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Publication details, including instructions for authors and subscription information:

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Published online: 17 Mar 2008.

To cite this article: Kentaro Okuma , Toshiro Yamamoto , Takafumi Shirokawa , Tsugio Kitamura & Yuzo Fujiwara (1997) Reaction of Thiobenzophenones with Benzyne, Phosphorus, Sulfur, and Silicon and the Related Elements, 120:1, 331-332, DOI:

[10.1080/10426509708545534](https://doi.org/10.1080/10426509708545534)

To link to this article: <http://dx.doi.org/10.1080/10426509708545534>

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## Reaction of Thiobenzophenones with Benzyne

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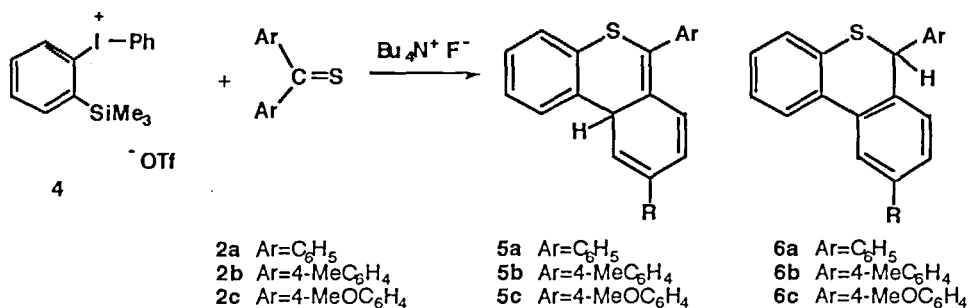
Reaction of thiobenzophenones with phenyl[2-(trimethylsilyl)-  
phenyl]iodonium trifluoromethanesulfonate in the presence of  
tetrabutylammonium fluoride afforded the corresponding adducts, which  
are the first examples of benzyne-thiobenzophenone adducts.

### INTRODUCTION

Benzyne is a reactive intermediate and reacts with many dienes to afford the corresponding cycloadducts. Benzenediazonium 2-carboxylate (**1**) is a well known benzyne precursor. Thiobenzophenone **2a** reacts with **1** to afford benzo-1,3-oxathian-4-one (**3**).<sup>1</sup> However, relatively few reports on the reaction of thione with benzyne. Recently, one of the authors has developed a new type of reagent, [2-(trimethylsilyl)-phenyl](phenyl)iodonium trifluoromethanesulfonate (**4**),<sup>2</sup> which found to be a good benzyne precursor. We report herein the reaction of thiobenzophenones with **4**, which forms completely different products previously reported.

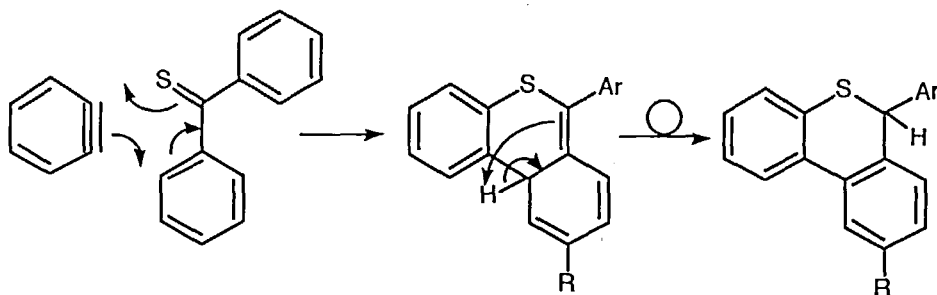
### RESULTS AND DISCUSSION

Treatment of **4** with 4,4'-dimethylthiobenzophenone (**2b**) followed by the addition of tetrabutylammonium fluoride at room temperature resulted in the formation of cycloadduct (**5b**) and its rearranged product (**6b**) in 15% and 45% yields, respectively.



Scheme 1.

When this reaction was carried out in refluxing toluene, the obtained products were only the rearranged one (**6**). When the present reaction was carried out at 0 °C, the ratio of unrearranged **5** were higher. Thus, the reaction might proceed as follows: when the benzyne was formed, thiobenzophenone immediately attacked benzyne to afford the corresponding Diels-Alder adduct **5**. This adduct further rearomatized to give the rearranged product **6** (Scheme 2).



Scheme 2.

Recently, many kinds of benzyne precursors were developed. However, the properties of thiobenzophenones are difficult to reconcile with the properties of the precursors of benzyne and also with the reaction conditions where benzyne is generated; acidic or basic conditions and the presence of oxidizing reagents or strong nucleophiles should be avoided. Because of this limitation, no report describing the reaction of benzyne with thiones in the actual sense has appeared. This reaction requires only fluoride anion at room temperature and can be carried out under very mild conditions. The present result is the first true example of the reaction of thioketones with benzyne.

## REFERENCES

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