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Conversion of trifluoromethyl groups into nitrile functions during cyclization of hexafluoroiodoalkanes with sodium amide

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Abstract

The cyclization of $(CF_3)_2CHCH_2CIR^1CHR^2R^3$ (**1**) (**1a**: $R^1=Me$, $R^2=R^3=H$; **1b**: $R^1=H$, $R^2=R^3=Me$; **1c**: $R^1=R^2=H$, $R^3=Bu^n$) with sodium amide occurs with conversion of trifluoromethyl groups to cyano functions or with their replacement by hydrogen atoms.

Introduction

The conversion of a trifluoromethyl group into the nitrile function is a little known phenomenon. It has been sporadically reported (for example, refs. 1 and 2) that trifluoromethyl-substituted olefins can be transformed by ammonia into the corresponding nitriles. In the course of our studies on the preparation and reaction of fluorinated alkyl halides [3], we observed that the cyclization of 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)alkanes (**1**) with sodium amide occurred with partial or complete loss of trifluoromethyl groups. The trifluoromethyl groups were either converted to cyano functions or replaced by hydrogen atoms. These conversions are unusual and we now report our results [4].

Experimental

1,1,1-Trifluoro- (**11b**) and 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) were obtained from the corresponding nonafluorobutanesulfonates by treatment with iodide [3]. IR spectra were taken as liquid films on a Bruker FT-IR IFS 48 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained on a Bruker WM 400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) relative to Me_4Si as an internal standard, and coupling constants are in Hertz. MS spectra were recorded on a Varian MAT 711 instrument, EI, 70 eV at 200 °C. GC–MS analysis was

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undertaken on a Hewlett–Packard 5890A/MSD 5970 instrument. Boiling points are uncorrected.

1,1,1-Trifluoro-4-iodo-4-methyl-2-(trifluoromethyl)pentane (1a) (nc)

To 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) (1.5 g, 5.4 mmol) placed in a heavy wall glass tube was added a spatula tip of azobisisobutyronitrile (AIBN). The glass tube was cooled in liquid nitrogen, evacuated, charged by gaseous transfer with a 5 mol excess of 2-methylpropene (**12a**) and sealed *in vacuo*. After the glass tube has been placed in a steel tube, the reaction mixture was heated at 65 °C for 6–16 h [88% conversion (GC)].

The tube was allowed to cool to ambient temperature and was opened after being cooled in liquid nitrogen. Excess alkene was removed at room temperature under aspirator pressure by using a rotary evaporator. The 93% pure product thus obtained could be purified by chromatography on silica gel on elution with CCl_4: yield 1.6 g **1a** (88%). Compound **1a** was sensitive to light. Reaction temperatures of *ca.* 80 °C led to complete conversion, but the purity of the crude product was diminished to 80–86%. IR: 2990–2878, 1470–1064, 969, 916, 876, 832, 728, 669 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.97 (s, 6H, CH_3), 2.26 (d, 2H, $J=3.9$, CH_2), 3.06 (m, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 37.9 (s, CH_3), 42.5 (s, CH_2), 43.7 (s, CI), 47.9 (sept, $J=28$, CH), 123.7 (q, $J=281$, CF_3). MS, *m/e* (relative intensity): 319 (<1), 207 (100), 187 (5), 167 (17), 147 (2), 77 (9), 55 (49). HRMS calcd. for $C_7H_9F_6^+$: 207.0608; found: 207.0608.

1,1,1-Trifluoro-4-iodo-5-methyl-2-(trifluoromethyl)hexane (1b) (nc)

