preparation of 2-(Trimethylstannylmethyl)thiophene*.—A small amount (*ca.* 1 $cm^3$) of 2-chloromethylthiophene was added under $N_2$ to a mixture of oven-dried Mg turnings (6.1 g, 0.25 mol), a small crystal of iodine, and anhydrous diethyl ether (300 $cm^3$). When reaction began a mixture of more of the chloride (to a total of 33.2 g, 0.25 mol) and trimethyltin chloride (50 g, 0.25 mol) was added dropwise. The mixture was stirred overnight, then saturated aqueous $NH_4Cl$ was carefully added with cooling, and the ethereal layer was separated, washed, dried ($Na_2SO_4$), and distilled under reduced pressure to give 2-*(trimethylstannylmethyl)thiophene* (75%), b.p. 88 °C at 7 mmHg (Found: C, 36.4; H, 5.4. $C_8H_{14}SSn$ requires C, 36.8; H, 5.4%).

*Rate Measurements*.—Rates for $RCH_2SiMe_3$ were measured spectrophotometrically as previously described;[11] the wavelengths used were (R=) furyl, 242; thienyl, 254; benzo[*b*]furanyl, 278; benzo[*b*]thiophenyl, 270 nm. A wavelength of 270 nm was used for 2-(trimethylstannylmethyl)thiophene.

*Calculations*.—Minimum basis set (STO-3G) *ab initio* calculations were carried out using the Gaussian 70 package.[12] Standard geometries[13] were used for $CH_3$ and $CH_2^-$ groups, and experimental geometries for the thiophene,[14] furan,[15] and benzo-furan and -thiophene[16] rings. The values of $\Delta E$ shown in Table 1 are given by the differences in energy between the neutral and anionic species.

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