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REGIOSPECIFIC OXIDATIVE CYCLIZATION OF N-METHYLSULFONYLAMINES INTO PYRROLIDINES

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Summary : In the framework of the approach to remote oxidative functionalization of organic compounds of various classes, which is currently under exploration by us and which is based on reactions of element-centred free radicals, the regiospecific oxidative cyclization of N-methylsulfonylalkylamines 3 into N-methylsulfonylpyrrolidines 4 has been accomplished. The more facile isomerisation of intermediate sulfonamidyl radicals 8 with 1,5-H shift in comparison with their carboxamidyl analogues 16 is, in our opinion, the chemical proof of different electronic configurations of radicals 8 (σ structure) and 16 (predominantly π structure) generated under identical conditions using $Na_2S_2O_8$-$CuCl_2$ system.

INTRODUCTION

One of the most important methodological problems of organic synthesis is the elaboration of regioselective introduction of new functional groups thus providing new routes to various polyfunctional compounds. The prominent contribution to this field is made by reactions of one-electron oxidation proceeding via intermediate organic cation radicals and free radicals.

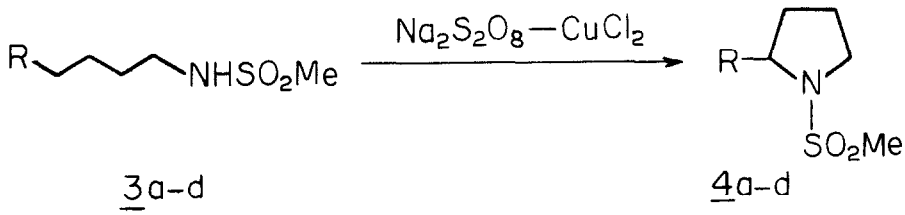
Our studies of transformations of element-centred organic radicals and cation radicals with odd electron at oxygen and nitrogen atoms[1-5] allowed to create general methods for remote regioselective functionalization of carbonyl compounds, whereupon a new substituent and the group in the final product are separated by a polymethylene chain.

The general principle of the approach is the initial generation of element-centred cation radicals upon one-electron oxidation of carbonyl compounds (ketones, and carboxylic acids and their derivatives). These cation radicals undergo a 1,5-H and 1,6-H shift[6,7] to rearrange, either directly (for ketones) or following deprotonation (for carboxylic acids and their derivates) into corresponding oxygen- and nitrogen-centred radicals. Intra- or intermolecular oxidative substitution in the latter affords final products of

RESULTS AND DISCUSSION

The photolytic rearrangement of N-chloroalkanesulfonamides into 3- and 4-chloroalkanesulfonamides[12,13] and cyclization of arenesulfonamides into sultams by addition of intermediate sulfonamidyl radicals to aromatic nucleus[14] seem to be the most remarkable intramolecular reactions of sultams.

We have found that N-methylsulfonylalkylamines (3a-d) under the action of $Na_2S_2O_8$-$CuCl_2$ system (molar ratio of 3:$Na_2S_2O_8$:$CuCl_2$=1:1:1) in aqueous medium at 90° undergo regiospececific cyclization into N-methylsulfonylpyrrolidines (4a-d)



3a-d 4a-d

R = H(a), Me(b), Et(c), Pr(d)

The efficiency of the formation of N-methylsulfonylpyrrolidines 4 increases on passing from 3a to 3b and then decreases from 3b to 3c,d (Table 1). Thus, although intramolecular oxidative cyclization of sulfonamides studied into sulfonylpyrrolidines is regiospecific since no other oxidation products were detected, its efficiency is to considerable extent dependent on the nature of C-4 substituent in the starting 3, the yield of 4 being lowest when this atom is primary in 3a and substantially increased when it is secondary in 3b-d. This influence of the substrate's structure on oxidative cyclization of 3 into 4 parallels that found for oxidative lactonization of alkanoic acids[2].

Table 1. Oxidation of N-methylsulfonylamines 3a-d in $Na_2S_2O_8$-$CuCl_2$*

Substrate	Conversion (%)	N-methylsulfonylpyrrolidine, yield (%) based on 3 converted (on the starting 3)
3a	27	4a, 82 (22)
3b	39	4b, 94 (37)
3c	37	4c, 71 (26)
3d	32	4d, 78 (25)

*90°C, 5 h, 3 (50 mmol), $Na_2S_2O_8$ (50 mmol), $CuCl_2 \cdot 2H_2O$ (50 mmol), 150 ml water.

