

## Reversible Reactions in Matrices of Silicon-centred Radicals with the C-H Bonds of Adamantane

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At room temperature, silacyclopentyl radicals exchange hydrogen or deuterium reversibly with the C-H or C-D bonds of adamantane in a matrix causing specific deuteration or de-deuteration at  $>\text{Si-H}$  or  $>\text{Si-D}$  bonds in the radical.

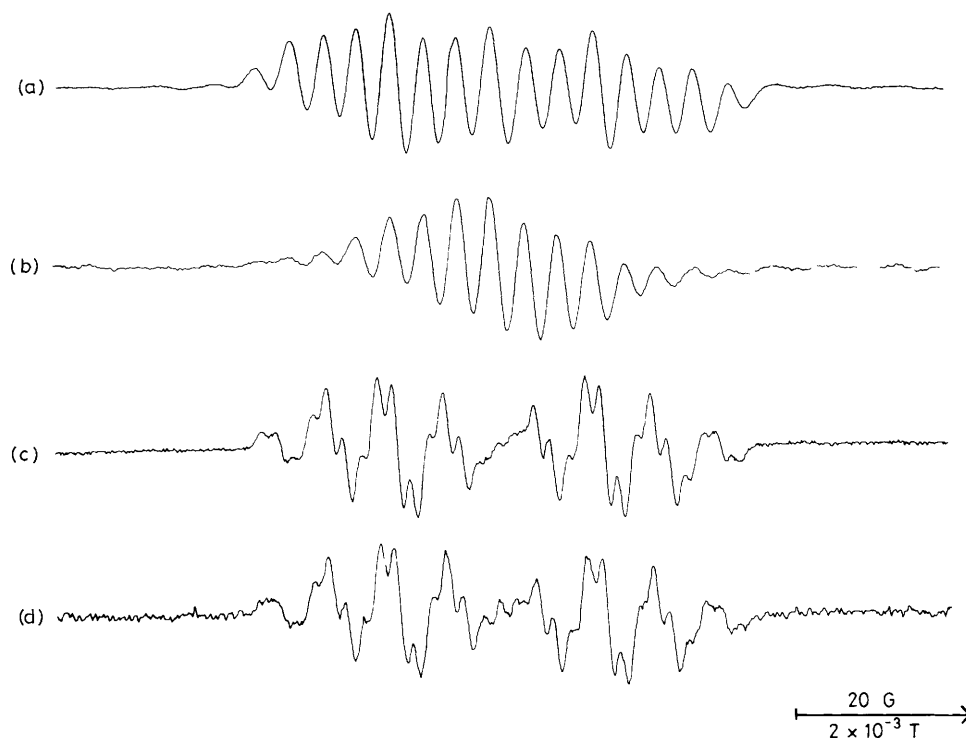
The main thrust of studies on free radicals in adamantane matrices has been on structural work, though some reactivity studies have been made.<sup>1,2</sup> Hydrogen abstraction reactions of the trapped radicals may be involved in the decay of radicals at high temperatures;<sup>2</sup> a minor amount of hydrogen exchange between cyclohexanonyl radicals with a perdeuterioadamantane matrix has been observed,<sup>2</sup> but equilibration of  $\alpha$ -protons in a radical with matrix protons has not hitherto been reported.

As part of a study of conformational effects on silicon-centred radicals, we  $\gamma$ -irradiated (4 h, 0.6 krad/min) silacyclopentane in an adamantane matrix at 77 K. After warming to 15 °C, e.s.r. spectra were obtained (c in Figure 1) which were analysed in terms of a doublet (23.4 G)<sup>†</sup> and three triplet splittings (7.4, 5.7, and 1.6 G) with a further possible triplet of ca. 0.3 G buried in the line width. The spectrum is very temperature dependent: at -135 °C, the doublet remains almost unchanged at 23.3 G, but the best analysis of the other couplings is in terms of doublets of 11.2, 7.3, 4.5, 3.7, and 3.6 G with further possible couplings of <1 G buried in the line shape (a in Figure 1). We interpret the spectrum as showing a twisted conformation of the radical, related to the  $C_2$  conformation shown for silacyclopentane by electron diffraction and microwave spectroscopy.<sup>3</sup> This leads to different environments for each of the nine protons in the radical, but at

