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REACTION OF 3,3,5,5-TETRAMETHYLTHIOLANE-2,4-DITHIONE WITH BENZYNE: NOVEL FORMATION OF BENZODITHIOLE

Kentaro Okuma*[†], Taeko Tsubone[†], Toshiyuki Shigetomi[†], Kosei Shioji[†],
and Yoshinobu Yokomori[‡]

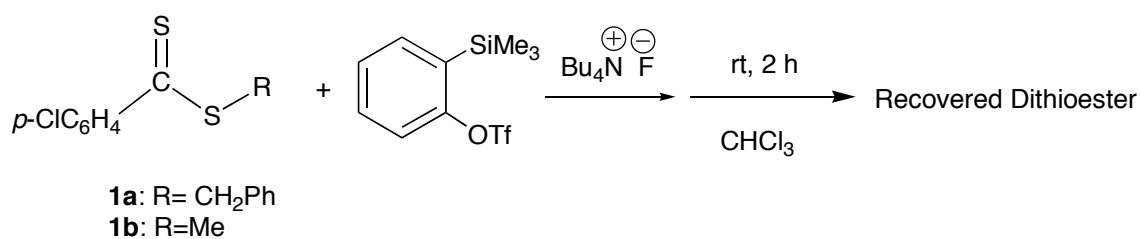
[†]Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-0180, Japan; [‡]National Defense Academy, Hashirimizu, Yokosuka, 239-8686, Japan. e-mail kokuma@fukuoka-u.ac.jp

Abstract – Reaction of 3,3,5,5-tetramethylthiolane-2,4-thione with benzyne gave a new type of benzodithiole in 78% yield. Dithioester's thiocarbonyl group initially attacked benzyne to afford the corresponding betaine, which finally rearranged to give benzodithiole. On the other hand, reaction of cyclic dithiolactone with benzyne recovered the starting dithiolactone in almost quantitatively.

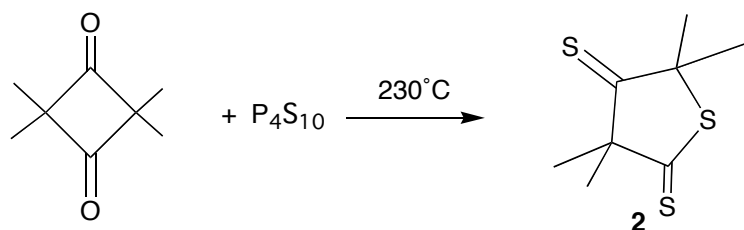
The chemistry of thiones has been studied extensively in recent years because of their unique and interesting properties.¹ Benzyne is a reactive intermediate that reacts with many dienes to afford the corresponding cycloadducts.² Because of our ongoing interest in the exploration of reactive benzyne for the synthesis of functionalized S-heterocycles, we attempted the synthesis of benzothietes and benzothianes.³ The results have prompted us to investigate the reaction of dithioesters with benzyne, which is reported herein.

We first attempted the reaction of simple dithioesters with benzyne. *o*-Trimethylsilylphenyl trifluoromethanesulfonate was used as the benzyne precursor.⁴ Treatment of benzyl dithio-*p*-chlorobenzoate (**1a**)⁵ with benzyne led to the recovery of the starting dithioesters (Scheme 1).

We next attempted the reaction of cyclic dithioester. Recently, we have reported the synthesis of 3,3,5,5-tetramethylthiolane-2,4-thione (**2**) by thermolysis of 2,2,4,4-tetramethylcyclobutane-1,3-dione with tetraphosphorus decasulfide (Scheme 2).⁶

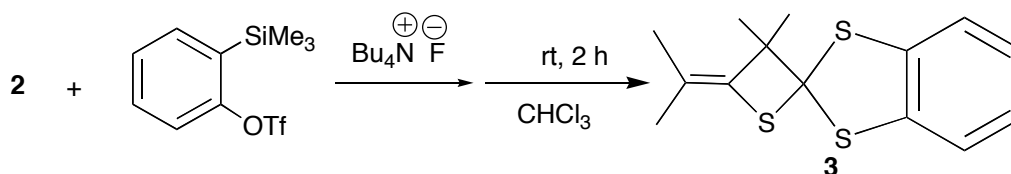


Scheme 1.



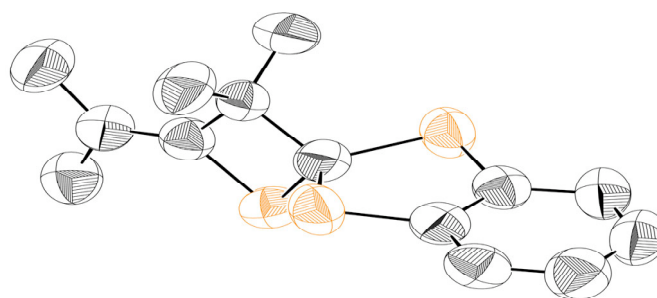
Scheme 2.

