nese(II) sulfate. The oxidized components were removed by filtration. Separation of the components was effected by concentrating the solution in ethanol to about 125 ml. On cooling slowly to 0 °C a crystalline *Substance B1* separated out. The substance was recrystallized from acetic acid, m.p. 158 °C. ^{1}H NMR (60 MHz, DMSO-d_6): δ 0.88 (CH_3), 1.30 (CH_2), 2.20 (CH_2CO_2H), 3.30 ($CHOH$). MS of B1 showed no molecular ion. Prominent peaks were observed at *m/e* 113, 155, 157, 173, and 229 corresponding to the fragments outlined in a previous communication.[4] IR comparison with authentic 9,10,12,13-tetrahydroxystearic acid (sativic acid) demonstrated a complete agreement. Found: C 62.58; H 10.25; O 27.24. Calc. for $C_{18}H_{36}O_6$: C 62.04; H 10.41; O 27.55.

On evaporation of the filtrate above, a crystalline mass remained. This was purified by recrystallization from acetic acid and chloroform. A *Substance B2*, yield 170 mg, m.p. 125 °C, snow-white crystals, was finally obtained. Anal. $C_{18}H_{36}O_4$: C, H, O. MW (osmometric in pyridine): Found 308, calc. 316.5. IR(KBr) and ^{1}H NMR (in DMSO-d_6) spectra agreed completely with those of an authentic sample of 9,10-dihydroxystearic acid.

In the mass spectrum, dominant and characteristic peaks were found. HrMS (*m/e*): 281 ($M-H_2O-OH$), 280 ($M-2H_2O$), 229 ($M-C_6H_{12}-OH$), 185 ($HO^+=CH-CH=CH-(CH_2)_6-CO_2H$), 175 ($HO-CH_2-(CH_2)_7-C(OH)=^+OH$) and 173 ($HO^+=CH-(CH_2)_7-CO_2H$). The base peak at *m/e* 155 corresponded to the fragment $HO^+=CH-(CH_2)_6-CH=C=O$.

1. Gibbs, R. D. *Chemotaxonomy of Flowering Plants*, McGill-Queen's University Press, London 1974, p. 500.
2. Pollard, A. C. and Piper, S. H. *Biochem. J. 25* (1931) 2111.
3. Lapworth, A. and Mottram, E. N. *J. Chem. Soc. 127* (1925) 1628.
4. Solberg, Y. *Z. Naturforsch. 30 C* (1975) 445.

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Stable α-Chloro-β-oxosulfenyl Chlorides: a Novel Class of Compounds Formed from Ketones and Thionyl Chloride

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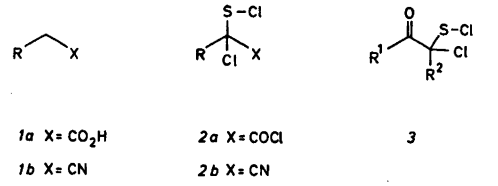
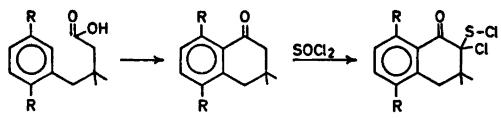
Reaction of monosubstituted acetic acids *1a* or acetonitriles *1b* with thionyl chloride in the presence of a tertiary amine, or Et_2O/HCl, respectively, produces α-chlorosulfenyl chlorides *2a* and *2b*.[1-7] By analogy, α-chloro-β-oxosulfenyl chlorides *3* have been invoked as transient intermediates in reactions between ketones and thionyl chloride leading to 3-thietanones and benzo[*b*]thiophenes.[8,9] The first stable representatives of this class of organic sulfur compounds are described in the following.



1a X = CO_2H *2a* X = COCl *3*

1b X = CN *2b* X = CN



4a R = H *5a* R = H *6a* R = H

4b R = CH_3 *5b* R = CH_3 *6b* R = CH_3

When the hindered ketones *5a* and *5b* are allowed to react with thionyl chloride, without any added catalyst, two products are formed, to which the structures *6a* and *6b* are assigned on the basis of elemental analysis and spectroscopic properties, see Experimental.

Though various pathways to the formation of *6a* and *6b* can be envisioned,[9] the evidence is insufficient to warrant further comments at this stage.

