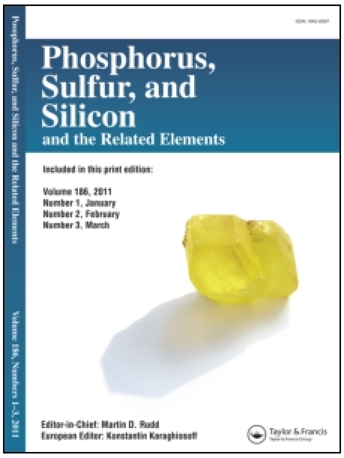

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SODIUM BOROHYDRIDE REDUCTION OF AROMATIC SULFONYL AZIDES IN THE PRESENCE OR ABSENCE OF TELLURIUM

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To cite this Article Obafemi, Craig. A. and Onigbinde, Adebayo O.(1991) 'SODIUM BOROHYDRIDE REDUCTION OF AROMATIC SULFONYL AZIDES IN THE PRESENCE OR ABSENCE OF TELLURIUM', Phosphorus, Sulfur, and Silicon and the Related Elements, 57: 1, 75 — 81

To link to this Article: DOI: 10.1080/10426509108038833

URL: http://dx.doi.org/10.1080/10426509108038833

Phosphorus, Sulfur, and Silicon, 1991, Vol. 57, pp. 75–81
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SODIUM BOROHYDRIDE REDUCTION OF AROMATIC SULFONYL AZIDES IN THE PRESENCE OR ABSENCE OF TELLURIUM

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(Received January 1, 1990; in final form August 15, 1990)

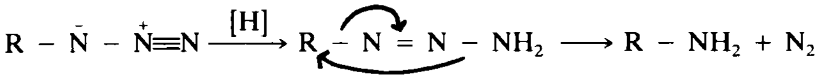
Some aromatic sulfonyl azides have been reduced, in various solvents, with sodium borohydride, in the presence or absence of Te element to the corresponding sulfonamides. Other functionals groups like the imino group may also be reduced.

Key words: Sulfonyl azides; reduction; sodium borohydride; tellurium; aryl sulfonamides; acetic acid.

INTRODUCTION

One of the most important method of preparation of amines (RNH_2) is the reduction of N-containing compounds like nitrocompounds ($R—NO_2$), nitriles ($R—CN$), amides ($RCONR_2$) oximes ($RR'C═NOH$), carbonyl compounds (involving reductive amination: e.g., $R—CHO \xrightarrow[H_2/Ni]{NH_3} RCH_2NH_2$) and azido compounds ($R—N_3$).

The azido group (N_3) is commonly converted to the amino group (NH_2) by catalytic hydrogenation, usually carried out at low hydrogen pressure in the presence of catalysts such as platinum oxide, palladium on carbon or Raney nickel.[1-2] The azido group has a dipolar character and it is converted to the amino group most probably through the following route:

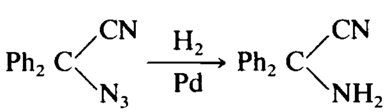


$$R - \overset{-}{N} - \overset{+}{N}{\equiv}N \xrightarrow{[H]} R - N = N - NH_2 \longrightarrow R - NH_2 + N_2$$

Using this method, azidoketones may be converted to aminoalcohols.[2] For example, catalytic hydrogenation of benzoylazidomethane:

$$C_6H_5COCH_2N_3 \xrightarrow[Pd]{H_2} C_6H_5COCH_2NH_2 \xrightarrow[Pd]{H_2} C_6H_5CH(OH)CH_2NH_2$$

On the other hand, the cyano group in azidonitriles is left untouched:[1]

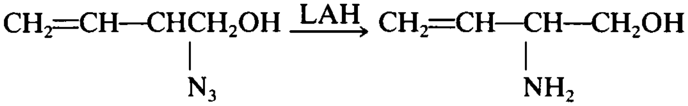


$$Ph_2C\begin{smallmatrix}CN\\N_3\end{smallmatrix} \xrightarrow[Pd]{H_2} Ph_2C\begin{smallmatrix}CN\\NH_2\end{smallmatrix}$$

Lithium aluminium hydride (LAH) has also been used:

$$\begin{array}{l}4R—N_3 + LiAlH_4 \longrightarrow (R—NH)_4AlLi + 4N_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_2O \\ \qquad\qquad\qquad\qquad\qquad\qquad 4R—NH_2\end{array}$$

