estimated based on the enones reacted. [Yields and retention times on column D (temperature) are given for each adduct below.]

All the cycloadducts showed only aliphatic protons in the NMR spectra, and gave weak parent peaks with base peaks of molecular ions corresponding to the respective enone plus hydrogen in the mass spectra. The carbonyl absorptions in the IR spectra of **5a–d**, **6**, and **7a–c** were at 1715 cm^{-1} and of **8a–c** at 1710 cm^{-1}. 6-(3-Cyclohexenyl)bicyclo[4.3.0]nonan-7-one (**9**) was identified with the authentic sample prepared from **2** and 3-bromocyclohexene using the method of Stork et al.[11] The other products were identified with the authentic materials.

Irradiation of 1. Four isomeric cycloadducts **5a–d** were obtained: **5a** [21%, 10.6 min (140 °C)]; **5b** [35%, 13.7 min (140 °C)], mp 59–61 °C; **5c** [12%, 15.6 min (140 °C)]; **5d** [5%, 18.4 min (140 °C)].

Irradiation of 2. Cis-anti-trans cycloadduct **6**, adduct **9**, bicyclo[4.3.0]nonan-7-one (1%), and 3,3′-bicyclohexenyl were obtained. **6** [84%, 12.3 min (150 °C)], mp 70–71 °C. 2,4-Dinitrophenylhydrazone mp 184–185 °C. Anal. Calcd for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.58; N, 14.06. Found: C, 63.25; H, 6.47; N, 14.02. **9** [3%, 17.7 min (150 °C)]: IR 1725, 720 cm^{-1}; NMR δ 0.90–2.60 (m, 20 H), 5.25–5.80 (m, 2 H); mass spectrum *m/e* 218 (M^+), 138, semicarbazone mp 238–240 °C. Anal. Calcd for $C_{16}H_{25}ON_3$: C, 69.78; H, 9.15; N, 15.26. Found: C, 69.62; H, 9.29; N, 15.05.

Irradiation of 3. Three isomeric cycloadducts **7a–c**, bicyclo[5.3.0]-decan-8-one (3%), and 3,3′-bicyclohexenyl were obtained. **7a** [7%, 11.0 min (160 °C)]. **7b** [82%, 14.7 min (160 °C)], mp 47–48 °C. Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.48; H, 10.60. **7c** [5%, 20.1 min (160 °C)].

Irradiation of 4. Three isomeric cycloadducts **8a–c**, bicyclo[6.3.0]-undecan-9-one (1%), and 3,3′-bicyclohexenyl were obtained. **8a** [3%, 12.4 min (170 °C)]. **8b** [79%, 17.0 min (170 °C)], mp 91–92 °C. Anal. Calcd for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 82.63; H, 10.79. **8c** [5%, 23.0 min (170 °C)].

Quantum Yield Measurement. A 0.13 M solution of **2** in cyclohexene was irradiated to about 3% conversion. After irradiation the calibrating compound was added and the amount of **6** determined by GLC (column C). Actinometry was by the ferrioxalate method.

Quenching of Photocycloaddition of 2 with Cyclohexene. A 0.05 M solution of **2** in cyclohexene was used with added piperylene (0.01–0.5 M).

Registry No.—**1**, 10515-92-1; **2**, 22118-00-9; **3**, 769-32-4; **4**, 38262-50-9; **5a**, 62264-61-3; **5b**, 62319-07-7; **5c**, 62319-08-8; **5d**, 62319-09-9; **6**, 58595-14-5; 6 2,4-DNPH, 62264-62-4; **9** semicarbazone, 62264-63-5; **7a**, 62264-64-6; **7b**, 62319-10-2; **7c**, 62356-50-7; **8a**, 62264-65-7; **8b**, 62319-11-3; **8c**, 62319-12-4; cyclohexene, 110-83-8.

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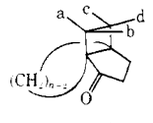
(2) Cargill et al. reported that four isomeric cycloadducts were obtained on irradiation of **1** with cyclohexene in methylene chloride,[1b] which is in agreement with our result.

