

small hfc's and weak CIDNP effects can be expected. During the CIDNP experiment part of the  $H_1$  spectrum clearly shows emission whereas  $H_1$  is obscured by the strong enhanced absorption of  $H_4$ . We note further that a localized radical cation, **5a,b**, although incompatible with the observed polarization, cannot be ruled out as a primary oxidation product, which rearranges rapidly ( $\tau \leq 10^{-9}$  s) to the doubly allylic, resonance stabilized **3**.

The formation of **3** requires a rehybridization of  $C_4$  and  $C_2$ . This structure may permit some overlap between the  $\pi$  orbitals of the two allylic systems at  $C_4$  and  $C_2$  or at  $C_2$  and  $C_4$ . However, significant overlap can be achieved only at the expense of severe distortion.

The radical cation **3** is an interesting example of an emerging family of radical cations, which have structures quite unlike their parent molecules. In fact, the radical cations resemble the geometries of transition states of the corresponding thermal isomerizations. A detailed discussion of these radical cations is in preparation.

**F-2,4-Dimethyl-3-ethyl-3-pentyl and F-2,4-Dimethyl-3-isopropyl-3-pentyl: Stable tert-Perfluoroalkyl Radicals Prepared by Addition of Fluorine or Trifluoromethyl to a Perfluoroalkene**

Kirby V. Scherer, Jr.,\* Taizo Ono, Kouichi Yamanouchi, Richard Fernandez, and Philip Henderson

Department of Chemistry  
University of Southern California  
Los Angeles, California 90089-1062

Harold Goldwhite

Department of Chemistry, California State University  
Los Angeles, California 90032

Received June 7, 1984

Revised Manuscript Received October 31, 1984

Addition of  $F_2$ , at ambient temperature and pressure, to *F*-3-isopropyl-4-methyl-2-pentene (**1**) or *F*-2,4-dimethyl-3-ethyl-2-pentene (**2**)<sup>1-3</sup> gives the hindered free radical *F*-2,4-dimethyl-3-ethyl-3-pentyl (**3**) in concentrations as high as 3 M! Radical **3** is stable at room temperature to dimerization, disproportionation,  $O_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ , or aqueous acid or base, and, at 70 °C, GC and decomposes by  $\beta$ -scission with a half-life of 1 h at 100 °C. This easy synthesis of **3**, the first air-stable alkyl radical,<sup>4</sup> and its clean thermolysis at 80–120 °C make it an attractive new source of  $CF_3$ .<sup>6</sup> While evidence for radical intermediates in the fluorination of alkenes is not new,<sup>7,8</sup> such radicals have not previously been observed directly.

We discovered **3** while repeating the fluorination of **1** and **2** at 30 and 100 °C as described by von Halasz, Kluge, and Martini<sup>3</sup>

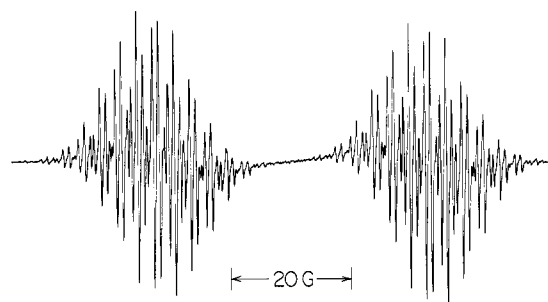


Figure 1. ESR spectrum of radical **3**.

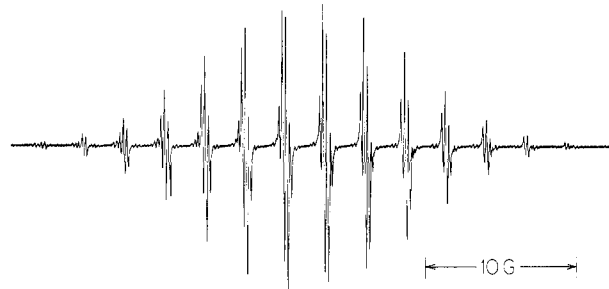
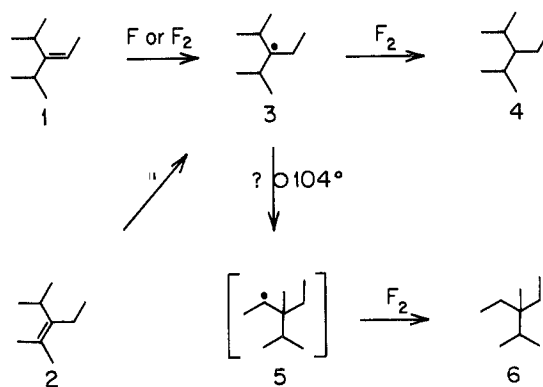


Figure 2. ESR spectrum of radical **7**.

