Tetrahedron Letters, Vol. 33, No. 41, pp. 6161-6164, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

Facile Conversion of Trifluoroacetyltriphenylsilane 2,4,6-Triisopropylbenzenesulfonylhydrazone to 2,2,2-Trifluorodiazoethane.An Unusual Example of the Bamford-Stevens Reaction

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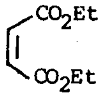
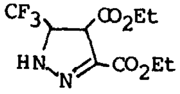
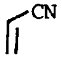
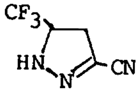
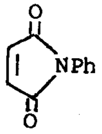
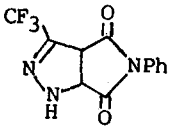
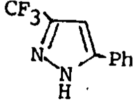
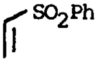
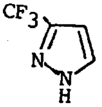
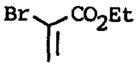
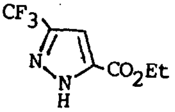
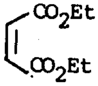
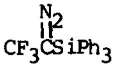
Abstract: Trifluoroacetyltriphenylsilane 2,4,6-triisopropylbenzenesulfonylhydrazone(**1**) reacted with dipolarophiles in the presence of Et_3N to produce trifluoromethylated pyrazoles or pyrazolines in good yields. The reaction was found to proceed through the intermediacy of 2,2,2-trifluorodiazoethane, and this unusual conversion of **1** to 2,2,2-trifluorodiazoethane was studied from the mechanistic viewpoint.

The Bamford-Stevens reaction[1] has been widely used to synthesize diazo compounds from the corresponding ketones, including trifluoromethylketones[2] and acylsilanes[3]. In all these syntheses,a hydrazone is converted to the corresponding diazo compound in the presence of a suitable base, and no unusual results have been observed. In the previous paper[4],we have reported an efficient synthesis of trifluoroacetyltriphenylsilane and its facile transformation into 2,2-difluoro enol silyl ethers. As a further exploration on the synthetic utility of trifluoroacetyltriphenylsilane, we have recently investigated the reactivity of trifluoroacetyltriphenylsilane 2,4,6-triisopropylbenzenesulfonylhydrazone(1) towards bases in an attempt to obtain 1-triphenylsilyl-2,2,2-trifluorodiazoethane(**2**) through the Bamford-Stevens reaction. Herein, we wish to report our results.

Trifluoroacetyltriphenylsilane 2,4,6-triisopropylbenzenesulfonylhydrazone[5], which was synthesized in a high yield from trifluoroacetyltriphenylsilane and 2,4,6-triisopropylbenzenesulfonylhydrazine in acetonitrile in the presence of a catalytic amount of conc. hydrochloric acid, was extremely sensitive to base, and it could be decomposed even by such a weak base as triethylamine. Thus, when triethylamine was added to a colorless solution of **1** in THF, there appeared an intense yellow coloration, indicating the formation of a diazo compound. To our surprise,instead of the expected diazo compound **2**, triphenylsilanol was obtained almost quantitatively. Initially, we supposed that 2 might be decomposed during the isolation, therefore, we made an attempt to trap 2 by a dipolarophile to form the cycloaddition product. We found that, when a dipolarophile was present, the yellow color faded gradually, but the product obtained was a trifluoromethylated pyrazole or pyrazoline without the silicon moiety and triphenylsilanol was isolated as a byproduct. A variety of trifluoromethylated pyrazoles or pyrazolines were obtained via this way[6], as illustrated in Table 1.

Interestingly, when Et_2O was used as the solvent and solid K_2CO_3 as the base in the

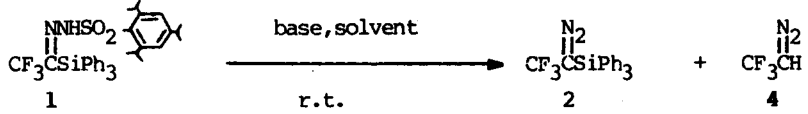
Table 1. Pyrazoles and pyrazolines obtained from $1^{a)}$

