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Do reactions of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane require fluoride anion catalysis?

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A B S T R A C T

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (cyclic dimer of hexafluorothioacetone (**1**)) was shown to react with a variety of organic substrates in the absence of metal fluoride catalyst at elevated temperature in DMSO or DMF solvents. While the reactions of vinyl ethers, phenyl vinyl sulfide, dienes and anthracenes under these conditions led to the formation of expected cycloadducts, the reaction of 1,5-cyclooctadiene resulted in the formation of the product derived from an ene reaction with hexafluorothioacetone (HFTA). In contrast to results reported for the CsF catalysed process, 2-vinylnaphthalene reacted with **1** to produce a compound that resulted from reaction with two molecules of HFTA. The structure of this adduct was established using single crystal X-ray diffraction. The formation of similar products was also observed in non-catalysed reactions of styrene and 2-methylstyrene with **1**. Interestingly, no product of this type was observed in reaction of 4-MeO-styrene with **1**, which instead led to the high yield formation of the corresponding thietane. The reaction of **1** with 1,3-cyclohexadiene was carried out in various organic solvents: the reaction in DMSO and DMF was significantly faster than in acetonitrile, tetrahydrofurane or hexane.

1. Introduction

The cyclic dimer of hexafluorothioacetone (2,2,4,4-terakis(trifluoromethyl)-1,3-dithietane (**1**)) is a valuable synthon which has been used to prepare a variety of fluorine-containing martials. It has been shown to react to give hexafluorothioacetone (HFTA) cycloaddition products with vinyl ethers [1–3] vinyl sulfides [2], vinyl amides [4], various dienes [5–7], styrenes [5,8], fluoroolefins [2,9]. It has also been shown to give the product of HFTA insertion into allylic C–H bond with certain hydrocarbon olefins [10–12]. Most of these reactions were carried out in the presence of an alkali metal fluoride catalyst (either KF or CsF), since in earlier publications [1,5,9] it was suggested that the catalyst was required to induce the equilibrium between **1** and monomeric hexafluorothioacetone.

In contrast, a significant number of reactions of **1** have been reported that did *not* contain metal fluoride catalyst, including substrates such as phosphorous, arsenic, germanium and silicon cyanides [13–15], thiourea, dithiooxamide and cyanoformamidines [16–18], 1,1-dimethoxyethylene [3], *N*-vinylamides [4], azoles [19], *N*-alkyl(aryl)imidazoles [20].

In order to further elucidate the chemical behavior of **1**, we undertook a separate study of its reported reactions, but in the *absence* of alkali metal fluoride catalysts. The observed results demonstrate that when using a polar *nucleophilic* solvent, the majority of the reactions involving **1** *do not* require the catalyst.

2. Results and discussion

Previously [7] we reported that the reaction of **1** with quadricyclane (**2**) carried out in diglyme in the presence of CsF catalyst resulted in rapid formation of the corresponding cycloadduct **3**. Interestingly, the formation of the same product, albeit at a significantly slower rate, was observed when this reaction was carried out at ambient temperature *in the absence* of either catalyst or solvent [7]. Intrigued by this result, we repeated the reaction of **1** with **2** in the absence of catalyst, but using a polar aprotic solvent—dimethylsulfoxide (DMSO). Surprisingly, at 50 °C, the reaction was complete (by ^{19}F NMR) after 10 min. to give a high yield of **3** (Eq. (1)).

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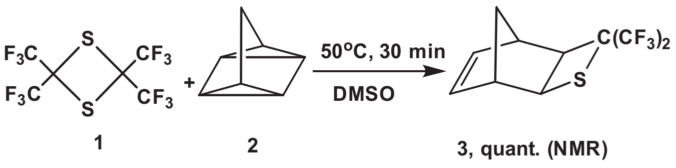
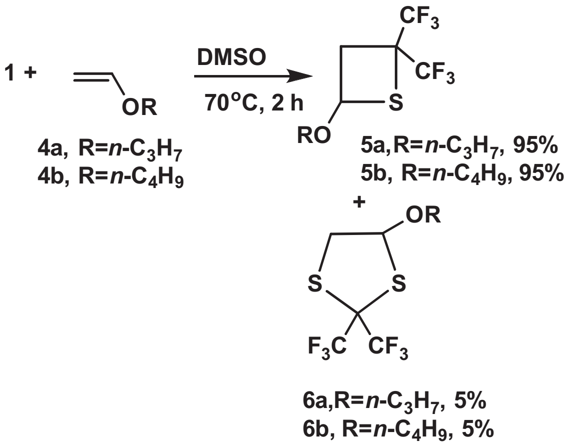


(1)

