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ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 120–125

One-pot process to prepare 1,1,2,2-tetrafluoroindane from substituted 2,2-difluorostyrene and sodium chlorodifluoroacetate

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Received 28 June 2006; revised 16 October 2006; accepted 18 October 2006
Available online 7 November 2006

Abstract—Reaction of 2,2-difluorostyrenes and sodium chlorodifluoroacetate in diglyme solution at 180 °C gave 1-aryl-2,2,3,3-tetrafluorocyclopropane as a primary product. After prolong reaction under the same condition, the 1,1,2,2-tetrafluoroindanes can be isolated as the only product in good yields. All the tetrafluorocyclopropanes and tetrafluoroindanes were well characterized by spectroscopic analyses.
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1. Introduction

Scientific and commercial interests in fluorine chemistry burgeoned after 1980, largely fueled by the need to replace industrial chlorofluorocarbons and the rapidly growing practical opportunities for organofluorine compounds in crops' protection, medicine, and diverse materials' applications.[1] In addition to our interest in the synthetic applications and spectroscopic studies of halocyclopropanes,[2] we attempted to extend our studies on the preparation of multifluorocyclopropanes. The addition of carbene on the double bond or triple bond to form the corresponding three-membered ring compounds is the most common process. Dibromocarbene and dichlorocarbene can be generated by the treatment of haloform with strong base. However, fluoroform cannot be used in the same fashion to form difluorocarbene. Numerous methods can be used to generate difluorocarbene for the preparation of *gem*-difluorocyclopropanes and *gem*-difluorocyclopropenes, such as thermal decomposition of $ClCF_2CO_2Na$, $PhHgCF_3$, or $FSO_2CF_2COOTMS$ or Ph_3P/CF_2Br_2 and Zn/CF_2Br_2.[3] On the other hand, difluorocarbene is often found as an electrophile toward multiple bond containing electron-rich substituents. Very few reports on the reaction between difluorocarbene and substituted styrenes were reported. Few attempts to prepare 1,1-difluoro-2-phenylcyclopropane gave poor yields.[3b,f] In this work, we attempt to prepare 1-aryl-2,2,3,3-tetrafluorocyclopropanes by the treatment of difluorocarbene, which was generated by thermal decomposition of $ClCF_2CO_2Na$, and 2,2-difluorostyrenes. The tetrafluorocyclopropanes were formed as the initial products, which were then converted into a tetrafluoroindanes along the progress of reaction. This one-pot process to prepare indanes is a merit to report.

2,2-Difluorostyrenes **1** were prepared by the reaction of $ClCF_2CO_2Na$ and the corresponding benzaldehyde in the presence of PPh_3.[4] Diglyme was used as a solvent to allow a higher reaction temperature for the decomposition of $ClCF_2CO_2Na$ to generate difluorocarbene. In order to obtain a good reaction, the purification of diglyme is necessary. When the mixture of 2,2-difluorostyrenes and $ClC_2F_2CO_2Na$ in diglyme was heated at 180 °C, the reaction was monitored by using TLC analysis. Difluorostyrenes disappeared within 2 h. However, upon the progress of reaction, the second product **3** formed along with the formation of cyclopropane **2** within 1 h as shown in Scheme 1. Results are summarized in Table 1.

The cyclopropane **2** could be isolated for characterization. In the case of styrene, the crude mixture contained **1a**, **2a**, and **3a** with the relative area ratio obtained from GC/MS analysis is 34:64:2. Tetrafluorocyclopropanes were purified by means of HPLC with RP-18 column and $MeOH/H_2O$ as an eluent. The proton on the cyclopropane ring appears at δ 3.47 (tt, 1H, J=19.6, 2.8 Hz). The splitting pattern is due to two fluorine atoms in cis-position and the other two at trans-position. The signals of ^{13}C NMR for the carbon containing two fluorine atoms display the complicated coupling patterns (δ 106, ddt, J=307, 304, 11.5 Hz). The $^{19}F[^1H]$ spectra also display different coupling patterns for two geminal fluorine atoms at the same carbon (d, J=183 Hz vs dd, J=167, 5 Hz). It might indicate that the asymmetrical structure of cyclopropane ring is due to the large size of fluorine atom compared to

Keywords: Difluorostyrene; Sodium chlorodifluoroacetate; Difluorocarbene; Tetrafluorocyclopropanes; Tetrafluoroindanes.
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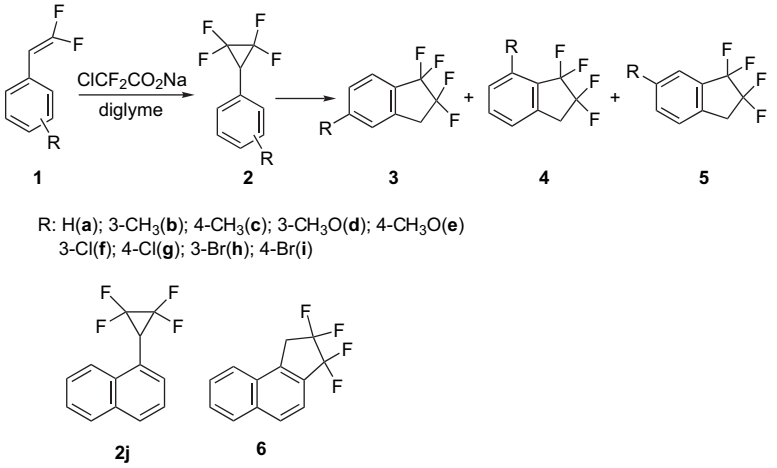
doi:10.1016/j.tet.2006.10.041



Scheme 1.