Entry	Dipolarophiles	Time(day)	Pyrazoles or Pyrazolines$^{b)}$		Yield(%)$^{c)}$
1		2		**(3a)**	86
2		1		**(3b)**	92
3		3		**(3c)**	77
4		50		**(3d)**	63
5		4		**(3e)**	96
6		5		**(3f)**	89
7		2$^{d)}$	**(3a)**		42
			 $CF_3C(=N_2)SiPh_3$	**(2)**	43

a) The reaction was performed at room temperature, using THF as solvent and Et_3N as base unless otherwise stated. b) New products were characterized by ^1H NMR, ^{19}F NMR, MS, and C, H, F, N elemental analyses. c) Isolated yield based on **1**. d) Et_2O was used as solvent and K_2CO_3 as base.

presence of diethyl maleate, then, besides **3a**, **2** could also be obtained(entry 7 in Table 1). However, **2** was inert to those dipolarophiles listed in Table 1. This implies that 3 did not result from **2** but possibly from an intermediate which is either unstable or difficult to isolate. This prompted us to reinvestigate the reactivity of **1** towards bases. We found that the reaction of 1 with base is more complex than that of the other hydrazones and two diazo compounds are formed depending upon the kind of solvent and base used; one of them is the expected **2** and the other, the key intermediate from which 3 results, is confirmed to be the 2,2,2-trifluorodiazoethane(**4**)[7].For example, **1** was completely transformed to **4** in THF by the action of Et_3N while in hexane **2** was formed in 100% by the action of K_2CO_3. Some typical results are depicted in Table 2. As mentioned above, fluorine-free acylsilane hydrazones have been converted normally to the

Table 2. Effect of solvent and base on the distribution of **2** and **4**$^{a)}$



Entry	Solvent	Base$^{b)}$	Molar ratio(%)$^{c)}$ 2	4
1	THF	Et_3N	0	100
2	Et_2O	Et_3N	58	42
3	CH_3OH	Et_3N	0	100
4	CH_3OH	K_2CO_3	0	100
5	Hexane	K_2CO_3	100	0
6	THF	K_2CO_3	11	89
7	THF	$Et_3N^{d)}$	0	100

a) Under all the following conditions, **1** was converted quantitatively to **2** and/or **4** as indicated by ^{19}F NMR using $C_6H_5CF_3$ as an internal standard. b) Equal molar amount of base was used unless otherwise stated. c) Estimated by ^{19}F NMR. d) 10 mol% of Et_3N was used.

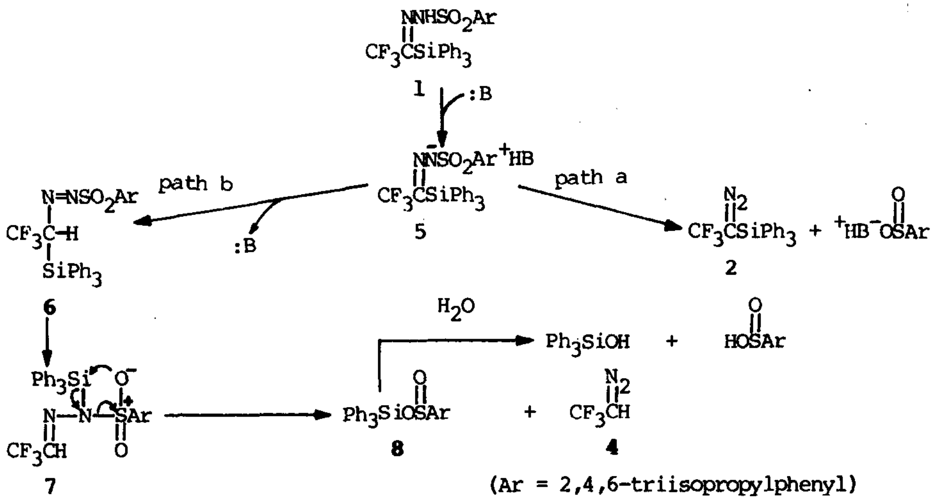
corresponding diazo compounds[3]; so, this unusual conversion of **1** to 2,2,2-trifluorodiazoethane represents a new aspect of the Bamford-Stevens reaction.