(3) Generally, photocycloaddition of the cyclic enone to an alicyclic olefin gives a number of stereoisomers.[1] In the present case, the formation of four stereoisomers is possible, and the nomenclature is as follows:



cis-anti-trans, bridging a to d
cis-syn-trans, bridging b to c
cis-anti-cis, bridging a to c
cis-syn-cis, bridging b to d

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(7) Melting points are uncorrected. Infrared spectra were recorded using a JASCO IR-G spectrometer. NMR spectra were obtained in a JEOL JNM-PS-100 spectrometer using CCl_4 as a solvent and Me_4Si as an internal standard. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC separation was conducted on a Varian Aerograph 90-P gas chromatograph. Phosphorescence spectra were recorded on a Hitachi MPF-3 spectrometer.

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Oxidation of L-Cystine by Dimethyl Sulfoxide. Cysteic Acid–Sulfoxide Compounds

Orville G. Lowe

The Author's Consulting Laboratory, Los Angeles, California 90027

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The oxidation of disulfides to sulfonic acids by dimethyl sulfoxide (Me_2SO) has been described;[1] however, L-cystine is insoluble in Me_2SO and satisfactory oxidation is not accomplished without modification of the procedure. The needed changes are an increase in the amount of halogen or hydrogen halide catalyst to about twice the number of moles of L-cystine and a significantly lower reaction temperature. With an appropriately high concentration of mixed I_2–HCl catalyst, oxidation occurs smoothly at room temperature, the water necessary for stoichiometry (eq 1) and reaction moderation being supplied through the use of concentrated hydrochloric acid.

$$(SCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH)_2 + 5CH_3\overset{\displaystyle O}{\overset{\|}{S}}CH_3 + H_2O \xrightarrow{cat} 2HO_3SCH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH + 5CH_3SCH_3 \quad (1)$$

Addition of acetone to the reaction mixture gave abundant precipitate, but this was not the expected L-cysteic acid (CysA). Accumulated evidence—high weight of product, acidic and oxidizing properties, elemental analysis, conversion to CysA by solvent extraction or vacuum drying, and ready formation by direct combination of CysA and Me_2SO—established that this was a 1:1 compound of CysA and Me_2SO.

My obtaining this molecular complex led to investigation of related compounds. It was found that CysA also dissolves in tetramethylene sulfoxide (TMSO) and, on addition of acetone, the corresponding TMSO compound precipitates. CysA has quite limited solubility in methyl phenyl sulfoxide, so, in this instance, no complex is obtained. The combinations DL-cysteic acid–Me_2SO and DL-homocysteic acid with both Me_2SO and TMSO were also checked. The corresponding molecular complexes were obtained; though, with DL-homocysteic acid, these were syrups from which it appeared that the compounds slowly crystallized.

The explanation for formation of these compounds would appear to lie in the ability of the oxygen of sulfoxides such as Me_2SO and TMSO to serve as a proton acceptor.[2] Such salts of strong acids have been reported[3] though the mole ratio is not always 1:1. CysA and, most likely, the other cysteic acids exist as the ammonium sulfonate zwitterion,[4] the carboxyl group being un-ionized. This leads to the interpretation of the subject compounds as carboxylic acid salts or associates of sulfoxides. These have also been investigated and isolated.[5] Those that I have obtained differ in being significantly more stable and amenable to characterization.

Experimental Section

General. The Me_2SO, iodine, hydrochloric and hydrobromic acids, and solvents were reagent grade. Other materials were a quality,

commercial grade and used directly except TMSO, which was dried over molecular sieves and distilled.

Melting points are by the capillary method and uncorrected. Those of CysA were obtained by inserting the capillary into the heating bath about 10 °C below the expected decomposition temperature. Elemental analysis are by Elek Microanalytical Laboratories, Torrance, Calif., and C. F. Geiger, Ontario, Calif.