Table 1. Yields of tetrafluorocyclopropanes **2** and tetrafluoroindanes **3**, **4**, **5** after either 1 h or 12 h reaction period

Entry	Styrenes **1**	Yields (%) after 1 h	Yields (%) after 12 h		
		Cyclopropanes	Indanes		
		2	**3**	**4**	**5**
1	H (**1a**)	40	52		
2	3-Me (**1b**)	46	32	32	
3	4-Me (**1c**)	35			68
4	3-OMe (**1d**)	48	29	43	
5	4-OMe (**1e**)	57			65
6	3-Cl (**1f**)	37	36	39	
7	4-Cl (**1g**)	58			72
8	3-Br (**1h**)	34	43	38	
9	4-Br (**1i**)	41			69

that of hydrogen atom. For the mass spectra, the $[M-CF_2]^+$ ions are as the base peak except for the compounds containing bromine or chlorine as a substituent on the phenyl ring, in which loss of a halide is a preferential process.

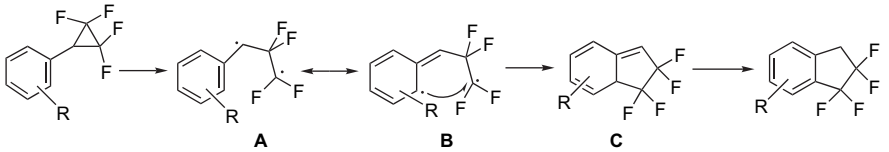
When the reaction mixture was allowed to further react for 12 h, tetrafluorocyclopropanes **2** could be completely converted into tetrafluoroindanes **3**. For 3-substituted styrenes, the reaction led to two indane isomers, which were separated by means of HPLC using RP-18 column and $MeOH/H_2O$ as an eluent. From the ^{13}C NMR analysis, two sets of triple–triple coupling patterns were observed for both carbons containing two fluorine atoms. The EI mass spectra display that the molecular ions remain as the base peak with relatively few fragmentations. This fact indicates the presence of compounds that have very stable skeleton. The distributions of indane isomers (i.e., 5- and 7-substituted, **3** and **4**) from 3-substituted tetrafluorocyclopropanes do not show much difference upon the change of the substituents. The reaction mechanism can be rationalized as a radical process (Scheme 2). Under the reaction condition, a Cα–Cβ bond of the cyclopropane ring can be ruptured to form structure **A** via the homolytic cleavage. The radical at Cα will undergo resonance to form structure **B**, in which the radical locates at C2 position. After a bond formation, the ring-closure proceeds to form structure **C** followed by a hydrogen transfer resulted in tetrafluoroindane product. The prototype thermal rearrangement involving competing diradical concerted and stepwise mechanisms had been studied in the vinylcyclopropane–cyclopentene rearrangement.[5] However, the photochemical rearrangement of unfluorinated arylcyclopropanes mainly yielded propene derivatives.[6] The driving force for the ring-opening process can be rationalized as the increase of ring strain[7] and lowering the activation energy of decomposition of the ring[8] by the increase of the fluorine content. The stronger carbon–fluorine bond prohibits the elimination of fluorine atom to form the propene and allows the cyclization to form the indanes.

Tetrafluorocyclopropane undergoes a ring-opening reaction to form indanes via a radical process. The driving force for this process can be rationalized as the carbon–carbon bond of cyclopropane ring is weakened by the presence of multifluorine atoms on the ring.

2. Experimental section

2.1. General

Experiments were performed under a dry nitrogen atmosphere. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 400, 100, and 376 MHz on Bruker Advance-400, respectively, at ambient temperature. Chemical shifts for samples



Scheme 2.

in $CDCl_3$ solution are reported in δ units relative to TMS (^1H and ^{13}C) and trifluoromethylbenzene (at −63.9 ppm, ^{19}F). Mass spectra were obtained from GC/MS (Fisons 8000 series coupled with Finnigan MD-800) at an ionization potential of 70 eV. Elemental analyses were performed at the Instrumental Analytic Center at National Chung Hsien University. All 2′,2′-difluorostyrenes were prepared by the reaction of sodium chlorodifluoroacetate and the corresponding benzaldehyde.[3] Diglyme was distilled from calcium hydride.

2.2. 1-Aryl-2,2,3,3-tetrafluorocyclopropanes (2a–2j) from 2′,2′-difluorostyrenes (1a–1j)

