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Perfluoro-1,2-di-t-butylvinyl radical stable in an inert medium [1]

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Abstract

The perfluoro-1,2-di-t-butylvinyl radical has been generated by direct fluorination of perfluorodi-t-butylacetylene or by the addition of the perfluorodi-t-butyl radical to perfluoro-t-butylacetylene in perfluorodiamyl ether. The radical was identified by its ESR spectrum, and appeared to be quite stable in an inert medium.

Keywords: Perfluoro-di-t-butylvinyl radicals; Stability; ESR spectroscopy; Synthesis; Mass spectrometry

1. Introduction

The high strength of C–F bonds in perfluorinated free radicals excludes their decay due to disproportionation reactions. Dimerization of these radicals is also suppressed in the case of the radical centre hindered by bulky groups and, as a result, such radicals (for example, perfluorocumyl [1], perfluorodiisopropylmethyl [2]) are stable in an inert medium.

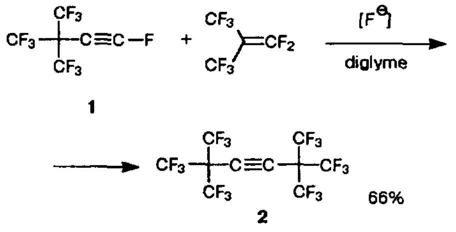
As the bulk of the hindering substituents increases, the organofluorine radicals become more stable and do not react even with oxygen (the perfluorodiisopropylethylmethyl radical) [3]. Some can be isolated in preparative quantities [4–6].

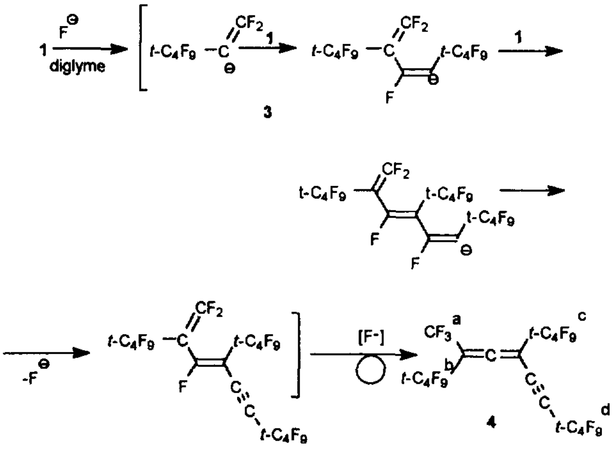
The purpose of the present study was to elucidate the effect of the bulk of the substituents on the stabilities of perfluorinated vinyl radicals.

2. Results and discussion

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 most stable of the radicals prepared. $(Me_3Si\text{–}\dot{C}{=}C(OCF_3)\text{–}SiMe_3)$ has a half-life ($t_{1/2}$) of 530 s (at −60 °C). The major routes for the decay of the vinyl radicals studied were most likely their disproportionation and decomposition.

The addition of radical particles to acetylenes containing bulky fluoroalkyl substituents may be a promising route for obtaining stable fluorinated vinyl radicals. In order to synthesize acetylenes of such structure, we studied the interaction of perfluoro-t-butylacetylene (**1**) [8] with the perfluoro-t-butyl anion generated from perfluoroisobutene and CsF in a polar aprotic solvent. It turned out that this reaction gave perfluoro-1,2-di-t-butylacetylene (**2**) in a satisfactory yield:





The reaction mixture was also shown to contain compound **4**, the trimerization product of the starting acetylene **1**, along with acetylene **2**. The formation of product **4** is likely to be

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[1] In memory of the late Lev Solomonovich German.

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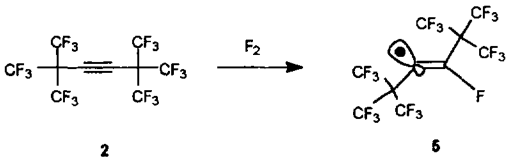
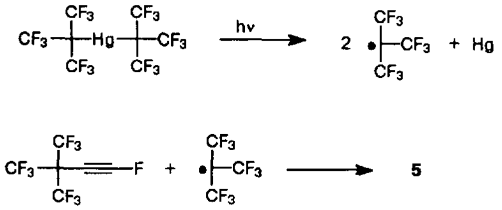
associated with the ease of competitive generation of the vinyl anion **3** and may be presented by the scheme shown above. In fact, acetylene **1** can be easily converted to trimer **4** in the presence of catalytic amounts of CsF in diglyme.

