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Trifluoroethylation of olefins with trichlorotrifluoroethane

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Abstract

1,1,1-Trichlorotrifluoroethane was added to seven different olefins using a redox system, giving adducts having the CF_3CCl_2–C–CCl– subunit. Selective addition to the exocyclic double bond in limonene was observed. The adducts were dechlorinated by catalytic reduction or with tri-n-butyltin hydride. The two-step sequence thus provided a method for appending the trifluoroethyl group (CF_3CH_2–) to olefins.

Introduction

Chlorofluorocarbons (CFCs) of the methane and ethane series are becoming increasingly useful reagents for the construction of more elaborate organic compounds containing fluorine. The activation of CFCs by copper salts, in particular, has played a significant role in the utilization of CFCs for this purpose. Assher and Vofsi [1] found that the addition of CCl_4 to olefins was catalyzed by Cu^I salts, and, via rapid chlorine-atom transfer, oligomerization and hydrogen-atom abstraction by the intermediate radicals ($CCl_3-C-C\cdot$) were suppressed. Later, Burton and Kehoe [2] extended this chemistry to the reaction of CF_3CCl_3 and $CF_2ClCFCl_2$ with 1-octene. More recently, CF_3CCl_3–olefin addition products were effectively utilized as key intermediates in the synthesis of a variety of heterocycles [3].

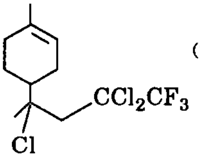
The possibility of utilizing the CF_3CCl_3–olefin adducts as a source of hydrofluorocarbons (HFCs) was of interest, due to the potential use of HFCs as replacements for CFCs in a variety of applications. In principle, three general procedures with broad scope and scale-up potential are possible for the preparation of hydrofluorocarbons from the CFC–olefin adducts: (a) total Cl–F exchange; (b) partial Cl–F exchange followed by reductive dechlorination; and (c) reductive dechlorination without exchange. In this paper a variant of (c) is reported, namely the addition of CF_3CCl_3 to olefins, followed by reductive dechlorination to give trifluoromethyl aliphatic compounds. The two-step procedure thus adds a two-carbon unit (CF_3CH_2-) to an olefin.

Results and discussion

Table 1 shows the results of the addition of CF_3CCl_3 to olefins **1–7** by Burton and Kehoe's method, which consists of heating the olefin and chlo-

TABLE 1

Addition of CF_3CCl_3 to olefins

Olefin	Product	Yield (%)	Boiling point (°C/mmHg)
isobutylene (**1**)	$CF_3CCl_2CH_2CCl(CH_3)_2$ (**1a**)	70	78–82/52
1-butene (**2**)	$CF_3CCl_2CH_2CHClCH_2CH_3$ (**2a**)	62	89–91/48
cis-2-butene (**3**)	$CF_3CCl_2CH(CH_3)CHClCH_3$ (**3a**)	55	77–85/48
1-hexene (**4**)	$CF_3CCl_2CH_2CHCl(CH_2)_3CH_3$ (**4a**)	63	88–89/15
$H_2C{=}C(CF_3)CH_3$ (**5**)	$CF_3CCl_2CH_2CCl(CH_3)CF_3$ (**5a**)	40	72/60
$(CH_3)_2CHCH{=}CH_2$ (**6**)	$CF_3CCl_2CH_2CHClCH(CH_3)_2$ (**6a**)	58	75–76/20
limonene (**7**)	 (**7a**)	65	88–91/0.3

rofluorocarbon in t-butanol in the presence of CuCl–$CuCl_2$ and ethanolamine at *c.* 85 °C. Earlier reports [2] indicated that the reaction was sensitive to the amine co-catalyst. In confirmation of this finding, adduct **3a** was formed in 45% distilled yield using *N*,*N*-dimethylethylenediamine as the co-catalyst, compared to a 55% yield with ethanolamine. However, the same reaction using ethylenediamine was extremely slow. Sensitivity to the amine is most likely a manifestation of steric and electronic factors affecting the ability of the copper–amine complex to produce the $CF_3CCl_2\cdot$ radical or form copper(III) oxidative insertion complexes [4]. Diastereomer ratios in the reaction of **3** with CF_3CCl_3 using the two different amines were different [5.3:1 (*N*,*N*-dimethylethylenediamine) versus 4.4–4.6:1 (ethanolamine)] and higher than the diastereomer ratios (3:1) observed [1] in CCl_4 additions to this olefin. The dependence of the isomer ratios on the amine is consistent with chlorine-atom transfer from a Cu^{II}–amine complex to the intermediate $CF_3CCl_2CH(CH_3)CH(CH_3)\cdot$ radical since the two Cu complexes would have slightly different steric preferences.

