

## Mechanism and Rate Constant for Rearrangement of Radicals $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{CH}_2\dot{\text{C}}\text{HCF}_3$ to $\text{Ph}\dot{\text{C}}\text{HCH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$ with 1,5-Hydrogen Migration

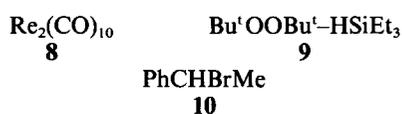
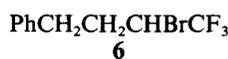
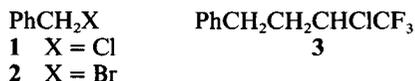
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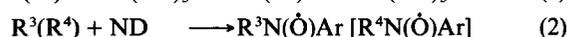
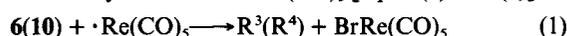
The intramolecular mechanism of the rearrangement of radicals  $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{CH}_2\dot{\text{C}}\text{HCF}_3$  ( $\text{R}^1$ ) to  $\text{Ph}\dot{\text{C}}\text{HCH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$  ( $\text{R}^2$ ) with 1,5-hydrogen migration has been elucidated using EPR spectroscopy and the rate constant of isomerization  $k_{is} = 5.0(\pm 0.3) \times 10^4 \text{ s}^{-1}$  at 22 °C has been determined.

Rearrangement of radicals involving 1,5-hydrogen migration ranks high in the list of known rearrangements of short-lived radicals in the liquid phase.<sup>1,2,3</sup> In ref. 3 it is shown that the rearrangement yields depend essentially on the nature of the substituent at the  $\alpha$ -position relative to the carbon atom from which the hydrogen atom migrates.

The telomerization of 3,3,3-trifluoropropene (TFP) with  $\text{PhCH}_2\text{X}$ ; X = Cl **1**, X = Br **2** on initiation by  $\text{Fe}(\text{CO})_5$  + dimethylformamide (DMF), was performed in order to find examples of the rearrangements. Using **1** the following substances were obtained:  $\text{PhCH}_2\text{CH}_2\text{CHClCF}_3$ , **3**,  $\text{PhCH}=\text{CHCH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$ , **4** and  $\text{PhCHClCH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$ , **5**, while compound **2** gave  $\text{PhCH}_2\text{CH}_2\text{CHBrCF}_3$ , **6**, **4** and  $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CHBrCF}_3$ , **7**. To explain the formation of both **4** and **5** from **1**, and **4** from **2** we propose that in both cases the radical involving two TFP monomer units  $\text{PhCH}_2\text{CH}_2\text{CH}(\text{CF}_3)\text{CH}_2\dot{\text{C}}\text{HCF}_3$  ( $\text{R}^1$ ) is partially (when X = Br) or completely (when X = Cl) isomerized into the radical  $\text{Ph}\dot{\text{C}}\text{HCH}_2\text{CH}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{CF}_3$  ( $\text{R}^2$ ) with 1,5-hydrogen migration. Compounds **3**, **4**, **5**, **6** and **7** were isolated and their compositions and structures were confirmed by elemental analysis and data from their <sup>13</sup>C NMR and mass spectra. In order to prove the occurrence of the rearrangement of  $\text{R}^1$  and  $\text{R}^2$  the mechanism was investigated and the rate constant for isomerization determined using EPR spectroscopy.

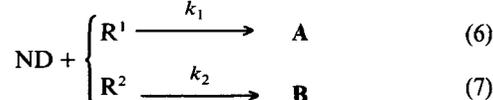
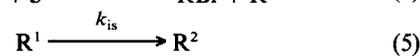
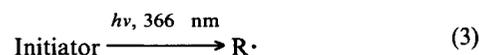


Radicals  $\text{R}^1$  were generated by removal of bromine from **7** with the radicals  $\cdot\text{Re}(\text{CO})_5$  or  $\cdot\text{SiEt}$ , obtained from the photochemical decomposition of  $\text{Re}_2(\text{CO})_{10}$  **8** or the system  $\text{Bu}^t\text{OO-Bu}^t\text{-HSi}(\text{Et})_3$  **9**.<sup>5</sup> Nitrosodurene (ND) was used as a spin trap for the identification of intermediate radicals. A benzene solution of **7** was irradiated with light ( $\lambda = 366 \text{ nm}$ ) in the presence of **8** or system **9**, in the resonator of a 'Radiopan' SX/47 spectrometer, (lamp DRS-500). Signals due to radicals  $\text{R}^1\text{N}(\dot{\text{O}})\text{Ar}$  **A** ( $a_N = 12.49$ ,  $a_{\beta\text{-H}} = 1.85$ ,  $a_F = 5.25 \text{ G}$ ) and  $\text{R}^2\text{N}(\dot{\text{O}})\text{Ar}$  **B** ( $a_N = 13.8$ ,  $a_{\beta\text{-H}} = 3.9 \text{ G}$ )† ( $\text{Ar} = 2,3,5,6\text{-Me}_4\text{C}_6\text{H}$ ) were simultaneously observed. The correctness of the assignments of the EPR signals to radicals **A** and **B** was established by comparison with the hyperfine splitting (hfs) constants for spin-adducts of the radicals  $\text{PhCH}_2\text{CH}_2\dot{\text{C}}\text{HCF}_3$  ( $\text{R}^3$ ) ( $a_N = 12.49$ ,  $a_{\beta\text{-H}} = 1.85$ ,  $a_F = 5.25 \text{ G}$ ) and  $\text{Ph}\dot{\text{C}}\text{HMe}$  ( $\text{R}^4$ ) ( $a_N = 13.8$ ,  $a_{\beta\text{-H}} = 3.9 \text{ G}$ ) with ND, which were generated by removal of bromine from **6** and  $\text{PhCHBrMe}$  **10** by the radicals  $\cdot\text{Re}(\text{CO})_5$  [eqns. (1) and (2)].



