

Preparation and Reactions of 2-Chloroperfluorocycloalkenylcopper Reagents

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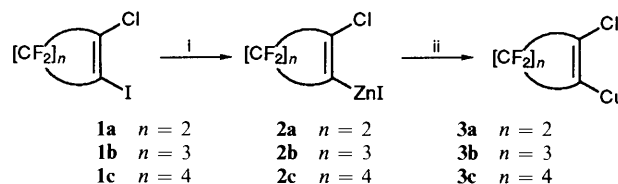
1-Chloro-2-iodoperfluorocycloalkenes react with activated zinc powder in dimethylformamide solvent at room temperature to give 2-chloroperfluorocycloalkenylzinc reagents. Treatment of these organozinc reagents with copper(I) bromide at 0 °C or at room temperature provides a simple route to the corresponding 2-chloroperfluorocycloalkenylcopper. The yield is excellent. These organocopper reagents, which are stable at room temperature in the absence of oxygen and/or moisture, can be used for the production of C–C bonds *via* reactions with alkyl, aryl and acyl halides. Reaction of these organocopper reagents with acyl halides leads to previously unreported acylated polyfluorocycloalkenes.

Fluoroalicyclic derivatives of various metals and metalloids are known.^{1–3} Polyfluorocycloalkenyl Grignard reagents can be obtained by exchange of a vinylic halogen with ethylmagnesium bromide,⁴ although these reagents are very unstable at room temperature. Fluorocycloalkenyllithiums are also prepared by displacement of hydrogen or iodine atoms with methyl-lithium.^{5,6} On the other hand, butyllithium is employed for the preparation of 1-chloro-2-lithio-perfluorocycloalkenes.⁷ These reagents exhibit high reactivity with halogens, water, carbon dioxide or acetaldehyde. They decompose at –10 to 15 °C. The low thermal stability and reactivity of previously reported fluoroalicyclic derivatives of metals and metalloids prompted a development of metal reagents which would be thermally more stable and yet show higher reactivity towards a variety of substrates. Even though vinylcopper reagents derived from acyclic polyfluoroolefins have received special attention,⁸ no report on analogous organocopper derivatives of alicyclic polyfluoroolefins is available. These organocopper derivatives could play an invaluable role in the synthesis of polyfluorocycloalkene derivatives. In this paper we report the convenient synthesis of fluorocycloalkenylcopper reagents (namely, 2-chlorotetrafluorocyclobut-1-enylcopper **3a**, 2-chlorohexafluorocyclopent-1-enylcopper **3b** and 2-chlorooctafluorocyclohex-1-enylcopper **3c** and the utilization of these reagents as intermediates for the synthesis of polyfluorocycloalkene derivatives, which have not been reported in the literature.

Results and Discussion

The usefulness of alkenylcopper and alkenylcuprate reagents in organic synthesis is well documented.⁹ The low thermal stability of fluorinated vinyl-lithium and Grignard reagents has generally limited their use in synthesis, but a few recent reports on the fluorinated vinylcopper reagents indicate otherwise.⁸ The present work is focused on the preparation and synthetic applications of alicyclic fluorinated vinylcopper reagents. Fluorinated alkenylzinc reagents are good precursors for the corresponding copper reagent. Previous attempts to prepare 2-chloroperfluorocycloalkenylzinc reagents (2-chlorotetrafluorocyclobut-1-enylzinc reagent **2a**, 2-chlorohexafluorocyclopent-1-enylzinc reagent **2b**, 2-chlorooctafluorocyclohex-1-enylzinc reagent **2c**) from the corresponding lithium reagents with zinc chloride have not been successful.¹⁰ In previous work^{11,12} we successfully prepared these zinc reagents **2** by direct reaction of the iodide derivatives (1-chloro-2-iodotetra-

fluorocyclobutene **1a**, 1-chloro-2-iodohexafluorocyclobutene **1b**, 1-chloro-2-iodooctafluorocyclohexene **1c**) with zinc metal. The iodide derivatives **1** react readily with activated zinc powder in dimethylformamide (DMF) at room temperature. After a short induction period, these reactions become exothermic. The colour changes from grey to brown, and the reaction is complete in about one hour. Yields are quantitative. These zinc reagents exhibit good thermal stability. Even at 80 °C they show no appreciable decomposition for 3 days in DMF under nitrogen. These zinc reagents are sensitive to moisture, being readily hydrolysed to reduced olefins. Upon addition of copper(I) bromide to a filtered solution of a zinc reagent **2** at 0 °C, or at room temperature, the corresponding copper reagent was formed (Scheme 1). The yields determined

