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Journal of Fluorine Chemistry 120 (2003) 93–96
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

Short communication

Reactions of highly branched fluoroolefins with methyllithium and methylmagnesium bromide: formations of unexpected polyfluorocyclobutene and polyfluoropentadiene compounds

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Received 7 October 2002; received in revised form 7 November 2002; accepted 16 November 2002

Abstract

Introduction of a methyl group into hexafluoropropene trimers was achieved by reactions with organometallic carbon nucleophiles. Unusual cyclization and defluorination occurred simultaneously with a formation of methylated polyfluoroolefins: excess methyllithium provided a polyfluorocyclobutene compound, while a polyfluoropentadiene derivative was formed by use of excess methyllithium.

Keywords: Hexafluoropropene trimer; Organolithium reagent; Grignard reagent; Cyclization; Defluorination

Hexafluoropropene oligomers, available from a hexafluoropropene monomer [1], have been used as synthetic intermediates for various industrially manufactured goods, viz. surfactants, liquid crystals and inert fluids. Hexafluoropropene trimers, especially, have interesting reactivities, such as forming persistent perfluoroalkyl radicals [2,3], due to their highly branched frameworks with electronegative bulky substituents. Several reactions of hexafluoropropene oligomers with nucleophilic reagents have been reported [4–6], however, with regard to the reaction with organometallic nucleophiles, only one report has been published about the reactions of hexafluoropropene dimers with organomagnesium and organolithium reagents [7]. Now we wish to report reactions of hexafluoropropene trimers with oraganometallic nucleophiles with an emphasis on the unusual cyclization and defluorination reactions.

Highly branched hexafluoropropene trimers, perfluoro-(4-methyl-3-isopropyl-2-pentene) (**T-2**) and perfluoro-(3-ethyl-2,4-dimethyl-2-pentene) (**T-3**), were prepared by oligomerization of a hexafluoropropene monomer under the presence of a fluoride anion and a crown ether [8]. The reactions of trimers, **T-2** and **T-3**, with organometallic nucleophiles, CH_3Li–LiBr and CH_3MgBr, were carried out in anhydrous ether at 0 °C for 5 h (Schemes 1 and 2). A typical procedure for the reactions of hexafluoropropene trimers with organometallic nucleophiles is as follows. To a suspension of perfluoro-(3-ethyl-2,4-dimethyl-2-pentene) (**T-3**, 0.453 g, 1.0 mmol) in 5 ml of ether, was dropped an ethereal solution of CH_3Li–LiBr (1.5 M, 2.4 ml) cooled with ice. After stirring for 5 h at 0 °C, a resulting white suspension was heated to 50 °C and was trap-to-trap distilled with a vacuum line system (1 mmHg). Crude products (0.469 g) were obtained by repetitive distillation and the product distribution was determined by ^{19}F and ^{1}H NMR. All samples used for analysis were purified by a preparative GC and were identified by FT-IR, GC, GC–MS, ^{1}H, ^{13}C, and ^{19}F NMR. The results on the reaction of **T-2** and **T-3** with CH_3Li and CH_3MgBr were summarized in Table 1.

Reactions of **T-3** with CH_3Li or with CH_3MgBr provided two structural isomers of mono-methylated compounds (**1** and **2**) in moderate to good yields (entries 1 and 4). Likewise with **T-2**, either CH_3Li or CH_3MgBr provided mono-methylated compounds **7** and **8** in moderate yields (entries 8 and 11). Interestingly, an excess use of oraganometallic nucleophiles provided unexpected products (**5**, **6** and **9**) in addition to the normal adducts such as bis-methylated fluoroolefins (**3** and **4**) and/or a tris-methylated fluoroolefin (**10**): either

