1,1-Difluoro-2-triphenylsiloxybuta-1,3-diene as a Potentially Useful Fluorine-containing Building Block: Preparation and [4 + 2] and [2 + 2] Cycloadditions

Fuqiang Jin, Yuanyao Xu* and Weiyuan Huang*

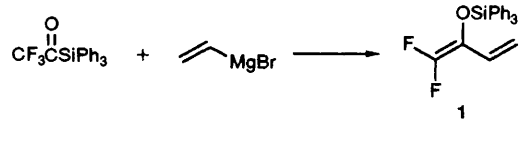
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

1,1-Difluoro-2-triphenylsiloxybuta-1,3-diene has been conveniently prepared and undergoes [4 + 2] or [2 + 2] cycloadditions with various olefins.

The usefulness of buta-1,3-dienes bearing one siloxy group in synthetic organic chemistry has been well recognized,[1] while their fluorine-containing analogues, *e.g.* fluorinated buta-1,3-dienes with a siloxy group, are much less exploited.[2] In the course of our studies directed at searching for new versatile and useful fluorine-containing building blocks, we became interested in exploring the synthetic utility of novel fluorinated buta-1,3-dienes bearing a siloxy group. We report here our preliminary results on the cycloadditions of a previously unknown fluorinated buta-1,3-diene—1,1-difluoro-2-siloxybuta-1,3-diene.

The title compound **1** was conveniently prepared in high yield (96%) from trifluoroacetyltriphenylsilane and vinylmagnesium bromide according to a procedure recently reported by us[3] [eqn. (1)]. **1** was found to be labile and easily polymerized in its pure state, however, it was stable in benzene and could be stored at 0 °C for several weeks without significant deterioration.

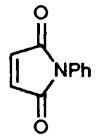
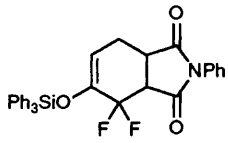
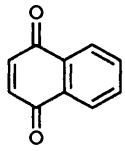
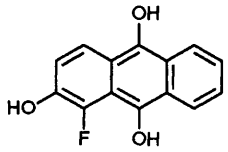
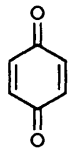
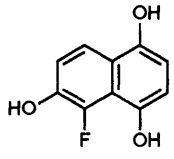
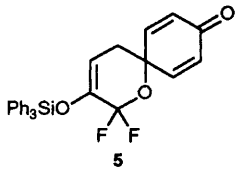
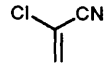
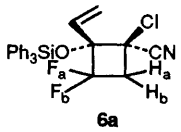
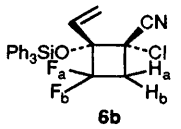
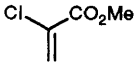
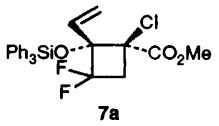
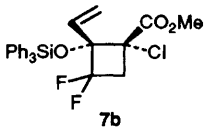
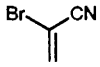
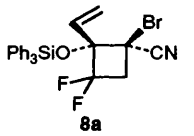
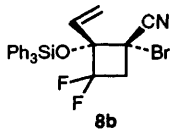
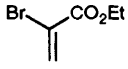
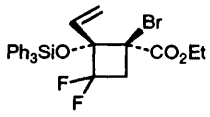
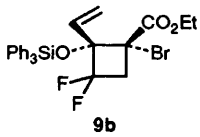
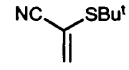
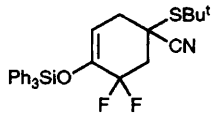
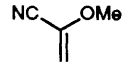
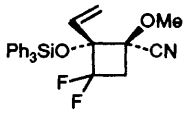
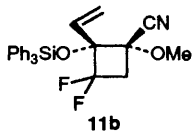
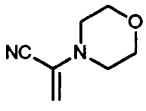
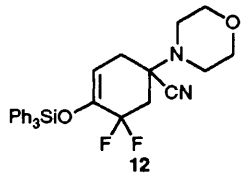
As a structurally typical buta-1,3-diene, its cycloadditions with various olefins were examined. The results are summarized in Table 1.



(1)

1

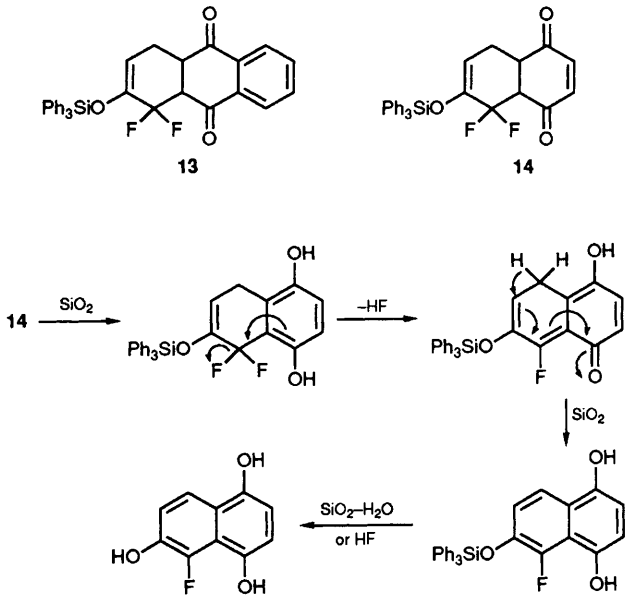
Table 1 Cycloadditions of 1,1-difluoro-2-triphenylsiloxybuta-1,3-diene **1** with various olefins[a]

