Muonic Alkyl Radicals with α- or β-Phosphorus Substituents: $(EtO)_2P(O)\dot{C}HCH_2Mu$ and $H_2\dot{C}CH(Mu)P(O)(OEt)_2$

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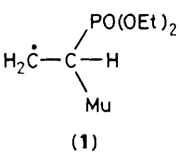
The magnitudes of the muon–electron hyperfine coupling constants for the title radicals show that the muonium atom favours the out-of-plane site for the α-P substituted radical, but is constrained towards the in-plane site for the β-P substituted radical.

While many alkyl radicals containing muonium atoms β- to the trigonal carbon are known,[1] there has been little work on muonic radicals containing hetero-atoms, especially 'heavy-atom' substituents,[2] and we know of no previous work on muonic phosphorus-containing radicals.

We have succeeded in detecting both radicals (**1**) and (**2**) (Figure 1), the results making an interesting contrast. The hyperfine coupling for (**1**) is less than a'(Mu) for $\dot{C}H_2CH_2Mu$ at room temperature[1,3] [*ca.* 37.2 G (1 G = 10^{-4} T): a'(Mu) = the true coupling divided by 3.184, the ratio of the muon and proton magnetic moments], whereas that for (**2**) is close to that for muonic ethyl.

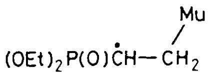
The ratio of the muon coupling in $H_2\dot{C}CH_2Mu$ to the methyl proton coupling in $H_2\dot{C}–CH_3$[1] is *ca.* 1.4. This large isotope effect is, at least in part, caused by the muonium atom exhibiting a preference for the 'out-of-plane' site. For radical (**2**), this remains the case, the α-$P(O)(OEt)_2$ group having no specific effect on the muon coupling. However, for radical (**1**), the muon coupling is clearly reduced relative to $H_2\dot{C}CH_2Mu$, suggesting that the $P(O)(OEt)_2$ group dominates the conformation in this case.

It is well established, both from the large hyperfine coupling to ^{31}P nuclei in β-positions,[4] and the small couplings to



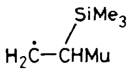
(**1**)

a' (Mu) = 29.88 G

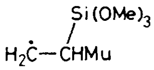


(**2**)

a' (Mu) = 37.03 G



(**3**)



(**4**)

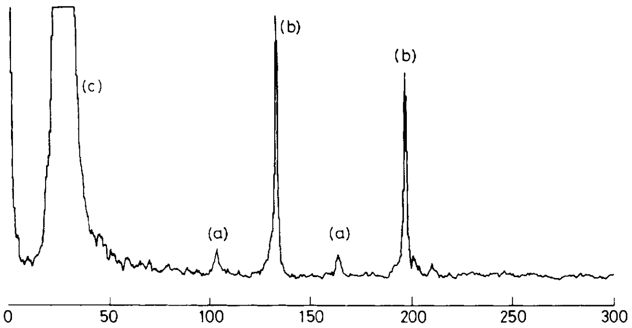


Figure 1. Muon spin rotation (μ.s.r.) spectrum recorded during muon implantation in $CH_2{=}CHP(O)(OEt)_2$, showing features assigned to: (a) $(EtO)_2P(O)CHMu\dot{C}H_2$ and (b) $CH_2Mu\dot{C}HP(O)(OEt)_2$; (c) is the signal from muons in diamagnetic environments.

β-protons[4] in normal protiated radicals of type (**1**), that the preferred conformation is indeed that in which the σ–π overlap for the C–P bond is maximised.

These results are in line with those recently obtained[2] for radicals (**3**) and (**4**). In both these radicals, *a*′(Mu) is less than that in $\dot{C}H_2CH_2Mu$, and falls on cooling, in contrast with the result for $H_2\dot{C}CH_2Mu$ where the coupling increases on cooling.[1,3] Thus, again, we conclude that the heavy atom substituents (SiR_3) dominate over the bound muonium atom for the conformational control of these radicals. However, when compared with the corresponding protiated species,[2,5] there is still a large muon isotope effect (*ca.* 1.4) for these radicals, suggesting that the mean conformations are still skewed in favour of the muon to some extent.

Finally, we note that the muon hyperfine coupling for the $H_2\dot{C}CHMuSi(OMe)_3$ radical (29.09 G) is slightly less than that for the phosphorus-containing radical, $H_2\dot{C}CHMuP(O)(OEt)_2$ (29.88 G) at room temperature. This fall on going from Si to P accords with the concept of conformational control through hyperconjugative electron transfer from the C–X bond, since this is expected to be stronger for C–Si than for C–P σ-electrons.

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