In order to investigate the new regioselective oxidative cyclization of 3 into sulfonylpyrrolidines 4 in more details and to reveal some other oxidative systems which induce this cyclization, a study was made of the oxidation of 3c by means of $Na_2S_2O_8$ in presence of different salts (Table 2).

We have shown that the selectivity of oxidation of 3c is decreased when $CuCl_2$ is omitted or substituted by other salts listed. In the absence of $CuCl_2$

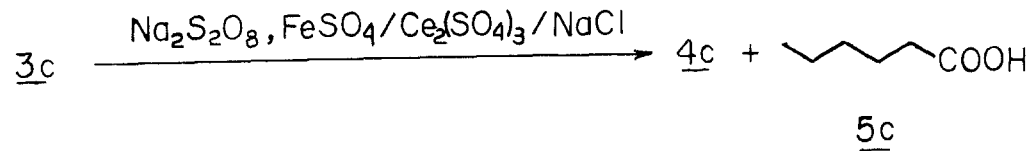
hexanoic acid 5c is formed together with 4c from 3c. Alteration of the $Na_2S_2O_8$-$CuCl_2$ ratio does not increase the yield of 4c.

Table 2. Oxidation of N-methylsulfonylhexylamine 3c in $Na_2S_2O_8$-M^nX_n*

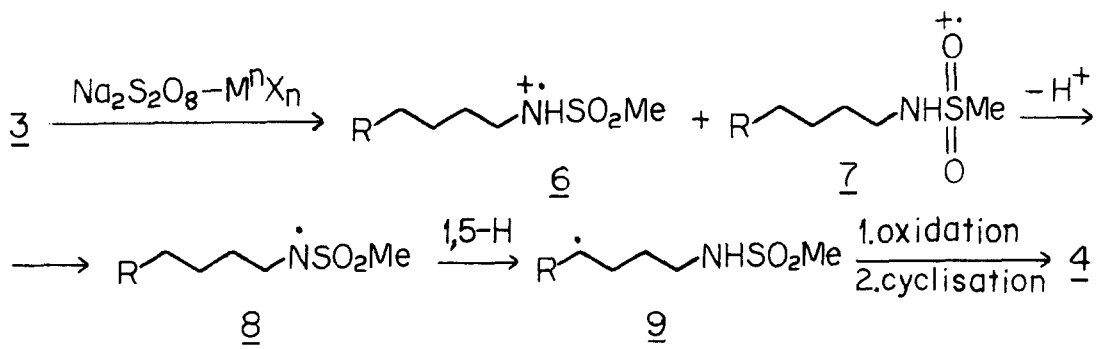
M^nX	Molar ratio $Na_2S_2O_8$:M^nX_n	Conversion of 3c (%)	Reaction products, yield (%) based on 3c converted (on the starting 3c)	
			(4c)	hexanoic acid (5c)
-	-	26	58 (15)	15 (4)
$CuCl_2$	1:1	37	71 (26)	-
$CuCl_2$	1:2	35	70 (24)	-
$CuCl_2$	2:1**	40	61 (24)	-
$FeSO_4$	1:1	24	33 (8)	40 (10)
$Ce_2(SO_4)_3$	1:1	15	30 (5)	5 (1)
NaCl	1:2	10	10 (1)	25 (3)

* 90°C, 5 h; 3c (50 mmol), $Na_2S_2O_8$ (50 mmol), 150 ml water.

** 100 mmol $Na_2S_2O_8$.

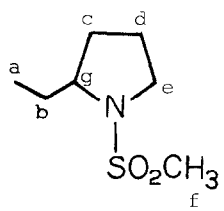


We suggest the mechanism of sulfonylpyrrolidines 4 formation involves one-electron oxidation of starting sulfonamides 3 by $Na_2S_2O_8$-M^nX_n systems to nitrogen-centred cation radicals (6a-d) or, less probably, to oxygen-centred cation radicals (7a-d). These cation radicals eliminate proton to give sulfonamidyl radicals (8a-d) which undergo a 1,5 H-shift to rearrange into C-centred 4-(methylsulfonylamino)alkyl radicals (9a-d). Oxidation of the latter to corresponding cations $R\overset{+}{C}H(CH_2)_3NHSO_2Me$ or N-methylsulfonyl-4-chloroalkylamines $RCHCl(CH_2)_3NHSO_2Me$ (in the presence of $CuCl_2$) and subsequent cyclization afford 4a-d.

