Tetrahedron Letters,Vol.25,No.19,pp 2039-2042,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

BORON TRIFLUORIDE PROMOTED REACTION OF BENZENESULPHENANILIDES WITH ALKENES-ARYLAMINOSULPHENYLATION OF ALKENES.

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Summary: The addition of benzenesulphenanilides to alkenes in the presence of boron trifluoride provides a practicable synthetic procedure for the arylaminosulphenylation of alkenes.

Considerable attention has been long devoted to the preparation and synthetic applications of sulphenamides.[1] Several procedures are now available for the synthesis of sulphenamides,[2] which have been proven to be useful sulphenyl-transfer reagents in the synthesis of sulphides,[3a] disulphides,[3b-d] trisulphides,[3e] sulphenate esters,[3f] and sulphenamides.[3g]

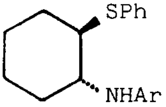
The reaction of sulphenamides with alkenes,[4] leading to aminosulphenylation of alkenes, might be another potentially useful synthetic application of sulphenamides. Aminosulphenylation[4,5] of alkenes represents an important synthetic process whose utility stems from the fact that the resulting β-amino-sulphides can be converted into a number of nitrogen compounds by appropriate substitution or elimination of the sulphur substituent. However, to our knowledge reactions of sulphenamides with alkenes have been virtually unexplored so far.[4] We now wish to report our preliminary results from a study of the reaction of a series of substituted benzenesulphenanilides (**1a-f**) with alkenes in the presence of boron trifluoride etherate, which show that sulphenanilides (**1**) generally react with alkenes to give aminosulphenylation products. Treatment of (**1a-f**) in cyclohexene with 1.5 equiv. of $BF_3.Et_2O$ at room temperature brought about smooth reactions which were completed within several minutes. After hydrolysis of the reaction mixtures, column chromatography led to the isolation of the trans-adducts (**2**)[6] in fair to good yields in all cases examined except for the methoxy-substituted sulphenanilides (**1e**) and (**1f**) which gave (**2e-f**) in rather low yields (Table).

The trans-geometry in (**2a-f**) was established in two cases by alternate reactions and assumed for the remaining examples. The product of trans-addition of PhSCl to cyclohexene was converted to (**2a**) and (**2d**) on treatment with $AgBF_4$

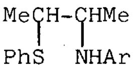
followed by the appropriate substituted aniline.[7]

PhSNHAr

(1)



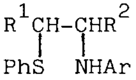
(2)



$$\underset{PhS}{MeCH}-\underset{NHAr}{CHMe}$$

(3) threo

(4) erythro



$$\underset{PhS}{R^1CH}-\underset{NHAr}{CHR^2}$$

(5) $R^1 = H$, $R^2 = Ph$

(6) $R^1 = H$, $R^2 = n\text{-}C_4H_9$

(7) $R^1 = n\text{-}C_4H_9$, $R^2 = H$

a: Ar = $4\text{-}NO_2C_6H_4$ c: Ar = Ph e: Ar = $4\text{-}OMeC_6H_4$ g: Ar = $3\text{-}NO_2C_6H_4$

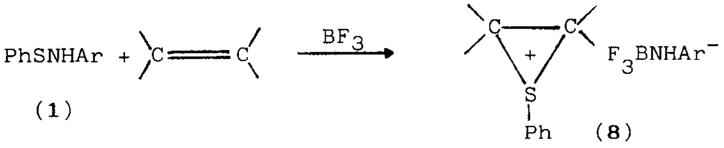
b: Ar = $4\text{-}ClC_6H_4$ d: Ar = $4\text{-}MeC_6H_4$ f: Ar = $3\text{-}OMeC_6H_4$

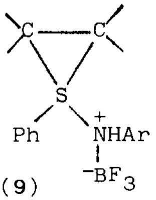
Thus, the addition of sulphenanilides (**1**) is highly stereoselective and appears to proceed with retention in the geometry of the groups in the starting alkene, as evidenced from the reactions of (**1a**) and (**1b**) with cis- and trans-but-2-enes which led to threo- and erythro-aminosulphides (**3a-b**)[6,8] and (**4a-b**),[6,8] respectively (Table).