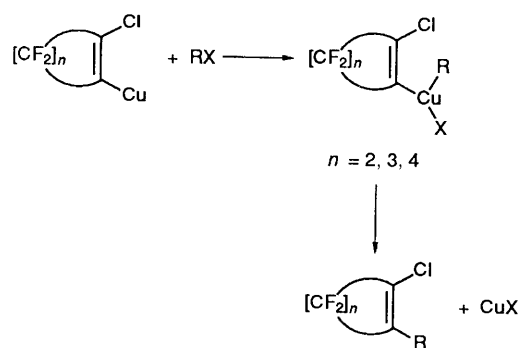


Scheme 1 Reagents and conditions: i, Zn, DMF, room temp.; ii, CuBr

by ¹⁹F NMR analysis^{11,12} were 92% (**3a**), 96% (**3b**) and 98% (**3c**). Unlike the zinc reagents **2**, the copper reagents **3** could not be prepared directly by the reaction of the metal with 1-chloro-2-iodoperfluorocycloalkenes **1**. Treatment of compounds **1** with copper powder in DMF provided only the corresponding dimeric coupling product.¹³ The copper reagents were found to be quite stable at room temperature in the absence of oxygen and/or moisture. Reagents **3a** showed 2% loss of activity after 1 day, and 30% loss of activity after 7 days at room temperature in DMF under nitrogen. The other copper reagents (**3b**, **3c**) exhibit similar stability, a loss of only 10% activity even after 7 days at room temperature. At higher temperatures (>80 °C), they undergo rapid decomposition to give reduced olefins and tars. This excellent stability allows their use in large-scale preparations and utilization over an extended period in a variety of synthetic reactions without any significant change in activity. Table 1 summarizes the results of the preparation of the metal reagents. The ¹⁹F NMR signal of the allylic fluorines in the metal reagents **2** and **3** is shifted downfield by 4–7 ppm from that of the allylic fluorines adjacent to iodine in iodide derivatives **1**. The copper reagents **3** participate in a variety of alkylations as summarized in Table 2. They react with alkyl

halides in DMF at room temperature. The yields are quite good for benzyl bromide and allyl halide, but the reaction rates are very slow with methyl and phenyl iodides. Park¹⁴ reported a synthetic route to alkyl derivatives of polyfluorocycloalkenes, in which a 1,2-dichloroperfluorocycloalkene was alkylated by Grignard reagents. The present method offers advantages over the previously reported method in versatility and facility of reaction. A mechanistic interpretation other than a highly discriminatory nucleophilic substitution is conceivable. Currently, a mechanism involving oxidative addition and reductive elimination can explain the reactivity of organo-copper reagents. Copper(III) complexes have been postulated as reaction intermediates.¹⁵ Oxidative addition of an alkyl halide to the copper(I) reagent would yield a planar copper(III) intermediate, as illustrated in Scheme 2.

Reductive elimination of two organic ligands from the copper(III) intermediate would lead to a coupled product and Cu^I species. To demonstrate the synthetic utility of the reagents **3** we prepared a number of previously unreported compounds through treatment of reagents **3** with acid halides. The results from these reactions are summarized in Table 3. Acylation proceeded readily and the yields were excellent for the cyclopentenylcopper reagent **3b** and the cyclohexenylcopper reagent **3c**. The low yields of acylation of the copper reagent **3a** are presumably due to its decomposition in DMF. Burton and co-workers¹⁶ reported that the acylation of trifluorovinyl-copper in DMF results in its decomposition as the reaction product reacts with DMF. Reaction of the organocopper



Scheme 2

reagent **3a** with acid chlorides was carried out at low temperature (-20°C) to minimize the decomposition; however, even then yields were low to moderate. These reactions are nearly complete after 10 min at room temperature and most give reduced olefins and unidentified tars as byproducts. While the copper reagents have been under observation only in DMF as solvent,¹⁶ the zinc reagents participate in a similar functionalization reaction involving CuBr mediation in glyme solvents. Fortunately, the zinc reagent **2a** was readily formed in a glyme solvent. With the zinc reagent **2a** thus prepared, the acylation reaction proceeded to give high yields with CuBr as the catalyst at room temperature. The results of acylation of the copper reagent **3a** in glymes are summarized in Table 4. Although the metathesis of the 2-chlorotetrafluorocyclobut-1-enylzinc reagent **2a** with copper(I) bromide in DMF gave a stable copper reagent **3a**, the ¹⁹F NMR spectrum of species **2a** in glyme solvents remained unchanged upon addition of CuBr. In the presence of CuBr, however, the reactivity of the zinc reagent **2a** is greatly enhanced. This change in reactivity suggests the formation of an intermediate copper reagent, which is responsible for the reactivity in the acylation.

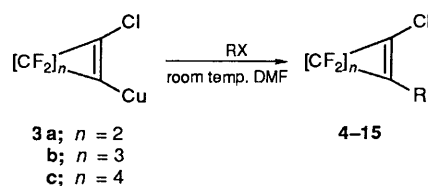
The low solubility of CuBr in glyme solvents and the poor stabilization of the resultant copper reagent **3a** in glymes are believed to be responsible for the production of the copper reagent **3a** in low concentration. Nevertheless, fresh copper reagent is produced until the end of the reaction during the course of the acylation. In conclusion, we present here a simple,

Table 1 Preparation of metal reagents

Reagent	Yield ^a (%)	δ_{F} ^b
2a	97	-110.2, -103.7
2b	98	-100.9, -112.0, -127.8
2c	99	-101.2, -112.8, -138.4
3a ^c	92	-109.0, -102.4
3b ^c	96	-98.8, -110.7, -127.3
3c ^c	98	-98.8, -112.0, -138.3

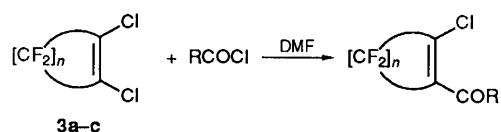
^a ¹⁹F NMR yield vs. PhCF₃. ^b Chemical shifts are relative to CFCl₃. Measurements were made in CDCl₃ with TFA as external standard. ^c Copper reagent was prepared from the zinc reagent. Yield is based on starting material used.

