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Preliminary Note

Diels–Alder reaction of 1-phenylsulfonyl-3,3,3-trifluoropropyne with 1,3-dienes

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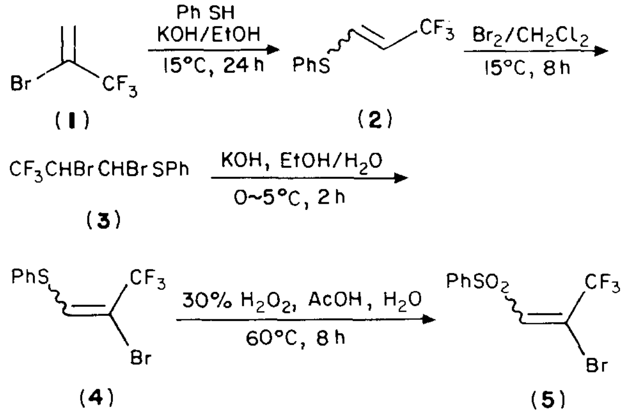
Abstract

1-Phenylsulfonyl-3,3,3-trifluoropropyne, prepared *in situ* from 1-phenylsulfonyl-2-bromo-3,3,3-trifluoropropene and triethylamine, reacted with 1,3-dienes to give the [4+2] cycloadducts and/or 2-trifluoromethylphenyl phenylsulfone in good to excellent yield.

The synthesis of specifically trifluoromethylated molecules is an ongoing area of research due to the unique physical and biological properties imparted by the CF_3 group [1–3]. Utilization of the appropriate CF_3-containing compounds as building blocks is one of the most promising approaches for introducing a CF_3 group into molecules because of its high selectivity and reactivity. For this reason, many versatile CF_3-containing building blocks have been developed in order to prepare various functionalized trifluoromethylated compounds [4–6].

Recently, Taguchi *et al.* reported the use of 1-phenylsulfonyl-3,3,3-trifluoropropene as a new building block in its reaction with 1,3-dienes to synthesize CF_3-containing cycloadducts [7]. We herein wish to report that 1-phenylsulfonyl-3,3,3-trifluoropropyne, prepared *in situ* from 1-phenylsulfonyl-2-bromo-3,3,3-trifluoropropene (**5**) and triethylamine also acts as a building block via its Diels–Alder reactions with 1,3-dienes. The results obtained show that there is some difference between 1-phenylsulfonyl-3,3,3-trifluoropropene and 1-phenylsulfonyl-3,3,3-trifluoropropyne, as in the latter case not only the expected cyclic adducts but also derived trifluorinated sulfones were obtained.

Compound **5** was prepared from 2-bromo-3,3,3-trifluoropropene. Addition of benzenethiol (KOH, EtOH, 15 °C, 24 h) gave the corresponding sulfide **2** [8], which was then treated with bromine to give compound **3**.



Scheme 1.

Dehydrobromination (KOH, $EtOH/H_2O$), followed by oxidation (30% H_2O_2, AcOH, H_2O) provided **5** as a 1:1 isomeric mixture in high overall yield (>85%)* (Scheme 1).

1-Phenylsulfonyl-3,3,3-trifluoropropyne was prepared by treating **5** with triethylamine in Et_2O at 15 °C for 4 h. After the usual work-up, 1-phenylsulfonyl-3,3,3-trifluoropropyne was obtained in 30% yield. However, this compound decomposed to a significant extent even at low temperature.

In order to circumvent this drawback, an alternative method was tested. Compound **5** as a precursor of 1-phenylsulfonyl-3,3,3-trifluoropropyne was used directly as a dienophile in the presence of triethylamine in order to effect the Diels–Alder reaction with 1,3-dienes. Thus, compound **5** (1 equiv.), 1,3-dienes (1.2 equiv.) and Et_3N (3.5 equiv.) in ether or toluene were stirred to give the anticipated cycloadducts and/or 2-trifluoromethylphenyl phenylsulfone in yields ranging from 75% to 98%. The results are summarized in Table 1.

2-Trifluoromethylphenyl phenylsulfone was assumed to be formed from the two substrates as follows (**6d**, **6e**, Table 1) (Schemes 2 and 3). Thus, for **6d**, the cyclic silyl ethers **8a** and **8b** were first formed and then detrimethylsilyation, followed by protonation and dehydration, gave the cyclic cations **10a** and **10b**. A 1,2-shift, followed by the loss of a proton, provided the product **7d**. For **6e**, 2-trifluoromethylphenyl phenyl-

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*Compound **4**: B.p. 66–68 °C/0.4 mmHg. Compound **5**: IR ν_{max} (cm^{-1}): 1600 (C=C); 1330; 1180 (S=O); 1130 (C–F). ^1H NMR (CCl_4) δ: 7.0 (s, =CH); 7.3–7.8 (m, Ar–H) ppm. ^{19}F NMR (CCl_4, CF_3COOH) δ: −18 (s, CF_3, *trans* isomer); −10 (s, CF_3, *cis* isomer) ppm. MS *m/z*; 316 (M^++2); 314 (M^+); 233; 109; 77; 69. HRMS: $C_9H_6BrF_3O_2S$, Calc.: 313.9233. Found: 313.9188.