Experimental. ^{1}H NMR were recorded on a Varian 360 instrument, and ^{13}C NMR on a Bruker WH-90 at 22.63 MHz with broad band noise ^{1}H-decoupling. Long relaxation times are indicated by an *a*. The mass spectrum of *6a* was recorded on a Perkin-Elmer 270 instrument; exact measurement was performed on an AEI MS 3074 instrument. The spectrum of *6b* was recorded on a DuPont 21-492 instru-

ment. Melting points are uncorrected. The thionyl chloride used was Fluka *"puriss. p.a. farblos"*. Use of a technical grade gave up to 10 % lower yields of darker coloured products.

The acids *4a* and *4b* were prepared conventionally[10,11] from benzyl chloride and 2,5-dimethylbenzyl chloride,[12] respectively. Cyclization with polyphosphoric acid gave the ketones.[13] The ketone *5b* was also prepared by allowing *4b* (2.20 g) to react with thionyl chloride (0.78 ml; excess thionyl chloride must be avoided, see below) in benzene (2.2 ml) for 18 h at 20 °C. Addition of methanol, removal of the solvents *in vacuo*, and crystallization from light petroleum (3 ml) at −80 °C gave colourless crystals. Yield 1.74 g (86 %), m.p. 58 – 60 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.03 (6 H, s, aliphatic methyl), 2.22 (3 H, s), 2.42 (2 H, s, methylene α to carbonyl), 2.60 (3 H, s), 2.67 (2 H, s, benzylic methylene), 6.92 (1 H, d, *J* 7.6 Hz), 7.13 (1 H, d, *J* 7.6 Hz). ^{13}C NMR ($DCCl_3$): δ 200.6[a] (C1), 53.9 (C2), 32.5[a] (C3), 41.6 (C4), 28.4 (aliphatic methyl), 19.7 and 23.1 (aromatic methyl), 129.7, 130.5[a], 133.9, 134.2[a] 138.3[a], 141.7[a] (aromatic ring carbon). A selective decoupling experiment showed the protons at δ 2.42 to be coupled to the carbon resonating at 53.9 ppm, confirming the assignment.

2-Chloro-2-chlorosulfenyl-3,4-dihydro-3,3 dimethyl-1-(2H)-naphthalenone 6a and the corresponding *3,3,5,8-tetramethyl derivative 6b*. The ketone *5a* (1.74 g) was dissolved in thionyl chloride (3.6 ml). The temperature rose from 22 to 32 °C and a brisk evolution of gas started after *ca.* 2 min. Crystallization set in after 30 – 45 min, and the mixture was allowed to stand at room temperature for 3 h. Recrystallization from ligroin (80/100, 10 ml) at 0 °C gave yellow crystals of the sulfenyl chloride *6a*. Yield 2.18 g (79 %), m.p. 120 – 122 °C; recrystallization from toluene afforded an analytical specimen, m.p. 124 – 126 °C. Anal $C_{12}H_{12}Cl_2OS$: C, H, Cl, S. ^{1}H NMR δ 1.23 (3 H, s), 1.50 (3 H, s), 3.00 (1 H, d, *J* 18 Hz), 3.36 (1 H, d, *J* 18 Hz), 7.07 – 7.74 (3 H, m), 8.07 – 8.22 (1 H, m). ^{13}C NMR ($DCCl_3$): δ 184.2[a] (C1), 92.7[a] (C2), 44.5[a] (C3), 42.8 (C4), 25.2 and 26.1 (aliphatic methyl), 127.4, 128.8, 129.2[a], 129.2[a], 134.3, 139.2[a] (aromatic ring carbon). MS [*m/e* (% rel. int.)]: 273.9963 (22, M), calc. for $C_{12}H_{12}Cl_2OS$ 273.9986; 239 (26), 207 (7), 203 (30), 171.0824 (43), calc. for $C_{12}H_{11}O$ 171.0810; 153 (45), 152.0067 (100), calc. for C_8H_5ClO 152.0029; 149 (40), 118.0418 (80), calc. for C_8H_6O 118.0419.