Oxidation of L-Cystine. Iodine (1.5 g, 11.8 mg-atoms) was dissolved with stirring in a mixture of 24 g (99.9 mmol) of L-cystine and 150 mL of Me_2SO. Gradually, 18 mL (216 mmol) of concentrated hydrochloric acid was added. Stirring at room temperature was continued for 24 h by which time all L-cystine had dissolved and some dimethyl sulfide appeared as a second phase.[6]

The oxidation was also conducted by using 18 mL (160.2 mmol) of concentrated hydrobromic acid in place of the iodine and hydrochloric acid and heating for 6.75 h at 75 °C with distillation of dimethyl sulfide.

CysA–Me_2SO Compound. Acetone (375 mL) was gradually stirred into the mixture obtained by I_2–HCl catalyzed oxidation. After cooling in an ice bath for 2 h, the precipitate was filtered off, reslurried with an 8% solution of Me_2SO in acetone, again collected, and rinsed with acetone. Obtained was 46.5 g (94% yield) of CysA–Me_2SO compound. This sintered at 160 °C, then decomposed at about 180 °C. Recrystallization was accomplished by dissolving in Me_2SO and adding acetone but without change in the decomposition temperature, $[\alpha]^{25}_D$ +5.92° (11%, water). Other solvents such as ethyl acetate or chloroform could be used in place of acetone.

Anal. Calcd for $C_5H_{13}NO_6S_2$: C, 24.28; H, 5.30; N, 5.67; S, 25.93. Found: C, 24.64; H, 5.40; N, 5.45; S, 26.03. Calcd neut equiv, 247.3. Found, 248.3. Calcd % Me_2SO for $C_3H_7NO_5S{\cdot}C_2H_6OS$, 31.59. Found by reduction with 57% hydriodic acid,[7] 31.65.

Conversion of CysA–Me_2SO Compound to CysA. A. By Solvent Extraction. CysA–Me_2SO compound (10 g, 40.5 mmol) was mixed with 40 mL of methanol and repeatedly triturated over a 1.5-h period. CysA was filtered off and rinsed with fresh methanol. Obtained was 6.45 g (94% yield), mp 273–274 °C dec (lit.[8] mp 274 °C dec). Recrystallization from water gave CysA monohydrate, mp 272–274 °C dec (lit.[9] mp 278 °C dec), $[\alpha]^{25}_D$ +8.45° (7.4%, anhydrous basis, water) (lit.[10] +8.66°). Identification was confirmed by comparing the IR spectrum with that of authentic material.

Acetonitrile or ethanol could be used in place of methanol in this extraction.

B. By Vacuum Drying. CysA–Me_2SO compound (0.8838 g, 3.58 mmol) was heated for 9 h at 120 °C (10 mm). The residual CysA weighed 0.6022 g, mp 260–263 °C dec (lit.[8] mp 274 °C dec). Calcd wt loss for $C_3H_7NO_5S{\cdot}C_2H_6OS$, 31.59. Found, 31.86.

Direct Formation of CysA–Me_2SO Compound. On treating 1.10 g (5.90 mmol) of CysA monohydrate with 4 mL of Me_2SO, it dissolved slowly, and stirring and some heating were used to complete solution. Acetone (5 mL) was added to start precipitation. Later 2 mL more was added. After cooling in an ice bath, CysA–Me_2SO compound was filtered off and given a final rinse with acetone. Obtained was 1.37 g (94% yield) identical with that described above.

Other Cysteic Acid–Sulfoxide Compounds. About 2.9 mmol of the cysteic acid was treated with 2 mL of Me_2SO or 6–8 mL of TMSO. Solution occurred gradually and was usually completed with gentle heating. Precipitation was by addition of acetone. Yields were about 90%. Where possible, recrystallization was by dissolving in the same sulfoxide followed by addition of acetone. The appropriate cysteic acid was recovered by treating with methanol.

