Tetrahedron 65 (2009) 6320–6324

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Reaction of difluorocarbene with propargyl esters and efficient synthesis of difluorocyclopropyl ketones

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ARTICLE INFO

Article history:
Received 29 April 2009
Received in revised form 3 June 2009
Accepted 5 June 2009
Available online 10 June 2009

Keywords:
Difluorocyclopropane
Difluorocyclopropene
Difluorocyclopropyl ketone
Difluorocarbene

ABSTRACT

Difluorocarbene generated from $FSO_2CF_2CO_2SiMe_3$ (TFDA) at 120 °C could reacted with terminal alkynes having an ester group at the α position to the triple bond. Difluorocyclopropenes were further converted to difluorocyclopropyl ketones under alkaline condition. Mechanism for the conversion was studied.

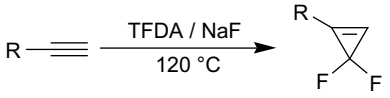
1. Introduction

Three-membered carbocycles are versatile building blocks in organic synthesis, which are extremely important and interesting for their unique structural and electronic properties.[1] Although the introduction of fluorine atoms into these compounds could significantly alter their chemical properties,[2] the fluorinated analogues such as difluorocyclopropenes and difluorocyclopropanes have been less studied. This might be due to the shortage of efficient and convenient synthetic methods for these compounds. The most possible and direct route to these fluorinated analogues might be through the addition of difluorocarbene to double or triple bonds.[3] Recently, we found that difluoro(methylene)cyclopropanes can be readily prepared from the direct difluorocyclopropanation of allenes, using $FSO_2CF_2CO_2Si(CH_3)_3$ (TFDA) as the difluorocarbene precursor.[3f] The difluorocarbene addition to phenylacetylene did give the corresponding difluorocyclopropene structure.[3a–e] However, the terminal difluorocyclopropene was not stable and decomposed readily on standing even at room temperature. As an extension of our studies on highly strained three-membered ring compounds and our interest in difluorocarbene chemistry,[4] we investigated the synthesis of terminal difluorocyclopropenes and their chemical conversions.

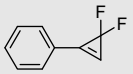
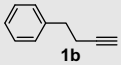
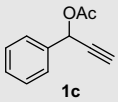
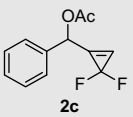
2. Results and discussion

Trimethylsilyl fluorosulfonyldifluoroacetate (TFDA) was found to be an efficient difluorocarbene precursor, which can be used to

Table 1
Reaction of alkynes with difluorocarbene



1a-c **2a-c**

Entry	Alkyne	Product	Yield (%)
1	 **1a**	 **2a**	65[a]
2	 **1b**	—[b]	—[b]
3	 **1c**	 **2c**	45
4[c]	**1c**	—	—

[a] **2a** was unstable, see Ref. 3a.
[b] No addition product was detected and the alkyne kept inert in the reaction.
[c] $ClCF_2COONa$ (10 equiv) was used as the difluorocarbene reagent and no addition product was detected.

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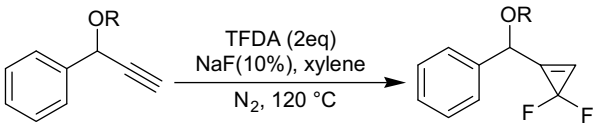
doi:10.1016/j.tet.2009.06.019

