Preparation of 1-Aryl-2-bromo-3,3-difluorocyclopropenes

Shaw-Tao Lin[a]*, Li-Chwen Chen[a] and Chun-Jen Lee[b]

[a]Department of Applied Chemistry, Providence University, Sha-Lu, Taichung Hsien, Taiwan 433, P.R. China
[b]Department of Chemical Engineering, Hsiuping Institute of Technology, Ta-Lee, Taichung Hsien, Taiwan 412, P.R. China

1-Aryl-2-bromo-3,3-difluorocyclopropanes were prepared from the reaction of 2',2'-difluorostyrene and dibromocarbene instead of from 1-aryl-2-haloacetylenes and difluorocarbene. These results are rationalised by the energy gap between $HOMO_{(styrene)}$, $HOMO_{(acetylene)}$ and $LUMO_{(CX2)}$. The title compounds were converted to methyl arylpropynoate in MeOH solution in quantitative yield.

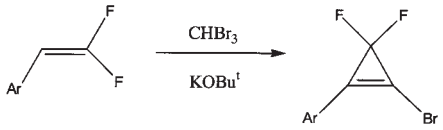
Keywords: 1-aryl-2-bromo-3,3-difluorocyclopropanes

Carbene addition to carbon–carbon double bond is a common process to prepare cyclopropanes. However, a few reports concern the addition of carbenes to the carbon–carbon triple bond leading to cyclopropenes.[1,2] Dehydrohalogenation of dihalocyclopropanes could give the corresponding cyclopropenes at low temperature without isolation, but it led to ring-opened products at an ambient temperature.[3] 1-Arylpolychlorocyclopropenes have been prepared from the Friedel–Crafts reaction by reaction of tetrachlorocylopropenes and arenes in the presence of $AlCl_3$.[4] Difluorocyclopropenes have been obtained *via* an exchange reaction of polychlorocyclopropenes using either SbF_3 or KF as fluorine sources,[5] dehalogenation of dichlorodifluorocyclopropanes using Zn,[6] and dehydrohalogenation of chlorodifluoro-cyclopropanes using base.[7] The direct preparation of difluorocyclopropenes *via* a [1 + 2] process was carried out by the addition of difluorocarbene to carbon–carbon triple bond having a strongly electron-withdrawing group.[8] Few reports concern the preparation of aryldifluorocyclopropanes by means of [1 + 2] process.[9] In general, the reactivity of alkenes with carbenes is higher than that of alkynes. In our previous work,[l0] we have successfully prepared 1-aryl-2-chloro-3, 3-difluorocyclopropenes by reaction of 2',2'-difluorostyrenes and chloroform in the presence of base and a phase transfer reagent.[l1] The function of base is to generate the dichlorocarbene as well as to eliminate hydrogen chloride to yield the cyclopropenes. Herein, we report the preparation of 1-aryl-2-bromo-3,3-difluorocyclopenes by reaction of 2', 2'-difluorostyrenes and bromoform in the presence of $KOBu^t$.[12]

Results and discussion

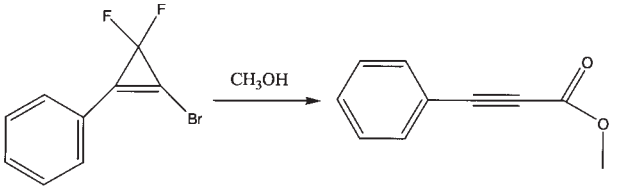
1-Aryldifluorocyclopropenes have been prepared by the reaction of styrenes and difluorocarbene in poor yield. In the present work, 2',2'-difluorostyrenes instead of styrenes were used to prepare difluorocyclopropenes. Thus, 1-aryl-2',2'-difluorostyrenes **1**, readily obtained from the reaction of the corresponding benzaldehydes and sodium chloro-fluoroacetate,[l1a] were treated with bromoforrn and $KOBu^t$ in hexane at ambient temperature for 24 h. The product was diluted with water, extracted with hexane and separated by chromatography to give the corresponding 1-aryl-2-bromo-3,3-difluorobromocyclopropenes **2** as the only products (Scheme 1). The structure of **2** was confirmed on the basis of the lack of resonance signals for cyclopropyl protons in the ^1H NMR spectra along with the molecular weight obtained from mass spectroscopic and elemental analyses. The characteristic fragment ions of $[M–Br]^+$ are also the base peaks for this series of compounds.[l0]

