In all experiments, with the exception of the preparation of (XI), the ethereal extracts were washed with water, dried over  $MgSO_4$ , and fractionated.

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#### ELECTRON TRANSFER IN REACTIONS OF tert-PERFLUOROALKYL BROMIDES

### WITH ALKENES AND NUCLEOPHILES

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Tertiary perfluoroalkyl bromides ( $R_FBr$ ) in nonpolar solvents under mild conditions can be added to the multiple bond of terminal alkenes, alkynes, and butadiene. Slow addition to alkenes at 20°C is accelerated in proton-donating solvents and is catalyzed by readily oxidizable nucleophiles. Bromination of the multiple bond and formation of  $R_FBr$  reduction products suggests a radical-chain mechanism initiated by electron transfer to the R<sub>F</sub>Br molecule.

The high energy (65-70 kcal/mole) for homolytic cleavage of the C-Br bond [1] in perfluoroalkyl bromides (R<sub>F</sub>Br) limits their use as perfluoroalkylating agents in organic synthesis. In contrast to R<sub>F</sub>I [2], perfluoroalkylation of olefins with R<sub>F</sub>Br was successful under drastic conditions (autoclave, 180°C) only with the most reactive tertiary perfluoroalkyl bromides [3]. Primary R<sub>F</sub>Br alkylate unsaturated compounds only in the presence of electrondonating catalysts [Zn, CuCl, Pd(PPh<sub>3</sub>)<sub>4</sub>] [4-7]. The role of the catalyst in these reactions consists of electron transfer to the R<sub>F</sub>Br molecule with formation of an intermediate anionradical, whose dissociation generates a reactive perfluoroalkyl radical.

In the present work we show that tertiary  $R_FBr$  (I) in organic solvents can be added to terminal olefins even at about 20°C in the presence of any catalysts. The addition rate at 20°C is small, and the adduct yield after 3-5 days usually does not exceed 10%. The formation of adduct (II) is accompanied by side reactions — bromination of the olefin multiple bond, leading to dibromide (III), and reduction of  $R_FBr$  monohydroperfluoroalkane (IV). Solvent polarity has no appreciable effect on the rate of the process. However, compound (II) is formed ten times more rapidly in proton-donating solvents than in EtOAc (see below).

The addition of t-R<sub>F</sub>Br to terminal olefins in nonpolar solvents at 20°C is also significantly accelerated by catalytic amounts (5-10 mole %) of nucleophiles (NaN<sub>3</sub>, NaNO<sub>2</sub>, KSCN, Bu<sub>4</sub>NBr). Thus the addition of compound (Ia) to hexene-1 is accelerated tenfold in the presence of 0.1 M NaN<sub>3</sub> in EtOAc and 45-fold in the presence of 0.1 M Bu<sub>4</sub>NBr. An increase in

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nucleophile concentration leads to a sharp acceleration in the bromination of the multiple bond and reduction of  $R_FBr$ . At an initial  $Bu_4NBr:(Ia)$  ratio of 1:1, dibromide (III) is the major reaction product, and  $R_FBr$  is reduced primarily to  $R_FH$  (IV).

Effect of the  $Bu_4NBr$  Concentration in the Reaction of  $R_FBr$  (Ia) with Hexene-1 in EtOAc on the Ratio of Adduct (II) and Dibromide (III)

Bu₄NBr: (Ia)	(II) : (III)
1:10	12,5
1:2	2.8
1:1	0.60
3:2	0,56

To elucidate the mechanism of nucleophilic catalysis, we studied the reaction of perfluoro-tert-hexyl bromide (Ia) with nucleophiles of the type  $Bu_4NX$  (X = Cl, Br, I). We found that in the presence of (Ia) halide anions were readily oxidized to halogens both in polar (CH<sub>3</sub>CN) and nonpolar solvents (dichloroethane,  $CH_2Cl_2$ ). The reduction products of (Ia) were 2-H-perfluoro-2-methylpentane (IV) and perfluoro-2-methylpentene-2 (V). The overall reaction scheme probably includes an initial electron transfer from the halide anion to the R<sub>F</sub>Br molecule with formation of intermediate anion-radical (VI), which dissociates to carbanion R<sub>F</sub><sup>-</sup> and a bromine radical. Carbanion R<sub>F</sub><sup>-</sup> is stabilized by capturing a proton from the solvent (SH) or by eliminating F<sup>-</sup>. This unusual pathway for dissociation of the t-R<sub>F</sub>Br (VI) anion-radical was proposed earlier on the basis of quantum-chemical calculations by the AM-1 method [8].