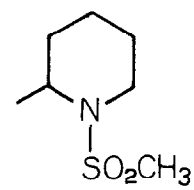


The highest yield of sulfonylpyrrolidine is obtained from 3b, oxidation of which produces 1-methyl-4-(methylsulfonylamino)butyl radical 9b stabilised due to conjugation with a CH_3-group and this is in agreement with the mechanism suggested. One could expect, due to analogues reasons, the isomerisation of the radicals 8b-d with competitive 1,6-H shift followed by oxidation and cyclization to provide 2-R-N-methylsulfonalpiperidines (10a-c) isomeric to 4b-d to be most probable for 8c that is the precursor of 4c or possibly of 10b.

Careful examination of a specimen of 4c was made with the use of ^1H n.m.r. spectroscopy with double homonuclear resonance (difference mode). Irradiation of a signal at 3.60 p.p.m. caused alterations in the region of 1.50-2.10 p.p.m., while the region of CH_3-resonances at 0.89-1.35 p.p.m. remained unaffected. Irradiation of a signal at δ = 0.89 caused a response in region δ = 1.50 solely. The signal at δ = 3.60 was not disturbed when a region of 1.10-1.35 (where the CH_3-C-group of 10b was expected of resonate) was irradiated. In our opinion these data rule out the formation of 10b together with 4c, thus the rearrangement of the sulfonamidyl radical 8c with 1,5-H shift proceeds with complete regiospecificity.

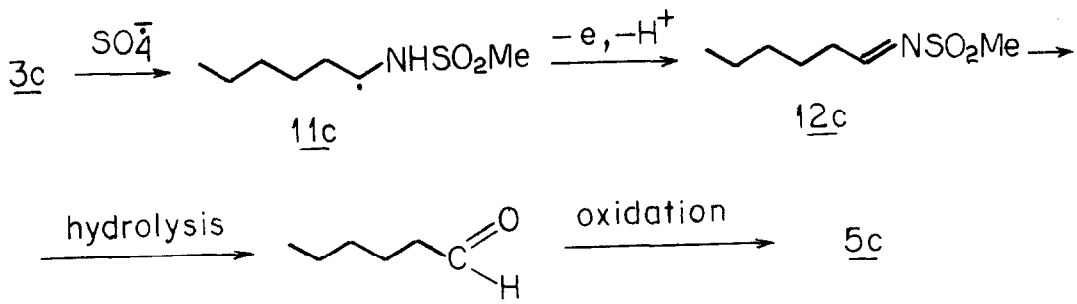


a	0.89	p.p.m.
b-d	1.50-2.10	p.p.m.
e	3.35	p.p.m.
f	2.75	p.p.m.
g	3.60	p.p.m.



4c 10b

One-electron oxidation in the systems without $CuCl_2$ (Table 2) is initiated in certain extent by the anion radicals $SO_4^{-\cdot}$[15]. Due to inherent electrophilic character they abstract H atom preferably from a methylene group in α-position to $NHSO_2Me$-group in 3c to produce the radical (11c) which is oxidized into imine (12c). The latter undergoes hydrolysis under the reaction conditions to give hexanal, oxidation of which then affords hexanoic acid 5c. A possibility of facile oxidation of aldehydes into acids in $Na_2S_2O_8$-containing systems has been demonstrated by us earlier[10].



An alternative pathway to 12c, namely, oxidative deprotonation of 8c, seems less probable because 5c was not detected among the products of oxidation of 3c in $Na_2S_2O_8$-$CuCl_2$, cupric ion being well-known to oxidize effectively organic radicals into unsaturated compounds.

Thus the oxidation studied of sulfonamides by means of $Na_2S_2O_8$-$CuCl_2$ is a rare example of completely regiospecific rearrangement of element-centred radicals.

It should be note that alkylamines themselves, $R(CH_2)_4NH_2$, are oxidized by this system into alkanenitriles $R(CH_2)_3CN$. In addition, alkanoic acids $R(CH_2)_3COOH$, 2,2-dichloroalkanals $R(CH_2)_2CCl_2CHO$ and 1-chloroalkanes $R(CH_2)_4Cl$ are formed as a result of oxidative deamination and chlorination[10]. No pyrrolidines which could possibly be formed upon Hoffmann-Löffler cyclization of aminyl radicals $R(CH_2)_4\dot{N}H$ (13) were detected[16,17].