Table 2
Reaction of terminal alkynes with different α substituents



1d-j **2d-j**

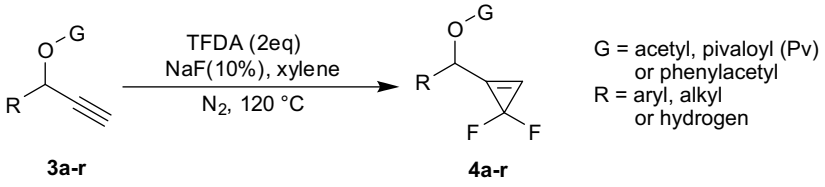
Entry	Alkyne	R	Product	Yield (%)
1	**1d**	Diethoxyphosphoryl	**2d**	—[c]
2	**1e**	4-Chlorophenyl	**2e**	—[c]
3	**1f**	Benzoyl	**2f**	49,[a] —[d]
4	**1g**	Cyclohenxanecarbonyl	**2g**	67,[a] 49[b]
5	**1h**	Ethylsuccinyl	**2h**	53,[a] 50[b]
6	**1i**	Phenylacetyl	**2i**	66,[a] 65[b]
7	**1j**	Pivaloyl	**2j**	78,[a] 61[b]

[a] Determinated by ^{19}F NMR.
[b] Isolated yield.
[c] No adduct was detected.
[d] The adduct decomposed readily after the reaction.

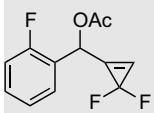
construct the highly strained ring compounds.[3,5] We reexamined the addition reaction of difluorocarbene derived from TFDA with terminal alkynes (Table 1). Although the product **2a** was not stable, the addition of difluorocarbene with phenylacetylene did occur under this condition (entry 1). In the case of 'normal' terminal alkyne like **1b**, no reaction happened (entry 2). Much to our surprise, the addition of difluorocarbene to alkyne **1c** with an acetoxy group at the α position to the triple bond could proceed smoothly to give **2c** as a stable compound in 45% yield (entry 3). However, no desired addition product could be detected when $ClCF_2COONa$ was used as the difluorocarbene precursor (entry 4).[3i] Having the desired product, the next step was to screen the reaction condition for optimized yield of the addition. It was found that **2c** could be isolated in 59% when xylene was used as the solvent at 120 °C for 35 min (See Supplementary data).

The above results have shown that an α substituted acetoxy group in alkynes is necessary for the reaction. With the optimized reaction conditions in hand, we further investigated the reaction of other α substituted alkynes. As shown in Table 2, no addition

Table 3
Addition of difluorocarbene to propargyl esters

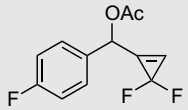


3a-r **4a-r**



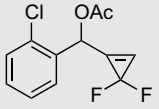
4a

63%[a]/54%[b]



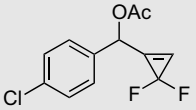
4b

51%[a]/46%[b]



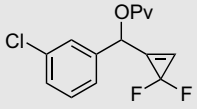
4c

63%[a]/52%[b]



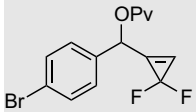
4d

57%[a]/46%[b]



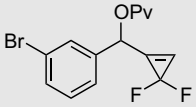
4e

44%[a]/33%[b]



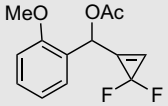
4f

73%[a]/37%[b]



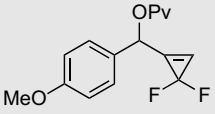
4g

53%[a]/48%[b]



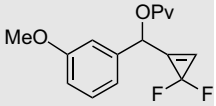
4h

73%[a]/55%[b]



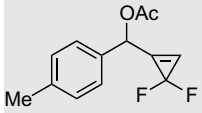
4i

60%[a]/55%[b]



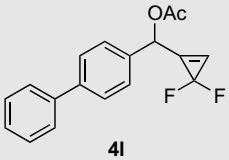
4j

54%[a]/35%[b]



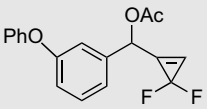
4k

60%[a]/51%[b]



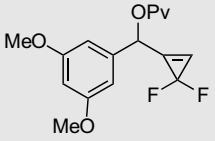
4l

64%[a]/53%[b]



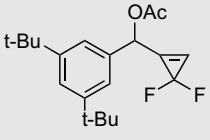
4m

51%[a]/45%[b]