 $C_{3}F_{7}(CF_{3})_{2}CBr + Br^{-} \longrightarrow C_{3}F_{7}(CF_{3})_{2}CBr^{+} (VI) + Br^{-}$   $C_{3}F_{7}\bar{C}(CF_{3})_{2} + Br^{-}$   $C_{3}F_{7}\bar{C}(CF_{3})_{2} + Br^{-}$   $C_{3}F_{7}C(CF_{3})_{2}H \qquad C_{2}F_{5}CF = C(CF_{3})_{2}$   $2Br^{-} \longrightarrow Br_{2} \qquad (IV) \qquad (V)$ 

Reversible oxidation of anion halides is observed at positive potentials - I<sup>-</sup> at 0.3 V, Br<sup>-</sup> at 0.7 V, and Cl<sup>-</sup> at 1.2 V relative to saturated calomel electrode [9] - while irreversible reduction of (Ia) takes place at -0.09 V relative to saturated calomel electrode [10]. According to formal thermodynamics, electron transfer from anion X<sup>-</sup> to (Ia) occurs "against the potential" and is an endothermic process requiring considerable energy expenditure. In accordance with an increase in the difference between the oxidation potential of donor X<sup>-</sup> and the reduction potential of acceptor (Ia),  $\Delta E = E_D^{\text{ox}} - E_A^{\text{red}}$ , we observed a decrease of the oxidation-reduction process. Thus under identical conditions (20°C, dichloroethane, Bu<sub>4</sub>NX:R<sub>F</sub>Br = 2:1), the overall yield of reduction products (IV) and (V) after 3 h was 100% for I<sup>-</sup>, 56% for Br<sup>-</sup>, and 30% for Cl<sup>-</sup>. Reagents whose redox potentials are in the cathodic region react with t-R<sub>F</sub>Br rapidly and exothermically. Compound (Ia) in acetone is reduced quantitatively by Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O or Na<sub>2</sub>S·5H<sub>2</sub>O to (IV) and (V) and the reaction is accompanied by evolution of Br<sub>2</sub>.

Based on these results, we propose the following scheme of nucleophilic catalysis for the addition of  $R_FBr$  to the multiple bond. The first step of the reaction consists of elec-

tron transfer from the nucleophile to  $R_FBr$  with formation of an intermediate anion-radical. Dissociation of  $R_FBr$  produces a perfluorocarbanion and a bromine radical, which is added to the multiple bond and initiates a radical-chain process. In this process the  $R_FBr$  molecule serves as an effective chain propagator. The ratio of the yield (n) of adduct (II) and dibromide (III) shows the number of chain propagation steps per initial electron transfer. At low nucleophile concentrations in nonpolar solvents n reaches a value of 40.

$$\begin{split} R_{F}Br + Nu^{-} \rightarrow R_{F}Br^{-} + Nu^{*} \\ R_{F}Br^{-} \rightarrow R_{F}^{-} + Br^{*} \\ R_{F}^{-} + SH \rightarrow R_{F}H (IV) + S^{-} \\ Br^{*} + H_{2}C = CHR \rightarrow BrCH_{2}CHR \\ BrCH_{2}CHR + R_{F}Br \rightarrow BrCH_{2}CH(Br)R (III) + R_{F}^{*} \\ R_{F}^{*} + CH_{2} = CHR \rightarrow R_{F}CH_{2}CHR \\ R_{F}CH_{2}CHR + R_{F}Br \rightarrow R_{F}CH_{2}CH(Br)R (II) + R_{F}^{*}, \text{etc.} \end{split}$$