Treatment of **2** with *o*-trimethylsilylphenyl trifluoromethanesulfonate in chloroform followed by the addition of tetrabutylammonium fluoride resulted in the formation of spiro[1,3-benzodithiole-2,2'-[3',3']dimethyl-[2']-(propan-[2'']-ylidene)thietane] (**3**) in 78% yield (Scheme 3).



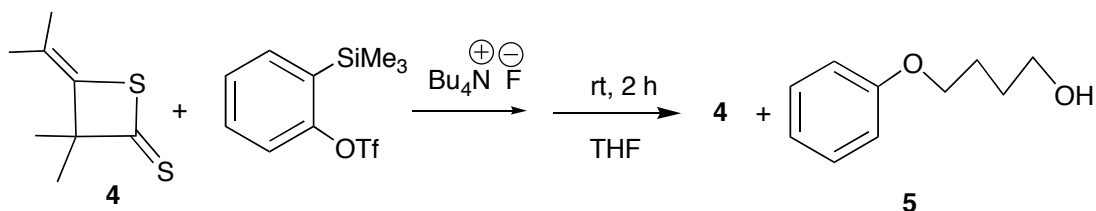
Scheme 3.

The structure of **3** was confirmed by spectroscopic analysis. The ¹H NMR spectrum of **3** displayed signals at δ 1.41, 1.66, and 1.73 that were assigned to the three methyl protons (1:2:1 ratio), and those at δ 7.05 and 7.18 that were assigned to the aromatic protons. The ¹³C NMR spectrum of **3** indicated the presence of three methyl, two quaternary, two olefinic and three aromatic carbons. The structure was finally determined by X-Ray crystallographic analysis. Its ORTEP structure is shown in Figure 1.⁷

Figure 1. ORTEP Drawing of Compound (**3**).

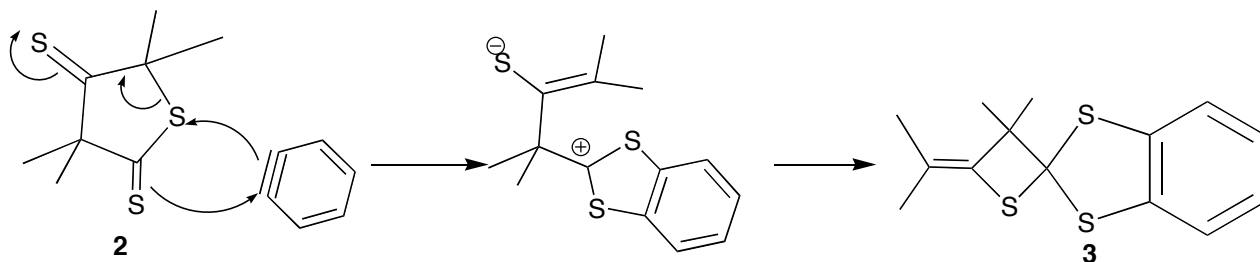
To confirm the reactivity of benzyne with dithiolactone, we next attempted the reaction of dithiolactone

(**4**)⁸ with benzyne. When the reaction was carried out in THF, starting **4** was recovered along with 4-phenoxybutanol (**5**) (15%), which was surmised to be the product of benzyne and THF.⁹ Thus, the thione moiety in **2** plays an important role in this reaction (Scheme 4).



Scheme 4.

The reaction is speculated to proceed as follows. The dithioester thiocarbonyl group initially attacked benzyne to afford the corresponding betaine, which produced the final product, benzodithiole (**3**) (Scheme 5).



Scheme 5.

A similar reaction was reported by Nakayama *et al.*, who performed the 1,3-dipolar cycloaddition reaction of 1,3-benzodithiole-2-thione with benzyne to afford bicyclic sulfonium salts by trapping with HCl.¹⁰ Paquer *et al.* reported that the reaction of dithiocinnamates with benzyne gave cinnamaldehydes via 1,3-dipolar cycloaddition.¹¹ 1,3-Benzodithioles were previously synthesized by reacting *o*-phenylenetrithiocarboxylate with methyl lithium.¹² However, to our knowledge, there is no report of the formation of the spiro compound of benzodithiole from dithioester.

In summary, we have succeeded in reacting cyclic dithioesters with benzyne, affording unusual heterocyclic compounds, whereas noncyclic dithioesters gave miscellaneous products along with starting dithioesters.

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 7. Compound (**3**): Colorless crystals, mp 98-99 °C (hexane): ¹H NMR (CDCl₃) δ 1.41 (s, 3H, CH₃), 1.67 (s, 6H, CH₃), 1.73 (s, 3H, CH₃), 7.00-7.22 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ 20.3 (CH₃), 22.0 (CH₃), 27.5 (CH₃), 61.9 (q), 84.3 (S-C-S), 119.7 (=C), 122.0, 125.9, 129.8 (=C), 136.5 (Ar). Crystallographic data of Compound (**3**): C₁₄H₁₆S₃ M = 280.48, a = 8.3540(4), b = 16.3130(7), c = 20.6840(9) Å, V = 2818.8(2) Å³, T = 298 K, orthorhombic, space group = Pbc₂a, Z = 8. The final R and wR were 0.0639 and 0.1899, respectively, using 2559 reflections.
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