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1,3-Dichloro-4,4,4-trifluorobut-2-ene as a 4-carbon building block containing a trifluoromethyl group

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Abstract

The preparation, isomerization, and utility of $CF_3CCl{=}CHCH_2Cl$ as a 4-carbon reagent for the incorporation of a trifluoromethyl group is described. The regiochemistry observed for charged intermediates derived from $CF_3CCl{=}CHCH_2Cl$ was consistent with MNDO calculated partial charges at C-1 and C-3. The anion-stabilizing and cation-destabilizing effects of the trifluoromethyl group were dominant.

Keywords: 1,3-Dichloro-4,4,4-trifluorobut-2-ene; Isomerization; Trifluoromethyl

1. Introduction

The incorporation of trifluoromethyl groups as a means of altering the biological activity of organic compounds is well established [1,2]. Direct methods, involving CF_3 transfer reagents [3–6] have been developed for this purpose, and "building blocks" of 3, 4, or more carbons containing a trifluoromethyl group continue to be developed [7–12].

Petrov [13] described the synthesis of $CF_3CF{=}CHCH_2Cl$ from the reaction of chlorosulfonic acid with pentafluorobutene ($C_2F_5CH{=}CH_2$) and its use in the preparation of CF_3-$CF{=}CHCH_2X$ compounds (X = halogens, $-OCF(CF_3)_2$). The related $CF_3CCl{=}CHCH_2Cl$ (**1**), in contrast, was reported as an intermediate in the preparation of $C_2F_5CH{=}CH_2$ [14]. A few simple derivatives via S_N2 displacement of the allylic chlorine, similar to those derived from Petrov's $R_fCF{=}CHCH_2Cl$ were also reported. Since **1** was readily prepared from relatively inexpensive starting materials, and appeared to have suitable functionality which would offer synthetic versatility, a more detailed study was undertaken to evaluate **1** as a 4-carbon reagent for the incorporation of a trifluoromethyl group.

2. Results and discussion

Compound **1** was prepared by the thermal dehydrochlorination of $CF_3CCl_2CH_2CH_2Cl$ (**2**), which in turn, was made by the addition of CF_3CCl_3 to ethylene [14]. While vapor phase dehydrochlorination

$$CF_3CCl_3 + CH_2{=}CH_2 \rightarrow \underset{(2)}{CF_3CCl_2CH_2CH_2Cl} \rightarrow \underset{(1)}{CF_3CCl{=}CHCH_2Cl}$$

of **2** over Cr_2O_3 at 285 °C cleanly produced **1**, liquid phase dehydrochlorination in the presence of a variety of bases was more complex, producing varying amounts of three dehydrochlorination products and higher boiling materials, depending on the base used and the reaction temperature. The main dehydrochlorination product, using either NaOH in ethylene glycol or NaOMe in methanol, was $CF_3CCl_2CH{=}CH_2$ (**3**, b.p. 73–75 °C). It has been shown previously that **3** is a kinetic dehydrochlorination product which can be isomerized to the thermodynamic product **1** (b.p. 100–101 °C) with LiCl in DMF [14]. NMR analysis of crude volatile (b.p. < 105 °C) products from the dehydrochlorination of **2** with $NaOCH_3$ in methanol indicated a third volatile product in addition to **1** and **3**, not readily separable from **1**. When NaI was reacted with this mixture, both **1** and **3** were converted into the primary iodide, $CF_3CCl{=}CHCH_2I$ (**4**). However, as

$$CF_3CCl_2(CH_2)_2Cl\ (2)$$

$$CF_3CCl_2CH{=}CH_2\ (3)$$

$$+$$

$$\xrightarrow{NaOMe} CF_3CHClCH{=}CHCl\ (5) \xrightarrow{NaI}$$

$$+$$

$$CF_3CCl + CHCH_2Cl\ (1)$$

$$CF_3CH{=}CHCH_2I\ (4) + CF_3CHClCH{=}CHCl\ (5)$$

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expected of an S_N2' reaction [15], the formation of the iodide **4** from **3** (18 h at 55 °C) was much slower compared with the same reaction using pure **1** (4 h at 25 °C). The third dehydrochlorination product (**5**) was unreactive under these conditions. Separation of **5** from **4** provided essentially pure **5** (b.p. 98–99 °C), which was identified as $CF_3CHClCH{=}CHCl$.