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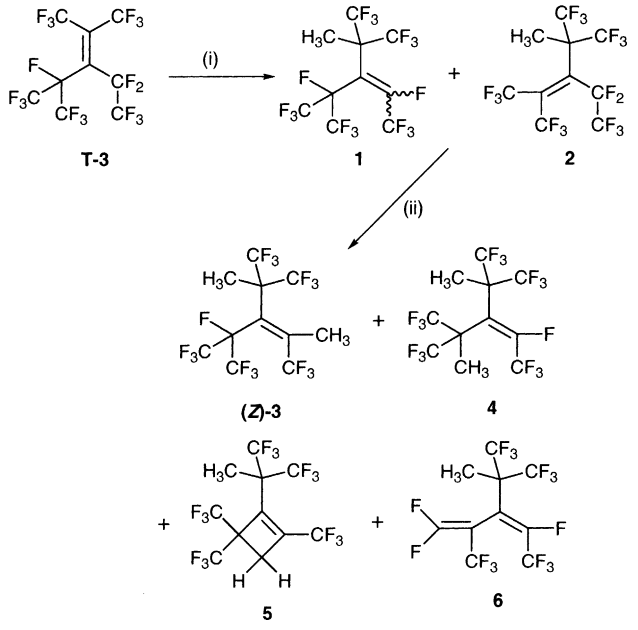
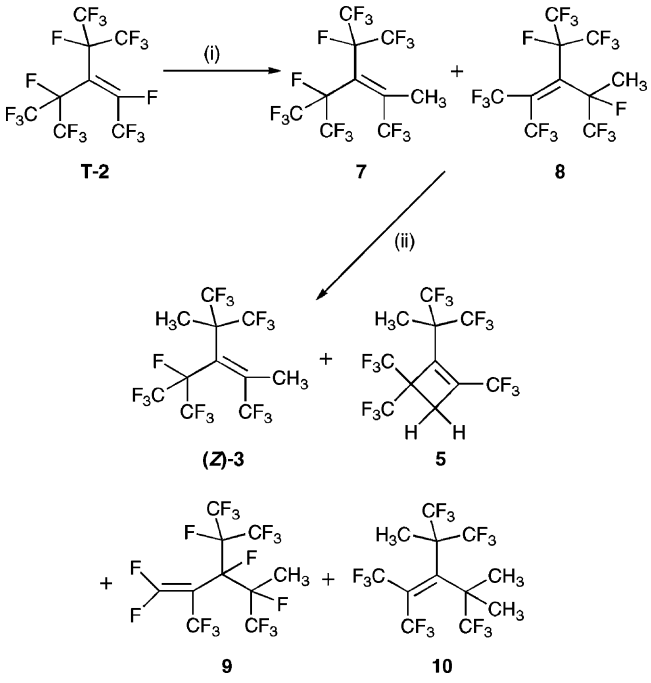
0022-1139/02/$ – see front matter
PII: S0022-1139(02)00311-1



Scheme 1. Reagents and conditions: (i) CH_3Li or CH_3MgBr; (ii) excess of CH_3Li or CH_3MgBr.



Scheme 2. Reagents and conditions: (i) CH_3Li or CH_3MgBr; (ii) excess of CH_3Li or CH_3MgBr.

