Reaction of 1-chloroperfluorocycloalkene derivatives with nucleophiles

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Abstract

1-Acetyl-2-chloroperfluorocycloalkenes and 1-benzoyl-2-chloroperfluorocycloalkenes have been prepared by the coupling of 2-chloroperfluorocycloalkenyl copper reagent with acetyl chloride and benzoyl chloride, respectively. Similarly, 1-chloro-2-(*p*-nitrophenyl)perfluoro-cyclopentene and -cyclohexene were prepared by the reaction of 2-chloroperfluorocyclo-pentenyl and -hexenyl copper reagent with *p*-nitroiodobenzene.

The compounds contain not only highly activated double bonds but also charge-stabilizing groups in vinylic positions. The reaction of these compounds has been studied with various nucleophiles. They were very susceptible to nucleophilic attack at the chlorine-bonded carbon atom. Cyclobutene and cyclopentene derivatives underwent interesting nucleophilic displacement reactions of vinylic chlorine with alkoxide, amine and triethyl phosphite without allylic rearrangement under mild conditions. The stabilization effect to the generated carbanion intermediate by the acyl or *p*-nitrophenyl group undoubtedly dictates selectivity.

However, additional factors must be considered in cyclohexene derivatives in which both 'inward' and 'outward' eliminations occur from methoxide ion attack on perfluoroacyclohexene derivatives. Also the order of activating power for a double bond has been found to be benzoyl > acetyl ≫ *p*-nitrophenyl and 1-chlorotetrafluorocyclobutene derivatives were more reactive than 1-chlorohexafluorocyclopentene derivatives towards the various nucleophiles.

Introduction

Nucleophilic substitution reactions of halogenated alicyclic olefins have received considerable attention because of their mechanistic and synthetic importance [1]. Alicyclic polyfluorinated olefins were subsequently found to yield unsaturated products, and the mechanism illustrated in Scheme 1 has been advanced as a compromise between a concerted displacement of vinylic halide and an addition–elimination of hydrogen halide, the differentiation between which cannot be made on the basis of available data.

The results of Park *et al.* on the reaction of halogenated cycloalkenes with alkoxide ion have been rationalized by empirical rules which are referred to as 'Park's carbanionic theory' [2]. The main assumption is that, even when the double bond is substituted by mildly electron-attracting halogens, the substitution intermediate is a carbanion. Nucleophilic attack is assumed to always give the carbanion best stabilized by substituents in the α-position to the negative charge. However, carbanionic theory does not fit all types of nucleophilic reaction, including the substitution reactions of halogenated cycloalkenes with complex metal hydrides. Franz and Burton have pointed out that a ring size effect is very important in the reaction of cyclic fluoroolefins with alkoxide nucleophiles [3]. Although many results on the nucleophilic displacement reactions of fluorinated cycloalkenes have been reported [1, 4], studies on the fluorinated cycloalkenes, which contain vinylic substituents other than halogen, have been quite limited [5]. In most studies, the halogenated cycloalkenes which do not have highly activated double bonds and charge-stabilizing groups in vinylic positions underwent vinylic displacement and displacement with rearrangement in nucleophilic reactions. Recently, we have synthesized perfluorocycloalkene derivatives containing various vinylic substituents, by using alicyclic fluorinated vinylcopper reagents [6]. In this paper, we wish to report the results obtained from the reactions of perfluorocycloalkenes, containing electron-withdrawing groups at the vinylic position, with severable nucleophiles. For this work, 1-acetyl-2-chloroperfluorocycloalkenes (**Ia**, **IIa**, **IIIa**), 1-benzoyl-2-chloroperfluorocycloalkenes (**Ib**, **IIb**, **IIIb**) and 1-chloro-2-(*p*-nitrophenyl)perfluorocycloalkenes (**IIc**, **IIIc**) were selected because these

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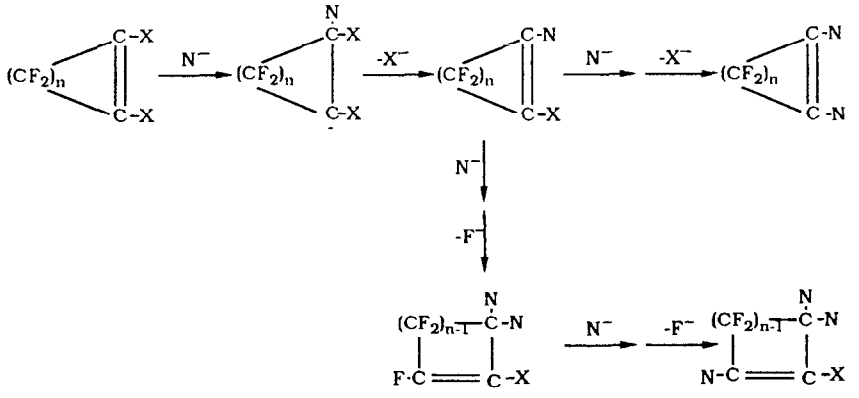


