Reaction of Thiopivalophenones with Benzyne. Formation of 2*H*-Benzo[b]thietes

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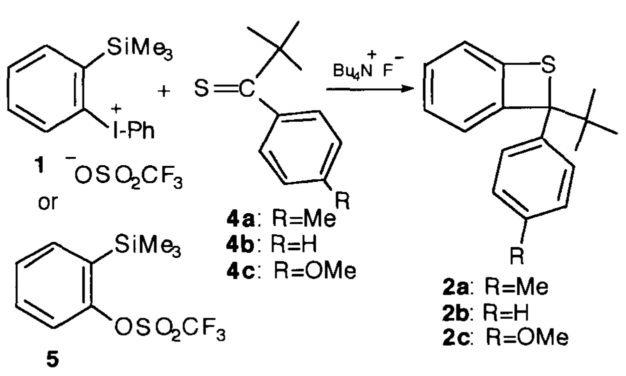
Reaction of thiopivalophenone with phenyl[2-(trimethylsilyl)-phenyl]iodonium trifluoromethanesulfonate in the presence of tetrabutylammonium fluoride afforded the corresponding [2+2] cycloadduct, 2-*tert*-butyl-2-*p*-tolyl-2H-benzo[b]thiete, in 58% yield. On the other hand, reaction of thiopivalophenone with benzenediazonium 2-carboxylate gave 2-*tert*-butyl-2-*p*-tolyl-benzo[d][3,1]oxathiane-6-one in 82% yield. The difference in the reactivity might be owing to the leaving group ability.

Benzyne is a reactive intermediate and reacts with many dienes to afford the corresponding cycloadducts.[1] However, there is relatively few reports on the reaction of thiones with benzyne.[2] The reaction of thiophosgene or 1,2-dithiol-3-thiones with benzyne initially afforded the corresponding [2+2] or [3+2] cycloadducts.[3] Recently, we have reported that the reaction of thiobenzophenones with benzyne generated from benzyne precursor, phenyl[2-(trimethylsilyl)phenyl]iodonium trifluoromethanesulfonate (**1**),[4] gave exclusively [4+2] adducts.[5] 2H-Benzo[b]thietes (**2**) are interesting compounds because of their unique reactivity toward dienophiles.[6] These compounds were generally synthesized by photolysis or flash vacuum pyrolysis of the corresponding precursors. One possible way to prepare **2** is by a 1,2-cycloaddition of a thiocarbonyl group to benzyne. However, the reaction of benzenediazonium 2-carboxylate (**3**), which is a well known benzyne precursor, with thiobenzophenones did not afford **2** but the corresponding benzoxathiane-6-one.[7] These results prompted us to investigate the reactivity of **1** with thiopivalophenones (**4**) whether **2** will be produced. We report herein the reaction of thiopivalophenones with benzyne.

Thiopivalophenones (**4a-c**) were prepared by the reaction of pivalophenones with tetraphosphorus decasulfide.[8] The reaction of **1** with *p*-methylthiopivalophenone (**4a**) in the presence of tetrabutylammonium fluoride afforded 2-*tert*-butyl-2-*p*-tolyl-2H-benzo[b]thiete (**2a**), 1,2-cycloadduct, in 58% yield (Scheme 1). When this reaction was carried out by using *o*-trimethylsilylphenyl triflate (**5**) as a benzyne precursor, **2a** was obtained in 12% yield.[9] In every case, no other cycloadducts such as [4+2] cycloadducts were identified. The result is shown in Table 1.



Scheme 1.

Table 1. Reaction of benzyne with **4**

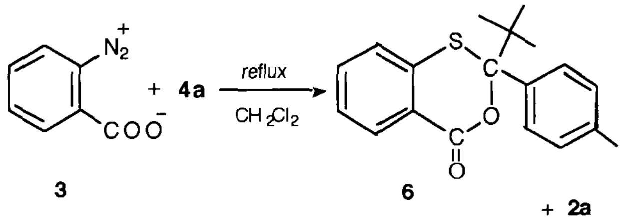
Run	Precursor	4	Solvent	2 (Yield/%)	Recovered 4 (%)
1	1 (2 eq)	**4a**	CH_3CN	**2a** 48	30
2	1 (4 eq)	**4a**	CH_3CN	**2a** 58	32
3	1 (2 eq)	**4a**	CH_2Cl_2	**2a** 49	30
4	5 (2 eq)	**4a**	CH_3CN	**2a** 19	9
5	5 (4 eq)	**4a**	CH_3CN	**2a** 24	22
6	5 (2 eq)	**4a**	CH_2Cl_2	**2a** 12	20
7	1 (2 eq)	**4b**	CH_2Cl_2	**2b** 51	11
8	1 (2 eq)	**4c**	CH_2Cl_2	**2c** 44	35

The structure of **2** was determined by their ^1H, and ^{13}C NMR spectra.[10] The best yields were obtained by the use of **1** as a benzyne precursor in dichloromethane solution at room temperature (Runs 3,7, and 8).

