(internal alkene), 87453-10-9; (*E*)-**21**, 87452-88-8; (*Z*)-**21**, 87453-11-0; **22**, 87452-89-9; **23**, 56694-87-2; **24**, 87452-90-2; **25** (terminal alkene), 87452-91-3; **25** (internal alkene), 87453-12-1; **26**, 87452-92-4; **27**, 87452-93-5; **28**, 87452-94-6; **29** (terminal alkene), 87452-95-7; **29** (internal alkene), 87453-13-2; **33**, 87452-96-8; **34**, 87452-97-9; **35**, 539-52-6; **36**, 87452-98-0; **37**, 87452-99-1; **38**, 87453-00-7; (*E*)-**39**, 83670-82-0; **40**, 624-57-7; **41a**, 87453-01-8; **41b**, 87453-02-9; **42a**, 87453-03-0; **42b**, 87453-04-1; **43**, 87453-05-2; **44**, 87453-06-3; **45**, 4351-11-5; **46**, 87453-07-4; **47**, 87453-08-5; **48**, 87453-09-6; (±)-**49**, 73191-64-7; (±)-**50**, 73210-04-5; BF_3·OEt_2, 109-63-7; $EtAlCl_2$, 563-43-9; Et_2AlCl_2, 96-10-6; Al_2O_3, 1344-28-1; $Ti(OiPr)_3Cl$, 20717-86-6; ZnI_2, 10139-47-6; (3-furyl)chloromethane, 14497-29-1; 1-bromo-2-methylpropene, 3017-69-4; 3-chloro-2-methylpropene, 563-47-3; 4-chloro-2-methyl-2-butene, 503-60-6; 4-iodo-2-methyl-1-butene, 53750-52-0; 5-iodo-2-methyl-2-pentene, 43161-11-1; (*E*)-epoxygeranyl chloride, 43119-82-0.

α-Oxo Sulfones.[1] 4. Correction of a Pretended α-Oxo Sulfone by an Unambiguous Synthesis of the Revised Structure

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By an independent synthesis the oxidation product of 1,1-dichloro-2,2-dimethyl-1-(phenylthio)-3-butene (**1**) was shown not to be α-oxo sulfone "**2**" as published earlier but a phenylsulfonyl γ-butyrolactone, **3**. This synthesis involves the intramolecular reaction of a sulfenic carboxylic mixed anhydride with an olefinic bond. A rationale for the formation of **3** from **1** is presented.

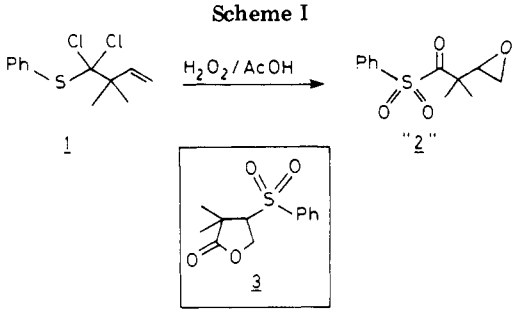
α-Diketones and α-disulfones are both stable and well-defined structures. In contrast, only a few isolable and well-characterized examples of α-oxo sulfones have been described.[2] Recently, several reports dealing with α-oxo sulfones were critically reviewed by us.[2] In many instances the suggested α-oxo sulfone structure was proven to be incorrect or at least questionable. In this context our attention[3] was drawn to the oxidation of 1,1-dichloro-2,2-dimethyl-1-(phenylthio)-3-butene (**1**) with hydrogen peroxide (30%) in acetic acid, giving aliphatic α-oxo sulfone "**2**" (Scheme I).[4]

In view of our experience[1] with established α-oxo sulfones the reported properties[4] were not in line with those expected for **2**. First, the high stability toward hydrolysis is incompatible with structure **2** as α-oxo sulfones are very sensitive to water.[1] Second, the IR absorption at 1790 cm^{-1} is not typical for an α-oxo sulfone (~1700 cm^{-1})[2] but rather is suggestive of a γ-lactone. One of us (B.Z.)[5] proposed on the basis of the provided spectral data the γ-lactone structure **3** as a possible alternative for "**2**". The aim of this investigation is to devise an unambiguous synthesis for **3** and to establish the true nature of the product "**2**" obtained by Parham and Groen.[4]

First of all we ensured that the reported[4] preparation of "**2**" could be repeated. This was found to be the case; even the yield of "**2**" could be considerably improved by a slight modification of the procedure.

