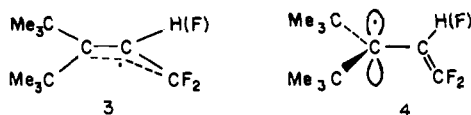


Persistent Cyclopropyl Radicals with Novel Configurations¹

Sir:

Geminal *tert*-butyl groups frequently have a profound effect on the lifetime and conformation of carbon-centered radicals.² New examples of these phenomena are provided by a family of persistent radicals which can be generated by UV photolysis directly in the cavity of an EPR spectrometer of a mixture of di-*tert*-butyldiazomethane, $(\text{Me}_3\text{C})_2\text{C}=\text{N}^+=\text{N}^-$, a fluorinated organic halide, R_fX , and a hexaalkylditin, in hydrocarbon solvents.³ All of these radicals have the structure $(\text{Me}_3\text{C})_2\dot{\text{C}}\text{R}_f$, with two exceptions. The exceptions are the persistent radicals, **1** and **2**, which are formed when R_fX is $\text{CF}_2=\text{CHBr}$ and $\text{CF}_2=\text{CFI}$, respectively. For the reasons outlined below, we assign a 2,2-di-*tert*-butyl-3,3-difluorocyclopropyl structure to **1** and **2**. These are the first persistent cyclopropyls to be reported. Of greater interest is their configuration which corresponds to a radical center that is planar for **1** and only slightly pyramidal for **2**. These configurations are unique for cyclopropyls which have an α -H or α -F. Previous studies by EPR spectroscopy^{4,5} and by chemical trapping⁶ on cyclopropyls with an α -H have indicated that such radicals are distinctly nonplanar, though there is rapid inversion on the EPR time scale^{4,5} and trapping generally indicates complete configurational equilibration.⁶ However, with an α -F the pyramidal geometry is static on the EPR time scale⁵ and trapping generally gives products with partial or complete retention of configuration.⁶

The EPR parameters for **1** and **2** (see Figure 1) are not consistent with the anticipated allylic structure whether it be a planar, delocalized allyl, **3**, or a perpendicular,⁷ localized allyl, **4**. The equivalence of the two fluorines in the CF_2 groups



of **1** and **2** can only be achieved in an allylic structure if there is rapid rotation about the C-CF₂ bond. This might be able to occur in the delocalized, planar allyl⁸ but would be extremely unlikely in the perpendicular allyl because the bond in question is, formally, a double bond. On the other hand, the planar allyl structure is not consistent with the 22.3-G hydrogen hyperfine splitting (hfs) in **1**. A radical with structure **3** has the hydrogen in the nodal plane and a^{H} would be ≤ 5 G.⁸ Finally, the large difference in the g values for **1** and **2** implies that their radical centers must reside at the unique CH and CF positions, respectively, rather than at the common $(\text{Me}_3\text{C})_2\text{C}$ or CF_2 positions.

Comparison of the EPR parameters (at -75 °C) for **1** and **2** in isopentane with those reported by Kawamura et al.⁵ (at -108 °C) for the structurally related 2,2-dimethylcyclopropyls **5** and **6** (see Figure 1), and with related radicals,⁵ serves to confirm the structures that we have assigned. However, there are also important differences. Thus, the equivalence of the fluorines of the CF_2 group in **2** indicates that this radical inverts much more rapidly than **6**; i.e., the barrier to inversion for **2** is much smaller than the barrier for **6**. That **2** is *not* completely planar is indicated by the fact that the $M_I = 0$ lines (the central line of each triplet) due to the β -fluorines are somewhat broadened at -75 °C. Lowering the temperature to slow the dynamic process which produces this broadening caused these lines to broaden beyond detection at -140 °C. At this temperature there is also a very severe broadening of the other lines in the spectrum, probably because of the reduced rate of radical tumbling. The fluorine hfs for **2** did not change significantly from 0 to -100 °C. The reduced magnitude of the α -F hfs for