Table 2 Reaction of copper reagents with alkyl halides



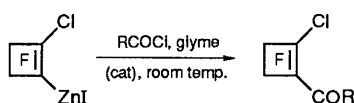
Entry	Reagent	RX	Time (t/h)	Product (R)	Yield ^a (%)
1	3a	CH ₂ =CHCH ₂ Cl	1	4 CH ₂ CH=CH ₂	87
2	3a	PhCH ₂ Br	48	5 CH ₂ Ph	78
3	3a	MeI	120	6 Me	42
4	3a	PhI	120	7 Ph	47
5	3b	CH ₂ =CHCH ₂ Br	0.5	8 CH ₂ CH=CH ₂	90
6	3b	PhCH ₂ Br	48	9 CH ₂ Ph	76
7	3b	MeI	160	10 Me	59
8	3b	PhI	120	11 Ph	52
9	3c	CH ₂ =CHCH ₂ Br	2	12 CH ₂ CH=CH ₂	71
10	3c	PhCH ₂ Br	55	13 CH ₂ Ph	61
11	3c	MeI	160	14 Me	52
12	3c	PhI	140	15 Ph	50

^a Isolated yields. Yields are based on starting 1-chloro-2-iodoperfluorocycloalkene used.

Table 3 Reaction of copper reagents with acid halides

Entry	Reagent	R	Temperature (T/°C)	Time (t/h)	Product (R)	Yield ^a (%)
13	3a	Me	-20	5	16	43
14	3a	Et	-20	5	17	58
15	3a	Ph	-20	5	18	53
16	3a		-20	5	19	38
17	3a		-20	5	20	32
18	3b	Me	0	1	21	74
19	3b	Et	0	1	22	78
20	3b	Ph	0	1	23	89
21	3b	PhCH ₂	0	1	24	63
22	3b	Me ₂ N	room temp.	24	25	52
23	3b		0	1	26	76
24	3b		0	1	27	85
25	3b		0	1	28	82
26	3c	Me	room temp.	2	29	79
27	3c	Et	room temp.	2	30	87
28	3c	Ph	room temp.	2	31	88
29	3c		room temp.	2	32	82
30	3c		room temp.	2	33	84
31	3c		room temp.	2	34	59

^a Isolated yields. Yields are based on starting 1-chloro-2-iodoperfluorocycloalkene used.

Table 4 Reaction of zinc reagent 2a with acyl halides in glyme solvent containing a catalytic CuBr

Entry	R	Solvent	Time (t/h)	Product (R)	Yield ^a (%)
13	Me	Triglyme	12	21	87
14	Et	Triglyme	12	22	85
17		Triglyme	12	27	73
32		Monoglyme	12	35	58

^a Isolated yields.

mild method for the preparation of fluorinated cycloalkenyl-copper reagents in high yield. These organometallic compounds, which satisfy the criteria for the preparation of stable and reactive fluorinated cycloalkenyl organometallic reagents, have been utilized in the synthesis of a variety of substituted fluorocycloalkene derivatives.

Experimental

General.—¹H NMR spectra were recorded on a Varian T-60A or Varian FT-80A NMR spectrometer, and chemical shifts are reported from tetramethylsilane as internal standard. ¹⁹F NMR spectra were recorded on a Varian FT-80 A NMR spectrometer with trifluoroacetic acid (TFA) as external

standard. Chemical shifts were reported relative to CFCl_3 (δ_{F} of 77), and J -values are given in Hz. ^{19}F NMR yields were determined by comparison of the peak integrations using PhCF_3 as the internal standard. IR spectra were recorded on a Perkin-Elmer Model 267 grating spectrometer with KBr pellets or thin films. Mass spectra were recorded on a Hewlett-Packard 5985A GC/MS system using the electron impact (EI) method. B.p.s determined during distillation were uncorrected. M.p.s were determined on a Hoover Capillary melting point apparatus and are uncorrected.

Materials.—1-Chloro-2-iodoperfluorocycloalkenes were prepared by the known procedure.¹⁷ Thiophene-2-carbonyl (2-thenoyl) chloride,¹⁸ thiophene-2,5-dicarbonyl dichloride¹⁹ and 2-furoyl chloride²⁰ were prepared according to the literature. All solvents were stored under nitrogen in brown bottles capped with a rubber septum. DMF was distilled from P_2O_5 under reduced pressure and stored over 4 Å molecular sieves under nitrogen. Triglyme (TG) and monoglyme (MG) were distilled from CaH_2 . Unless otherwise indicated, all other reagents were purified prior to use in the usual manner. Copper(I) bromide was purchased from Aldrich Chemical Co. and was purified by a method similar to that of Osterlof.²¹ Zinc powder was activated by washing successively with dil. HCl and then distilled water and dried *in vacuo* overnight at 120 °C. Reactions were conducted at room temperature unless otherwise indicated.

2-Chlorotetrafluorocyclobut-1-enylzinc Iodide 2a.—A 50 cm^3 , two-neck, round-bottom flask fitted with condenser was charged with activated zinc powder (3.4 g, 52 mmol) and dry DMF (35 cm^3) under nitrogen. To this mixture was added 1-chloro-3,3,4,4-tetrafluoro-2-iodocyclobutene **1a** (10 g, 35 mmol) dropwise. After the induction period of several minutes, an exotherm occurred; addition of compound **1a** was maintained at such a rate as to maintain a reasonable exotherm. The reaction mixture was stirred until the mild exotherm subsided. Then, the excess of zinc was removed by filtration through a medium fritted glass filter (Schlenk funnel). ^{19}F NMR analysis of the resultant solution indicated a 97% yield of product **2a**; $\delta_{\text{F}}(\text{CDCl}_3)$ –103.7 (m) and –110.2 (m).

2-Chlorohexafluorocyclopent-1-enylzinc Iodide 2b.—98% Yield; $\delta_{\text{F}}(\text{CDCl}_3)$ –100.9 (2 F), –112.0 (2 F) and –127.8 (2 F).

2-Chlorooctafluorocyclohex-1-enylzinc Iodide 2c.—99% Yield; $\delta_{\text{F}}(\text{CDCl}_3)$ –101.2 (2 F), –112.8 (2 F) and –138.4 (4 F).

