Radical Addition of 2,2,2-Trifluoroethyl Iodide to Terminal Alkenes

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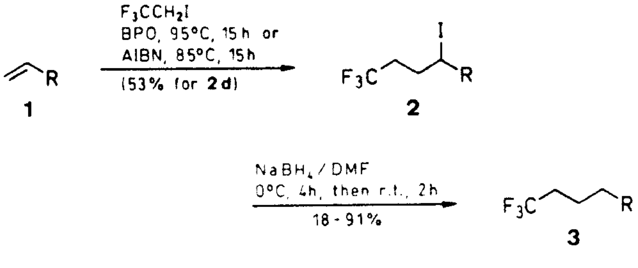
2,2,2-Trifluoroethyl iodide adds to terminal alkenes under free radical conditions in good yields if the radical initiator is added in successive portions to the reaction mixture. Reduction of the resulting secondary iodides with sodium borohydride gives the corresponding trifluoroethyl-substituted products in overall yields of 40–60%. The reaction seems to be restricted to vinyl double bonds.

The majority of methods for the preparation of compounds having a trifluoromethyl substituent have been designed to arrive at given target molecules.[1–9] Introduction of this group into olefins is mostly based on the use of trifluoromethyl iodide. This reactive compound adds to double bonds with classical radical initiators[10–14] or in the presence of metal carbonyls as catalysts.[15] Its introduction by nucleophilic substitution of halogen via trifluoromethyl copper as reagent, in bromo- and iodoalkanes, has also been reported; the latter compound has been prepared from trifluoromethyl iodide and metallic copper in hexamethylphosphoric triamide.[16]

The reagent, 2,2,2-trifluoroethyl iodide, is less expensive and, as a liquid, easier to handle. It is readily available from 2,2,2-trifluoroethanol.[17a] However, the formation of the 2,2,2-trifluoroethyl radical is expected to proceed slowly, since the trifluoromethyl group destabilizes adjacent radical centers.[17b] Its addition on the triple bond of an alkynol under free radical conditions has been reported to fail.[18] The cross-coupling with either *cis*- or *trans*-tributyl(2-phenylethenyl)stannane has been shown to proceed both to the (*trans*-4,4,4-trifluoro-1-butenyl)benzene in the presence of palladium(0) as catalyst in moderate yields (35 and 38%, respectively).[19] Finally, preliminary experiments in our laboratory have shown that this reagent did not react with double bonds in the presence of ruthenium(II) as a catalyst under conditions where the addition of carbon tetrachloride and chloroform proceeds in good yield[20] and also that its addition to double bonds failed in the presence of triiron dodecacarbonyl.[15]

In the present paper we report the successful addition of 2,2,2-trifluoroethyl iodide to vinyl double bonds with dibenzoyl peroxide (BPO) or 2,2′-azobisisobutyronitrile (AIBN) as initiators. In fact, conversion yields of 70% to iodide **2** were obtained when the initiator was added in four successive portions of 2.0 mol% each. After the first three additions the mixture was left to react for 3 hours and after the last portion for 6 hours. With BPO and AIBN the optimum reaction temperature was 95°C and 85°C, respectively. The iodide **2** was not isolated but directly reduced with sodium borohydride in dimethylformamide at 0°C.



1–3	R	1–3	R
a	Bu	**d**	n-$C_{12}H_{25}$
b	n-C_6H_{13}	**e**	$(CH_2)_{14}OAc$
c	n-C_8H_{17}	**f**	$(CH_2)_2CH=CH_2$

Both initiators gave similar yields. By using BPO the major byproduct was iodobenzene which is not reduced by borohydride and which is difficult to eliminate if the boiling point of the trifluoromethyl derivative is similar. By using AIBN as initiator the main side-product was that formed by the addition of isobutyronitrile to the double bond. The latter was difficult to eliminate from high boiling fluorinated products. Consequently, AIBN ought to be used for the synthesis of volatile compounds and BPO for those having higher boiling points.

As an example, the addition of 2,2,2-trifluoroethyl iodide to 1-tetradecene (**1d**) was studied in some detail. The resulting iodoalkane **2d** was isolated by distillation in 53% yield and 97.2% purity. On distillation, decomposition was observed, therefore, it was proposed that in further preparations isolation of intermediate **2** be omitted. Reduction of aliquots of the isolated **2d** in diethyl ether with aqueous hydrochloric acid and aqueous acetic acid gave important amounts of hydrogen iodide elimination products, therefore poor yields of **3d** were obtained. Good results were achieved by reduction of the iodoalkane **2d** with sodium borohydride according to Vol'pin et al.[21] where trifluorohexadecane (**3d**) was obtained in 91% yield.