The homologous chloride *6b* may be prepared as above, but was obtained also directly from the corresponding acid *4b* (2.20 g) and thionyl chloride (2.6 ml). Addition of pyridine (0.1 ml) catalyzed the reaction and gave a higher yield. Crystallization took place after about 3 h at *ca.* 20 °C. The reaction mixture was allowed to stand for 24 h. It was dissolved in a mixture of ligroin (80/100 °C, 10 ml) and toluene (1 ml) at reflux temperature and decanted from a small amount of a brown oil (mainly pyridine hydrochloride). Crystallization at 0 °C gave yellow crystals of *6b*. Yield 2.56 g (84 %), m.p. 122 – 124 °C. Recrystallization from ethanol produced an analytical sample, m.p. 124 – 125 °C. Anal. $C_{14}H_{16}Cl_2OS$: C, H, Cl, S. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.25 (3 H, s), 1.46 (3 H, s), 2.23 (3 H, s), 2.59 (3 H, s), 2.95 (2 H, s; no splitting could be detected on a Varian HA-100 instrument), 7.11 (1 H, d, *J* 7.8 Hz), 7.27 (1 H, d, *J* 7.8 Hz).

^{13}C NMR ($DCCl_3$): δ 187.7[a] (C1), 94.9[a] (C2), 43.6[a] (C3), 41.6 (C4), 25.5 and 26.4 (aliphatic methyl), 19.4 and 22.5 (aromatic methyl), 127.9[a], 130.5, 133.9[a], 134.7, 138.1[a], 140.2[a] (aromatic ring carbon). MS [*m/e* (% rel. int.)]: 302.0308 (33, M), calc. for $C_{14}H_{16}Cl_2OS$ 302.0299; 267.0608 (21 [M − Cl]), calc. for $C_{14}H_{16}ClOS$ 267.0610; 235.0881 (54, [M − SCl]), calc. for $C_{14}H_{16}ClO$ 235.0889; 231.0841 (12, [M − Cl_2]), calc. for $C_{14}H_{15}OS$ 231.0843; 199.1085 (24, [M − SCl_2]), calc. for $C_{14}H_{15}O$ 199.1122; 181.0408 (58, rearrangement), calc. for $C_{10}H_{10}ClO$ 181.0420; 177.0365 (43, rearrangement), calc. for $C_{10}H_9OS$ 177.0374; 146.0732 (100, odd-electron acylium ion), calc. for $C_{10}H_{10}O$ 146.0731. The loss of sulfur and chlorine is expected.[1] The base peak of *6a* at *m/e* 152 does not have a counterpart (at *m/e* 180) in the spectrum of *6b*.

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1. Simon, M. S., Rogers, J. B., Saenger, W. and Gougoutas, J. Z. *J. Am. Chem. Soc. 89* (1967) 5338.
2. Krubsack, A. J. and Higa, T. *Tetrahedron Lett.* (1968) 5149.
3. Krubsack, A. J. and Higa, T. *Tetrahedron Lett.* (1972) 4823.
4. Krubsack, A. J. and Higa, T. *Tetrahedron Lett.* (1973) 125.
5. Krubsack, A. J. and Higa, T. *Tetrahedron Lett.* (1973) 4515.
6. Higa, T. and Krubsack, A. J. *J. Org. Chem. 40* (1975) 3037.
7. Ohoka, M., Kojitani, T., Yanagida, S., Okahara, M. and Komori, S. *J. Org. Chem. 40* (1975) 3540.
8. Krubsack, R. S., Sehgal, R. and Loong, W.-A. *J. Org. Chem. 40* (1975) 3179.
9. Krubsack, A. J., Higa, T. and Slack, W. E. *J. Am. Chem. Soc. 92* (1970) 5258.
10. Prout, F. S., Hartman, R. J., Huang, E. P.-Y., Korpics, C. J. and Tichelaar, G. R. *Org. Synth. Coll. Vol IV* (1963) 93.

11. Wideqvist, S. *Acta Chem. Scand. 3* (1949) 303.
12. Akin, R. B., Stamatoff, G. S. and Bogert, M. T. *J. Am. Chem. Soc. 59* (1937) 1268.
13. Bell, V. L. and Cromwell, N. H. *J. Org. Chem. 23* (1958) 789.

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Resolution and Absolute Configuration of 2-Hydroxylamino-1-phenylpropane (*N*-Hydroxyamphetamine)

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In recent years it has been well established that *N*-hydroxyphenylalkylamines are formed during the metabolism of several phenylalkylamines.[1–4] These aliphatic hydroxylamines are unstable compounds which further metabolize or undergo chemical conversion to various compounds.

