

1,3-Cycloaddition of Benzyne to Thiophens

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Summary Benzyne, generated from diphenyliodonium-2-carboxylate, reacts with various thiophens by addition to the sulphur and β -carbon to give, after loss of an acetylene moiety, benzo[*b*]thiophens in low but reproducible yields.

DURING a study¹ of the solution-phase reactions of various thiophens (**1**) with benzyne generated from diphenyliodonium-2-carboxylate,² the formation of benzo[*b*]thiophens in low but reproducible yields was repeatedly observed (Table). A similar observation was reported some years

ago from the gas-phase reaction of thiophen and benzyne generated from phthalic anhydride, and was rationalized by a mechanism which predicted that both β -carbons of the thiophen were lost and both α -carbons were retained in the product (**2**).³ Aside from the improbability of portions of this mechanism as revealed by more recent studies,⁴ the substitution patterns of the benzo[*b*]thiophens (**2**) in the Table clearly contradict this prediction. Instead, it appears that adjacent α - and β -carbons of the thiophens (**1**) are either retained as C-2 and C-3 of the product (**2**), respectively, or they are lost entirely.

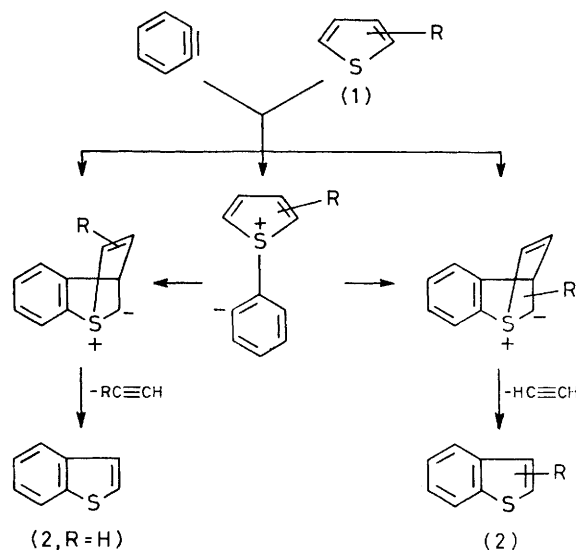
TABLE. Yields^a of benzo[*b*]thiophens (2).^b

Thiophen (1) R	Benzo[<i>b</i>]thiophen (2) R	% Yield
a ; H	H	0.5
b ; 2-Br	H	1.5
c ; 3,4-Br ₂	3-Br	3.8
d ; 2-Me	2-Me	ca. 0.5 ^c
	H	0.5
e ; 3-Me	H	0.5
f ; 2,5-Me ₂	2-Me	3.0
g ; 2-OMe	H	1.0

^a Identification based on g.c.-m.s. comparison with authentic materials. Yields are g.c.-determined. ^b Conditions and major products are given in ref. 2. ^c Incomplete resolution from other components of the reaction mixture.

Although details such as the sequence and timing of the steps cannot be specified as yet, the mechanism must involve a 1,3-cycloaddition of benzyne to the sulphur and β -carbon of the thiophen ring and expulsion of an acetylene moiety composed of the α - and β -carbons of the unattacked side of the thiophen ring. With monosubstituted thiophens, the unsubstituted side is preferentially attacked for (**1b**, **e**, and **g**) but for 2-methylthiophen (**1d**) either side may react. An illustrative mechanism incorporating these features is shown in the Scheme.†

Benzyne is known to participate in 1,3-cycloaddition reactions,⁵ including several with mesoionic five-membered heterocycles.⁶ Two recent examples closely related to the mechanism in the Scheme involve the stepwise attack of benzyne on the sulphur atoms of dithiin dioxides⁷ or 2,1,3-benzothiadiazoles,⁸ followed by attack at a β -carbon and elimination of an acetylene or a nitrile, respectively. All these examples, however, involve species relatively more



SCHEME.

dipolar or less aromatic than thiophen. Although 1,3-cycloaddition to a thiophen ring had previously been considered to explain certain photochemical reactions, this hypothesis was eliminated⁹ thereby leaving the present reaction as the first apparent example of this phenomenon.

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† Added in proof. A similar mechanism has been recently proposed to explain the reactions of cyclic thioenol ethers with di methyl acetylenedicarboxylate (K. Gollnick and S. Fries, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 832).

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