Scheme I



(Scheme I). We wanted samples of **4** and **6** for another study, but doubted structure **6** because of the novel 1,2- $CF_3$  shift proposed by the authors to explain its formation. We did, however, obtain **6** as described by von Halasz et al. and concluded, based on F NMR and negative ion MS,<sup>9</sup> that the structure was correct. In following the fluorination at room temperature by F NMR, we noted line broadening suggesting the presence of a paramagnetic species. ESR examination revealed a strong signal,  $G = 2.00286$ , and upon diluting and degassing we obtained the spectrum shown in Figure 1 and assigned to **3**. This spectrum shows >90 lines and is not yet completely analyzed, but its main feature is a 45.0-G doublet, consistent with a conformationally locked structure in which one  $\beta$ -fluorine of the  $C_2F_5$  group is nearly eclipsed with the half-filled p orbital, while the other lies near its nodal plane.<sup>10</sup> A space-filling (CPK) model of **3** cannot be assembled unless the in-plane  $\beta$ -F's are replaced by H's, and "decomposes" if rotation of the  $C_2F_5$  is attempted. The 45-G coupling is too low for an  $\alpha$ -F in a 2° radical but is within the range reported for  $\beta$ -couplings.<sup>11,12</sup> Radical **3** gives an intense  $M^-$  in its negative ion MS<sup>9</sup> and reacts slowly with  $F_2$  at room temperature to give **4**. These data, plus the fact that **3** is the only radical detected by ESR during fluorination of either **1** or **2** at room temperature, conclusively establish its structure.

(1) Burnskill, W.; Flowers, W. T.; Gregory, R.; Haszeldine, R. N. *J. Chem. Soc. D* 1970, 1444-1446. Dmowski, W.; Flowers, W. T.; Haszeldine, R. N. *J. Fluorine Chem.* 1977, 9, 94-96.

(2) Ishikawa, N.; Sekiya, A. *Nippon Kagaku Kaishi* 1972, 2214-2215. Ishikawa, N.; Maruta, M. *Nippon Kagaku Kaishi* 1977, 1411-1415.

(3) von Halasz, S. P.; Kluge, F.; Martini, T. *Chem. Ber.* 1973, 106, 2950-2959.

(4) Russian workers<sup>5</sup> report that low concentrations of air-stable radicals of unassigned structure form upon radiolysis of some fluorocarbons; we believe that their spectrum "d" is due to **3**.

(5) Allayarov, S. R.; Barkalov, I. M.; Gol'danskii, V. I.; Kiryukhin, D. P. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* 1983, 32, 1105-1107.

(6) U.S. and foreign patents applied for.

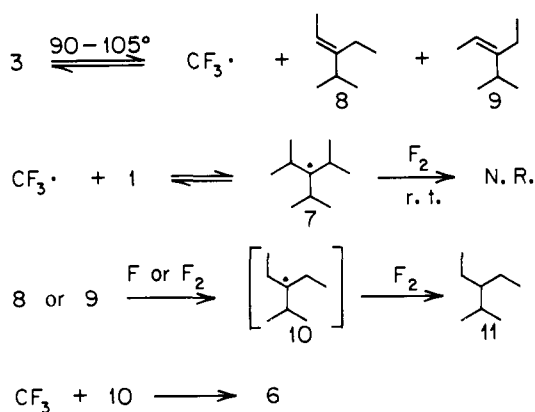
(7) Miller, W. T., Jr.; Stoffer, J. O.; Fuller, G.; Currie, A. C. *J. Am. Chem. Soc.* 1964, 86, 51-56.

(8) Rogers, A. S. *J. Phys. Chem.* 1965, 69, 254-257.

(9) Scherer, K. V., Jr.; Yamanouchi, K.; Ono, T. *J. Fluorine Chem.* 1982, 21, 48. With NCl, **4** shows no  $M^-$  but gives fragments of  $m/e$  419 ( $M - CF_3$ , 0.5%), 369 ( $M - C_2F_5$ , 100%), and 319 ( $M - C_3F_7$ , 53.2%), consistent with the assigned structure and the behavior of model compounds.

(10) Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* 1972, 94, 6485-6495.

Scheme II



Radical **3** is prepared by bubbling undiluted  $F_2$  into the neat mixture of **1** + **2** in a narrow-mouth Teflon-FEP<sup>13</sup> bottle, at a rate such that most of the  $F_2$  reacts (**HOOD!**); we have had no fires or explosions. Reaction of **1** and **2** and formation of **3** and **4** can be followed by GC;<sup>14</sup> **3** reaches a maximum in 15–20 h and then declines by about 3% per h. alkene **1** reacts faster than **2** and gives a higher yield of **3**.

