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Mechanism and Rate Constant for Rearrangement of Radicals $PhCH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3$ to $Ph\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3$ with 1,5-Hydrogen Migration

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The intramolecular mechanism of the rearrangement of radicals $PhCH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3$ (R^1) to $Ph\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3$ (R^2) with 1,5-hydrogen migration has been elucidated using EPR spectroscopy and the rate constant of isomerization $k_{is} = 5.0(\pm 0.3) \times 10^4\ s^{-1}$ 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.[1,2,3] In ref. 3 it is shown that the rearrangement yields depend essentially on the nature of the substituent at the α-position relative to the carbon atom from which the hydrogen atom migrates.

The telomerization of 3,3,3-trifluoropropene (TFP) with $PhCH_2X$; X = Cl **1**, X = Br **2** on initiation by $Fe(CO)_5$ + dimethylformamide (DMF), was performed in order to find examples of the rearrangements. Using **1** the following substances were obtained: $PhCH_2CH_2CHClCF_3$ **3**, $PhCH{=}CHCH(CF_3)CH_2CH_2CF_3$ **4** and $PhCHClCH_2CH(CF_3)CH_2CH_2CF_3$ **5**, while compound **2** gave $PhCH_2CH_2CHBrCF_3$ **6**, **4** and $PhCH_2CH_2CH(CF_3)CH_2CHBrCF_3$ **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 $PhCH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3$ (R^1) is partially (when X = Br) or completely (when X = Cl) isomerized into the radical $Ph\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3$ (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 ^{13}C NMR and mass spectra. In order to prove the occurrence of the rearrangement of R^1 and R^2 the mechanism was investigated and the rate constant for isomerization determined using EPR spectroscopy.

$PhCH_2X$
1 X = Cl
2 X = Br

$PhCH_2CH_2CHClCF_3$ **3**

$PhCH{=}CHCH(CF_3)CH_2CH_2CF_3$ **4**

$PhCHClCH_2CH(CF_3)CH_2CH_2CF_3$ **5**

$PhCH_2CH_2CHBrCF_3$ **6**

$PhCH_2CH_2CH(CF_3)CH_2CHBrCF_3$ **7**

$Re_2(CO)_{10}$ **8**

Bu^tOOBu^t–$HSiEt_3$ **9**

PhCHBrMe **10**

Radicals R^1 were generated by removal of bromine from **7** with the radicals $\cdot Re(CO)_5$ or $\cdot SiEt$, obtained from the photochemical decomposition of $Re_2(CO)_{10}$ **8**[4] or the system Bu^tOOBu^t–$HSi(Et)_3$ **9**.[5] Nitrosodurene (ND) was used as a spin trap for the identification of intermediate radicals. A benzene solution of **7** was irradiated with light (λ = 366 nm) in the presence of **8** or system **9**, in the resonator of a 'Radiopan' SX/47 spectrometer, (lamp DRSH-500). Signals due to radicals $R^1N(\dot{O})Ar$ **A** ($a_N = 12.49$, $a_{\beta-H} = 1.85$, $a_F = 5.25$ G) and $R^2N(\dot{O})Ar$ **B** ($a_N = 13.8$, $a_{\beta-H} = 3.9$ G)† (Ar = 2,3,5,6-Me_4C_6H) 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 $PhCH_2CH_2\dot{C}HCF_3$ (R^3) ($a_N = 12.49$, $a_{\beta-H} = 1.85$, $a_F = 5.25$ G) and $Ph\dot{C}HMe$ (R^4) ($a_N = 13.8$, $a_{\beta-H} = 3.9$ G) with ND, which were generated by removal of bromine from **6** and PhCHBrMe **10** by the radicals $\cdot Re(CO)_5$ [eqns. (1) and (2)].

$$\mathbf{6(10)} + \cdot Re(CO)_5 \longrightarrow R^3(R^4) + BrRe(CO)_5 \quad (1)$$

$$R^3(R^4) + ND \longrightarrow R^3N(\dot{O})Ar\ [R^4N(\dot{O})Ar] \quad (2)$$

The formation of radicals of type R^2 can be rationalised in terms of both an intermolecular removal of a benzyl hydrogen from the initial compound **7** by radicals R^1 and intramolecular isomerization of radicals R^1 into R^2 with 1,5-hydrogen migration. Consequently, for the intermolecular mechanism the ratio of the concentration of the radicals [**A**]/[**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 (0.127–0.008 mol dm^{-3}), the ratio of signal intensities, depending on the nitroxide, remains unchanged. These results indicate that the radicals R^2 are formed as a result of the intramolecular rearrangement of the radicals R^1 with 1,5-hydrogen migration, and the process can be described in terms of the mechanism in eqns. (3)–(7).

$$\text{Initiator} \xrightarrow{h\nu,\ 366\ \text{nm}} R\cdot \quad (3)$$

$$R\cdot + \mathbf{3} \longrightarrow RBr + R^1 \quad (4)$$

$$R^1 \xrightarrow{k_{is}} R^2 \quad (5)$$

$$ND + \begin{cases} R^1 \xrightarrow{k_1} \mathbf{A} & (6) \\ R^2 \xrightarrow{k_2} \mathbf{B} & (7) \end{cases}$$

† $G = 10^{-4}$ T.

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

$$\left.\begin{matrix}\mathbf{A}\\ \mathbf{B}\end{matrix}\right\} + R^1(R^2) \xrightarrow{k_0} \text{non-radical products} \qquad (8)$$

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

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

The ratio $[\mathbf{A}]_{st}/[\mathbf{B}]_{st}$ depends directly upon the concentration of ND (8.64–2.32 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),

$$\frac{d[R^iN(\dot{O})Ar]_{st}}{d[ND]_0} = \frac{k_r}{k_0} \qquad (10)$$

where $R^i = R^3$, $k_r = k_1$ or $R^i = R^4$, $k_r = k_2$, considering that $k_0 = 2 \times 10^8$ dm^3 $mol^{-1}s^{-1}$.[8] The rate constants k_1 and k_2 at 22 °C are equal to $(3.9 \pm 0.6) \times 10^6$ and $(1.2 \pm 0.3) \times 10^6$ dm^3 mol^{-1} 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, $k_{is} = (5.0 \pm 0.3) \times 10^4$ s^{-1}.

A comparison of the activation energy, calculated by us for rearrangement of R^1 to R^2 and equal to 5.8 kcal mol^{-1} (on taking the value of the pre-exponential factor as 10^9 s^{-1};[3] 1 cal = 4.184 J), with the activation energies for the rearrangement of the radicals $XCH_2CH_2CH_2CH_2\dot{C}Cl_2$ into $X\dot{C}HCH_2CH_2CH_2CCl_2H$ [X = Cl (E_a = 10.5 kcal mol^{-1}); Me (9.5); Et (9.2); $SiEt_3$ (7.3); $CH_2CH_2SiEt_3$ (9.3)] and $\dot{C}H_2(CH_2)_4CO_2Me$ into $Me(CH_2)_3\dot{C}HCO_2Me$ (E_a = 6.3 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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