At normal reaction temperatures (85–95 °C), pressures generated using the isomeric butenes were generally less than 50 psig, and the reactions were therefore conveniently run in glass pressure vessels. The reaction proceeded well for terminal olefins, but was found to be comparatively sluggish for the internal olefin, *cis*-2-butene. In order to determine the potential selectivity that might be realized in a competitive experiment, CF_3CCl_3 was reacted together with limonene. The intermediate $CF_3CCl_2\cdot$ radical could add to either the endocyclic or exocyclic double bond, resulting in a tertiary carbon radical. In the event, however, only addition to the disubstituted exocyclic double bond was observed. Previously, Or *et al.* [5] concluded that, in the CuCl-catalyzed addition of CCl_4 to four different olefins in acetonitrile solutions at 110 °C, the olefin played no role in the rate-determining step.

Electron-deficient olefins also reacted sluggishly. The reaction of CF_3CCl_3 with 3,3,3-trifluoropropene, for example, failed to give the expected addition product, but **1a** was formed instead. Similarly, the more reactive CCl_4 did not provide $CF_3CHClCH_2CCl_3$ [6], but rather $CCl_3CH_2CCl(CH_3)_2$ as the major product (identical with an authentic sample prepared from CCl_4 and isobutylene) which presumably arose via dehydration of the t-butanol solvent (as did **1a**). The reaction with 2-trifluoromethylpropene (**5**), however, was successful, in contrast with the reported failure of the benzoyl peroxide-catalyzed addition of CBr_2F_2 to this olefin [7].

Adducts **1a–7a** displayed characteristic strong IR bands near 1255, 1205 and 1180 cm^{-1}.

The reduction of adducts **1a–6a** was then studied. Catalytic reduction was desirable for reasons of scale-up potential and economy.

Although catalytic reduction of organic halides in the presence of base is well established, few catalytic reductive dechlorinations have been reported for hydrofluorochlorocarbons of this type under *neutral* conditions. Catalytic reductive defluorinations, on the other hand, have been observed for simple alkyl fluorides (e.g. isopropyl fluoride) at *c.* 250 °C over Pd/C [8]. When adducts **1a–3a** were passed over Pd/C or Pt/C at *c.* 250 °C in a flow system at atmospheric pressure, the corresponding trifluoromethyl compounds were obtained in good yield (Table 2). The reductions were moderately exothermic (20–30 °C) and surprisingly clean, in view of the potential defluorination which might have occurred under these conditions. With this system, the reactor effluent was initially greater than 90% of the desired hydrofluorocarbon, but the crude product was generally not above 85% with the remainder being primarily monochloro and dichloro compounds. Reductions were effected under much milder conditions (50–80 °C) using neat tributyltin hydride. Alternatively, the procedure of Corey and Suggs [9] was modified with good results. Tributyltin hydride (1 equiv.) was allowed to react with the adduct,

TABLE 2

Reduction of adducts **1a–6a**

Adduct	Product	Yield (%)	Method[a]
1a	$CF_3(CH_2)_2CH(CH_3)_2$ (**1b**)	57	A
1a	$CF_3(CH_2)_2CH(CH_3)_2$ (**1b**)	73	B
2a	$CF_3(CH_2)_4CH_3$ (**2b**)	67	C
3a	$CF_3CH_2CH(CH_3)CH_2CH_3$ (**3b**)	65	C
4a	$CF_3(CH_2)_6CH_3$ (**4b**)	68	D
5a	$CF_3(CH_2)_2CH(CF_3)CH_3$ (**5b**)	79	B
6a	$CF_3(CH_2)_3CH(CH_3)_2$ (**6b**)	55	D

[a] Method A: H_2, 0.5% Pt/C; method B: $(Bu^n)_3SnH$; method C: H_2, 1% Pd/C; and method D: $(Bu^n)_3SnH/NaBH_4$.

followed by the addition of ethanol and 1 equiv. $NaBH_4$ to regenerate the tin hydride. The process was repeated to complete the reduction of the trichloro adduct.