The synthetic plan for lactone **3** is outlined in Scheme II. The essential feature of this sequence is that dimethylvinylacetic acid **7** is transformed into the carboxylic sulfenic mixed anhydride **8**. The formation of such (unstable) mixed anhydrides has been reported previously.[7] These species react with olefinic double bonds in a similar fashion[7,8] as is known for sulfenyl halides.[9] It should be noted that this proposed lactone formation in fact resembles the iodolactonization of the sodium salt of **7** with iodine which leads to the corresponding 3-iodo-2,2-dimethyl-γ-butyrolactone.[10]

Scheme I



Treatment of carboxylic acid[11] **7**, prepared by an improved procedure (see Scheme III and the Experimental

(1) For α-oxo sulfones **3**, see: Schank, K.; Werner, F. *Liebigs Ann. Chem.* **1980**, 1477.
(2) Schank, K.; Werner, F. *Liebigs Ann. Chem.* **1979**, 1977.
(3) We (K.S. and A.F.) are obliged to Dr. H.-G. Schmitt from Bayer AG, Leverkusen (FRG), for bringing ref 4a to our attention.
(4) (a) Parham, W. E.; Groen, S. H. *J. Org. Chem.* **1966**, *31*, 1694. (b) Groen, S. H. Thesis, University of Groningen, The Netherlands, 1966.
(5) Ph.D. ceremony of S. H. Groen, University of Groningen, The Netherlands, March 4, 1966.
(6) We first tried to prepare lactone **3** from methallyl phenyl sulfone. Isomerization to an α,β-unsaturated sulfone and simultaneous conjugate addition of cyanide by treatment with sodium hydrogen carbonate and sodium cyanide in ethanol at 80 °C for 3 days gave 2,2-dimethyl-3-(phenylsulfonyl)propanenitrile (yield 40%; mp 87–90 °C). Subsequent methanolysis (methanol/HCl/-20 °C) followed by hydrolysis (methanol/KOH/20 °C) led to 2,2-dimethyl-3-(phenylsulfonyl)propanoic acid (yield 62%; mp 142 °C). Attempts to ring close this compound via reaction of its dilithio derivative with methylene iodide failed. Presumably, the carbon atom α to the sulfonyl group is too sterically shielded for an alkylation reaction.
(7) (a) Havlik, A. J.; Kharash, N. *J. Am. Chem. Soc.* **1956**, *78*, 1207. (b) Brydon, A.; Cameron, G. G.; Hogg, D. R. *Int. J. Sulfur Chem., Part A* **1972**, *A2*, 289. (c) Putnam, R. E.; Sharkey, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 6526. (d) Bell, P. A.; Hogg, D. R.; Robertson, A. *J. Chem. Soc., Perkin Trans 1* **1978**, 1246.
(8) One could argue that conversion of **7** to **9** may be envisaged without the intermediacy of **8**. However, the carboxylate of **7** is probably a better nucleophile with regard to benzenesulfenyl chloride than the olefin. The intermediate **8** is relevant in understanding the formation of **3** from **1** (Scheme III).
(9) Kühle, E. "The Chemistry of the Sulfenic Acids"; Georg Thieme Verlag: Stuttgart, 1973; pp 44–52.
(10) Bougault, J. *Ann. Chim. Phys.* **1908**, *14* (8), 145, 166.