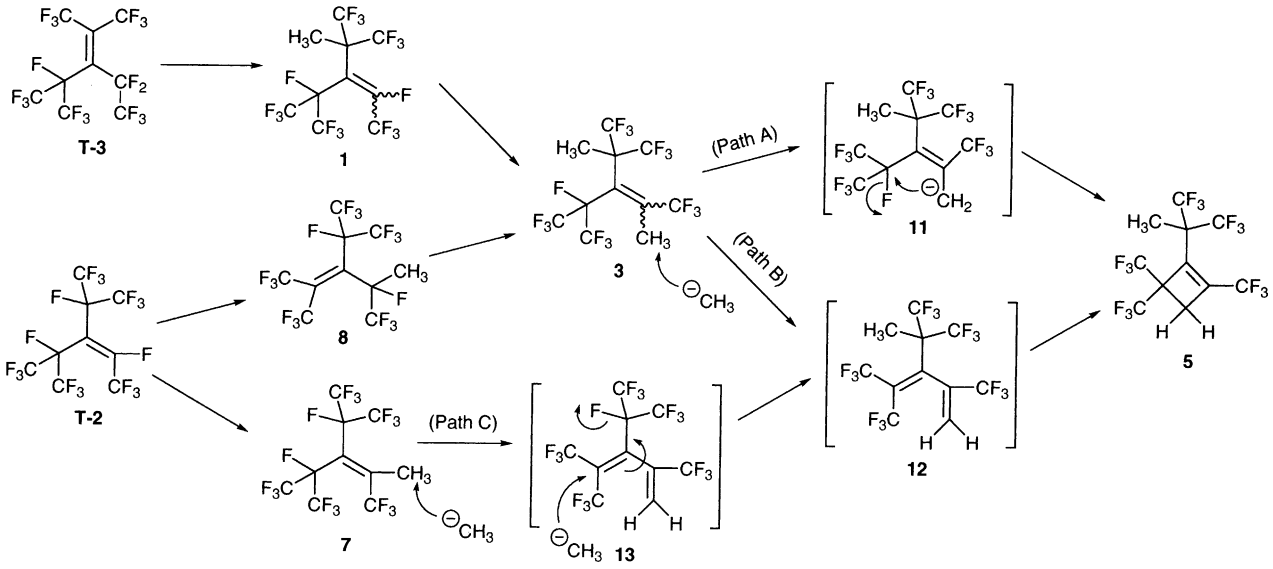
Table 1
Reactions of hexafluoropropene trimers **T-3** and **T-2** with organometallic nucleophiles

Entry	Trimers (mmol)	Nucleophiles (mmol)	Products (percentage yield)[a]			Recovery of trimers (%)
			Mono-CH_3	Bis- and tris-CH_3	Others	
1	**T-3** (1.9)	CH_3Li (2.3)	(*E*)-**1** (30), (*Z*)-**1** (36), **2** (12)	(*Z*)-**3** (6.3), **4** (2.9)		11
2	**T-3** (1.9)	CH_3Li (4.8)	(*E*)-**1** (4.6), (*Z*)-**1** (35), **2** (1.9)	(*Z*)-**3** (31), **4** (14)	**5** (6.2)	0
3	**T-3** (1.0)	CH_3Li (3.6)	(*Z*)-**1** (24)	(*Z*)-**3** (30), **4** (16)	**5** (29)	0
4	**T-3** (1.9)	CH_3MgBr (1.2)	(*E*)-**1** (28), (*Z*)-**1** (11), **2** (23)			31
5	**T-3** (1.5)	CH_3MgBr (2.0)	(*E*)-**1** (40), (*Z*)-**1** (12), **2** (15)		**6** (26)	0
6	**T-3** (1.5)	CH_3MgBr (3.8)	(*E*)-**1** (31), (*Z*)-**1** (10), **2** (11)		**6** (32)	0
7[b,c]	**T-3** (1.0)	CH_3MgBr (3.6)	(*E*)-**1** (8.5), (*Z*)-**1** (5.5)	(*Z*)-**3** (11)	**5** (10), **6** (20)	0
8	**T-2** (1.9)	CH_3Li (2.3)	**7** (47), **8** (20)	(*Z*)-**3** (2.6)	**5** (1.1)	0
9	**T-2** (1.9)	CH_3Li (4.8)	**7** (25), **8** (11)	(*Z*)-**3** (4.9)	**5** (27)	0
10[b]	**T-2** (1.0)	CH_3Li (3.6)	**7** (5.3)	**10** (17)	**5** (49)	0
11	**T-2** (1.5)	CH_3MgBr (1.8)	**7** (22), **8** (40)		**9** (9.2)	0
12	**T-2** (1.5)	CH_3MgBr (4.8)	**7** (32), **8** (39)		**5** (1.2), **9** (7.8)	0

[a] Determined by ^{19}F and ^{1}H NMR otherwise noted.
[b] Determined by GC.
[c] Several high-boiling products were also obtained.

