Reaction Pathways for the Cyclization of *ortho*-Thioalkyl and *ortho*-Thioaryl Substituted Phenyl Radicals with Alkynes. Reaction of *o*-Methylthioarenediazonium Tetrafluoroborates with Alkynes to give 2-Substituted Benzo[*b*]thiophenes

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An easily effected aromatic annelation is described involving reaction of *o*-thioalkyl and *o*-thioaryl substituted phenyl radicals with alkynes to give 2-substituted benzo[*b*]thiophenes; the mechanism is discussed.

Radical displacement reactions at bivalent sulphur of disulphides or thiosulphones are well established[1] while those at sulphur of sulphides are less usual and are known only when the bond between sulphur and the departing radical is relatively weak or when the displacement is intramolecular.[2] Homolytic substitutions at a sulphur atom which is part of an aromatic ring are uncommon and have been reported only in the case of 1,2,3-benzothiadiazole.[3] We describe here a versatile synthesis of 2-substituted benzo[*b*]thiophenes occurring through an annelation process involving an S_Hi substitution at sulphur.
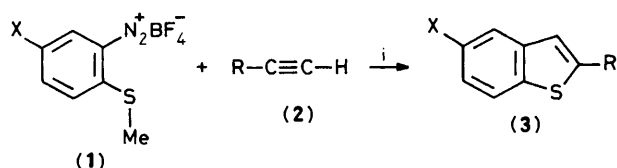
The reaction of *o*-methylthioarenediazonium tetrafluoroborates (1) (5 mmol) at room temperature with alkynes (2) (25 mmol) in acetone solution in the presence of NaI or freshly prepared copper powder, or in dimethyl sulphoxide deoxygenated with nitrogen and containing $FeSO_4$, gives benzo[*b*]thiophenes (3) (Scheme 1 and Table 1).

High yields were obtained in the reactions involving arylacetylenes, but yields were lower with but-3-yn-2-one and ethyl propiolate (see Table 1).

This synthesis is of interest since it provides 2-arylbenzo[*b*]thiophenes in high yields without the concomitant formation of the 3-substituted analogues,[4] and it also provides 2-acetyl- and 2-ethoxycarbonylbenzo[*b*]thiophenes which are not always obtainable directly from benzo[*b*]thiophene.[5]

With the aim of establishing the mechanism of the displacement at sulphur the diazonium salts (4) and the *N*-nitrosoacetanilide (5) were prepared.

The reaction of the tetrafluoroborate (4a) (5 mmol) with phenylacetylene (25 mmol) in acetone in the presence of freshly prepared copper powder or in deoxygenated dimethyl sulphoxide containing $FeSO_4$ provided (3a), hexa-1,5-diene, and phenyl hex-5-enyl sulphide. The same products were obtained from the decomposition of the *N*-nitrosoacetanilide (5) at room temperature in acetone in the presence of phenylacetylene. A similar reaction of the tetrafluoroborate (4b) gave biphenyl, 2-phenyldibenzothiophene, and biphenyl-4-yl phenyl sulphide, together with (3a).†
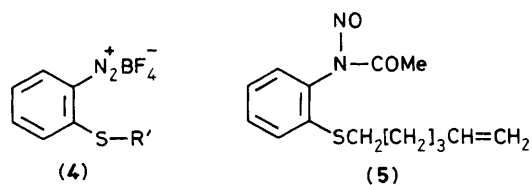
These results can be rationalized by assuming the mechanism shown in Scheme 2; the tetrafluoroborate (4), *via* electron transfer, gives rise to the corresponding diazenyl radical which affords the aryl radical (6) by fast loss of nitrogen. Addition of (6) to phenylacetylene leads to the vinyl radical (7) which then cyclizes, *via* an S_Hi mechanism, to give the sulphuranyl radical (8). The latter can be oxidized to the corresponding cation (9) with which it is assumed to be in equilibrium; both (8) and (9) may provide the benzo[*b*]thiophene (3) either by loss of R˙' or *via* an E_2 process, depending on R'. Moreover radical (6a) would lead to phenyl hex-5-enyl sulphide by hydrogen abstraction, whereas radical (6b) would afford 2-phenyldibenzothiophene *via* an intramolecular aromatic S_H2 reaction and biphenyl-4-yl phenyl sulphide by hydrogen abstraction.