Regarding the mechanism of addition of t-RFBr to the multiple bond of terminal olefins in the absence of nucleophiles or any electron donors, it seems improbable that homolysis of the C-Br bond, whose energy in RFBr is 65-70 kcal/mole, can be accomplished under such mild conditions (20°C,  $CH_2Cl_2$ ). However, bromination of the multiple bond with formation of dibromide III, the formal olefin oxidation product, as well as the formation of monohydroperfluoroalkane (IV), the formal reduction product of  $R_FBr$ , shows that the redox process takes place in the reaction of RyBr with olefins. At first glance electron transfer from olefin (oxidation potential  $E^{OX} = +2.8 V$ ) to t-R<sub>F</sub>Br (reduction potential  $E^{red} = -0.1 V$ ) seems highly improbable. Such transfer should be a strongly endothermic process, since the free energy change  $\Delta G = E_D^{\text{ox}} - E_A^{\text{red}} = +2.9 \text{ eV}$ . According to the terminology of Marcus [11], in this case the driving force for this process is missing. However, such formal thermodynamic analysis is based on data relating to the formation of an isolated cationradical donor (olefin) and anion-radical acceptor (RFBr). In the given reaction electron transfer probably occurs in the collision complex of two neutral particles (olefin and RFBr) and may take place "intraspherically," when the transition state is in the form of a contact ion-radical pair [12]. In this case Coulombic interaction of the emerging charges q in the cation- and anion-radicals at distance r between charge centers should stabilize the transition state and lower the activation energy barrier  $\Delta G^{\neq}$ :

$$\Delta G^{\neq} = E_{\mathrm{D}}^{\mathrm{ox}} - E_{\mathrm{A}}^{\mathrm{red}} - \frac{q_1 q_2 e^2}{r_{\mathrm{D},\mathrm{A}}}.$$

Since the difference between the redox potentials of olefin and RpBr is very large (2.9 V) and the reaction nevertheless takes place at 20°C, we must conclude that Coulombic stabilization in this case is very significant. This may be associated with the low degree of charge delocalization in the olefin cation-radical and the RpBr anion-radical, and also with the small distance ( $r_{DA}$ ) between charge centers in the transitional contact ion-radical pair.

It should be stressed that the reaction of  $t-R_FBr$  with olefins at 20°C is slow and cannot be used for preparative purposes. However, perfluoro-tert-hexyl bromide (Ia) and perfluoro-1-methylcyclopentyl bromide (Ib) readily add to terminal olefins in high yields even at 80°C in nonpolar solvents in the absence of any electron donors:

$$\begin{split} R_{F}Br + CH_{2} = CHR \xrightarrow{EtOAc} R_{F}CH_{2}CHBrR + R_{F}H \\ (Ia, b) & (VII), (VIII) & (IV) \\ R = C_{4}H_{9}, C_{5}H_{11}. \end{split}$$

The yield of additon products (VII, VIII) in other solvents  $(CH_2Cl_2, CH_3CN, CF_3CH_2OH)$  decreases markedly. Addition of t-R<sub>F</sub>Br to butadiene under the same conditions is accompanied by formation of telomeric products (IX) at a low butadiene conversion:

$$\begin{array}{rcl} R_{\rm F} {\rm Br} + {\rm CH}_2 = {\rm CHCH} = {\rm CH}_2 \xrightarrow[80^{\circ}, \ 12\,{\rm h}]{} {\rm R}_{\rm F} ({\rm CH}_2 {\rm CH} = {\rm CHCH}_2)_n {\rm Br} \\ ({\rm Ia, \ b}) & ({\rm IXa, \ b}), \\ R_{\rm F} = {\rm C}_3 {\rm F}_7 {\rm C} ({\rm CF}_3)_2, \ ({\rm IXa, \ n = 1}) \ 22,6\,\%, \ ({\rm IXa, \ n = 2}) \ 76\,\%. \end{array}$$

**N/O** 1

$$R_F = F$$
 (IXb,  $n = 1$ ) 43,5%, (IXb,  $n = 2$ ), 56,4%.