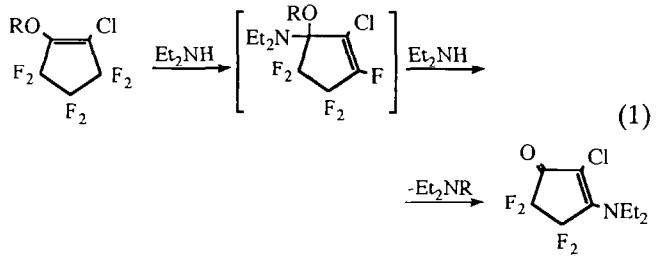
Scheme 1.

compounds contain not only highly activated double bonds but also charge-stabilizing groups at the vinylic position (Fig. 1).

Results and discussion

Reactions with diethylamine

Miller and co-workers have reported that the reaction of 1-alkoxy-2-chlorohexafluorocyclopentene with secondary amines gives aminoketones, as rearranged products [eqn. (1)] [7].



(1)

In our studies, we have found that the reaction of 2-chloroperfluorocycloalkenes (**I**, **II**, and **III**, respectively), containing acetyl, benzoyl or *p*-nitrophenyl groups at the vinylic position, with diethylamine gave stable monosubstituted tertiary perfluorocycloalkenylamines in good yield without rearrangement [eqn. (2)].

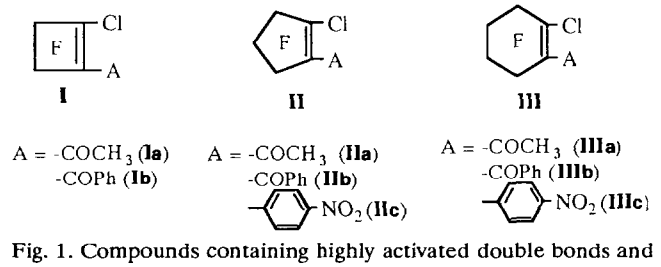
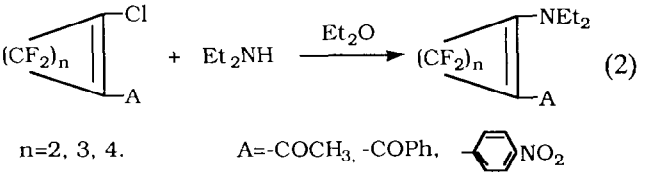


Fig. 1. Compounds containing highly activated double bonds and charge-stabilizing groups at the vinylic position.



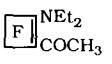
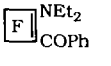
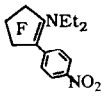
(2)

n=2, 3, 4. A=-$COCH_3$, -COPh,

This significant result was considered to be due to the stability of the carbanion intermediate in the nucleophilic displacement reaction of fluoro-olefins. Thus, 1-acetyl-2-chloroperfluorocycloalkenes (**Ia**, **IIa** and **IIIa**) reacted very smoothly with diethylamine to give the monoamino compounds, i.e. 1-acetyl-2-diethylaminoperfluorocycloalkenes (**1**, 89%; **2**, 90%, **3**, 90% yield). The reactions of the 1-benzoyl-2-chloroperfluorocycloalkenes (**Ib**, **IIb**, **IIIb**) with diethylamine proceeded at a slightly faster rate than those of the 1-acetyl-2-chloroperfluorocycloalkenes. The yields were 91% (**4**), 93% (**5**) and 95% (**6**). 1-Chloro-2-(*p*-nitrophenyl)-hexafluorocyclopentene (**IIc**) reacted with diethylamine at the reflux temperature of diethylether over a prolonged period to give a monosubstituted product, 1-diethylamine-2-(*p*-nitrophenyl)hexafluorocyclopentene (**7**, 86% yield). However, 1-chloro-2-(*p*-nitrophenyl)octafluorocyclohexene (**IIIc**) did not react under these conditions. These results are summarized in Table 1.