Previously, 2H-benzo[b]thietes were obtained by flash vacuum pyrolysis (1000 °C, 0.05 Torr) of benzo[b]thiophene-1,1-oxide,[6] by gas phase dehydration (700 °C) of *o*-mercaptobenzyl alcohol,[11] or by flash vacuum pyrolysis (600 °C) of 2,4,6-trineopentylbenzenesulfenic acid.[12] Recently, Meier has found that 2-oxa-4H-3,1-benzoxathiin decomposed at 140 °C to give 2H-benzo[b]thiete (**2d**).[6] Thus, this is the first practical synthesis of 2H-benzo[b]thietes under mild conditions.

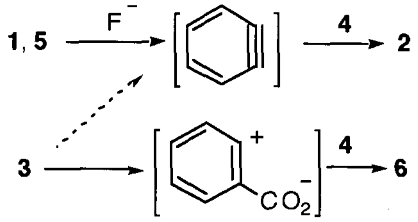
In a previous paper, we have reported that the reaction of thiobenzophenones with **1** affords the corresponding [4+2] cycloadducts.[5] How do we account for the difference in the reactivity? A bulky *tert*-butyl group prevents to make a plane between phenyl and carbonyl in **4**. PM3 calculation suggests that the dihedral angle between carbonyl and phenyl group of the most stable structure in **4b** is 60°. Actually, the maximum wave length (n, π^*) of **4b** is 560 nm, which is 34 nm shorter than that of thiobenzophenone (594 nm).[8,13] Thus, **4** is too hard to act as diene toward dienophiles.

Benzenediazonium 2-carboxylate (**3**) is a well known benzyne precursor. Dittmer and Tokunaga *et al.* reported that this reagent does not act as benzyne toward thiobenzophenone.[7] On the other hand, Nakayama *et al.* reported that the reaction of carbon disulfide or trithiocarbonates with **3** gave [3+2] dipolar addition products.[14] In this case, **3** acted as a benzyne precursor. In order to confirm its reactivity toward **3**, the reaction of **4a** with **3** was carried out. 2-*tert*-Butyl-2-*p*-tolylbenzo[d][3,1]oxathiane-6-one (**6**) was obtained in 82% yield along with a small amount of **2a** (8%)(Scheme 2).



Scheme 2.

Thus, **3** did not act as a benzyne precursor in the present reaction. As shown in Scheme 3, the present results have shown that **1** and **5** are good benzyne precursors under mild conditions in contrast with **3**.



Scheme 3.

In summary, the present reaction provides a practical method for the synthesis of 2H-benzo[b]thiete derivatives. The reaction proceeds under mild conditions (room temperature, neutral and aprotic solvent).

References and Notes

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10 Satisfactory mass spectra were obtained for all new compounds. Selected ^{1}H and ^{13}C NMR spectra of **2a** and **2c**. **2a**: ^{1}H NMR (CDCl$_3$) δ=1.08 (s, 9H, *tert*-Butyl), 2.32 (s, 3H, Tol-Me), 6.97 (d, 1H, *J*=7.6 Hz, *o*-H), 7.03 (d, 2H, *J*=8.4 Hz, Tol *meta*-H), 7.09 (t, 1H, *J*=7.6 Hz), 7.19, 7.23, 7.40 (d, 2H, J=8.4 Hz, Tol *ortho*-H). ^{13}C NMR (CDCl$_3$) δ=20.9 (Tol-Me), 26.9 (*tert*-Butyl-Me), 37.1 (*tert*-Butyl-C), 81.0 (C-S), 121.9, 123.2, 123.6, 127.1, 129.2, 129.5, 136.1, 136.9, 140.0, 145.1. **2c**: ^{1}H NMR (CDCl$_3$) δ=1.08 (s, 9H, *tert*-Butyl), 3.78 (s, 3H, OMe), 6.80 (d, 2H, *J*= 8.4 Hz, *meta* H), 7.00 (d, 1H, *J*=7.6 Hz, *ortho*-H), 7.12 (t, 1H, *J*=7.0 Hz, *para*-H), 7.19 (t, 1H, *J*=8.0 Hz, *meta*-H), 7.21 (d, 1H, *J*=7.6 H, *meta*H), 7.43 (d, 2H, *J*=8.4 Hz). ^{13}C NMR (CDCl$_3$) δ=26.7 (*tert*-Butyl-Me), 38.2 (*tert*-Butyl-C), 55.3 (MeO), 80.9 (C-S), 111.9 (*meta*-C), 121.7 (C-6), 122.9 (C-3), 123.6 (C-4), 128.7 (C-5), 130.6 (*ortho*-C), 132.3, 140.0, 145.2, 158.2 (*para*-C).

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