The addition of t- $R_FBr$  to the terminal triple bond is more difficult; longer heating or the use of proton-donating solvents is required. In the case of phenylacetylene, telomeric products are formed and  $R_FBr$  conversion does not exceed 50%.

$$\begin{array}{c} R_{F}Br + HC \equiv CBu \xrightarrow[80^{\circ}, 100 \text{ h}]{\text{EtOAc}} & R_{F}CH = CBr(Bu) \\ (Ia, b) & (X), 90\% \\ & \text{conversion of (I)} 24 - 30\% \\ R_{F}Br + HC \equiv CPh \xrightarrow[120^{\circ}, 80 \text{ h}]{\text{AcOH}} & R_{F}(CH = CPh)_{2}Br + R_{F}H \\ (Ia) & (X1), 46\% & (IV), 19\% \\ & \text{conversion of (Ia)} 50\% \end{array}$$

### EXPERIMENTAL

PMR and <sup>19</sup>F NMR spectra were obtained on a Bruker WP-200 SY (200 MHz) spectrometer, with TMS and CF<sub>3</sub>COOH as internal standards. Mass spectra were obtained on a Varian MAT CH-8 spectrometer. Raman spectra were obtained on a Ramanor HG-2S spectrometer, with Arlaser pumping (5145 Å).

# Addition of tert-Perfluoroalkyl Bromides to Alkenes and Alkynes

<u>6-Bromo-4,4-bis(trifluoromethyl)-1,1,1,2,2,3,3-heptafluorodecane (VIIa) (typical experiment).</u> A mixture consisting of 10.2 g (0.025 mole) of compound (Ia) and 4.2 g (0.05 mole) hexene-1 in 12 ml EtOAc was heated in a glass ampul ( $80^{\circ}$ C, 12 h). The volatile components were removed in a vacuum ( $20^{\circ}$ C, 60 mm) and the residue was distilled. A 11.5-g (93.1%) yield of compound (VII) was obtained, bp 78°C (10 mm), which, according to its PMR and <sup>19</sup>F NMR spectra, was identical to the known sample [7]. GLC data showed that the low-boiling fraction contained 0.5 g (6%) 2-H-perfluoro-2-methylpentane (IV), which, according to its <sup>19</sup>F NMR spectrum, was identical to the known sample.

1-(2-Bromohexy1)-1-trifluoromethyloctafluorocyclopentane (VIIb) was obtained from compound (Ib) and hexene-1 in EtOAc (80°C, 12 h) in a yield of 88%, bp 89°C (4 mm). Its PMR and <sup>19</sup>F NMR spectra were identical to those of the known sample [7].

<u>6-Bromo-4,4-bis(trifluoromethy1)-1,1,1,2,2,3,3-heptafluoroundecane (VIII)</u> was obtained from compound (Ia) and heptene-1 in EtOAc (80°C, 12 h) in a yield of 88%, bp 98°C (10 mm). Its PMR and <sup>19</sup>F NMR spectra were identical to those of the known sample [8].