The formation of cyclopropenes presumably proceeded by the addition of dibromocarbene to 2',2'-difluorostyrenes followed by the elimination of hydrogen chlorine in the presence of a strong base. The existence of an aryl group incorporating two fluorine atoms would increase the possibility of removing a benzylic hydrogen by base. The relatively poor yields are due to the labile cyclopropene, which might decompose either during the column purification or by thermal decomposition.



2a - 2j

a: C_6H_5; **b:** 3-$CH_3C_6H_4$; **c:** 4-$CH_3C_6H_4$; **d:** 3-CH_3O-C_6H_4; **e:** 4-CH_3O-C_6H_4; **f:** 3-ClC_6H_4; **g:** 4-ClC_6H_4; **h:** 3-BrC_6H_4; **i:** 4-BrC_6H_4; **j:** 4-FC_6H_4; **k:** naphthenyl-



Scheme 1

An alternative process to prepare 1-phenyl-2-bromo-3, 3-difluorocyclopropene was the addition of difluorocarbene, generated from a mixture of CH_2Br_2, CBr_2F_2 and KOH, to bromophenylacetylene.[l3] Analysis of the product by GC/MS suggested that the mixture contained the title compound (19.5%) along with 2',2'-dibromostyrene (17.1%), 1', 2'-dibromostyrenes (11.4%), and tribromostyrene (52.0%). Formation of polybromostyrenes indicated that a radical process might be involved.[l4] A number of attempts to prepare the title compound from the reaction of dibromostyrene[l4] and difluorocarbene, generated from $CBr_2F_2/PPh_3/Zn$. $CBr_2F_2/CH_2Br_2/KOH$. $ClCF_2COONa$/heat. and $CBr_2F_2/Zn/I_2$ failed. No reaction was observed from the reaction of chlorophenylacetylene and difluorocarbene under same conditions.[l4a,l5]

In general, in the addition of dihalocarbene to multiple bond, the dihalocarbenes are classified as electrophiles, while, the multiple bonds serve as the nucleophile, *i.e.*, the LUMO orbital of carbene will accept an electron pair from the HOMO orbital of multiple bond. The orientation of the addition of dihalocarbene and styrenes or phenylacetylene can be rationalised by the energy gap between the HOMO of multiple bond and LUMO of carbene. The energies of HOMO and LUMO orbitals for dihalocarbenes and 2',2'-dihalostyrene and 1-halo-2-phenylacetylenes obtained from AM1 calculation are shown in Table 1. From this we see that the singlet carbenes with lower LUMO energy level than that of triplet shall favour the addition to dihalostyrenes. While, reactions of

*Correspondence. E-mail: sdlin@Pu.edu.tw

Table 1 Calculated energies (eV) of HOMO of dihalostyrenes and halophenyl-acetylenes, LUMO of carbenes and the energy gaps between LUMO and HOMO

	E_{HOMO} / ΔE / E_{LUMO}	Ph-CH=CX_2			Ph-C≡CX		
		X: F	Cl	Br	X: F	Cl	Br
		–9.091	–9.413	–9.581	–9.303	–9.193	–9.288
:CF_2	s-0.297	8.794	9.116	9.284	9.006	8.896	8.991
	t 2.509	11.600	11.922	12.090	11.812	11.702	11.797
:CCl_2	s-1.105	7.986	8.308	8.476	8.198	8.088	8.183
	t 0.148	9.239	9.561	9.729	9.451	9.341	9.436
:CBr_2	s-0.910	8.181	8.503	8.671	8.393	8.283	8.378
	t-0.569	8.522	8.844	9.012	8.734	8.624	8.719

[a]$\Delta E = E_{LUMO(carbene)} - E_{HOMO(styrene\ or\ acetylene)}$; s., singlet carbene; t., triplet carbene.

difluorostyrenes with dibromocarbene or dichlorocarbene are the more favoured processes because of the smaller energy gap.

