DETECTION OF AN
α-MUONIUM-SUBSTITUTED METHYL
RADICAL

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Reported here is the first observation of an α-Muonium-substituted methyl radical. The key to the success of this experiment was the use of a more stable precursor, trimethylsilyldiazomethane, in lieu of the prototypical diazomethane. The radical, \( \cdot \text{CHMuSi(CH}_3\text{)}_3 \) was observed by TF-\( \mu \text{SR} \), with \( A_\alpha = 187.6(2) \text{ MHz} \). This result is compared to literature values for the proton analogue and the isotope effect is discussed.

1. Introduction

Muonium-substituted free radicals are typically formed by addition of muonium to one end of a carbon-carbon double bond such that the unpaired electron is left on the adjacent carbon. Since by convention the site of the unpaired electron is labelled "α", the point of muonium attachment is invariably the "β" carbon. Addition of muonium to a conjugated bond system still results in a β-radical, as the Mu ends up on a carbon adjacent to one of the "α" carbons of the delocalized spin system. Thus, all muonium-substituted radicals reported to date belong to the class of β-radicals. With this in mind, we sought a route to an α-substituted radical. Such a radical would increase the scope of studies of the isotope effect on both structure and hyperfine interactions. In particular, the archetypal α-radical, \( \cdot \text{CH}_2\text{Mu} \) (muonium-substituted methyl) would be invaluable in a study of out-of-plane bending at a radical centre, since substitution of Mu for H would have a large effect on the reduced mass of that motion.

Our previous attempts to detect \( \cdot \text{CH}_2\text{Mu} \) failed, almost certainly due to the extreme reactivity of the chosen precursor, \( \text{CH}_2\text{N}_2 \) (dia-
zomethane). However, we have recently synthesized the more stable derivative trimethylsilyldiazomethane and detected in transverse field the corresponding α-muonium-substituted radical ·CHMuSi(CH₃)₃. In contrast to diazomethane, which required specialized handling and the use of added safety measures due to its high reactivity and toxicity, the trimethylsilyl derivative proved to be stable under prolonged storage and easy to handle under operating conditions at TRIUMF. These properties make trimethylsilyldiazomethane the reagent of choice not only for μSR, but also for a wide variety of synthetic organic chemistry applications [1]. The μSR technique offers a unique method of furthering our understanding of the behaviour of this compound on a short timescale during initial radical formation. Information on the geometry and lifetime of the radical will be very useful in interpreting final product composition in those syntheses where an intermediate α-substituted radical is formed.

2. Synthesis

Since trimethylsilyldiazomethane has only recently become commercially available, it was necessary to synthesize the compound at the time of this study. The chosen method was by reaction of an organometallic derivative of chloromethyltrimethylsilane with a diazo transfer reagent [2], as shown below:

\[
\text{(CH₃)₃SiCH₂MgCl} \rightarrow \text{2H₂O} \rightarrow \text{(CH₃)₃SiCHN₂ + (PhO)₂P(O)NH₂} \quad (1)
\]

Specifically, a Grignard reagent and diphenylphosphoryl azide (both purchased from Aldrich) were reacted in diethyl ether at -10°C for 12 hours, after which water was added and the standard workup performed. The product (yellow liquid, bp 96°C) was further concentrated by distillation from hexane. Yield and purity were determined by ¹H NMR with dibenzyl added as an internal calibrant. This solution was stored under N₂ and away from light to avoid photoreaction. To increase the volume of sample to that required by the μSR apparatus a two-fold dilution was required, bringing the final sample concentration to 0.84 M.

3. μSR Experiment

The trimethylsilyldiazomethane solution was first freeze-pump-thawed to remove O₂, then transferred under N₂ to a glass sample cell with a thin