Compound **1b** was prepared as described for **1a** by heating 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) (2.4 g, 8.6 mmol), AIBN and a 5 mol excess of 3-methyl-1-butene (**12b**) at 80 °C for 10 h [98% conversion (GC)] to yield **1b** (2.5 g, 84%) which was sensitive to light. Lower reaction temperatures (65 °C) led to a purer crude product at a lower conversion (50%). Purification was carried out as mentioned above for **1a**. IR: 2969–2879, 1467–1138, 934, 884, 725, 672 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.96, 1.02 (2d, 3H each, $J=6.5$, CH_3), 1.28–1.35 [m, 1H, $CH(CH_3)_2$], 2.06–2.13, 2.29–2.36 (2m, 1H each, CHH), 3.26–3.36 (m, 1H, $CHCF_3$), 4.20–4.23 (m, 1H, CHI). ^{13}C NMR ($CDCl_3$): δ 19.5, 22.6 (2s, CH_3), 32.9 (s, CH_2), 35.3, 44.8 (2s, CH), 48.9 (sept, $J=28$, $CHCF_3$), 123.6, 123.9 (2q, $J=280$, CF_3). MS, *m/e* (relative intensity): 347 (<1), 333 (<1), 318 (<1), 221 (76), 181 (3), 159 (4), 153 (5), 73 (7), 69 (18). 55(15), 43(100). HRMS calcd. for $C_8H_{11}F_6^+$: 221.0765; found: 221.0765.

1,1,1-Trifluoro-4-iodo-2-(trifluoromethyl)nonane (1c) (nc)

1,1,1,3,3,3-Hexafluoroisopropyl iodide (**11a**) (8.4 g, 30.2 mmol), a spatula tip of AIBN and a 5 mol excess of 1-heptene (**12c**) were sealed in a heavy wall glass tube *in vacuo*. After the glass tube had been placed in a steel tube, the reaction mixture was heated at 65 °C for 6–8 h [complete conversion (GC)]. Work-up and purification as mentioned for **1a** yielded 11.0 g of **1c**

(97%). Compound **1c** was sensitive to light. IR: 2962–2862, 1469–1120, 930, 724, 672 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J=6.9$, CH_3), 1.23–1.36 [m, 4H, (C*H_2*$)_2CH_3$], 1.37–1.48, 1.50–1.60 (2m, 1H each, C*HH*–C_3H_7), 1.70–1.79, 1.86–1.95 (2m, 1H each, C*HH*–C_4H_9), 2.13, 2.27 (2ddd, 1H each, CH–C*HH*–CHI), 3.26–3.37 (m, 1H, $CHCF_3$), 4.08–4.15 (m, 1H, CHI). ^{13}C NMR ($CDCl_3$): δ 13.9 (s, CH_3), 22.4, 29.1, 30.9 (3s, CH_2), 33.4 (s, CHI), 35.0, 41.0 (2s, CH_2), 49.0 (sept, $J=28$, CH), 123.5, 123.7 (2q, $J=280$, CF_3). MS, *m/e* (relative intensity): 374 (<1), 319 (<1), 318 (<1), 249 (42), 207 (14), 167 (8), 57 (75), 43 (100). HRMS calcd. for $C_{10}H_{15}F_6^+$: 249.1078; found: 249.1074.