Overall yields for the two-step sequence were moderate (32–51%) although the experimental procedures are simple. The process is a useful alternative to the reaction of a carboxylic acid with SF_4 where the appropriate acid, equipment or experience in handling SF_4/HF is lacking. With the appropriate choice of reducing agent, the procedure appears to be both a general and versatile method* for appending the trifluoroethyl group to olefins.

Experimental

1,1,1-Trichlorotrifluoroethane was obtained from a commercial bulk sample (93% purity) and was used without further purification for **1a–6a**; 99% pure material was used for **7a**. Except for **7a**, yields of distilled products were calculated on the basis of limiting reagent added (usually olefin); conversions were not determined. A 300 ml glass pressure bottle (Andrews Glass Co.) equipped with a magnetic stir bar, pressure gauge and needle valve was used for the olefin additions. ^1H NMR spectra were recorded in $CDCl_3$ and ^{19}F NMR spectra in the same solvent with internal $CFCl_3$ using a Varian EM-390 spectrometer. ^{19}F NMR data are reported as ppm upfield (negative values) from $CFCl_3$.

2,2,4-Trichloro-1,1,1-trifluoro-4-methylpentane (1a)

A 300 ml glass pressure bottle was charged with 0.5 g catalyst (50:50 weight mixture of CuCl and $CuCl_2 \cdot H_2O$), 75 ml t-butanol, 3.0 g ethanolamine and 50 g CF_3CCl_3, and evacuated briefly. Isobutylene (14.6 g) was then added, and the contents heated in an oil bath to 85 °C for 2.5 d. At this time the pressure in the vessel was 0 psig. The cooled reaction mixture was poured into 200 ml water and the lower organic layer separated. The aqueous layer was extracted with 2×50 ml CH_2Cl_2, and the combined organic layers washed with 2×100 ml water. After drying (Na_2SO_4), the volatiles were removed by rotary evaporation. Vacuum distillation (6 in. packed column) of the residue gave 44.4 g (70% yield) of the title compound (98% purity); b.p., 78–82 °C/52 mmHg. ^1H NMR δ: 2.9 (s, 2H); and 1.9 (s, 6H) ppm. ^{19}F NMR δ: -82.0 (s) ppm. Anal.: Calcd. for $C_6H_8Cl_3F_3$: C, 29.60; H, 3.31%. Found: C, 29.59; H, 3.20%.

1,1,1-Trifluoro-4-methylpentane (1b)

The hydrogenation reactor used in this example was comprised of a 1 in. glass tube having an internal volume of *c*. 100 cm^3. Heat was applied by means of electrical heating tape wrapped around the outside of the tube.

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*Using similar methodology, i.e. addition of a halocarbon to an olefin followed by reduction, $-CF_2H$ [10], $-CF_2Br$ [10], $-CF_3$ [11], $-CF{=}CF_2$ [12] and $-CF_2Cl$ [13] groups have been appended to olefins.