2.2.1. Preparation of 1-phenyl-2,2,3,3-tetrafluorocyclopropane (2a); typical procedure. A two-necked round bottom flask (100 mL) was equipped with a pressure-equalizing additional funnel and a condenser. This system was flame-dried under reduced pressure and then flashed with nitrogen stream to exclude the moisture. To a pre-heated 2′,2′-difluorostyrene (2.0 g, 14.3 mmol) in diglyme (15 mL) at 180 °C, a solution of $ClCF_2CO_2Na$ (7.6 g, 50 mmol) in diglyme (25 mL) was added from an additional funnel for 1 h. Slow addition of $ClCF_2CO_2Na$ solution is recommended to avoid too vigorous evolution of CO_2. The mixture was stirred at the same temperature for 1 h after complete addition. After the mixture was cooled to ambient temperature, the mixture was poured into H_2O (50 mL) and then extracted with *n*-hexane (50 mL×3). The hexane layer was washed with H_2O (50 mL×3), dried ($MgSO_4$), and filtered. The resultant hexane solution was concentrated and purified by washing through silica gel column with *n*-hexane. The mixture contained **1a**, **2a**, and **3a** (relative area ratio from GC/MS analysis is 34:64:2). Further purification by using HPLC (RP-18, 25 mm×25 cm, 10 μm) with MeOH/H_2O=10:1 as an eluent gave **2a** as the yellow liquid (1.1 g, yield 40%); bp 151 °C; ^1H NMR δ 3.46 (tt, 1H, J=19.6, 2.8 Hz), 7.31–7.33 (m, 2H), 7.36–7.44 (m, 3H); ^{13}C NMR δ 37.3 (t, J=11.5 Hz, Cα), 106.1 (ddt, J=307.0, 304.3, 11.5 Hz, Cβ, Cβ′), 125.3 (C1), 129.5 (C2, C6), 128.5 (C3, C5), 128.8 (C4); ^{19}F NMR δ −139.63 (d, 1F, J=182.7 Hz, Fa), −151.07 (d, 1F, J=182.7 Hz, Fb), −139.63 (dd, 1F, J=166.2, 5.3 Hz, Fa′), −151.07 (dd, 1F, J=166.2, 5.3 Hz, Fb′); EIMS m/z 190 ($M^{+\bullet}$, 42), 151 (12), 140 (100). Anal. Calcd for $C_9H_6F_4$: C, 56.85; H, 3.18. Found: C, 56.81; H, 3.22.

2.2.2. 1-(3-Tolyl)-2,2,3,3-tetrafluorocyclopropane (2b). Yellow liquid, yield 46%, bp 168 °C; ^1H NMR δ 2.46 (s, 3H), 3.47 (tt, 1H, J=19.6, 2.8 Hz), 7.19 (d, 2H, J=8 Hz), 7.28 (s, 1H), 7.36 (t, 1H, J=7.6 Hz); ^{13}C NMR δ 37.3 (t, J=11.5 Hz, Cα), 106.2 (ddt, J=307.6, 304.0, 11.5 Hz, Cβ, Cβ′), 125.2 (C1), 130.1 (C2), 138.7 (C3), 129.3 (C4), 128.7 (C5), 126.5 (C6), 21.1 (–CH_3); ^{19}F NMR δ −139.63 (d, 1F, J=183.1 Hz, Fa), −151.04 (d, 1F, J=183.1 Hz, Fb), −139.63 (dd, 1F, J=165.8, 4.5 Hz, Fa′), −151.04 (dd, 1F, J=165.8, 4.5 Hz, Fb′); EIMS m/z 204 ($M^{+\bullet}$, 75), 189 (51), 169 (12), 154 (100), 153 (63), 133 (33). Anal. Calcd for $C_{10}H_8F_4$: C, 58.83; H, 3.95. Found: C, 58.86; H, 3.91.

2.2.3. 1-(4-Tolyl)-2,2,3,3-tetrafluorocyclopropane (2c). Yellow liquid, yield 35%, bp 164 °C; ^1H NMR δ 2.37 (s, 3H), 3.40 (tt, 1H, J=20.0, 2.8 Hz), 7.10 (d, 2H, J=9.2 Hz), 7.21 (d, 2H, J=9.2 Hz); ^{13}C NMR δ 37.0 (t, J=11.5 Hz, Cα), 106.1 (ddt, J=307.9, 303.9, 11.5 Hz, Cβ, Cβ′), 122.2 (C1), 129.5 (C2, C6), 129.3 (C3, C5), 138.5 (C4), 21.1 (–CH_3); ^{19}F NMR δ −139.82 (d, 1F, J=182.7 Hz, Fa), −151.25 (d, 1F, J=182.7 Hz, Fb), −139.82 (dd, 1F, J=166.9, 5.6 Hz, Fa′), −151.25 (dd, 1F, J=166.9, 5.2 Hz, Fb′); EIMS m/z 204 ($M^{+\bullet}$, 79), 189 (51), 169 (11), 154 (100), 153 (69), 133 (48). Anal. Calcd for $C_{10}H_8F_4$: C, 58.83; H, 3.95. Found: C, 58.73; H, 4.06.

2.2.4. 1-(3-Methoxyphenyl)-2,2,3,3-tetrafluorocyclopropane (2d). Yellow liquid, yield 48%, bp 186 °C; ^1H NMR δ 3.81 (s, 3H), 3.42 (tt, 1H, J=9.2, 2.8 Hz), 6.82 (s, 1H), 6.88 (d, 1H, J=8.8 Hz), 6.90 (d, 1H, J=8.4 Hz), 7.31 (t, 1H, J=8 Hz); ^{13}C NMR δ 37.2 (t, J=11.5 Hz, Cα), 106.0 (ddt, J=307.6, 304.3, 11.5 Hz, Cβ, Cβ′), 126.5 (C1), 115.2 (C2), 159.8 (C3), 114.0 (C4), 129.8 (C5), 121.7 (C6), 55.3 (–OCH_3); ^{19}F NMR δ −139.57 (d, 1F, J=182.7 Hz, Fa), −151.03 (d, 1F, J=182.7 Hz, Fb), −139.57 (dd, 1F, J=166.6, 4.5 Hz, Fa′), −151.03 (dd, 1F, J=166.6, 4.5 Hz, Fb′); EIMS m/z 220 ($M^{+\bullet}$, 69), 189 (21), 170 (100), 140 (58), 127 (70). Anal. Calcd for $C_{10}H_8OF_4$: C, 54.55; H, 3.66. Found: C, 54.67; H, 3.70.