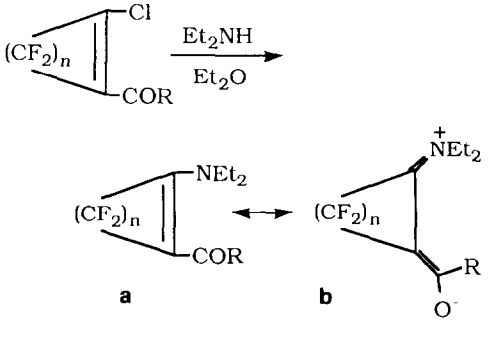
The ^1H NMR spectra of 1-acetyl-2-diethylaminotetrafluorocyclobutene (**1**) and of 1-benzoyl-2-diethylaminotetrafluorocyclobutene (**4**) show methylene protons at 3.8 ppm and 3.5 ppm, and at 4.0 ppm and 3.6 ppm, respectively, which are totally deshielded compared with normal methylene protons in amines. In the ^{19}F NMR spectra, the fluorines adjacent to amino groups are deshielded 11.7 ppm (−113.8 to −102.1 ppm) in 1-acetyl-2-diethylaminotetrafluorocyclobutene (**1**) and by 17.9 ppm (−113.2 ppm to −95.3 ppm) in 1-benzoyl-2-diethylaminotetrafluorocyclobutene (**4**) compared with the vinylic chloro compound.

TABLE 1. The reaction of the 2-chloroperfluorocycloalkene derivatives **I**, **II**, and **III**, respectively, with diethylamine

Entry No.	Reagent	Reaction conditions		Product		Yield (%)[a]
		Time (h)	Temp. (°C)			
1	**Ia**	1	r.t.		**(1)**	89
2	**IIa**	2	r.t.		**(2)**	90
3	**IIIa**	8	r.t.		**(3)**	90
4	**Ib**	1	r.t.		**(4)**	91
5	**IIb**	1	r.t.		**(5)**	93
6	**IIIb**	6	r.t.		**(6)**	95
7	**IIc**	72	reflux		**(7)**	86
8	**IIIc**	90	reflux			

[a]Isolated yield.

In the ^1H NMR and ^{19}F NMR spectra of 1-acetyl- and 1-benzoyl-hexafluorocyclopentenes **2** and **5**, we observed a deshielded peak which was quite similar to that of the tetrafluorocyclobutene derivatives. This observation indicates that the contribution of resonance hybrid 'b' is more important than the contribution of structure 'a' [eqn. (3)].



(3)

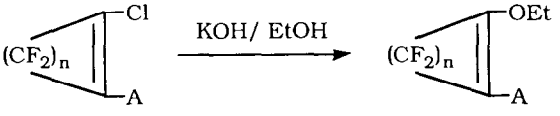
n=2, 3.
R=-CH_3, -Ph

In the IR spectra, absorption bands attributed to stretching of the C=O and cyclic C=C bonds are at lower frequencies compared with the vinylic chloro compounds. This is probably due to delocalization of the electrons from nitrogen to the carbonyl group, so that the resonance hybrid 'b' makes an important contribution.

Reaction with EtOH/KOH

Displacement of the vinylic halogen from fluorinated cyclo-olefins by alkoxide ions is well known. The product distribution varied with the alcohol and olefin used [1, 8].

Here, we have studied the reaction of 2-chloroperfluorocycloalkenes **I**, **II** and **III** with potassium hydroxide dissolved in absolute ethanol [eqn. (4)].



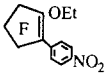
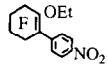
(4)

n=2, 3. A=-$COCH_3$, -COPh, -

These reactions were found to be exothermic and cooling was required. As shown in Table 2, 1-acetyl-2-chlorotetrafluorocyclobutene (**Ia**), 1-benzoyl-2-chlorotetrafluorocyclobutene (**Ib**) and hexafluorocyclopentene (**IIa**, **IIb**) derivatives react rapidly with KOH/EtOH solution at 0 °C to give monosubstituted products in good yield.

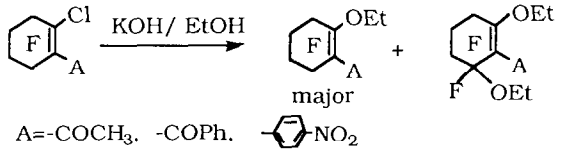
1-Chloro-2-(*p*-nitrophenyl)hexafluorocyclopentene (**IIc**) reacted smoothly with KOH/EtOH solution at room temperature, a result fully consistent with an inductively stabilized carbanion intermediate on the basis of the previously presented Park's carbanionic

TABLE 2. The reaction of the 2-chloroperfluorocycloalkene derivatives **I**, **II** and **III** with KOH/EtOH

Entry No.	Reagent	Reaction conditions		Product		Yield (%)[a]
		Time (h)	Temp. (°C)			
1	**Ia**	0.5	0		**(8)**	73
2	**IIa**	0.5	0		**(9)**	74
3	**IIIa**	0.5	0		**(10)**	45
					**(11)**	18
4	**Ib**	0.5	0		**(12)**	88
5	**IIb**	0.5	0		**(13)**	82
6	**IIIb**	0.5	15		**(14)**	54
					**(15)**	20
7	**IIc**	3	r.t.		**(16)**	72
8	**IIIc**	20	r.t.		**(17)**	65

[a]Isolated yield.

