Cleavage of 5-Nitro-2-(trimethylsilylmethyl)thiophene by Methanolic Sodium Methoxide. U.V. Spectroscopic and Solvent Isotope Effect Evidence for Generation of the Anion [5-$O_2N \cdot C_4H_2S \cdot CH_2$-2]$^-$

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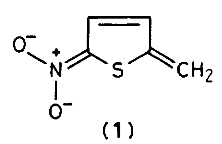
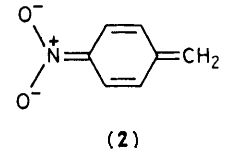
The reaction of 5-nitro-2-(trimethylsilylmethyl)thiophene with NaOMe–MeOH involves generation of the observable anion [5-$O_2N{\cdot}C_4H_2S{\cdot}CH_2$]$^-$ with a solvent isotope effect *k*(MeOH)/*k*(MeOD) of 0.5, followed by protonation of the anion with a solvent isotope effect of 10; the results confirm that cleavages of $RSiMe_3$ compounds by NaOMe–MeOH involve separation of the anions R^-, and that the isotope effect in the reaction of R^- with MeOH depends greatly on the degree of conjugative delocalization of the negative charge, not just on the acidity of RH.

In a series of papers we have built a case for our view that in cleavage by NaOMe–MeOH of organotrimethylsilanes, $RSiMe_3$, where R can be of a wide range of types, the carbanion R^- separates in the rate determining step and then rapidly acquires a proton from the solvent to give RH (see, *e.g.* refs. 1—4). (In contrast, with many organotin compounds the carbanion is never free, a solvent proton being transferred to R as the metal–carbon bond is broken.[1,5]) The case was based on indirect evidence from solvent isotope effects, but we have now obtained direct evidence for the separation of the anion [5-$O_2N \cdot C_4H_2S \cdot CH_2$-2]$^-$ in the cleavage of 5-nitro-2-(trimethylsilylmethyl)thiophene, 5-$O_2N \cdot C_4H_2S \cdot CH_2SiMe_3$-2.

When 2-(trimethylsilylmethyl)thiophene, $C_4H_3S \cdot CH_2SiMe_3$-2 reacts with 2.03 M NaOMe–MeOH at 50 °C there is a progressive change in the u.v. spectrum (involving a hypsochromic shift and a fall in absorption in the long wavelength region studied) to that of the product, $C_4H_3S \cdot Me$-2. The observed first order rate constant, *k*, is $0.53 \times 10^{-5}\ s^{-1}$, and the specific rate constant, k_s (= *k*/[NaOMe]) is $0.26 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$; for reaction in NaOMe–MeOD k_s is $0.52 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$, and thus the solvent isotope effect k_s(MeOH)/k_s(MeOD) is 0.50, as expected for a rate determining transition state in which the MeO^- ligand is substantially or fully attached to silicon as R^- leaves.[1—5] Similarly, with the much more reactive 3-$O_2N \cdot C_4H_2S \cdot CH_2SiMe_3$-2 in 0.001 M NaOMe–MeOH there is a progressive change in the spectrum to that of 3-$O_2N \cdot C_4H_2S \cdot Me$-2; the value of k_s is 5.5 $dm^3\ mol^{-1}\ s^{-1}$ at 25 °C, and that of k_s(MeOH)/k_s(MeOD) is 0.69, a value in line with those observed for some other highly reactive $RSiMe_3$ compounds.[6] After allowance for temperature differences and the effects of the base concentration on k_s,[7] the ratio of k_s for the 3-nitro compound relative to that for $C_4H_3S \cdot CH_2SiMe_3$-2 is *ca.* 1.7×10^7.

In contrast, in cleavage of 5-$O_2N \cdot C_4H_2S \cdot CH_2SiMe_3$-2, by 0.001—0.005 M base, there is initially a rise in the absorption and a bathochromic shift of $\lambda_{max.}$ from 348 to 375 nm; with 0.001 M base, *k* for this process is $11.5 \times 10^{-3}\ s^{-1}$ at 15 °C (the value of k_s at 25 °C is *ca.* 4.5 times that for the 3-nitro-isomer), and k_s(MeOH)/k_s(MeOD) is 0.71, similar to that for the 3-nitro isomer. Subsequently the spectrum changes to that of 5-$O_2N \cdot C_4H_2S \cdot Me$-2 ($\lambda_{max.}$ 325 nm), the first order rate constant for this process being $1.6 \times 10^{-3}\ s^{-1}$; *i.e.*, the rate is 7 times smaller than that for the first step at the base concentration used. Moreover, whereas the observed rate constant for the first step (studied at 15 °C) is proportional to the base concentration, that of the second step is independent of that concentration in the range 0.001—0.01 M (studied at 25 °C).† (Because of this difference, at very low base concentrations the first step becomes rate determining.) The value of *k*(MeOH)/*k*(MeOD) for the second step (at 25 °C) is 10, in satisfactory agreement with that of 9 observed (by mass spectrometry) for the product ratio RH/RD obtained on cleavage by NaOMe in 1:1 MeOH–MeOD, the product isotope effect, p.i.e.