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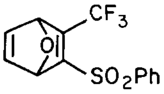
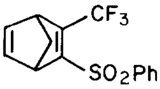
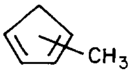
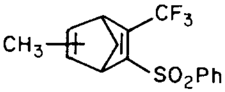
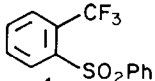
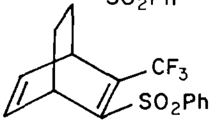
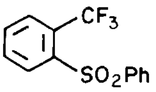
TABLE 1. Diels–Alder reactions of 1-phenylsulfonyl-2-bromo-3,3,3-trifluoropropene (**5**) and triethylamine with 1,3-dienes **6**

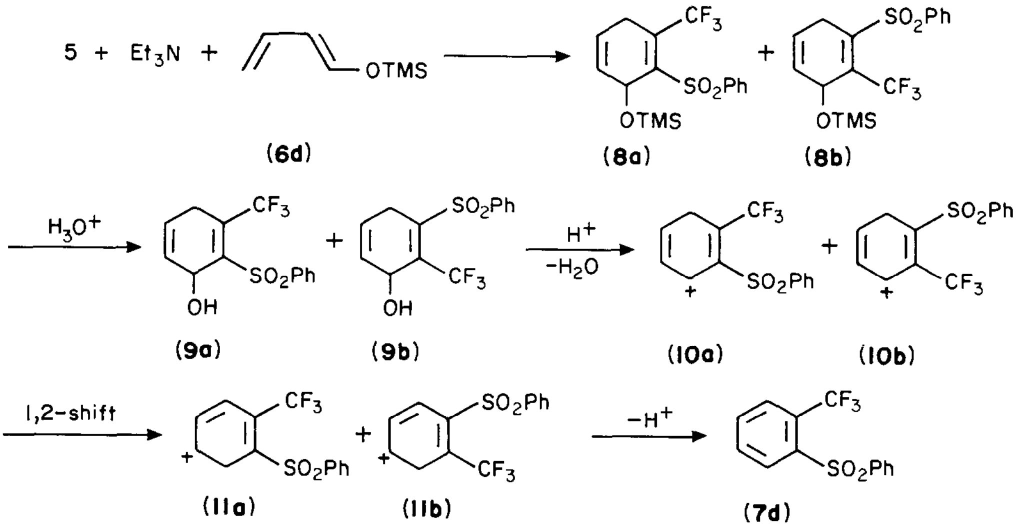
Entry No.	1,3-diene (**6**)	Conditions[a]	Product (**7**)	Yield[b] (%)	M.p. (°C)
1	 **6a**	A	 **7a**	98	66–67
2	 **6b**	A	 **7b**	95	72–74
3[c]	 **6c**	A	 **7c**	75	70–72
4	 **6d**	B	 **7d**	80	89–90
5[d]	 **6e**	B	 **7e**	70	81–82
			 **7d**		89–90

[a] Method A: Reactions were carried out with **5** (4 mmol), **6a–c** (5 mmol) and Et_3N (14 mmol) in Et_2O (5 ml) at r.t. for 2–4 h. Method B: Reactions were carried out with **5** (4 mmol), **6d–e** (5 mmol) and Et_3N (14 mmol) in toluene (5 ml) at 60 °C for 4–6 h.

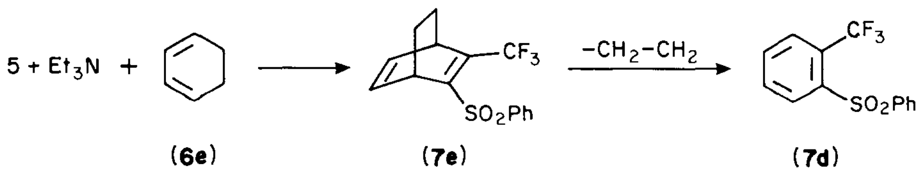
[b] Isolated yield. Satisfactory spectra and microanalytical data were obtained for all new compounds.

[c] 1:1 Isomer.

[d] Ratio of **7d**/**7e** was 7:3.



Scheme 2.



Scheme 3.

sulfone was formed through the retro-Diels–Alder reaction of **7e**.

In summary, we have demonstrated the preparation of 1-phenylsulfonyl-2-bromo-3,3,3-trifluoropropene and its utilization in the presence of triethylamine as a new CF_3-containing building block in a manner equivalent to 1-phenylsulfonyl-3,3,3-trifluoropropyne. This compound gave trifluoromethylated cyclic adducts via a Diels–Alder reaction with 1,3-dienes.

Acknowledgement

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