

Preliminary note

[4 + 2] and [2 + 2] cycloadditions of 1,1-difluoro-2-triphenylsiloxybuta-1,3-diene with electron-deficient alkynes

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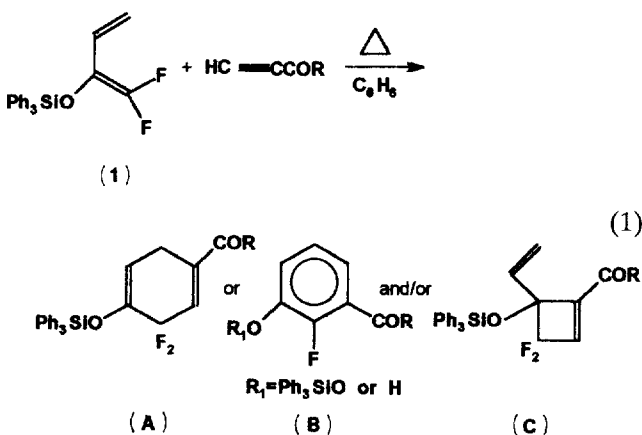
Abstract

1,1-Difluoro-2-triphenylsiloxybuta-1,3-diene undergoes [4 + 2] and/or [2 + 2] cycloadditions with electron-deficient alkynes to give cyclobutenes and arenes.

Keywords: Cycloadditions; Electron-deficient alkynes; Difluorotriphenylsiloxybutadiene; NMR spectroscopy; IR spectroscopy; Mass spectrometry

We have recently reported the synthesis of a novel siloxy-bearing fluorodiene, 1,1-difluoro-2-triphenylsiloxybuta-1,3-diene (**1**), and described its cycloadditions with various olefins [1]. Because of its unique combination of substituents, this fluorodiene exhibits a greatly enhanced tendency to undergo [2 + 2] cycloadditions with captodative olefins [1]. As part of our continuing studies on the reactivity of this fluorodiene in cycloadditions, we have investigated its cycloadditions with electron-deficient alkynes. We report here our results.

On heating, **1** reacted readily with electron-deficient alkynes yielding various products (Eq. (1)). Thus, A or B or both B and C were obtained depending on the alkyne used. The results are summarized in Table 1.



As shown in Table 1, with the exception of propynal (entry 1) and ethynyl methyl ketone (entry 2), **1** reacted with electron-deficient alkynes to produce both [2 + 2] adducts (type C) and arylated [4 + 2] adducts (type B) (entries 3-7). With ethynyl methyl ketone, only the arylated [4 + 2] adduct **3** (type B) was obtained, whilst in the case of propynal the [4 + 2] adduct **2** (type A) was formed. The formation of various kinds of products in these cycloadditions may be attributed to two concurrent reaction paths, i.e. the concerted [4 + 2] and diradical cycloadditions, as illustrated in Scheme 1.

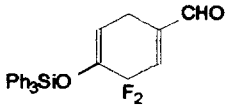
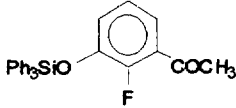
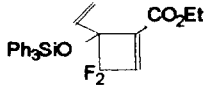
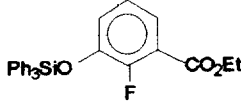
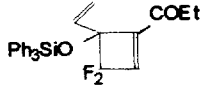
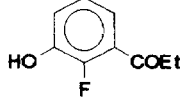
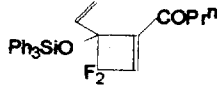
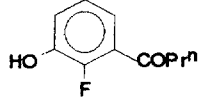
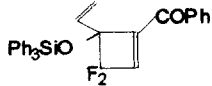
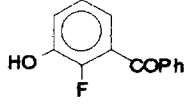
Following the concerted [4 + 2] cycloaddition path, a [4 + 2] cycloadduct **8** is first formed from **1** and the alkyne. Adduct **8** is unstable under the reaction conditions and converts to B ($R_1 = \text{Ph}_3\text{Si}$) via dehydrofluorination. It should be mentioned that B thus formed may be desilylated on chromatography leading to desilylated products ($R_1 = \text{H}$) such as **5b**, **6b** and **7b**. However, **1** may also react with the alkyne via a diradical cycloaddition path forming intermediate **9** and resulting in the formation of A or C by either [4 + 2] or [2 + 2] ring closure.

