Acta Chemica Scandinavica B 32 (1978) 31—35

Cathodic Cleavage of α-Benzenesulfonylnitriles

BO LAMM and KJELL ANKNER

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg, Sweden

The cathodic reduction of a series of α-benzenesulfonylnitriles comprising benzenesulfonylacetonitrile and seven α-substituted alkyl and aryl derivatives thereof has been studied at mercury in *N*,*N*-dimethylformamide solution. Polarographic half-wave potentials and preparative electrolysis product distributions are given. The compounds all undergo cleavage to yield benzenesulfinate ion and mononitriles, with the exception of the α-phenylsubstituted one, which also gives some dinitrile. The latter product is thought to result from dimerization of the radical formed in a one-electron process.

The cathodic reduction of α-sulfonylnitriles has never been investigated. A related class of compounds, the β-ketosulfones, has been studied electrochemically by Lamm and Samuelsson.[1–3] In weakly alkaline (pH 8) aqueous *N*,*N*-dimethylformamide (DMF), β-ketosulfones were found to yield ketones *via* cleavage of a carbon-sulfur bond. The behaviour in acidic solution was not investigated.

Simple nitriles may be cathodically reduced to amines in acidic solution.[4] A different type of reaction, loss of cyanide ion through carbon-carbon bond cleavage, has been observed under conditions involving solvated electrons.[5] Since sulfones generally undergo carbon-sulfur bond cleavage,[5] it is reasonable to assume that α-sulfonylnitriles will yield nitriles upon cathodic cleavage according to the reaction

$$R^1SO_2CR^2R^3CN + 2e^- + H^+ \rightarrow R^1SO_2^- + CHR^2R^3CN.$$

However, the presence of two electroactive groups in the same molecule can sometimes lead to surprises. For example, benzonitriles of the type *p*-$RCOC_6H_4CN$ (R = H or CH_3) have been shown [4] to undergo reduction to benzylamines in sulfuric acid solution, even though the carbonyl group is generally more easily reduced than the cyano group. We therefore felt that a study of some α-sulfonylnitriles would be worth while.

The compounds chosen for study can be represented by the formula $PhSO_2CHRCN$, where R = H, Me, Et, Pr, Bu, Ph, and Bzl. Also, the disubstituted compound $PhSO_2C(Et)_2CN$ was included. For the synthesis of the α-Et, α-Pr, and α-Bu compounds, ion-pair alkylation [7] was employed. Separation of the monoalkyl compounds from their non- and dialkylated analogues was difficult, requiring chromatography on silica gel.

RESULTS AND DISCUSSION

Polarography. Half-wave potentials, obtained at a dropping mercury electrode, are given in Table 1. The supporting electrolyte was 0.4 M tetraethylammonium perchlorate (TEAP) in DMF, and a silver iodide-coated silver wire in 0.1 M tetrabutylammonium iodide (TBAI) was used as a reference electrode.[8] Methyl phenyl sulfone, which is known [8] to give an irreversible two-electron wave under these conditions, was included for comparison. Since the diffusion coefficients for the compounds studied should be similar, it could be concluded from the data obtained that they all give irreversible two-electron waves except for compound *5*, which gives an apparent one-electron wave. The reason for this is that the substrate is acidic enough to serve as its own proton donor. Half of the material reaching the mercury electrode is reduced in a two-electron process, and the other half is rendered electroinactive by con-

Table 1. Polarographic half-wave potentials *vs.* Ag,AgI/0.1 M TBAI in DMF. Substrate conc. 5×10^{-4} M, supporting electrolyte 0.4 M TEAP in DMF.

Compound		$E_{1/2}$/V
$PhSO_2CH_2CN$	(*1*)	−1.42
$PhSO_2CH(Me)CN$	(*2*)	−1.41
$PhSO_2CH(Et)CN$	(*3a*)	−1.39
$PhSO_2CH(Pr)CN$	(*3b*)	−1.42
$PhSO_2CH(Bu)CN$	(*3c*)	−1.42
$PhSO_2C(Et)_2CN$	(*4*)	−1.45
$PhSO_2CH(Ph)CN$	(*5*)	−1.15 [a]
$PhSO_2CH(Bzl)CN$	(*6*)	−1.12
$PhSO_2Me$		−1.93
$PhSO_2Bzl$		−1.80

[a] Wave height in the absence of phenol half of that of all the other compounds.

version to its conjugate base. When phenol is added as a proton donor, the wave height of *5* is doubled.