The principal features of the present transformation, which are important for delineating the mechanism, are as follows. (a) The transformation of **1** to **4** with aqueous workup is always accompanied by the formation of triphenylsilanol. (b) Unlike that in the common Bamford-Stevens reaction, even a catalytic amount of base (10 mol%, entry 7 in Table 2) is able to induce a complete conversion of **1** to **4**. Based on these two facts, the reaction mechanism is proposed as that shown in Scheme 1. The reaction appears to involve two pathways, path a and path b; the first of which leads to the formation of **2**, thus represents a common Bamford-Stevens reaction, and the other demonstrates a base catalyzed reaction which consists of a base induced 1,3-hydrogen migration(**1**→**5**→**6**) followed by an unusual 1,3-silicon migration from carbon to nitrogen(**6**→**7**)[8], thereby resulting in the formation of **4** from **7** through the elimination of **8**, which is moisture-sensitive and leads to triphenylsilanol.

The existence of **8** has been verified by ^{29}Si NMR and ^{1}H NMR. We found that the oily residue, obtained after removal of solvent from a reaction mixture of **1** and a catalytic amount of Et_3N in carefully dried THF, absorbed at δ_{TMS} -7.38(s, upfield negtive) (**1**: δ_{TMS} -25.72(s), **2**: δ_{TMS} -14.81(s), Ph_3SiOH: δ_{TMS} -16.19(s)) in ^{29}Si NMR[9] and its ^{1}H NMR data were consistent with the structure of **8**. This oil was found easy to hydrolyze and the absorption at δ_{TMS} -7.38 disappeared after hydrolysis; instead, a new signal at δ_{TMS} -16.19 emerged, which corresponds to the silicon of triphenylsilanol.

It is well known that 2,2,2-trifluorodiazoethane is a useful trifluoromethylated diazo compound[10], but the hazard in its handling and its preparation through nitrosation

Scheme 1. A proposed mechanism



(Ar = 2,4,6-triisopropylphenyl)

of 2,2,2-trifluoroethylamine[11] largely limits its use. Thus, our finding described above provides an efficient and practical synthesis of 2,2,2-trifluorodiazoethane under very mild conditions and also has demonstrated the usefulness in its application as shown by the syntheses of trifluoromethylated pyrazoles and pyrazolines. In summary, we have disclosed a safe and convenient variant of 2,2,2-trifluorodiazoethane.

Acknowledgment:We thank the National Science Foundation of China and Academia Sinica for their financial support.

References and Notes

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5. **1**, 86% yield, m.p. 158-160°C; ^{19}F NMR(CCl_4)δ_{TFA} -14.2(s,downfield negative); ^{1}H NMR ($CDCl_3$)δ 1.16(d,J=9Hz,12H), 1.28(d,J=9Hz,6H),2.92(hept,J=9Hz,1H),3.84(hept,J=9Hz,2H), 7.16-7.70(m,17H),8.44(s,1H); IR(KCl) 3200,1590,1560,1420,1330,1280,1190,1100,740,700, 690 cm^{-1}; MS,m/e,637(M+1). Elem. anal. calcd. for $C_{35}H_{39}F_3N_2O_2SSi$: C,66.09; H,6.17; N,4.39; F,8.95. Found:C,66.55; H,6.30; N,3.86; F,8.63.
6. General procedure: Triethylamine(50mg,0.5mmol) was added to a solution of **1**(318mg,0.5 mmol) and a dipolarophile(1mmol) in THF(6ml) placed in a reaction tube,then, the tube was capped and stood at room temperature until the yellow color of the solution disappeared. After usual aqueous workup, pyrazole or pyrazoline(3) and triphenylsilanol were obtained.
7. **4**, b.p.12°C(lit.[11]13-13.5°C/752mm), ^{19}F NMR(CD_3OD)δ_{TFA} -20.3(s); ^{1}H NMR(CD_3OD)δ 5.10(s).
8. In their studies on cycloaddition reactions of silyldiazoalkanes,Brook et al proposed the occurrence of a 1,3-silyl migration from C to N from the mechanistic viewpoint[12].
9. ^{29}Si NMR Spectra were recorded in THF-$CDCl_3$ on JEOL FX-90 with Me_4Si as an external standard.
10. See, for example:(a) Tordeux, M.; Wakselman, C. J. Fluorine Chem. **1981**, 17, 299; (b) Fields, R.; Tomlinson, J. P. J. Fluorine Chem. **1979**, 14, 19 ; (c) Mock, M.L.; Hartman, M. E. J. Org. Chem. **1977**, 42, 466.
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(Received in China 29 July 1992)