Photolytic rearrangement of N-haloalkylacetamides into 4-haloalkylacetamides and subsequent base-induced cyclization into corresponding N-acetylpyrrolidines was reported[18]. At the same time low yields of products with functionalized acyl moiety were observed during photolysis of N-bromo-N-methylpentanamide[19]. It was concluded that the 1,5-H shift from N-alkyl moiety of carboxamides is more energetically favoured than that from an acyl moiety and was attributed to orbital and stereoelectronic control in intermediate carboxamidyl radicals with π electronic configuration[18].

Here we have shown that N-hexylacetamide (14) is almost inert towards $Na_2S_2O_8$-$CuCl_2$ system. Cyclization of N-methylpentanamide into γ-valerolactone in the same system was observed only with poor yield[2]. Comparison of our and literature data thus shows that the chemical behaviour of radicals $R(CH_2)_4\dot{C}ONCH_3$ (15) and $CH_3\dot{C}ON(CH_2)_4R$, (16) R=H or alkyl, depends in principle on the generation mode which obviously determines electronic configuration of these radicals. This is not unexpected since ESR studies and quantum-chemical calculations of carboxamidyl radicals have revealed them to exist in ground state in two electronic configurations π and σ [9,20-23], the former being more reactive with respect to intramolecular H-shift. It is quite probable that in the case of $Na_2S_2O_8$-$CuCl_2$ system and in some other cases when functionalization is absent or strongly inhibited, it is the σ form of the carboxamidyl radicals that is generated. The recently detected chemical nonequivalence of π and σ forms of acyloxyl radicals[24] supports this viewpoint.

Unlike carboxamidyl and acyloxyl radicals the sulfonamidyl radicals which are structurally similar to 8a-d exist exclusively in σ_N configuration as follows from ESR studies[25,26] and quantum chemical calculations[27]. This, obviously, determines their rather facile isomerization with 1,5-H shift in comparison with carboxamidyl radicals 15 and 16.

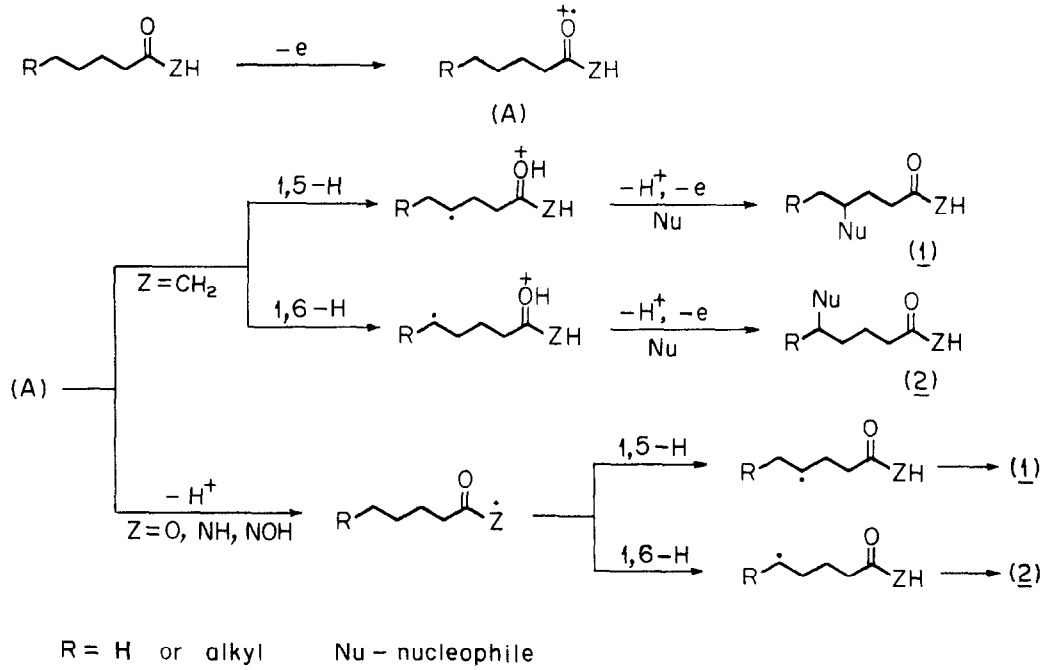
We suppose that the rearrangement with H-shift can be regarded as a chemical probe for electronic configuration of amidyl radicals of different types. Those posessing π configuration undergo rearrangement while for radicals with σ configuration this rearrangement is untypical.

