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Synthetic utility of 3-(perfluoro-1,1-dimethylbutyl)prop-1-ene. Part VI ☆. A free-radical addition of CCl_4 and CBr_4 and dehydrohalogenation of the adducts

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Abstract

Heating the title compound **1** in excess CCl_4 and in the presence of a free-radical initiator (t-butyl peroxide) at 120 °C afforded 1,1,1,3-tetrachloro-4-(perfluoro-1,1-dimethylbutyl)butane (**2**) as the main product together with considerable amounts of cyclic dimer, 1,4-bis(perfluoro-1,1-dimethylbutyl)cyclohexane (**3**). Reaction of **1** with CBr_4 at 120 °C gave 1,1,1,3-tetrabromo-4-(perfluoro-1,1-dimethylbutyl)butane (**4**) as the sole product while at 220 °C a mixture of 1,2-dibromo-3-(perfluoro-1,1-dimethylbutyl)propane (**5**) and 1,1-dibromo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-diene (**6**) was formed. Treatment of adducts **2** and **4** with methanolic potassium hydroxide at ambient temperature gave mixtures of 1,1,3-trihalo-4-(perfluoro-1,1-dimethylbutyl)but-1-enes (**7**) or (**8**) and 1,1-dihalo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-dienes (**9**) or (**6**) in ratios depending on the adduct to base ratio and on the reaction conditions. Using an excess of the base and reflux temperature, adduct **4** and diene **6** were converted into methyl 4-(perfluoro-1,1-dimethylbutyl)buten-3-oate (**10**).

Keywords: Synthetic utility; Free-radical addition; Perfluorodimethylbutylprop-1-ene; Dehydrohalogenation; Adduct formation; Carbon tetrachloride; Carbon tetrabromide; Reaction mechanism; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

In the first part of this series [1] we reported that the oxidation of 3-(perfluoro-1,1-dimethylbutyl)-prop-1-ene (**1**) with 3-chloroperbenzoic acid in chloroform contaminated with ca. 0.8% of carbon tetrachloride gives, besides the expected oxirane, considerable amounts of 1,1,1,3-tetrachloro-4-(perfluoro-1,1-dimethylbutyl)butane (**2**) deriving from a free-radical addition of a CCl_4 molecule across the double bond of **1**. That result suggests a simple method of prolongation of the carbon chain of compound **1** by one unit via addition of a carbon tetrahalide. Dehydrohalogenation of the adducts should lead to new highly halogenated alkenes and dienes containing 10 carbon atoms in their molecules.

In the present paper we report a t-butyl peroxide-initiated addition of carbon tetrachloride and carbon tetrabromide to compound **1** and the dehydrohalogenation reactions of the adducts.

2. Results and discussion

The attempted reaction of compound **1** with carbon tetrachloride at reflux temperature failed; GLC analysis revealed only unreacted substrates. This failure was evidently due to too low a reaction temperature. According to the literature data [2] decomposition of t-butyl peroxide to produce radicals at a reasonable rate requires temperatures above 100 °C; hence, all the following reactions were carried out at 120 °C in a thick-wall glass ampoule fitted with a Rotaflo valve. The ratio of CCl_4 to **1** was found to be a critical factor. With a 10-fold excess of carbon tetrachloride, a complex mixture of products was formed which contained about 20% of a high boiling oligomeric fraction. The best results were obtained using a 50-fold excess of carbon tetrachloride: two compounds were formed in a 86:13 ratio with only trace amounts (1%) of other products. The major component was the expected adduct, 1,1,1,3-tetrachloro-4-(perfluoro-1,1-dimethylbutyl)butane (**2**) but, surprisingly, the minor component of the reaction mixture was found to be a cyclic dimer of **1**,

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1,4-bis(perfluoro-1,1-dimethylbutyl)cyclohexane (3) (Scheme 1).