2.2.5. 1-(4-Methoxyphenyl)-2,2,3,3-tetrafluorocyclopropane (2e). Yellow liquid, yield 58%, bp 172 °C; ^1H NMR δ 3.83 (s, 3H), 3.41 (tt, 1H, J=19.6, 2.4 Hz), 6.95 (dt, 2H, J=8.8, 2 Hz), 7.25 (d, 2H, J=8.4 Hz); ^{13}C NMR δ 36.7 (t, J=11.5 Hz, Cα), 106.2 (ddt, J=307.7, 304.1, 11.5 Hz, Cβ, Cβ′), 117.0 (C1), 130.6 (C2, C6), 114.3 (C3, C5), 159.8 (C4), 55.1 (–OCH_3); ^{19}F NMR δ −140.49 (d, 1F, J=182.4 Hz, Fa), −151.88 (d, 1F, J=182.4 Hz, Fb), −140.49 (dd, 1F, J=165.4, 4.9 Hz, Fa′), −151.88 (dd, 1F, J=165.4, 4.9 Hz, Fb′); EIMS m/z 220 ($M^{+\bullet}$, 80), 189 (62), 170 (100), 155 (93), 127 (78). Anal. Calcd for $C_{10}H_8OF_4$: C, 54.55; H, 3.66. Found: C, 54.49; H, 3.69.

2.2.6. 1-(3-Chlorophenyl)-2,2,3,3-tetrafluorocyclopropane (2f). Yellow liquid, yield 37%, bp 170 °C; ^1H NMR δ 3.41 (tt, 1H, J=18.8, 2.4 Hz), 7.20 (d, 1H, J=7.2 Hz), 7.3–7.7 (m, 3H); ^{13}C NMR δ 36.7 (t, J=11.5 Hz, Cα), 105.8 (ddt, J=308.4, 304.0, 11.5 Hz, Cβ, Cβ′), 127.1 (C1), 129.6 (C2), 134.8 (C3), 128.9 (C4), 130.1 (C5), 127.6 (C6); ^{19}F NMR δ −139.53 (d, 1F, J=183.1 Hz, Fa), −150.77 (d, 1F, J=183.1 Hz, Fb), −139.53 (dd, 1F, J=167.3, 4.9 Hz, Fa′), −151.77 (dd, 1F, J=167.3, 4.9 Hz, Fb′); EIMS m/z 226 [$(M+2)^{+\bullet}$, 3], 224 ($M^{+\bullet}$, 10), 189 (100), 176 (31), 174 (95), 139 (41), 119 (30). Anal. Calcd for $C_9H_5ClF_4$: C, 48.13; H, 2.24. Found: C, 48.11; H, 2.16.

2.2.7. 1-(4-Chlorophenyl)-2,2,3,3-tetrafluorocyclopropane (2g). Yellow liquid, yield 58%; bp 178 °C; ^1H NMR δ 3.40 (tt, 1H, J=19.2, 2.8 Hz), 7.23 (d, 2H, J=8.4 Hz), 7.37 (dt, 2H, J=8.8, 2 Hz); ^{13}C NMR δ 36.6 (t, J=11.5 Hz, Cα), 105.8 (ddt, J=308.4, 304.0, 11.5 Hz, Cβ, Cβ′), 123.7 (C1), 130.8 (C2, C6), 129.1 (C3, C5), 134.8 (C4); ^{19}F NMR δ −139.80 (d, 1F, J=178.9 Hz, Fa), −151.11 (d, 1F, J=178.9 Hz, Fb), −139.80 (dd, 1F, J=162.8, 3.8 Hz, Fa′), −151.11 (dd, 1F, J=162.8, 3.8 Hz, Fb′); EIMS m/z 226 [$(M+2)^{+\bullet}$, 2], 224 ($M^{+\bullet}$, 7), 189 (100), 176 (33), 174 (94), 139 (30), 119 (21). Anal. Calcd for $C_9H_5ClF_4$: C, 48.13; H, 2.24. Found: C, 48.11; H, 2.33.

2.2.8. 1-(3-Bromophenyl)-2,2,3,3-tetrafluorocyclopropane (2h). Yellow liquid, yield 34%, bp 184 °C; ^1H NMR

δ 3.37 (tt, *J*=19.2, 2.4 Hz), 7.23 (d, 2H, *J*=7.2 Hz), 7.45 (s, 1H), 7.49 (t, 1H, *J*=6.8 Hz); ^{13}C NMR δ 36.6 (t, *J*=11.5 Hz, Cα), 105.7 (ddt, *J*=308.6, 303.9, 11.5 Hz, Cβ, Cβ′), 117.4 (C1), 132.4 (C2), 122.8 (C3), 131.8 (C4), 130.3 (C5), 128.1 (C6); ^{19}F NMR δ −139.57 (d, 1F, *J*=182.7 Hz, Fa), −150.75 (d, 1F, *J*=182.7 Hz, Fb), −139.57 (dd, 1F, *J*=167.7, 4.5 Hz, Fa′), −150.75 (dd, 1F, *J*=67.7, 4.15 Hz, Fb′); EIMS *m*/*z* 270 [(M+2)$^{+\bullet}$, 3], 268 (M$^{+\bullet}$, 3), 220 (43), 218 (44), 189 (100), 169 (23), 139 (30), 119 (37). Anal. Calcd for $C_9H_5BrF_4$: C, 40.18; H, 1.87. Found: C, 40.03; H, 1.93.