 $\frac{1-\text{Bromo-5},5-\text{bis}(\text{trifluoromethyl})-6,6,7,7,8,8,8-\text{heptafluorooctene-2} (IXa, n = 1) \text{ and}}{1-\text{bromo-9},9-\text{bis}(\text{trifluoromethyl})-10,10,11,11,12,12,12-\text{heptafluorodeca-2},6-\text{diene} (IXa, n = 2)} were obtained from 0.025 mole of compound (Ia) and 0.03 mole butadiene-1,3 in EtOAc (80°C, 12 h) with 20% conversion of butadiene-1,3. The yield of <math>\text{CF}_3^2\text{CF}_2^3\text{CF}_2^4\text{C}(\text{CF}_3^1)_2\text{CH}_2\text{CH}=\frac{\text{b}}{\text{CH}}_2\text{Br}}{(\text{XIa, n = 1})} \text{ was } 22.6\%, \text{ bp } 60°C (1 \text{ mm}). Found, \%: C 27.15, H 1.42. C_{10}\text{H}_6\text{Br}_{13}. Calculated, \%: C 27.58, H 1.38. PMR spectrum (CD_3\text{CN}, \delta, ppm): 5.97 m (H^a), 5.88 m (H^b), 4.03 d (CH_2\text{Br}), 3.09 d (CH_2\text{R}). ^{19}\text{F} NMR spectrum (CD_3\text{CN}, \delta, ppm): -14.7 (2CF_3^1), 2.2 (CF_3^2), 28.79 (CF_3^3), 44.59 (CF_2^4). Raman spectrum: vC=C 1678 cm^{-1}. The yield of CF_3^2\text{CF}_2^3\text{CF}_2^4 \cdot C(CF_3^1)_2\text{CH}_2\text{CH}=CHCH_2\text{CH}_2\text{CH}=CHCH_2\text{Br} (XIa, n = 2)$  was 76%, bp 104°C (1 mm). Found, \%: C 32.42, H 2.36, F 48.94. C\_{14}\text{H}\_1\text{2}\text{Br}\_{13}. Calculated, \%: C 33.09, H 2.26, F 48.72. PMR spectrum (CD\_3\text{CN}, \delta, ppm): 5.75 m (H^a, H^c), 5.54 m (H^b, H^d), 4.0 d (CH\_2\text{Br}), 3.01 d (CH\_2\text{R}), 2.15 m (CH\_2\text{CH}\_2). ^{19}\text{F} NMR spectrum (CD\_3\text{COCD}\_3, \delta, ppm): -14.8 (2CF\_3^1), 2.02 (CF\_3^2), 28.7 (CF\_2^3), 44.6 (CF\_2^4). Raman spectrum: vC=C 1672 cm^{-1}. Mass spectrum: M<sup>+</sup> 508, 506; M<sup>+</sup> - Br 428, 427.

 $\frac{1-(4-\text{Bromobuten-2-y1})-1-\text{trifluoromethyloctafluorocyclopentane (IXb, n = 1) and 1-(8-bromoocta-2,6-dienyl)-1-trifluoromethyloctafluorocyclopentane (IXb, n = 2) were obtained from 0.025 mole of compound (Ib) and 0.03 mole butadiene-1,3 in EtOAc (80°C, 12 h) with a butadiene-1,3 conversion of 24%. The yield of compound (IXb, n = 1) was 43.5%, bp 55-56 °C (1 mm). Found, %: C 28.87, H 1.51. C<sub>10</sub>H<sub>6</sub>BrF<sub>11</sub>. Calculated, %: C 28.91, H 1.44. PMR spectrum (CD<sub>3</sub>CN, <math>\delta$ , ppm): 6.0 m (H<sup>a</sup>), 5.87 m (H<sup>b</sup>), 4.0 d (CH<sub>2</sub>Br), 2.91 d (CH<sub>2</sub>R<sub>F</sub>). <sup>19</sup>F NMR spectrum (CD<sub>3</sub>CN,  $\delta$ , ppm): -16.92 (CF<sub>3</sub>), CF<sub>2</sub><sup>1</sup> (AB-quartet), 37.0 and 40.22, J<sub>AB</sub> = 262.5 Hz, 53.5 and 56.2 [CF<sub>2</sub><sup>2</sup> (AB-quartet), J<sub>AB</sub> = 260 Hz]. Raman spectrum: vC=C 1678 cm<sup>-1</sup>. The



yield of (IX, n = 2) was 56.4%, bp 114-115°C (1 mm). Found, %: C 36.31, H 2.29.  $C_{14}H_{12}BrF_{11}$ . Calculated, %: C 35.8, H 2.56. PMR spectrum ( $CD_3CN$ ,  $\delta$ , ppm): 5.76 m ( $H^a$ ,  $H^b$ ), 5.54 m ( $H^b$ ,  $H^d$ ), 4.0 d ( $CH_2Br$ ), 2.85 d ( $CH_2R_F$ ), 2.15 m ( $CH_2CH_2$ ). <sup>19</sup>F NMR spectrum ( $CD_3CN$ ,  $\delta$ , ppm): -16.72 ( $CF_3$ ), 38.5 and 40.0 ( $CF_2$ <sup>1</sup>, AB-quartet, J<sub>AB</sub> = 265 Hz), 53.1 and 55.8 ( $CF_2$ <sup>2</sup>, AB-quartet, J<sub>AB</sub> = 252.5 Hz). Raman spectrum:  $\nu C=$ C 1673 cm<sup>-1</sup>. Mass spectrum:  $M^+$  - Br 390, 389.