2-Chlorotetrafluorocyclobut-1-enylcopper 3a.—To a filtered solution of reagent **2a** prepared from iodide **1a** (5 g, 17.5 cm^3) and activated zinc powder (1.7 g, 26 mmol) in DMF (20 cm^3) at 0 °C was added CuBr (2.5 g, 17.5 mmol). The reaction mixture was stirred for 1 h and allowed to warm up to room temperature. ^{19}F NMR analysis indicated a 92% yield of the organocopper reagent **3a** from starting iodide. This solution was used for subsequent functionalization reactions; $\delta_{\text{F}}(\text{CDCl}_3)$ –102.4 (m) and –109.6 (m).

2-Chlorohexafluorocyclopent-1-enylcopper 3b.—To a filtered solution of reagent **2b** prepared from iodide **1b** (6.73 g, 20 mmol) and activated zinc powder (1.83 g, 28 mmol) in dry DMF (20 cm^3) was added CuBr (2.86 g, 20 mmol). After the reaction mixture had been stirred for 1 h, ^{19}F NMR analysis indicated a 96% yield of organocopper reagent **3b**; $\delta_{\text{F}}(\text{CDCl}_3)$ –98.8 (2 F), –110.7 (2 F) and –127.3 (2 F).

2-Chlorooctafluorocyclohex-1-enylcopper 3c.—To a filtered

solution of reagent **2c** prepared from iodide **1c** (5.80 g, 15 mmol) and activated zinc powder (1.30 g, 20 mmol) in dry DMF (13 cm^3) was added CuBr (2.86 g, 20 mmol). The reaction mixture was stirred for 2 h, when ^{19}F NMR analysis showed 98% yield; $\delta_{\text{F}}(\text{CDCl}_3)$ –98.2 (2 F), –112.0 (2 F) and –138.3 (4 F).

1-Allyl-2-chlorotetrafluorocyclobutene 4.—The copper reagent **3a** was prepared from 1-chloro-2-iodotetrafluorocyclobutene **1a** (5 g, 17.5 mmol), activated zinc powder (1.7 g, 26 mmol) and CuBr (2.5 g, 17.5 mmol) in DMF (20 cm^3). To this solution was added allyl chloride (1.3 g, 17.5 mmol). After being stirred for 1 h the reaction mixture was flash distilled. The distillate was washed with water to remove DMF and was then dried over anhydrous magnesium sulphate. Fractional distillation of the crude product gave compound **4** (3.0 g, 87%), b.p. 117 °C (Found: C, 41.8; H, 2.4; F, 37.7; Cl, 17.5. $\text{C}_7\text{H}_5\text{ClF}_4$ requires C, 41.92; H, 2.51; F, 37.89; Cl, 17.68%); $\delta_{\text{F}}(\text{CDCl}_3)$ –112.8 (m) and –114.3 (m); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.81–3.14 (2 H, br d), 5.10–5.37 (2 H, td) and 5.75 (1 H, m); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 3090, 2990 and 1650.

1-Benzyl-2-chlorotetrafluorocyclobutene 5.—B.p. 56–57 °C (3 mmHg) (Found: C, 52.4; H, 2.8; F, 30.2; Cl, 14.2. $\text{C}_{11}\text{H}_7\text{ClF}_4$ requires C, 52.71; H, 2.82; F, 30.33; Cl, 14.15%); $\delta_{\text{F}}(\text{CDCl}_3)$ –111.8 (m) and –113.4 (m); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.58 (2 H, m) and 7.21 (5 H, m).

1-Chloro-3,3,4,4-tetrafluoro-2-methylcyclobutene 6.—B.p. 83 °C (Found: C, 34.0; H, 1.7; F, 43.4; Cl, 20.4. $\text{C}_5\text{H}_3\text{ClF}_4$ requires C, 34.41; H, 1.73; F, 43.55; Cl, 20.31%); $\delta_{\text{F}}(\text{CDCl}_3)$ –113.0 (m) and –113.7 (m); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.94 (3 H, m); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1585.

1-Chloro-3,3,4,4-tetrafluoro-2-phenylcyclobutene 7.—B.p. 70–71 °C (15 mmHg) (Found: C, 51.5; H, 2.1; F, 32.1; Cl, 15.0. $\text{C}_{10}\text{H}_5\text{ClF}_4$ requires C, 50.76; H, 2.13; F, 32.12; Cl, 14.98%); $\delta_{\text{F}}(\text{CDCl}_3)$ –112.0 (m) and –113.0 (m); $\delta_{\text{H}}(\text{CDCl}_3)$ 7.46 (m).

1-Allyl-2-chlorohexafluorocyclopentene 8.—B.p. 58–59 °C (50 mmHg) (Found: C, 38.3; H, 2.0; F, 45.4; Cl, 14.3. $\text{C}_8\text{H}_5\text{ClF}_6$ requires C, 38.34; H, 2.01; F, 45.50; Cl, 14.15%); $\delta_{\text{F}}(\text{CDCl}_3)$ –110.0 (2 F), –112.7 (2 F) and –129.2 (2 F); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.15–3.40 (2 H, br d), 5.12–5.45 (2 H, td) and 5.62–6.15 (1 H, m); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1630; m/z 252 ($\text{M}^+ + 2$, 30.9%), 250 (M, 90.7) and 145 (100).