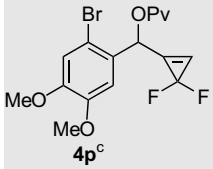
4n

61%[a]/58%[b]



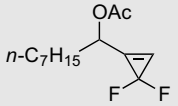
4o

74%[a]/43%[b]



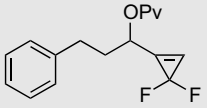
4p[c]

57%[a]/30%[b]



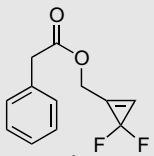
4q

45%[a]/39%[b]



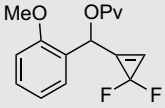
4r

62%[a]/60%[b]



4s

65%[a]/29%[b]



4t

45%[a]/35%[b]

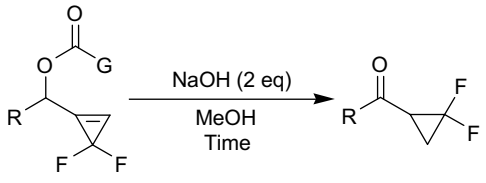
[a] Determined by ^{19}F NMR.
[b] Isolated yield.
[c] 5 equiv TFDA was used.

reaction happened when the α position of the triple bond was substituted with phosphoryloxy (entry 1) or aryloxy (entry 2) group. The reaction with alkyne containing a benzoyloxy substitutent was similar to that with phenylacetylene. The easy decomposition of the adduct made the isolation difficult (entry 3). As for other carboxy substituted alkynes, the reaction could proceed very well to give the adducts **2g–j** with satisfied yields (entries 4–7), which indicated the strong neighboring group effect existed in the difluorocarbene addition to terminal alkynes. Further evidence is needed to elucidate the underlying mechanism for this inherent effect.

Then a variety of propargyl esters with α substituted carboxy groups were applied to the reaction (Table 3). Both aryl and alkyl propargyl esters could be converted to the corresponding difluorocyclopropenes in moderate yields. The carboxy group of the alkyne had some influence on the reaction. Increasing the hindrance of the ester group would depress the addition of difluorocarbene to the triple bond. Compared with **4h**, the yield of **4t** decreased significantly when the acetyl was substituted by pivaloyl. However, as it might be seen from the yield of **4q** and **4r**, bulky ester group on alkyl propargyl esters would favor the difluorocarbene addition. It should be noted that all of these terminal difluorocyclopropenes are stable at room temperature when exposed to air for long time.

An ester functionality is most commonly used to protect the hydroxyl group. We carried out the deprotection by hydrolysis with NaOH in anhydrous methanol. To our surprise, the deprotected product rearranged readily to give the *gem*-difluorocyclopropyl ketone under the alkaline reaction condition (Table 4). However, this reaction only worked well for the aryl-substituted difluorocyclopropenes, while not for the alkyl-substituted ones (entry 10). Longer reaction time and more amounts of NaOH were necessary to complete the reaction for those difluorocyclopropenes with substituents at the *ortho* position of the aryl ring (entries 2, 5). The reaction was not affected by the electronic properties of the substituents on the aryl ring, giving the corresponding difluorocyclopropyl ketones[6] in moderate to good yields.

