

# 액정 재료용 유기 불소 화합물의 제조에 관한 연구

정 연 태

부경대학교 공과대학 사진정보공학과

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## Preparation of New Fluorinated Organic Compounds for Liquid Crystal Material

*Yeon-Tae Jeong*

Dept. of Photographic Science and Information Technology,

College of Engineering, Pukyong National University

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### Abstract

상온의 DMF 용매에서 1-클로로-2-요오도옥타플루오로시클로헥산과 활성 아연 분말을 반응시켜 2-클로로옥타플루오로시클로헥스-1-에닐 아연시약을 거의 정량적인 수율로 합성하였다. 이 유기 아연시약을 실온에서 1 시간 동안 브롬화제일구리(CuBr)와 반응시키는 아주 간편한 방법으로 2-클로로옥타플루오로시클로헥스-1-에닐 구리시약을 정량적인 수율로 얻을 수 있었다. 이 구리시약은 질소 분위기 하에서는 실온에서 매우 안정한 특성을 나타내었다. 이 구리시약을, 새로운 액정 재료용 유기 불소 화합물을 제조하기 위하여, 여러 가지 할로겐화 알킬 또는 할로겐화 아실 화합물과의 반응을 통하여 이제까지 합성할 수 없었던 여러 가지 폴리플루오로시클로헥센 유도체들을 합성하였다.

### 1. Introduction

Liquid crystal materials provide an interesting area that requires a most advance and has been widely developed for display industry. Dainippon Ink reports the use of fluorinated materials, for example fluorinated tolans, to achieve high-purity nematic materials. These fluorinated compounds exhibit not only high stability for heat and light but also another good properties for liquid crystal material as a large  $n_e$  and  $\Delta n$ . There are increasing interests in fluorinated organic compounds as liquid crystal material.

In the present paper, preparation of polyfluorocycloalkene derivatives is studied for the

use as liquid crystal materials.

Polyfluorocycloalkene derivatives of various metals and metalloids are known for the synthesis of polyfluorocycloalkene derivatives.<sup>1-3)</sup> Polyfluorocycloalkenyl Grignard reagents can be obtained by exchange of a vinylic halogen with ethylmagnesium bromide,<sup>4)</sup> although these reagents are very unstable at room temperature. Fluorocycloalkenyllithiums are also prepared by displacement of hydrogen or iodine atoms with methylolithium.<sup>5,6)</sup> For the preparation of 1-chloro-2-lithio-perfluorocycloalkenes butyllithium is employed.<sup>7)</sup> These reagents exhibit high reactivity with halogens, water, carbon dioxide and acetaldehyde. They decompose around -10 to 15°C. The low thermal stability and reactivity of previously reported fluorocycloalkene derivatives of metal and metalloids prompted a development of metal reagents which would be thermally more stable but show higher reactivity towards a variety of substrates.

We now report the preparation and reaction of polyfluorocyclohexenylcopper reagent 3 as intermediate for the synthesis of polyfluorocyclohexene derivatives which can be used as liquid crystal materials. They are also important compounds in our continuing studies of organometallic reagents derived from polyfluorocyclopentene<sup>8)</sup>, -butene<sup>9)</sup> and -propene.<sup>10)</sup>

## 2. Experimental

2.1 *General.* <sup>1</sup>H-NMR spectra were recorded on a Bruker AM-300 NMR spectrometer, and chemical shifts are reported from tetramethylsilane as internal standard. <sup>19</sup>F-NMR spectra were recorded on a Varian FT-80A NMR spectrometer with trifluoroacetic acid(TFA) as external standard. Chemical shifts were reported relative to CFCl<sub>3</sub>( $\delta_F$  of 77), and J-values are given in Hz. <sup>19</sup>F-NMR yields were determined by comparison of the peak integrations using PhCF<sub>3</sub> 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 uncorrected. All reactions were performed at room temperature under nitrogen.

2.2 *Materials.* 1-chloro-2-iodooctafluorocyclohexene was prepared by the known procedure.<sup>15)</sup> Thiophene-2-carbonyl (2-thenoyl)chloride,<sup>16)</sup> thiophene-2,5-dicarbonyl dichloride<sup>17)</sup> and 2-furoyl chloride<sup>18)</sup> 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<sub>2</sub>O<sub>5</sub> under reduced pressure and stored over 4 Å molecular sieves under nitrogen. 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.<sup>19)</sup> Zinc powder was activated by washing successively with dil. HCl and then distilled water and dried *in vacuo* overnight at 120°C.