Entry	Olefins	React. cond. *T*/°C (*t*/h)	Products[b]	Yield[c] (%)
1		90(9)	 **2**	63
2		110(20)	 **3**	45
3		90(10)	 **4**	69
			 **5** (4:5 45:55)	
4		90(5)	 **6a**	91
			 **6b** (6a:6b 43:57)	
5		100(14)	 **7a**	77
			 **7b** (7a:7b 44:56)	
6		90(6)	 **8a**	86[d]
			 **8b** (8a:8b 42:56)	
7		110(12)	 **9a**	66
			 **9b** (9a:9b 38:62)	
8		100(5)	 **10**	87
9		110(12)	 **11a**	71[d]
			 **11b** (11a:11b 47:53)	
10		110(6)	 **12**	81

[a] All the reaction were conducted in benzene in a capped thick-walled tube by using **1** (1 equiv.) and the olefin (1.5 equiv.). [b] All the new compounds were fully characterized by ^{19}F NMR, ^{1}H NMR, IR, MS and C, H, F elemental analyses or HRMS. [c] Isolated yield based on **1**. [d] Isolated as a mixture of the corresponding two isomers.

As the results show, the diene has normal reactivity towards typical dienophiles leading to [4 + 2] cycloadducts (entries 1, 2 and 3, Table 1). It is interesting to note that, in the case of 1,4-benzoquinone (entry 3, Table 1), besides the carbocyclic product **4**,[4] **5** was obtained as the main product resulting from a hetero Diels–Alder reaction with the quinone acting as a carbonyl dienophile. It should be mentioned that compounds **3** and **4** were not the direct reaction products, but they were formed during isolation (chromatography on silica gel) from the intermediates **13** and **14** respectively, which were detectable in the crude reaction products by ^{19}F NMR, possibly through a sequence of dehydrofluorination and desilylation as exemplified by the formation of **4** (Scheme 1).

Unexpectedly, reaction of **1** with olefins with captodative (cd) substitution, which are also known to be good dienophiles,[5] gave [2 + 2] cycloadducts except in the cases of



Scheme 1 Formation of **4**

α-*tert*-butylthioacrylonitrile (entry 8, Table 1) and α-morpholino acrylonitrile (entry 10, Table 1). Thus, **1** can serve both as a 1,3-diene in Diels–Alder reactions and also as an efficient partner in [2 + 2] cycloadditions to cd olefins. Though gem-difluorine substitution could result in a greater tendency of the ethylene derivatives to undergo [2 + 2] cycloadditions,[5] no [2 + 2] cycloadduct could be detected in a reaction system from heating a mixture of 1,1-difluoro-2-triphenylsiloxy-1-propene[6] and 2-chloroacrylonitrile in benzene at 110 °C for 6 h, suggesting that the tendency of **1** to undergo [2 + 2] cycloadditions was greatly enhanced by the presence of an extra vinyl group.

It is noteworthy that, in the cases of α-*tert*-butylthioacrylonitrile and α-morpholino acrylonitrile which are two of the most effective cd olefins, we obtained [4 + 2] adducts only. This might be attributed to their stronger dienophilic character as compared to that of other cd olefins.[7]

The assignment of the configurations of **6a** and **b** was based on their X-ray structures. Interestingly, **6a** and **b** were quite different in their ^{1}H NMR and ^{19}F NMR (referenced to TFA): ^{1}H NMR of **6a** gave δ 2.77 (m, 1 H, H_a) and 3.40 (m, 1 H, H_b) [$\Delta\delta(H_a - H_b) = 0.63$]; ^{19}F NMR +23.1 (m, 1 F, F_a) and +28.9 (m, 1 F, F_b) [$\Delta\delta(F_a - F_b) = 5.8$], while ^{1}H NMR for **6b** at δ 3.10 (m, 2 H, H_a and H_b) [$\Delta\delta(H_a - H_b) = 0$] and ^{19}F NMR gave +19.1 (m, 1 F, F_a) and +29.3 (m, 1 F, F_b) [$\Delta\delta(F_a - F_b) = 10.2$]. By correlation of their ^{1}H NMR and ^{19}F NMR spectra with those of **6a** and **b**, the structures of other pairs of [2 + 2] cycloadducts were assigned.

From a synthetic standpoint, products **6–12** are all extremely versatile intermediates for further synthetic routes. Thus, more studies on cycloadditions of **1** should find a wide use in the construction of complex fluorinated molecules.

Further investigation on the utilization of **1** as a fluorine-containing building block is in progress.

We thank National Natural Science Foundation of China and Academia Sinica for their financial support.

Received, 8th December 1992; Com. 2/06539H

References

1 E. W. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981, p. 254.
2 M. Schlosser, *J. Fluorine Chem.*, 1991, **54**, 192.
3 F. Jin, Y. Xu and W. Huang, *J. Chem. Soc., Perkin Trans. 1*, 1993, 795.
4 Generally, *p*-quinones react with 1,3-dienes to give carbocycles; see, D. L. Boger and S. N. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*', Harcourt Brace Jovanovich, New York, 1987, p. 94.
5 Ch. De Cock, S. Piettre, F. Lahourse, Z. Janousek, R. Merenyi and H. G. Viehe, *Tetrahedron*, 1983, **41**, 4183.
6 F. Jin, B. Jiang and Y. Xu, *Tetrahedron Lett.*, 1992, **33**, 1221.
7 H. G. Viehe, Z. Janousek and R. Merenyi, *Acc. Chem. Res.*, 1985, **18**, 148.