On the other hand, difluorocabene possesses a higher LUMO energy level leading to addition reaction to neither styrenes nor phenylacetylenes. In this system, the double bond acts as a better nucleophile than that of the triple bond to accept carbenes. Although, the higher HOMO–LUMO energy gap between difluorocarbene and bromoacetylene was observed from the calculation. However, the reaction of bromoacetylene and difluorocarbene yielded difluoro-cyclopropene along with polybromo-products suggested that this reaction is not a simple 1 + 2 concerted addition process but possible a radical process as described in the literature.[16]

Polyhalocyclopropenes (Br or C1) are decomposed by either alcohols or water.[17] Difluorocyclopropenes seem to be more stable than their chloro-counterparts and we were able to isolate them from an aqueous solution. This might be attributed to the high bond energy of the carbon–fluorine bond in bromodifluorocyclopropenes compared to that of the carbon–chlorine bond in trichlorocyclopropenes. No decomposition was observed when a pure compound prepared for GC/MS analysis was allowed to stand in an aqueous methanol solution ($MeOH/H_2O$: 4/1) for a week at room temperature. This series of compounds can be stored in a deep freeze without decomposition for more than one month. Bromodifluorocyclopropenes are decomposed by methanol under reflux to form methyl phenylpropiolate.[18] While, the solvolysis reactions of chlorodifluorocyclopropenes and trichlorocyclopropenes led to hydroxycyclopropenones, alkoxycyclopropenone or 2-aryl-3-chloroacrylic acid in the presence of water or alcohols.[17] The differences in the products might be due to the bromine atom behaving as a good leaving group to form a triple bond. Direct methanolysis of the product from **2a** gave good yields of methyl arylpropioylate.

Experimental

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 250, 62.86 (Bruker AC-250), and 282.22 MHZ (Varian VXR-300), respectively, at ambient temperature. Chemical shifts for samples in $CDC1_3$ solution are reported in δ units relative to TMS (^{1}H and ^{13}C) and trifluorobenzene (at –63.9 ppm, ^{19}F). Mass spectra were obtained from GC/MS (Fisons 8000 series coupled with Finnigan MD-800) at an ionisation potential of 70 eV. Elemental analyses were performed at the Instrumental Analysis Center at National Chung Hsien University. A11 2',2'-difluorostyrenes were prepared from the reaction of sodium chlorodifluoroacetate and the corresponding benzaldehyde. 1-Bromo-2-phenylacetylene was prepared from dehydrobromination of 2',2'-dibromostyrene by aqueous KOH solution.

1-AryI-2-bromo-3,3-difluorocyclopropenes from 2',2'-diflouro-styrenes

Typical procedure: Bromoform $CHBr_3$ (0.80 ml, 8.9 mmol) was added dropwisely to a mixture of 2',2'-difluorostyrene (**la**, 0.5 g, 3.6 mmol) and $KOBu^t$ (1.7 g, 14.8 mmol) in *n*-hexanes (15 ml) on an ice-bath with stirring. After stirring at that temperature for 10 min, the ice-bath was removed and the mixture was stirred at ambient temperature. The progress of reaction was traced by using TLC analysis. Once, benzaldehyde had disappeared from the TLC plate (usually less then 12 h), the mixture was poured into ice-water (70 ml) and then extracted with *n*-hexane (20 ml × 3). The organic layer was washed with H_2O (20 ml × 3), dried ($MgSO_4$) and filtered. The resultant was purified by chromatography on a silica gel column with *n*-hexane as an eluent to give **2a**; yield 62%, f.p. –14°C; ^{1}H NMR. 7.48–7.67 (m, 5H); ^{13}C NMR. 99.14(t, *J*=16.0 Hz), 101.88 (t, *J*=281.0 Hz), 122.32, 129.19, 129.46, 131.86, 134.31 (t, *J*=13.0Hz); ^{19}F NMR. –106.39; IR . 1767, 1323, 1048 cm^{-1}; MS *m/z*(%) 230(M^+, 2), 151(100), 101(19); Anal. Calcd. for $C_9H_5BrF_2$: C, 46.79; H, 2.18. Found: C, 46.54; H, 2.34.