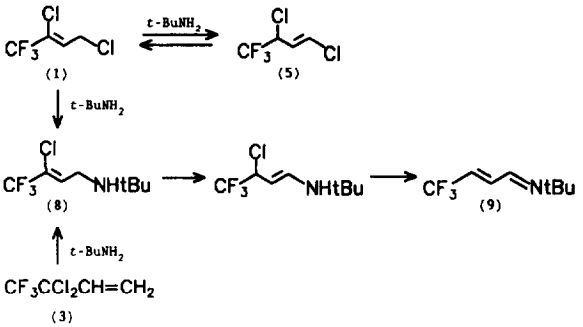
When **2** was dehydrochlorinated at 0–10 °C using sodium methoxide in methanol, the combined selectivity for **1**, **3**, and **5** (in the ratio 7:59:35, respectively) was approximately 95%. High-boiling products were tentatively identified by GC-MS (following an aqueous workup) as the fluoroether $CH_3OCF_2CHClCH{=}CHCl$ (or $CH_3OCF_2CCl{=}CHCH_2Cl$) and two esters derived from its hydrolysis, namely, methyl esters of dichlorobutenoic acid. Presumably, the high-boiling by-products are derived from $CF_2{=}CClCH{=}CHCl$, which is the product of fluoride ion loss from the anion, $CF_3CCl{=}CHCHCl^-$. Protonation of this anion at C-3 explains the formation of **5**.

The proposed isomerization of **1** to **5** was demonstrated independently. Treating **1** with $NaOCH_3$ in methanol at 0–10 °C for 2 h resulted in a 35% conversion to **5**, while by-products accounted for < 1% of the product mixture.

Calculated partial charges (MNDO) for the appropriate LUMO/HOMO for charged species derived from **1** (Table 1), are in agreement with the regiochemistry observed in the protonation of the anion of **1** (isomerization of **1** to **5**).

The above results suggest that deprotonation of **1** may be a significant side reaction with basic nucleophiles, competing with S_N2 displacement of the allylic chlorine. Displacement of the allylic chlorine with neutral or weakly basic nucleophiles has provided access to the corresponding iodide, bromide, acetate, and alcohol (via acetate hydrolysis), in good (73%–82%) yield [14,16]. Similarly, the reaction of **1** with sodium benzenesulfinate gave the corresponding sulfone ($CF_3CCl{=}CHCH_2SO_2Ph$, **6**) in 65% yield, while the reaction of **1** with sodium phenolate provided $CF_3CCl{=}CHCH_2OPh$ (**7**) in only 42% yield.

With *t*-$BuNH_2$, **1** gave $CF_3CCl{=}CHCH_2NHtBu$ (**8**) in 39% yield. To avoid competing deprotonation, an S_N2' reaction on the isomeric **3** was attempted. When **3** was treated with excess *t*-butylamine in DMF, the formation of $CF_3CCl{=}CHCH_2NHtBu$ (**8**) was indeed observed. However, the reaction did not stop at this stage, but produced the non-chlorinated, α,β-unsaturated imine, $CF_3CH{=}CHCH{=}NtBu$ (**9**) as the principle product (45% yield). A similar result was obtained when either **1** or **5** were treated with excess *t*-butylamine. **1** and **5** reacted at a comparable rate, but faster than **3**, indicating a base catalyzed equilibration of these isomers with *t*-butylamine. Pure **8** was also shown to react with *t*-$BuNH_2$ in DMF to give imine **9**, confirming that it is an intermediate in the conversion of **1**, **3**, or **5** to **9**. The conversion of **8** to **9** most likely involves the isomerization of **8** to $CF_3CHClCH{=}CHNHtBu$, followed by rapid loss of HCl.