Table 4
Conversion of difluorocyclopropenes to difluorocyclopropyl ketones

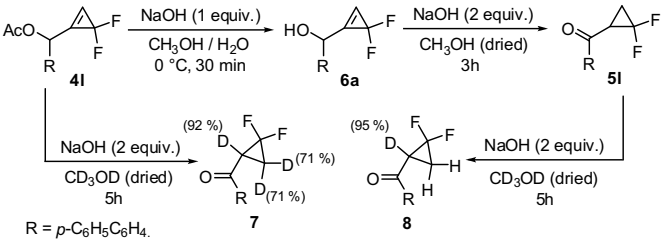


4 **5**

Entry	R	G	Time (h)	Product	Yield[a] (%)
1	*p*-F–Ph–	Acetyl, **4b**	5	**5b**	85
2	*o*-Cl–Ph–	Acetyl, **4c**	72[b]	**5c**	75
3	*p*-Cl–Ph–	Acetyl, **4d**	5	**5d**	99
4	*m*-Cl–Ph–	Pivaloyl, **4e**	5	**5e**	71
5	*o*-CH_3O–Ph–	Acetyl, **4h**	101[b]	**5h**	66
6	*p*-CH_3O–Ph–	Pivaloyl, **4i**	5	**5i**	89
7	*m*-CH_3O–Ph–	Pivaloyl, **4j**	5	**5j**	94
8	*p*-CH_3–Ph	Acetyl, **4k**	5	**5k**	72
9	*p*-Ph–Ph–	Acetyl, **4l**	5	**5l**	82
10	$CH_3(CH_2)_6$–	Acetyl, **4q**	5	—[c]	—[c]

[a] Isolated yield.
[b] 4 equiv of NaOH was used in the reaction.
[c] No desired product detected.

In order to gain insights into the mechanism for the conversion of difluorocyclopropenes to difluorocyclopropyl ketones,[6] a series of conditional experiments were conducted (Scheme 1). In wet methanol, deacetylation of **4l** occurred rapidly to give the unstable α-hydroxyl difluorocyclopropene **6a**, which subsequenty rearranged to

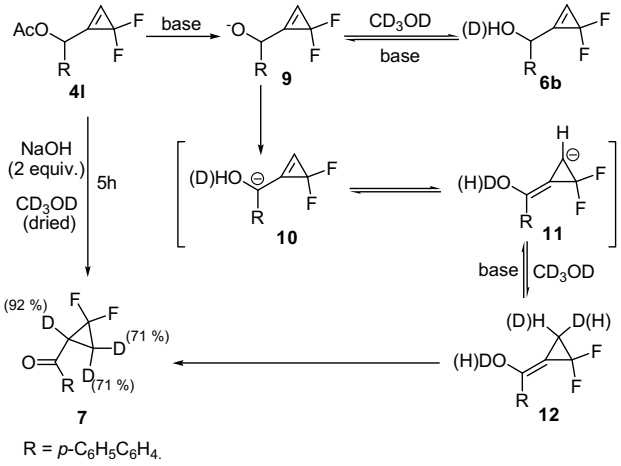


4l **6a** **5l** **7** **8**

Scheme 1. Deuterium-labeling experiment.

5l under the same reaction condition as that in Table 4. The α-hydrogen of **5l** was deuterated quite easily under basic condition to give **8**, while the methylene hydrogens of the cyclopropane ring remained inert. However, when the reaction was performed in CD_3OD, the cyclopropane ring hydrogens of the product were mostly deuterated, affording difluorocyclopropyl ketone **7** with a deuterium content of 71% as determined by ^1H NMR.

Based on the above results, a plausible reaction mechanism was proposed similar to a propargylic alcohol rearrangement under the alkaline condition.[7] Deacetylation of **4l** under basic condition first led to the formation of the intermediate **9** (Scheme 2), which could either abstract a proton to give **6b** or convert to **10** through proton transfer from carbon to oxygen. Allylic rearrangement of **10** would give **11**. Subsequent deuteration of active allylic hydrogens could afford the final product.



4l **9** **6b** **10** **11** **12** **7**

Scheme 2. Proposed mechanism for the formation of difluorocyclopropyl ketones.

3. Conclusion

In conclusion, the difluorocarbene addition to terminal alkynes was realized through the introduction of a carboxy group at the α-position to the triple bond. The corresponding difluorocyclopropenes were further converted to difluorocyclopropyl ketones under alkaline condition. A deuterium-labeling technique was adopted to elucidate the mechanism for this conversion. Further investigation into the reaction of difluorocyclopropenes and difluorocyclopropyl ketones is currently under way in our laboratory.