LAH is a strong reducing agent that reduces most reducable functional groups. It also reduces all types of azides. With azidoketones, LAH yields amino-alcohols,[3] while with olefinic azides, the double bonds are not affected[4]: e.g.,



$$CH_2{=}CH{-}\underset{\underset{N_3}{|}}{C}HCH_2OH \xrightarrow{LAH} CH_2{=}CH{-}\underset{\underset{NH_2}{|}}{C}H{-}CH_2OH$$

Sodium borohydride ($NaBH_4$) is a milder reducing agent than LAH. It was found to be less effective than LAH. For example, it gives negligible or no reduction products with monofunctional and aromatic azides, while azidoketones give azidoalcohols.[5] e.g.,

$$C_6H_5COCH_2N_3 \xrightarrow{NaBH_4} C_6H_5CH(OH)\ CH_2N_3$$

The use of more vigorous reaction conditions with $NaBH_4$ results in the formation of aniline ($C_6H_5NH_2$) starting with benzoylazidomethane ($C_6H_5COCH_2N_3$).[6]

There have been reports on the conversion of organosulfonyl azides to organosulfonamides. Probably the first report of sulfonyl azide reduction was by Reagen and Nickon[7] where the sulfonyl azides were converted to the sulfonamides by irradiation in 2-propanol in the absence of oxygen:

$$RSO_2N_3 + (CH_3)_2\ CHOH \xrightarrow{hv} RSO_2NH_2 + (CH_3)_2CO + N_2$$

Lee and Closson[8] also reported the conversion of a sulfonyl azide to the corresponding *N*,*N*-dimethylsulfonamide derivative, using sodium hydride (NaH) as the reducing agent in refluxing tetrahydrofuran(THF) in the presence of iodomethane.

In addition, Obafemi[9] reported that an azidosulfonyl-iminoindoline could be converted to its aminosulfonylimino-indoline derivative by catalytic hydrogenation.

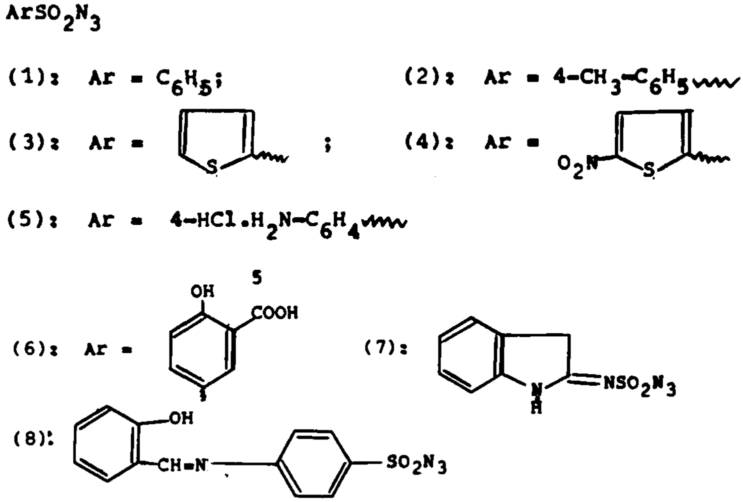
Also, Franco Rolla[10] reported the conversion of azides to amines using $NaBH_4$ under Phase-Transfer-Conditions (PTC), employing hexadecyltributylphosphosphonium bromide as the PTC reagent. In the work, 4-toluenesulfonyl azides was reduced to 4-toluenesulfonamide in about 94% yield.

The use of reducing agents containing tellerium (Te) element started recently and has been on the increase. For example, Uchida *et al.*[11] have recently used $NaBH_4$ and catalytic amount of Te to partially reduce 4-nitrobenzenes at room temperature.

In the present work, a study was undertaken to know the effect of $NaBH_4$ on various aromatic sulfonyl azides in the presence of catalytic amounts of Te and in various solvents at room temperature.

RESULTS AND DISCUSSION

The following aromatic-sulfonyl azides were studied:



The sulfonyl azides (1)–(6) were prepared by the treatment of the respective sulfonyl chlorides with sodium azide in aqueous acetone.[12] Compound (7) was prepared as reported earlier.[9] Compound (8) was prepared with the following scheme:

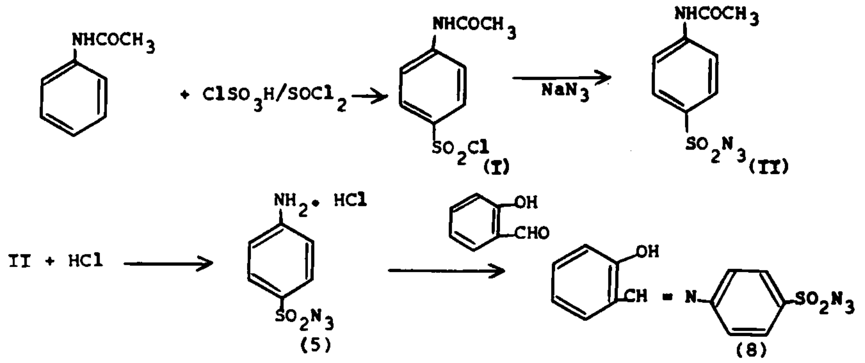


Table I shows the infrared data and some assignments for the sulfonyl azides. The functional groups, N_3, SO_2, NO_2, C=N, C=O, show their characteristic stretching frequencies in the expected regions.