During investigations of the chemical and biological properties of *N*-hydroxyphenylalkylamines access to the optical isomers of 2-hydroxylamino-1-phenylpropane (*N*-hydroxyamphetamine, *1*) became desirable. Thus by using optically active substrates information could be gained as to the stereochemical properties of the nitroso compounds formed during autoxidation of *1*.[5] Furthermore pure enantiomers of *1* were needed to assess the influence of its chirality on the enzymatic binding during metabolism.[6]

N-Hydroxyamphetamine was resolved into its (+)- and (−)-enantiomers using (+)- and (−)-tartaric acid, respectively. Five recrystallizations from 5 % solutions in ethanol were required to produce salts with constant physical properties. The absolute configuration of (+)-*1* was established by reduction to (*S*)-amphetamine with $LiAlH_4$. Consequently (+)-*1* can be assigned the (*S*)-configuration.

A synthetic route leading to optical isomers of *1* was recently reported.[7] Optically pure amphetamine was converted into the benzylimine, oxidation of which with *m*-chloroperbenzoic acid, gave the 3-phenyloxaziridine. Subsequent acidic hydrolysis yielded *1*. Although no optical rotations were presented, dextrorotatory amine was claimed to yield dextrorotatory *N*-hydroxylamine. Our results confirm this statement. As *1* easily forms crystalline tartrates resolution is a convenient alternative to the production of the optical antipodes. Racemic *1* can be prepared in reasonable good yield (35 %) by partial reduction of 1-phenyl-2-nitropropene-(1),[8] or in excellent yield (80 %) by a modification[9] of the method of Borch *et al.*[10] utilizing 1-phenyl-2-propanone oxime and cyanoborohydride.

Experimental. Melting points were determined in an electrically heated metal block using open capillary tubes and calibrated Anschütz thermometers. Optical rotations were measured with a Perkin-Elmer 141 spectropolarimeter.

2-Hydroxylamino-1-phenylpropane was prepared in up to 35 % yield by $LiAlH_4$ reduction of 1-phenyl-2-nitro-propene(1).[8] The phenylnitropropene used as the starting material was from seizures and was kindly supplied by the National Laboratory of Forensic Science. The compound contained some impurities and was recrystallized from ethanol (96 %) prior to use.

Resolution of 2-hydroxylamino-1-phenylpropane(1). Racemic *1* (8.0 g, 0.05 mol) was added to a hot solution of (+)-tartaric acid (7.9 g, 0.05 mol) in 300 ml of ethanol (abs.). The solution was kept at room temperature overnight. The salt obtained (11.4 g, m.p. 152–154 °C) required five recrystallizations from 5 % solutions in ethanol (96 %) before it exhibited constant physical properties. Yield 3.5 g (44 %) of resolved (+)-hydrogen tartrate m.p. 163–164 °C, $[\alpha]_D^{23}$ +21.3° (*c* 1.0, H_2O).

Refrigeration of the initial filtrate yielded 2.0 g of pure (−)-*1*-(+)-tartrate, m.p. 143–145 °C, $[\alpha]_D^{23}$ +6.3° (*c* 1.0, H_2O).

The combined filtrates from the above resolution were concentrated *in vacuo* and the residue was dissolved in saturated $NaHCO_3$-solution (25 ml). Extraction with $CHCl_3$ (2 × 25 ml), subsequent drying (Na_2SO_4) and evaporation of the solvent yielded 4.1 g of recovered hydroxylamine. This was added to a hot solution of (−)-tartaric acid (4.4 g, 0.027 mol) in ethanol (96 %). Two recrystallizations from the latter solvent gave 1.3 g of resolved (−)-hydrogen tartrate with constant physical properties, m.p. 164–165 °C, $[\alpha]_D^{23}$ −21.4° (*c* 1.0, H_2O).

The total yield of salts containing resolved (−)-*1* was 3.3 g (41 %).

(S)- and (R)-2-Hydroxylamino-1-phenylpropane. The hydroxylamines were obtained from the resolved (+)- and (−)-hydrogen tartrates by dissolution in saturated $NaHCO_3$-solutions and extraction with chloroform as described above. (*S*)-2-Hydroxylamino-1-phenylpropane, m.p. 79–80 °C (from light petroleum), $[\alpha]_D^{23}$ +1.9° (*c* 1.0, EtOH) +21.2° (*c* 1.0, CH_2Cl_2). (*R*)-2-Hydroxylamino-1-phenylpropane obtained from (+)-tartrate m.p. 79–80 °C $[\alpha]_D^{23}$ −20.6° (*c* 1.0, CH_2Cl_2), obtained from (−)-tartrate m.p. 79–80 °C, $[\alpha]_D^{23}$ −1.9° (*c*