For the other compounds, there is no change in the wave height or the half-wave potential when phenol is added. This indicates that the potential-determining step cannot contain a proton from the medium, a behaviour shared by methyl phenyl sulfone.[8] No second wave is observed.

The α-benzenesulfonylnitriles are easier to reduce than methyl phenyl sulfone and benzyl phenyl sulfone (Table 1), and they have far more anodic half-wave potentials than simple nitriles. For example, benzonitrile in DMF has $E_{1/2} = -2.74$ *vs.* $Ag/AgClO_4$.[4] The currents are diffusion controlled, as was found by studying the influence of the mercury pressure.[9]

The change in half-wave potential is small when the carbon is substituted with one or two alkyl groups. However, when there is a phenyl or a benzyl group in the α position, reduction is easier. The cleavage mechanism involves the initial formation of a radical anion, which undergoes fragmentation to a radical and a sulfinate ion. Stabilization of the incipient radical by the substituent is possible both for *5*, in which a benzylic radical is formed, and *6*, involving a β-phenethyl radical. The relative stability of the latter type of radical is well documented in the literature.[10]

Electrolyses. Some of the compounds were reduced at mercury under potentiostatic conditions in DMF solution with TEAP as the supporting electrolyte. Phenol was present as a proton donor. The reaction products were identified by GLC and/or ^1H NMR analyses. Table 2 summarizes the results.

All the compounds undergo cleavage between the sulfonyl group and the α carbon atom, giving a nitrile and benzenesulfinate ion. In some, but not all, cases, the formation of the latter anion was verified by alkylation to methyl phenyl sulfone after the electrolysis.

Substrate *1* gives acetonitrile and benzenesulfinate ion. The acetonitrile was identified *via* GLC, but no quantitative determination was made because of the difficulty in separating it from diethyl ether. The benzenesulfinate ion was converted to methyl phenyl sulfone with methyl iodide. This reaction is almost quantitative,[11] and the yield of sulfone therefore represents that of sulfinate ion.

Other possible products from *1* could have been β-(benzenesulfonyl)ethylamine from reduction of the cyano group, or methyl phenyl sul-

Table 2. Results from preparative electrolyses in DMF containing TEAP and phenol.

Compound		E/V [a]	F mol^{-1} [b]	Percent yield of $MeSO_2Ph$	Nitrile
$PhSO_2CH_2CN$	(*1*)	−1.60	2.5	64	− [c]
$PhSO_2CH(Me)CN$	(*2*)	−1.60	2.2	− [d]	75
$PhSO_2C(Et)_2CN$	(*4*)	−1.55	3.1	58	86
$PhSO_2CH(Ph)CN$	(*5*)	−1.40	1.1	− [d]	45; 30 [e]
$PhSO_2CH(Bzl)CN$	(*6*)	−1.35	1.5	48	58

[a] Cathode potential *vs.* Ag,AgI/0.1 M TBAI in DMF. [b] Electricity consumption. [c] Not quantitatively determined. [d] No alkylation performed in this run. [e] Yields of $PhCH_2CN$ and PhCH(CN)CH(CN)Ph, respectively.

fone from loss of the cyano group. No amine was detected, which is not surprising; the acidity of the medium was far too low to allow protonation of the cyano group. The observed coulometry also contradicts this reaction mode, since reduction to amine is a four-electron process.

No conclusion could be drawn about the possible cyanide loss, since methyl phenyl sulfone was present from alkylation of benzenesulfinate ion. Therefore, the electrolysis was repeated, this time omitting the alkylation step. No methyl phenyl sulfone was present in the catholyte, which precludes a cathodic cleavage at the cyano group.

Compound *2* gave propionitrile and benzenesulfinate as the exclusive products. The higher homologs were not tried in preparative runs. The diethyl compound, *4*, was electrolyzed to yield diethylacetonitrile and benzenesulfinate ion. For reference purposes, diethylacetonitrile was independently synthesized from 3-chloropentane and sodium cyanide.

For *5*, the electricity consumption was 1.1 F mol^{-1} although phenol was present as a proton donor (compare the polarographic value of $n=2$). The products were benzyl cyanide and the dimeric product *meso*-2,3-diphenylsuccinonitrile. The formation of dimer is thought to be a consequence of the relative stability of the intermediate, a benzylic radical. The possibility that the dimer is produced *via* an S_N2 attack of a carbanion on *5*, benzenesulfinate acting as a leaving group, cannot be excluded but appears unlikely.