The substantial acidity of the methylene hydrogens in **1** is consistent with studies by Klabunde and Burton [17] on the carbanion stabilizing ability of α-halogens and trifluoromethyl groups. The acidifying effect is in the order $CF_3 > Cl > F$, as demonstrated by the following pKa values (in DMSO/MeOH at 37 °C) [16]: $CF_3CHClCF_3$, 12.6; CF_3CCl_2H, 17.2; CF_3CHFCF_3, 18.0; $CF_3CHPhCF_3$, 17.9. Deprotonation of **1** produces a carbanion which is vinylogously related to $CF_3CCl_2^-$, and thus **1** should be substantially more acidic than CF_3CCl_2H and more acidic than $CF_3CF{=}CHCH_2Cl$ by approximately 5 pKa units.

When sulfone **6** was treated with NaOMe/MeOH under the same conditions which isomerized **1** to **5**, no C=C bond migration took place, indicating that the charge in the corresponding anion, $CF_3CCl{=}CHCH(SO_2Ph)^-$, is primarily on C-1, adjacent to phenylsulfonyl group. In contrast, Martin et al. [7] observed C=C bond migration in the preparation of $(CF_3)_2CHCH{=}CHSO_2$-*p*-tolyl from $(CF_3)_2C{=}CHCH_2Br$ (basic workup). Thus the magnitude of the acidifying effect of $ArSO_2$ apparently lies between that of $(CF_3)_2C{=}CH$ and $CF_3CCl{=}CH$. For comparison, the equilibrium acidity of $(PhSO_2)_2CH_2$ in DMSO solution is 12.3 [18].

As predicted by the calculated charges for the $CF_3CCl{=}CHCH_2^+$ cation (Table 1), the $CF_3CCl{=}CH$ group in **1** directed Friedel–Crafts arylation at C-1. Refluxing **1** in benzene in the presence of $FeCl_3$ gave $PhCH_2CH{=}CClCF_3$ (**10**), along with some $(Ph)_2CHCH{=}CClCF_3$. The formation of **10** rather than the rearranged product, $Ph(CF_3)CClCH{=}CH_2$, indicates the controlling influence of the CF_3 group in the carbocation, $CF_3CCl{=}CHCH_2^+$, which overrides the stabilizing influence of the secondary chlorine.

Catalytic reduction of **10** provided a simple route to 4,4,4-trifluorobutylbenzene (**11**; 61% yield), which represents a simple and attractive alternative to previous methods which involve either hazardous [19] or expensive [20] reagents.

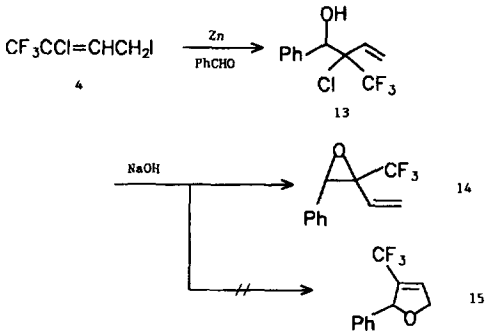
Calculated charges for the anion $CF_3CCl{=}CHCH_2^-$ indicate that it should react with electrophiles at C-3. The Grignard reagent derived from **1**, however, was not stable.

Table 1
Partial charge

Species	C-1	C-3
$CF_3CCl{=}CHCH_2^+$	+0.396	+0.208 (LUMO)
$CF_3CCl{=}CHCH_2^-$	−0.311	−0.502 (HOMO)
$CF_3CCl{=}CHCHCl^-$	−0.224	−0.474 (HOMO)

Attempts to perform Grignard reactions using **1** or its corresponding allylic bromide or iodide failed, even in the presence of benzaldehyde. Magnesium was consumed, however, when refluxed with **1** in THF. The main product was CF_2=$CClCH$=CH_2 (**12**), in 34% yield. Barr [21] previously prepared this diene by dehydroiodination of CF_2=$CClCH_2CH_2I$ in about 10% yield. **1** was also reduced with Zn in aqueous HCl to give a mixture of 5 products, including **12**, *E*/*Z*-CF_3CCl=$CHCH_3$ and *E*/*Z*-CF_3CH=$CHCH_3$.