Lewis acids have long been known to promote not only [4 + 2] but also [2 + 2] cycloadditions [2,3]. An extended study on the effect of Lewis acids on the cycloaddition of **1** with electron-deficient alkynes shows that, in cases studied here, Lewis acid greatly facilitates [2 + 2] cycloaddition. Thus, in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, compound **1** reacted with alkynes to yield [2 + 2] cycloadducts (type C) exclusively. Apparently, this [2 + 2]

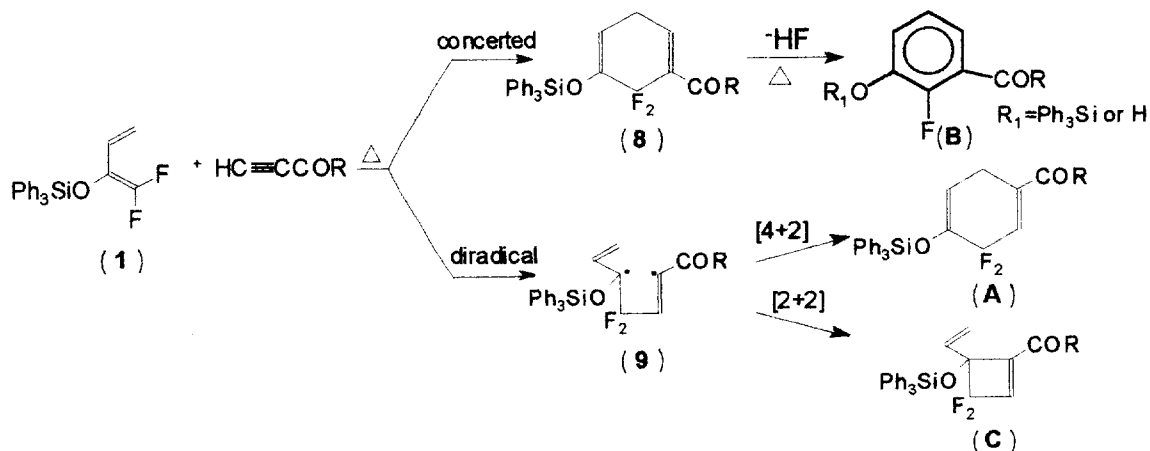
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Table 1

Cycloadditions of 1,1-difluoro-2-triphenylsiloxybuta-1,3-diene (**1**) with electron-deficient alkynes ^a

Entry	Alkyne	Reaction conditions Temp. (°C)/time (h)	Product ^b	Melting point (°C)	Yield (%) ^c	
1	HC≡CCHO	100/8		(2)	126–128	71
2	HC≡CCOCH ₃	110/15		(3)	97–98	43
3	HC≡CCO ₂ Et	90/11		(4a)	92–93	57
				(4b)	oil (4a/4b 45:55) ^d	
4	HC≡CCOEt	110/15		(5a)	oil	68
				(5b)	78–80 (5a/5b 44:56) ^d	
5	HC≡CCO ⁿ Pr	110/10		(6a)	oil	64
				(6b)	85–87 (6a/6b 43:57) ^d	
6	HC≡CCOPh	110/10		(7a)	113	67
				(7b)	115–117 (7a/7b 49:51) ^d	
7	HC≡CCOPh	rt/6 ^e		(7a)		83
8	HC≡CCO ⁿ Pr	rt/6 ^e		(6a)		73
9	HC≡CCOEt	rt/6 ^e		(5a)		59

^a All reactions were conducted in benzene in a capped thick-walled tube using 1 equiv. of **1** and 1.5 equiv. of the alkyne.^b All new compounds were fully characterized by ¹⁹F NMR, ¹H NMR, IR, MS and C, H, F elemental analyses or HRMS.^c Isolated yields based on **1**.^d The ratio of **a** to **b** was determined via their isolated yields.^e 1 equiv. of BF₃·Et₂O was used.



Scheme 1.

cycloaddition proceeds via the ion-pair intermediate 10 as shown in Scheme 2.

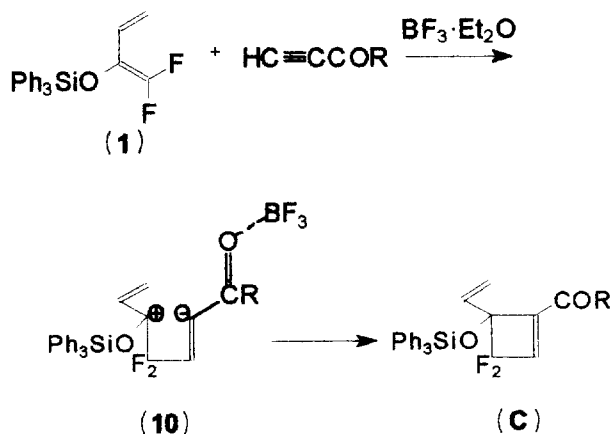
The establishment of the structures of cycloadducts 2-7 was based on their spectral and microanalytical data. The ¹H NMR spectrum of 2, a cycloadduct of type A, displayed a methylene proton signal with a tdd pattern ($J=14.4, 2$ Hz) at δ 2.84 ppm due to coupling of the methylene protons with fluorine atoms as well as with two olefinic protons. In addition, a signal with a tt pattern ($J=6, 2$ Hz) and δ 6.44 ppm was assigned to the olefinic proton at the carbon vicinal to the carbon-bearing fluorine atoms, while a multiplet at δ 5.28 ppm (the coupling constant of this olefinic proton with the fluorine atoms was <2 Hz) was exhibited by the olefinic proton at the carbon neighboring the methylene group. The fluorine atoms in 2 resonated at $\delta_{\text{TFA}} + 10.55$ ppm in the ¹⁹F NMR spectrum as a td signal ($J=14, 6$ Hz), which was compatible with the data from the ¹H NMR spectra. The C, H, F microanalytical data of 2 were also consistent with its structure. The ¹H NMR spectrum of 3, a cycloadduct of type B, displayed an aryl proton signal as a triplet at δ 6.86 ppm; in addition, the ¹⁹F NMR spectrum of 3 showed