Thus, it is the different electronic properties of N-centred radicals of three types, aminyl 13, carboxamidyl 15 and 16 and sulfonamidyl 9, generated under essentially identical conditions by the action of $Na_2S_2O_8$-$CuCl_2$ system upon respective substrates, that enabled the latter radicals to be used for regiospecific synthesis of sulfonylpyrrolidines 4.

Treatment of 4 with hydrobromic acid in the presence of phenol affords smoothly the corresponding 2-R-pyrrolidines (17a-d). This, together with the simplicity of conducting 3 → 4 oxidation, allows to consider the latter as a new, effective method for building the pyrrolidines ring.

The reaction studied is an additional example which illustrates the possibility of wide application of remote oxidative functionalization for organic synthesis.

oxidative functionalization. The known preference of radical rearrangements with 1,5-H shift determines the regioselectivity of a reaction and preponderance of γ-C-functionalized products. The regioselectivity of the process is also influenced to considerable extent by the nature of a carbonyl substrate to be oxidized.

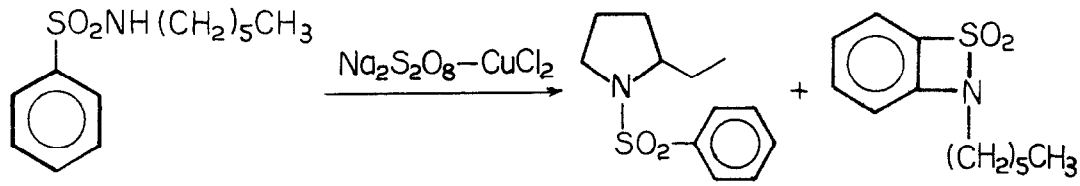


Direct, one-pot remote oxidations of ketones into 1,4- and 1,5-diketones were conducted with $Na_2S_2O_8$-$FeSO_4$[1], and those of alkanoic acids into γ- and δ-lactones with the $Na_2S_2O_8$-$CuCl_2$ system[2]. The latter oxidative system converts alkanehydroxamic acids, that are the precursors of N-centred hydroxyamidyl and O-centred amidoxyl radicals, into lactones and 3-chloroalkanoic acids[3]. Studies on diastereoselectivity of the oxidative lactonization of 3-methylpentanoic acid[4] and on stereochemistry of oxidative chlorination of cyclohexanecarboxylic acid[5] allowed to prove some steps of the mechanism of remote oxidative functionalization.

The simultaneous use of two powerful one-electron oxidants - sodium peroxydisulfate and cupric chloride - to induce the remote functionalization led to simplification of the existing synthetic methods. Thus, e.g. lactones can now be easily prepared from carboxamides in one-step[2], without recourse to the known three-step procedure which involves synthesis of N-halocarboxamides, their photolytic rearrangement, and subsequent hydrolysis[8,9].

As a development of these studies and investigations of oxidative transformations of nitrogen-centred radicals of various classes[2,3,10,11] we now report on directive oxidative cyclization of N-methylsulfonylalkylamines into N-methylsulfonylpyrrolidines.

Oxidative cyclization of N-phenylsulfonylhexylamine (18) with $Na_2S_2O_8$-$CuCl_2$ proceeds in two alternative pathways to give mixtures of N-phenylsulfonyl-2-ethyl-pyrrolidine (19) and the isomeric sultam, 1,1-dioxo-2-hexyl-1,2-benzothiazetidine (20) in 1:3 ratio, total yield of 19 and 20 being 90% based on sulfonylamine 18 converted, its conversion being 45%. The sultam 20 is obviously a product of intramolecular addition of intermediate sulfonamidyl radical to aromatic nucleus.



