A Map of Nucleophilic Substitution at Silicon in Solution

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The course of nucleophilic substitution at silicon involving a pentacoordinate intermediate is mapped in solution;[1] the method involves correlating the extent of nucleophile–silicon bond-making (as determined by the pyridone ring carbon chemical shifts) with the coordination state of the silicon (as inferred from the ^{29}Si NMR chemical shifts); the reaction under study is the displacement of X (X = OR, F, Cl, Br, OSO_2CF_3) by oxygen in an intramolecular reaction of a series of *N*-dimethylsilylmethyl pyridones.

Despite its deceptive simplicity the mechanism of nucleophilic substitution at silicon is still controversial and an area of active current research.[2,3] We sought to test our solution mapping method[4] by examining a straightforward nucleophilic displacement at silicon. Accordingly a series of compounds **1** (X = OR, F, Cl, Br, OSO_2CF_3; Y = H, $3NO_2$, 3-OMe, 5-Cl, 6-Cl, 6-Me) was prepared and their ^{1}H, ^{13}C and ^{29}Si NMR spectra have been obtained. From these spectra a map of nucleophilic substitution at the silicon nucleus has been drawn. The method[3] involves determining the position of a particular compound on the reaction continuum, **2**, **3**, and **4** by analysing the ^{13}C (or ^{1}H) NMR chemical shifts of the pyridone ring and comparing them with model compounds for the extremes **2** and **4**. The method was tested by using *N*-methylpyridone as the model for **2**.[4]

Whereas *N*-methylpyridone serves well as a general model we used **5** in this study, having established, by ^{29}Si NMR and by comparison of the ^{13}C NMR spectra with *N*-methylpyridone, that the disiloxane is purely tetracoordinate. The model for **4** is then determined by silylation of **5** with trimethylsilyl trifluorosulphonate[5] to give **6**.

Fig. 1 shows the variation of the extent of reaction (*i.e.* the extent of Si–O bond formation) for the unsubstituted series **1** (Y = H; X = F, Cl, Br, OSO_2CF_3) together with the model disiloxane **5** (OSi) and its silylated derivative; **6** (OSi+). The extent of reaction follows the expected order[2,3] with the leaving group ability TfO > Br > Cl > F. Figs. 2 and 3 shows the same effect, except for the $3-NO_2$ and 6-Me substituted series. In each case the 0 and 100% reactions refer to the appropriate **5** and its silylated derivative. The same general trend in leaving-group ability is followed in both cases, but the relative extent of reaction is modified by the substituent. With the strongly electron-withdrawing $3-NO_2$ group the extent of reaction for each leaving group is significantly less than for the unsubstituted series. Conversely, the reactions are all more advanced for the 6-Me series. For example, the extent of reaction for the fluorides is 12%, $3-NO_2$; 30%, H and 40%, 6-Me, and for the chlorides 40%, $3-NO_2$; 50%, H and 70%, 6-Me. The Si–O bond in the $3-NO_2$ substituted silyl trifluorosulphonate is only 80% formed, whereas for the H and 6-Me derivatives the Si–O bonds are around 90% formed. Other derivatives were also studied and for the fluorides the


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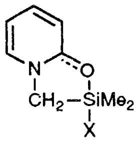
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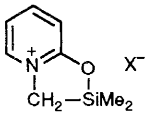
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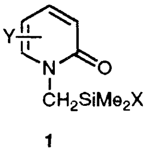
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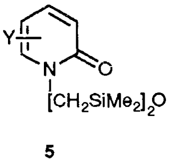
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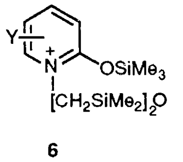
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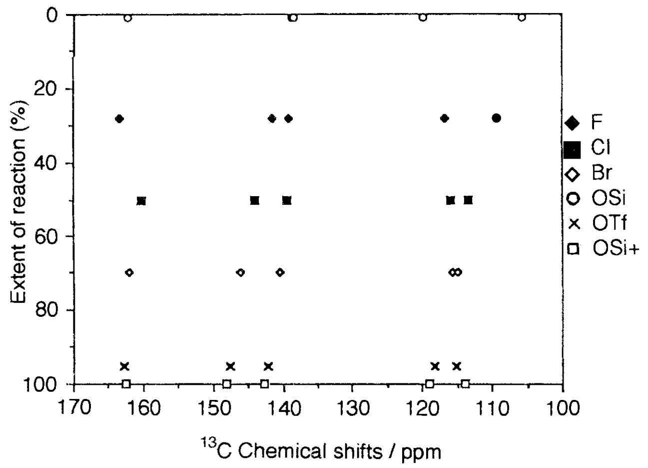