a singlet signal at $\delta_{\text{TFA}} + 54.0$ ppm. This suggests that the triplet at δ 6.86 ppm in the ¹H NMR spectrum stems from an H-H coupling and not from an H-F coupling. Obviously, the signal at δ 6.86 ppm was given by the proton located at the carbon *meta* to the carbon substituted by the acetyl group and was a pseudo triplet (a dd signal with an identical coupling constant of 9 Hz) due to coupling of this proton with its two neighboring protons. The establishment of such an orientation for the substituents in 3 was further supported by the fact that 8 readily eliminates HF to give 3 since the methylene protons in 8 are located at the γ position of an α,β -unsaturated carbonyl system and are thus activated while those in 2 are not. The appearance of three vinylic protons at δ 5.34, 5.55 and 5.93 ppm, respectively, and a more downfield olefinic proton at δ 6.57 ppm in the ¹H NMR spectrum of 4a is compatible with the structure of a cycloadduct of type C. Selected spectral and microanalytical data for 2, 3, 4a and 4b are as follows.

Compound 2: IR (KCl) (cm^{-1}): 1700; 1600; 1420; 1110; 710; 690. ¹H NMR (CDCl_3) δ : 2.84 (tdd, $J=14.4, 2$ Hz, 2H); 5.28 (m, 1H); 6.64 (tt, $J=6, 2$ Hz, 1H); 7.20-7.70 (m, 15H); 9.52 (s, 1H) ppm. ¹⁹F NMR (CDCl_3) δ_{TFA} : +10.55 (upfield, td, $J=14, 6$ Hz) ppm. MS m/z (relative intensity): 418 (15.43); 398 (40.17); 369 (1.56); 259 (100). HRMS: Calc. for $\text{C}_{25}\text{H}_{20}\text{F}_2\text{O}_2\text{Si}$: 418.1201. Found: 418.1224.

Compound 3: IR (KCl) (cm^{-1}): 1680; 1600; 1110; 910; 690. ¹H NMR (CDCl_3) δ : 2.48 (s, 3H); 6.86 (pseudo t, $J=9$ Hz, 1H); 7.30-7.75 (m, 17H) ppm. ¹⁹F NMR (CCl_4) δ_{TFA} : +54.0(s) ppm. MS m/z (relative intensity): 412 (48.42); 397 (20.81); 369 (1.31); 355 (20.25); 259 (100). Analysis: Calc. for $\text{C}_{26}\text{H}_{21}\text{F}_2\text{O}_2\text{Si}$: C, 75.70; H, 5.13; F, 4.60%. Found: C, 75.53; H, 5.09; F, 4.87%.

Compound 4a: IR (KCl) (cm^{-1}): 1720; 1610; 1590; 1290; 1110; 710; 690. ¹H NMR (CDCl_3) δ : 1.17 (t, $J=7$ Hz, 3H); 4.01 (q, $J=7$ Hz, 2H); 5.34 (d, $J=11$ Hz, 1H); 5.55 (d, $J=17$ Hz, 1H); 5.93 (dd, $J=17, 11$ Hz,



Scheme 2.

1H); 6.57 (s, 1H); 7.29–7.65 (m, 15H) ppm. ^{19}F NMR (CCl_4) δ_{TFA} : +29.7 (d, $J=220$ Hz, 1F); +35.0 (d, $J=220$ Hz, 1F) ppm. MS m/z (relative intensity): 462 (6.16); 385 (100); 259 (82.86). HRMS: Calc. for $\text{C}_{27}\text{H}_{24}\text{F}_2\text{O}_3\text{Si}$: 462.1463. Found: 462.1472.

Compound **4b**: IR (neat) (cm^{-1}): 1680; 1590; 1110; 710; 690. ^1H NMR (CDCl_3) δ : 1.26 (t, $J=7$ Hz, 3H); 4.24 (q, $J=7$ Hz, 2H); 6.80 (pseudo t, $J=9$ Hz, 1H); 7.20–7.70 (m, 17H) ppm. ^{19}F NMR (CCl_4) δ_{TFA} : +53.5 (s) ppm. MS m/z (relative intensity): 442 (21.89); 397 (19.81); 365 (15.72); 259 (100); 243 (7.46). HRMS: Calc. for $\text{C}_{27}\text{H}_{23}\text{FO}_3\text{Si}$: 442.1400. Found: 442.1420.

In conclusion, the diversity of the reactivity of **1** in cycloadditions indicates that **1** is not only a synthetically useful intermediate in fluorine chemistry but also an interesting diene for the theoretical study of cycloadditions.

Further studies on the cycloaddition of **1** with other kinds of dienophiles are in progress.

References

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