 $\frac{6-\text{Bromo-4},4-\text{bis}(\text{trifluoromethyl})-1,1,1,2,2,3,3-\text{heptafluorodecene-5}(Xa)}{0.025 \text{ mole of compound (Ia) and 0.03 mole hexyne-1 in EtOAc (80°C, 100 h) with (Ia)} conversion of 24%. Yield 90%, bp 89°C (2 mm). Found, %: C 29.96, H 2.12, F 49.75. C<sub>12</sub>H<sub>10</sub>-$ 

BrF<sub>13</sub>. Calculated, %: C 29.93, H 2.08, F 51.35.  $CF_3^2 CF_2^3 CF_2^4 C(CF_3^1)_2 CH=CBrCH_2(CH_2)_2 CH_3$ . PMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 5.97 s (CH=C), 2.54 t (CH<sub>2</sub><sup>a</sup>), 1.34-1.58 m (2CH<sub>2</sub><sup>b</sup>), 0.93 t (CH<sub>3</sub>). <sup>19</sup>F NMR spectrum (CD<sub>3</sub>COCD<sub>3</sub>,  $\delta$ , ppm): -15.6 (2CF<sub>3</sub><sup>1</sup>), 2.5 (CF<sub>3</sub><sup>2</sup>), 30.2 (CF<sub>2</sub><sup>3</sup>), 45.3 (CF<sub>2</sub><sup>4</sup>).

1-(2-Bromohexene-1-y1)-1-trifluoromethyloctafluorocyclopentane (Xb) was obtained from



0.025 mole of compound (Ib) and 0.03 mole hexyne-1 in EtOAc (80°C, 100 h). At 30% conversion of (Ib) the yield of (Xb) was 90%, bp 82°C (12 mm). Found, %: C 32.17, H 2.27, F 45.51.  $C_{12}H_{10}BrF_{11}$ . Calculated, %: C 32.5, H 2.26, F 47.17. PMR spectrum (CCl<sub>4</sub>,  $\delta$ , ppm): 5.83 s (CH=C), 2.45 t (CH<sub>2</sub><sup>a</sup>), 1.25-1.7 m (2CH<sub>2</sub><sup>b</sup>), 0.95 t (CH<sub>3</sub>). <sup>19</sup>F NMR spectrum (CD<sub>3</sub>COCD<sub>3</sub>,  $\delta$ , ppm): -14.72 (CF<sub>3</sub>), CF<sub>2</sub><sup>1</sup> (AB-quartet), 32.89 and 41.58, J<sub>AB</sub> = 260 Hz), CF<sub>2</sub><sup>2</sup> (AB-quartet) 52.52 and 53.25, J<sub>AB</sub> = 258 Hz.

 $\frac{1-\text{Bromo-5,5-bis}(\text{trifluoromethyl})-6,6,7,7,8,8,8-\text{heptafluoro-1,3-diphenyloctadiene-1,3}}{\text{CF}_3^2\text{CF}_2^4\text{C}(\text{CF}_3^{-1})_2\text{CH}=\text{C}(\text{C}_6\text{H}_5)\text{Br}(\text{XI})} \text{ was obtained from 0.025 mole of compound}} (Ia) and 0.03 mole phenylacetylene in glacial acetic acid (110°C, 78 h). After heating, CH_3COOH was washed off with water; the lower layer was separated, dried with MgSO<sub>4</sub>, and distilled. At 50% conversion of (Ia) the yield of compound (XI) was 45.6%, bp 112°C (0.02 mm). Found, %: H 2.19, F 40.37. C_{22}H_{12}\text{BrF}_{13}. Calculated, %: H 1.99, F 40.96. PMR spectrum (CCl<sub>4</sub>, 6, ppm): 7.32 m (8H), 7.17 m (2H), 6.97 d (H<sup>a</sup>), 5.66 br.s (H<sup>b</sup>). <sup>19</sup>F NMR spectrum (CD_3COCD_3, <math>\delta$ , ppm): -16.6 (2CF<sub>3</sub><sup>-1</sup>), 2.3 (CF<sub>3</sub><sup>-2</sup>), 30.0 (CF<sub>2</sub><sup>-3</sup>), 45.5 (CF<sub>2</sub><sup>-4</sup>). Raman spectrum:  $\nu$ C=C 1598 cm<sup>-1</sup>. Mass spectrum: M<sup>+</sup> 604, 602, M<sup>+</sup> - Br 524, 523. GLC data showed that the low-boiling fraction contains 0.98 g of compound (IV), yield 19%.