*2-Chlorooctafluorocyclohex-1-enylzinc iodide 2.* A 50cm<sup>3</sup>, two-neck, round-bottom flask fitted with condenser was charged with activated zinc powder(1.3g, 20mmol) and dry DMF(15cm<sup>3</sup>) under nitrogen. To this mixture was added 1-chloro-2-iodooctafluorocyclohexene 1(5.8g, 15mmol) dropwise. After the induction period of several minutes, an exotherm occurred; addition of compound 1 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(Schrenk funnel). <sup>19</sup>F-NMR analysis of the resultant solution indicated a 99% yield of product 2;  $\delta_F(\text{CDCl}_3)$  -100.9(2 F), -101.2(2 F) and -138.4(4 F).

*2-Chlorooctafluorocyclohex-1-enylcopper 3.* To a filtered solution of reagent 2 prepared from iodide 1 (5.8g, 15mmol) and activated zinc powder(1.3g, 20mmol) in dry DMF(15cm<sup>3</sup>) was added CuBr(2.9g, 20mmol). The reaction mixture was stirred for 2 h, then <sup>19</sup>F-NMR analysis showed 98% yield of organocopper reagent 3 from starting iodide. This solution was used for subsequent functionalization reactions;  $\delta_F(\text{CDCl}_3)$  -98.2(2 F), -112.0(2 F) and -138.3(4 F).

*1-Allyl-2-chlorooctafluorocyclohexene 4.* The copper reagent 3 was prepared from 1-chloro-2-iodooctafluorocyclohexene 1(5.8g, 15mmol), activated zinc powder(1.3g, 20mmol) and CuBr(2.9g, 20mmol) in DMF(15cm<sup>3</sup>). To this solution was added allyl bromide(1.8g, 15mmol). After being stirred for 2h 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*(3.2g, 71%), b.p. 40-42°C(65mmHg) (Found: C, 35.7; H, 1.6; F, 50.6; Cl, 11.7. C<sub>9</sub>H<sub>5</sub>ClF<sub>8</sub> requires C, 35.96; H, 1.68; F, 50.57; Cl, 11.79%);  $\delta_F(\text{CDCl}_3)$  -114.1(2 F), -115.7(2 F), -138.5(2 F) and -139.7(2 F);  $\delta_H(\text{CDCl}_3)$  3.15-3.50(2 H, br d), 5.0-5.35(2H, br), 5.45-6.0(1H, m);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3090, 2950 and 1650; m/z 302(M<sup>+</sup> + 2, 2.5%) and 300(M, 30.5).

*1-Benzyl-2-chlorooctafluorocyclohexene 5.* B.p. 64-66°C(2.5mmHg) (Found: C, 44.35; H, 2.0; F, 43.3; Cl, 10.1. C<sub>13</sub>H<sub>7</sub>ClF<sub>8</sub> requires C, 44.53; H, 2.01; F, 43.35; Cl, 10.11%);  $\delta_F(\text{CDCl}_3)$  -114.3(2F), -115.0(2F), -138.0(2F) and -139.4(2F);  $\delta_H(\text{CDCl}_3)$  4.05(2H, s) and 7.15-7.55(5H, m);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  3070 and 1640; m/z 352(M<sup>+</sup> + 2, 32%) and 350(M, 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-methylcyclohexene 6. B.p. 50-52°C (98mmHg) (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(2F), -115.1(2F) and -138.5(4F);  $\delta_H(CDCl_3)$  1.93(3H, 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 7. B.p. 64-66°C (35mmHg) (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(2F), -112.5(2F) and -136.4(4F);  $\delta_H(CDCl_3)$  6.92-7.76(5H, 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-chlorooctafluorocyclohexene 8. To a solution of reagent 3 prepared from iodide 1 (5.8g, 15mmol), activated zinc powder(1.3g, 20mmol) and CuBr(2.9g, 20mmol) in DMF(15  $cm^3$ ) was added acetyl chloride(1.2g, 15 mmol). The reaction mixture was stirred for 2 h and was then flash distilled. The distillate was washed with water( $3 \times 40cm^3$ ) and dried over anhydrous  $MgSO_4$ . Fractional distillation of the crude product gave compound 8(3.64g, 79%), b.p. 67-68°C (77mmHg) (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(2F), -116.8(2F), -138.0(2F) and -139.7(2F);  $\delta_H(CDCl_3)$  2.55(3H, s);  $\nu_{max}(neat)/cm^{-1}$  1730 and 1650; m/z 304 ( $M^+ + 2$ , 6.7%), 302(M, 19.1) and 287(M- $CH_3$ , 100).