reaction of **T-3** and **T-2** with a 3.6 molar excess of CH_3Li (entries 3 and 10) gave a polyfluorocyclobutene derivative **5** in 29 and 49% yields, respectively.[1] Spectral data for **5** are—^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.71 (br s, 3H, CH_3), 2.93 (br s, 2H, –CH_2–); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.4 (q, J_{CH} 134.0, $(CF_3)_2(CH_3)C$), 30.8 (t, J_{CH} 148.5, CH_2), 53.1 (sep, J_{CF} 28.6, $(CF_3)_2(CH_3)C$), 55.7 (sep t, J_{CF} 31.2, J_{CH} 4.5, $(CF_3)_2C$), 117.6 (q, J_{CF} 272.4, CF_3), 122.5 (q, J_{CF} 282.5, $(CF_3)_2C$), 122.8 (q, J_{CF} 286.1, $(CF_3)_2(CH_3)C$), 133.0 (m, C=C–C$(CF_3)_2(CH_3)$), 147.1 (qt, J_{CF} 41.8, J_{CH} 7.6, =C–CF_3); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$ as an internal standard) δ: −64.9 (sep, J_{FF} 9.3, 3F, CF_3), −68.7 (s, 6F, $(CF_3)_2$), −70.9 (q, J_{FF} 9.3, 6F, $(CF_3)_2(CH_3)C$); GC–MS (EI, 70 eV) *m/z*: 422 (M^+, 5.8), 403 (M^+ − F, 5.0), 383 (5.2), 353 (13), 333 (31), 313 (16), 263 (10), 145 (62), 69 (100), 65 (31), 51 (26); IR (cm^{-1}): 1477 ($\nu_{C=C}$). In contrast, excess amounts of CH_3MgBr reacted with **T-3** to give a polyfluorobutadiene compound **6** in 20–32% yields (entries 5–7; see

[1] These yields are determined by ^{19}F and ^{1}H NMR. The isolation of **5** and **6** in pure form was difficult because of very close boiling points to methylated fluoroolefins. Both **5** and **6** were separable only with a preparative GC: an isolated yield of **5** was about 10–15%, while that of **6** was below 5% because (*E*)- and (*Z*)-**1** have very close retention times.

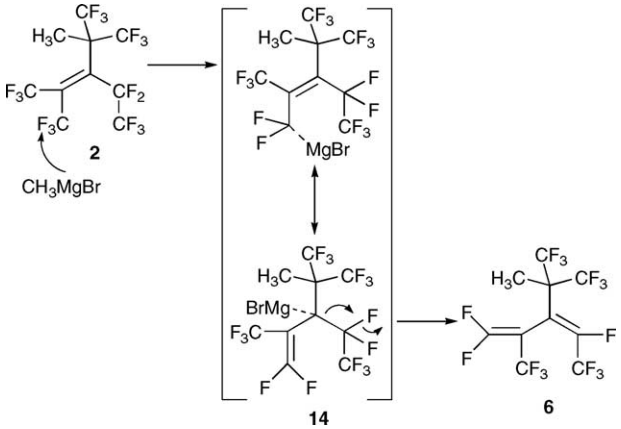


Scheme 3.