1,1,1-Trifluoro-4-iodo-2-methylnonane (**1d**) *(nc)*

Compound **1d** was prepared as described for **1c** by heating 1,1,1-trifluoroisopropyl iodide (**11b**) (1.1 g, 4.9 mmol), AIBN and a 5 mol excess of 1-heptene (**12c**) at 110 °C for 16 h [complete conversion (GC)] to yield **1d** (1.3 g, 82%) which was sensitive to light. The mixture of diastereomers (diastereomer **I** and **II** in the ratio of 41:59) were separated by distillation using a fractionating column (diastereomer **I**, b.p., 42–44 °C/7×10^{-2} mbar; diastereomer **II**, b.p., 42–45 °C/6×10^{-2} mbar). IR: 2959–2860, 1468–1016 cm^{-1}. The IR spectra of the diastereomer **1dI** and **1dII** were almost identical. ^1H NMR of **1dI** ($CDCl_3$)*: δ 0.88 (t, 3H, $J=6.9$, CH_2C*H_3*), 1.12 (d, 3H, $J=7.0$, CHC*H_3*), 1.19–1.36 [m, 4H, (C*H_2*$)_2CH_3$], 1.37–1.45, 1.47–1.58 (2m, 1H each, C*HH*–C_3H_7), 1.61–1.69, 1.75–1.84 (2m, 1H each, C*HH*–C_4H_9), 1.83–1.91, 2.05–2.12 (2ddd, 1H each, CH–C*HH*–CHI), 2.41–2.52 (m, 1H, $CHCF_3$), 4.11–4.18 (m, 1H, CHI). ^1H NMR of **1dII** ($CDCl_3$)*: δ 0.89 (t, 3H, $J=6.9$, CH_2C*H_3*), 1.05 (d, 3H, $J=6.9$, CHC*H_3*), 1.22–1.35 [m, 4H, (C*H_2*$)_2CH_3$], 1.36–1.45, 1.47–1.58 (2m, 1H each, C*HH*–C_3H_7), 1.49 (ddd, 1H, CH–C*H*H–CHI), 1.70–1.78, 1.88–1.97 (2m, 1H each, C*HH*–C_4H_9), 2.16 (ddd, 1H, CH–CH*H*–CHI), 2.45–2.59 (m, 1H, $CHCF_3$), 3.96–4.03 (m, 1H, CHI). ^{13}C NMR of **1dI** ($CDCl_3$): δ 13.8, 13.9 (2s, CH_3), 22.5, 29.0, 30.9 (3s, CH_2), 35.4 (s, CHI), 38.4 (q, $J=26$, *C*HCF_3), 40.5, 41.9 (2s, CH_2), 128.1 (q, $J=280$, CF_3). ^{13}C NMR of **1dII** ($CDCl_3$): δ 11.4, 13.9 (2s, CH_3), 22.5, 29.1, 31.0 (3s, CH_2), 34.8 (s, CHI), 39.0 (q, $J=27$, *C*HCF_3), 39.6, 41.4 (2s, CH_2), 128.1 (q, $J=279$, CF_3). MS of **1dI**, *m/e* (relative intensity): 320 (1), 264 (1), 195 (29), 153 (10), 57 (100), 55 (32). MS of **1dII**: 195 (24), 153 (7), 57 (100), 55 (28). HRMS calcd. for $C_{10}H_{18}F_3^+$: 195.1360; found: for **1dI**, 195.1363; for **1dII** 195.1362.

Reaction of 1,1,1-trifluoro-4-iodo-4-methyl-2-(trifluoromethyl)pentane (**1a**) *with sodium amide: synthesis of 2,2-dimethyl-1-(trifluoromethyl)cyclopropane carbonitrile* (**3a**) *(nc) and 2,2-dimethylcyclopropane carbonitrile* (**4a**)

To a stirred suspension of sodium amide (5 mol excess) in THF (30 ml) under nitrogen was added dropwise 1,1,1-trifluoro-4-iodo-4-methyl-2-

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*Assignments of peaks to protons were by SDF experiments.

(trifluoromethyl)pentane (**1a**) (2.0 g, 6.0 mmol). After stirring at room temperature for 2 d, the volatile contents were condensed in a trap cooled to −78 °C. The remaining product contained in the residue was collected by twice adding dry THF (30 ml), followed by short stirring and subsequent condensation in a trap (−78 °C). The contents of the traps were combined, the solvent was removed from the combined collected fractions under slightly reduced pressure, affording a mixture of **3a** and **4a** in the ratio of 1:4; total yield, 390 mg (*ca.* 60%). Purification and separation was undertaken by chromatography on silica gel using first CCl_4 for the removal of nonpolar impurities, followed by rapid change to $CHCl_3$. Whereas **4a** could be isolated analytically pure, the purification of **3a** was more difficult. **3a**: IR: $\nu_{CN} = 2246$ cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.34 (s, 3H, CH_3), 1.40 (d, 1H, $J = 6.0$, C*H*H), 1.44 (s, 3H, CH_3), 1.53 (d, 1H, $J = 5.9$, CH*H*). ^{13}C NMR ($CDCl_3$): δ 19.0, 24.7 (2s, CH_3), 26.3 (s, CH_2), 26.7 [s, *C*$(CH_3)_2$], 115.9 (s, CN), 123.4 (q, $J = 275$, CF_3)[†]. GC–MS, *m/e*: 163, 162, 148, 143, 136, 128, 122, 121, 102, 94, 69, 67, 61, 42. **4a**: IR: 3085–2874, 2238, 1448, 1383, 1126, 1033, 981 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (dd, 1H, $J = 5.1$, $J = 5.1$, H_{cyc}), 0.93 (dd, 1H, $J = 8.7$, $J = 4.9$, H_{cyc}), 1.10 (s, 3H, CH_3), 1.14 (dd, 1H, $J = 8.8$, $J = 5.4$, H_{cyc}), 1.26 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 10.1 (s, CH), 20.4 [s, *C*$(CH_3)_2$], 21.7 (s, CH_3), 21.9 (s, CH_2), 24.6 (s, CH_3), 120.6 (s, CN). MS, *m/e* (relative intensity): 95 (12), 94 (41), 80 (57), 68 (100), 67 (53), 55 (61), 53 (86), 41 (55), 39 (69) HRMS calcd. for $C_6H_8N^+$: 94.0657; found: 94.0656.

