Tetrahedron Letters, Vol.30, No.7, pp 815-816, 1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

ISOLATION OF UNSYMMETRICAL DISULPHIDES AND TRISULPHIDES AS BY-PRODUCTS IN THE COURSE OF ELECTROCHEMICAL REDUCTION OF DITHIOLE-THIONES.

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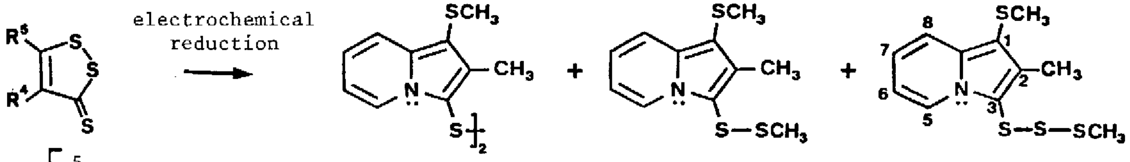
Abstract - Unsymmetrical disulphides and trisulphides were obtained after electrochemical reduction of 1,2-dithiole-3-thiones in N,N dimethylformamide as by-products in addition to the major symmetrical disulphide.

In a previous paper[1], we reported the electrochemical reduction of 1,2-dithiole-3-thiones (1, 2, 3) in N,N-dimethyformamide. These compounds underwent a reversible 1-electron addition affording thiyl anion radicals. These latters were subsequently converted into ring-fused thiyl radicals which dimerized. Controlled potential electrolysis afforded a convenient route to the symmetrical disulphides (4, 7, 10) which were obtained in good yield.

However, relatively little attention has been given to the by-products due to the difficulties appearing during the course of isolation i.e., especially, chromatographic analyses.

The results we report show that use of preparative TLC[1] followed by reversed phase TLC (acetonitrile) permitted separation of compounds 5, 8, 11 and 6, 9, 12 as the unsymmetrical disulphides and the corresponding trisulphides (table).



1: R^5 = 2-pyridyl
R^4 = CH_3

4 5 6

The unsymmetrical disulphide electrochemically obtained[3] and the one isolated after reaction with thiolate ions[2] exhibit similar structural data (^{1}H N.M.R., mass and U.V.-visible spectra). Therefore, we are almost undoubtedly dealing with the same kind of product.

The use of MS-MS spectrometry[3] as an additional technique enabled us to establish the structure of compounds 6, 9 and 12. In support, a strong tendency was observed for the unsymmetrical disulphide and for the trisulphide to generate the corresponding symmetrical disulphide. Similar results were previously reported in the literature[4].

Although these by-products were obtained in relatively poor yield, their isolation is motivated by two reasons:

- Whereas the preparation of symmetrical trisulphides is straightforward and well documented[5-7], the synthesis of unsymmetrical trisulphides is more complex[4,8]. Furthermore, few trisulphides have been electrochemically isolated as yet[9].
- The presence of unsymmetrical disulphides and trisulphides are in agreement with the

occurrence of radical type reactions as established in the reaction pathway given in ref. 1.

Table: Products and yield of controlled potential electrolysis.

Starting material	Products	yield %
1: R^5= 2-pyridyl R^4= CH_3	4 5 6	55 15 15
2: R^5= 2-pyridyl R^4= $COOC_2H_5$	7 8 9	65 5 10
3: R^5= 2-pyrazinyl R^4= CH_3	10 11 12	55 5 10

References and notes

1 - M. Largeron, T. Martens and M.B. Fleury, J. Electroanal. Chem., 252, (1988), 99.

2 - M. Largeron, T. Martens and M.B. Fleury, Tetrahedron, 43, (1987), 3421.

3 - Mass spectrum of 5 (E.I.): m/z = 255 ($M^{+\cdot}$); m/z = 208 (M - SCH_3) 100%; m/z = 193 (M - SCH_3 - CH_3).
^{1}H N.M.R., 270 MHz, $CDCl_3$, δ: 2.20, 2.50, 2.55 {s, 3H, SCH_3 (1), CH_3 (2), SCH_3 (3)}, 6.75 {ddd, 1H, H (6), $J(H_6-H_7)$ = 7 Hz, $J(H_6-H_5)$ = 7 Hz, $J(H_6-H_8)$ = 1 Hz}, 7.00 {ddd, 1H, H (7), $J(H_7-H_6)$ = 7 Hz, $J(H_7-H_8)$ = 9 Hz, $J(H_7-H_5)$ = 1 Hz}, 7.75 {dd, 1H, H (8), $J(H_8-H_7)$ = 9 Hz, $J(H_8-H_6)$ = 1 Hz}, 8.45 {dd, 1H, H (5), $J(H_5-H_6)$ = 7 Hz, $J(H_5-H_7)$ = 1 Hz}.
Mass spectrum of 6 (E.I.): m/z = 287 ($M^{+\cdot}$); m/z = 240 (M - SCH_3); m/z = 208 (M - {S - SCH_3}) 100%; m/z = 193 (M - {S - SCH_3} - CH_3).
MS-MS: daughters of 287: m/z = 208
daughters of 208: m/z = 193 (208 - CH_3); 175 (208 - SH).
^{1}H N.M.R., 270 MHz, $CDCl_3$, δ: 2.20, 2.50, 2.60 {s, 3H, SCH_3 (1), CH_3 (2), SCH_3 (3)}, 6.75 {ddd, 1H, H (6), $J(H_6-H_7)$ = 7 Hz, $J(H_6-H_5)$ = 7 Hz, $J(H_6-H_8)$ = 1 Hz}, 7.00 {ddd, 1H, H (7), $J(H_7-H_6)$ = 7 Hz, $J(H_7-H_8)$ = 9 Hz, $J(H_7-H_5)$ = 1 Hz}, 7.80 {dd, 1H, H(8), $J(H_8-H_7)$ = 9 Hz, $J(H_8-H_6)$ = 1 Hz}, 8.45 {dd, 1H, H (5), $J(H_5-H_6)$ = 7 Hz, $J(H_5-H_7)$ = 1 Hz}.

4 - P.K. Singh, L. Field and B.J. Sweetman, J. Org. Chem., 53, (1988), 2608.

5 - D.N. Harpp, D.K. Ash, T.G. Back, J.G. Gleason, B.A. Orwig and W.F. Vanhorn, Tetrahedron Lett., 41, (1970), 3551.

6 - K. Sirakawa, O. Aki, T. Tsujikawa and T. Tsuda, Chem. Pharm. Bull., 18, (1970), 235.

7 - A.L. Schroll and G. Barany, J. Org. Chem., 51, (1986), 1866.

8 - A.W. Mott and G. Barany, Synthesis, 8, (1984), 657.

9 - Q.N. Porter, J.H.P. Utley, P.D. Machion, V.L. Pardini, P.R. Schumacher and H. Viertler, J. Chem. Soc. Perkin Trans 1, (1984), 973.

Acknowledgements: The authors thank Dr. B. MONEGIER DU SORBIER from RHONE-POULENC for mass spectra and fruitful discussions.

(Received in France 24 November 1988)