footnote 1). Spectral data for **6** are—^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.67 (s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 15.7 (q, J_{CH} 133.42, $(CF_3)_2(CH_3)C$), 55.2 (m, $(CF_3)_2(CH_3)C$), 82.4 (m, $CF_3C{=}CF_2$), 105.8 (dqm, J_{CF} 19.6, J_{CH} 5.1, $(CF_3)FC{=}C$), 117.5 (qd, J_{CF} 276.5, 40.8, $(CF_3)FC{=}C$), 121.2 (qm, J_{CF} 271.15, $CF_3C{=}CF_2$), 123.5 (qq, J_{CF} 291.1, 3.9, $(CF_3)_2(CH_3)C$), 153.4 (dq, J_{CF} 220.5, 43.4, $(CF_3)FC{=}C$), 158.0 (dd, J_{CF} 181.8, 169.6, $CF_3C{=}CF_2$); ^{19}F NMR ($CDCl_3$, 282 MHz, $CFCl_3$ as an internal standard) δ: −58.8 (s, 3F, $(CF_3)FC{=}C$), −66.5 (qd, J_{FF} 11.7, 9.9, 1F, $CF_3C{=}CF_2$), −67.4 (q, J_{FF} 4.0, 3F, $CF_3C{=}CF_2$), −67.6 (m, 1F, $CF_3C{=}CF_2$), −68.7 (d, J_{FF} 23.1, 3F, $(CF_3)(CF_3)(CH_3)C$), −69.9 (dqd, J_{FF} 23.1, 9.9, 9.9, 3F, $(CF_3)(CF_3)(CH_3)C$), −92.8 (sep, J_{FF} 23.1, 1F, $(CF_3)FC{=}C$); GC–MS (EI, 70 eV) *m/z*: 408 (M^+, 11), 389 ($M^+ - F$, 6.4), 339 (13), 243 (12), 69 (100), 65 (18), 51 (18); IR (cm^{-1}): 1736, 1670 ($\nu_{C=C}$). Polyfluorocyclobutene **5** and polyfluorobutadiene **6** were thermally stable and could be handled in the air. No methanol-insoluble polymers were obtained in the reactions with CH_3Li or with CH_3MgBr.

Formation of methyl adducts, **1**–**4**, **7**, **8** and **10**, was explained by the well-established addition–elimination mechanism (Ad_N-E) [9,10], while polyfluorocyclobutene **5** and polyfluoropentadiene **6** could not be explained by such a mechanism. Probable pathways for the formation of **5** were presented in Scheme 3. The cyclized product **5** was commonly seen in the reaction of **T-2** and **T-3** with excess CH_3Li. Two reaction intermediates, **11** (path A) and **12** (paths B and C), are conceivable for the last cyclization step (Scheme 3). If the path A is the case, a rather unusual intramolecular S_N2 mechanism should be followed. However, the same kind of mechanism was previously reported by Chambers et al. on the cyclization reaction of perfluoro-3,4-dimethylhexa-3-ene [11]. Although the ring size is different, four-membered in our case and five-membered in the Chambers et al.'s case, there is a common feature, that is, a very congested perfluoro-system into which an incipient anionic nucleophile is compressed by the large steric strain energy. If the path B is taken, the thermally prohibited 2 + 2 cyclo-addition should be followed. However, it is well known that such a 2 + 2 cyclization proceeds in the perfluoro-system as is exemplified in the 2 + 2 cyclo-dimerization of tetrafluoroethylene. Therefore, the path B cannot be discarded. Moreover, changes of the product distribution on **7** and **5** (yields of **5** increased with the decrease of the yields of **7**) found in entries 8–10 support the existence of path C that passes through **13**. All other characterized products **1**, **3**, **7** and **8** are reasonably explained as is illustrated in the Scheme 3.

In contrast with CH_3Li, an excess use of CH_3MgBr caused one more unusual product **6** of which structure was confirmed by ^{1}H, ^{19}F, and ^{13}C NMR and GC–MS. Since pentadiene **6** was only detected by the reactions of **T-3** with CH_3MgBr, a tentative formation mechanism involving **2** (available only from **T-3**) was presented in Scheme 4. Less reactive CH_3MgBr is likely to attack the terminal allylic CF_3



Scheme 4.

group instead of the double bond of **2**, leading to the intermediate **14**, and then the diene structure **6** through the subsequent defluorination. Although the C–F activation promoted by magnesium [12,13] and zinc [14] metals has been reported recently, this defluorination promoted by a Grignard reagent has no precedent to the best of our knowledge. It is just our surprise to find that such a reactive diene **6** survived throughout the reaction under the presence of a Grignard reagent. More detailed studies about cyclization and defluorination and about the differences between CH_3Li and CH_3MgBr are under way.

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