Cyclic voltammetry studies on substituted arenesulfonhydrazides

J. Chem. Research (S), 2000, 6–7
J. Chem. Research (M), 2000, 0129–0149

Ulf Ragnarsson,[a]* Leif Grehn,[a] Hernani L.S. Maia[b] and Luis S. Monteiro[b]

[a] *Department of Biochemistry, University of Uppsala, Biomedical Center, PO Box 576, SE-751 23 Uppsala, Sweden*
[b] *Departamento de Quimica, Universidade do Minho, Gualtar, P-4700-320 Braga, Portugal*

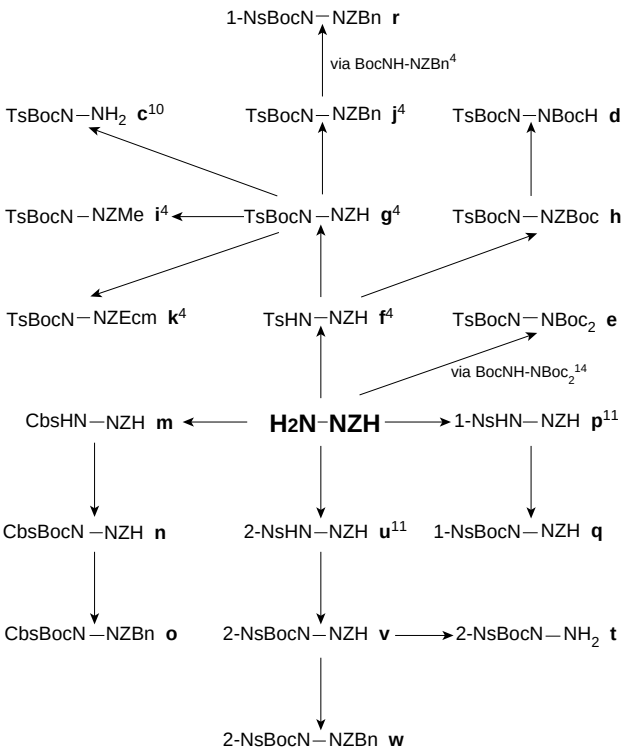
Additional Z and Boc groups on the vicinal nitrogen of sulfonyl hydrazines have no significant effect on the cathodic potential of the sulfonyl functions as measured by cyclic voltammetry, whereas a Boc group on the geminal nitrogen invariably gives rise to shifts of about 0.2 V to less negative potential similar to those previously observed for derivatives of amines.

In the course of work aiming at the synthesis of multisubstituted hydrazines, a large number of precursors, derivatives and analogues of ZNH-NTsBoc[4] **(1g)** (Z=benzyloxycarbonyl; Ts=4-toluenesulfonyl; Boc=*t*-butyloxycarbonyl) were prepared and a selection of them also studied with respect to the cleavage of their sulfonyl groups. Most of these studies were initially performed by cyclic voltammetry (CV), a technique recently explored in work dealing with sulfonamides and sulfonylcarbamates.[6] In the present paper complementing CV data related to the sulfonhydrazides **1a-w** are presented.

Several of the compounds **1b-w** have been described previously but most of them are novel ones, the syntheses of which are described in the full-text version of this publication. An overview of the synthetic transformations involving **1c–k**, **1m–r** and **1t–w** is presented in the following scheme:

The CV peak potentials *vs.* SCE (E_P) of the arenesulfonhydrazides **1a-w** are listed in Table 1.