The structure of dimer **3** has been demonstrated unequivocally by elemental analysis (identical to that of **1**) and by MS, ^{1}H and ^{13}C NMR investigations. The mass spectrum exhibited a number of high molecular weight fragmentation ions, the highest with $m/z = 692$ $(M - C_2H_4)^+$ indicating a dimeric structure. The ^{1}H NMR spectrum of compound **3** exhibited only three signals with 1:2:2 intensities which implies a highly symmetric structure with perfluoroalkyl groups in positions 1 and 4. These two large substituents are assumed to occupy thermodynamically preferable equatorial positions and to inhibit inversion of the cyclohexane ring. In fact, the spectrum showed differentiation between axial and equatorial protons (3.03 and 2.70 ppm, respectively) and coupling between geminal protons ($^2J_{HH} = 17$ Hz). Couplings between axial CH group protons (4.63 ppm) and axial and equatorial CH_2 group protons (7.70 and 2.34 Hz, respectively) were also observed (see Fig. 1).

Besides signals corresponding to the perfluoroalkyl chains, the non-proton-decoupled ^{13}C NMR spectrum of compound **3** exhibits the presence of CH and CH_2 groups (47.0 ppm, d; 40.1 ppm, t). The magnitude of the carbon-to-proton coupling in the higher field signal ($^1J_{CH} = 26$ Hz) is characteristic for CH_2 groups in a six-membered ring [3].

Surprisingly, cyclic dimer **3** is not formed in the absence of carbon tetrachloride; heating alkene **1** and t-butyl peroxide in the absence of carbon tetrachloride gave a complex mixture of polymeric products but no dimer **3** was formed. Also, prolonged heating of adduct **2** at 120 °C gave no compound **3**. Hence, it seems probable that the formation of **3** is initiated by radicals generated from carbon tetrachloride. The hypothetical reaction mechanism is shown in Scheme 2.

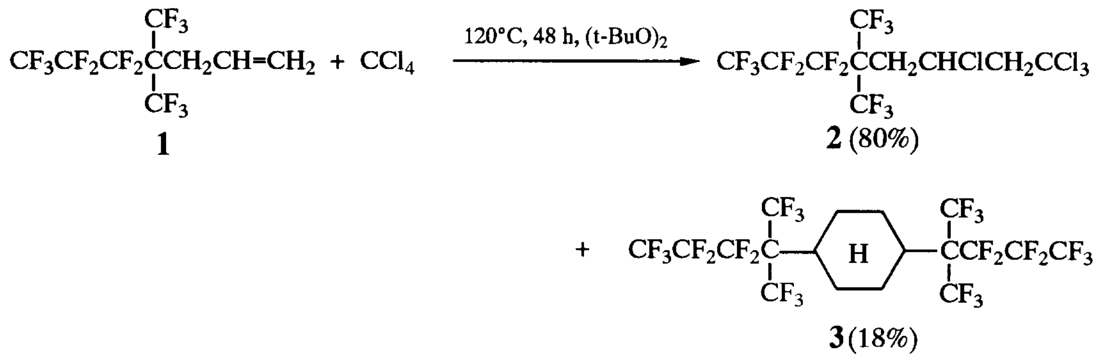
Since no product arising from the addition of two chlorine atoms across the double bond of **1** was observed, it seems more probable that the cyclization reaction is initiated by trichloromethyl radicals rather than by chlorine radicals. A trichloromethyl radical can either add to the terminal carbon to give adduct **2** or abstract a proton from the methylene group adjacent to the perfluoroalkyl group to produce an allylic radical i, which in turn combines with the second molecule of alkene **1**. The dimeric radical ii undergoes a proton migration from the activated methylene group to give the rearranged radical iii which then cyclizes. Cyclic radical iv abstracts a proton from alkene **1** to give compound **3** and reproduces radical i.

The addition of carbon tetrabromide to alkene **1** does not require excess of the former or solvent. The best results were obtained by heating equimolar amounts of the reagents and some t-butyl peroxide at 120 °C when 1,1,1,3-tetrabromo-4-(perfluoro-1,1-dimethylbutyl)butane (**4**) was obtained in 77% yield. Addition also took place in the absence of free-radical initiator but the yield of **4** did not exceed 51%. The reaction of alkene **1** with carbon tetrabromide was not accompanied by formation of the cyclic adduct **3**.