The proposed mechanism seems reasonable in the light of the following considerations; first, the reaction of (4a) with phenylacetylene gives (3a) and hexa-1,5-diene but none of the products expected from an elimination of the hex-5-enyl group
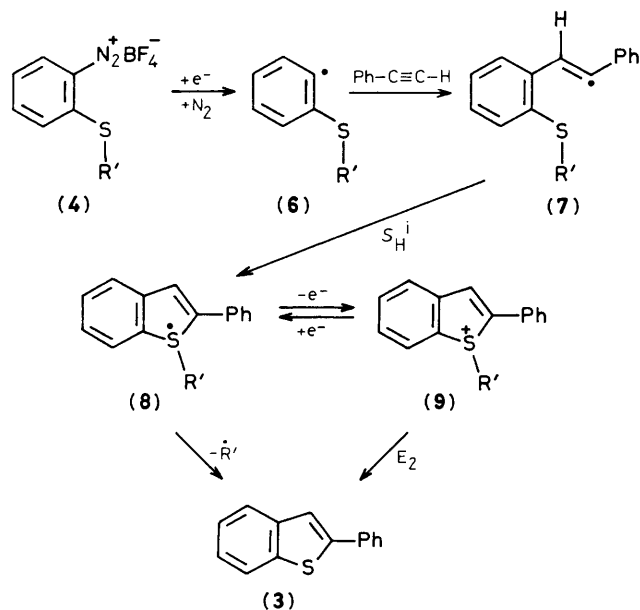
Table 1. Substituted benzo[*b*]thiophenes (3).

Product	R	X	% Yield[a]	M.p. ($t/^\circ$C)	Ref.
(3a)	Ph	H	95	174—175	7
(3b)	Ph	Cl	95	190—191	b
(3c)	Ph	OMe	95	143—144	b
(3d)	Ph	Me	80	157—159	5
(3e)	m-MeOC$_6$H$_4$	H	80	88—89	b
(3f)	m-MeOC$_6$H$_4$	Cl	71	120—121	b
(3g)	m-MeOC$_6$H$_4$	OMe	70	85—86	b
(3h)	m-MeOC$_6$H$_4$	Me	55	85—87	b
(3i)	p-ClC$_6$H$_4$	H	75	200—202	b
(3j)	p-ClC$_6$H$_4$	Cl	85	164—165	b
(3k)	p-ClC$_6$H$_4$	OMe	82	177—179	b
(3l)	p-ClC$_6$H$_4$	Me	73	219—221	b
(3m)	CO$_2$Et	H	75	33—35	8
(3n)	CO$_2$Et	Cl	40	79—80	9
(3o)	CO$_2$Et	OMe	58	65—67	10
(3p)	CO$_2$Et	Me	50	69—70	b
(3q)	COMe	H	37	86—88	b
(3r)	COMe	Me	55	113—115	b

[a] Yields were calculated for pure product based on starting tetrafluoroborate decomposed in acetone with Cu powder. [b] New compound; satisfactory ^{1}H n.m.r. and mass spectra and elemental analyses were obtained.

Scheme 1. *Reagents*: i, acetone, NaI; acetone, Cu powder; or dimethyl sulphoxide, $FeSO_4$.

† Biphenyl and hexa-1,5-diene were determined by g.l.c.; in addition, biphenyl was also separated from the reaction mixture by column chromatography and identified by spectra comparison with an authentic specimen; the structure of hexa-1,5-diene was confirmed by ^{13}C n.m.r. spectroscopy.

a; R' = hex-5-enyl
b; R' = biphenyl-4-yl

Scheme 2

either as a radical or as a cation.[6] In fact, no methylcyclopentane, hex-1-ene, fluorocyclohexane, or cyclohexane could be detected in the reaction mixture. Thus, (3a) and hexa-1,5-diene conceivably arise from (9) *via* a bimolecular elimination, E_2. Secondly, the reaction of (4b) and phenylacetylene affords (3a) and biphenyl, but none of the products expected from an elimination of the biphenyl group as a cation (4-fluorobiphenyl could not be detected). Therefore, (3a) is obtained directly from (8) by detachment of the biphenyl-4-yl radical which abstracts hydrogen from the solvent giving biphenyl.

From the dichotomy of the mechanism by which 2-phenylbenzo[b]thiophene is produced, the sulphuranyl radical (8) can be presumed to be a true intermediate.

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