The tube was mounted vertically and packed with small glass rings in the lower one-third of the tube, followed by 25 cm^3 of a mixture of 0.5% Pt on carbon (4–8 mesh, 10 cm^3) and 3 mm glass helices (15 cm^3), and the remainder of the tube packed with glass rings. The organic material (**1a**) was fed into the top of the reactor by means of a syringe pump at the rate of 1 cm^3 every 9 min. The reactor was heated first with N_2 purge to *c.* 230 °C near the center of the reactor (skin temperature) and then with H_2. The reactor exit was connected to two Dry-Ice/acetone baths and a water scrubber. The organic material (total 32.6 g) was fed into the reactor, which increased the temperature to *c.* 250 °C, being fairly constant at 250 °C thereafter. The hydrogen flow rate was adjusted as necessary after the organic flow was started to maintain a slow bubble rate in the water scrubber in order to ensure that an excess of hydrogen was present. After all the organic material had been added, heating was continued at 250 °C with H_2 flow for 0.5 h and with N_2 flow for 0.5 h. After warming the cold traps to room temperature, 14.9 g of crude product was collected, which was shown by GC methods to be 87% 1,1,1-trifluoro-4-methylpentane and *c.* 5% under-reduced (monochlorinated) material. Distillation gave 10.6 g (57% yield) of **1b** (99% purity); b.p., 65–67 °C (lit. [14] b.p., 66.3 °C). ^{1}H NMR δ: 1.7–2.3 (m, 2H); 1.2–2.3 (m, 3H); and 0.93 (d, 6H) ppm. ^{19}F NMR δ: -67.7 (t, $J=11$ Hz) ppm.

*2,2,4-Trichloro-1,1,1-trifluorohexane (**2a**)*

A glass pressure bottle was charged with 1.0 g 1:1 (wt.) $CuCl/CuCl_2 \cdot 2H_2O$, 3.0 g ethanolamine, 55 g CF_3CCl_3 and 75 ml t-butanol, and evacuated briefly. 1-Butene (16.7 g) was then added and the mixture stirred and heated to 85 °C for 15 h, at which time the pressure in the vessel was 0 psig. Work-up as described for **1a** gave 63.5 g crude product, which on vacuum distillation (47–48 mmHg) gave 44.0 g (62% yield) of 97.5% pure 2,2,4-trichloro-1,1,1-trifluorohexane; b.p., 82–91 °C (mainly 89–91 °C). ^{1}H NMR δ: 4.33 (m, 1H); 2.77 (apparent triplet, 2H); 1.7–2.2 (m, 2H); and 1.1 (t, 3H) ppm. ^{19}F NMR δ: -81 (s) ppm. Anal.: Calcd. for $C_6H_8Cl_3F_3$: C, 29.60; H, 3.31%. Found: C, 29.50; H, 3.26%.

*1,1,1-Trifluorohexane (**2b**)*

The reactor in this example was similar to that described for **1b**, except that 10 cm^3 of 1% palladium on (4–8 mesh) carbon was used instead of platinum on carbon, and the temperature was measured internally using a thermocouple in the center of the catalyst bed. A total of 40.7 g of **2a** was passed over the bed with hydrogen gas over a period of 4.67 h. The temperature inside the reactor was 220 °C before the organic flow was started, but increased to 244 °C with organic material and hydrogen gas passing over the catalyst bed. The crude material consisted of 86% of the desired HFC and *c.* 12% under-reduced material. Distillation gave 15.6 g (67% yield) 1,1,1-trifluorohexane; b.p., 74–76 °C (lit. [15] b.p., 70 °C). ^{19}F NMR δ: -67.8 (t, $J=11$ Hz) ppm. The infrared spectrum of the product was identical to that of 1,1,1-trifluorohexane made by the reaction of SF_4 with hexanoic acid.

*2,2,4-Trichloro-1,1,1-trifluoro-3-methylpentane (**3a**)*

In a manner analogous to the preparation of **1a**, **3a** was prepared by heating a mixture of CF_3CCl_3 (80.5 g), 75 ml t-butanol, 3 g ethanolamine, 1.0 g CuCl and *cis*-2-butene (13.0 g) for 17 h at *c.* 90 °C. The product (31.1 g; 55% yield; b.p., 77–85 °C/48 mmHg) was comprised of a mixture of diastereomers in a ratio of *c.* 4.6:1. ^{19}F NMR δ: major isomer at -76 ppm and minor isomer at -75.7 ppm. Apparent ^1H NMR of major isomer δ: 4.8 (dq, 1H); 3.0 (dq, 1H); 1.6 (d, 3H); and 1.4 (d, 3H) ppm. Anal.: Calcd. for $C_6H_8Cl_3F_3$: C, 29.60; H, 3.31%. Found: C, 29.31; H, 3.33%.

