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

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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.

The title compound **1** was conveniently prepared in high yield (96%) from trifluoroacetyltriphenylsilane and vinylmag-

nesium bromide according to a procedure recently reported by us³ [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.



Table 1 Cycloadditions of 1,1-difluoro-2-triphenylsiloxybuta-1,3-diene 1 with various olefins^a

Entry C	Diefins	React. cond. <i>T</i> /°C (<i>t</i> /h)	Products ^b	Yield ^c (%)	Ent	try Olefins	React. cond. <i>T</i> /°C (<i>t</i> /h)	Products	Yield ^c (%)
1	O NPh	90(9)	Ph ₃ Sio F F O	63	6	BrCN	90(6)	Ph ₃ SiOCN F 8a	86 ^d
2		110(20)		45				Ph ₃ SiOBr F 8b (8a:8b 42:56)	
3		90(10)	HO F OH	69	7	Bry CO ₂ Et	110(12)	Ph ₃ SiOCO ₂ Et	66
			Ph ₃ SiO F F					Ph ₃ SIO ⁵ F 9b (9a:9b 38:62)	
Cار_ 4	CN TI	90(5)	5 (4:5 45:55) Ph ₃ SioCN	91	8	NC SBu ^t	100(5)	Ph ₃ SiO F 10	87
	11				9	NCOMe	110(12)	Ph ₃ SiOCN F 11a	71 ^d
_ CI~	_CO₂Mθ		F6 H6 (6a:6b 43:57)					Ph ₃ SiO	
2	Í	100(14)		//	10		110(6)	(11a:11b 47:53)	81
			F 7b (7a:7b 44:56)			II		F F 12	

^{*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 ¹⁹F NMR, ¹H 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 ¹⁹F 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-1propene⁶ 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

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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 ¹H NMR and ¹⁹F NMR (referenced to TFA): ¹H NMR of **6a** gave $\delta 2.77 \text{ (m, 1 H, H_a)}$ and 3.40 (m, 1 H, H_b) $[\Delta\delta(H_a - H_b) = 0.63]$; ¹⁹F 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 ¹H NMR for **6b** at δ 3.10 (m, 2 H, H_a and H_b) $[\Delta\delta(H_a - H_b) = 0]$ and ¹⁹F 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 ¹H NMR and ¹⁹F 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 fluorinecontaining building block is in progress.

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