Perfluoro-1,2-di-*tert*-butylvinyl radical stable in an inert medium

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The high strength of the C—F bond in organofluorine compounds and in their free radicals excludes disproportionation of the latter.[1] Dimerization of these radicals is also suppressed when the radical center is hindered by bulky groups, and as a result such radicals are stable in an inert medium (for instance, perfluorocumyl[2] or perfluorodiisopropylmethyl radicals[3]).

As the volume of the hindering substituents increases the organofluorine radicals become more stable and do not react even with oxygen (perfluorodiisopropylethylmethyl radical).[4] Some of them can be isolated in preparative quantities.[5,6]

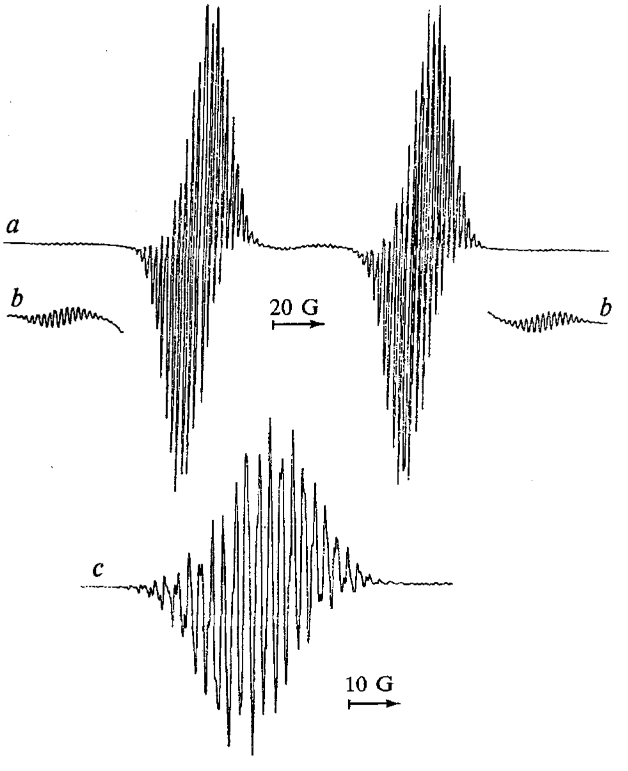
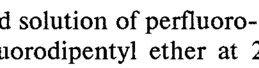
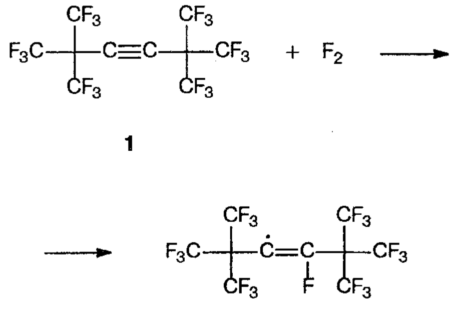


Fig. 1. *a.* ESR spectrum of the perfluoro-1,2-di-*tert*-butylvinyl radical at 20 °C. *b.* ESR spectra of satellites from interaction of an unpaired electron with ^{13}C carbon nuclei at a tenfold increase in gain. *c.* Low-field component of the ESR spectrum of the dilute solution of 1,2-di-*tert*-butylvinyl radical.

The purpose of this study is to elucidate the effect of bulky substituents on the stability of perfluorinated vinyl radicals.

Branched vinyl radicals have been generated previously[7] by the addition of radicals to acetylene derivatives R—C≡C—R, where R = CMe_3, $SiMe_3$, *etc.* The half-life time, $\tau_{1/2}$, for the most stable of the generated radicals  $Me_3Si{-}\dot{C}{=}\underset{OCF_3}{C}{-}SiMe_3$ is 530 s at −60 °C. The major routes for the decay of the vinyl radicals studied are likely to be disproportionation or decomposition.

In order to obtain perfluorinated vinyl radicals in an inert medium we conducted the direct fluorination of a saturated solution of perfluoro-di-*tert*-butylacetylene (**1**) in perfluorodipentyl ether at 25 °C. After 30—40 s of bubbling with F_2, the solution became rose colored. The intense ESR spectrum of radical **1a** (Fig. 1) is characterized by hyperfine interaction (HFI) of an unpaired electron with the fluorine nuclei ($a_{F(\beta)}$ = 89 G, $a_{F(\gamma)}$ (9 F) = 2.0 G, $a_{F(\delta)}$ = 4.75 G) and with ^{13}C nuclei: a_C = 116.0 G, g = 2.0026. The high value of the HFI constant with ^{13}C nuclei, which is typical of vinyl radicals,[8] and the unusually high HFI constant with the β-fluorine atom point to the formation of the perfluoro-1,2-di-*tert*-butylvinyl radical (**1a**).



1

1a

Radical **1a** is stable in the absence of oxygen. When the tube (with **1a**) is opened in air the radical decays, and the rose color of the solution disappears.

[†] Deceased in 1994.

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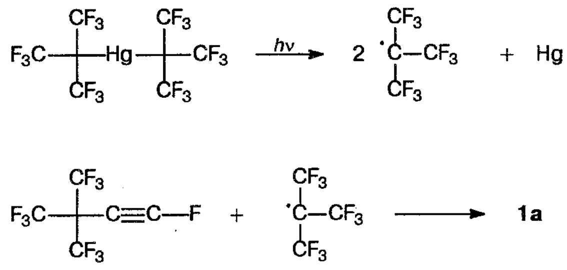
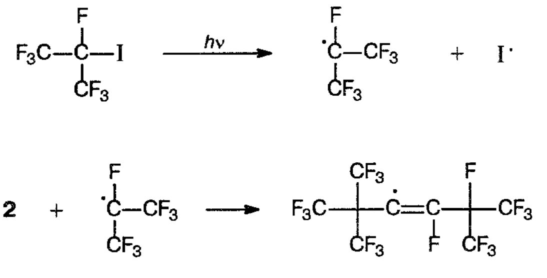
An ESR spectrum identical to the spectrum of **1a** is recorded in the counter synthesis of this radical by the addition of perfluoro-*tert*-butyl radical to perfluoro-*tert*-butylacetylene (**2**).



2

The addition of the perfluoroisopropyl radical to acetylene **2** results in the formation of the vinyl radical (**2a**).



2a

The ESR spectrum of radical **2a** is characterized by interaction of an unpaired electron with fluorine nuclei: $a_{F(\beta)}(1\ F) = 86.0$ G, $a_{F(\gamma)}(1\ F) = 15.25$ G, $a_{F(\gamma)}(9\ F) = a_{F(\delta)}(6\ F) = 2.5$ G. Radical **2a** decays within 10 s after the UV light is switched off. One can assume that radical **2a** reacts with I_2, which is accumulated quickly in the solution as a result of photolysis of perfluoroisopropyl iodide.

Thus, we have obtained for the first time a stable perfluorinated vinyl radical **1a** whose concentration in perfluorodipentyl ether remained unchanged at 20 °C during one month of observation.

ESR spectra were recorded on a Varian E-12 radiospectrometer. The tubes were thoroughly vented with argon before fluorination. A DRSh-1000 lamp was used for UV-irradiation. Acetylenes **1** and **2** were synthesized using the procedure reported previously.[9]

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