In order to obtain perfluorinated vinyl radicals in an inert medium, we have conducted the direct fluorination of a saturated solution of perfluoro-di-t-butylacetylene (**2**) in perfluorodiamyl ether at 25 °C. After bubbling F_2 for 30–40 s the solution became rose-coloured. The intensive ESR spectrum of radical **5** was recorded in this case (Fig. 1), characterized by hyperfine interaction (HFI) of the unpaired electron with fluorine nuclei–aF(β) = 89 G; aF(γ) (9F) = 2.0 G; aF(δ) = 4.75 G– and with ^{13}C nuclei–a_C = 116.0 G; g = 2.0026. The high value of the HFI constant with a ^{13}C nucleus, typical of vinyl radicals [9], and the unusually high HFI constant with the β-fluorine atom point to the formation of the perfluoro-1,2-di-t-butylvinyl radical **5**:

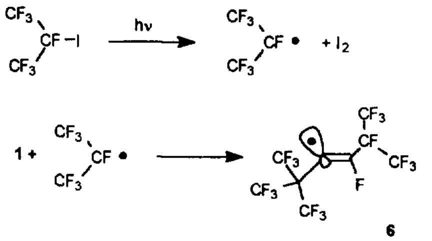


Radical **5** is stable in the absence of oxygen. If a tube (with **5**) is opened in air, the radical decays and the rose colour of the solution disappears.

An ESR spectrum identical to the spectrum of **5** is recorded in an alternative synthesis of this radical by the addition of the perfluoro-t-butyl radical to perfluoro-t-butylacetylene (**1**):



The addition of the perfluoroisopropyl radical to acetylene **1** results in formation of the vinyl radical **6**:



The ESR spectrum of radical **6** (Fig. 2) is characterized by the interaction of the unpaired electron with fluorine nuclei: aF(β) (1F) = 86.0 G; aF(γ) (1F) = 15.25 G; aF(γ) (9F) = aF(δ) (6F) = 2.5 G. Radical **6** decays within 10 s after switching the UV light off. It maybe assumed that radical **6** reacts with I_2 which accumulates quickly in the solution as a result of the photolysis of perfluoropropyl iodide.

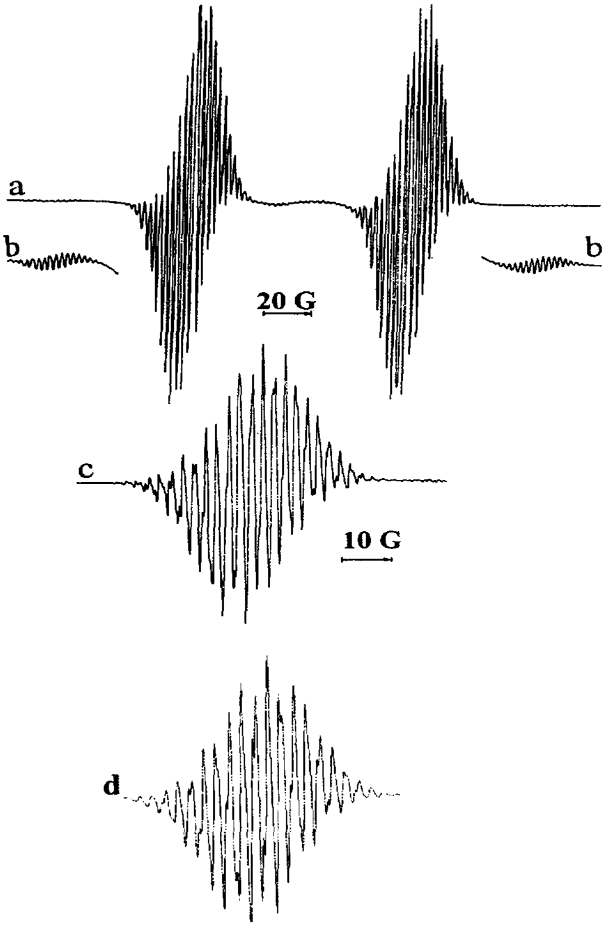


Fig. 1. (a) ESR spectrum of the perfluoro-1,2-di-t-butylvinyl radical **5** at 20 °C. (b) ESR spectra of satellites from the interaction of an unpaired electron with ^{13}C carbon nuclei at a 10-fold increase in gain. (c) Low-field component of ESR spectrum of a dilute solution of the 1,2-di-t-butylvinyl radical. (d) Computer simulation of the low-field component of the ESR spectrum of **5**.

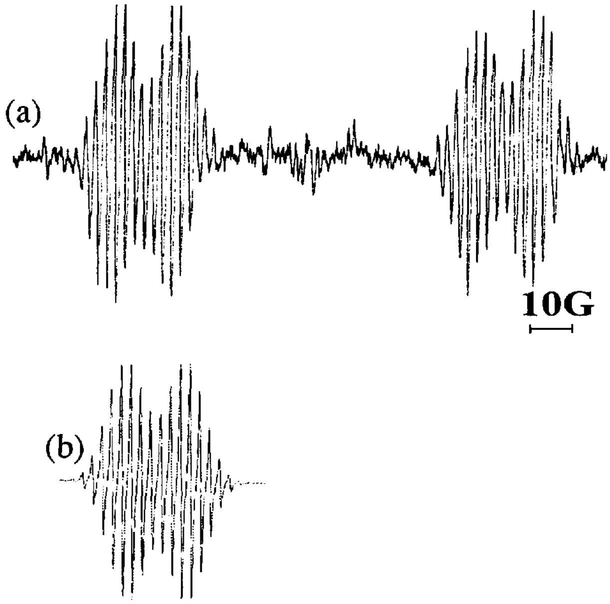


Fig. 2. (a) ESR spectrum of the perfluoro-1-t-butyl-2-isopropylvinyl radical **6** at 20 °C. (b) Computer simulation of the low-field component of the ESR spectrum of **6**.