When dilute (ca.  $10^{-3}$  M) **3** in excess **1** (or **1** + **2**) is heated to 90–100 °C, its spectrum disappears over several hours and is replaced by that of tris-(*F*-isopropyl)methyl (*F*-2,4-dimethyl-3-isopropyl-3-pentyl) (**7**),  $G = 2.00302$ , shown (recorded at room temperature) in Figure 2. The ESR spectrum of **7** shows splitting by three equivalent  $\beta$ -F's,  $a = 2.38$  G, and 18 equivalent  $\gamma$ -F's,  $a = 2.65$  G; these small couplings fit a structure in which the  $\beta$ -F's are locked in the nodal plane of the  $sp^2$  carbon but are not consistent with radical **5**, proposed by von Halasz et al.<sup>3</sup> to explain the formation of **6**, since **5** has an  $\alpha$ -F that should cause a splitting of about 65 G.<sup>11</sup> Radical **7** fails to react even with 1.3 atm of  $F_2$  over 300 h at room temperature.<sup>15</sup> Inspection of a model shows that both faces of its trivalent central carbon are completely shielded by the close-packed  $CF_3$ 's. The rate of conversion of **3** into **7** (in excess **1**) is indistinguishable from the rate of unimolecular decomposition of **3**. The disappearance of **3** and **7** was followed by ESR in *F*-2-methylpentane solution, using excess  $I_2$  to trap the  $CF_3$ 's, and showed first-order kinetics, with half-lives of 60 and 110 min, respectively, at 100 °C. The formation of **7** from **3** is necessarily an intermolecular process. While our results do not exclude the intramolecular 1,2- $CF_3$  shift proposed by von Halasz et al.,<sup>3</sup> we prefer to accept the rule that 1,2-alkyl shifts occur in free radicals only by elimination and readdition<sup>16</sup> and propose that perfluoroalkane **6** arises from **1** or **2** as shown in Scheme II.  $CF_3$  radicals from  $\beta$ -scission of **3** may "park" on **1** while *F*-alkenes **8** and **9** react with  $F_2$  to form the intermediate *F*-3-isopropyl-3-pentyl (**10**). Radical **10** may then react with  $F_2$  to give **11** or with a  $CF_3$ · to give **6**. Alkenes **8** and **9** are formed in an 8:3 ratio when **3** is heated in air, and **11** is a product of the 104 °C fluorination of **1** + **2**.<sup>17</sup> Elimination–readdition of  $CF_3$ ·'s during the fluorination, without excessive loss by reaction with  $F_2$ , is surprising but possible if dissolved  $[F_2]$  at 104 °C is low enough and the rates of reaction of  $F_2$  with **10** and  $CF_3$ · are comparable to the rates of reaction of  $CF_3$ · with **1** and **10**.

(11) Lloyd, R. V.; Rogers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 1512–1515.

(12) Maletesta, V.; Forrest, D.; Ingold, K. U. *J. Phys. Chem.* **1978**, *82*, 2370–2373.

(13) "Teflon-FEP" is a trademark of E. I. du Pont de Nemours and Co.

(14) Fomblim N-VAC 40/11 (we thank Montedison USA for a sample) or SE-30 stationary phase; for analysis of **3**, use injector and detector temperatures  $\geq 100$  °C.

(15) Analysis by ESR; a 10% change might not have been detected.

(16) Beckwith, A. L. J.; Ingold, K. U. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Chapter 4.

(17) New compounds, except radicals, have been fully characterized by  $F$  NMR and low-resolution NCI-GC/MS; for  $C_xF_y$  compounds with  $x > 19$ , unit resolution is sufficient to assign a unique composition to any ion. Radical **10** has been identified by ESR.

**Acknowledgment.** We thank the Green Cross Corporation for financial support and G. Millhauser, G. King, Dr. P. Fajer, Dr. E. Fajer, Dr. P. Krusic, and Prof. L. Dalton for some of the ESR measurements.

**Registry No.** **1**, 30320-27-5; **2**, 30320-26-4; **3**, 93683-27-3; **4**, 50285-18-2; **6**, 50285-19-3; **7**, 93683-28-4; **8**, 58621-72-0; **9**, 58621-71-9; **10**, 93683-29-5; **11**, 354-97-2;  $F_2$ , 7782-41-4.