1-Benzyl-2-chlorohexafluorocyclopentene 9.—B.p. 62–63 °C (3 mmHg) (Found: C, 47.8; H, 2.4; F, 38.1; Cl, 11.7. $\text{C}_{12}\text{H}_7\text{ClF}_6$ requires C, 47.9; H, 2.35; F, 37.9; Cl, 11.79%); $\delta_{\text{F}}(\text{CDCl}_3)$ –107.5 (2 F), –113.3 (2 F) and –128.3 (2 F); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.60 (2 H, m) and 7.40 (5 H, m); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1605.

1-Chloro-3,3,4,4,5,5-hexafluoro-2-methylcyclopentene 10.—B.p. 59–61 °C (100 mmHg) (Found: C, 32.0; H, 1.3; F, 50.9; Cl, 15.7. $\text{C}_6\text{H}_3\text{ClF}_6$ requires C, 32.09; H, 1.35; F, 50.77; Cl, 15.79%); $\delta_{\text{F}}(\text{CDCl}_3)$ –112.0 (2 F), –112.7 (2 F) and –129.3 (2 F); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.85–2.05 (br s); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1620; m/z 226 ($\text{M}^+ + 2$, 29.9%), 224 (M, 92.1) and 155 (100).

1-Chloro-3,3,4,4,5,5-hexafluoro-2-phenylcyclopentene 11.—B.p. 69–69.9 °C (10 mmHg) (Found: C, 46.0; H, 1.7; F, 39.85; Cl, 12.3. $\text{C}_{11}\text{H}_5\text{ClF}_6$ requires C, 46.10; H, 1.76; F, 39.78; Cl, 12.37%); $\delta_{\text{F}}(\text{CDCl}_3)$ –106.9 (t, J_{FF} 4), –111.1 (t, J_{FF} 4) and –128.7 (m); $\delta_{\text{H}}(\text{CDCl}_3)$ 6.9–7.7 (m); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1590; m/z 288 ($\text{M}^+ + 2$, 12.6%), 288 (M, 38.7) and 204 (100).

1-Allyl-2-chlorooctafluorocyclohexene 12.—B.p. 40–42 °C

(65 mmHg) (Found: C, 35.7; H, 1.6; F, 50.6; Cl, 11.7. $C_9H_5ClF_8$ requires C, 35.96; H, 1.68; F, 50.57; Cl, 11.79%); $\delta_F(CDCl_3)$ -114.1 (2 F), -115.73 (2 F), -138.49 (2 F) and -139.74 (2 F); $\delta_H(CDCl_3)$ 3.15–3.50 (2 H, br d), 5.0–5.35 (2 H, br), 5.45–6.0 (1 H, m); $\nu_{max}(neat)/cm^{-1}$ 3090, 2950 and 1650; m/z 302 ($M^+ + 25\%$) and 300 (M, 30.5).

1-Benzyl-2-chlorooctafluorocyclohexene 13.—B.p. 64–66 °C (2.5 mmHg) (Found: C, 44.35; H, 2.0; F, 43.3; Cl, 10.1. $C_{13}H_7ClF_8$ requires C, 44.53; H, 2.01; F, 43.35; Cl, 10.11%); $\delta_F(CDCl_3)$ -114.30 (2 F), 7114.95 (2 F), -137.97 (2 F) and -139.40 (2 F); $\delta_H(CDCl_3)$ 4.05 (2 H, s) and 7.15–7.55 (5 H, m); $\nu_{max}(neat)/cm^{-1}$ 3070 and 1640; m/z 352 ($M^+ + 2$, 32%) and 350 (M, 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-methylcyclohexene 14.—B.p. 50–52 °C (98 mmHg) (Found: C, 30.5; H, 1.1; F, 55.1; Cl, 12.8. $C_7H_3ClF_8$ requires C, 30.62; H, 1.10; F, 55.36; Cl, 12.91%); $\delta_F(CDCl_3)$ -114.8 (2 F), -115.1 (2 F) and -138.5 (4 F); $\delta_H(CDCl_3)$ 1.93 (3 H, s); $\nu_{max}(neat)/cm^{-1}$ 1650; m/z 276 ($M^+ + 2$, 29.5%), 274 (M, 90.1) and 239 (M - Cl, 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-phenylcyclohexene 15.—B.p. 64–66 °C (35 mmHg) (Found: C, 42.7; H, 1.5; F, 45.0; Cl, 10.3. $C_{12}H_5ClF_8$ requires C, 42.81; H, 1.50; F, 45.16; Cl, 10.53%); $\delta_F(CDCl_3)$ -110.3 (2 F), -112.5 (2 F) and -136.4 (4 F); $\delta_H(CDCl_3)$ 6.92–7.76 (5 H, m); $\nu_{max}(neat)/cm^{-1}$ 1640; m/z 338 ($M^+ + 2$, 9.8%), 336 (M, 30.5) and 77 (Ph, 100).

1-Acetyl-2-chlorotetrafluorocyclobutene 16.—To a precooled (-20 °C) solution of reagent **3a** prepared iodide **1a** (5 g, 17.5 mmol), activated zinc powder (1.7 g, 26 mmol) and CuBr (2.5 g, 17.5 mmol) in DMF (20 cm³) was added acetyl chloride (1.4 g, 17.5 mmol). The reaction mixture was stirred at -20 °C for 5 h, and was then slowly warmed to room temperature. The reaction mixture was flash distilled. The distillate was washed with water to remove DMF and dried over anhydrous magnesium sulphate. Fractional distillation of the crude product gave **compound 16** (1.5 g, 43%), b.p. 64–66 °C (50 mmHg) (Found: C, 35.3; H, 1.4; F, 37.4; Cl, 17.4. $C_6H_3ClF_4O$ requires C, 35.58; H, 1.49; F, 37.52; Cl, 17.50%); $\delta_F(CDCl_3)$ -111.2 (m) and -113.8 (m); $\delta_H(CDCl_3)$ 2.43 (s); $\nu_{max}(neat)/cm^{-1}$ 1710 and 1629; m/z 204 ($M^+ + 2$, 6.7%), 202 (M, 19.5) and 187 (M - CH₃, 100).