Thus, we have obtained a stable perfluorinated vinyl radical **5** for the first time whose concentration in perfluorodiamyl ether remains unchanged at 20 °C for several months.

3. Experimental details

3.1. General

ESR spectra were recorded on a Varian E-12 radiospectrometer. Before fluorination the tubes were vented thoroughly with argon. ^{19}F NMR spectra were recorded on a Brucker WP200 SY spectrometer at 188.3 MHz (CF_3COOH as internal reference).

*3.2. Preparation of perfluoro-1,2-di-t-butylacetylene (**2**)*

Perfluoroisobutene (6 g, 0.03 mol) was introduced gradually into a mixture of dry CsF (0.5 g, 0.0033 mol) and 10 ml of anhydrous diglyme at 20 °C and stirred for 10 min; then acetylene **1** (6 g, 0.223 mol) in diglyme (5 ml) was added gradually. The reaction mixture was stirred for 1 h at 20 °C (5% trimer **4** and 95% compound **2**, GLC) and poured into ice; the organic layer was distilled over conc. H_2SO_4 to give **2** (7 g, 66%), b.p. 95–98 °C, m.p. 27 °C. Analysis: Calc. for $C_{10}F_{18}$: C, 25.97; F, 74.02%. Found: C, 25.77; F, 74.58. ^{19}F NMR δ: -9.2 (s, CF_3) ppm. MS (m/z, relative intensity, %): 462 $[M]^+$ (0.5); 443 $[M-F]^+$ (3); 374 $[M-CF_4]^+$ (9); 355 $[M-CF_4-F]^+$ (12); 305 $[M-F-2CF_3]^+$ (8); 286 $[M-2CF_4]^+$ (4); 255 $[C_7F_9]^+$ (3); 205 $[C_6F_7]^+$ (3); 167 $[C_6F_5]^+$ (3); 117 $[C_5F_3]^+$ (3); 93 $[C_3F_3]^+$ (1); 69 $[CF_3]^+$ (100).

*3.3. Preparation of compound **4***

A mixture of dry CsF (0.02 g), anhydrous diglyme (5 ml) and compound **1** (2 g) was stirred at 20 °C for 20 min. The lower layer was then separated and distilled to afford product **4** (1.5 g, 75%), b.p. 77 °C/10 Torr. Analysis: Calc. for $C_{18}F_{30}$: C, 27.48; F, 72.52%. Found: C, 27.57; F, 72.25. ^{19}F NMR δ: -19.3 (d, $3F^a$); -12.7 (q, $9F^b$); -11.7 (s, $9F^c$); -9.3 (s, $9F^d$) ppm; $J(a\text{–}b) = 7$ Hz. MS (m/z, relative intensity, %): 786 $[I]^+$ (10); 767 $[I-F]^+$ (15); 717 $[I-NF_3]^+$ (2); 672 $[C_{17}F_{25}]^+$ (5); 629 $[C_{16}F_{23}]^+$ (15); 567 $[C_{14}F_{21}]^+$ (4); 541 $[C_{15}F_{19}]^+$ (3); 479 $[C_{13}F_{17}]^+$ (3); 429 $[C_{12}F_{15}]^+$ (2); 341 $[C_{11}F_{11}]^+$ (2); 181 $[C_4F_7]^+$ (2); 69 $[CF_3]^+$ (100).

*3.4. Preparation of radical **5***

Method a

A 10% solution of perfluoro-di-t-butylacetylene in perfluorodiamyl ether (0.4 ml) was placed in a tube of 4 mm diameter and vented by dry argon; then F_2 (20% in N_2) was bubbled into the tube through a Teflon capillary tube of internal diameter 0.5 mm for 4 min at 25 °C. The solution became rose-coloured. Its ESR spectrum is given in Fig. 1.

Method b

A 10% solution of perfluoro-t-butylacetylene and perfluorodi-t-butylmercury in perfluorodiamyl ether placed in a quartz tube was thoroughly degassed by venting of argon. The photolysis was carried out by the focused light of a DPSh-1000 mercury lamp directly in the resonator of the Varian-E12A ESR spectrometer at 20 °C.

*3.5. Preparation of radical **6***

To a 10% solution of perfluoro-*t*-butylacetylene in perfluorodiamyl ether, $ICF(CF_3)_2$ (5% by volume) was added. A quartz tube containing the solution obtained was irradiated directly in the resonator of the ESR spectrometer at 20 °C. The ESR spectrum of radical **6** is given in Fig. 2.

Acknowledgements

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