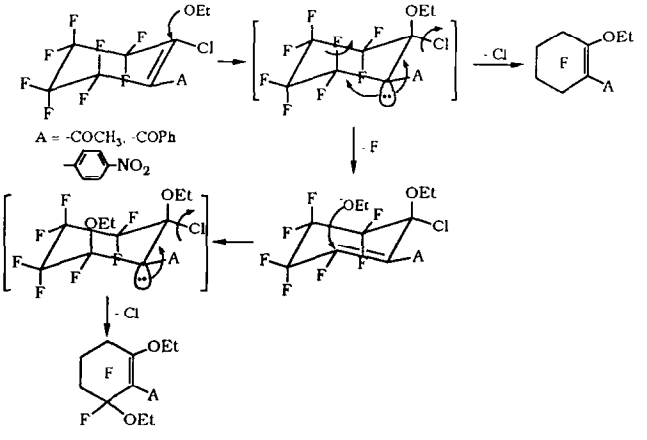
theory [2]. 2-Chloro-octafluorocyclohexene derivatives **III** yielded two main products which are separable by column chromatography [eqn. (5)].



(5)

This observation may be explained by 'inward' and 'outward' elimination as suggested by Tatlow and co-workers [9]. Thus, the product distribution results from a competition pathway between an electronically favored 'inward' elimination of Cl from C(Cl)OR and a stereochemically favored '*trans*-outward' elimination of F from C(F)F as shown in Scheme 2.

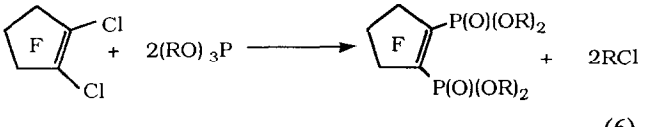
The fluorinated vinylic carbon is susceptible to a second nucleophilic attack to form the disubstituted products **11** and **15**.



Scheme 2.

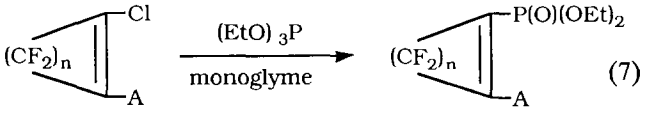
Reaction with triethyl phosphite

Frank has reported that the reaction of trialkyl phosphites with 1,2-dichloroperfluorocycloalkenes provides tetra-alkylperfluoro-1-cycloalkene-2-ylene phosphonates via displacement of both chlorine atoms [eqn. (6)] [10].



(6)

1-Acetyl-2-chlorotetrafluorocyclobutene (**Ia**), 1-benzoyl-2-chloro-tetrafluorocyclobutene (**Ib**) and -hexafluorocyclopentene (**IIa, IIb**) reacted readily with triethyl phosphite to give the corresponding products. 1-Chloro-2-(*p*-nitrophenyl)hexafluorocyclopentene (**IIc**) reacted slowly with triethyl phosphite to give a monophosphonated product [eqn. (7)].



(7)

n=2, 3. A=-$COCH_3$, -COPh, -$C_6H_4NO_2$

However, the perflourocyclohexene derivatives **IIIa, IIIb** and **IIIc** which are less reactive than the corresponding four- and five-membered cyclic compounds do not react with triethyl phosphite under these conditions. A qualitative measurement of the substituent effect on the reactions of 1-acyl-2-chlorotetrafluorocyclobutene (**Ia, Ib**), 1-acyl-2-chlorohexafluorocyclopentene (**IIa, IIb**) and 1-chloro-2-(*p*-nitrophenyl)-hexafluorocyclopentene (**IIc**) with triethyl phosphite was obtained.

As shown in Table 3, reaction of 1-acetyl-2-chlorotetrafluorocyclobutene (**Ia**), 1-acetyl-2-chlorohexafluorocyclopentene (**IIa**), and 1-benzoyl-2-chlorohexafluorocyclopentene (**IIb**) required 6 h, 8h and 2 h, respectively, on refluxing in monoglyme to complete reaction.

Finally, we have synthesized new alicyclic polyfluoroolefin derivatives in good yield.

Experimental

General

^{1}H NMR spectra were recorded on a Varian T-60A or Varian TF-80A NMR spectrometer, chemical shifts being reported from tetramethylsilane as internal standard. ^{19}F NMR spectra were recorded on a Varian FT-80A NMR spectrometer with trifluoroacetic acid (TFA) as external standard. ^{19}F NMR yields were determined by comparison of peak integrations using $PhCF_3$ as the internal standard (shifts negative upfield). IR spectra were recorded on a Perkin-Elmer model 267 grating spectrometer using KBr pellets or thin films. Mass spectra were recorded on a Hewlett Packard 5985A GC–MS system using electron impact. Melting points were determined on a Hoover Capillary melting point apparatus and are uncorrected.