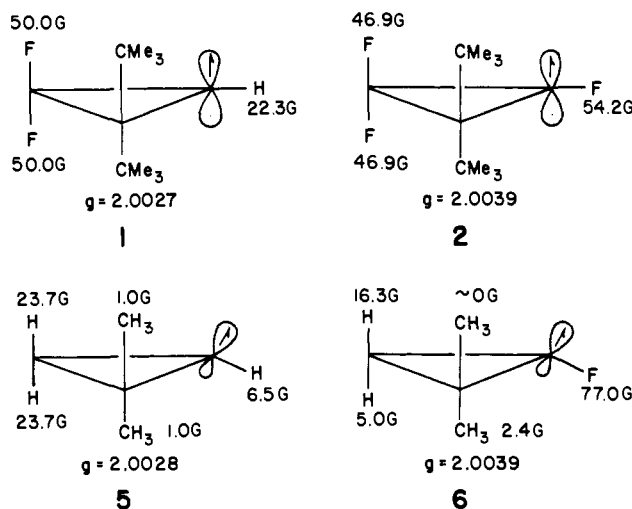


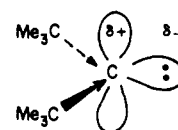
Figure 1. EPR parameters for cyclopropyls.

2 also indicates that this radical is less pyramidal than **6** and that it may well be less pyramidal than the "slightly bent" radicals $\text{CH}_2\text{F}\cdot$ ($a^{\text{F}} = 64.3$ G),⁹ $\text{CH}_3\text{CHF}\cdot$ (59.2 G),¹⁰ and $(\text{CH}_3)_2\text{CF}\cdot$ (60.9 G).¹⁰ The near planarity of **2** is also indicated by a ^{13}C hfs of 51.5 G which can be observed at high gain and is presumably due to the α -carbon (cf, $a^{13\text{C}} = 54.8$ G for $\text{CH}_2\text{F}\cdot$).⁹

Although the α - ^{13}C hfs for **1** could not be determined, its α -H hfs, which is constant in the temperature range -20 to -140 °C, is closely comparable with the values found for such planar (or nearly planar) radicals as $\text{CH}_3\cdot$ ($a^{\text{H}} = 23.0$ G),⁴ $\text{CH}_3\text{CH}_2\cdot$ (22.4 G),⁴ and $(\text{CH}_3)_2\text{CH}\cdot$ (22.1 G).⁴ In addition, the β -fluorines show no sign of magnetic inequivalence even at -140 °C (though $a^{\text{F}\beta}$ shows a small negative temperature coefficient).¹¹ For these reasons, we believe that **1** must be a planar cyclopropyl radical.

We attribute the unusual configuration of **1** and **2** to steric repulsion between the *tert*-butyl groups and the α -hydrogen or α -fluorine. The electronic effect of the two β -fluorines may also promote planarity.¹²

Radicals **1** and **2** are not formed unless ditin is present. Photolysis of hydrocarbon solutions of di-*tert*-butyldiazomethane and $\text{CH}_2=\text{CHBr}$ with or without the ditin does not give any persistent radical. We suggest that **1** and **2** are produced by an initial addition of di-*tert*-butylcarbene to the fluoro olefin and a subsequent abstraction of the Br or I from the cyclopropane by the trialkyltin radical. A possible reason why di-*tert*-butylcarbene adds only to the two electron-poor olefins is that it is a nucleophilic rather than an electrophilic species, reacting via its σ orbital rather than via its p orbital.¹³ Its nucleophilic reactivity may arise from steric hindrance of the p orbital combined with the electronic (+I) effect of the *tert*-butyl groups.



In conclusion, we note that **1** and **2** are not only the first persistent cyclopropyl radicals, they are also the first alkyl radicals to be made persistent by *tert*-butyl groups that are not attached directly to the radical center.² They decay with first order kinetics ($\tau_{1/2} = \sim 50$ s for **1** and ~ 25 min for **2** in cyclopentane at 25 °C).¹⁴ Possible decay mechanisms which are currently under investigation include reaction with the solvent, β scission, and intramolecular H-atom transfer.