(1)


(2)

Monitoring of the ^1H n.m.r. spectrum shows that Me_3SiOMe is completely formed in the first step, in which the singlet from the CH_2SiMe_3 protons disappears, but the singlet from the Me group of 5-$O_2N \cdot C_4H_2S \cdot Me$-2 appears, and grows progressively, only in the second step.

It can be concluded that the first step in the cleavage of the 5-nitro-compound involves separation of the anion [$O_2N \cdot C_4H_2S \cdot CH_2$]$^-$, which is probably best regarded as the nitronate ion (**1**), although there must be some contribution from the carbanion structure; by analogy with anions derived from polynitrotoluenes,[8] anion (**1**) would be expected to absorb at longer wavelengths than the parent thiophene compound. The subsequent step involves slow proton transfer (not base dependent) from the solvent to the methylene carbon, the transfer being about half complete in the transition state.

It can be assumed that a similar stepwise process takes place in cleavage of 3-$O_2N \cdot C_4H_2S \cdot CH_2SiMe_3$-2, but because the anion is less stable the first step is slower and the second faster than with the 5-nitro isomer, so that at the base concentrations used the first step is rate determining or the two steps proceed together. The p.i.e. for the compound, 10, is the same as that for the 5-nitro-isomer within experimental error.

There is nothing abnormal about the rate of the initial (cleavage) step for the 5-nitro compound; in fact, the ratio of k_s for this step to that for cleavage of $C_4H_3S \cdot CH_2SiMe_3$-2, *ca.* 8×10^7 (at 50 °C), is remarkably close to the corresponding ratio for *p*-$O_2N \cdot C_6H_4 \cdot CH_2SiMe_3$ and $C_6H_5 \cdot CH_2SiMe_3$, *viz.* 2.3×10^7 (at 25 °C). There is no reason to doubt that cleavage of the *p*-nitrobenzyl compound also involves initial formation of the anion, and furthermore, since conjugative effects are known not to be much greater in [5-X $\cdot C_4H_2S \cdot CH_2$-2] than in [*p*-X $\cdot C_6H_4 \cdot CH_2$]$^-$ species,[9] that the anion is close in structure to the nitronate species (**2**). The fact that the value of the solvent isotope effect *k*(MeOH)/*k*(MeOD) for protonation of the anion (**1**), and that of the p.i.e, are the same within experimental error as that of the p.i.e. for *p*-$O_2N \cdot C_6H_4 \cdot CH_2SiMe_3$,[3] confirms our view that the p.i.e.

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† The 5-$O_2N{\cdot}C_4H_2S{\cdot}Me$-2 is formed immediately if the solution is acidified when the first step is complete.

corresponds to the kinetic isotope effect for reaction of R^- with MeOH and MeOD,[1—4] and also suggests that the reactivity of the anion (**1**) towards MeOH may not be greatly different from that of (**2**).

It is noteworthy that 5-nitro-2-(trimethylsilymethyl)-thiophene is only *ca.* 5 times as reactive as 5-nitro-2-trimethylsilylthiophene, $5\text{-}O_2N \cdot C_4H_2S \cdot SiMe_3\text{-}2$,[4] and this implies that the acidities of $5\text{-}O_2N \cdot C_4H_2S \cdot Me\text{-}2$ (at the Me group) and $5\text{-}O_2N \cdot C_4H_3S$ (at the 2-position) are rather similar, but whereas the isotope effect for the reaction of the anion (**1**) with MeOH and MeOD is 10, that for the reaction of the 5-nitrothienyl-2-anion (given by the p.i.e.) is 1.1.[4] This confirms our view that the kinetic isotope effect for the reaction with MeOH depends much more on the degree to which a carbanion R^- is stabilized by conjugative delocalization than on the acidity of RH.[4]

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