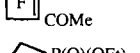
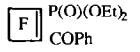
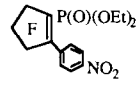
Materials

Diethyl ether and monoglyme were distilled from potassium hydroxide pellets. Triethyl phosphite was distilled from sodium. 1-Acetyl-2-chloroperfluorocycloalkenes (**Ia, IIa, IIIa**), 1-benzoyl-2-chloroperfluorocycloalkenes (**Ib, IIb, IIIb**), and 1-chloro-2-(*p*-nitrophenyl)perfluorocycloalkenes (**IIc, IIIc**) were prepared according to literature methods [6].

Preparation of 1-acetyl-2-diethylaminotetrafluorocyclobutene (1)

To a solution of diethylamine (2.2 g, 30 mmol) in diethyl ether (25 cm^3) was added 1-acetyl-2-chlorotetrafluorocyclobutene (3.04 g, 15 mmol) in diethyl ether (10 cm^3) at room temperature. After stirring for 1 h,

TABLE 3. The reaction of the 2-chloroperfluorocycloalkene derivatives **I, II,** and **III** with triethyl phosphite

Entry No.	Reagent	Reaction conditions		Product		Yield (%)[a]
		Time (h)	Temp. (°C)			
1	**Ia**	6	reflux		**(18)**	77
3	**IIa**	8	reflux		**(19)**	78
3	**Ib**	4	45		**(20)**	87
4	**IIb**	2	reflux		**(21)**	88
5	**IIc**	72	reflux		**(22)**	72
6	**IIIa–c**	48	reflux			

[a]Isolated yield.

the reaction mixture was filtered. The filtrate was washed with water and dried over anhydrous magnesium sulfate. It was then evaporated and the residue distilled to give pure compound **1** (3.2 g, 89%), b.p. 50–52 °C/0.6 mmHg. (Analysis: Found: C, 50.28; H, 5.39; F, 31.72; N, 5.91%. $C_{10}H_{13}F_4NO$ requires: C, 50.21; H, 5.48; F, 31.77; N, 5.86%. ^{19}F NMR ($CDCl_3$) δ: −102.1 (m, 2F); −111.5 (m, 2F) ppm. ^1H NMR ($CDCl_3$) δ: 3.80 (q, 2H); 3.35 (q, 2H); 2.13 (s, 3H); 1.20 (t, 3H); 1.10 (t, 3H) ppm. IR ν_{max} (neat) (cm^{-1}): 1695; 1630.

1-Acetyl-2-diethylaminohexafluorocyclopentene (**2**): B.p. 41–42 °C/0.1 mmHg. (Analysis: Found: C, 45.62; H, 4.51; F, 39.76; N, 4.92%. $C_{11}H_{13}F_6NO$ requires: C, 45.68; H, 4.53; F, 39.42; N, 4.84%). ^{19}F NMR ($CDCl_3$) δ: −97.7 (2F); −109.9 (2F); −128.4 (2F) ppm. ^1H NMR ($CDCl_3$) δ: 1.15 (t, 6H); 2.40 (s, 3H); 3.50 (q, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1680; 1590. MS *m/z*: 289 (M^+, 61.6%); 274 ($M-CH_3$, 33.8); 240 (100); 226 (70.9).

1-Acetyl-2-diethylamino-octafluorocyclohexene (**3**): B.p. 65–66 °C/2 mmHg. (Analysis: Found: C, 42.53; H, 3.92; F, 45.10; N, 4.21%. $C_{12}H_{13}F_8NO$ requires C, 42.48; H, 3.86; F, 44.81; N, 4.13%). ^{19}F NMR ($CDCl_3$) δ: −99.8 (2F); −109.8 (2F); −133.4 (4F) ppm. ^1H NMR ($CDCl_3$) δ: 1.15 (t, 6H); 2.39 (s, 3H); 3.25 (q, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1690; 1560. MS *m/z*: 339 (M^+, 10.3%); 71 (30.8); 40.3 (100).

1-Benzoyl-2-diethylaminotetrafluorocyclobutene (**4**): B.p. 135–136 °C/11 mmHg. (Analysis: Found: C, 59.71; H, 5.01; F, 25.73; N, 4.60%. $C_{15}H_{15}F_4NO$ requires: C, 59.80; H, 5.02; F, 25.23; N, 4.65%). ^{19}F NMR ($CDCl_3$) δ: −95.3 (m); −109.0 (m) ppm. ^1H NMR ($CDCl_3$) δ: 1.3 (t, 3H); 1.4 (t, 3H); 3.6 (q, 2H); 4.0 (q, 2H); 7.5–8.0 (m, 5H) ppm. IR ν_{max} (cm^{-1}): 1675; 1620; 1040. MS *m/z*: 301 (M^+, 12.6%); 77 (100).