Table II shows the reaction conditions and products of reduction. $NaBH_4$ reduces benzenesulfonyl- and 2-thiopohenesulfonyl azides to the corresponding sulfonamide, at room temperature without the use of Te within 20 minutes. Addition of Te only increases the yield slightly.

Nitration of 2-thiophenesulfonyl azide under reflux conditions gave a mixture of the 4-nitro- and 5-nitro-2-thiophenesulfonyl azide as yellow oil (see experimental section).

Reduction of the 5-nitro-2-thiophenesulfonyl azide in THF with $NaBH_4$ alone reduces the azido group, as monitored by ir. When the reduction was carried out in the presence of tellurium, both the azido absorption band at 2100 cm^{-1} and the nitro absorption band at 1380 cm^{-1} disappeared. New bands appeared at 3320 and

TABLE I

Infrared Data and Assignments for Sulfonyl Azides (1)–(8)

Compd No.	ν_{N_3}	ν_{as} S=O	ν_{sym} S=O	ν_{as} N=O	ν_{sym} N=O	$\nu_{C=O}$	$\nu_{C=N}$	ν_{S-N}	ν_{C-H}
1	2130	1370	1160						
2	2120	1380	1165						
3	2100	1360	1160						3080
4	2105	1365	1160	1570	1340				3080
5	2100	1370	1165					920	
6	2140	1365	1160			1690			
7	2140	1360	1160				1590(b)		
8	2108	1365	1155				1612		

TABLE II

Reaction Conditions and Products of Reaction

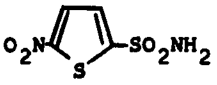
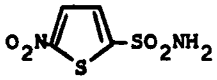
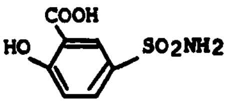
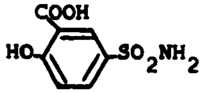
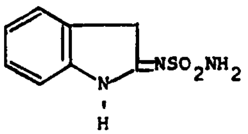
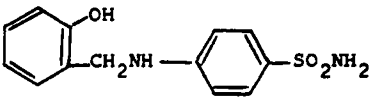
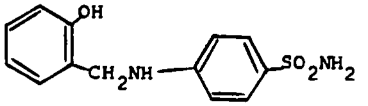
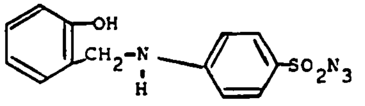
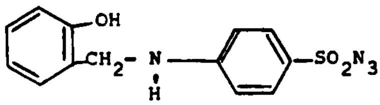
	Substrate (mmole)	$NaBH_4$ (mmole)	Te (mmole)	Temp.	Time (Min.)	Product	Yield[a,b] %
(1)	5.5	54.6	—	r.t	20	$PhSO_2NH_2$	75
(1)	5.5	54.6	0.55	r.t	20	$PhSO_2NH_2$	80
(1)	5.5	54.6	0.55	r.t	60	—	—[c]
(2)	5.1	51	—	r.t	60	$TolSO_2NH_2$	68
(2)	5.1	51	0.51	r.t	60	$TolSO_2NH_2$	85
(2)	5.1	51	0.51	r.t	60	—	—[c]
(3)	5.3	53	—	r.t	60	2-$ThSO_2NH_2$	77
(3)	5.3	53	0.53	r.t	60	2-$ThSO_2NH_2$	85
(3)	5.3	53	0.53	r.t	60	—	—[c]
(4)	4.3	43	—	r.t	60		78
(4)	4.3	43	0.43	r.t	60		86
(4)	4.3	43	0.43	r.t	60	—	—[c]
(5)	4.3	43	—	r.t	30	4-H_2N—$C_6H_4SO_2NH_2$	60
(5)	4.3	43	0.43	r.t	30	4-$H_2NC_6H_4SO_2NH_2$	85
(6)	8.2	82	—	r.t	30		68
(6)	8.2	82	0.82	r.t	30		88
(6)	8.2	82	0.82	r.t	30	—	—[c]
(7)	4.2	4.2	0.42	r.t	60		62