When a mixture of **1**, carbon tetrabromide and t-butyl peroxide was heated at 220 °C for a short period (0.5 h), 1,2-dibromo-4-(perfluoro-1,1-dimethylbutyl)-propane (**5**) and 1,1-dibromo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-diene (**6**) were obtained instead of adduct **4** (Scheme 3). Diene **6** was evidently formed by thermal dehydrobromination of adduct **4**. The latter was found to be unstable and lost bromine on standing at room temperature under daylight.

Dehydrohalogenation of adducts **2** and **4** with methanolic potassium hydroxide at ambient temperature proceeded stepwise and gave mixtures of 1,1,3-trihalo-4-(perfluoro-1,1-dimethylbutyl)but-1-enes (**7**) or (**8**) and 1,1-dihalo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-dienes (**9**) or (**6**) in ratios depending on the adduct to base proportion and on the reaction time (Scheme 4).

Alkenes **7** and **8** are unstable and slowly eliminate the second molecule of halogen halide, even in the absence of a base. In the case of **8** this process was slow enough to allow measurement of the ^{1}H NMR spectra of this alkene in the mixture of products obtained by quenching the reaction at an early stage. The spectrum exhibited typical ABX patterns for the



Scheme 1.

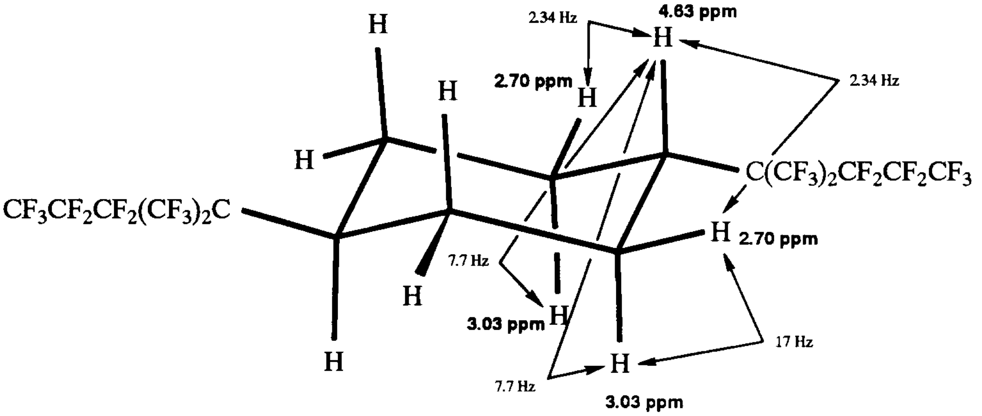
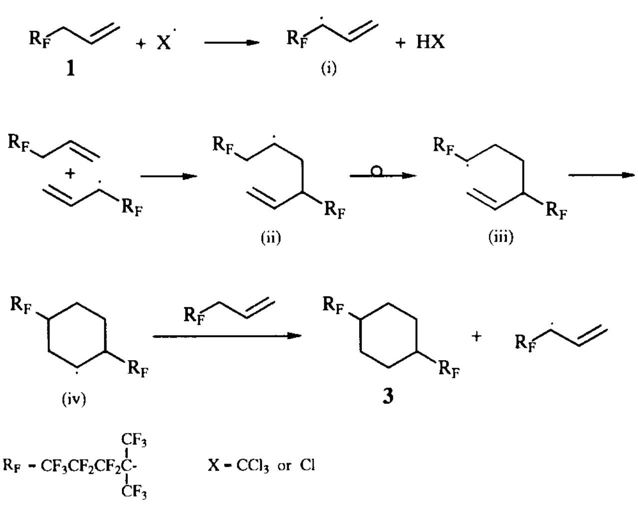


Fig. 1. Chemical shifts (δ, ppm) and coupling constants (*J*, Hz) associated with the structure of 1,4-bis(perfluoro-1,1-dimethylbutyl)cyclohexane (**3**) as determined from its ^{1}H NMR spectrum.



Scheme 2.