*Reaction of 1,1,1-trifluoro-4-iodo-5-methyl-2-(trifluoromethyl)hexane (**1b**) with sodium amide: synthesis of 2-(1-methylethyl)-1-(trifluoromethyl) cyclopropane carbonitrile (**3b**) (nc) and 2-(1-methylethyl)cyclopropane carbonitrile (**4b**) (nc)*

Synthesis, work-up and purification was performed as described for **3a** and **4a** by reacting 1,1,1-trifluoro-4-iodo-5-methyl-2-(trifluoromethyl)hexane (**1b**) (1 g, 2.9 mmol) with a 5 mol excess of sodium amide in THF (30 ml) under nitrogen at room temperature for 2 d to yield a mixture of **3b** and **4b** in the ratio of 1:4.5; total yield, 30%. From compound **4b** both isomers were formed in the ratio of 56:44. Neither separation of the isomers by chromatography nor an assignment of *cis* nor *trans* configuration, respectively, was possible. From cyclopropane **3b** only one isomer was found. **3b**: IR; $\nu_{CN} = 2234$ cm^{-1}. GC–MS, *m/e*: M^+ was missing, 162, 142, 122, 102, 77, 69, 56. **4b** (mixture of isomers): IR: 2962–2874, 2236, 1467, 1384, 1367, 1163, 1050 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.75–1.43 [m, 11H, H_{cyc}, $CH(CH_3)_2$]. ^{13}C NMR ($CDCl_3$): δ 1.8, 2.5 (2s, 2×*C*HCN), 13.1, 13.4 (2s, 2×CH_2), 21.2, 21.4, 21.6, 21.9 (4s, 2×2CH_3), 26.5, 29.2 (2s, 2×CH), 31.0, 32.2 [2s, 2×*C*$H(CH_3)_2$], 120.7, 122.0 (2s, 2×CN). GC–MS, *m/e*: M^+ was missing, 94, 81, 80, 67, 56.

[†] Value for *C*—CF_3 could not be observed, probably because of its very low intensity.

Reaction of 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)nonane (1c) with sodium amide: synthesis of 2-pentyl-1-(trifluoromethyl)cyclopropane carbonitrile (3c) (nc), trans-*1,1,1-trifluoro-2-(trifluoromethyl)-3-nonene (5) (nc) and* trans-*1,1,1-trifluoro-2-(trifluoromethyl)-4-nonene (6) (nc)*