2.2.9. 1-(4-Bromophenyl)-2,2,3,3-tetrafluorocyclopropane (2i). Yellow liquid, yield 41%, bp 198 °C; ^{1}H NMR δ 3.38 (tt, *J*=19.2, 2.4 Hz), 7.16 (d, 2H, *J*=8.4 Hz), 7.52 (d, 2H, *J*=8.4 Hz); ^{13}C NMR δ 36.6 (t, *J*=11.5 Hz, Cα), 105.7 (ddt, *J*=308.5, 303.0, 11.5 Hz, Cβ, Cβ′), 124.2 (C1), 132.2 (C2, C6), 131.1 (C3, C5), 123.0 (C6); ^{19}F NMR δ −139.63 (d, 1F, *J*=183.1 Hz, Fa), −150.92 (d, 1F, *J*=183.1 Hz, Fb), −139.63 (dd, 1F, *J*=166.9, 4.5 Hz, Fa′), −150.92 (dd, 1F, *J*=166.9, 4.5 Hz, Fb′); EIMS *m*/*z* 270 [(M+2)$^{+\bullet}$, 1], 268 (M$^{+\bullet}$, 1), 220 (39), 218 (39), 169 (15), 139 (20), 119 (32). Anal. Calcd for $C_9H_5BrF_4$: C, 40.18; H, 1.87. Found: C, 40.24; H, 1.90.

2.2.10. 1-Naphthyl-2,2,3,3-tetrafluorocyclopropane (2j). Yellow solid, yield 43%, mp 32–34 °C; ^{1}H NMR δ 3.78 (tt, 1H, *J*=19.2, 1.2 Hz), 7.48 (t, 1H, *J*=8 Hz), 7.55–7.66 (m, 3H), 7.90 (t, 3H, *J*=8 Hz); ^{13}C NMR δ 36.4 (t, *J*=11.5 Hz, Cα), 106.2 (ddt, *J*=306.3, 304.8, 11.5 Hz, Cβ, Cβ′), 121.6, 123.3, 125.3, 126.3, 127.1, 127.8, 128.8, 129.4, 132.5, 133.6; ^{19}F NMR δ −139.11 (d, 1F, *J*=183.1 Hz, Fa), −149.34 (d, 1F, *J*=183.1 Hz, Fb), −139.11 (dd, 1F, *J*=164.3, 5.6 Hz, Fa′), −149.34 (dd, 1F, *J*=164.3, 4.95 Hz, Fb′); EIMS *m*/*z* 240 (M$^{+\bullet}$, 78), 239 (25), 219 (24), 190 (61), 189 (42), 188 (31), 170 (100). Anal. Calcd for $C_{13}H_8F_4$: C, 65.01; H, 3.36. Found: C, 65.02; H, 3.41.

2.3. 1,1,2,2-Tetrafluoroindanes (3–5) from 1-aryl-2,2,3,3-tetrafluorocyclopropanes (2a–2j)

2.3.1. Preparation of 1,1,2,2-tetrafluoroindane (3a); typical procedure. Same procedure for preparation of tetrafluorocyclopropane was carried except for the longer heating period. The progress of conversion from tetrafluorocyclopropane to tetrafluoroindane was monitored by using either TLC or GC/MS. In most cases, 12 h is required for this reaction. The products were isolated by using vacuum distillation. The isomers of indane from 3-substituted arylcyclopropane were separated by using HPLC (RP-18, 25 mm×25 cm, 10 μm) with MeOH/H_2O=10: 1 as an eluent for spectroscopic characterization.

2.3.2. 1,1,2,2-Tetrafluoroindane (3a). Yellow liquid, yield 52%, bp 72 °C/20 torr; ^{1}H NMR δ 3.48 (t, 2H, *J*=12.4 Hz), 7.33 (d, 1H, *J*=8.4 Hz), 7.44 (t, 1H, *J*=7.6 Hz), 7.54 (t, 1H, *J*=7.6 Hz), 7.62 (d, 1H, *J*=7.6 Hz); ^{13}C NMR δ 121.7 (tt, *J*=260.0, 25.7 Hz, C1), 118.8 (tt, *J*=254.7, 25.7 Hz, C2), 38.2 (t, *J*=25.3 Hz, C3), 125.6 (C4), 124.1 (C5), 129.0 (C6), 132.9 (C7), 136.6 (tt, *J*=7.6, 6.0 Hz, C3a), 132.3 (t, *J*=4.2 Hz, C7a); ^{19}F NMR δ −112.00 (t, 2F, *J*=3.8 Hz, C1–F), −118.52 (t, 2F, *J*=3.8 Hz, C2–F); EIMS *m*/*z* 190 (M$^{+\bullet}$, 100), 169 (21), 151 (26), 140 (64). Anal. Calcd for $C_9H_6F_4$: C, 56.85; H, 3.18. Found: C, 56.88; H, 3.24.

2.3.3. 5-Methyl-1,1,2,2-tetrafluoroindane (3b) and 7-methyl-1,1,2,2-tetrafluoroindane (4b). Yellow liquid, yield 65% (**3b/4b**=1:1), bp 70 °C/28 torr. Anal. Calcd for $C_{10}H_8F_4$: C, 58.83; H, 3.95. Found: C, 58.78; H, 3.89.