Radical addition of 2,2,2-trifluoroethyl iodide seems to be restricted to vinyl double bonds. In our hands the following double bond types gave no detectable amounts of addition products: methylene double bond in 2-methyl-1-tetradecene; disubstituted *cis* and *trans* double bonds in 1,3- and 1,4-cyclohexadiene and *trans*-3-hexene. Reaction of 1,5-hexadiene (**1f**) gave as major product 1,1,1-trifluorooctene (**3f**) in 18% yield (59% GC) accompanied by only 6% (20% GC) of the bis-addition product, 1,1,1,10,10,10-hexafluorodecane (**4**), i.e., less than predicted on the basis of statistical considerations (34% and 43%, respectively). It is interesting to note that 1,5-hexadiene (**1f**) gave no cyclic derivatives confirming the findings of Brace et al. in the radical addition of perfluoropropyl iodide on this same compound (contrary to the analogous reaction of 1,6-heptadiene with perfluoroalkyl iodide).[22]

Finally, it seems that the presence of aliphatic hydroxy groups seriously affects the radical addition of 2,2,2-trifluoroethyl iodide. Under our standard conditions 10-undecen-1-ol gave only very low conversion (less than 6%). This problem is easy circumvented by the use of the corresponding acetates. The reaction between 15-hexadecenyl acetate (**1e**), obtained by the copper(I) bromide catalyzed coupling of the Grignard reagent of 1-bromo-10-undecene[23] and 5-iodo-1-pentyl acetate,[24] and 2,2,2-trifluoroethyl iodide gave 18,18,18-trifluoro-15-iodooctadecyl acetate (**2e**) in 70% conversion and the acetate **3e** of 99.7% purity was obtained in 42% yield.

Almost all the trifluoromethyl compounds synthesized failed to give correct and reproducible microanalyses. Both the carbon and hydrogen percentages were too low and they were systematically decreasing between successive analyses. The only compound that gave reproducible and correct results was 18,18,18-trifluorooctadecyl acetate (**3e**). 1,1,1-Trifluoro-4-iodohexadecane gave a just acceptable elemental analysis.

In mass spectrometry, all the trifluoroalkanes **3a**–**3d** gave the expected series of fragments $C_nH_{2n+1}^+$, $C_nH_{2n}^+$ and $C_nH_{2n-1}^+$. There is probably also a $CF_3C_nH_{2n}^+$ series of fragment but at low mass resolution it is not distinguishable from the $C_nH_{2n-1}^+$ series (the m/z = 69 correspond to both CF_3^+ and $C_5H_9^+$ fragments).

The ^1H NMR spectrum of 1,1,1-trifluorooctane in *d*-chloroform and in d_6-benzene measured at 200 MHz is shown in the Figure. The multiplet attributed to the methylene protons α to the trifluoromethyl group is complex due to the strong coupling between the protons of the aliphatic chain. Neither higher field (360 MHz) nor two dimensional coupling resolved (2D–J) experiments helped a detailed interpretation and attribution of all transitions was not possible. It is interesting to note the very pronounced solvent effect both for the structure of the multiplet and for the difference in the chemical shifts. Nevertheless, the examples depicted in the Figure are typical for all our products and may be used for diagnostic purposes.

Table 1. Physical Properties of the Synthesized Compounds

Product	Yield (%)	mp (°C) or bp (°C)/mbar	n_D^{20}[b]	d^{20}[c] (g cm^{-3})
2d	53	98–105/0.054	1.4656	1.235
3a	37	120–121	1.3681	0.945
3b	40	160–162	1.3863	0.936
3c	53[a]	90.5–92.5/20	1.3999	0.919
3d	36[a]	55–60/0.04	1.4186	0.914
3e	42[a]	40.5–41.5	–	–
3f	18	117–118.5	1.3712	0.971
4	6	156–158	1.3562	1.083

[a] BPO instead of AIBN, 95°C instead of 85°C.
[b] Confidence limit at the 95% confidence level Δ_{95} = 0.0005.
[c] Δ_{95} = 0.001 g cm^{-3}.