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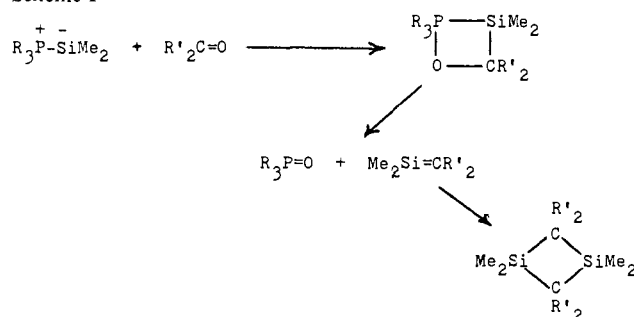
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Reactions of Hexamethylsilacyclopropane with Carbonyl Compounds in the Presence of Tertiary Phosphines. The Possible Intermediacy of a Dimethylsilylenephosphorane

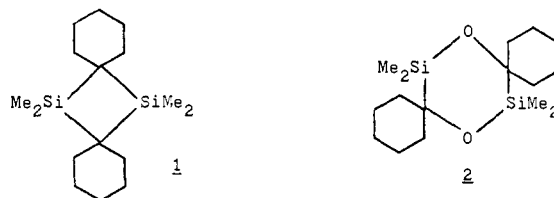
Sir:

The SiC₂ ring of hexamethylsilacyclopropane (hexamethylsilirane) is highly reactive as a result of its high ring strain.^{1,2} At 70-80 °C hexamethylsilirane undergoes dimethylsilylene transfer reactions to suitable substrates such as organosilicon hydrides,^{1b} dimethyldimethoxysilane,^{1b} internal olefins,^{1c} and internal acetylenes.^{1e,3} We became interested in the possible preparation and synthetic utilization of a silylenephosphorane, R₃P⁺-Si⁻Me₂, an interesting and potentially reactive organosilicon/phosphorus intermediate which had not been reported previously. In particular, we were interested in the reactions of such an intermediate with aldehydes and ketones. A possible reaction course which is a simple analog of the well-known Wittig reaction of alkylidenephosphoranes is shown in Scheme I.

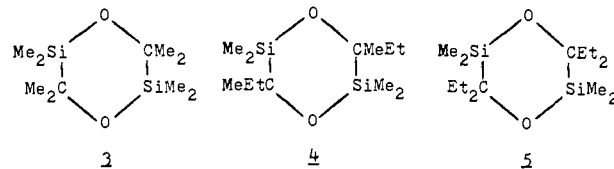
Scheme I



To examine this possibility, a solution containing 3.60 mmol of triphenylphosphine, 3.99 mmol of cyclohexanone, and 3.64 mmol of hexamethylsilirane^{1a} in 1 mL of benzene was stirred and heated at 75 °C under argon for 14 h. Removal of benzene at reduced pressure, followed by addition of hexane and cooling to -60°C gave white crystals of triphenylphosphine (87% recovery). GLC examination of the filtrate showed the presence of a single product, mp 100-102 °C, 26% yield, which was identified not as **1**, but rather as the 1,4-dioxo-2,5-disilacy-



clohexane derivative **2**. Its C, H analysis was in agreement with this formulation; its mass spectrum showed the expected molecular ion at m/e 312; its ¹H NMR spectrum showed signals due to methyl substituents on silicon and to cyclohexylidene groups in the correct integrated ratio. Similar reactions using acetone, methyl ethyl ketone, and diethyl ketone were carried out and gave **3** (53%), **4** (13%, mixture of isomers) and **5** (3%), respectively. The product yield of the hexamethylsilirane-



triphenylphosphine-cyclohexanone reaction could be improved by using an excess of the phosphine and of the ketone. A still better yield of **2** was obtained (48%) in a reaction carried out at 110 °C in which the silirane was added slowly to the phosphine-ketone mixture during the course of 2 h. Even more substantial yield improvement was achieved when the latter procedure was used in a reaction in which triphenylphosphine was replaced by dimethylphenylphosphine. Thus a reaction of 5.26 mmol of Me₂PhP, 1.5 mmol of cyclohexanone, and 0.83 mmol of hexamethylsilirane was carried out by adding the silirane to the hot (120 °C) phosphine-ketone solution (under argon) over a 2-h period and heating the resulting mixture for another 2 h at 120 °C. Product **2** was obtained in 92% yield (GLC). A similar reaction carried out at 98 °C with diethyl ketone gave **5** in 72% yield. Pivaldehyde also was found to react with the hexamethylsilirane-dimethylphenylphosphine system at 75 °C (18.5 h) to give **6** in 97% yield.