18 19 20

EXPERIMENTAL

G.l.c. analyses were carried out on LKhM-8MD chromatograph fitted with a flame-ionization detector. Columns used were 2000x3 mm with 1.5% PEG (mol. weight 20 000), treated with H_3PO_4 [28], on Chromosorb P-AW (120-140 mesh) and 3000x4 mm with 1% Carbowax 20M, treated with 3% Na_3PO_4 and 0.5% NaOH on Celite-545 (52-60 mesh). ^{1}H-NMR spectra were run for solutions in $CDCl_3$ and CCl_4 and recorded with a "Varian-DA 60 JL" (60 MHz) and a "Bruker WM-250" (250 MHz) spectrometer. Chemical shifts are presented in δ scale with tetramethylsilane (TMS) used as an internal standard. Mass spectra were obtained on a "Varian-MAT CH-6" instrument with a direct inlet system and ionizing voltage of 70 eV. IR-spectra were taken on a "Perkin-Elmer 577" spectrometer for thin layers and pellets with KBr.

$Na_2S_2O_8$ was a commercially available analytical grade sample; $CuCl_2$, NaCl, $FeSO_4$, $Ce_2(SO_4)_3$ were available reagent grade samples used without additional purification.

Synthesis of N-methylsulfonylalkylamines. General procedure. Methanesulfonylchloride (11.4g, 0.1 mol) was added dropwise to a vigorously stirred solution of 0.1 mol of an alkylamine and 0.1 mol of triethylamine in 50 ml of anhydrous ether at a rate providing gentle boiling of a reaction mixture. Then (after 0.5 h) the residue of triethylamine chlorohydrate was filtered off and the solution was evaporated. N-Methylsulfonylalkylamines thus obtained were purified by distillation in vacuo or recrystallization from ether.

N-Methylsulfonylamine 3a. Yield 81%; b.p. 103-104°/0.15 torr; m.p. (crystallized on standing) 21-29°; IR (film): 3285, 2960, 2935, 2870, 1470, 1430, 1415, 1380, 1320, 1150, 1080 cm^{-1}; ^{1}H NMR (CCl_4): 0.95(t, 3H), 1.20-1.70 (m, 4H), 2.90(c, 3H), 3.10(m, 2H), 5.45(t, 1H); MS: m/e (rel.int.): 152 (M^++1, 2), 151(M^+, 6), 136(11), 122(5), 110(30), 109(20), 108(100), 96(70), 80(13), 79(90).

N-Methylsulfonylpentylamine 3b. Yield 80%; b.p. 112-114°/0.1 torr.; m.p. (christallized on standing) 37°; ^{1}H NMR (CCl_4): 0.90(t, 3H), 1.10-1.60(m, 6H), 2.90(s, 3H), 3.10(m, 2H), 5.20(t, 1H); MS: m/e (rel.int.): 165(M^+, 4), 136(2), 110(10), 109(8), 108(100), 96(18), 86(7), 79(19), 70(29), 69(8).

N-Methylsulfonylhexylamine 3c. Yield 86%; m.p. 40° (from ether); ^{1}H-NMR (CCl_4): 0.91 (t, 3H), 1.25-1.70(m, 8H), 2.95(s, 3H), 3.10(m, 2H), 5.15(t, 1H); MS: m/e (rel.int.): 180(M^+, 7), 164(1), 150(1), 122(3), 110(40), 109(27), 108(100), 100(57), 96(90), 84(90), 79(57).

N-Methylsulfonylheptylamine 3d. Yield 83%; m.p. 58° (from ether); ^{1}H-NMR (CCl_4): 0.90 (t, 3H), 1.10-1.70(m, 10H), 2.90(s, 3H), 3.10 (m, 2H), 5.40 (t, 1H); MS: m/e (mol.int.): 194(M^++1, 38), 193(M^+, 7), 164(3), 150(6), 122(5), 114(80), 110(30), 109(40), 108(100), 96(40).

Oxidation of N-methylsulfonylalkylamines in $Na_2S_2O_8$-$CuCl_2$ system. General procedure: A solution of $Na_2S_2O_8$ (11.9 g, 0.05 mol) in water (50 ml) was added dropwise to a vigorously stirred mixture of 3 (0.05 mol) and $CuCl_2 \cdot 2H_2O$ (8.55 g, 0.05 mol) in water (100 ml) at 90°. The mixture was heated at the same temperature for 5h with vigorous stirring. On cooling the mixture was extracted with ether (2x100 ml) and chloroform (100 ml). The combined extracts were dried ($MgSO_4$), then evaporated, and the residue was analysed by ^{1}H-NMR and g.l.c. to determine the conversion of starting 3 and yield of 4 obtained. This residue was dissolved in toluene (100 ml) and treated with NaH, its amount being equivalent to that of the unreacted 3, to remove the starting sulfonamide 3 in form of its Na-salt. A mixture thus prepared was filtered, and removal of a solvent gave sulfonylpyrrolidine 4, its purity was confirmed by ^{1}H-NMR and g.l.c. Initial 3 was recovered upon acidification of its Na-salt and was quite suitable for repeated oxidation.