Table 2. Spectroscopic Data of the Synthesized Compounds

Product	IR (film) ν (cm^{-1})	^1H NMR (CDCl$_3$/TMS) δ, J (Hz)	^{13}C NMR (CDCl$_3$/TMS) δ, J (Hz)	MS (70 eV) m/z (%)
2d	2960, 2930, 1470, 1445, 1390, 1255, 1145, 840, 725	4.08 (tt, 1H, J = 4.7, 8.1), 2.60–1.60 (m, 6H), 1.27 (br s, 20H), 0.89 (t, 3H, J = 6.4)	126.82 (q, J = 276), 40.72, 35.65, 34.31 (q, J = 28), 32.88 (q, J = 2.9), 31.94, 29.65, 29.61, 29.55, 29.42, 29.34, 28.77, 22.68, 14.03	279 (M^+ − I, 4), 153 (5), 85 (26), 83 (6), 71 (47), 70 (4), 69 (16), 57 (100), 56 (11), 55 (42), 43 (92)
3a	2960, 2930, 1470, 1440, 1390, 1255, 1150, 840, 735	2.20–1.90 (m, 2H), 1.56 (m, 2H), 1.31 (br s, 8H), 0.90 (t, 3H, J = 6.6)	127.39 (q, J = 276), 33.82 (q, J = 28), 31.63, 28.89, 28.74, 22.59, 21.91 (q, J = 2.8), 14.01	168 (M^+, 1), 139 (6), 99 (12), 85 (6), 71 (29), 69 (8), 57 (100), 43 (99)
3b	2960, 2930, 1470, 1445, 1390, 1260, 1145, 840, 725	2.20–1.90 (m, 2H), 1.56 (m, 2H), 1.28 (br s, 12H), 0.89 (t, 3H, J = 6.5)	127.36 (q, J = 276), 33.80 (q, J = 28), 31.87, 29.35, 29.23, 28.75, 22.66, 21.88 (q, J = 2.8), 14.01	196 (M^+, 3), 167 (11), 85 (26), 71 (59), 57 (82), 43 (100)
3c	2960, 2930, 1470, 1445, 1390, 1255, 1145, 840, 725	2.20–1.90 (m, 2H), 1.55 (m, 2H), 1.28 (br s, 16H), 0.89 (t, 3H, J = 6.5)	127.35 (q, J = 276), 33.79 (q, J = 28), 31.92, 29.58, 29.38, 29.32, 29.20, 28.74, 22.68, 21.87 (q, J = 2.8), 14.04	224 (M^+, 2), 167 (4), 153 (7), 139 (7), 85 (30), 71 (45), 69 (9), 57 (100), 43 (99)
3d	2930, 2855, 1465, 1440, 1390, 1255, 1145, 840, 725	2.20–1.90 (m, 2H), 1.55 (m, 2H), 1.27 (br s, 24H), 0.89 (t, 3H, J = 6.5)	127.34 (q, J = 276), 33.80 (q, J = 28), 31.96, 29.68, 29.63, 29.58, 29.38, 29.20, 28.74, 22.70, 21.88 (q, J = 2.9), 14.05	280 (M^+, 2), 167 (7), 153 (9), 139 (5), 85 (34), 71 (63), 69 (11), 57 (100), 43 (68)
3e	2930, 2860, 1730, 1470, 1440, 1390, 1270, 1140, 1040, 840	4.06 (t, 2H, J = 6.7), 2.20–1.90 (m, 2H), 2.05 (s, 3H), 1.50 (m, 4H), 1.27 (br s, 26H)	170.97, 127.32 (q, J = 276), 64.58, 33.77 (q, J = 28), 29.62, 29.54, 29.33, 29.24, 29.15, 28.68, 25.93, 21.84 (q, J = 2.8), 20.82	367 (M^+ + 1, 2), 306 (2), 111 (6), 97 (17), 83 (35), 70 (20), 69 (37), 57 (29), 56 (25), 55 (49), 43 (100)
3f	3080, 2980, 2940, 2870, 1465, 1440, 1390, 1255, 1145, 1040, 915	5.81 (ddt, 1H, J = 17.1, 10.2, 6.7), 5.01 (ddt, 1H, J = 17.1, 2.0, 1.5), 4.96 (ddt, 1H, J = 10.2, 2.0, 1.1), 2.06 (m, 4H), 1.55 (m, 2H), 1.42 (m, 4H)	138.50, 127.31 (q, J = 276), 114.58, 33.76 (q, J = 28.4), 33.40, 28.47, 28.16, 21.75 (q, J = 2.9)	166 (M^+, 10), 97 (2), 83 (4), 70 (3), 69 (30), 56 (43), 55 (100), 42 (60), 41 (79)
4	2940, 2870, 1470, 1440, 1390, 1260, 1150, 990, 835	2.20–1.90 (m, 4H), 1.54 (m, 4H), 1.34 (m, 8H)	127.31 (q, J = 276), 33.76 (q, J = 28.4), 28.92, 28.61, 21.84 (q, J = 2.9)	230 (M^+ − HF, 3), 139 (18), 125 (5), 69 (21), 56 (9), 43 (100), 42 (12)