1-Benzoyl-2-diethylaminohexafluorocyclopentene (**5**): M.p. 53–54 °C (from hexane/CH_2Cl_2). (Analysis: Found: C, 55.12; H, 4.28; F, 32.56; N, 4.19%. $C_{16}H_{15}F_6NO$ requires: C, 54.70; H, 4.30; F, 32.45; N, 3.99%). ^{19}F NMR ($CDCl_3$) δ: −97.2 (2F); −108.7 (2F); −126.3 (2F) ppm. ^1H NMR ($CDCl_3$) δ: 1.20 (t, 6H); 3.35 (q, 4H); 7.4–8.0 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1650; 1590; 1010. MS *m/z*: 351 (M^+, 20.0%); 105 ($PhCO^+$, 75.6); 77 (100).

1-Benzoyl-2-diethylamino-octafluorocyclohexene (**6**): M.p. 48–50 °C (from hexane/CH_2Cl_2). (Analysis: Found: C, 51.09; H, 3.75; F, 37.63; N, 3.53%. $C_{17}H_{15}F_8NO$ requires: C, 50.88; H, 3.77; F, 37.88; N, 3.49%). ^{19}F NMR ($CDCl_3$) δ: −102.3 (2F); −110.0 (2F); −132.9 (4F) ppm. ^1H NMR ($CDCl_3$) δ: 1.12 (t, 6H); 3.1 (q, 4H); 7.2–7.8 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1660; 1590. MS *m/z*: 401 (M^+, 15.4%); 105 ($PhCO^+$, 89.9); 77 (100).

1-Diethylamino-2-(*p*-nitrophenyl)hexafluorocyclopentene (**7**): M.p. 79–80 °C. (Analysis: Found: C, 48.85; H, 3.89; F, 30.78; N, 7.65%. $C_{15}H_{14}F_6N_2O_2$ requires: C, 48.92; H, 3.83; F, 30.95; N, 7.61%). ^{19}F NMR ($CDCl_3$) δ: −100.8 (2F); −109.8 (2F); −126.5 (2F) ppm. ^1H NMR ($CDCl_3$) nδ: 0.97 (t, 6H); 3.05 (q, 4H); 7.51–8.23 (m, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1595; 1535; 1360. MS *m/z*: 368 (M^+, 6.6]); 306 (70); 278 (100).

Preparation of 1-Acetyl-2-ethoxytetrafluorocyclobutene (8)

To a solution of 1-acetyl-2-chlorotetrafluorocyclobutene (3.04 g, 15 mmol) in ethanol (60 cm^3) was added potassium hydroxide (0.84 g, 15 mmol) in ethanol (15 cm^3) slowly at 0 °C. After being stirred for 30 min, the reaction mixture was diluted with water (200 cm^3) and extracted with diethyl ether. The extract was washed with water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled to give compound **8** (73%), b.p. 80–82 °C/10 mmHg. (Analysis: Found: C, 45.42; H, 3.76; F, 35.64%. $C_8H_8F_4O_2$ requires: C, 45.29; H, 3.80; F, 35.82%). ^{19}F NMR ($CDCl_3$) δ: −108.3 (m); −113.4 (m) ppm. ^1H NMR ($CDCl_3$) δ: 1.44 (t, 3H); 2.30 (s, 3H); 4.60 (q, 2H) ppm.

1-Acetyl-2-ethoxyhexafluorocyclopentene (**9**): B.p. 76–77 °C/4.2 mmHg. (Analysis: Found: C, 40.98; H, 3.01; F, 43.56%. $C_9H_8F_6O_2$ requires: C, 41.23; H, 3.08; F, 43.49%). ^{19}F NMR ($CDCl_3$) δ: −106.4 (2F); −113.9 (2F); −130.3 (2F) ppm. ^1H NMR ($CDCl_3$) δ: 1.58 (t, 3H); 2.56 (s, 3H); 4.63 (q, 2H) ppm. IR ν_{max} (neat) (cm^{-1}): 1695; 1610; 1020. MS *m/z*: 262 (M^+, 2.6%); 247 ($M-CH_3$); 219 (100).