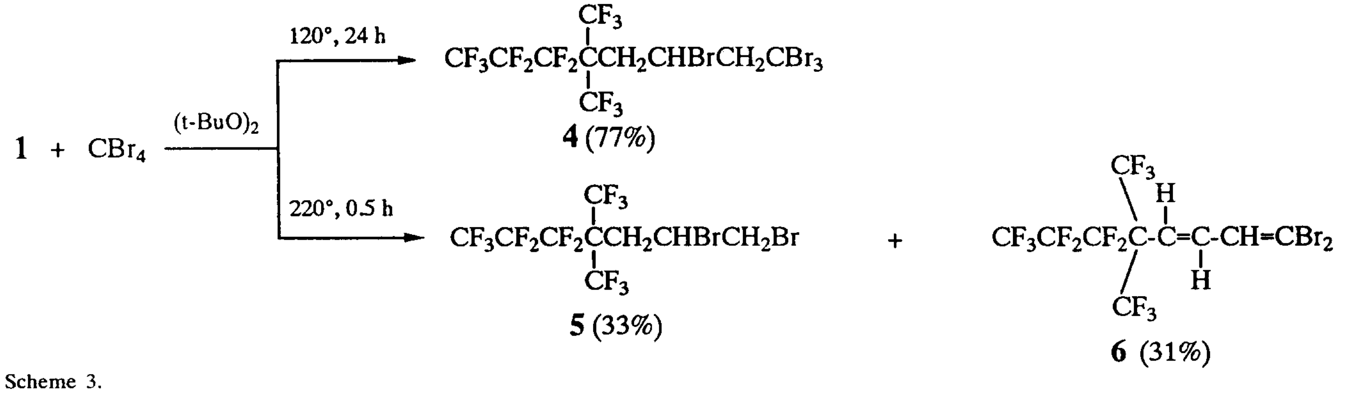
$-CH_2CHX-$ part of the molecules. Alkene **7** was too unstable to be isolated or to enable its NMR spectrum to be measured.

Dibromodiene **6** is also thermally unstable, such that attempted distillation resulted in decomposition; the analytical sample was obtained by preparative GLC. In contrast, dichlorodiene **9** is quite stable (no sign of decomposition during distillation) and hence this perfluoroalkyl-substituted diene seems to be a synthetically useful compound.

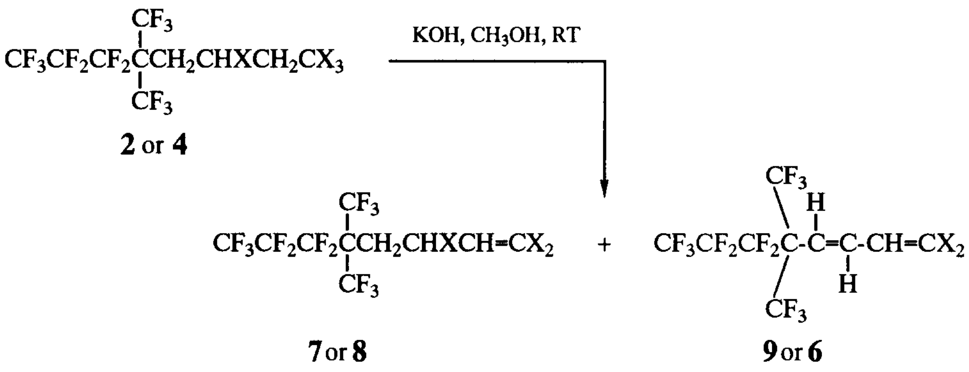
As evidenced by large coupling constants between the vinylic protons on the C-3 and C-4 carbon atoms, dienes **6** and **9** are formed exclusively as *trans* isomers; no signals of the *cis* isomers were detected in the ^{1}H NMR spectra. The exclusive formation of *trans* isomers suggests a concerted *E*2 elimination mechanism [4].

When refluxed for 0.5 h in an excess of methanolic potassium hydroxide, dibromodiene **6** (or adduct **4**) was converted in 75% yield into methyl 4-(perfluoro-1,1-dimethylbutyl)buten-3-oate (**10**). Analogous treatment of dichlorodiene **9** for 4 h resulted in only 10% conversion into **10**.

