Boron Trifluoride-promoted Reaction of 4′-Nitrobenzenesulphenanilide and Its *N*-Methyl Derivative with Alkynes

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4′-Nitrobenzenesulphenanilide and its *N*-methyl derivative react with alkynes in the presence of boron trifluoride–diethyl ether presumably affording thiirenium ion intermediates, which are trapped by acetonitrile to give eventually β-acetamidinovinyl sulphides.

In previous papers we have shown that boron trifluoride–diethyl ether transforms the sluggish benzenesulphenanilides (**1**) into highly reactive species (probably anilide–BF_3 complexes) which can undergo nucleophilic displacement at sulphur by alkenes presumably leading to thiiranium ion intermediates from which azasulphenylation adducts are ultimately formed. In benzene these reactions generally afford arylamino sulphides,[1] whereas in nitrile solvents amidino and/or amido sulphides are smoothly produced.[2]

We now report preliminary results from a related study of the addition of 4′-nitrobenzenesulphenanilide (**1a**) and its *N*-methyl derivative (**1b**) to alkynes in the presence of boron trifluoride–diethyl ether. To our knowledge electrophilic additions of sulphenamides to alkynes have not been explored so far.

Treatment of the benzenesulphenanilide (**1a**) in benzene containing a five-fold excess of hex-1-yne with boron trifluoride–diethyl ether (1.5 equiv.) at room temperature brought about smooth reaction of the anilide (**1a**) within *ca.* 1 h. After hydrolysis, column chromatography gave, in addition to the aniline (**2a**)[1—3] and diphenyl disulphide (**3**),[1—3] (*E*)-2-fluoro-1-(phenylthio)hex-1-ene (**4**) (22%).† The same reaction carried out in the presence of phenylacetylene afforded an inseparable mixture of (*E*)- (**5**)† and (*Z*)-1,2-bis(phenylthio)styrene (**6**)† (20%) in 70:30 ratio, as indicated by ^1H n.m.r. spectroscopy, together with the aniline (**2a**) and the disulphide (**3**). These findings showed at first sight that hex-1-yne and phenylacetylene should be capable of effecting nucleophilic displacement at the sulphur atom of the anilide (**1a**)–BF_3 complex possibly leading to thiirenium ions (**7**).

These might have been trapped by either fluoride from the tetraborate counterion ($ArNHBF_3^-$) or by the disulphide (**3**) to give eventually the adducts (**4**) or (**5**,**6**) (Scheme 1). Intermediacy of thiirenium ions (**7**) was suggested to some extent by the observed regioselectivity and stereoselectivity.

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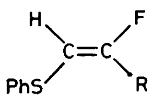
† Satisfactory analyses and ^1H n.m.r., i.r., and mass spectral data were obtained for all new compounds.

$ArNR^1SPh$ **(1)** $ArNHR^1$ **(2)** $PhSSPh$ **(3)**

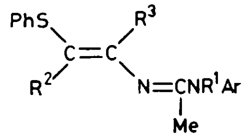


(4) R = Bu^n

$PhSCH{=}CPhSPh$

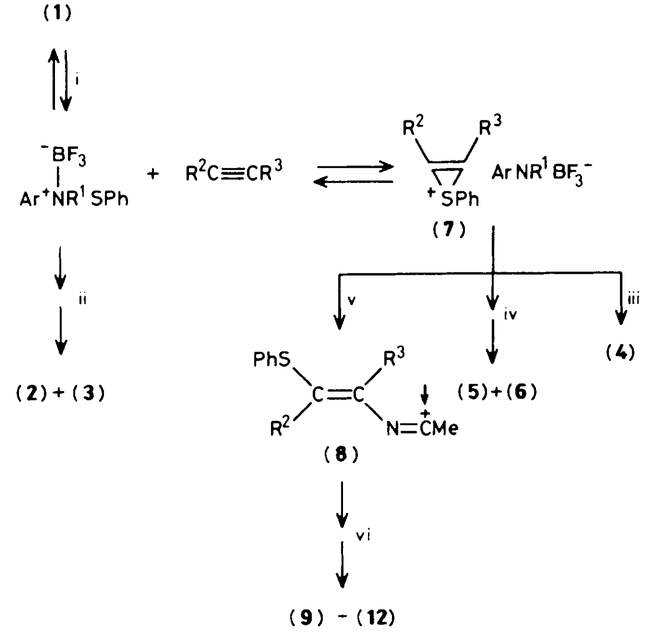
(5) *E*

(6) *Z*



(9) $R^2 = H$, $R^3 = Bu^n$
(10) $R^2 = H$, $R^3 = Ph$
(11) $R^2 = Me$, $R^3 = Pr^n$
(12) $R^2 = Pr^n$, $R^3 = Me$

a; $R^1 = H$, Ar = $C_6H_4NO_2$-*p*
b; $R^1 = Me$, Ar = $C_6H_4NO_2$-*p*



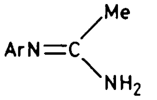
Scheme 1. *Reagents*: i, $BF_3{\cdot}Et_2O$; ii, + (**1**); iii, benzene; iv, benzene, + PhSSPh; v, MeCN; vi, $ArNR^1BF_3^-$.