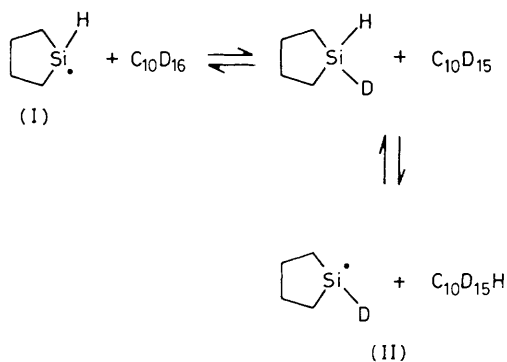
high temperatures the C-H protons become equivalent in pairs. The assignments of the couplings and their temperature dependence (fully reversible) will be discussed in more detail in the full paper. The large doublet is assigned as due to the Si-H proton; it appears probable on the basis of UMINDO<sup>4</sup> calculations and the conformational dependence of coupling constants shown by pyramidal carbon-centred radicals such as fluoroalkyl radicals,<sup>5</sup> that the largest of the high temperature triplet splittings (and hence the 11.2 and either the 3.7 or the 3.6 G coupling shown at low temperatures) is due to the  $\beta$ -protons having approximately 120° dihedral angles with respect to the singly occupied orbital. The doublet splitting from the Si-H proton is significantly greater than that for dimethylsilyl (17.0, 17.3 G)<sup>6</sup> but Si-H couplings are known to be very sensitive to minor structural changes.<sup>7</sup>

To confirm the doublet coupling as being due to Si-H, we prepared the deuteriated radical (II) from  $\text{CH}_2[\text{CH}_2]_3\text{SiD}_2$ . At -135 °C we obtained a spectrum (b in Figure 1) which analysed in terms of doublets of 11.5, 7.5, 4.7, 3.5, and 2.5 G and a 1 : 1 : 1 deuterium triplet of 3.8 G in good agreement with the constants expected from the protiated radical, and a direct comparison of the auto-correlograms<sup>8</sup> of the protiated and deuteriated radical confirmed the Si-H splitting as being ca. 23.3 G. Much to our surprise, as the sample of the deuteriated compound was warmed to room temperature, the spectrum changed to that of the protiated radical (I) (d in Figure 1). Re-cooling gave the low-temperature spectrum of the protiated radical. These observations were confirmed by prepar-

<sup>†</sup> 1 G = 10<sup>-4</sup> T.



**Figure 1.** E.s.r. spectra of silacyclopentane in adamantane,  $\gamma$ -irradiated at 77 K then recorded at the temperature indicated. (a)  $C_4H_{10}Si$  at  $-135^\circ C$ , (b)  $C_4H_8D_2Si$  at  $-135^\circ C$ , (c)  $C_4H_{10}Si$  at room temp., (d)  $C_4H_8D_2Si$  at room temp.



**Scheme 1**

ing the protiated radical from  $\overline{CH_2[CH_2]_3SiH_2}$  in perdeuterioadamantane: at  $-121^\circ C$ , the low temperature spectrum of the protiated radical was observed, but at  $25^\circ C$ , the spectrum changed to that of the deuteriated radical.

We interpret these changes as being due to reversible hydrogen or deuterium abstraction from the matrix. Silyl radical abstractions from alkanes are endothermic,<sup>9</sup> will have a significant activation energy, and should only take place at relatively high temperatures; the reverse reactions should always be faster, leading to deuterium incorporation from  $C_{10}D_{16}$  as in Scheme 1. Deuterium is incorporated or removed only at Si-H or Si-D bonds in the radical.

Reactions of this type appear to be localised at particular matrix positions and do not lead to extensive exchange of hydrogen and deuterium in molecules away from the original radical centres, since if a sample of  $\overline{CH_2[CH_2]_3SiD_2}$  in adamantane is irradiated, warmed to room temperature to convert the deuteriated into the protiated radical, further

heated to destroy the radicals, then cooled and re-irradiated, the deuteriated radical spectrum is seen once again.

In addition to the insight this system gives into hydrogen transfer reactions in adamantane matrices, the technique outlined here provides a method of preparing radicals deuteriated at a silicon centre without the need for preparing deuteriated precursors, and the method should be applicable to other systems, provided that the central atom forms bonds to hydrogen that are weaker than the C-H bonds in adamantane.

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