4. Experimental section

4.1. General information

^1H NMR spectra were recorded on a Bruker AM 300 (300 MHz) spectrometer with TMS as an internal standard (negative for

upfield). ^{19}F NMR spectra were recorded on a Bruker AM 300 (282 MHz) with $CFCl_3$ as an external standard (negative for upfield). ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz) spectrometer with $CDCl_3$ as an internal standard (negative for upfield). The solvent for NMR measurement was $CDCl_3$, which were purchased from Cambridge Isotope Laboratories, Aldrich or Acros. MS and HRMS were recorded on a Hewlett–Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer. Elementary analyses were obtained on a Perkin–Elmer 2400 Series II Elemental Analyzer. Infrared spectra were measured with a Perkin–Elmer 983 spectrometer. TLC analysis was performed on silica gel plates, column chromatography over silica gel (mesh 300–400). All solvents were purified by standard methods. $FSO_2CF_2COOSiMe_3$ (TFDA),[5] propargyl compounds **1d**,[8] **1e**[9] were prepared as described in the literature.[10]

4.2. Synthesis of propargylic ester substrates

To a solution of ethynylmagnesium bromide (90 mL, 45 mmol, 0.5 M in THF) was added slowly to a solution of benzaldehyde (3.18 g, 30 mmol) in 10 mL THF at −20 °C within 30 min. Then the cold bath was removed. The reaction mixture was stirred for an additional 4 h at room temperature till TLC showed that benzaldehyde was consumed. The reaction was quenched by addition of 10 mL saturated aqueous ammonium chloride, and the viscous residue was extracted with Et_2O. The combined organic layers were dried with Na_2SO_4 overnight, and concentrated by rotary evaporation to yield the propargylic alcohol, which was further purified by chromatography on a silica gel column (ethyl acetate/petroleum ether=1:10). Yield 1-phenylprop-2-yn-1-ol as a yellow oil, 3.2 g, 80%. ^1H NMR (300 MHz, $CDCl_3$): δ=2.65 (s, 1H), 2.58–2.86 (br, 1H), 5.42 (s, 1H), 7.29–7.42 (m, 3H), 7.49–7.56 (m, 2H).

To a solution of 1-phenylprop-2-yn-1-ol (1.32 g, 10 mmol) in 15 mL CH_2Cl_2 at 0 °C was added DMAP (123 mg, 1 mmol), triethylamine (2.1 mL, 15 mmol), Ac_2O (2.0 mL, 15 mmol), and the reaction mixture was stirred for 2 h. After addition of an appropriate volume of aqueous water, the reaction was extracted with CH_2Cl_2. The combined organic layer was washed twice with saturated NaCl aqueous, dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether=10:1) to give the desired propargylic acetate **1c** in almost quantitative yield as a yellow oil.[10a] ^1H NMR (300 MHz, $CDCl_3$): δ=1.97 (s, 3H), 2.56 (d, J=2.0 Hz, 1H), 6.35 (d, J=2.0 Hz, 1H), 7.21–7.31 (m, 3H), 7.39–7.46 (m, 2H).