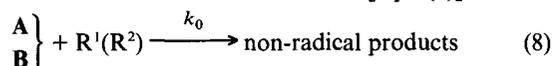
The formation of radicals of type  $\text{R}^2$  can be rationalised in terms of both an intermolecular removal of a benzyl hydrogen from the initial compound **7** by radicals  $\text{R}^1$  and intramolecular isomerization of radicals  $\text{R}^1$  into  $\text{R}^2$  with 1,5-hydrogen migration. Consequently, for the intermolecular mechanism the ratio of the concentration of the radicals  $[\text{A}]/[\text{B}]$  will depend on the concentration of **7**; if this dependence is not observed, the intermolecular mechanism cannot be operating.

On changing the concentration of **7** approximately 15-fold ( $0.127\text{--}0.008 \text{ mol dm}^{-3}$ ), the ratio of signal intensities, depending on the nitroxide, remains unchanged. These results indicate that the radicals  $\text{R}^2$  are formed as a result of the intramolecular rearrangement of the radicals  $\text{R}^1$  with 1,5-hydrogen migration, and the process can be described in terms of the mechanism in eqns. (3)–(7).



†  $G = 10^{-4} \text{ T}$ .

Radicals **A** and **B** achieve stationary concentrations by interaction of radicals  $R^1$  and  $R^2$  with them [eqn. (8)].



The isomerization rate constant,  $k_{is}$ , was determined from eqn. (9) (see, e.g., ref. 7).

$$[\mathbf{A}]_{st}/[\mathbf{B}]_{st} = \frac{k_1[\text{ND}]_0}{k_{is}} + \frac{k_1 k_0([\mathbf{A}]_{st} + [\mathbf{B}]_{st})}{k_2 k_{is}} \quad (9)$$

The ratio  $[\mathbf{A}]_{st}/[\mathbf{B}]_{st}$  depends directly upon the concentration of ND ( $8.64\text{--}2.32 \text{ mmol dm}^{-3}$ ) in accordance with expression (9). It can be assumed that the capacity of the radicals  $R^1$  and  $R^2$  to bind to ND will not differ from that of the radicals  $R^3$  and  $R^4$ . The rate constants for binding of radicals  $R^3$  and  $R^4$  to ND were calculated to determine  $k_{is}$  by using eqn. (10),

$$\frac{d[\mathbf{R}^i\text{N}(\dot{\text{O}})\text{Ar}]_{st}}{d[\text{ND}]_0} = \frac{k_r}{k_0} \quad (10)$$

where  $R^i = R^3$ ,  $k_r = k_1$  or  $R^i = R^4$ ,  $k_r = k_2$ , considering that  $k_0 = 2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .<sup>8</sup> The rate constants  $k_1$  and  $k_2$  at 22 °C are equal to  $(3.9 \pm 0.6) \times 10^6$  and  $(1.2 \pm 0.3) \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . From the experimental results and values for  $k_1$  and  $k_2$  and by using eqn. (9) the rate constant for rearrangement of  $R^1$  into  $R^2$  with 1,5-hydrogen migration,  $k_{is}$  was determined; at 22 °C,  $k_{is} = (5.0 \pm 0.3) \times 10^4 \text{ s}^{-1}$ .

A comparison of the activation energy, calculated by us for rearrangement of  $R^1$  to  $R^2$  and equal to  $5.8 \text{ kcal mol}^{-1}$  (on

taking the value of the pre-exponential factor as  $10^9 \text{ s}^{-1}$ ,<sup>3</sup>  $1 \text{ cal} = 4.184 \text{ J}$ ), with the activation energies for the rearrangement of the radicals  $\text{XCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\dot{\text{C}}\text{Cl}_2$  into  $\text{X}\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_2\text{CCl}_2\text{H}$  [ $\text{X} = \text{Cl}$  ( $E_a = 10.5 \text{ kcal mol}^{-1}$ ); Me (9.5); Et (9.2); SiEt<sub>3</sub> (7.3); CH<sub>2</sub>CH<sub>2</sub>SiEt<sub>3</sub> (9.3)] and  $\dot{\text{C}}\text{H}_2(\text{CH}_2)_4\text{CO}_2\text{Me}$  into  $\text{Me}(\text{CH}_2)_3\dot{\text{C}}\text{HCO}_2\text{Me}$  ( $E_a = 6.3 \text{ kcal mol}^{-1}$ ) (see ref. 3 and references therein) which occur with 1,5-hydrogen migration it is clear that the isomerization studied in the present work is an energetically more favoured process than similar rearrangements, which were studied before.

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