1-Chloro-3,3,4,4-tetrafluoro-2-propionylcyclobutene 17.—B.p. 66–67 °C (20 mmHg) (Found: C, 38.9; H, 2.3; F, 35.1; Cl, 16.4. $C_7H_5ClF_4O$ requires C, 38.82; H, 2.33; F, 35.09; Cl, 16.37%); $\delta_F(CDCl_3)$ -110.6 (m) and -113.5 (m); $\delta_H(CDCl_3)$ 1.50 (3 H, t) and 2.68 (2 H, q); $\nu_{max}(neat)/cm^{-1}$ 1720 and 1635; m/z 218 ($M^+ + 2$, 9.7%), 216 (M, 27.3) and 187 (M - CH₂CH₃, 100).

1-Benzoyl-2-chlorotetrafluorocyclobutene 18.—B.p. 75–76 °C (1 mmHg) (Found: C, 49.95; H, 1.8; F, 28.7; Cl, 13.4. $C_{11}H_5ClF_4O$ requires C, 49.93; H, 1.90; F, 28.72; Cl, 13.40%); $\delta_F(CDCl_3)$ -106.9 (m) and -113.2 (m); $\delta_H(CDCl_3)$ 7.52 (3 H, m) and 7.90 (2 H, m); $\nu_{max}(neat)/cm^{-1}$ 3080, 1675 and 1610; m/z 266 ($M^+ + 2$, 8.8%), 264 (M, 26.2) and 105 (PhCO⁺, 100).

1-Chloro-3,3,4,4-tetrafluoro-2-(2-furoyl)cyclobutene 19.—B.p. 58–60 °C (1.5 mmHg) (Found: C, 42.4; H, 1.2; F, 30.0; Cl, 13.95. $C_9H_3ClF_4O_2$ requires C, 42.46; H, 1.19; F, 29.85; Cl, 13.93%); $\delta_F(CDCl_3)$ -106.9 (m) and -113.2 (m); $\delta_H(CDCl_3)$ 6.62 (dd), 7.42 (dd) and 7.70 (dd).

1-Chloro-3,3,4,4-tetrafluoro-2-(2-thenoyl)cyclobutene 20.—B.p. 70–72 °C (1.5 mmHg) (Found: C, 40.0; H, 1.1; F, 28.2; Cl,

13.0. $C_9H_3ClF_4OS$ requires C, 39.94; H, 1.12; F, 28.08; Cl, 13.10%); $\delta_F(CDCl_3)$ -107.1 (m) and 113.3 (m); $\delta_H(CDCl_3)$ 7.0–7.35 (m), 7.45–7.75 (br d) and 7.50–8.0 (dd).

1-Acetyl-2-chlorohexafluorocyclopentene 21.—To a precooled (0 °C) solution of reagent **3b** prepared from iodide **1b** (6.73 g, 20 mmol), activated zinc powder (1.83 g, 28 mmol) and CuBr (2.86 g, 20 mmol) in DMF (20 cm³) was added acetyl chloride (1.57 g, 20 mmol). The reaction mixture was stirred at 0 °C for 1 h and was then slowly warmed to room temperature. The reaction mixture was flash distilled. The distillate was washed with water and dried. Fractional distillation of the crude product gave **compound 21** (3.73 g, 74%), b.p. 73–74 °C (50 mmHg) (Found: C, 33.3; H, 1.2; F, 45.0; Cl, 14.9. $C_7H_3ClF_6O$ requires C, 33.29; H, 1.20; F, 45.14; Cl, 14.04%); $\delta_F(CDCl_3)$ -108.3 (t, J_{FF} 4), -114.8 (t, J_{FF} 4) and -130.5 (m); $\delta_H(CDCl_3)$ 2.55 (s); $\nu_{max}(neat)/cm^{-1}$ 1720 and 1625; m/z 254 ($M^+ + 2$, 8.2%), 252 (M, 23.7%) and 237 (M - CH₃, 100).

1-Chloro-3,3,4,4,5,5-hexafluoro-2-propionylcyclopentene 22.—B.p. 54.5–56 °C (6 mmHg) (Found: C, 36.2; H, 1.85; F, 42.7; Cl, 13.4. $C_8H_5ClF_6O$ requires C, 36.04; H, 1.89; F, 42.77; Cl, 13.30%); $\delta_F(CDCl_3)$ -108.3 (2 F), -114.9 (2 F) and -130.6 (2 F); $\delta_H(CDCl_3)$ 1.20 (3 H, t) and 2.68 (2 H, q); $\nu_{max}(neat)/cm^{-1}$ 1730 and 1620; m/z 268 ($M^+ + 2$, 6.8%), 266 (M, 19.6) and 237 (M - CH₂CH₃, 100).

1-Benzoyl-2-chlorohexafluorocyclopentene 23.—B.p. 62–63 °C (0.1 mmHg) (Found: C, 45.9; H, 1.6; F, 36.4; Cl, 11.3. $C_{12}H_5ClF_6O$ requires C, 45.9; H, 1.60; F, 36.23; Cl, 11.27%); $\delta_F(CDCl_3)$ -108.0 (2 F), -113.9 (2 F) and -127.7 (2 F); $\delta_H(CDCl_3)$ 7.05–7.85 (m); $\nu_{max}(neat)/cm^{-1}$ 1690 and 1610; m/z 316 ($M^+ + 2$, 7.0%), 314 (M, 20.1) and 105 (PhCO, 100).