2-Bromo-1-(3-tolyl)-3,3-difluorocyclopropene **2b**: yield 48%; m.p. ^{1}H NMR . 2.42(s, 3H), 7.32–7.45(m, 4H); ^{13}C NMR . 21.19, 98.71(t, t=16.0 Hz), 101.95(t, *J*=281.0 Hz), 122.12, 126.59, 129.05, 129.94, 12.69, 134.26(t, *J*=13.0 Hz), 139.11; ^{19}F NMR . –106.39; IR 1766, 1325, 1046cm^{-1}; MS *m/z*(%) 244(M^+, 1), 165(100), 115(11); Anal. Calcd. for $C_{10}H_7BrF_2$: C, 49.01; H, 2.88. Found: C, 48.94; H, 2.74.

2-Bromo-1-(4-tolyl)-3,3-difluorocyclopropene **2c**: yield 66.2 %, m.p. 35.9–36.9°C; ^{1}H NMR δ 2.42(s, 3H), 7.30(dd, *J*=8.0Hz, 2H), 7.54(dd, *J*=8.0Hz, 2H); ^{13}C NMR δ 21.80, 97.65(t, *J*=16.0Hz), 102.00(t, *J*=280.Hz), 119.49, 129.45, 129.90, 134,14(t, *J*=13.0Hz), 142.60; ^{19}F NMR δ -106.42; IR ν 1766, 1327, 1044 cm^{-1}; MS *m/z*(%.) 244(M^+, 2), 165(100), 115 (16). Anal. Calcd. for $C_{10}H_7BrF_2$: C,49.01; H,2.88. Found: C, 48.92; H, 3.09

2-Bromo-1-(3-methoxyphenyl)-3,3-difluorocyclopropene **2d**: yield 53.7 %, m.p. 3.0°C; ^{1}H NMR δ 3.86 (s, 3H), 7.06–7.12 (m, 2H), 7.23 (s, 1H), 7.41 (t, 1H, *J*=7.8Hz); ^{13}C NMR δ 55.49, 99.37(t, *J*=15.8Hz), 101.85(t, *J*=281.4Hz), 114.07, 118.80, 121.91, 123.31, 130.31, 134.32(t, *J*=13.0Hz), 159.96; ^{19}F NMR . –106.31; IR ν 1767, 1318, 1043 cm^{-1}; MS *m/z*(%) 260(M^+,3), 181(100), 166(4), 138(37). Anal. Calcd for $C_{10}H_7OBrF_2$: C, 46.01; H, 2.70. Found: C, 45.89; H, 2.89

2-Bromo-1-(4-methoxyphenyl)-3,3-difluorocyclopropene **2e**: yield 55.4%, m.p. 36.8–37.1°C; ^{1}H NMR δ 3.87(s, 3H), 6.99(dd, 2H, *J*=8.8Hz), 7.59(d, 2H, *J*=8.8Hz); ^{13}C NMR δ 55.49, 95.60 (t, *J*=16.1Hz), 102.06(t, *J*=280.8Hz), 114.65, 114.74, 131.38, 133.56(t, *J*=12.5Hz), 162.29; ^{19}F NMR δ -106.40; IR ν 1767, 1323, 1031cm^{-1}; MS: *m/z*(%) 260(M+,1), 181(100), 138(29); Anal. Calcd. for $C_{10}H_7OBrF_2$: C, 46.01; H, 2.70. Found: C, 45.82; H, 2.80