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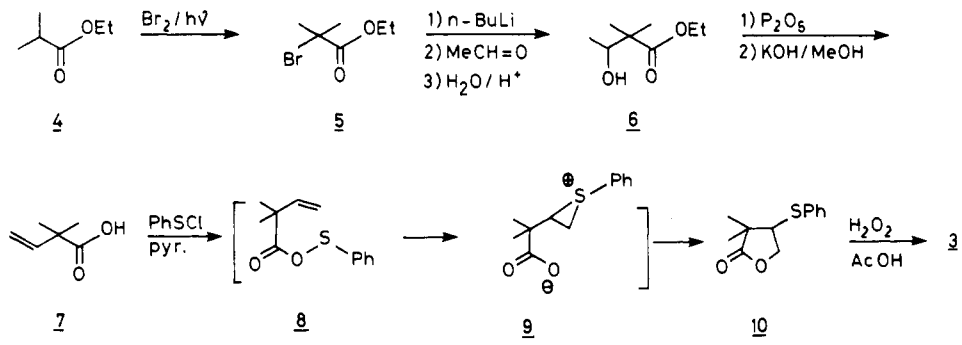
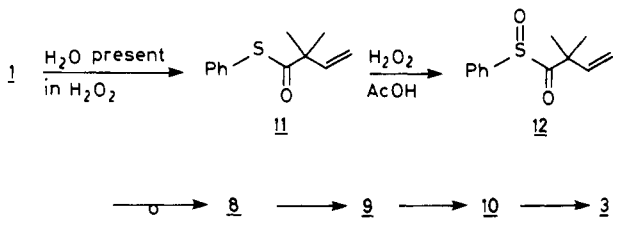
Scheme II



Scheme III



Section), with benzenesulfenyl chloride in the presence of 1 equiv of pyridine gave γ-butyrolactone **10** as the predominant product. The major byproduct, diphenyl disulfide, probably arises from a disproportionation[7d] of intermediate **8**. The spectral features of this compound are in full accord with lactone structure **10**. Subsequent oxidation of lactone **10** with hydrogen peroxide in acetic acid gave phenylsulfonyl-substituted lactone **3** in excellent yield. The thus-obtained product **3** is identical in all respects with the pretended α-oxo sulfone "**2**" prepared according to Scheme I. Therefore, the oxo sulfone structure "**2**" is incorrect and must be revised to lactone **3**.

The formation of sulfonyl lactone **3** upon oxidation of **1** is rationalized as is shown in Scheme III. As observed by Parham and Groen,[4] dichloride **1** is readily hydrolyzed to give *thiolo* ester **11**. Oxidation of **11** at sulfur now leads to the notoriously unstable acyl sulfoxide **12** (cf. ref 12). Compounds of this type are reported[13] to isomerize instantaneously, even at low temperature, to give carboxylic sulfenic mixed anhydrides. Accordingly, acyl sulfoxide **12** isomerizes to mixed anhydride **8** which then, as outlined in Scheme II, will produce lactone **10**. A final oxidation of this sulfide leads to isolated sulfonyl lactone **3**. An alternative sequence of events involving an oxidation of dichloride **1** to an α,α-dichloro sulfoxide, followed by a hydrolysis to **11**, is unlikely because it is well-known that α,α-dihalo sulfoxides are reluctant toward hydrolysis.[14]

Experimental Section

All melting and boiling points are uncorrected; melting points were determined automatically with a Fus-O-mat.[15] Infrared spectra were recorded with a Beckmann IR-33 or IR-4230. ^1H NMR spectra were obtained with Varian EM-360 and A-60 spectrometers (that of **3** also with a Bruker WH-90). TLC analysis were performed on SiO_2, Type 60 F-254 (Merck). Elemental analyses were carried out by the method of Walisch.[16] 1,1-Dichloro-2,2-dimethyl-1-(phenylthio)-3-butene (**1**) was synthesized according to ref 4a.