Compound *6* was found to give dihydrocinnamonitrile but no dimer. For identification, dihydrocinnamonitrile was independently synthesized from 2-chloroethylbenzene and sodium cyanide. The electricity consumption was less than 2 F mol^{-1}, so that the absence of dimer is surprising.

The alkylation of *1* gives mixtures of non-, mono-, and dialkylated products, which are difficult to separate. This detracts from the synthetic usefulness of the method.

To summarize, it has been shown that α-benzenesulfonylnitriles are exclusively cleaved between the sulfonyl group and the α carbon atom upon cathodic reduction at mercury in DMF solution containing phenol.

EXPERIMENTAL

Syntheses

Benzenesulfonylacetonitrile (1). To a suspension of 164 g (1 mol) of sodium benzenesulfinate in 600 ml of DMF at 80 °C was added 82 g (1.1 mol) of freshly distilled chloroacetonitrile at such a rate that the temperature did not exceed 80 °C. The reaction mixture was stirred at the same temperature for 3 h. After cooling, the sodium chloride was filtered off and the DMF was evaporated *in vacuo*. The crude product was recrystallized three times from ethanol. Yield 80 g (45 %), m.p. 112 °C, lit.[12] 114 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 4.12 (2 H, s), 7.5–8.1 (5 H, m).

2-Benzenesulfonylpropionitrile (2). Using the same procedure as above, this compound was prepared in 54 % yield from 2-chloropropionitrile, m.p. 69–70 °C, lit.[13] 72 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.67 (3 H, d, J 7.0 Hz), 3.95 (1 H, q, J 7.0 Hz), 7.5–8.1 (5 H, m). The 2-chloropropionitrile was prepared in 25 % overall yield from 2-chloropropionic acid *via* conversion to the amide and dehydration with diphosphorus pentoxide.[14]

2-Benzenesulfonylbutyro-, valero-, and capronitrile (3a–c). Alkylation of *1* with ethyl-, propyl-, and butyl iodide, respectively, was performed in dichloromethane–water using ion-pair extraction with tetrabutylammonium as the cation,[7] the reaction mixtures being stirred for 3 h. In each run, 4.5 g (25 mmol) of *1* was employed. The crude reaction products were chromatographed on a silica gel column. The eluent was toluene, which was gradually changed to dichloromethane. The eluate was continuously analyzed with a Pye LCM 2 flame ionization detector. The monoalkyl compounds *3a–c* thus obtained were colourless oils. The pure fractions represented only 10–20 % yield. ^{1}H NMR (60 MHz, $CDCl_3$): *3a*, δ 1.13 (3 H, t, J 7.5 Hz), 2.0 (2 H, m), 3.97 (1 H, dd, J 5.0 and 9.5 Hz), 7.5–8.1 (5 H, m); *3b*, δ 1.0 (3 H, t, J 6.0 Hz), 1.75 (4 H, m), 3.97 (1 H, dd, J 5.0 and 9.5 Hz), 7.5–8.1 (5 H, m); *3c*, δ 1.0 (3 H, t, J 5.5 Hz), 1.2–2.4 (6 H, m), 3.97 (1 H, dd, J 5.0 and 10.0 Hz), 7.5–8.1 (5 H, m).

2-Benzenesulfonyl-2-ethylbutyronitrile (4). Using ion-pair alkylation,[7] this time with a twofold excess of ethyl iodide, the compound was prepared in 54 % yield, m.p. 74–76 °C, lit.[15] 78 °C. The compound could also be prepared through conventional alkylation in THF, sodium hydride being used as a base. Yield 42 %, same m.p. as above. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.26 (6 H, t, J 7.5 Hz), 1.98 (4 H, q, J 7.5 Hz), 7.5–8.1 (5 H, m).

2-Benzenesulfonyl-2-phenylacetonitrile (5). Bromination of benzyl cyanide in 0.1 mol scale yielded the α-bromo derivative.[16] Due to its lachrymatory properties, the crude product was not distilled but directly used in the next step.