CysA–TMSO Compound. This darkened, then decomposed at 215–216 °C. Anal. Calcd for $C_7H_{15}NO_6S_2$: N, 5.13; S, 23.46. Found: N, 4.87; S, 23.61.

DL-Cysteic Acid–Me_2SO Compound. This showed partial melting at 161–165 °C followed by gradual decomposition. Anal. Calcd for $C_5H_{13}NO_6S_2$: N, 5.67; S, 25.93. Found: N, 5.82; S, 26.08.

DL-Homocysteic Acid–Me_2SO Compound. Addition of acetone resulted in formation of a syrup. This was extracted with fresh acetone until the extract would no longer rapidly decolorize added aqueous $KMnO_4$ solution. This syrup gradually crystallized. Its aqueous solution decolorized aqueous $KMnO_4$. Anal. Calcd for $C_6H_{15}NO_6S_2$: N, 5.36; S, 24.54. Found: N, 4.31; S, 20.75. Ratio: S to N, 2.1.

DL-Homocysteic Acid–TMSO Compound. A syrup was obtained as with Me_2SO. After exhaustive extraction with acetone, its aqueous solution continued to rapidly decolorize $KMnO_4$ solution.

Registry No.—L-Cysteic acid, 498-40-8; L-cystine, 56-89-3; Me_2SO, 67-68-5; cysA–Me_2SO compound, 60643-99-4; TMSO, 1600-44-8; cysA–TMSO compound, 60644-00-0; DL-cysteic acid, 3024-83-7; DL-cysteic acid–Me_2SO compound, 62337-55-7; DL-homocysteic acid, 504-33-6; DL-homocysteic acid–Me_2SO compound, 60644-01-1; DL-homocysteic acid–TMSO compound, 62337-56-8.

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anhydro-2-Mercaptothiazolo[3,2-*f*]phenanthridinium Hydroxide, a Mesoionic Thiazole Ring System Containing Exocyclic Sulfur

Kevin T. Potts* and Samuel J. Chen

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Jacob Szmuszkovicz

Research Laboratories, The Upjohn Company, Kalamazoo, Michigan 49001

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The synthesis of mesoionic ring systems with exocyclic sulfur atoms by a direct ring closure sequence is usually effective only in those systems with a nitrogen atom adjacent to the carbon bearing the sulfur, as in the 1,3,4-oxadiazole,[1] 1,3,4-thiadiazole,[1,2] and 1,2,4-triazole[3] ring systems. In these cases an isothiocyanate is presumed to be the reactive intermediate. Interconversion of mesoionic systems by the use of a reactive dipolarophile, such as the reaction of *anhydro*-2,4-diphenyl-5-hydroxy-3-methylxanthylium hydroxide with carbon disulfide to give *anhydro*-2,4-diphenyl-5-mercapto-3-methylthiazolium hydroxide,[4] requires an exceptionally reactive substrate and has only been successful in the above example, although the hydrolytic rearrangement of the *anhydro*-5-hydroxy-1,3,4-thiadiazolium hydroxide system to the corresponding *anhydro*-5-mercapto-1,3,4-oxadiazolium hydroxide system is well documented.[1] We now describe a direct approach that has been successful in the synthesis of the title ring system.

6-Oxo-5(6*H*)-phenanthridineacetic acid (**1**, R = H; X = O) when refluxed in pyridine for 1 h with an equimolar quantity of P_4S_{10} gave *anhydro*-2-mercaptothiazolo[3,2-*f*]phenanthridinium hydroxide (**2**), characterized further by the ready formation of 2-methylthiothiazolo[3,2-*f*]phenanthridinium iodide (**3**) on reaction with methyl iodide. Use of the methyl ester of **1** (R = CH_3; X = O) in toluene required 21.5 h of reflux for the formation of **2** whereas, if the reaction were run for shorter periods (45 min), no **2** was formed, the product isolated being the corresponding thioester **1** (R = CH_3; X = S). Confirmation of the structure of **2** was obtained by an alternative synthesis. Cyclization of **1** (R = H; X = O) with dicyclohex-