The drastic difference observed in the rate of methanolysis between dienes **6** and **9** in favour of the former, suggests an S_N2 mechanism for the replacement of halogen atoms by the methoxide group. Thus, it seems probable that due to the strong electron-withdrawing effect of the perfluoroalkyl group, which is transmitted via the conjugated double bonds, initial nucleophilic attack of the methoxide ion is directed on to the terminal carbon atom and results in addition of a methanol molecule. The subsequent S_N2 substitution of two hal-



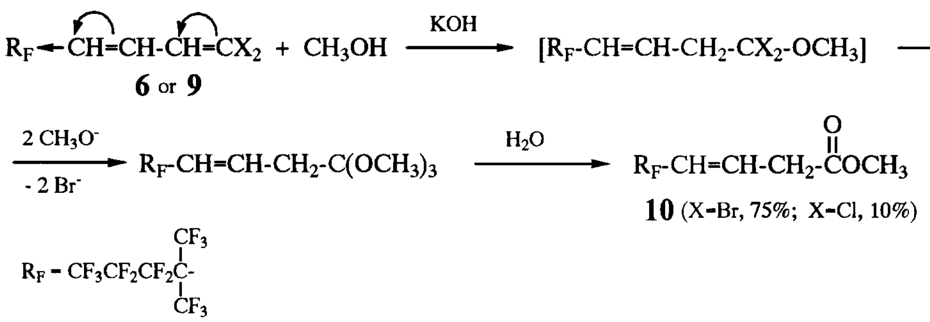
Scheme 3.



Compounds: **2, 7, 9**; X = Cl
4, 8, 6; X = Br

Reaction conditions	Products (yields)
2 : KOH - 1 : 1; 2 h	**7** (30%); **9** (16%)
- 1 : 4; 3 h	**7** (7%); **9** (93%)
4 : KOH - 1 : 1; 1 h	**8** (56%); **6** (22%)
- 1 : 3; 0.25 h	**8** (25%); **6** (63%)
- 1 : 3; 2 h	**8** (3%); **6** (94%)

Scheme 4.



Scheme 5.

ogen atom gives an orthoester which, when poured into water, hydrolyzes to the final product **10** (Scheme 5).

For the case of the alternative replacement of halogens by an addition–elimination mechanism (Ad_NE), the relative methanolysis rates of compounds **6** and **9** should be exactly opposite [5].

3. Experimental details

Boiling points were determined during distillation and are uncorrected. Most of the ^{1}H NMR spectra were recorded with a Varian 200 MHz spectrometer but the ^{1}H and ^{13}C NMR spectra of dimer **3** were obtained with a Bruker 500 MHz spectrometer, all in $CDCl_3$ solutions. The ^{19}F NMR spectra of the perfluorinated part of all compounds were within the limits reported previously [1] and are therefore not quoted. The IR spectra were measured with a Perkin-Elmer 1640 instrument and the mass spectrum of compound **3** with an AMD-604 spectrometer at 70 eV.

GLC analyses were performed with a Shimadzu GC-14A chromatograph using a 3.5m × 2 mm column packed with 5% silicon oil SE-52 on Chromosorb G. For preparative work, a GCHF-18.3 apparatus (Germany) equipped with a 4 m × 10 mm column was used.