2-Bromo-1-(3-chlorophenyl)-3,3-difluorocyclopropene **2f**: yield 66.4 %, m.p. 39.1–39.5°C; ^{1}H NMR δ 7.42–7.55 (m, 3H), 7.63 (s, 1H); ^{13}C NMR δ 101.02 (t, *J*=16.0Hz), 101.39(t, *J*=282.0Hz), 123.86, 127.46, 129.17, 130.53, 131.91, 133.32(t, 6 *J*=13.0Hz), 135.29; IR ν 1766, 1321, 1050cm^{-1}; MS *m/z*(%) 264(M^+,1), 185(100), 187(37), 150(21); Anal. Calcd. for $C_{10}H_4ClBrF_2$: C, 40.72; H,1.52. Found: C, 39.68; H, 1.72

2-Bromo-1-(4-chlorophenyl)-3,3-difluorocyclopropene **2g**: yield 64.9 %, m.p. 30.6–31.0°C; ^{1}H NMR δ 7.47 (d, 2H, *J*=8.5Hz), 7.58 (d, 2H, *J*=8.5Hz); ^{13}C NMR δ 99.82 (t, *J*=16.0Hz), 101.48 (t, *J*=282.0Hz), 120.72, 129.64, 130.61, 133.31(t, *J*=13.0Hz); ^{19}F NMR δ -106.39; IR ν; 1767, 1322, 1053cm^{-1}; MS *m/z*(%) 264(M^+,1), 185(100), 187(34), 150(19); Anal. Calcd. for $C_{10}H_4ClBrF2$: C, 40.72; H,1.52. Found: C, 39.75; H, 1.54

2-Bromo-1-(3-bromophenyl)-3,3-difluorocyclopropene **2h**: yield 59.3%, m.p. 45.0–46.0°C; ^{1}H NMR δ=7.39(t, 1H, *J*=7.8Hz), 7.58 (d, 1H, *J*=7.8Hz), 7.67(d, 1H, *J*=7.8Hz), 7.78(s, 1H); ^{13}C NMR δ 101.04(t, *J*=16.0Hz), 101.37(t, *J*=282.Hz), 123.15, 124.10, 127.91, 130.73, 132.05, 133.16(t, *J*=13.0Hz), 134.80; ^{19}F NMR δ 106.30; IR: ν; 1767, 1320, 1053 cm^{-1}; MS *m/z*(%) 308(M^+,1), 229(100), 231(100), 150(59); Anal. Calcd. for $C_{10}H_4Br_2F_2$: C, 34.88; H, 1.30. Found: C, 35.12; H, 1.14

2-Bromo-1-(4-bromophenyl)-3,3-difluorocyclopropene **2i**: yield 66.2 %, m.p. –6.5°C; ^{1}H NMR δ 7.51(d, 2H, *J*=8.3Hz), 7.65(d, 2H, *J*=8.3Hz); ^{13}C NMR: δ 100.04 (t, *J*=15.9Hz), 101.47(t, *J*=281.8Hz), 121.17, 126.62, 130.72, 132.63, 133.44(t, *J*=13.1Hz); ^{19}F NMR δ -106.43; IR ν; 1765, 1321, 1051cm^{-1}; MS *m/z*(%) 308(M^+,1), 229(100), 231(97), 150(53); Anal. Calcd. for $C_{10}H_4ClBrF_2$: C, 34.88; H, 1.30. Found: C, 34.69; H, 1.24