Although the Grignard reagent derived from **1** lost fluoride ion too rapidly to be trapped by benzaldehyde, the organozinc reagent derived from iodide **4** readily added to benzaldehyde in THF. As is typically observed for allylic organozinc reagents [22], the product of the addition was the rearranged, homoallylic alcohol **13** (76% yield). Treatment of **13** with aqueous NaOH gave epoxide **14**, and not dihydrofuran **15** via an intramolecular S_N2' displacement, a result consistent with Baldwin's rules for ring closure [23] and portended by the sluggishness observed in the conversion of **3** to **4**.



4 13 14 15

3. Conclusion

Compound **1** has considerable synthetic utility. The allylic chlorine is readily replaced by neutral and weakly basic nucleophiles and thus **1** may be considered a synthon for cation **16**. Reduction of S_N2 products of the type CF_3CCl=$CHCH_2X$ provides a convenient route to $CF_3(CH_2)_3X$ compounds. Strongly basic nucleophiles may give lower yields of the corresponding S_N2 products due to deprotonation of **1**, followed by rearrangement and/or loss of fluoride ion. The complementary synthon of anion **17** is provided by the zinc reagent derived from iodide **4**.

16 17

The acidity of the methylene hydrogens plays an important role in the chemistry of **1** and its derivatives. It can be anticipated that compounds having the CF_3CCl=$CHCH$ grouping will in general be susceptible to deprotonation, isomerization, and S_N2' displacement of chloride ion.

4. Experimental details

NMR spectra were recorded in $CDCl_3$ solution with a Finnegan TSQ-700, 360 MHz multinuclear spectrometer. Chemical shifts are reported in ppm downfield from standard (TMS for ^1H and ^{13}C, $CFCl_3$ for ^{19}F). MNDO calculations were performed using the MOPAC program resident in the CAChe™ Scientific WorkSystem, Version 3.5.

4.1. Mixture of $CF_3CCl_2CH_2CH_2Cl$ dehydrochlorination products (1, 3, and 5)

Sodium methoxide (135.0 g, 2.495 mol) in 550 ml methanol was added over 100 min with mechanical stirring to 411.0 g (1.907 mol) $CF_3CCl_2CH_2CH_2Cl$ (**2**) in 200 ml MeOH at 0–10 °C. Stirring was continued for 20 h, and the reaction mixture poured into 3 L water. The lower product layer was washed twice with 100 ml water and dried (Na_2SO_4), providing 308.1 g of crude product. Distillation gave 6.0 g forerun, 133.2 g of **3**, b.p. 73–75 °C, 94.7 g of a mixture of **1** and **5**, b.p. 97–105 °C, 20.7 g of starting material **2**, b.p. 123–127 °C, 33 g intermediate cuts and 16.1 g pot residue. Thus the combined yield of dehydrochlorination products, **1, 3, and 5**, based on unrecovered starting material was 70%. The ratio of **3:5:1** was 59:35:7 as determined by GC and ^{19}F NMR data.

Higher boiling products were identified from GC-MS of the pot residue. $CH_3OCF_2CHClCH$=$CHCl$ (or CH_3OCF_2CCl=$CHCH_2Cl$) MS (*m*/*z*): 194 (1.0) P+4; 192 (5.8) P+2; 190 (9.5) P; 157 (2.9); 155 (7.5) P-Cl; 113 (1.5); 111 (9.3); 109 (14.3) $C_3H_3Cl_2$; 81 (100) CH_3OCF_2. Isomer of methyl dichlorobutenoate: 168 (0.2) P; 135 (21.4); 133 (67.2) P-Cl; 113 (11); 111 (64.6); 109 (100) $C_3H_3Cl_2$; 105 (18.0) P-C_2H_4Cl; 59 (66) $COOCH_3$; 49 (7.6) CH_2Cl; 39 (35); other isomer of methyl dichlorobutenoate: 172 (9.7) P+4; 170 (59.7) P+2; 168 (100) P; 153 (24.0) P-CH_3; 135 (19.0); 133 (57.4) P-Cl; 117 (58.1) P-CH_3-HCl; 109 (81) P-$COOCH_3$; 59 (76.0) $COOCH_3$; 49 (20.8) CH_2Cl.