1-Chloro-3,3,4,4,5,5-hexafluoro-2-(phenylacetyl)cyclopentene 24.—B.p. 84–86 °C (0.1 mmHg) (Found: C, 47.6; H, 2.1; F, 34.7; Cl, 10.7. $C_{13}H_7ClF_6O$ requires C, 47.51; H, 2.15; F, 34.69; Cl, 10.79%); $\delta_F(CDCl_3)$ -107.5 (2 F), -114.5 (2 F) and -130.3 (2 F); $\delta_H(CDCl_3)$ 4.18 (2 H, s) and 7.15–7.55 (5 H, m); $\nu_{max}(neat)/cm^{-1}$ 1725 and 1620; m/z 330 ($M^+ + 2$, 1.6%), 328 (M, 4.9) and 91 (PhCH₂, 100).

1-Chloro-2-(dimethylcarbamoyl)hexafluorocyclopentene 25.—B.p. 75–76 °C (1.5 mmHg) (Found: C, 34.2; H, 2.1; F, 40.5; Cl, 12.6. $C_8H_6ClF_6NO$ requires C, 34.12; H, 2.15; F, 40.48; Cl, 12.59%); $\delta_F(CDCl_3)$ -109.1 (t), -114.4 (t) and -130.2 (m); $\delta_H(CDCl_3)$ 2.87 (3 H, s) and 2.95 (3 H, s); $\nu_{max}(neat)/cm^{-1}$ 1680 and 1630; m/z 283 ($M^+ + 2$, 16.2%), 281 (M, 47.1) and 246 (M - Cl, 100).

1-Chloro-3,3,4,4,5,5-hexafluoro-2-(2-furoyl)cyclopentene 26.—B.p. 61–63 °C (0.7 mmHg) (Found: C, 39.4; H, 1.0; F, 37.3; Cl, 11.5. $C_{10}H_3ClF_6O_2$ requires C, 39.43; H, 0.99; F, 37.43; Cl, 11.64%); $\delta_F(CDCl_3)$ -108.2 (2 F), -114.7 (2 F) and -130.3 (2 F); $\delta_H(CDCl_3)$ 6.15 (1 H, dd), 7.33 (1 H, d) and 7.71 (1 H, d); $\nu_{max}(neat)/cm^{-1}$ 1680 and 1570; m/z 306 ($M^+ + 2$, 15.2%), 304 (M, 45.2) and 95 (M - C₅H₆Cl, 100).

1-Chloro-3,3,4,4,5,5-hexafluoro-2-(2-thenoyl)cyclopentene 27.—B.p. 64–66 °C (0.2 mmHg) (Found: C, 37.5; H, 0.9; F, 35.8; Cl, 11.1. $C_{10}H_3ClF_6OS$ requires C, 37.46; H, 0.94; F, 35.55; Cl, 11.06%); $\delta_F(CDCl_3)$ -108.6 (2 F), -114.2 (2 F) and -130.3 (2 F); $\delta_H(CDCl_3)$ 7.17 (1 H, dd), 7.53 (1 H, d) and 7.83 (1 H, d); $\nu_{max}(neat)/cm^{-1}$ 1685 and 1570; m/z 322 ($M^+ + 2$, 4.5%), 320 (M, 11.9%) and 111 (M - C₅F₆Cl, 100).

2,5-Bis-(2-chlorohexafluorocyclopent-1-enecarbonyl)thiophene 28.—M.p. 119–121 °C (From hexane-CH₂Cl₂) (Found: C,

34.3; H, 0.4; F, 40.9; Cl, 12.8. $C_{16}H_2Cl_2F_{12}O_2S$ requires C, 34.49; H, 0.36; F, 40.92; Cl, 12.73%; $\delta_F(CDCl_3)$ -107.9 (4 F), -113.8 (4 F) and 130.1 (4 F); $\delta_H(CDCl_3)$ 7.65 (2 H, s); $\nu_{max}(KBr)/cm^{-1}$ 1675 and 1530; m/z 560 ($M^+ + 4$, 1.8%), 558 ($M^+ + 2$, 7.1), 556 (M, 12.2) and 347 (M - C_5F_6Cl , 100).

1-Acetyl-2-cyclooctafluorocyclohexene 29.—To a solution of reagent **3c** prepared from iodide **1c** (5.80 g, 15 mmol), activated zinc powder (1.30 g, 20 mmol) and CuBr (2.86 g, 20 mmol) in DMF (13 cm³) was added acetyl chloride (1.18 g, 15 mmol). The reaction mixture was stirred for 2 h and was then flash distilled. The distillate was washed with water (3 × 40 cm³) and dried over anhydrous MgSO₄. Fractional distillation of the crude product gave compound **28** (3.64 g, 79%), b.p. 67–68 °C (77 mmHg) (Found: C, 31.7; H, 1.0; F, 50.1; Cl, 11.7. $C_8H_3ClF_8O$ requires C, 31.76; H, 1.00; F, 50.24; Cl, 11.72%; $\delta_F(CDCl_3)$ -114.0 (2 F), -116.8 (2 F), -138.0 (2 F) and -139.7 (2 F); $\delta_H(CDCl_3)$ 2.55 (3 H, s); $\nu_{max}(neat)/cm^{-1}$ 1730 and 1650; m/z 304 ($M^+ + 2$, 6.7%), 302 (M, 19.1) and 287 (M - CH₃, 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-propionylcyclohexene 30.—B.p. 70–72 °C (38 mmHg) (Found: C, 34.2; H, 1.6; F, 48.2; Cl, 11.2. $C_9H_5ClF_8O$ requires C, 34.14; H, 1.59; F, 48.01; Cl, 11.20%; $\delta_F(CDCl_3)$ -114.3 (2 F), -117.0 (2 F), -137.3 (2 F) and -140.0 (2 F); $\delta_H(CDCl_3)$ 1.2 (3 H, t) and 2.8 (2 H, q); $\nu_{max}(neat)/cm^{-1}$ 1730 and 1650; m/z 318 ($M^+ + 2$, 3.4%), 316 (M, 10.8) and 109 (100).

