Muonium-containing Vinyl Radicals

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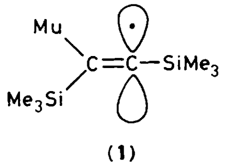
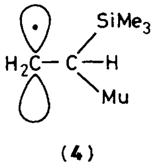
Exposure of trimethylsilylacetylene and bis(trimethylsilyl)acetylene to positive muons gave radicals whose muon–electron hyperfine coupling constants establish that the corresponding vinyl radicals were formed.

A range of muonic radicals derived from formal addition of muonium (Mu) to alkenes have recently been characterised,[1] but little is known about the corresponding triple-bond adducts.[2] Our endeavours to detect addition to acetylene and alkyl substituted acetylenes have not been successful, but we have been able to produce adducts from the silylated derivatives, $Me_3SiC{\equiv}CH$ and $Me_3SiC{\equiv}CSiMe_3$.

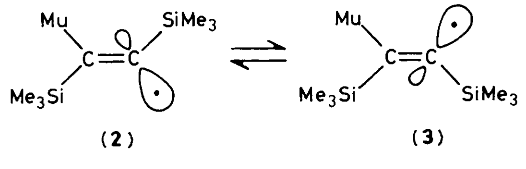
The resulting muon–electron hyperfine coupling constants, 591.4 and 732.4 MHz for the mono- and di-silyl derivatives (at *ca.* 298 K) are so large that the species must be vinyl radical derivatives. It is convenient to use reduced coupling constants, which allow for the difference between the muon and proton magnetic moments. The result, $a' = 82.2$ G (1 G = 10^{-4} T), for the disilyl derivative (the largest value yet obtained for a muonated organic radical) can then be compared with the value obtained for the corresponding hydrogen derivative (72.4 G).[3] This gives an isotope ratio of 1.14 which is close to the minimum observed for such radicals, and is only observed for radicals in which 'rotational' effects are unimportant.[2] The large magnitudes for A(Mu) and A(H) show that the limiting 'linear' structures (**1**) cannot be correct, and also that fast averaging between bent structures, equation (1), is also not occurring, since in both cases we expect ^{1}H coupling constants close to 52 G, on the basis of low temperature e.s.r. data[4] for $CH_2{=}\dot{C}H$. We suggest, in agreement with Ingold *et al.*,[3] that the *trans*-structure, (**2**), is strongly favoured over the *cis*-structure (**3**), and that averaging, which would probably lead to severe line broadening, is not occurring. [Indeed, such line broadening caused by equilibria such as (1) may help to explain our inability to detect muonated adducts of other



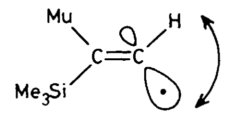
(**1**)



(**4**)



(**2**) (**3**) (1)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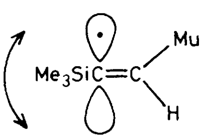
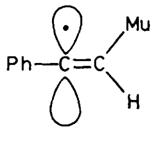

(6)


(7)

acetylenes.] It is of interest to compare this result with our recent results for radical (**4**).[5] In this case, the –SiMe$_3$ unit tends to favour the 'out-of-plane' site so that σ–π delocalisation involving the C–SiMe$_3$ σ-electrons is more important than that involving the C–Mu electrons. For radical (**2**) delocalisation involving the C–Mu bond is clearly favoured. This probably arises because of large Me$_3$Si · · · Me$_3$Si repulsion in the *cis* conformer (**3**), rather than for electronic reasons.

Although it is clear that a vinyl radical is formed, the result for the mono-silyl derivative ($a' = 66.4$ G) does not enable us to distinguish conclusively between the two modes of addition, giving radicals (**5**) or (**6**). In our work on the corresponding alkene, addition to the C=C unit occurred on either side, two distinct radicals being detected.[5] The issue is made more complicated by the possibility of 'inversion,' indicated by the double-headed arrows. We hope to be able to make the distinction between (**5**) and (**6**) either by determining the hyperfine coupling to the unique proton in the muonated radical,[2] or by studying the e.s.r. spectrum of the corresponding hydrogen atom adduct, which, so far as we know, has not yet been observed.

Unfortunately, we are not able to make structural predictions from the results for radical (**7**) since the reduced muon coupling in this case (47.1 G) is much smaller because of delocalisation into the benzene ring.[2]

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