Thiirenium ions (**7**) would be expected to undergo ring opening with *trans*-stereoselectivity and Markovnikov orientation.[4]

More significant results were obtained when these reactions were carried out in acetonitrile. Under similar conditions the anilide (**1a**) reacted in acetonitrile with hex-1-yne to give the Markovnikov adduct (**9a**) (50%; m.p. 110—111 °C)† and with phenylacetylene to afford the corresponding adduct (**10a**), which was obtained as an oil in comparable yield.† ^{1}H N.m.r., i.r., and mass spectral data and chemical evidence were consistent with the proposed structural assignment of the enamidines (**9a,10a**). In particular, the ^{1}H n.m.r. spectra of the compounds (**9a**) and (**10a**) showed a three-proton singlet [MeC(=N)–] at δ *ca.* 2.0, a one-proton singlet in the vinylic region at δ 5.5 and 6.37, respectively, and a broad singlet at δ 6.6—6.7 (NH). The mass spectra exhibited, in addition to the

$PhSCHR^1COR^2$

(13) $R^1 = H$, $R^2 = Bu^n$
(14) $R^1 = H$ $R^2 = Ph$
(15) $R^1 = Me$, $R^2 = Pr^n$
(16) $R^1 = Pr^n$, $R^2 = Me$



(17) Ar = $C_6H_4NO_2$-*p*

molecular ion, strong fragmentation ions ascribable to M^+ − PhS and $ArN{\equiv}CMe^+$. Upon hydrolysis in dioxane–aqueous 4 M-HCl at reflux the enamidines (**9a**) and (**10a**) gave the keto sulphides (**13**)[5] and (**14**)[6] respectively and the acetamidine (**17**).[7]

Analogous reaction of the anilide (**1a**) with hex-2-yne gave an 80% yield of an inseparable mixture of the two regioisomers (**11a**)† and (**12a**)† in 60:40 ratio. Hydrolysis of this isomeric mixture gave the corresponding keto sulphides (**15**)[8] and (**16**)† in about the same ratio.

However, our present spectral and chemical evidence does not allow a definite structural assignment of the enamidines (**9a—12a**). These can theoretically exist in a number of geometrical and tautomeric forms. At this stage we tentatively assign the (*E*)-configuration (regarding the C=C double bond) to all these compounds (**9a—12a**) on the basis of the reasonable assumption that thiirenium ions (**7**) might be actually involved in their formation (*vide infra*).

As for the anilide (**1a**), the *N*-methyl derivative (**1b**) reacted with hex-1-yne in acetonitrile to afford the Markovnikov adduct (**9b**), albeit in low yield (18%). Interestingly, we found that the initially formed adduct (**9bA**)† was converted into a geometrical isomer (**9bB**)† slowly on standing at room temperature and fairly rapidly by adsorption on silica gel. In fact, both these isomeric compounds (**9bA** and **B**) exhibited one olefinic proton at δ 5.30 and 5.43, respectively, in the ^{1}H n.m.r. spectrum. Both isomers, upon hydrolysis, gave the keto sulphide (**13**).

A similar trend was encountered in the reaction of the anilide (**1b**) with phenylacetylene, which led to the separation of a 50:50 mixture of the two corresponding adducts (**10bA** and **B**) (20%).† In this case also, complete isomerisation of the enamidine (**10bA**) to (**10bB**) was subsequently observed. We believe that the enamidines (**9b,10b**) might be first formed as the (*E,Z*)-isomers (**9bA,10bA**); these would then isomerize to the (*E,E*)-isomers (**9bB,10bB**) by inversion at the C=N double bond. (*Z*)-Amidines have been shown to be formed initially in the reaction of amines with nitrilium ions and then to rearrange to the (*E*)-isomers.[9]

In the light of the above results it may be inferred that electrophilic addition of the activated anilides (**1a** and **b**) to alkynes can occur smoothly probably to give thiirenium ions (**7**). These would be effectively captured by acetonitrile to give nitrilium ions (**8**), from which the enamidines (**9—12**) would be ultimately produced by subsequent attack by $ArNR^1BF_3^-$ (Scheme 1).

Intermediacy of thiirenium ions (**7**) in these reactions is strongly suggested by both the exclusive occurrence of Markovnikov adducts with terminal alkynes and the general high stereoselectivity apparently exhibited. Thus, our present results provide the first examples of sulphenamide addition to alkynes leading to stereoselective and regioselective amidinosulphenylation of alkynes. Furthermore, our reactions appear to provide a new synthetic route to enamidines, a class of compounds of theoretical and synthetic interest, but still little known.[9a,10]

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