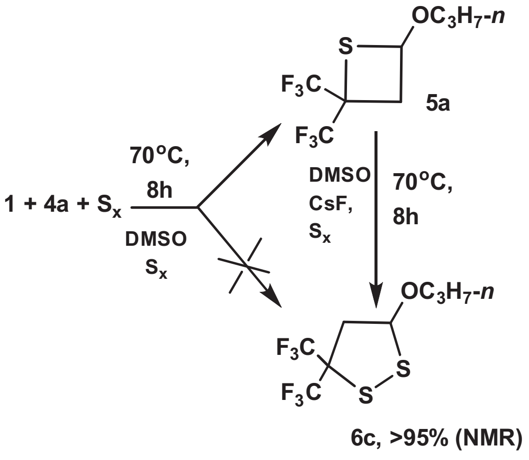
We also examined other previously reported KF or CsF catalyzed reactions of **1** by running the reactions in the absence of catalyst. To our surprise, the majority of these reactions *did not* require metal fluoride catalysis, as long as the reaction was carried out in a polar solvent such as DMSO or DMF.

One example, the reaction of alkylvinyl ethers **4a,b** with **1** in DMSO (70 °C, 2 h) led to high yields of previously reported [2] thietanes **5a** and **5b**, along with smaller amounts of 1,3-dithiolanes **6a** and **6b** (Eq. (2), Table 2).



(2)

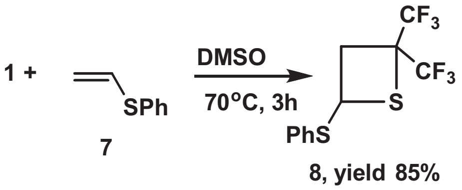
When one equivalent of sulfur was included in this reaction (DMSO, 70 °C, 24 h) the major product was compound **5a** (and trace amount of **6a**), rather than the expected 1,2-dithiolane **6c** [2]. However, when dry CsF catalyst was added to the existing reaction mixture, complete conversion of **5a** into **6c** was observed within 8 h at 70 °C. (Eq. (3))



(3)

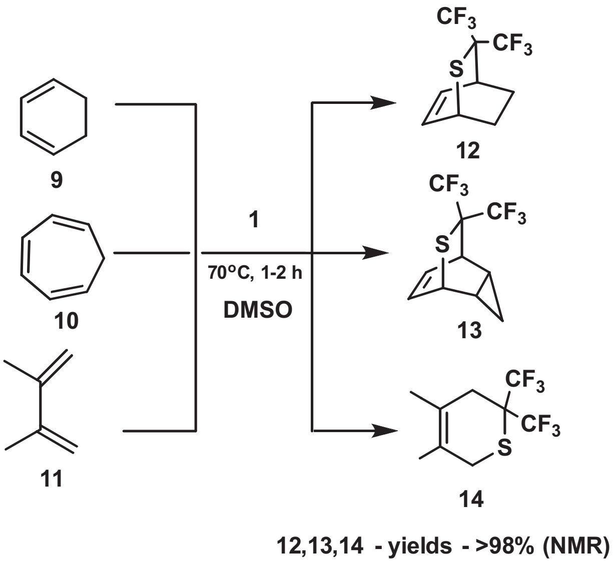
This experiment demonstrated that while the formation of thietane **5a** does not require catalyst, the ring-expansion process leading to **6c** is catalyzed by CsF. It is likely that in this case CsF reacts with elemental sulfur (rather than **5a**), converting it into an anionic species that is then able to react with **5a**.

Phenylvinyl sulfide (**7**), under similar reaction conditions, was completely consumed after 3 h at 70 °C to give thietane **8** in 85% isolated yield (Eq. (4)). The structure of this material was established by single crystal X-ray diffraction.



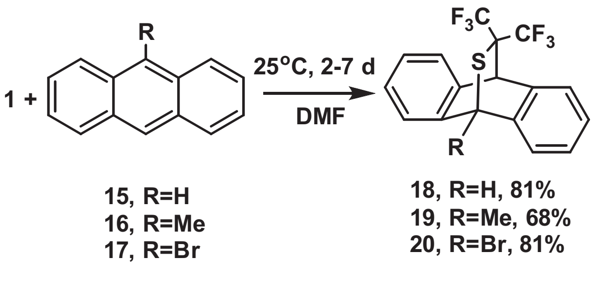
(4)

1,3-Cyclohexadine (**9**), 1,3,5-cycloheptatriene (**10**) and 2,3-dimethyl-1,3-butadiene (**11**) all readily reacted with **1** at elevated temperature in DMSO to produce the corresponding cycloadducts **12–14** in nearly quantitative yields.



(5)

The reaction of anthracenes **15–17** with **1** were carried out at ambient temperature in DMF. Although these reactions were relatively slow (2–7 days), the corresponding cycloadducts **18–20** were isolated in 68–81% yield.



(6)

In the case of substituted anthracenes **16** and **17**, the formation of only one regioisomer was observed. The structures of products **18–20** were established by single crystal X-ray diffraction. Compounds **19** and **20** both were shown to exist as the isomer