4.2. Separation of $CF_3CHClCH$=$CHCl$ (5)

Sodium iodide (15 g, 0.1 mol) was dissolved in 100 ml acetone. To this was added 92.3 g (0.52 mol) of the fraction boiling at 97–105 °C (comprised of **1** and **5**) obtained from the dehydrochlorination of **2** described above. The mixture was stirred 2 h at room temperature, filtered, and diluted with 250 ml water. The organic layer was washed with 100 ml each of water and 5% aq. $NaHSO_3$, and distilled twice over a little Cu powder to give 27.2 g of **5**, b.p. 98–100 °C. ^1H NMR δ: 6.58 (d, 1 H, J=13.3 Hz); 6.04 (dd, 1 H, J=9.0 and 13.3 Hz); 4.63 (dq, 1 H, J=9.0 and 6.4 Hz) ppm. ^{19}F NMR δ: −74.8 (d, J=6.4 Hz) ppm.

4.3. 1-(phenylsulfonyl)-4,4,4-trifluoro-3-chlorobut-2-ene (6)

A solution of 18 g $CF_3CCl{=}CHCH_2Cl$ and 20 g sodium benzenesulfinate in 100 ml methanol was refluxed for 17 h. The solution was then concentrated on the rotovap and the residue treated with 250 ml water. The crude yellow solid was washed with water and air dried (18.6 g, 65% yield). Pure $PhSO_2CH_2CH{=}CClCF_3$, m.p. 86–87 °C, was obtained as a white solid after two recrystallizations from 60% ethanol–water (14.9 g, 52% yield). ^{1}H NMR δ: 7.9 (2 H); 7.7 (1 H); 7.6 (2 H); 6.57 (t, J=7.9 Hz, 1 H); 4.1 (d, J=7.9 Hz, 2 H) ppm. ^{19}F NMR δ: −70.1 ppm. IR (cm^{-1}): 3065; 2998; 2945; 1659 (C=C); 1320 (-SO_2-); 1154. Analysis: Calc. for $C_{10}H_8ClF_3O_2S$ (284.68): C, 42.19%; H, 2.83%. Found: C, 42.08; H, 2.92%.

4.4. 1,1,1-trifluoro-2-chloro-4-phenoxybut-2-ene (7)

A solution of phenol (9.4 g, 0.1 mol), 4.0 g (0.1 mol) NaOH, and 18 g (0.1 mol) $CF_3CCl{=}CHCH_2Cl$ in 80 ml 50% MeOH–water was refluxed 1.5 h. The mixture was diluted with 50 ml water, and extracted with 2×50 ml ether. The combined ether layers were washed with 5% aq. NaOH, water, and dried (Na_2SO_4). Distillation gave 9.9 g (42% yield) of $PhOCH_2CH{=}CClCF_3$, b.p. 79 °C at 5 mm Hg. ^{1}H NMR δ: 7.27 (2 H); 6.97 (1 H); 6.86 (2 H); 6.70 (1 H, tq); 4.72 (dq, J=5.1 and 2.1 Hz) ppm. ^{19}F NMR δ: −69.8 (major isomer) and −64.2 (minor isomer) ppm. Analysis: Calc. for $C_{10}H_8ClF_3O$ (236.62): C, 50.76; H, 3.41%. Found: C, 50.99; H, 3.49%.

4.5. N-(4,4,4-trifluoro-3-chloro-2-butenyl)-N-t-butylamine (8)

A solution of 17.9 g (0.1 mol) $CF_3CCl{=}CHCH_2Cl$, 21 ml (14.7 g, 0.2 mol) t-butylamine, 60 ml ether, and 40 ml DMF were stirred at room temperature for 65 h. The reaction mixture was poured into 100 ml 0.1 N NaOH. The ether layer was separated, washed with 50 ml water, 25 ml aqueous NaCl, and dried (Na_2SO_4). Distillation at 10 mm Hg gave 8.5 g (39% yield) of $CF_3CCl{=}CHCH_2NHC(CH_3)_3$, b.p. 50–52 °C. ^{1}H NMR δ: 6.57 (t, 1 H); 3.48 (m, 2 H); 0.9–1.2 (10 H) ppm. ^{19}F NMR δ: −70.0 ppm. MS (m/z): 215 (0.8) P; 202 (35.6); 200 (100); 145 (9.8); 143 (26.0). Analysis: Calc. for $C_8H_{13}ClF_3N$ (215.65): C, 44.55; H, 6.08; N, 6.49%. Found: C, 44.42; H, 6.11; N, 6.32%.