Thiophenol, 14.3 (0.13 mol), and potassium hydroxide, 7.3 g (0.13 mol), were dissolved in 100 ml of 95 % ethanol. Solid potassium carbonate, 5 g, was added. The mixture was heated to 50 °C, and the crude bromobenzyl cyanide was added dropwise during 1 h. The mixture was allowed to reflux for 2 h and was then diluted with 200 ml of water. The ethanol was evaporated *in vacuo* and the residue was extracted with chloroform. After washing and evaporation, 14 g of an oil remained. This was dissolved in 150 ml of glacial acetic acid, and 25 ml of 30 % hydrogen peroxide (about 0.25 mol) was added, whereupon the solution was heated to 60 °C for 3 h. It was then diluted with water and extracted with ether, the ether solution washed with water, dried over anhydrous sodium sulfate, filtered and evaporated and the residue recrystallized from ethanol. Yield 7.5 g (29 %) of colourless crystals, m.p. 147–148 °C, lit.[17] 148–150 °C. ^{1}H NMR (60 MHz, $CDCl_3$); δ 5.18 (1 H, s), 7.2–7.5 (5 H, m), 7.5–8.1 (5 H, m). In Ref. 17, the compound is only obtained as a by-product.

2-Benzenesulfonyl-2-benzylideneacetonitrile. A solution of 4.5 g (25 mmol) of *1*, 2.7 g (25 mmol) of freshly distilled benzaldehyde and 2 g of ammonium acetate in 75 ml of absolute ethanol was boiled under reflux for 10 min and allowed to stand for a few hours. The crystalline precipitate was filtered off and recrystallized from ethanol. Yield 3.7 g (55 %), m.p. 137 °C, lit.[18] 137–138 °C.

2-Benzenesulfonyl-2-benzylacetonitrile (6). Of the preceding compound, 3 g (11 mmol) were dissolved in 100 ml of ethanol and a few drops of conc. hydrochloric acid. Hydrogenation over 100 mg of 10 % palladium on charcoal in a Parr apparatus at an initial pressure of 0.35 MPa required 24 h. The solution was filtered and evaporated to dryness. Yield 3 g (100 %), m.p. 75 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 3.27 (2 H, m), 4.20 (1 H, dd, J 4.0 and 11.5 Hz), 7.22 (5 H, s), 7.5–8.1 (5 H, m).

Polarography

The DMF was purified as described earlier.[19] Tetraethylammonium perchlorate (TEAP) was prepared from the bromide by precipitation with sodium perchlorate in aqueous solution. The crude product was recrystallized five times from water and preelectrolyzed at a mercury pool to remove polarographically active impurities (*e.g.*, sodium ion).

A three-electrode polarograph similar to the Heath Model EUW 401 was used. The substrate concentration was 5×10^{-4} M, and that of TEAP, 0.4 M.

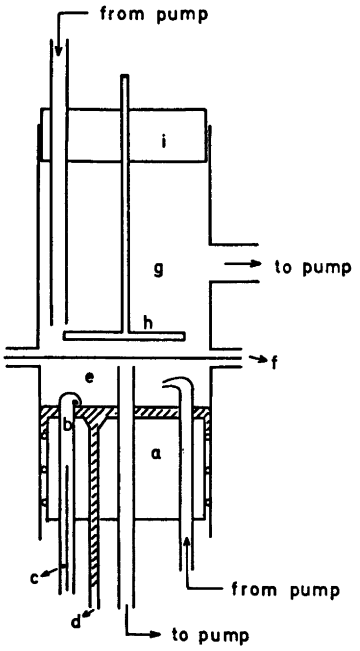

Fig. 1. Electrochemical cell. *a*, Teflon plug with sealing O-rings; *b*, reference electrode; *c*, silver wire; *d*, stainless steel tube, also serving as electrical connection; *e*, cathode compartment; *f*, ion-exchange membrane; *g*, anode compartment; *h*, stainless steel anode; *i*, cork stopper.

Electrolyses

A divided cell, constructed in this laboratory, was used. It is schematically shown in Fig. 1. The cell was constructed from two flat-flange joints, between which a cation exchange membrane (Amfion C-311) was clamped. The cathode surface was 20 cm^2. A Teflon plug with suitable entry and exit holes was used as a support for the mercury cathode. Sealing to the glass tube was provided by Viton O-rings.

The catholyte was circulated with a Normag all-glass centrifugal pump *via* an intermediate storage vessel, not shown in Fig. 1. The pumping speed could be adjusted so that the mercury surface did not wobble too much. The minimum useable catholyte volume was 80 ml. Electrical contact with the mercury was provided by a stainless steel tube which also served to introduce and drain the mercury. The reference electrode had a bent tip with a capillary hole and could be filled with 0.1 M TBAI solution in DMF. It also contained a silver iodide-coated silver wire.