1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-propionylcyclohexene 9. B.p. 70-72°C (38mmHg) (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(2F), -117.0(2F), -137.3(2F) and -140.0(2F);  $\delta_H(CDCl_3)$  1.2(3 H, t) and 2.8(2H, 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 10. B.p. 52-53°C (0.2mmHg) (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(2F), -116.5(2F), -137.7(2F) and -139.4(2F);  $\delta_H(CDCl_3)$  7.2-8.1(5H, m);  $\nu_{max}(neat)/cm^{-1}$  1690 and 1650; m/z 366( $M^+ + 2$ , 3%), 364(M, 9.0) and 105(PhCO, 100).

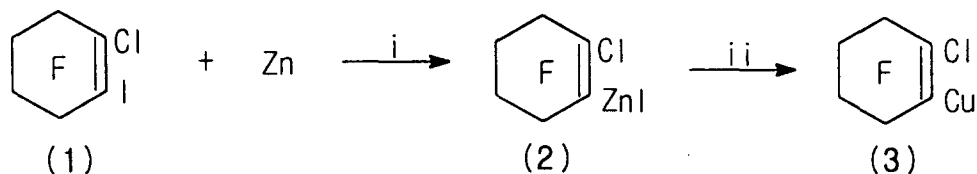
1-Chloro-3,3,4,4,5,5,6,6-octafluoro-2-(2-furoyl)cyclohexene 11. B.p. 86-88°C (2.5mmHg) (Found: C, 37.2; H, 0.9; F, 42.9; Cl, 10.1.  $C_{11}H_3ClF_8O_2$  requires C, 37.3; H, 0.85; F, 42.9; Cl, 10.00%);  $\delta_F(CDCl_3)$  -113.6(2F), -116.7(2F), -137.7(2F) and -139.5(2F);  $\delta_H(CDCl_3)$  6.65(1 H, br s), 7.3 (1H, br s) and 7.75(1H, 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 **12**. B.p. 90-91 °C (1.2mmHg) (Found: C, 35.5; H, 0.8; F, 41.1; Cl, 9.55. C<sub>11</sub>H<sub>3</sub>ClF<sub>8</sub>O<sub>2</sub>S requires C, 35.64; H, 0.82; F, 41.0; Cl, 9.57%); δ<sub>F</sub>(CDCl<sub>3</sub>) -113.6(2F), -116.6(2F), -137.9(2F) and -139.6(2F); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.2(1 H, br s), 7.6(1H, br s) and 7.8(1H, br s); ν<sub>max</sub>(neat)/cm<sup>-1</sup> 1670 and 1650; m/z 372(M<sup>+</sup> + 2, 2.6%), 370(M, 7.4) and 111(100).

2,5-Bis-(2-chlorooctafluorocyclohex-1-enecarbonyl)thiophene **13**. M.p. 86-88 °C (From hexene-CH<sub>2</sub>Cl<sub>2</sub>) (Found: C, 32.9; H, 0.25; F, 47.1; Cl, 10.7. C<sub>18</sub>H<sub>2</sub>Cl<sub>2</sub>F<sub>16</sub>O<sub>2</sub>S requires C, 32.90; H, 0.31; F, 46.26; Cl, 10.79%); δ<sub>F</sub>(CDCl<sub>3</sub>) -112.9(4F), -116.5(4F), -137.6(4F) and -139.1(4F); δ<sub>H</sub>(CDCl<sub>3</sub>) 7.65 (2H, s); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 1680 and 1650; m/z 658(M<sup>+</sup> + 2, 8.0%), 656(M, 11.0) and 397(100).