To a 5 mol excess of sodium amide, placed in a heavy wall glass tube under nitrogen, was added THF (80 ml) and 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)nonane (**1c**) (6.0 g, 16.0 mmol). The glass tube was cooled in liquid nitrogen, sealed *in vacuo*, placed in a steel tube and heated at 85–90 °C for 16 h [conversion 86–95% (GC)]. Temperatures above 100 °C were avoided. The tube was allowed to cool to ambient temperature and was opened after being cooled in liquid nitrogen. The contents were cautiously hydrolyzed and filtered, the residue was washed several times with diethyl ether and the layers were separated. After the aqueous phase had been thoroughly extracted with ether, evaporation of the combined ethereal solutions under slightly reduced pressure gave an oily crude product which was condensed into a trap (−78 °C) to remove the last remains of a solid impurity. Total yield was 70–80% of a mixture of **5**, **6** and both isomers of **3c** in the ratio of 69:24:6:1. Both alkenes **5** and **6** could be separated as a mixture (b.p., 39–42 °C/18 mbar) from the higher boiling **3c**. Compound **3c** was mixed with larger amounts of **5** and **6**. However, **3c** could be obtained pure, if this fraction was chromatographed on silica gel and eluted first with CCl_4, followed by rapid change to $CHCl_3$. From **3c**, only the main isomer was isolated, its configuration was not determined. **3c**: IR: 2960–2860, 2246, 1460–1044, 785, 733 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J=6.8$, CH_3), 1.22 (dd, 1H, $J=7.0$, $J=6.1$, H_{cyc}), 1.28–1.41 [m, 4H, $(CH_2)_2CH_3$], 1.47–1.70 [m, 6H, 2H_{cyc}, $(CH_2)_2-C_3H_7$]. ^{13}C NMR ($CDCl_3$): δ 13.8 (s, CH_3), 18.5 (s, $CH_{2,cyc}$), 20.2 (q, $J=39$, CCF_3), 22.4 (s, CH_2), 24.0 (s, CH), 28.0, 29.8, 31.2 (3s, CH_2), 115.0 (s, CN), 123.1 (q, $J=274$, CF_3). MS, *m/e* (relative intensity): 205 (2), 204 (7), 203 (7), 201 (12), 190 (28), 176 (13), 162 (13), 148 (14), 136 (7), 122 (35), 69 (90), 56 (80), 55 (97), 43 (58), 41 (100). **5**: IR (mixture of **5** and **6** in the ratio of 80:20): 2963–2863, 1674, 1470–1095, 971, 911, 858, 730, 680 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J=6.9$, CH_3), 1.31 [m, 4H, $CH_2)_2CH_3$], 1.42 (quint, 2H, $CH_2-C_3H_7$), 2.12 (pqd, 2H, $J=7.2$, $J=1.3$, $=CH-CH_2$), 3.41 (m, 1H, $CHCF_3$), 5.37 (dd, 1H, $J=15.3$, $J=9.5$, $CH-CH=$), 5.93 (dt, 1H, $J=15.3$, $J=6.8$, $=CH-CH_2$). ^{13}C NMR ($CDCl_3$): δ 13.8 (s, CH_3), 22.5, 28.2, 31.2, 32,5 (4s, CH_2), 52.5 (sept, $J=29$, $CHCF_3$), 114.1 (s, $=CH$), 123.1 (q, $J=280$, CF_3), 143.8 (s, $=CH$). MS (mixture of **5** and **6** in the ratio of 80:20), *m/e* (relative intensity): 249 (3), 248 (23), 219 (3), 206 (4), 187 (9), 145 (4), 70 (75), 69 (22), 57 (48) 56 (100), 55 (77), 43 (43), 42 (67), 41 (99). HRMS (mixture of **5** and **6** in the ratio of 80:20) calcd. for $C_{10}H_{14}F_6^+$: 248.0999; found 248.0995. **6**: ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3H, $J=6.9$, CH_3), 1.31 [m, 4H, $(CH_2)_2CH_3$], 2.02 (pq, 2H, $J=7.1$, $=CH-CH_2$), 2.52 (t, 2H, $J=6.7$ Hz, $CH-CH_2-CH=$), 2.87 (m, 1H, $CHCF_3$), 5.37 (dt, 1H, $CH-CH_2-CH=$)*, 5.60 (dt, 1H, $J=15.2$,

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*Values of the coupling constants could not be determined because of superposition on the $CH-CH=$ signal of **5**.

$J=6.8$, $=CH-CH_2$). ^{13}C NMR ($CDCl_3$): δ 13.7 (s, CH_3), 22.2, 27.1, 31.4, 32.1 (4s, CH_2), 49.0 (sept, $J=27$, $CHCF_3$), 123.5 (s, $=CH$), 124.0 (q, $J=281$, CF_3), 135.5 (s, $=CH$).