A comparison between the data for **1a** and **1b** or **1f** shows that the introduction of Boc and Z groups on the vicinal hydrazine nitrogen of tosylhydrazine has no significant effect on E_P as measured in this system (vitreous carbon cathode with DMF as solvent and Bu_4NBF_4 as supporting electrolyte). Replacement of Ts in **1f** with 2-Ns **(1u)** results in a shift to less negative potential of 0.43 V, whereas 1-Ns **(1p)** and Cbs **(1m)** give rise to shifts of 0.45 and 0.53 V, respectively. Compounds such as **1f**, **1u**, **1p** and **1m** easily undergo chemoselective acylation with Boc_2O (1 equiv.) and catalytic amounts of 4-dimethylaminopyridine (DMAP) on their more acidic, geminal nitrogens.[4] The shifts for the products, **1g**, **1v**, **1q** and **1n**, are 0.21 V, 0.15 V, 0.30 V and 0.20 V, respectively, in comparison with the starting materials. Similar effects of geminal Boc substitution were recorded for **1c** (0.18 V) and **1d** (0.20 V) and in one case also of such benzyl substitution for **1l** (0.17 V). Many years ago Singer and Sharpless prepared a BocTs-amine derivative and demonstrated that the Boc-group shifted the electrochemical cleavage potential of tosyl by 0.25 V to a less negative potential.[7] The overall data for geminally Boc-substituted arenesulfonhydrazides are thus in good agreement with this result as well as with those recently reported for *tert*-butyl sulfonylcarbamates.[6] Further substitution on the vicinal



Scheme

Table 1 CV peak potentials for substituted arenesulfonhydrazides RSO_2NR^1-NR^2R^3

Compound	RSO_2	R^1	R^2	R^3	$-E_P$[a]/V (*vs* SCE)
1a	Ts	H	H	H	2.38
1b	Ts	H	Boc	H	2.38
1c[10]	Ts	Boc	H	H	2.20
1d	Ts	Boc	Boc	H	2.18
1e	Ts	Boc	Boc	Boc	2.14
1f[4]	Ts	H	Z	H	2.32
1g[4]	Ts	Boc	Z	H	2.11
1h	Ts	Boc	Z	Boc	2.06
1i[4]	Ts	Boc	Z	Me	2.16
1j[4]	Ts	Boc	Z	Bn	2.14
1k[4]	Ts	Boc	Z	Ecm[b]	2.11
1l	Ts	Bn	Boc	H	2.21
1m	Cbs[c]	H	Z	H	1.79
1n	Cbs[c]	Boc	Z	H	1.59
1o	Cbs[c]	Boc	Z	Bn	1.63
1p[11]	1-Ns[d]	H	Z	H	1.87
1q	1-Ns[d]	Boc	Z	H	1.57
1r	1-Ns[d]	Boc	Z	Bn	1.61
1s	2-Ns[e]	H	Boc	H	1.97
1t	2-Ns[e]	Boc	H	H	1.77
1u[11]	2-Ns[e]	H	Z	H	1.89
1v	2-Ns[e]	Boc	Z	H	1.74
1w	2-Ns[e]	Boc	Z	Bn	1.82
$Ts-NH_2$					2.52

[a]Cathode: vitreous carbon. Solvent: DMF. Supporting electrolyte: Bu_4NBF_4 0.1 mol dm^{-3}. Substrate conc. ~0.005 mol dm^{-3}. [b]Ecm=ethoxycarbonylmethyl.[7] [c]Cbs=4-cyanobenzenesulfonyl (*Chem. Commun.*, 1997, 1381). [d]1-Ns=1-naphthalenesulfonyl. [e]2-Ns=2-naphthalenesulfonyl.

* To receive any correspondence.
Fax: +46 18 55 21 39; E-mail:urbki@bmc.uu.se

nitrogen with Boc **(1e** and **1h)**, benzyl **(1j**, **1o**, **1r** and **1w)** and other groups **(1i** and **1k)** induced only insignificant shifts in CV peak potentials.

Differences in cathodic potentials such as those presented here were the basis for selective electrolytic cleavage of one tosyl from ditosylated, mixed primary/secondary diamines.[12] Such differences between tosylamides and the corresponding *tert*-butyl tosylcarbamates also seem to explain why the latter are cleaved by magnesium in anhydrous methanol.[13] Based on these experiences we therefore predict that milder, more selective reductive conditions are in sight not only for compounds of the type studied above but also for ordinary sulfonamides and other protective groups, the electron affinity of which can be measured by CV.

This work was supported by the Swedish Natural Science Research Council (NFR) and the Fundaçao para a Ciência e a Tecnologia (Portugal). U.R. thanks the RSC for a journals grant for international authors.

Techniques used: Cyclic voltammetry, ^{1}H and ^{13}C NMR (data on all new compounds).

References: 15

Schemes: 2

Figure 1: CV of arenesulfonylhydrazines

Received, 18 August 1999; accepted, 14 October 1999
Paper 9/06709D

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