TABLE II (*Continued*)

	Substrate (mmole)	$NaBH_4$ (mmole)	Te (mmole)	Temp.	Time (Min.)	Product	Yield[a,b] %
(8)	3.3	33	—	r.t	30		55
(8)	3.3	33	0.33	r.t	30		90
(8)	3.3	33	—	r.t	30		82[c]
(8)	3.3	33	0.33	r.t	30		95[c]

[a] Isolated sulfonamide product.
[b] % yield in THF as solvent. Similar yields are obtained in DMSO, ethanol or isopropanol as solvents.
[c] Acetic acid as solvent.

3230 cm^{-1}, attributable to the NH_2 of sulfonamide group and a strong band at around 1305 cm^{-1} probably due to an overlap of both the NO_2 symmetric and SO_2 asymmetric stretching vibrations.

In the reduction of the Schiff base (8), reduction in acetic acid (AcOH) as solvent, with or without Te catalyst, left the azido group unaffected, while the imino group, (C=N), was reduced instantaneously (with the disappearance of the C=N absorption at 1612 cm^{-1} and appearance of the N—H absorption at 3340 cm^{-1}).

When the reaction was repeated using either EtOH or THF or DMSO as solvent instead of acetic acid, the C=N was reduced instataneously as observed with AcOH, but the azido group was also reduced (disappearance of bands at 1612 and 2108 cm^{-1} and appearance of N—H bands at 3380 (broad) and 3260 cm^{-1}).

On the other hand, the imino group in compound **7** was not affected in all the solvents (the broad band at 1590 cm^{-1} attributable to the $>C{=}NSO_2$— appeared in all the ir spectra of reduction products), only the azido group was reduced.

The azido group in all the sulfonyl azides (1)–(8) was not reduced in acetic acid as solvent even after prolonged stirring at room temperature. After about 24 h. a mixture of the starting sulfonyl azides and reduced sulfonamide product was obtained. This slow reaction may be due to the fact that acetic acid, which is present in excess, reacts with the $NaBH_4$.

EXPERIMENTAL

I.r spectra were recorded as potassium bromide discs on a Perkin-Elmer 727B spectrophotometer. The melting points were determined on a Gallenkamp instrument and represent uncorrected values. ^1H nmr spectra were determined with a Varian FT 80 machine.

All the chemical reactants used in this work were of reagent grade. The arylsulfonyl azides (1–3) were prepared by treating the corresponding sulfonyl chlorides with excess sodium azides in aqueous acetone.[12]

4- and 5-Nitro-2-thiophenesulfonyl azide, (**4**). Fuming nitric acid (55 mL) was added gradually from a dropping funnel to 2-thiophenesulfonyl azide (13.2 g, 70 mmole) with continuous stirring. There was an immediate green coloration. The mixture was then heated under reflux for 3 h., cooled and poured into crushed ice. The aqueous mixture was extracted with chloroform, washed with water, dried and evaporated to give light-yellow liquid (12.9 g). This was cooled in a freezer for 48 h. to give a small amount of light yellow needles (650 mg), which is the 4-nitro-2-thiophenesulfonyl azide, mp 52–54°C, (Found: C, 20.26; H, 0.91; N, 23.78. $C_4H_2N_4O_4S_2$ requires: C, 20.51; H, 0.86; N, 23.92). Nmr ($CDCl_3$): 8.69 (d, thiophene-5H), 8.38 (d, thiophene-3H). ν_{max} 3118 (C—H), 2140 (N_3), 1510, 1350 (NO_2), 1370, 1170 (SO_2) cm^{-1}.

The remaining light-yellow liquid is mainly the 5-nitro-2-thiophenesulfonyl azide (4), which did not crystallize upon long cooling. Nmr ($CHCl_3$): 7.78 (*d*, thiophene-3H), 7.20 (*d*, thiophene −4H). (Found: C, 20.30; H, 0.92; N, 23.70; $C_4H_2N_4O_4S_2$ requires: C, 20.51: H, 0.86; N, 23.92).

2-Hydroxy-5-Chlorosulfonylbenzoic acid. 2-Hydroxybenzoic acid (10 g, 72.5 mmole) was added portionwise to chlorosulfonic acid (54 mL) in a 150 mL flask, equipped with a condenser to which a gas trap was attached in an ice jacket. The mixture was heated to 70–80°C for 1½ h and then cooled in ice-water before pouring into a beaker containing crushed ice, to give crystals. This was filtered and dried. Yield = 11.1 g, 65%. Mp 161–163°C (lit.[13] mp 169–171°C).