2.3.4. 5-Methyl-1,1,2,2-tetrafluoroindane (3b). ^{1}H NMR δ 2.41 (s, 3H), 3.43 (t, 2H, *J*=12.4 Hz), 7.13 (s, 1H), 7.24 (d, 1H, *J*=8.4 Hz), 7.49 (d, 1H, *J*=8.4 Hz); ^{13}C NMR δ 121.9 (tt, *J*=260.1, 25.7 Hz, C1), 118.8 (tt, *J*=253.9, 25.4 Hz, C2), 38.1 (t, *J*=25.2 Hz, C3), 126.0 (C4), 143.6 (C5), 129.6 (C6), 123.9 (C7), 136.7 (tt, *J*=7.9, 5.6 Hz, C3a), 124.5 (t, *J*=25.7 Hz, C7a), 21.7 (–*C*H$_3$); ^{19}F NMR δ −111.24 (t, 2F, *J*=3.8 Hz, C1–F), −117.96 (t, 2F, *J*=3.8 Hz, C2–F); EIMS *m*/*z* 204 (M$^{+\bullet}$, 100), 189 (21), 169 (9), 154 (27), 140 (72), 135 (29).

2.3.5. 7-Methyl-1,1,2,2-tetrafluoroindane (4b). ^{1}H NMR δ 2.51 (s, 3H), 3.44 (t, 2H, *J*=12.4 Hz), 7.11 (d, 1H, *J*=8.4 Hz), 7.18 (d, 1H, *J*=7.6 Hz), 7.40 (t, 1H, *J*=7.6 Hz); ^{13}C NMR δ 121.5 (tt, *J*=259.6, 25.6 Hz, C1), 120.1 (tt, *J*=255.3, 25.6 Hz, C2), 38.2 (t, *J*=25.2 Hz, C3), 130.3 (C4), 132.6 (C5), 122.8 (C6), 137.0 (C7), 136.9 (tt, *J*=7.7, 5.9 Hz, C3a), 118.9 (t, *J*=25.4 Hz, C7a), 17.3 (–*C*H$_3$); ^{19}F NMR δ −111.73 (t, 2F, *J*=3.8 Hz, C1–F), −117.56 (t, 2F, *J*=3.8 Hz, C2–F); EIMS *m*/*z* 204 (M$^{+\bullet}$, 100), 189 (25), 184 (20), 169 (12), 154 (15), 140 (49), 135 (27).

2.3.6. 5-Methoxy-1,1,2,2-tetrafluoroindane (3d) and 7-methoxy-1,1,2,2-tetrafluoroindane (4d). Yellow liquid, yield 72% (**3d/4d**=1:1.5), bp: 87 °C/16 torr. Anal. Calcd for $C_{10}H_8OF_4$: C, 54.55; H, 3.66. Found: C, 54.58; H, 3.72.

2.3.7. 5-Methoxy-1,1,2,2-tetrafluoroindane (3d). ^{1}H NMR δ 3.89 (s, 3H), 3.43 (t, 2H, *J*=12.4 Hz), 6.79 (s, 1H), 6.95 (d, 1H, *J*=8.4 Hz), 7.52 (d, 1H, *J*=8.4 Hz); ^{13}C NMR δ 121.8 (tt, *J*=259.9, 25.9 Hz, C1), 118.8 (tt, *J*=253.1, 25.3 Hz, C2), 38.3 (t, *J*=25.6 Hz, C3), 115.5 (C4), 163.4 (C5), 109.9 (C6), 125.5 (C7), 138.6 (tt, *J*=7.7, 6.0 Hz, C3a), 124.3 (t, *J*=24.9 Hz, C7a), 55.5 (–O*C*H$_3$); ^{19}F NMR δ −111.01 (t, 2F, *J*=3.8 Hz, C1–F), −118.42 (t, 2F, *J*=3.8 Hz, C2–F); EIMS *m*/*z* 220 (M$^{+\bullet}$, 100), 201 (26), 189 (7), 170 (24), 156 (18), 127 (34).

2.3.8. 7-Methoxy-1,1,2,2-tetrafluoroindane (4d). ^{1}H NMR δ 3.91 (s, 3H), 3.43 (t, 2H, *J*=12.4 Hz), 6.85–6.89 (m, 2H), 7.47 (t, 1H, *J*=8.4 Hz); ^{13}C NMR δ 121.6 (tt, *J*=258.2, 25.6 Hz, C1), 119.4 (tt, *J*=257.5, 25.5 Hz, C2), 38.0 (t, *J*=25.4 Hz, C3), 110.5 (C4), 134.6 (C5), 122.8 (C6), 157.4 (C7), 138.7 (tt, *J*=7.3, 6.0 Hz, C3a), 119.4 (t, *J*=22.3 Hz, C7a), 55.6 (–O*C*H$_3$); ^{19}F NMR δ −112.31 (t, 2F, *J*=3.8 Hz, C1–F), −117.01 (t, 2F, *J*=3.8 Hz, C2–F); EIMS *m*/*z* 220 (M$^{+\bullet}$, 100), 201 (11), 189 (10), 170 (17), 140 (17), 127 (45).

2.3.9. 5-Chloro-1,1,2,2-tetrafluoroindane (3f) and 7-chloro-1,1,2,2-tetrafluoroindane (4f). Yellow liquid, yield 75% (**3f/4f**=1.0:1.1), bp 91 °C/15 torr. Anal. Calcd for $C_9H_5ClF_4$: C, 48.13; H, 2.24. Found: C, 48.17; H, 2.30.