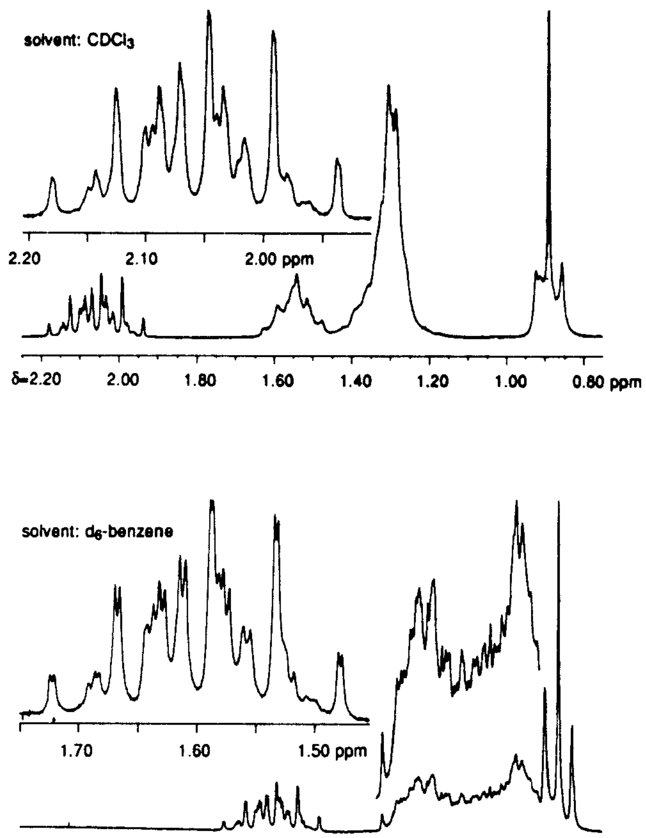


Figure. ^1H NMR spectra of 1,1,1-trifluorooctane (**3a**) in $CDCl_3$ and in d_6-benzene. The multiplet of the methylene in position α to the trifluoromethyl group is depicted in more detail.

Research grade 2,2,2-trifluoroethanol, TsCl, Et_3N, NaI, 1-hexene, 1,5-hexadiene, 1-octene, 1-decene, 1-tetradecene, tetrahydropyran, acetyl chloride, $ZnCl_2$, 10-undecen-1-ol, triphenylphosphine, NBS, anhydr. THF, 1,2-dibromoethane, $Fe_3(CO)_{12}$, $(Ph_3P)_3RuCl_2$, benzoyl peroxide (BPO), AIBN, $NaBH_4$ and DMF were purchased from Fluka (Buchs, Switzerland) and used as received. CH_2Cl_2 was refluxed then distilled over P_2O_5. 5-Iodopentyl acetate was prepared from tetrahydropyran and acetyl chloride in the presence of catalytic amount of $ZnCl_2$ and subsequent substitution of the chloride by NaI in acetone according to Williams et al.[24] 1-Bromo-10-undecene was prepared according to Chen et al.[23] by reacting 10-undecen-1-ol in CH_2Cl_2 with Ph_3P and (instead of CBr_4:) NBS.