3.1. Reaction of 3-(perfluoro-1,1-dimethylbutyl)prop-1-ene (1) with carbon tetrachloride

Carbon tetrachloride (240 ml), compound **1** (18 g 0.05 mol) and t-butyl peroxide (0.5 ml) were placed in a 500 ml pressure glass ampoule and heated at 120 °C for 48 h. Removal of excess CCl_4 under reduced pressure afforded an oily liquid (24 g) which was shown by GLC to consist of two products (87% and 13%). Both compounds were isolated by preparative GLC and identified, respectively, as 1,1,1,3-tetrachloro-4-(perfluoro-1,1-dimethyl)butane (**2**) (elemental analysis, ^{1}H and ^{19}F NMR spectra in agreement with the reported data [1]) and 1,4-bis(perfluoro-1,1-dimethylbutyl)cyclohexane (**3**) (nc). Analysis: Found: C, 29.7; H, 1.3; F, 68.5%. $C_{18}H_{10}F_{26}$ requires: C, 30.0; H, 1.4; F, 68.5%. ^{1}H NMR δ: 2.70 (d broadened, $CH_2(H_{eq})$, $^2J_{HH}=17.0$ Hz); 3.03 (dd, $CH_2(H_{ax})$, $^2J_{HH}=17.0$ Hz, $^3J_{HaxHax}=7.7$ Hz); 4.63 (tt, CH_{ax}, $^3J_{HaxHax}=7.7$ Hz, $^3J_{HaxHeq}=2.34$ Hz) ppm. ^{13}C NMR δ: 40.1 (t, CH_2, $^1J_{CH}=126$ Hz); 47.0 (d, CH, $^1J_{CH}=157.5$ Hz); 60.3 (nonet, $C-CF_3$, $^2J_{CF}=25.5$ Hz); 109.3 (t sxt, CF_2, $^1J_{CF}=272$ Hz, $^2J_{CF}=38$ Hz); 114.6 (tt, CF_2, $^1J_{CF}=270$ Hz, $^2J_{CF}=34$ Hz); 117.4 (qt, CF_3, $^1J_{CF}=290$ Hz, $^2J_{CF}=34$ Hz); 121.7 (q, $2CF_3$, $^1J_{CF}=290$ Hz) ppm. MS (70 eV) (*m/z*): 692 [21% $(M-C_2H_4)^+$]; 673 [10% $(M-C_2H_4F)^+$]; 653 [47% $(M-C_2H_5F_2)^+$]; 603 [15% $(M-C_3H_5F_3)^+$]; 503 [25% $(C_{13}H_5F_{19})^+$]; 373 [100% $(C_{10}H_8F_{13})^+$]; 169 [23% $(C_3H_7)^+$]; 69 [17% $(CF_3)^+$].

3.2. *Reactions of 3-(perfluoro-1,1-dimethylbutyl)prop-1-ene (1) with carbon tetrabromide*

Method A

Alkene **1** (7.2 g, 0.02 mol), carbon tetrabromide (6.7 g, 0.02 mol) and t-butyl peroxide (0.2 ml) were heated in a sealed glass ampoule at 120 °C for 48 h. The resulting brown liquid was shown by GLC to contain one major product (80%), a small amount of unreacted CBr_4 (9.5%) and numerous minor unidentified components. Vacuum distillation gave pure 1,1,1,3-tetrabromo-4-(perfluoro-1,1-dimethylbutyl)butane (**4**) (nc) (b.p. 136 °C/6 Torr, 10.7 g, yield 77%) as a colourless liquid. Analysis: Found: C, 17.4; H, 0.7; Br, 46.3; F, 35.6%. $C_{10}H_5Br_4F_{13}$ requires: C, 17.4; H, 0.7; Br, 46.2; F, 35.7%. ^{1}H NMR δ: 3.06 and 3.14 (AB, R_FCH_2, $^2J_{HH'}=17.6$ Hz); 3.55 and 3.80 (AB, CH_2CBr_3, $^2J_{HH'}=16.23$ Hz); 4.62 (m, CHBr) ppm.

Method B

Alkene **1** (1.8 g, 0.005 mol), carbon tetrabromide (1.7 g, 0.005 mol) and t-butyl peroxide (0.1 ml) were heated in a sealed glass ampoule at 220 °C for 30 min. After completion of the reaction, the resulting fuming brown liquid was poured into water (25 ml) and agitated for a few minutes; the organic layer was then separated, dissolved in ether (30 ml), washed with water until neutral and dried over $MgSO_4$. Removal of the solvent gave a brown oil (3.3 g) which was shown by comparative GLC analysis to consist of 1,2-dibromo-4-(perfluoro-1,1-dimethylbutyl)propane (**5**) (33%), 1,1-dibromo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-diene (**6**) (31%), unreacted alkene **1** (7%) and numerous minor unidentified components.

3.3. *Dehydrohalogenation of adducts 2 and 4*

A solution of adduct **2** or **4** (5 mmol) in methanol (1–3 ml) was added at ambient temperature to a stirred solution of potassium hydroxide (5, 15 or 20 mmol) in methanol (10 ml). An exothermic reaction occurred and a potassium halide immediately precipitated. The reaction mixture was stirred for the required time (Scheme 4), then poured into water. The organic layer was separated, dissolved in ether (30 ml), the solution washed with water and dried over $MgSO_4$. The residue obtained after removal of the solvent was subjected to GLC separation or distillation followed by ^{1}H NMR investigation. Yields of compounds **6**, **7**, **8** and **9** (%GLC) are given in Scheme 4.