2-Bromo-1-(4-fluorophenyl)-3,3-difluorocyclopropene **2j**: yield 46.9%, m.p. 29.9–30.9°C; ^{1}H NMR δ 7.15-7.29(m, 2H), 7.62-7.69(m, 2H); ^{13}C NMR δ 98.62(t, *J*=16.0Hz), 7 101.61 (t, *J*=281.0Hz), 116.86 (d, *J*=22.3Hz), 118.70, 131.76(d, *J*=9.0Hz), 133.3(t, *J*=13.1 Hz), 164.59(d, *J*=253.0 Hz); ^{19}F NMR δ -106.46, -106.93(d, *J*=6.2 Hz); IR 1762,1327,1048 cm^{-1}; MS *m/z*(%) 248 (M^+, 1), 169(100), 149(7), 119(6); Anal. Calcd. for $C_9H_4BrF_3$:C, 43.41;H,1.62. Found: C, 43.60; H, 1.72

2-Bromo-l-naphthalenyl-3,3-difluorocyclopropene **3**: yield 70.0%, m.p. ^{1}H NMR: δ 7.53–7.74(m, 3H), 7.87–8.04(m, 3H), 8.26(d, 1H, *J*=8.3Hz); ^{13}C NMR δ 99.50(t, *J*=15.7Hz), 101.78(t, *J*=280.8Hz), 119.71, 124.75, 125.30, 126.94, 128.11, 128.70, 130.22, 130.96, 132.78, 132.88(t, *J*=12.9Hz), 133.64; ^{19}F NMR δ -105.25; IR ν 1750, 1319, 1042 cm^{-1}; MS *m/z*(%) 280(M^+, 4), 201(100), 202(11), 181(14), 150(10); Anal. Calcd. for $C_{13}H_7BrF_2$: C, 55.55; H, 2.51. Found: C, 55.66; H, 2.38

Reaction of bromophenylacetylenes and difluorocarbene: Potassium hydroxide (60%), 1 cm^3) was added dropwise to a dichloromethane (2.0 ml) solution of bromophenylacetylene (0.lg, 0.55mmol), dibromodifluoromethane (0.2 ml), dibromomethane (0.2 ml) and phase-transfer catalyst (triethylbenzylammonium chloride, 20mg) in a three-necked flask with a condenser on an ice-bath with stirring for 1 h. After the addition was complete, the ice-bath was removed and the solution was stirred at ambient temperature for 5 days. The mixture was poured into ice-water (10 ml), and then extracted with diethyl ether (5 ml × 3). The organic layer was dried over $MgSO_4$ and analysed by GC/MS. The signals of compounds were verified by their retention time of authentic compounds and their mass spectra. The distribution of the products are obtained based on the peak areas from GC/MS analysis as 1-bromo-2,2-difluoro-3-phenylcyclopropene (19.5 %), 2',2'-dibromostyrene (17.1 %), 1',2'-dibromostyrene (11.4%), and tribromostyrene (52.0%).

Methyl 3-phenylpropynoate from methanolysis of 1-bromo-2–2-difluoro-3-phenylcyclopropene (**2a**). A mixture of **2a** (71 mg, 0.3 mmol) and methanol (1.5 ml) was heated under refluxing for 1 h. The pure methyl 3-phenylpropynoate was isolated in quantitative yield from removing solvent under reduced pressure and verified by comparing m.p. and spectra (IR, NMR).

Direct methanolysis of difluorocyclopropenes

Typical procedure: Bromoform (0.8cm^3, 8.9 mmol) was added dropwise to a mixture of 2',2'-difluorostyrene (la, 0.5 g, 3.6 mmol) and KOBu^t (1.7 g, 14.8 mmol) in n-hexane (15 ml) on an ice-bath with stirring. After stirring at that temperature for 10 min, the ice-bath was removed and the mixture was stirred at ambient temperature. The progress of reaction was followed by using TLC analysis. Once, benzaldehyde had disappeared from the TLC plate (usually less then 12 h), the mixture was poured into ice-water (70 ml) and then extracted with n-hexanes (3 × 20 ml). The organic layer was washed with H_2O (3 × 20 ml), dried ($MgSO_4$) and filtered. Methanol (l.0 ml) was added and then refluxed for 1 h. Methyl 3-(4-bromophenyl)propynoate was isolated in 95% yield.

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