2-Hydroxy-5-azidosulfonylbenzoic acid, (**6**). 2-Hydroxy-5-chlorosulfonylbenzoic acid (5.0 g, 21.1 mmole) was dissolved in acetone (50 mL) and sodium azide (2 molar equivalent) in water (5 mL) was added portionwise and the mixture stirred for about 5 h. The solvent was evaporated to afford the sulfonyl azide (4.5 g, 88%). Mp 176–179°C.

4-Acetamidobenzenesulfonyl azide. 4-Acetamidobenzenesulfonyl chloride (10.0 g, 43 mmole), prepared by treating acetanilide with chlorosulfonic acid and thionyl chloride, was dissolved in acetone (100 mL) and treated with sodium azide (8.4 g, 128 mmole) in water (10 mL). Acetone was distilled off and the resulting solid was filtered and dried to give the sulfonyl azide (9.2 g, 90%); mp 152–154°C. (Found: C, 39.81; H, 3.32; N, 23.25; $C_8H_8N_4O_3S$ requires: C, 40.00; H, 3.36; N, 23.32). ν_{max} 2131 (N_3), 1650 (C=O of amide), 1360, 1150 (SO_2) cm^{-1}.

4-Aminobenzenesulfonyl azide hydrochloride (**5**). 4-Acetamidobenzenesulfonyl azide (5.0 g, 21 mmole) and concentrated hydrochloric acid was heated under reflux for 1½ h and then cooled in ice until white crystals of compound **5** came out. This was filtered and dried under vacuum. Mp 166–168°C (dec.). (Found: C, 30.61; H, 3.00; N, 23.59; $C_6H_7ClN_4O_2S$ requires: C, 30.71; H, 3.01; N, 23.88).

N-[4-Azidosulfonylphenyl] Salicylideneimine (**8**). 4-Aminobenzenesulfonyl azide hydrochloride (1.0 g, 4.3 mmole was dissolved in a mixture of sodium acetate (0.7 g) and water 20 mL and alcohol (10 mL).

2-Hydroxybenzaldehyde (0.52 g, 4.3 mmole) was added and the whole mixture refluxed for 1 h. Upon cooling, a light-yellow precipitate was obtained (0.78 g, 61% yield). Mp 110–112°C (dec.) (Found: C, 51.60; H, 3.29; N, 18.98; $C_{13}H_{10}N_4O_3S$ requires: C, 51.65; H, 3.33; N, 18.85).

Typical Reduction Procedure:

Benzenesulfonyl azide (1.0 g, 5.5 mmole) was dissolved in tetrahydrofuran (or isopropanol or ethanol or dimethylsulfoxide) containing Te (70 mg, 0.55 mmole). The mixture was cooled in ice with stirring and sodium borohydride (2.1 g, 55 mmole) was added in small portions and stirring continued for about 20 min. at room temperature. Dilute H_2SO_4 was added to the mixture and then extracted with ether. The ether extract was washed with water and then dried with anhydrous sodium sulfate. Evaporation of the ether at room temperature afforded the pure white benzenesulfonamide.

Other products obtained, using similar procedure are: 2-Thiophenesulfonamide; mp 144–146° (lit.[12] 145–147°) 5-Nitro-2-thiophenesulfonamide; mp 134–136° (lit.[14] 136°) 4-Aminobenzenesulfonamide (identical with an authentic sample). 2-Hydroxy-5-sulfonamidobenzoic acid; mp 220–221 (dec.) (Found: C, 38.97; H, 3.18; N, 6.30; $C_7H_7NO_5S$ requires: C, 38.71; H, 3.25; N, 6.45). ν_{max} 3340, 3260 (N—H), 1670 (C=O), 1330, 1170 (SO_2) cm^{-1}.

2-Hydroxybenzyl(4′-azidosulfonylphenyl) amine; mp 98–100° (dec.). Found: C, 51.10; H, 3.82; N, 18.50; $C_{13}H_{12}N_4O_3S$ requires: C, 51.31; H, 51.10; N, 18.51). ν_{max} 3400 (broad, OH and NH), 2110 (N_3), 1350, 1150 (SO_2) cm^{-1}.

2-Hydroxybenzyl (4'-aminosulfonylphenyl) amine; mp 167–168°. (Found: C, 56.30; H, 5.28, N, 9.90; $C_{13}H_{12}N_2O_3S$ requires: C, 56.10; H, 5.07; N, 10.07). ν_{max} 3400 (broad), 3250 (OH, and NH), 1300, 1170 (SO_2) cm^{-1}.

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