N-Methylsulfonylpyrrolidine 4a. From 7.55 g (0.05 mol) of 3a 1.63 g (0.011 mol) of 4a was formed, yield 82% for converted 3a, conversion 27% (^{1}H-NMR, g.l.c.). The residue obtained after treatment of this mixture of 3a and 4a with NaH (0.88 g, 0.037 mol) was crystallized from ether to afford 4a (1.55 g); m.p. 68-68,5° (lit.[30]:70-71°); IR (KBr-pellet): 2990, 2940, 2900, 1490, 1480, 1425, 1410, 1330, 1250, 1200, 1150, 1110, 1060, 1010 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 1.92 (m, 4H), 2.74 (s, 3H), 3.27 (m, 4H); MS: m/e (rel.int.): 150(M^++1, 30), 149(M^+, 100), 148(90), 134(21), 122(22).

N-Methylsulfonyl-2-methylpyrrolidine 4b. Viscous oil, yield 94% for converted 3b, conversion 39%. IR(film): 2965, 2935, 2875, 1465, 1420, 1380, 1330, 1250, 1200, 1150, 1125, 1055, 1020 cm^{-1}; ^{1}H-NMR($CDCl_3$): 1.15 (d, 3H), 1.70-2.10 (m, 4H), 2.70 (s, 3H), 3.20 (m, 2H), 3.67 (m, 1H); MS: m/e (rel.int.): 164(M^++1, 14), 163(M^+, 22), 162(13), 150(19), 149(28), 148(100), 136(7), 122(9), 108(5), 84(36).

N-Methylsulfonyl-2-ethylpyrrolidine 4c. Yield 71% for converted 3c, conversion 37%. M.p. 35° (from ether); IR (KBr-pellet): 2970, 2935, 2870, 1460, 1415, 1380, 1330, 1245, 1195, 1150, 1120, 1060, 1000 cm^{-1}; ^{1}H-NMR($CDCl_3$): 0.89 (t, 3H), 1.50-2.10 (m, 6H), 2.75 (s, 3H), 3.35 (m, 2H), 3.60 (m, 1H); MS: m/e (rel.int.): 178(M^++1,4), 177(M^+, 2), 162(5), 150(8), 149(10), 148(100), 136(2), 122(1), 108(2), 84(14).

N-Methylsulfonyl-2-propylpyrrolidine 4d. Viscous oil. Yield 78% for converted 3d, conversion 32%. IR (KBr-pellet): 2970, 2930, 2870, 1465, 1410, 1380, 1330, 1250, 1200, 1150, 1120, 1055, 1005 cm^{-1}; ^{1}H-NMR ($CDCl_3$): 0.95 (t, 3H), 1.20-2.10 (m, 8H), 2.72 (s, 3H), 3.32 (m, 2H), 3.64 (m, 1); MS: m/e (rel.int.): 192(M^++1, 3), 191(M^+, 13), 190(2), 176(5), 162(8), 150(42), 149(55), 148(100), 108(15), 84(20).

Oxidation of N-methylsulfonylhexylamine 3c by $Na_2S_2O_8$ in the absence and in the presence of $FeSO_4$, $Ce_2(SO_4)_3$ or NaCl. Interaction of 3c with the oxidants mentioned was performed according to the general procedure given above, the amount of salts added ($FeSO_4$, $Ce_2(SO_4)_3$ or NaCl) is presented in Table 2. After completion of the reaction the mixture was extracted with ether and chloroform, the combined extracts were dried ($MgSO_4$) and evaporated. The amounts of unreacted 3c as well as the yields of sulfonylpyrrolidine 4c and hexanoic acid 5c were determined by means of ^{1}H-NMR and g.l.c.