Results and discussion

Cyclization of 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)alkanes (1)

We have attempted to synthesize trifluoromethyl-substituted cyclopropanes (**2**) from 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)alkanes (**1**) via a 1,3-elimination reaction of hydrogen iodide, using sodium amide as the base. The hexafluoroiodoalkanes **1a–c** investigated reacted smoothly with sodium amide, but in no case were the expected bis(trifluoromethyl)-substituted cyclopropanes **2a–c** obtained.

Reaction of **1a** or **1b** with sodium amide gave exclusively two cyclopropyl derivatives **3a**,**4a** or **3b**,**4b**, respectively. In **3a**,**b**, compared to cyclopropane **2**, one of the trifluoromethyl groups was converted to a cyano function and in **4a**,**b** one trifluoromethyl group was converted to a cyano function and the other replaced by a hydrogen.

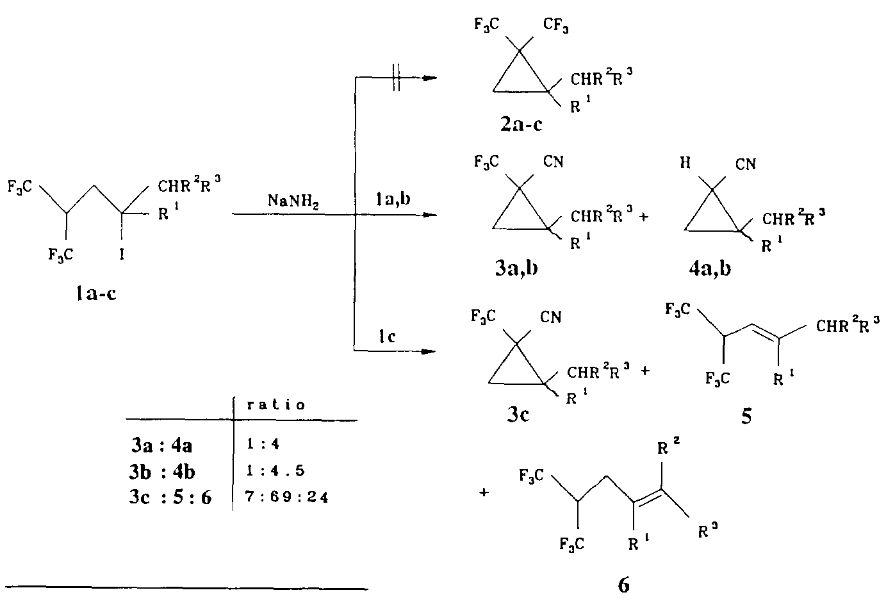
In contrast, treatment of 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)nonane (**1c**) with sodium amide resulted mainly in a 1,2-elimination of hydrogen iodide to form the isomeric olefins **5** and **6** (Scheme 1), with only a low yield of the cyclopropane derivative.

Evidently, the reaction of fluoroiodoalkanes **1a**,**b** with sodium amide begins with a 1,2-elimination of hydrogen fluoride, which is preferred to an elimination of hydrogen iodide. The difluoromethylene unit in **7a**,**b** thus obtained adds ammonia to form the 1-amino-1,1-difluoromethyl group, which is subsequently converted to the cyano group by dehydrofluorination to give **8a**,**b**. At the stage of the intermediate **8a**,**b**, further reaction yields either the cyclopropane derivative **3a**,**b** by a 1,3-elimination of hydrogen iodide, or the 2-aminodifluoromethyl-4-iodocarbonitrile **9a**,**b** by a 1,2-elimination of hydrogen fluoride and subsequent addition of ammonia. Excess sodium amide does not cause additional dehydrofluorination to the dicyano derivative, but a deprotonation of the amino function, elimination of difluoromethanimine, $HN=CF_2$, and formation of the carbanion **10a**,**b**, which finally expels the iodine forming the cyclopropyl carbonitrile **4a**,**b** (Scheme 2).

The base-induced elimination of difluoromethanimine could not be demonstrated experimentally. Difluoromethanimine itself is not stable and polymerizes under the reaction conditions used. However, it is known that treatment of trifluoromethylamine even with weak bases, e.g. triethylamine, results in the liberation of difluoromethanimine [5].