Oxidation of 1 with H_2O_2 (30%) in Acetic Acid. An 80-mL sample of hydrogen peroxide (30%) was added dropwise to a solution of 20 g (76 mmol) of **1** in 160 mL of acetic acid at 70 °C. After being stirred and heated at reflux for 3.5 h, the mixture was poured into ice–water. A white precipitate was formed that was recrystallized from ethanol. A second crop could be obtained by ether extraction and the usual workup. The total yield of white crystals was 8.2 g (42%) of "**2**": mp 107 °C (lit.[4a] mp 108–109 °C). Anal. Calcd for $C_{12}H_{14}O_4S$ (M_r = 254.3): C, 56.67; H, 5.55. Found: C, 56.64; H, 5.61. All spectral data were in accordance with those reported in ref 4.

Ethyl 2-Bromo-2-methylpropanoate (5). Ethyl isobutyrate (116.1 g, 1 mol) was irradiated and heated to reflux by using a 450-W photolamp, and then 159.8 g (1 mol) of bromine was added under stirring at a rate so that discoloration took place. Stirring was continued for 2 h followed by an immediate distillation of the reaction mixture to give **5**: Yield 175.4 g (90%); bp 161 °C (lit.[17] bp 160 °C).

Ethyl 3-Hydroxy-2,2-dimethylbutanoate (6). A solution of 175.4 g (0.9 mol) of **5** in 300 mL of absolute ether was cooled to −75 °C, and 625 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane (Merck, 20% excess) was added without letting the reaction temperature exceed −70 °C. After the addition was completed the temperature was allowed to rise to −20 °C. Then, after the mixture was cooled to −75 °C, 60 g (1.35 mol) (50% excess) of freshly distilled ethanal was added dropwise to the stirred reaction mixture. Stirring was continued overnight, allowing the reaction mixture to reach room temperature. Concentrated sulfuric acid (52.9 g, 0.54 mol) dissolved in 200 mL of absolute ether was slowly added to the mixture, the precipitated inorganic salt was removed by filtration, and the filtrate was distilled, affording **6**: 133 g (90%); bp 84–86 °C (13 torr) [lit.[18] bp 91 °C (13 torr)].

Ethyl 2,2-Dimethyl-3-butenoate. According to ref 18, 60 g of diphosphorus pentoxide was added under stirring to a solution of 133 g (0.83 mol) of **6** in 500 mL of dry benzene at room temperature. Stirring was continued overnight, and finally the black reaction mixture was heated under reflux for 1 h. Distillation of the solution obtained by decantation and filtration of the reaction mixture yielded ethyl ester of **7**: 74 g (63%); bp 142 °C (lit.[18] bp 141–142 °C).

2,2-Dimethyl-3-butenoic Acid (7). The ethyl ester of **7** (74 g, 0.52 mol) was stirred with a solution of 72.3 g (1.29 mol) of potassium hydroxide in 150 mL of methanol at room temperature until no more ester was present. Methanol was distilled off, and the residue was acidified with 63.3 g (0.65 mol) of concentrated sulfuric acid in 250 mL of absolute ether. Distillation yielded **7**: 36.5 g (62%); bp 85–86 °C (13 torr) [lit. bp 88 °C (16 torr),[4] 185 °C,[11] 99 °C (23 torr)[11]].

2,2-Dimethyl-3-(phenylthio)-γ-butyrolactone (10). Benzenesulfenyl chloride (7.9 g, 55 mmol) dissolved in 20 mL of dry