*1,1,1-Trifluoro-3-methylpentane (**3b**)*

In a manner analogous to **1b**, **3a** (55.8 g) was hydrogenated over 1% Pd on carbon at 241–248 °C (H_2 flow rate at 140 cm^3 min^{-1} and organic flow rate at 8.8 g h^{-1}) to give 30.8 crude product which was comprised of 80% 1,1,1-trifluoro-3-methylpentane and 13% under-reduced material (but essentially no trichlorinated material). Distillation gave 20.8 g of product; b.p., 66–68 °C (lit. [14] b.p., 62.5 °C) (65% yield). ^1H NMR δ: 1.7–2.3 (m, 3H); 1.15–1.7 (m, 2H); and 0.8–1.15 (m, 6H) ppm. ^{19}F NMR δ: -64.5 (t, $J=12$ Hz) ppm.

*2,2,4-Trichloro-1,1,1-trifluoro-octane (**4a**)*

A 300 ml glass pressure bottle was charged with 75 ml t-butanol, 1 g CuCl, 3 g ethanolamine, 50 g CF_3CCl_3 and 16.6 g 1-hexene. After evacuating briefly, the mixture was stirred and heated to 95–100 °C for 21 h. Work-up as described for **1a** gave 54.8 g crude material, which on distillation at 15 mmHg gave 33.7 g 96% pure 2,2,4-trichloro-1,1,1-trifluoro-octane; b.p., 88–88.5 °C (63% yield). ^1H NMR δ: 4.35 (m, 1H); 2.77 (overlapping dd giving apparent t, 2H); 1.7–2.1 (m, 2H); 1.15–1.7 (m, 4H); and 0.8–1.15 (distorted t, 3H) ppm. ^{19}F NMR δ: -80.7 ppm. Anal.: Calcd. for $C_8H_{12}Cl_3F_3$: C, 35.39; H, 4.45%. Found: C, 35.35; H, 4.55%.

*1,1,1-Trifluoro-octane (**4b**)*

Compound **4b** was prepared (68% yield from **4a**) in an analogous fashion as described for **6b** below; b.p., 120–123 °C. ^1H NMR δ: 1.7–2.3 (m, 2H); 1.1–1.7 (m, 10H); 0.8–1.0 (m, 3H) ppm. ^{19}F NMR δ: -67.7 (t) ppm.

*2,2,4-Trichloro-1,1,1,5,5,5-hexafluoro-4-methylpentane (**5a**)*

In the usual manner, 75 ml Bu^tOH, 82 g CF_3CCl_3, 1 g CuCl, 3 g ethanolamine and 19.1 g 2-trifluoromethylpropene were combined and heated to 90–95 °C for 22 h. Distillation of crude product gave 20.6 g (40% yield) of **5a**; b.p., 61–74 °C (mainly 71–73 °C) at 60 mmHg. ^1H NMR δ: 2.07 (s, 3H); 3.10 (d, $J=15$ Hz); 2.85 (d, $J=15$ Hz) ppm. ^{19}F NMR δ: -82.0 (two CF_3 singlets separated by 6 Hz). Anal.: Calcd. for $C_6H_5Cl_3F_6$: C, 24.23; H, 1.69%. Found: C, 24.17; H, 1.64%.

*1,1,1,5,5,5-Hexafluoro-4-methylpentane (**5b**)*

A 100 ml flask fitted with a thermometer, addition funnel and condenser was flushed with N_2 and charged with 105 mg AIBN, 51.5 (177 mmol) tri-n-butyltin hydride and heated to 55 °C. The addition of **5a** (16.6 g, 56 mmol) to the tin hydride was exothermic and controlled (1 h) to maintain a temperature of 70–80 °C. Heating was continued for 0.5 h. The mixture was cooled, the condenser was exchanged for a distillation column and volatiles were distilled into a −78 °C trap at 15 mmHg up to a pot temperature of 55 °C, affording 8.5 g (79% yield) of 95% pure **5b**. Redistillation gave 98% pure material; b.p., 84–86 °C/745 mmHg (lit. [16] b.p., 80 °C). ^{1}H NMR δ: 1.4–2.5 (m, 5H); 1.15 (d, $J=7$ Hz, 3H) ppm. ^{19}F NMR δ: −67.9 (t, $J=11$ Hz, 3F); −74.3 (d, $J=9$ Hz, 3F) ppm.