### Nucleophilic Catalysis for Addition of tert-Perfluoroalkyl Bromides to Alkenes

<u>Typical Experiment.</u> A mixture of 5 mmoles of compound (Ia) and 10 mmoles hexene-1 in 2 ml  $CH_2Cl_2$  (or EtOAc, 1,2-dichloroethane) in the presence of 0.5-5 mmoles  $Bu_4NBr$  (Et<sub>4</sub>NBr,  $Bu_4NC1$ , NaNO<sub>2</sub>, NaN<sub>3</sub>) was mixed for 3 days at about 20°C and analyzed by means of GLC, using known samples for comparison. The concentration of the components was determined chromatographically by use of an internal standard.

# Reaction of tert-Perfluoroalkyl Bromides with Bu4NX

A mixture of 0.85 mmole of compound (Ia) and 1.7 mmoles  $Bu_4NX$  (X = Cl, Br, I) in 5 ml 1,2-dichloroethane (or  $CH_3CN$ ) in the presence of 0.85 mmole heptane as internal standard was mixed at about 20°C. The mixture was analyzed chromatographically, determining the ratio of the original (Ia) to the sum of  $R_{\rm F}H$  (IV) and perfluoroolefin (V) at specific time intervals.

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### REACTION OF $\alpha$ -CYANOACRYLATES WITH FUNCTIONALLY SUBSTITUTED

THIOLS, ETHANEDITHIOL, AND HYDROGEN SULFIDE

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Functionally substituted thiols, i.e., thioglycolic acid and cysteamine and cysteine hydrochlorides, facilely undergo addition at the double bond of  $\alpha$ -cyanoacrylates, forming the corresponding adducts in quantitative yields: R'SCH<sub>2</sub>CH(CN)COOR [R' = CH<sub>2</sub>COOH; CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>·HCl; CH<sub>2</sub>CH(COOH)NH<sub>2</sub>·HCl]. Under similar conditions, the reaction with ethanedithiol gives the diadduct [CH<sub>2</sub>SCH<sub>2</sub>CH(CN)COOR]<sub>2</sub>; the monoadduct HSCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH(CN)COOR]<sub>2</sub> is formed in a significantly lower yield. Hydrogen sulfide does not undergo addition to  $\alpha$ -cyanoacrylate in the absence of a catalyst; S[CH<sub>2</sub>CH(CN)COOR]<sub>2</sub> is formed quantitatively in the presence of Et<sub>3</sub>N. In the presence of triethylamine, this sulfide undergoes intramolecular cyclization (the Ziegler-Thorpe reaction) with formation of 4-amino-5-cyano-3,5-bis(ethoxycarbonyl)thiacyclohex-3-ene.

Previously, we showed that, unlike other nucleophiles (water, alcohols, and amines) various sulfhydryl compounds (thiols and thiocarboxylic and thiophosphoric acids) do not cause polymerization of  $\alpha$ -cyanoacrylates (I), but facilely undergo addition to them, forming the corresponding adducts (II) in high yields [1].

$$CH_{2} = C(CN)COOR + R'SH \rightarrow R'SCH_{2}CH(CN)COOR$$
(I)
(II)

Therefore, it seems important to explore the possibility of extending this reaction to thiols containing various functional groups, in particular, of acid and basic nature and also to dithiols and hydrogen sulfide.

We have determined that thioglycolic acid reacts with ethyl cyanoacrylate (Ia, R = like other thiols, forming an adduct (IIa, R = Et;  $R' = CH_2COOH$ ) in virtually quantitative yield.

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