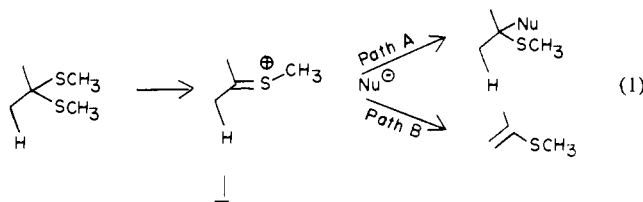
## Dimethyl(methylthio)sulfonium Tetrafluoroborate Initiated Organometallic Additions to and Macrocyclizations of Thioketals

Barry M. Trost\* and Toshio Sato

*McElvain Laboratories of Organic Chemistry  
Department of Chemistry, University of Wisconsin  
Madison, Wisconsin 53706*

Received July 23, 1984

Thioketals normally provide protection for carbonyl groups against nucleophilic additions. Nevertheless, the ready access of thioketals via lithiated thioacetals makes the notion of their direct reaction for further structural elaboration particularly important.<sup>1–4</sup> In trying to achieve such a goal, two requirements must be met—(1) the initiator used to form a reactive intermediate such as a thionium ion **1** (a thiocarbocation) must be compatible with the nucleophile and (2) the nucleophile must be sufficiently reactive to capture **1** via path A but devoid of basicity to avoid path B (see eq 1). We wish to report that allylstannanes are satis-



factory nucleophiles and DMTSF [dimethyl(methylthio)sulfonium fluoroborate (**2**)]<sup>2,5,6</sup> is an excellent initiator.

(1) Trost, B. M.; Vaultier, M.; Santiago, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 7929. Trost, B. M.; Reiffen, M.; Crimmin, M. *J. Am. Chem. Soc.* **1979**, *101*, 257. Pelter, A.; Ward, R. S.; Satyanarayana, P.; Collins, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 643. Reetz, M. T.; Giannis, A. *Synth. Commun.* **1981**, *11*, 315. Reetz, M. T.; Huttenhain, S.; Walz, P.; Lowe, U. *Tetrahedron Lett.* **1979**, 4971. Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860. Brinkmeyer, R. S. *Tetrahedron Lett.* **1979**, 207. Mizyuk, V. L.; Semenovskiy, A. V. *Tetrahedron Lett.* **1978**, 3603. Andersen, N. H.; Yamamoto, Y.; Denniston, A. D. *Tetrahedron Lett.* **1975**, 4547. Mukaiyama, T.; Narasaka, K.; Hokonok, H. *J. Am. Chem. Soc.* **1969**, *91*, 4315.

(2) Trost, B. M.; Murayama, E. *J. Am. Chem. Soc.* **1981**, *103*, 6529; *Tetrahedron Lett.* **1982**, 23, 1047. Kim, J. K.; Pau, J. K.; Caserio, M. C. *J. Org. Chem.* **1979**, *44*, 1544. For reaction with an ortho thio ester, see: Smith, R. A. J.; bin Manas, A. R. *Synthesis* **1984**, 166.

(3) For a few recent examples of generation of thionium ions from sulfides and  $\alpha$ -chloro sulfides, see: (a) Murayama, E.; Uematsu, M.; Nishio, H.; Sato, T. *Tetrahedron Lett.* **1984**, 25, 313. (b) Tamura, Y.; Tsugoshi, T.; Annoura, H.; Ishibashi, H. *Synthesis* **1984**, 326. (c) Magnus, P.; Gallagher, T.; Brown, P.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2105. (d) Hori, M.; Kataoka, T.; Shimizu, H.; Kataoka, M.; Tomoto, A.; Kishida, M. *Tetrahedron Lett.* **1983**, *24*, 3733. (e) Arai, K.; Ohara, Y.; Izumi, T.; Takakuwa, Y. *Tetrahedron Lett.* **1983**, *24*, 1531. (f) Wada, M.; Shigehisa, T.; Akiba, K. *Tetrahedron Lett.* **1983**, *24*, 1711. (g) Wada, M.; Shigehisa, T.; Kitani, H.; Akiba, K. *Tetrahedron Lett.* **1983**, *24*, 1715. (h) Fleming, I.; Iqbal, J. *Tetrahedron Lett.* **1983**, *24*, 327. (i) Lee, T. V.; Okonkwo, J. O. *Tetrahedron Lett.* **1983**, *24*, 323. (j) McKervey, M. A.; Ratananukul, P. *Tetrahedron Lett.* **1983**, *24*, 117. (k) Tamura, Y.; Choi, H. D.; Mizutani, M.; Ueda, Y.; Ishibashi, H. *Chem. Pharm. Bull.* **1982**, *30*, 3574. (l) Khan, H. A.; Paterson, I. *Tetrahedron Lett.* **1982**, 23, 2399. (m) Tamura, Y.; Maeda, H.; Akai, S.; Ishibashi, H. *Tetrahedron Lett.* **1982**, 23, 2209.

(4) For some recent reviews on thioacetal anions, see: Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357. Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943.