GC analyses were performed on a Hewlett-Packard (model 5890A) instrument equipped with a fused silica macrobore capillary column (i.d. = 0.30 mm; length = 25.0 m) with crosslinked methylsilicone as stationary phase. Retention indexes I_T/°C were calculated from isothermal chromatograms. IR spectra were recorded on a Perkin-Elmer 684 spectrophotometer. Elemental analyses were made with an instrument from Leco Corp. (St. Joseph MI, USA; model CHN-900). ^1H NMR spectra were recorded at 200 MHz and ^{13}C NMR spectra were measured at 50 MHz on a Bruker AC-P 200 spectrometer. Safety glass autoclaves were purchased from Ciba-Geigy (Basel, Switzerland). The fractional distillations were made in a spaltrohr microcolumn model MMS 150 from Fischer AG (Bonn, Germany).

15-Hexadecenyl Acetate (1e)

In a 250 mL flask, Mg (3.65 g; 150 mmol) was covered with anhydr. THF (40 mL) at r.t. 1,2-dibromoethane (0.47 g; 2.5 mmol) was added (activation of the Mg) then, after evolution of ethylene had stopped, a solution of 1-bromo-10-undecene (28.0 g; 120 mmol) in THF (60 ml) was added dropwise in 30 min. The mixture was refluxed during 2 h then cooled to r.t. The Grignard reagent was diluted with THF (50 mL) and transferred into a dropping funnel. In a 500 mL flask, CuBr (0.14 g; 1.0 mmol) was added to a solution of 5-iodopentyl acetate (25.6 g; 100 mmol) in THF (50 mL) and cooled to − 30 °C and the Grignard reagent was added dropwise from the funnel over a 2 h period while maintaining the temperature between − 30 and − 40 °C. The mixture was stirred for a further 3 h at the same temperature, then aq sat. NH_4Cl (100 mL) was added to the cold mixture which was now allowed to warm to r.t. and transferred to a separatory funnel where it was treated a second time with aq sat. NH_4Cl (100 mL). The aqueous phase was extracted with Et_2O (2 × 100 mL) and the combined organic phase was dried (Na_2SO_4). The solvent was removed on a rotary evaporator, the residue was dissolved in hexane (40 mL) and filtered on silica gel column (100 g). With further hexane (200 mL) were eluted 5.2 g of a mixture of 1-undecene and 1,21-docosadiene (Würtz product). Elution with hexane/EtOAc (80:20) (200 mL) gave after evaporation of the solvent pure 15-hexadecenyl acetate (**1e**) as a colorless liquid: 22.1 g (78%) of 98% purity (GC. I_{220} = 1988); d^{20} = 0.877 g cm^{-3}; n_D^{20} = 1.4558.

$C_{18}H_{34}O_2$	calc.	C 76.54	H 12.13
(282.5)	found	76.51	11.74

Trifluoroalkanes 2d and 3a–f; General Procedure:

In a safety glass autoclave previously purged with Ar, alkene **1a–f** (50.0 mmol) was placed together with CF_3CH_2I (60.0 mmol) and the radical initiator (1.0 mmol). The autoclave was closed and placed in an oil bath heated to 85 °C for AIBN or 95 °C for BPO. After 3 h at the appropriate temperature, the autoclave was allowed to cool and opened. Another portion of catalyst (1.0 mmol) was added and the autoclave was heated again for 3 h. This operation was repeated once more for a 3 h period and finally, after the fourth portion of radical initiator had been added, for 6 h. The autoclave was then allowed to cool. In a 500 mL two-necked flask equipped with a reflux condenser and a dropping funnel, $NaBH_4$ (125 mmol) was dissolved in DMF (255 mL) and the flask was cooled to 0 °C (ice bath). At this temperature a solution of the crude iodoalkane in DMF (45 mL) was added slowly within 45 min. After 3 h at 0 °C, the mixture was allowed to warm to r.t. and was stirred for a further 2 h. The mixture was now cooled again to 0 °C and H_2O (100 mL) was added carefully to hydrolyze the excess borohydride. The mixture was transferred to a separatory funnel and extracted with pentane (100 mL). The aqueous phase was separated and the organic upper layer was washed with H_2O (2 × 100 mL). The combined aqueous phase was extracted with a further portion of pentane (50 mL). The combined pentane extract was dried (Na_2SO_4) and filtered on silica gel (30 g). From the fraction eluted by pentane the solvent was distilled off in a 10 cm Vigreux column. The residue was fractionated in a Fischer Spaltrohr microcolumn. Usually a second distillation was necessary to separate the starting alkene.