4.6. N-(4,4,4-trifluorobutenylidene)-t-butylamine (9)

A mixture of 16.1 g (0.09 mol) $CF_3CCl_2CH{=}CH_2$ and 24.8 g (0.34 mol) t-butylamine in 50 ml DMF was stirred at room temperature for 5.5 days. The mixture was poured into 300 ml water, extracted 3×25 ml CH_2Cl_2, and the combined organic layers washed with 2×25 ml water, 1×25 ml brine, and dried (Na_2SO_4). Distillation provided 7.2 g (45% yield) of $CF_3CH{=}CHCH{=}NC(CH_3)_3$, b.p. 50 °C at 30 mm Hg. ^{1}H NMR δ: 1.24 (s, 9 H); 6.13 (dq, $J_{H\,H}$=15.9, $J_{H\,F}$=6.5 Hz, 1 H); 6.91 (ddq, J=15.9, 8.4, and 1.7 Hz, 1 H); 7.94 (d, J=8.4 Hz, 1 H) ppm. ^{19}F NMR δ: −65.4 (ddd) ppm. ^{13}C NMR δ: 29.5 (s); 58.7 (s); 123.1 (q, $^1J_{C\,F}$=269.6 Hz); 126.7 (q, $^2J_{C\,F}$=35.7 Hz); 138.2 (q, $^3J_{C\,F}$=6.6 Hz); 153.9 (s) ppm. IR (cm^{-1}): 1667; 1630. MS (m/z): 179 (2.6) P; 164 (82.3); 57 (100). MS (CI): 180 (M+1).

4.7. 1,1,1-trifluoro-2-chloro-4-phenylbut-2-ene (10)

A mixture of 10 ml benzene, 0.33 g $FeCl_3$, and 3.1 g $CF_3CCl{=}CHCH_2Cl$ was heated to reflux. After 0.5 h, HCl evolution subsided and an additional 0.9 g $FeCl_3$ was added which resumed HCl evolution. Reflux was continued 1.5 h, the mixture cooled and treated with 10 ml aq. HCl and 20 ml ether. The organic layer was washed with water, brine, and dried. Distillation gave 2.0 g (53% yield) of colorless $PhCH_2CH{=}CCl(CF_3)$, b.p. 92–97 °C at 19 mm Hg. ^{1}H NMR δ: 7.25 (5 H, m); 6.60 (1 H, t, J=7.4 Hz); 3.58 (2 H, d, J=7.4 Hz) ppm. (The minor Z-isomer is evident as a triplet at δ 6.28). ^{19}F NMR δ: −69.2 (major) and −62.0 (minor) ppm in a ratio of 96:4. MS (m/z): 220 (50.1 P; 222 (15.6) P+2; 165 (100). Analysis: Calc. for $C_{10}H_8ClF_3$ (220.62): C, 54.44; H, 3.65%. Found: C, 54.24; H, 3.66%. A minor product, identified by MS, was $(Ph)_2CHCH{=}CCl(CF_3)$.

4.8. (4,4,4-trifluorobutyl)benzene (11)

Twenty grams of $CF_3CCl{=}CHCH_2Ph$ (**10**) in 50 ml methanol containing 10 g KOAc was hydrogenated at 60 °C under 50 psi H_2 using 61 mg 5% Pd/C as catalyst. After filtering the mixture, the filtrate was poured into 125 ml water, and extracted with 3×50 ml ether. The combined ether fractions were washed with 50 ml aq. $NaHCO_3$, dried ($MgSO_4$), and distilled to give 10.4 g (61% yield) of 95% pure $PhCH_2CH_2CH_2CF_3$, b.p. 78–79 °C at 19 mm Hg. ^{1}H NMR δ: 7.2 (5 H); 2.65 (2 H, t, J=7.5 Hz); 2.05 (m, 2 H); 1.9 (m, 2 H) ppm. ^{19}F NMR δ: −66.5 (t, J=11 Hz) ppm. Analysis: Calc. for $C_{10}H_{11}F_3$ (188.20): C, 63.82; H, 5.89%. Found: C, 63.74%; H, 5.93%.

