

(총설 논문)

액정 재료용 새로운 유기 불소 화합물의 제조를 위한 플루오로할로게노시클로프로펜의 커플링 반응

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Coupling Reaction of Fluorohalogenocyclopropenes for Preparation of New Fluorinated Organic Compounds for Liquid Crystal Material

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The reaction of a variety of nucleophiles with fluorohalogenocyclopropenes has been considerably investigated.¹⁻³⁾ The nucleophilic substitution of 1,2-dichloro-3,3-difluorocyclopropene involved displacement of one or both chlorine atoms by iodine,⁴⁾ methoxy,^{5, 6)} or thiocyanide group.⁷⁾

Soulen and co-workers reported that the reductive coupling of 1-chloro-2-iodoperfluorocyclobutene, cyclopentene, and cyclohexene with copper powder and a trace amount of dimethylformamide gave the corresponding 2,2'-dichloroperfluoro-(bi-1-cycloalken-1-yl) derivatives.⁸⁾

There has, however, been no report on the coupling reaction of fluorohalogenocyclopropene derivatives.

In the previous paper⁹⁾ we reported the preparation of polyfluorocyclohexene

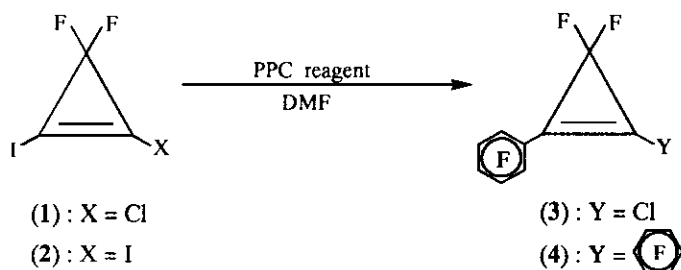
derivatives as new fluorinated organic compounds for liquid crystal material.

In this communication we report the coupling reaction of fluorohalogenocyclopropenes with pentafluorophenylcopper(PPC) reagent under a mild condition.

The coupling reaction of 1-chloro-2-iodo-3,3-difluorocyclopropene(1) with PPC reagent gave a 62% yield of 1-chloro-2-pentafluorophenyl-3,3-difluorocyclopropene(3), a colorless liquid, bp 72-73.5°C/10mmHg. The structure of (3) was determined by IR, ^{19}F -NMR, ^{13}C -NMR, and Mass spectra.¹⁰⁾

On the other hand, the reaction of 1,2-diiodo-3,3-difluorocyclopropene(2) with PPC reagent(1:2 molar ratio) gave the di-coupled product, 1,2-bispentafluorophenyl-3,3-difluorocyclopropene(4) in 58% yield. (4) is a colorless crystal, mp 62-63°C.¹¹⁾

Sepiol and co-workers reported the instability of 1,2-dithiocyano-3,3-difluorocyclopropene synthesized by nucleophilic substitution.⁷⁾ However, (4) was stable for a few months without decomposition.



A typical procedure is as follows: under an argon atmosphere, 1,2-diiodo-3,3-difluorocyclopropene(2)(1.64g, 5 mmol) was added in drops to a stirred solution of PPC reagent(10 mmol)^{12 14)} in dimethylformamide at -20°C. After stirring for 24 hours, the reaction mixture was warmed to room temperature and filtered with sintered glass funnel, then the filtrate was poured into water and extracted with n-hexane. The organic layer was dried and concentrated. Crystallization of the crude product from hexane/methylene chloride gave (4)(1.18g, 58%).

The above mentioned coupling reactions are synthetically useful in the preparation of previously inaccessible mono- and di-substituted-3,3-difluorocyclopropenes as new fluorinated organic compounds for liquid crystal material.

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- (10) (3): IR(neat film) 1770(m, $\nu_{C=C}$ of cyclopropene), 1640(m), 1490(vs), 1410(m), 1300-1330(vs), 1180(s), 1070(vs), 980(s), 900(m), 830(m), 700(m) cm^{-1} ; MS(m/z) 276(M⁺), 241(100%), 141; ¹⁹F-NMR spectra were measured in CDCl₃. Chemical shifts are reported in ppm with referenced to CFCl₃. -100.5(s, 2F), -129.5(m, 2F), -139.7(t, 1F), -152.5(m, 2F); ¹³C-NMR(CDCl₃) δ = 98.2(t, J_{C-F}=286 Hz), 99.1, 116.0, 121.3, 138.1(d, J_{C-F}=253 Hz), 144.1(d, J_{C-F}=262 Hz), and 145.2(d, J_{C-F}=256 Hz).
- (11) The structure of (4) could be confirmed by the following data: IR(KBr) 1830(w, $\nu_{C=C}$ of cyclopropene), 1670(m), 1510-1530(vs), 1470(m), 1310-1330(m, vs), 1130(m), 1100(m), 1060(s), 1000(s), 910(m), 810(s) cm^{-1} ; MS(m/z) 408(M⁺), 358(100%), 289, 179, 141; ¹⁹F-NMR -100.0(s, 2F), -128.7(m, 2F), -139.5(t, 1F), -152.4(m, 2F); ¹³C-NMR(CDCl₃) δ = 96.8(t, J_{C-F}=280 Hz), 100.6, 116.7, 138.2(d, J_{C-F}=254 Hz), 144.2(d, J_{C-F}=262 Hz), and 145.5(d, J_{C-F}=254 Hz). Details will be given in full paper.
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