1,1,1-Trifluorooctane (**3a**):

From 1-hexene (4.21 g, 50.0 mmol), CF_3CH_2I (12.6 g, 60.0 mmol) and AIBN (4 × 0.16 g, 4 × 1.0 mmol). Reduction with $NaBH_4$ (4.73 g, 125 mmol) afforded, after two fractional distillations, 3.10 g (37%) of colorless trifluoroalkane **3a** showing a purity of 97.6%). (GC, I_{60} = 788).

1,1,1-Trifluorodecane (**3b**):

From 1-octene (5.61 g, 50.0 mmol), CF_3CH_2I (12.6 g, 60.0 mmol) and AIBN (4 × 0.16 g, 4 × 1.0 mmol). Reduction with $NaBH_4$ afforded, after two fractional distillations, 3.92 g (40%) of colorless trifluoroalkane **3b** with a purity of 95.6%. (GC, I_{80} = 983).

1,1,1-Trifluorododecane (**3c**):

From 1-decene (7.00 g, 50.0 mmol), CF_3CH_2I and BPO (3 × 0.32 g, 3 × 1.0 mmol) and heating for three times 2 h at 95 °C. Reduction with $NaBH_4$ (4.73 g, 125 mmol) afforded after Kugelrohr distillation 6.88 g (61%) of trifluoroalkane **3c** with a purity of 95%. Further purification was accomplished by adding the compound **3c** to a sat. solution of urea in MeOH (200 mL). The precipitate was filtered and washed with Et_2O (4 × 20 mL). The dry precipitate was then dissolved in H_2O (100 mL) and extracted with Et_2O (2 × 20 mL). The organic phase was dried (Na_2SO_4) and the solvent evaporated. The residue gave, after Kugelrohr distillation 5.88 g (53%) of trifluorododecane **3c** showing a 98.1% purity. (GC, I_{100} = 1181).

1,1,1-Trifluoro-4-iodohexadecane (**2d**):

From 1-tetradecene (**1d**; 9.82 g; 50.0 mmol), CF_3CH_2I (10.3 g, 52.6 mmol) and BPO (4 × 0.32 g, 4 × 1.0 mmol). Distillation at 98-105 °C/5.4 × 10^{-2} mbar afforded 10.85 g (53%) of compound **2d** with a 97.2% purity (GC, I_{220} = 1892).

$C_{16}H_{30}F_3I$ calc. C 47.30 H 7.44
(406.3) found 47.21 7.16

1,1,1-Trifluorohexadecane (**3d**):

From 1,1,1-trifluoro-4-iodohexadecane (**2d**; 4.06 g, 10.0 mmol) and $NaBH_4$ (0.95 g, 25.0 mmol) in DMF (60 mL). The crude mixture was purified by the formation of urea inclusion complexes (*vide supra*: **3c**). Kugelrohr distillation of the resulting oil at 55-60 °C/4 × 10^{-2} mbar gave 2.55 g (91%) of trifluorohexadecane **3d** with a 97% purity (GC, I_{160} = 1562).

18,18,18-Trifluorooctadecyl Acetate (**3e**):

From 15-hexadecenyl acetate (**1e**; 42.4 g, 150 mmol), CF_3CH_2I (37.8 g, 180 mmol) and BPO (4 × 0.97 g, 4 × 3.0 mmol). Reduction with $NaBH_4$ (14.2 g, 375 mmol) in DMF (765 + 135 mL) afforded after two recrystallizations (94% weight EtOH) 23.1 g (42%) of pure acetate **3e** with a 99.7% purity (GC, I_{240} = 2137) and a mp of 40.5-41.5°C.

$C_{20}H_{37}F_3O_2$ calc. C 65.54 H 10.18
(366.5) found 65.50 10.31

1,1,1-Trifluoro-7-octene (**3f**) *and 1,1,1,10,10,10-hexafluorodecane* (**4**):

From 1,5-hexadiene (**1f**; 4.11 g, 50.0 mmol), CF_3CH_2I and AIBN (4 × 0.16 g, 4 × 1.0 mmol). Reduction with $NaBH_4$ afforded, after three fractional distillations, 1.49 g (18%) of alkene **3f** with a purity of 97% (GC, I_{60} = 775) and 0.76 g (6%) of alkane **4** showing a 93% purity (GC, I_{100} = 974).

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