Although the detailed criteria for the preferred elimination of hydrogen fluoride or hydrogen iodide are still not understood, the proposed mechanism might be the most probable reaction pathway.

Attempts to cyclize hexafluoroiodoalkanes **1** with other bases were unsuccessful. Moderately strong bases were not capable of abstracting a



	ratio
3a : 4a	1 : 4
3b : 4b	1 : 4 . 5
3c : 5 : 6	7 : 69 : 24

	R^1	R^2	R^3
1a-4a	CH_3	H	H
1b-4b	H	CH_3	CH_3
1c,1d,2c, 3c,5,6	H	H	n-C_4H_9

Scheme 1.

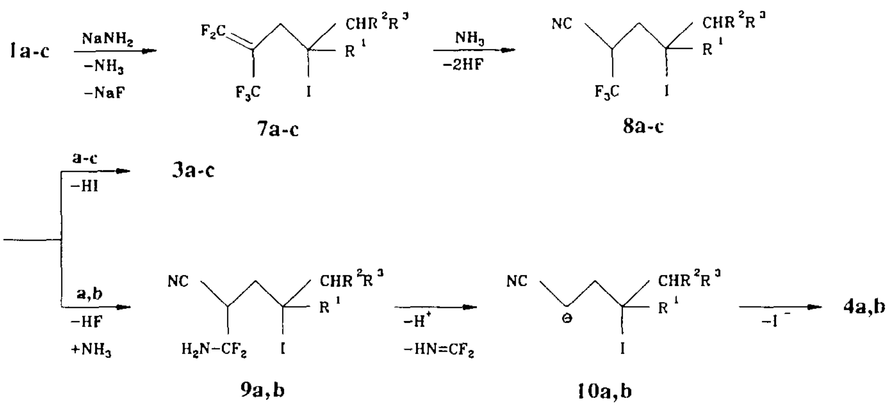
proton, and strong bases such as n-butyllithium, led to complete decomposition of the starting materials.

The behaviour of hexafluoroiodoalkanes 1 towards sodium amide, although possibly undesired, is an interesting novel reaction.

Synthesis of 1,1,1-trifluoro-4-iodo-2-(trifluoromethyl)alkanes (1)

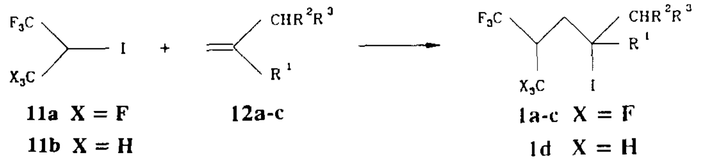
Hexafluoroiodoalkanes **1a–c** which were used in this study were prepared from 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) and olefins **12a–c**. Although the radical-initiated addition of perfluoroalkyl iodides to alkenes is well established and extensively studied [6, 7], and numerous investigations have been concerned with the improvement of the reaction conditions [7], little is known about the addition of partially fluorinated alkyl iodides, e.g. trifluoro- (**11b**) and hexafluoroisopropyl iodide (**11a**).

Indeed, 1,1,1-trifluoro- (**11b**) and 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) can be added to olefins in modest to good yields. While 1,1,1,3,3,3-hexafluoroisopropyl iodide (**11a**) reacted with 1-heptene (**12c**) under the same conditions reported for perfluoroisopropyl iodide (65 °C, 6 h, AIBN) [8], the addition of 1,1,1-trifluoroisopropyl iodide (**11b**) to **12c** needed more



	R^1	R^2	R^3
7a-10a	CH_3	H	H
7b-10b	H	CH_3	CH_3
7c,8c	H	H	n-C_4H_9

Scheme 2.



	R^1	R^2	R^3
12a	CH_3	H	H
12b	H	CH_3	CH_3
12c	H	H	n-C_4H_9

Scheme 3.

elevated temperatures (110 °C, 16 h, AIBN). Alkenes **12** with a methylene group gave hexafluoroiodoalkanes **1** in a clean reaction. Olefins with more substituted double bonds reacted with iodides **11** to give an increased number of products, due to the possibility of isomerization of the initially formed radical. Hence, the choice of suitable olefins is limited (Scheme 3).

References

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