Fig. 1 Variation of ^{13}C chemical shift with extent of reaction for some silylpyridones

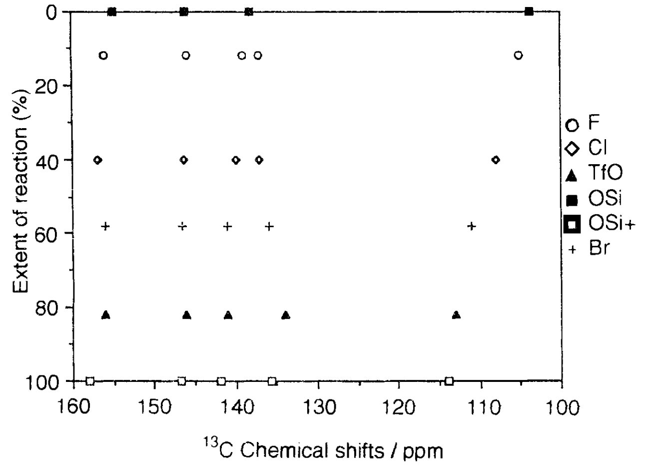


Fig. 2 Variation of ^{13}C chemical shifts with extent of reaction for some 3-NO_2 substituted silylpyridones

substituent effect decreases in the order 6-Me > 6-Cl > H > 5-Cl > 3-OMe > 3-NO_2.†

The 6-Cl substituent in **1** is electron-supplying by the resonance effect, which is particularly pronounced in the 6-position. By contrast, the 3-OMe group is electron-withdrawing as the resonance electron supply is suppressed in the 3-position.

The question arises as to the nature of the species being studied. There are two possible descriptions. Either there is a continuum of structures as the Si–X bond extends and the Si–O bond forms, or there are equilibria **2** $\rightleftharpoons$ **3** and **3** $\rightleftharpoons$ **4** which, in view of the single sets of resonances in the NMR spectra of each nucleus, must involve rapid exchange on the NMR time scale. X-Ray structural analysis[6] on chelated pentacoordinate silyl amides does indeed show that the Si–Cl bond length increases as the Si–O bond length decreases; it seems a reasonable assumption that solution structures can be similarly hybrid. We have no direct evidence, at present, to support this hypothesis. However, solutions of bromides in MeCN, which would be approximately 50% **4** if an equilibrium obtains, do not conduct electricity. Trifluorosulphonate derivatives do conduct electricity, consistent with their being essentially ionic.

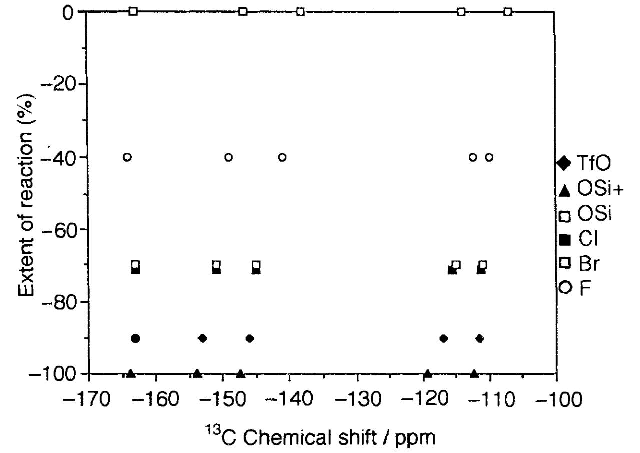
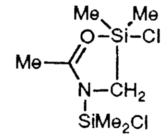


Fig. 3 Variation of ^{13}C chemical shift with extent of reaction for some 6-Me substituted silylpyridones