The anode was a stainless steel disk, and the anolyte was circulated with a second pump. The interelectrode distance was typically 10

mm, including the membrane. With 0.2 M TEAP solution in DMF in both compartments, the overall cell resistance was 20 Ω. For comparison, 0.5 M aqueous sodium hydroxide solution in the same cell showed about 0.5 Ω resistance.

A 15 A/30 V potentiostat, built in this laboratory, was used. It also included an integrator and an oscilloscope to check the system for stability.[20]

In all runs, the supporting electrolyte concentration was 0.2 M. The amount of substrate used in each run was 1 – 1.5 g, and 1 g of phenol was added as a proton donor. The anolyte was 0.2 M TEAP in DMF, to which 5 – 10 % (by volume) dimethyl sulfoxide had been added as a depolarizer. In the course of electrolysis, this was oxidized to dimethyl sulfone. After preelectrolysis, the substrate was added. The initial current was about 0.4 A, and the experiments were run to exhaustion, about 2 h.

Two different methods of work-up were used. *A*: To the catholyte was added 10 ml of methyl iodide, and the solution was kept at 50 °C for 2 h. It was then diluted with a large volume of water and extracted with ether. The organic phase was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The residue was analyzed by GLC and ^{1}H NMR. *B*: The alkylation with methyl iodide was omitted, otherwise the work-up was as in *A*.

Identification was easy since all mononitriles formed were available either as commercial samples or *via* independent syntheses. The *meso*-2,3-diphenylsuccinonitrile from *5* had m.p. 220 – 222 °C, lit.[21] 238 – 239 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 4.91 (2 H, s), 7.38 – 7.45 (10 H, m). For comparison, *racem.*-2,3-diphenylsuccinonitrile has [22] m.p. 164 °C.

Acknowledgements. We wish to thank Professor Lars Melander for his helpful criticism. A grant from the Swedish Natural Science Research Council defrayed the cost of chemicals and some pieces of equipment.

REFERENCES

1. Lamm, B. and Samuelsson, B. *Acta Chem. Scand. 24* (1970) 561.
2. Lamm, B. and Samuelsson, B. *Chem. Commun.* (1970) 1010.
3. Samuelsson, B. and Lamm, B. *Acta Chem. Scand. 24* (1970) 3070.
4. Manousek, O. and Zuman, P. *Chem. Commun.* (1965) 158.
5. Arapakos, P. G. and Scott, M. K. *Tetrahedron Lett.* (1968) 1975.
6. Horner, L. and Neumann, H. *Chem. Ber. 98* (1965) 1715.
7. Brändström, A. and Junggren, U. *Tetrahedron Lett.* (1972) 473.
8. Simonet, J. and Jeminet, G. *Bull. Soc. Chim. Fr.* (1971) 2754.
9. Fry, A. J. *Synthetic Organic Electrochemistry*, Harper and Row, New York 1972, p. 62.
10. Wilt, J. W. In Kochi, J. K., Ed., *Free Radicals*, Wiley, New York 1973, Vol. 1, pp. 345 – 356.
11. Meek, J. S. and Fowler, J. S. *J. Org. Chem. 33* (1968) 3422.
12. Tröger, J. and Hille, W. *J. Prakt. Chem.* [2] *71* (1905) 201.
13. Tröger, J. and Wunderlich, X. *Arch. Pharm. (Weinheim, Ger.) 253* (1915) 219.
14. Gattermann, L. *Die Praxis des Organischen Chemikers*, 41. Ed., Walter de Gruyter, Berlin 1962, p. 125.
15. Tröger, J. and Vasterling, P. *J. Prakt. Chem.* [2] *72* (1905) 323.
16. Robb, C. M. and Schultz, E. M. *Org. Synth. Coll. Vol. III* (1955) 347.
17. Dodson, R. M. and Turner, H. W. *J. Am. Chem. Soc. 73* (1951) 4517.
18. Balasubramanaian, M. *Synthesis of β-amino, α,β-unsaturated and bis-(aminoaryl) sulphones*, Diss., Annamalai University Annamalai 1954.
19. Lamm, B. and Simonet, J. *Acta Chem. Scand. B 28* (1974) 147.
20. Lamm, B. and Ankner, K. *Acta Chem. Scand. B 31* (1977) 375.
21. Davis, R. B. and Ward, J. A., Jr. *Org. Synth. Coll. Vol. IV* (1963) 392.
22. *Beilsteins Handbuch der organischen Chemie*, II. Erg.w. *9*, p. 667.

Received June 13, 1977.