(i) *trans*-1,1-Dibromo-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-diene (**6**) (nc): isolated by preparative GLC. Analysis: Found: C, 22.6; H, 0.5; Br, 30.0; F, 46.4%. $C_{10}H_3Br_2F_{13}$ requires: C, 22.6; H, 0.6; Br, 30.1; F, 46.5%. ^{1}H NMR δ: 5.80 (d, H-4, $^3J_{HH}=16.2$ Hz); 6.79 (dd, H-3, $^3J_{HH}=16.2$ and 10.2 Hz); 7.04 (d, H-2, $^3J_{HH}=10.2$ Hz) ppm. IR (film) (cm^{-1}): 1670 [ν(C=C)]. Attempted distillation (72 °C/7 Torr) resulted in decomposition.

(ii) 1,1,3-Trichloro-4-(perfluoro-1,1-dimethylbutyl)but-1-ene (**7**) (nc). This compound was too unstable to obtain its NMR spectrum. Its structure was elucidated on the basis of a similarity between the GL chromatograms of mixtures obtained from dehydrohalogenation of **2** and from **4**, and also on the fact that on standing it was transformed into **9**.

(iii) 1,1,3-Tribromo-4-(perfluoro-1,1-dimethylbutyl)but-1-ene (**8**) (nc): ^{1}H NMR identification only: δ: 2.96 and 3.07 (AB, CH_2, $^2J_{HH'}=16.3$ Hz); 5.07 (td, CHBr, $^3J_{HH}=10$ Hz and 3 Hz); 6.59 (d, $-CH=$, $^3J_{HH}=10$ Hz) ppm. Attempted distillation (83 °C/15 Torr) resulted in decomposition.

(iv) *trans*-1,1-Dichloro-4-(perfluoro-1,1-dimethylbutyl)buta-1,3-diene (**9**) (nc): isolated by distillation, b.p. 88–89 °C/20 Torr. Analysis: Found: C, 27.0; H, 0.7; Cl, 16.0; F, 55.9%. $C_{10}H_3Cl_2F_{13}$ requires: C, 27.2; H, 0.7; Cl, 16.1; F, 56.0%. ^{1}H NMR δ: 5.73 (d, H-4, $^3J_{HH}=16.3$ Hz); 6.88 (dd, H-3, $^3J_{HH}=16.3$ and 10.6 Hz); 6.51 (d, H-2, $^3J_{HH}=10.6$ Hz) ppm. IR (film) (cm^{-1}): 1670 [ν(C=C)].

3.4. *Methyl 4-(perfluoro-1,1-dimethylbutyl)buten-3-oate (10) (nc)*

Methanolic solutions of adduct **4** or diene **6** (5 mmol) and potassium hydroxide (20 mmol) were mixed together and when the exothermic reaction ceased the mixture was refluxed for 30 min. After cooling to room temperature, the precipitate of potassium bromide was filtered off, washed with a small amount of cold methanol and the combined methanolic solutions evaporated under reduced pressure to give a liquid (ca. 2 g) containing 75% of compound **10** and 20% of diene **6**. Preparative GLC separation gave pure methyl 4-(perfluoro-1,1-dimethylbutyl)buten-3-oate (**10**) (yield 75%). Analysis: Found: C, 30.4; H, 1.6; F, 59.0%. $C_{11}H_7F_{13}O_2$ requires: C, 31.6; H, 1.7; F, 59.1%. ^{1}H NMR δ: 3.25 (dd, CH_2, $^3J_{HH}=7.1$ Hz, $^4J_{HH}=1.5$ Hz); 3.73 (s, CH_3); 5.63 (d,

$R_FCH{=}$, $^3J_{HH} = 16.5$ Hz); 6.43 (dt, $=CH-$, $^3J_{HH} = 16.5$ and 7.1 Hz) ppm. IR (film) (cm^{-1}): 1748 [ν(C=O)]; 1643 [ν(C=C)].

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