2.3.10. 5-Chloro-1,1,2,2-tetrafluoroindane (3f). ^{1}H NMR δ 3.46 (t, 2H, J=12.4 Hz), 7.33 (s, 1H), 7.41 (d, 1H, J=8.4 Hz), 7.55 (d, 1H, J=8.4 Hz); ^{13}C NMR δ 121.4 (tt, J=260.5, 25.4 Hz, C1), 118.2 (tt, J=254.8, 25 Hz, C2), 38.0 (t, J=25.8 Hz, C3), 129.3 (C4), 139.2 (C5), 126.0 (C6), 125.4 (C7), 138.3 (tt, J=7.6, 6.0 Hz, C3a), 130.7 (t, J=24.7 Hz, C7a); ^{19}F NMR δ −111.88 (t, 2F, J=3.8 Hz, C1–F), −117.95 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 226 [(M+2)$^{+\bullet}$, 33)], 224 (M$^{+\bullet}$, 100), 205 (16), 189 (40), 174 (32), 169 (28).

2.3.11. 7-Chloro-1,1,2,2-tetrafluoroindane (4f). ^{1}H NMR δ 3.47 (t, 2H, J=12.4 Hz), 7.22 (d, 1H, J=7.6 Hz), 7.37 (d, 1H, J=8.4 Hz), 7.46 (d, 1H, J=7.6 Hz); ^{13}C NMR δ 121.1 (tt, J=259.7, 25.2 Hz, C1), 118.6 (tt, J=257.1, 25.9 Hz, C2), 37.9 (t, J=25.6 Hz, C3), 124.0 (C4), 134.1 (C5), 129.9 (C6), 131.8 (C7), 139.1 (tt, J=6.5, 6.2 Hz, C3a), 129.4 (t, J=21.8 Hz, C7a); ^{19}F NMR δ −113.01 (t, 2F, J=3.8 Hz, C1–F), −117.30 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 226 [(M+2)$^{+\bullet}$, 34], 224 (M$^{+\bullet}$, 100), 205 (14), 189 (49), 174 (18), 169 (34).

2.3.12. 5-Bromo-1,1,2,2-tetrafluoroindane (3h) and 7-bromo-1,1,2,2-tetrafluoroindane (4h). Yellow liquid, yield 81% (**3h/4h**=1.0:0.9), bp 106 °C/11 torr. Anal. Calcd for $C_9H_5BrF_4$: C, 40.18; H, 1.87. Found: C, 40.11; H, 1.96.

2.3.13. 5-Bromo-1,1,2,2-tetrafluoroindane (3h). ^{1}H NMR δ 3.47 (t, 2H, J=12.4 Hz), 7.49–7.50 (m, 2H), 7.58 (d, 1H, J=8.4 Hz); ^{13}C NMR δ 121.3 (tt, J=260.6, 25.4 Hz, C1), 118.2 (tt, J=255.2, 25.7 Hz, C2), 37.9 (t, J=25.7 Hz, C3), 128.9 (C4), 127.4 (C5), 132.2 (C6), 125.6 (C7), 138.5 (tt, J=7.6, 5.9 Hz, C3a), 131.2 (t, J=24.8 Hz, C7a); ^{19}F NMR δ −112.75 (t, 2F, J=3.8 Hz, C1–F), −118.69 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 270 [(M+2)$^{+\bullet}$, 98], 268 (M$^{+\bullet}$, 100), 250 (12), 249 (13), 220 (26), 218 (26), 189 (56), 169 (72).

2.3.14. 7-Bromo-1,1,2,2-tetrafluoroindane (4h). ^{1}H NMR δ 3.47 (t, 2H, J=12.4 Hz), 7.26 (d, 1H, J=7.6 Hz), 7.45 (d, 1H, J=7.6 Hz), 7.50 (d, 1H, J=7.6 Hz); ^{13}C NMR δ 121.1 (tt, J=260.7, 25.3 Hz, C1), 118.6 (tt, J=257.8, 25.8 Hz, C2), 37.8 (t, J=25.5 Hz, C3), 124.5 (C4), 133.9 (C5), 133.2 (C6), 119.3 (C7), 139.4 (tt, J=6.3, 6.0 Hz, C3a), 131.4 (t, J=22.9 Hz, C7a); ^{19}F NMR δ −113.79 (t, 2F, J=3.8 Hz, C1–F), −118.03 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 270 [(M+2)$^{+\bullet}$, 98], 268 (M$^{+\bullet}$, 100), 251 (10), 249 (10), 220 (10), 218 (11), 189 (58), 169 (68).

2.3.15. 6-Methyl-1,1,2,2-tetrafluoroindane (5c). Yellow liquid, yield 68%, bp 86 °C/20 torr; ^{1}H NMR δ 2.42 (s, 3H), 3.44 (t, 2H, J=12.4 Hz), 7.21 (d, 1H, J=8.4 Hz), 7.36 (d, 1H, J=8.4 Hz), 7.43 (s, 1H); ^{13}C NMR δ 118.9 (tt, J=254.6, 25.6 Hz, C1), 122.0 (tt, J=260.1, 25.5 Hz, C2), 37.8 (t, J=25.2 Hz, C3), 125.4 (C4), 133.9 (C5), 138.9 (C6), 124.1 (C7), 133.6 (tt, J=7.6, 6.0 Hz, C3a), 132.2 (t, J=23.9 Hz, C7a), 21.2 (–CH$_3$); ^{19}F NMR δ −112.67 (t, 2F, J=3.8 Hz, C1–F), −118.92 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 204 (M$^{+\bullet}$, 100), 189 (25), 169 (9), 154 (21), 140 (43), 135 (28). Anal. Calcd for $C_{10}H_8F_4$: C, 58.83; H, 3.95. Found: C, 58.79; H, 4.02.