Addition of sulphenanilides (**1a**), (**1d**) and (**1g**) to styrene gave the corresponding adducts (**5**)[6] in a highly stereoselective fashion; with hex-1-ene, (**1a**) gave only the aminosulphide (**6a**)[6,9] whereas (**1d**) afforded a mixture[6] of the regioisomers (**6d**) and (**7d**) in the ratio of 77:23 (Table). On the basis of our findings it might be assumed that boron trifluoride transforms the sluggish benzenesulphenanilides (**1**) into highly reactive species (presumably $PhSNHAr^+BF_3^-$)[10] which react with alkenes to afford episulphoniumtetraborate ion-pair intermediates (**8**) as shown in eq. 1 through a mechanism related to that generally suggested for the addition of sulphenyl chlorides to alkenes.[11,12]

The trans-stereospecific addition observed with but-2-enes and the exclusive (or predominant) formation of Markownikoff adducts from reaction with styrene and hex-1-ene would be consistent with the intermediacy of episulphonium ions,[12] although at this stage one cannot exclude the possibility of involvement of other cyclic intermediates such as sulphuranes (**9**), analogous to those also advanced in the sulphenyl chloride addition to alkenes.[11-13]

(1)





(9)

Table

Aminosulphenylation Products from the BF_3-Benzenesulphenanilide Reaction of Alkenes.[a]

Benzene-Sulphenanilide	Alkene	Product	Yield,[g] (%)
(1a)	Cyclohexene[b]	**(2a)**	94
(1b)	Cyclohexene[b]	**(2b)**	78
(1c)	Cyclohexene[b]	**(2c)**	52
(1d)	Cyclohexene[b]	**(2d)**	80
(1e)	Cyclohexene[b]	**(2e)**	27
(1f)	Cyclohexene[b]	**(2f)**	25
(1a)	*cis*-But-2-ene[c]	**(3a)**	88
(1b)	*cis*-But-2-ene[c]	**(3b)**	78
(1a)	*trans*-But-2-ene[c]	**(4a)**	88
(1b)	*trans*-But-2-ene[c]	**(4b)**	79
(1a)	Styrene[d]	**(5a)**	98
(1d)	Styrene[d]	**(5d)**	61
(1d)	Styrene[e]	**(5d)**	90
(1g)	Styrene[d]	**(5g)**	98
(1a)	Hex-1-ene[f]	**(6a)**	51
(1d)	Hex-1-ene[f]	**(6d)**+**(7d)**[h]	48

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[a] Carried out by treating a 0.05 M solution of the benzenesulphenanilide in the appropriate alkene or alkene-benzene mixture with 1.5 equiv. of $BF_3.Et_2O$ for 5-10 min. at room temperature. [b] Reaction solvent. [c] Saturated benzene solution. [d] 0.1 M Benzene solution. [e] 0.4 M Benzene solution. [f] *ca.* 30% Benzene solution. [g] All yields are for products isolated by column chromatography on silica gel. [h] Isomer ratio 77:23 as determined by hplc.

However, our observation[9] that the reaction of the sulphenanilide **(1a)** with hex-1-ene leads to oligomers, $C_6H_{12}C_6H_{11}SPh$ and $C_{12}H_{24}.4NO_2C_6H_4NHSPh$, in addition to the Markownikoff adduct **(6a)**, makes the intermediacy of an episulphonium species very likely, at least in this case.[7,12]

Finally, we wish to point out that data reported in the Table would indicate that the efficiency, by which substituted benzenesulphenanilides **(1)** react with alkenes to afford aminosulphenylation products, is largely sensitive to the nature of the N-aryl substituent. Although our present results do not allow to fully explain the effect of substituents observed, it would appear that these reactions represent a practicable general procedure for the arylaminosulphenylation of alkenes, particularly satisfactory when benzenesulphenanilides bearing an electron-attracting group are employed.

References and Notes

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(Received in UK 22 February 1984)