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In order to map completely the progress of the reaction it is necessary to correlate the Si–O bond formation with the coordination state of silicon. The X-ray crystal structure of **7** has been reported[7] and one silicon is completely pentacoordinate.[6,7] We have measured the ^{29}Si NMR chemical shifts in solution in $CDCl_3$ and found that the pentacoordinate silicon has a resonance at δ −42 and the four-coordinate silicon appears at δ 28. The ^{29}Si NMR chemical shifts of the H and 6-Cl substituted chlorosilanes, **1**, both appear at δ −40 and their extents of reaction, as measured by ^{13}C NMR, are both 50%. Confirmation that this represents the maximum extent of pentacoordination is found in the ^{29}Si NMR chemical shifts of the 3-OMe substituted chlorosilane, **1**, at −32 ppm, accompanied by a 44% extent of reactions from ^{13}C NMR, and the 6-Me substituted chlorosilane, **1**, δ −24, accompanied by a 70% extent of reaction. The 'reaction' is therefore least advanced with the electron-withdrawing 3-OMe substituent, then proceeds to a fully pentacoordinate intermediate with H and 6-Cl substituents, and then O–Si bond formation advances significantly with the 6-Me substituent with consequent weakening of the Si–Cl bond. We use these results to estimate the 'extent of pentacoordination' at silicon. The ^{29}Si NMR chemical shifts of Me_3SiCl, Me_3SiF, Me_3SiBr and the tetracoordinate silicon in **7** all appear within about ±2 ppm of +28 ppm, which is used as the limiting value for 0% pentacoordination. The assumption is made that −40 ppm represents complete pentacoordination for all derivatives of F, Cl and Br. This is reasonable in view of the chemical shift of both the 6-Me substituted fluorosilane, **1**, with ^{29}Si δ −35 and 40% reaction from the ^{13}C NMR data, and δ ^{29}Si δ −27 for the 3-NO_2 substituted bromosilane, **1**, with an extent of reaction about 60% from ^{13}C NMR data. A ^{29}Si NMR chemical shift of, say, −4 ppm, being the mean value of the two extremes, **2** and **3**, would therefore represent 50% pentacoordination and δ −40, would suggest 100% pentacoordination. The limiting value of the ^{29}Si NMR chemical shift of **4** is taken to be +40 from the chemical shift of *O*-trimethylsilylated *N*-methylpyridone. For species on the **3** and **4** manifold the ^{29}Si NMR chemical shift range is assumed to be between −40 and

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† The spectra of the fluoride series were obtained in $CDCl_3$ and CD_3CN. There was almost no difference in chemical shifts between the spectra in the different solvents in this series. The bromides provided a problem with solubility and a variety of solvents were used. The solvent is not important in determining the extent of reaction but variations make direct comparison difficult between, say, two differently substituted bromides.

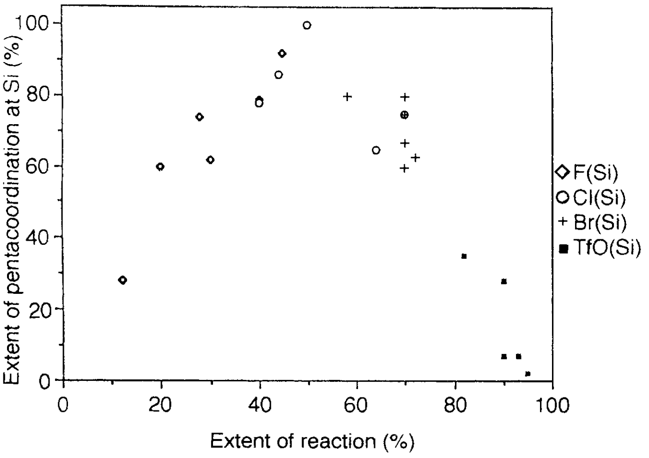

Fig. 4 Map of nucleophilic substitution at silicon

+40 ppm, and the extent of pentacoordination for intermediate species is readily obtained. For the whole series of compounds, **1**, the extent of pentacoordination at silicon was calculated as described above, and correlated with the extent of reaction as determined by ^{13}C NMR spectroscopy. Fig. 4 shows the completed map of substitution at **1**. The approach to the pentacoordinated intermediate is characterized by the fluorosilanes, which are the least powerful leaving groups; the chlorides are clustered around the pentacoordinate intermediate position; the bromides all have about 70% pentacoordination at silicon and 70% reaction, and finally the trifluorosulphonates which bear that excellent leaving group, are almost fully reacted. That the reaction proceeds through a genuine pentacoordinate intermediate is confirmed by the ^{29}Si NMR chemical shifts.

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References

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2 A. R. Bassindale and P. G. Taylor, *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, J. Wiley, Chichester, 1989, ch. 13.

3 R. J. P. Corriu and J. C. Young, *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, J. Wiley, Chichester, 1989, ch. 20.

4 A. R. Bassindale and M. Borbaruah, previous paper.

5 In a related study using the 2,2′-dipyridylamine ligand, various structures on the equivalent **2**, **3**, **4** continuum were observed, but the ligand, from the ^1H NMR spectra, apparently failed to show the anticipated relationship between the chemical shifts of the silylmethyl derivatives and the methylated ligand. D. Kummer, S. C. Chaudhry, J. Seifert, B. Deppisch and G. Mattern, *J. Organometal. Chem.*, 1990, **382**, 345.

6 A. A. Macharashvili, V. E. Shklover, Yu, T. Struchkov, G. I. Oleneva, E. P. Kramarova, A. G. Shipov and Yu. I. Baukov, *J. Chem. Soc., Chem. Commun.*, 1988, 683.

7 K. D. Onan, A. T. McPhail, C. H. Yoder and R. W. Hillyard Jr., *J. Chem. Soc., Chem. Commun.*, 1978, 209.