4.3. Typical procedure for the synthesis of difluorocyclopropenes 2c–j and 4a–t

Alkyne 1-phenylprop-2-ynyl acetate **1c** (0.45 g, 2.5 mmol), NaF (10.5 mg, 10% mol) and xylene (1 mL) were placed in a 30-mL Schlenk flask fitted with a magnetic stirring bar under N_2. After the mixture was heated to 120 °C (bath temperature), TFDA (1.25 g, 5 mmol) was added within a period of 30–35 min by a microinjection pump. The mixture was then stirred for an additional 30 min to ensure the substrate was consumed. After having cooled to room temperature, 100 μL trifluoromethyl benzene and 5 mL ethyl acetate were added to the glass flask for ^{19}F NMR test. Then the solvent was removed under reduced pressure. And the residual product was purified by chromatography on silica gel column (petrol ether/ethyl acetate=10:1). Yield **2c** as an oil, 59% yield based on **1c**. ^1H NMR (300 MHz, $CDCl_3$): δ=2.12 (s, 3H), 6.69 (s, 1H), 7.36–7.43 (m, 5H), 7.43–7.46 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.8 to 102.7 (m, 2F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=20.56, 69.52, 101.16 (t, J_{FC}=270.2 Hz), 119.17 (t, J_{FC}=11.8 Hz), 127.47, 128.92, 129.31, 134.72, 136.40 (t, J_{FC}=32.1 Hz), 169.52. IR (film): 3131, 1751, 1373, 1318, 1227, 1030, 699 cm^{-1}. MS (ESI): m/z: 247.0 [M+Na^+]. Anal. Calcd for $C_{12}H_{10}F_2O_2$: C, 64.28; H, 4.50. Found: C, 64.20; H, 4.61.

4.4. Typical procedure for the synthesis of 2,2-difluorocyclopropyl ketones (5)

To a stirred solution of **4b** (49 mg, 0.2 mmol) in MeOH (1.5 mL) was added NaOH (16 mg, 0.4 mmol). The reaction process was monitored by TLC. After complete conversion it was directly purified by flash chromatography on silica gel column. Compound **5b** was obtained as red oil, 42 mg, 85% yield. ^1H NMR (300 MHz, $CDCl_3$): δ=1.67–1.81 (m, 1H), 2.27–2.41 (m, 1H), 3.20–3.38 (m, 1H), 7.05–7.15 (m, 2H), 7.92–8.00 (m, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−103.9 (s, 1F), −124.2 (dt, J_1=148.2 Hz, J_2=12.4 Hz, 1F), −140.1 (dt, J_1=148.2 Hz, J_2=16.7 Hz, 1F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=15.63 (t, J_{FC}=10.9 Hz), 29.60 (t, J_{FC}=11.7 Hz), 111.45 (t, J_{FC}=286.2 Hz), 114.31, 116.07, 131.02, 131.12, 127.64–137.84 (m), 166.12 (d, J_{FC}=25.5 Hz), 188.88. IR (film): 3113, 3076, 2965, 1685, 1600, 1509, 1454, 1413, 1374, 1326, 1255, 1206, 1159, 1051, 1004, 959, 916, 854, 784 cm^{-1}. MS (EI): m/z: 200, 180, 151, 133, 123, 95, 75. HRMS (EI) calcd for $C_{10}H_7F_3O^+$: 200.0449; found: 200.0452.

4.5. Hydrolysis of difluorocyclopropenes 4l

To a stirred solution of **4l** (30 mg, 0.1 mmol) in wet MeOH (1 mL) was added NaOH (4 mg, 0.1 mmol). The mixture was kept under 0 °C and monitored by TLC. After complete conversion it was directly purified by flash chromatography on silica gel column to give compound **6a** as a while solid, 19 mg, 74% yield. ^1H NMR (300 MHz, $CDCl_3$): δ=2.53 (s, 1H), 5.83 (s, 1H), 7.33–7.74 (m, 10H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ=−102.6 to 101.5 (m, 2F) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ=69.20, 102.15 (t, J_{FC}=270.2 Hz), 118.66 (t, J_{FC}=11.9 Hz), 127.21, 127.37, 127.89, 128.01, 129.09, 137.48, 139.23 (t, J_{FC}=11.2 Hz), 140.56, 142.19. IR (film): 3386 (br), 3032, 2925, 1947, 1832, 1718, 1488, 1310, 1034, 842, 764, 698 cm^{-1}. MS (EI): m/z: 258, 236, 229, 209, 191, 181, 165, 152, 82. HRMS (EI) calcd for $C_{16}H_{12}F_2O^+$: 258.0856; found: 258.0852.

Acknowledgements

We thank the Chinese Academy of Sciences (Hundreds of Talents Program) and the National Natural Science Foundation (20772147) for financial support.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.019.

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