1-Benzoyl-2-chlorooctafluorocyclohexene 31.—B.p. 52–53 °C (0.2 mmHg) (Found: C, 42.7; H, 1.3; F, 41.5; Cl, 9.6. $C_{13}H_5ClF_8O$ requires C, 42.82; H, 1.38; F, 41.69; Cl, 9.72%; $\delta_F(CDCl_3)$ -113.5 (2 F), -116.5 (2 F), -137.7 (2 F) and -139.4 (2 F); $\delta_H(CDCl_3)$ 7.2–8.1 (5 H, m); $\nu_{max}(neat)/cm^{-1}$ 1690 and 1650; m/z 366 ($M^+ + 2$, 3%), 364 (M, 9.0) and 105 (PhCO, 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-(2-furoyl)cyclohexene 32.—B.p. 86–88 °C (2.5 mmHg) (Found: C, 37.2; H, 0.9; F, 42.9; Cl, 10.1. $C_{11}H_3ClF_8O_2$ requires C, 37.3; H, 0.85; F, 42.9; Cl, 10.00%; $\delta_F(CDCl_3)$ -113.6 (2 F), -116.7 (2 F), -137.7 (2 F) and 139.5 (2 F); $\delta_H(CDCl_3)$ 6.65 (1 H, br s), 7.3 (1 H, br s), 7.75 (1 H, br s), $\nu_{max}(neat)/cm^{-1}$ 3140, 1680 and 1560; m/z 356 ($M^+ + 2$, 3.3%), 354 (M, 9.1) and 95 (100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-(2-thenoyl)cyclohexene 33.—B.p. 90–91 °C (1.2 mmHg) (Found: C, 35.5; H, 0.8; F, 41.1; Cl, 9.55. $C_{11}H_3ClF_8OS$ requires C, 35.64; H, 0.82; F, 41.0; Cl, 9.57%; $\delta_F(CDCl_3)$ -113.6 (2 F), -116.6 (2 F), -137.9 (2 F) and -139.6 (2 F); $\delta_H(CDCl_3)$ 7.2 (1 H, br s), 7.6 (1 H, br s), 7.8 (1 H, br s), $\nu_{max}(neat)/cm^{-1}$ 1670 and 1650; m/z 372 ($M^+ + 2$, 2.6%), 370 (M, 7.4) and 111 (100).

2,5-Bis-(2-chlorooctafluorocyclohex-1-enecarbonyl)thiophene 34.—M.p. 86–88 °C (From hexane-CH₂Cl₂) (Found: C, 32.9; H, 0.25; F, 47.1; Cl, 10.7. $C_{18}H_2Cl_2F_{16}O_2S$ requires C, 32.90; H, 0.31; F, 46.26; Cl, 10.79%; $\delta_F(CDCl_3)$ -112.9 (4 F), -116.5 (4 F), -137.6 (4 F) and -139.1 (4 F); $\delta_H(CDCl_3)$ 7.65 (2 H, s); $\nu_{max}(KBr)/cm^{-1}$ 1680 and 1650; m/z 658 ($M^+ + 2$, 8.0%), 656 (M, 11.0), and 397 (100).

2,5-Bis-(2-chlorotetrafluorocyclobutene-1-carbonyl)thiophene 35.—A 50 cm³, two-neck, round-bottom flask fitted with a condenser was charged with activated zinc powder (1.7 g, 26 mmol) and monoglyme (20 cm³) under nitrogen. To this mixture were added a 1.0 mol dm⁻³ solution of diethylzinc in hexane (0.1 cm³) and the iodide **1a** (5 g, 17.5 mmol). The mixture was heated with a heat-gun. After a short induction period, an exothermic reaction took place. The reaction mixture was stirred to cool it to room temperature. Then, excess of zinc was removed by pressure filtration of the reaction mixture through a Schlenk funnel. ¹⁹F NMR analysis of the resultant solution indicated a quantitative yield of the zinc reagent **2a**. To the filtered solution of reagent **2a** were added CuBr (0.5 g, 3.5 mmol) and a solution of thiophene-2,5-dicarbonyl dichloride (1.81 g, 8.7 mmol) in methylene dichloride (5 cm³). The reaction mixture was stirred for 12 h under nitrogen, and then was flash filtered. Evaporation of the filtrate gave a crude product, which was recrystallized from a mixture of hexane and methylene dichloride to give compound **35** (2.30 g, 58%) as yellow needles, m.p. 106–107 °C (Found: C, 36.7; H, 0.4; F, 33.3; Cl, 15.5. $C_{14}H_2Cl_2F_8O_2S$ requires C, 36.78; H, 0.44; F, 33.25; Cl, 15.51%; $\delta_F(CDCl_3)$ -107.1 (m) and -114.3 (m); $\delta_H(CDCl_3)$ 7.63 (s); $\nu_{max}(KBr)/cm^{-1}$ 1680; m/z 460 ($M^+ + 4$, 2.7%), 458 (M + 2, 6.3), 456 (M, 15.7) and 397 (M - C₄F₄Cl, 100).

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