2.3.16. 6-Methoxy-1,1,2,2-tetrafluoroindane (5e). Yellow liquid, yield 65%, bp 106 °C/10 torr; ^{1}H NMR δ 3.40 (t, 2H, J=12.4 Hz), 3.84 (s, 3H), 7.21 (d, 1H, J=9.2 Hz), 7.07–7.09 (m, 2H); ^{13}C NMR δ 122.0 (tt, J=260, 25.4 Hz, C1), 118.8 (tt, J=254.9, 25.8 Hz, C2), 37.5 (t, J=25.2 Hz, C3), 126.7 (C4), 120.6 (C5), 160.1 (C6), 107.5 (C7), 138.4 (tt, J=7.7, 6.0 Hz, C3a), 133.2 (t, J=24.1 Hz, C7a), 55.6 (–OCH$_3$); ^{19}F NMR δ −112.00 (t, 2F, J=3.8 Hz, C1–F), −117.87 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 220 (M$^{+\bullet}$, 100), 201 (14), 170 (30), 127 (52). Anal. Calcd for $C_{10}H_8OF_4$: C, 54.55; H, 3.66. Found: C, 54.62; H, 3.66.

2.3.17. 6-Chloro-1,1,2,2-tetrafluoroindane (5g). Yellowish liquid, yield 72%, bp 95 °C/10 torr; ^{1}H NMR δ 3.42 (t, 2H, J=12.4 Hz), 7.23 (d, 1H, J=8.4 Hz), 7.46 (d, 1H, J=8.4 Hz), 7.55 (s, 1H); ^{13}C NMR δ 121.6 (tt, J=260.5, 25.5 Hz, C1), 118.2 (tt, J=255.9, 25.9 Hz, C2), 37.6 (t, J=25.3 Hz, C3), 127.1 (C4), 133.3 (C5), 134.7 (C6), 124.2 (C7), 135.0 (tt, J=7.5, 5.7 Hz, C3a), 133.7 (t, J=24.4 Hz, C7a); ^{19}F NMR δ −112.36 (t, 2F, J=3.8 Hz, C1–F), −118.25 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 226 [(M+2)$^{+\bullet}$, 35], 224 (M$^{+\bullet}$, 100), 205 (14), 189 (57), 174 (35), 169 (40). Anal. Calcd for $C_9H_5ClF_4$: C, 48.13; H, 2.24. Found: C, 48.10; H, 2.26.

2.3.18. 6-Bromo-1,1,2,2-tetrafluoroindane (5i). Yellow liquid, yield 69%, bp 89 °C/7 torr; ^{1}H NMR δ 3.42 (t, 2H, J=12.4 Hz), 7.21 (d, 1H, J=8.4 Hz), 7.66 (d, 1H, J=8.4 Hz), 7.75 (s, 1H); ^{13}C NMR δ 121.4 (tt, J=260.7, 25.3 Hz, C1), 118.0 (tt, J=256.1, 25.9 Hz, C2), 37.8 (t, J=25.3 Hz, C3), 127.3 (C4), 136.1 (C5), 122.3 (C6), 127.4 (C7), 135.4 (tt, J=7.2, 6.0 Hz, C3a), 134.2 (t, J=24.5 Hz, C7a); ^{19}F NMR δ −112.34 (t, 2F, J=3.8 Hz, C1–F), −118.26 (t, 2F, J=3.8 Hz, C2–F); EIMS m/z 270 [(M+2)$^{+\bullet}$, 98], 268 (M$^{+\bullet}$, 100), 251 (10), 249 (11), 220 (20), 218 (20), 189 (66), 169 (84). Anal. Calcd for $C_9H_5BrF_4$: C, 40.18; H, 1.87. Found: C, 40.12; H, 1.93.

2.3.19. 1,1,2,2-Tetrafluoro-2,3-dihydro-1*H*-cyclopenta(*a*)naphthalene (6). Yellow solid, yield 79%, mp 40–42 °C; ^{1}H NMR δ 3.75 (t, 2H, J=12 Hz), 7.58–7.69 (m, 4H), 7.84 (d, 1H, J=8.8 Hz), 7.89 (d, 1H, J=8.8 Hz); ^{13}C NMR δ 121.9 (tt, J=260.4, 25.4 Hz, C1), 119.7 (tt, J=254.2, 25.5 Hz, C2), 36.9 (t, J=26.0 Hz, C3), 135.0 (tt, J=8.7, 5.9 Hz, C3a), 125.7 (t, J=23.9 Hz, C9a), 119.2, 124.0, 127.5, 128.2, 128.9, 129.8, 135.2; ^{19}F NMR δ −112.00 (t, 2F, J=3.8 Hz, C1–F), −118.52 (t, 2F, J=3.8 Hz, C2–F) EIMS m/z 240 (M$^{+\bullet}$, 100), 239 (28), 221 (34), 190 (45), 170 (36). Anal. Calcd for $C_{13}H_8F_4$: C, 65.01; H, 3.36. Found: C, 64.93; H, 3.39.

Acknowledgements

Financial support by the National Science of the Republic of China (NSC 94-2113-M-126-005) and the technique supporting by NCHC are gratefully acknowledged.

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