N-Hexylacetamide 14. Acetylchloride (12 g, 0.15 mol) was added dropwise at -5° for 0.5 h to a stirred mixture of hexylamine (12.6 g, 0.125 mol) and NaOH (5 g, 0.125 mol) in water (50 ml). The mixture was stirred for 0.5 h at 20°, heated 0.5 h at 50° and extracted with ether (3x100 ml). Extract was washed with water, dried ($MgSO_4$) and evaporated. Distillation of the residue afforded 14 (11 g, yield 64%), b.p. 152°/14 torr; IR(film): 3340, 3070, 1640 cm^{-1}; ^{1}H-NMR (CCl_4): 0.95 (t, 3H), 1.20-1.50 (m, 8H), 2.00 (s, 3H), 3.15 (m, 2H), 7.90 (t, 1H); MS: m/e (rel.int.): 143(M^+ 19), 128(19), 114(52), 100(33), 86(56), 73(84), 72(72), 60(60), 43(100), 44(86).

Interaction of N-hexylacetamide 14 with system $Na_2S_2O_8$-$CuCl_2$. A solution of $Na_2S_2O_8$ (11.9 g, 0.05 mol) in water (50 ml) was added dropwise at 90° to a mixture of 14 (7.15 g, 0.05 mol) and $CuCl_2 \cdot 2H_2O$ (8.55 g, 0.05 mol) in water (100 ml). The reaction mixture was kept at the same temperature for 5 h, on cooling extracted with ether (3x100 ml), extract was dried ($MgSO_4$) and evaporated. The residue contained only unreacted 14 (6.51 g), conversion 9%.

Cleavage of N-methylsulfonylpyrrolidines 4 to pyrrolidines 17. Cleavage of sulfonylpyrrolidines 4 was carried out on boiling with 48% HBr in the presence of phenol accordingly to[31], yields of pyrrolidines 17a-d 65-75%. Thus obtained: pyrrolidine (17a), b.p. 87°/750 torr; 2-methylpyrrolidine (17b), b.p. 100-101° torr, ^{1}H-NMR (CCl_4): 1.08 (d, 3H), 1.60-1.80 (m, 4H), 2.80 (t, 4H), 2.98 (m, 1H); 2-ethylpyrrolidine (17c), b.p. 124-126°/750 torr; 2-propylpyrrolidine (17d), b.p. 148°/750 torr.

N-Phenylsulfonylhexylamine 18. Benzenesulfonylchloride (5.3 g, 0.03 mol) was added dropwise to a solution of hexylamine (3.03 g, 0.03 mol) and triethylamine (3.03 g, 0.03 mol) in anhydrous ether (20 ml). After 2 h the mixture was filtered, filtrate evaporated, distillation of the residue afforded 18 (5.6 g, yield 85%), b.p. 149-150°/0.07 torr, which crystallized on standing, m.p. 22°; ^{1}H-NMR(CCl_4): 0.90 (t, 3H), 1.10-1.55 (m, 8H), 2.82 (m, 2H), 5.90 (t, 1H), 7.30-7.80 (m, 5H); MS: m/e (rel.int.): 241(M^+, 5), 198(1), 171(10), 170(100), 158(20), 140(80), 100(20), 77(68), 55(5), 51(14), 43(5).

Oxidation of N-phenylsulfonylhexylamine 18 in $Na_2S_2O_8$-$CuCl_2$ system were carried out analogously to the general procedure for the oxidation of N-methylsulfonylalkylamines 3. Reaction of 18 (4.82 g, 0.02 mol) with $Na_2S_2O_8$ (4.76 g, 0.02 mol) and $CuCl_2 \cdot 2H_2O$ (3.42 g, 0.02 mol) afforded a mixture, which contained 2.65 g (0.011 mole) of unreacted 18 (conversion 45%) and 1.94 g (yield 90% for converted 18) of a mixture of N-phenylsulfonyl-2-ethylpyrrolidine 19 and 1,1-dioxo-2-hexyl-1,2-benzothiazetidine 20 in a ratio 1:3 (based on g.l.c. and ^{1}H-NMR (250 MHz) spectral data). After treatment with NaH similarly to described above the mixture of 19 and 20 was obtained; MS: m/e 239(M^+); ^{1}H-NMR of 20 ($CDCl_3$): 0.95 (t, 3H), 1.70-2.00 (m, 6H), 3.25-3.35 (m, 2H), 3.60 (m, 1H), 7.50-7.85 (m, 5H); ^{1}H-NMR of 21 ($CDCl_3$): =.87 (t, 3H), 1.20-1.60 (m, 8H), 3.10 (t, 2H), 7.50-7.85 (m, 4H). The structure of 20 was confirmed by double homonuclear resonance which demonstrated that irradiation of the triplet at δ = 3.10 caused the response of the signal at 1.70 solely.

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