4.9. 1,1-difluoro-2-chloro-1,3-butadiene (12)

A 3-necked flask fitted with a dropping funnel and 12″ packed column with a distillation take-off head was charged with 3.5 g Mg (N_2 atmosphere). The Mg was activated by preparing the Grignard reagent from 0.6 g isopropyl bromide in dry THF. The THF solution was then removed, and the Mg washed with 5 ml THF. Dry THF (30 ml) was then added. 21.7 g of $CF_3CCl{=}CHCH_2Cl$ (purity 96%) was added over 1.5 h at 65 °C. Heating was continued for an additional 0.5 h. A total of 12.5 g crude product along with some THF distilled out. The crude distillate was washed with water and re-distilled to give 4.9 g (34% yield) of 99% pure $CF_2{=}CClCH{=}CH_2$, b.p. 45–46 °C (Ref. [21], 45–47 °C).

^{1}H NMR δ: 6.4 (1 H); 5.49 (1 H); 5.21 (1 H) ppm. ^{19}F NMR δ: −90.2 (1 F, J_{F-F} = 25.5 Hz); −86.5 (1 F) ppm. MS (m/z): 126 (27.7) P+2; 124 (89.6) P; 89 (100) P-Cl.

4.10. 1-Phenyl-2-chloro-2-(trifluoromethyl)but-3-en-1-ol (13)

10.2 g Zn powder was activated by treatment with 20 ml 1 N HCl, followed by washing with 25 ml ethanol and 2×25 ml ether. Residual ether was flushed out with a stream of nitrogen. Dry THF (70 ml) was then added, followed by 11.0 g (0.104 mol) benzaldehyde. The mixture was stirred mechanically while adding 27.0 g (0.0998 mol) $CF_3CCl{=}CHCH_2I$ (**4**) over 35 min with water bath cooling to maintain the temperature at 25–30 °C. Stirring was continued for 1 h. The slurry was filtered and the filtrate treated with 100 ml 2N HCl. The organic layer was separated and the aqueous phase extracted with 100 ml ether. The combined organic layers were combined, washed with water and dried (Na_2SO_4). Removal of volatiles at the pump gave 21.6 g of 95% pure product by GC analysis. Distillation provided 18.9 g (76% yield) of $PhCH(OH)CCl(CF_3)CH{=}CH_2$, b.p. 77 °C at 0.8 mm Hg. ^{1}H NMR (for major diastereomer) δ: 7.3 (Ar); 6.2 (dd, 1 H, J = 16.7 and 10.8 Hz, $C\underline{H}{=}CH_2$); 5.6 (2 H, $CH{=}C\underline{H_2}$); 5.1 (s, 1 H, $C\underline{H}OH$); 2.9 (bs, 1 H, OH) ppm. ^{19}F NMR δ: −71.7 ppm. IR (cm^{-1}): 3451 (OH); 1645 (weak); 1495; 1410; 1456; 1249; 1188; 1171; 730; 701. Analysis: Calc. for $C_{11}H_{10}ClF_3O$ (250.65): C, 52.71; H, 4.02%. Found: C, 53.09; H, 3.92%.

4.11. 2-(Trifluoromethyl)-2-vinyl-3-phenyloxirane (14)

Alcohol **13** (8.0 g, 31.9 mmol) was stirred with 18 ml 2 N NaOH at 85 °C for 0.5 h. The cooled reaction mixture was neutralized and the organic product taken up in 25 ml CH_2Cl_2, washed with 15 ml water, 15 ml aq. NaCl, dried (Na_2SO_4), and distilled at 5 mm Hg to give 4.7 g (22 mmol, 69% yield) of the oxirane, b.p. 59–63 °C (isomer ratio 10:1). ^{1}H NMR δ: 7.3 (5 H); 5.5 (m, 3 H); 4.5 (s, 1 H) ppm. ^{19}F NMR δ: −75.5 (s, major isomer); −69.2 (s, minor isomer) ppm. Analysis: Calc. for $C_{11}H_9F_3O$ (214.19): C, 61.68; H, 4.24%. Found: C, 61.63; H, 4.31%.

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