1-Acetyl-2-ethoxyoctafluorocyclohexene (**10**) and 1-acetyl-2,6-diethoxyheptafluorocyclohexene (**11**): Separation of two main compounds via chromatography (n-hexane/ethyl acetate = 10:1); yield, **10** (45%) and **11** (18%). Compound **10**: b.p. 55–57 °C/5 mmHg. (Analysis: Found: C, 38.15; H, 2.56; F, 48.64%. $C_{10}H_8F_8O_2$ requires: C, 38.47; H, 2.58; F, 48.69%). ^{19}F NMR (CDCl3) δ: −101.4 (2F); −111.6 (2F); −133.4 (4F) ppm. Compound **11**: B.p. 78–80 °C/5 mmHg. (Analysis: Found: C, 42.66; H, 3.92; F, 39.18. $C_{12}H_{13}F_7O_3$ requires: C, 42.61, H, 3.87; F, 39.32%). ^{19}F NMR ($CDCl_3$) δ: −115.5 (2F); −124.0 (1F); −127.2 (2F); −128.6 (2F) ppm.

1-Benzoyl-2-ethoxytetrafluorocyclobutene (**12**): B.p. 91–92 °C/0.4 mmHg. (Analysis: Found: C, 56.95; H, 3.70; F, 27.75%. $C_{13}H_{10}F_4O_2$ requires: C, 56.93; H, 3.68; F, 27.72%). ^{19}F NMR ($CDCl_3$) δ: −103.0 (2F); −108.7 (2F) ppm. ^1H NMR ($CDCl_3$) δ: 1.6 (t, 3H); 4.65 (q, 2H); 7.6–8.1 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1670; 1610. MS *m/z*: (M^+, 7.6%); 245 ($M-Et$, 12.4); 105 ($PhCO^+$, 100).

1-Benzoyl-2-ethoxyhexafluorocyclopentene (**13**): B.p. 87–89 °C/0.4 mmHg. (Analysis: Found: C, 51.95; H, 3.21; F, 36.82%. $C_{14}H_{10}F_6O_2$ requires: C, 51.86; H, 3.11; F, 35.16%). ^{19}F NMR ($CDCl_3$) δ: −103.8 (2F); −111.6

(2F); 127.2 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.35 (t, 3H); 4.25 (q, 4H); 7.5–8.1 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1690; 1610; 1020. MS *m/z*: 324 (M^+, 1.9%); 105 ($PhCO^+$), 100).

1-Benzoyl-2-ethoxyoctafluorocyclohexene (**14**) and 1-benzoyl-2,6-diethoxyheptafluorocyclohexene (**15**): Separation of two main compounds via chromatography (n-hexane/ethyl acetate = 10:1); yield, **14** (54%) and **15** (20%). Compound **14**: B.p. 62–64 °C/3.5 mmHg. (Analysis: Found: C, 48.01; H, 2.67; F, 40.58%. $C_{15}H_{10}F_8O_2$ requires: C, 48.14; H, 2.69; F, 40.62%). ^{19}F NMR ($CDCl_3$) δ: −101.3 (2F); −118.6 (2F); −124.3 (4F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.31 (t, 3H); 4.28 (q, 2H); 7.2–8.1 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1720; 1600; 1450. MS *m/z*: 105 ($PhCO^+$, 100); 77 (52.5). Compound **15**: B.p. 77–80/3 mmHg. (Analysis: Found: C, 51.23; H, 3.81; F, 33.61%. $C_{17}H_{15}F_7O_3$ requires: C, 51.01; H, 3.78; F, 33.23%). ^{19}F NMR ($CDCl_3$) δ: −117.5 (2F); −124.3 (1F); −127.2 (2F); −128.6 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.1 (t, 3H); 1.3 (t, 3H); 3.7 (q, 2H); 4.2 (q, 2H); 7.2–7.9 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1680; 1600; 1450. MS *m/z*: 249 (40.3%); 105 ($PhCO^+$, 100); 77 (51.2).

Preparation of 1-ethoxy-2-(p-nitrophenyl)hexafluorocyclopentene (16)

To a solution of 1-chloro-2-(*p*-nitrophenyl)hexafluorocyclopentene (1.66 g, 5 mmol) in ethanol (30 cm^3) was added dropwise potassium hydroxide (0.30 g, 5.3 mmol) in 95% ethanol (20 cm^3) at 0 °C. After addition, the reaction mixture was brought to room temperature and stirred for an additional 3 h at that temperature. Usual work-up gave compound **16** (1.31 g, 77%), m.p. 49–50 °C. (Analysis: Found: C, 45.83; H, 2.86; F, 33.32; N, 4.16%. $C_{13}H_9F_6NO_3$ requires: C, 45.76; H, 2.66; F, 33.41; N, 4.11%. ^{19}F NMR ($CDCl_3$) δ: −105.0 (2F); −11.4 (2F); −127.6 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.5 (t, 3H); 4.5 (q, 2H); 7.5–8.5 (m, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1645; 1610; 1350. MS *m/z*: 341 (M^+, 12.6%); 249 (100); 219 (63.2).