*2,2,4-Trichloro-1,1,1-trifluoro-5-methylhexane (**6a**)*

t-Butanol (75 ml), 0.5 g of a 1:1 mixture of CuCl and $CuCl_2 \cdot H_2O$, 3 g ethanolamine, 60 g CF_3CCl_3 and 10.6 g 3-methyl-1-butene were heated to 75–90 °C for 20 h. Work-up and distillation afforded 22.6 g (58% yield) of **6a**; b.p., 70–80 °C (mainly 75 °C) at 20 mmHg of 94% purity. Redistillation provided 98% pure material; b.p., 75–76 °C/20 mmHg (lit. [17] b.p., 40 °C/0.5–0.6 mmHg). ^{1}H NMR δ: 4.34 (m, 1H); 2.72 (d, 2H); 1.9–2.3 (m, 1H); 1.06 (t, (overlapping doublets) 6H) ppm. ^{19}F NMR δ: −80.7 (s) ppm. Anal.: Calcd. for $C_7H_{10}Cl_3F_3$: C, 32.65; H, 3.91%. Found: C, 32.48; H, 4.22%.

*1,1,1-Trifluoro-5-methylhexane (**6b**)*

In a manner similar to that described for **5b**, 18.1 g (0.070 mol) **6a** was added to 22.9 g (0.079 mol) tri-n-butyltin hydride in a 250 ml flask (initially at 50 °C) over 35 min (temperature 70 °C during the addition). The mixture was cooled to room temperature (water bath) and 100 ml anhydrous EtOH was added, followed by 1.5 g $NaBH_4$. After gas evolution had subsided, an additional 1.5 g $NaBH_4$ was added and the mixture refluxed for 0.75 h. The process of cooling, adding $NaBH_4$ and refluxing was repeated until the reaction was judged complete by GC methods (total 7 g $NaBH_4$). The cooled reaction mixture was poured into 100 ml water containing 20 ml CH_2Cl_2, and the aqueous layer extracted twice with 20 ml CH_2Cl_2. The combined organic layers were washed three times with 30 ml water, dried (Na_2SO_4) and distilled to give 5.9 g (55% yield) of **6b**; b.p., 90–91 °C. ^{1}H NMR δ: 1.7–2.3 (m, 2H); 1.1–1.7 (m, 5H); 0.9 (d, $J=6$ Hz, 6H) ppm. ^{19}F NMR δ: −67.4 (t, $J=11$ Hz) ppm. The pot residue was 95% pure tri-n-butyltin chloride by GC analysis.

*CF_3CCl_3-limonene adduct (**7a**)*

A mixture of 25 ml (39.5 g, 0.211 mol) CF_3CCl_3, 75 ml Bu^{t}OH, 0.5 g of a 1:1 mixture of $CuCl/CuCl_2 \cdot 2H_2O$, 3 g ethanolamine and 29.4 g (0.216 mol) of (R)−(+)−limonene were heated to 62–73 °C for 5 d. Work-up gave 56.9 g crude material. Distillation gave 6.7 g limonene and 34.9 g material of 95% purity; b.p., 78–100 °C/0.15–0.2 mmHg (65% yield based on unrecovered limonene). Some decomposition occurred in the pot during the distillation but, based on the GC analysis of the crude product before distillation and the NMR spectrum of the pot residue, addition to the endocyclic double bond did not occur. Redistillation at 0.3 mmHg gave an analytically pure sample of **7a**; b.p., 88–91 °C. ^1H NMR δ: 5.4 (bs, 1H); 2.96 and 2.83 (1H each, diastereotopic CH_2CCl_2); 1.1–2.2 (m, 13H) ppm. ^{19}F NMR δ: -81.7 (s) ppm. Anal.: Calcd. for $C_{12}H_{16}Cl_3F_3$: C, 44.54; H, 4.98%. Found: C, 44.32; H, 5.01%.

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