### 3. Results and Discussion

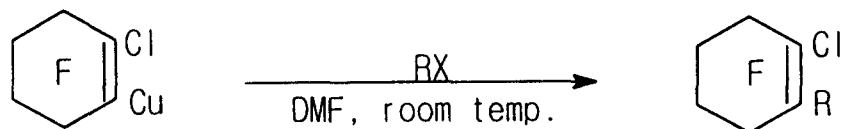
The usefulness of alkenylcopper and alkenylcuprate reagents in organic synthesis is well documented.<sup>11)</sup> The low thermal stability of fluorinated vinylolithium and Grignard reagents has generally limited their use in synthesis, but a few recent reports on the fluorinated vinylcopper reagents indicate otherwise.<sup>12)</sup> We previously reported on the preparation and synthetic applications of alicyclic fluorinated vinylcopper reagents.<sup>8-10)</sup> As our continuing study the present work is focused on the preparation and synthetic applications of 2-chlorooctafluoro-cyclohex-1-enylcopper reagent to synthesize polyfluorocyclohexene derivatives with rigid double bond for liquid crystal materials. Alicyclic fluorinated vinylzinc reagents are good precursors for the corresponding copper reagent. We easily prepared 2-chlorooctafluorocyclohex-1-enylzinc reagent **2** by direct reaction of 1-chloro-2-iodooctafluorocyclohexene **1** with zinc metal. The iodide compound **1** reacts readily with activated zinc powder in dimethylformamide(DMF) at room temperature. After a short induction period, this reaction becomes exothermic. The color changes from grey to brown, and the reaction is completed in about one hour. The yield is quantitative. This zinc reagent exhibits good thermal stability. Even at 80 °C it shows no appreciable decomposition for 3 days in DMF under nitrogen. This zinc reagent is sensitive to moisture, being readily hydrolyzed to a reduced olefin. Upon addition of copper(I) bromide to the filtered solution of zinc reagent **2** at room temperature, The copper reagent **3** was formed(Scheme 1). The yield determined by <sup>19</sup>F NMR analysis<sup>8,9)</sup> was 98%. Unlike the zinc reagent **2**, the copper reagent **3** could not be prepared directly by the reaction of the metal with 1-chloro-2-iodooctafluorocyclohexene.



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

Treatment of the iodide compound **1** with copper powder in DMF provided only the dimeric coupling product.<sup>13a</sup> The copper reagent **3** was found to be quite stable in the absence of oxygen and/or moisture and showed a loss of only 10% activity even after 7 days at room temperature in DMF under nitrogen. At higher temperatures (>80°C), it undergoes a rapid decomposition to give a reduced olefin and tar. This excellent stability allows its use in a large-scale preparation and utilization over an extended period in a variety of synthetic reactions without any significant change in activity. The copper reagent **3** participates in a variety of alkylations as summarized in <Table 1>. It reacts with alkyl halides in DMF at room temperature. The yield is good for allyl bromide, but the reaction rates are very slow with methyl and phenyl iodides. Park<sup>11</sup> reported a synthetic route to alkyl derivatives of polyfluorocyclohexene, in which a 1,2-dichlorooctafluorocyclohexene was alkylated by Grignard reagents. The present method offers advantages over the previously reported method in versatility and facility of reaction.

**Table 1.** Reaction of 2-chlorooctafluorocyclohex-1-enylcopper reagent with alkyl halides



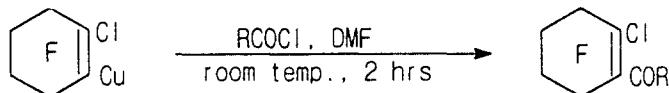
Entry	RX	Time(h)	Product(R)	Yield <sup>a</sup> (%)
1	CH <sub>2</sub> =CHCH <sub>2</sub> Br	2	CH <sub>2</sub> CH=CH <sub>2</sub>	71 (4)
2	PhCH <sub>2</sub> Br	55	CH <sub>2</sub> Ph	61 (5)
3	MeI	160	Me	52 (6)
4	PhI	140	Ph	50 (7)

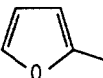
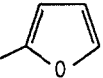
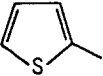
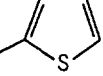
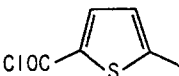
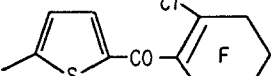
<sup>a</sup>Isolated yields. Yields are based on starting 1-chloro-2-iodo-octafluorocyclohexene used.

To demonstrate the synthetic utility of the reagent **3** we prepared a number of previously unreported compounds through treatment of the reagent **3** with acid halides. The results from these reactions are summarized in <Table 2>. Acylation proceeded readily and the yields were excellent.

In conclusion, we present here a simple, mild method for the preparation of 2-chlorooctafluorocyclohex-1-enylcopper reagent in a quantitative yield. This organometallic compound, which satisfies the criteria for the preparation of a stable and reactive 2-chlorooctafluorocyclohex-1-enyl organometallic reagent, has been utilized in the synthesis of a variety of substituted fluorocyclohexene derivatives.

**Table 2.** Reaction of 2-chlorooctafluorocyclohex-1-enylcopper reagent with acid halides



Entry	R	Product(R)	Yield <sup>a</sup> (%)
5	Me	Me	79(8)
6	Et	Et	87(9)
7	Ph	Ph	88(10)
8			82(11)
9			84(12)
10			59(13)

<sup>a</sup>Isolated yields. Yields are based on starting 1-chloro-2-iodo-octafluorocyclohexene used.

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