1-Ethoxy-2-(*p*-nitrophenyl)octafluorocyclohexene (**17**): M.p. 45–47 °C. (Analysis: Found: C, 42.92; H, 2.31; F, 38.63; N, 3.32%. $C_{14}H_9F_8NO_3$ requires:C, 42.98; H, 2.32; F, 38.85; N, 3.58%). ^{19}F NMR ($CDCl_3$) δ: −106.2 (2F); −115.1 (2F); −134.1 (4F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.32 (t, 3H); 4.1 (q, 2H); 7.6–8.5 (m, 4H) ppm.

Preparation of diethyl 2-acetyltetrafluoro-1-cyclobutene-1-yl phosphonate (18)

To a solution of 1-acetyl-2-chlorotetrafluorocyclobutene (2.02 g, 10 mmol) in monoglyme (30 cm^3) was added dropwise triethyl phosphite (1.66 g, 10 mmol) at room temperature. The reaction mixture was heated to reflux and stirred for 6 h. It was then evaporated and the residue distilled to give compound **18** (2.32 g, 77%), b.p. 74–75 °C/0.15 mmHg. (Analysis: Found: C, 39.69; H, 4.28; F, 25.02; P, 10.28%. $C_{10}H_{13}F_4O_4P$ requires: C, 39.48; H, 4.31; F, 24.99; P, 10.18%. ^{19}F NMR ($CDCl_3$) δ: −105.5 (m, 2F); −107.0 (m, 2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.4 (t, 6H); 2.57 (s, 3H); 4.27 (m, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1710; 1620; 1130. MS *m/z*: 304 (M^+, 16.2%); 259 (M−OEt, 27.9); 43 (CH_3CO^+, 100).

Diethyl 2-acetylhexafluoro-1-cyclopentene-1-yl phosphonate (**19**): B.p. 84–85 °C/0.8 mmHg. (Analysis: Found: C, 37.52; H, 3.64; F, 32.32; P, 8.82%. $C_{11}H_{13}F_6O_4P$ requires: C, 37.30; H, 3.70; F, 32.19; P, 8.75%). ^{19}F NMR ($CDCl_3$) δ: −107.4 (2F); −109.5 (2F); −130.6 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.4 (t, 6H); 2.6 (s, 3H); 4.0–4.4 (m, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1740; 1640; 1270. MS *m/z*: 354 (M^+, 9.0%); 283 (100); 262 (27.5).

Diethyl 2-benzoyltetrafluoro-1-cyclobutene-1-yl phosphonate (**20**): B.p. 119–120 °C/0.2 mmHg. (Analysis: Found: C, 49.27; H, 4.07; F, 21.06; P, 8.96%. $C_{15}H_{15}F_4O_4P$ requires: C, 49.19; H, 4.13; F, 20.75; P, 8.46%). ^{19}F NMR ($CDCl_3$) δ: −102.8 (m, 4F); ppm. ^{1}H NMR ($CDCl_3$) δ: 1.3 (t, 6H); 4.2 (m, 4H); 7.5–7.9 (m 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1710; 1630; 1060. MS *m/z*: 366 (M^+, 1.4%); 105 ($PhCO^+$, 100).

Diethyl 2-benzoylhexafluoro-1-cyclopentene-1-yl phosphonate (**21**): B.p. 109–110 °C/0.23 mmHg. (Analysis: Found: C, 46.32; H, 3.69; F, 27.68; P, 7.58%. $C_{16}H_{15}F_6O_4P$ requires: C, 46.16; H, 3.63; F, 27.39; P, 7.44%). ^{19}F NMR ($CDCl_3$) δ: −107.2 (2F); −109.3 (2F); −128.3 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.31 (t, 6H); 3.95–4.35 (m, 6H); 7.5–8.0 (m, 5H) ppm. IR ν_{max} (neat) (cm^{-1}): 1690; 1610; 1270. MS *m/z*: 416 (M^+, 2.4%); 138 (27.5); 105 ($PhCO^+$, 100); 77 (76.5).

Diethyl 2-(*p*-nitrophenyl)hexafluoro-1-cyclopentene-1-yl phosphonate (**22**): M.p. 153–154 °C. (Analysis: Found: C, 41.62; H, 3.21; F, 26.08; N, 3.32; P, 7.08%. $C_{15}H_{14}F_6NO_5P$ requires: C, 41.58; H, 3.26; F, 26.31; N, 3.23; P, 7.15%). ^{19}F NMR ($CDCl_3$) δ: −107.5 (2F); −111.0 (2F); −128.0 (2F) ppm. ^{1}H NMR ($CDCl_3$) δ: 1.18 (t, 6H); 3.84–4.22 (m, 4H); 7.51–8.38 (m, 4H) ppm. IR ν_{max} (neat) (cm^{-1}): 1610; 1580; 1350. MS *m/z*: 433 (M^+, 8.3%); 249 (100); 203 (36.8).

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