(11) Courtot, A. *Bull. Soc. Chim. Fr.* **1906**, *35*, 111.
(12) (a) Kumamoto, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2111. (b) Casida, J. E.; Gray, R. A.; Tilles, H. *Science (Washington, D.C.)* **1974**, *184*, 573, 4136. (c) Barton, D. H. R.; Manly, D. P.; Widdowson, D. A. *J. Chem. Soc., Perkin. Trans. 1* **1975**, 1568. (d) Wakui, T.; Nakamura, Y.; Motoki, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3081.
(13) (a) Chaves das Neves, H. J.; Machette, M. F. *Tetrahedron Lett.* **1977**, 187. (b) Sousa Lobo, M. J.; Chaves das Neves, H. J. *Ibid.* **1978**, 2171. (c) Chaves das Neves, H. J.; Da Silveira Godinko, L. *Tetrahedron* **1979**, *35*, 2063.
(14) (a) Hojo, M.; Yoshida, Z.-i. *J. Am. Chem. Soc.* **1968**, *90*, 4496. (b) Ogura, K.; Tsuchihashi, G. *J. Chem. Soc., Chem. Commun.* **1970**, 1689.
(15) Fus-O-Mat Type 1, W.C. Heraeus GmbH, D-6450 Hanau, FRG.
(16) Walisch, W. *Chem. Ber.* **1961**, *94*, 2314.
(17) Markownikoff, W. *Justus Liebigs Ann. Chem.* **1876**, *182*, 324, 336.
(18) Kwart, H.; Miller, R. K. *J. Am. Chem. Soc.* **1954**, *76*, 5403.

dichloromethane was added dropwise under stirring to a mixture of 6.3 g (55 mmol) of **7** and 4.5 g (57 mmol) of pyridine in 20 mL of dry dichloromethane at room temperature. Stirring was continued for 2 h, and the solution was washed successively with water, diluted hydrochloric acid, washed a second time with water, and then dried over calcium chloride. The solvent was removed by distillation and the residue fractionated under reduced pressure. The fraction boiling from 133 to 136 °C at 2×10^{-3} torr consisted of crude **10**. TLC analysis showed the presence of at least five further components; the main impurity was diphenyl disulfide. Further purification was performed by chromatography on silica gel with chloroform as the eluent, yielding **10** as a slightly pale yellow oil: 3.7 g (30%); IR (liquid) 1770 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 90 MHz, FT) δ 1.255, 1.287 (2 s, 6 H, 2 CH_3), 3.540, 3.625, 3.645, 3.729, 3.977, 4.078, 4.183, 4.395, 4.476, 4.496, 4.580 (ABX m, 3 H, CH-CH_2), 7.25-7.48 (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{14}O_2S$ (M_r = 222.3): C, 64.83; H, 6.35. Found: C, 64.79; H, 6.46.

2,2-Dimethyl-3-(phenylsulfonyl)-γ-butyrolactone (3). A large excess of 30% hydrogen peroxide (3.4 g) was added to a solution of 2.8 g (12.6 mmol) of lactone **10** in 65 mL of glacial acetic acid, and the mixture was heated under reflux for 3 h. After the mixture was poured into water, 2.1 g of the crystallized sulfone **3** could be collected by filtration immediately. Extraction of the aqueous phase with dichloromethane and the usual workup yielded a second crop of **3**. Recrystallization from ethyl acetate gave 3.1 g (95%) of **3** as white needles, mp 106 °C, identical with the substance obtained by the oxidation of **1**: IR (KBr) 1145, 1280, 1328 (SO_2), 1790 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, 90 MHz, FT) δ 1.421, 1.597 (2 s, 6 H, 2 CH_3), 3.632, 3.716, 3.736, 3.821, 4.114, 4.199, 4.218, 4.303, 4.395, 4.499, 4.606 (ABX m, 3 H, CH-CH_2), 7.54-7.96 (m, 5 H, C_6H_5). Anal. Calcd for $C_{12}H_{14}O_4S$ (M_r = 254.3): C, 56.67; H, 5.55. Found: C, 56.55; H, 5.59.

Registry No. **1**, 10276-07-0; **2**, 10276-08-1; **3**, 87279-52-5; **4**, 97-62-1; **5**, 600-00-0; **6**, 7505-94-4; **7**, 10276-09-2; 7 ethyl ester, 58544-20-0; **10**, 87279-53-6; MeCH=O, 75-07-0; methallyl phenyl sulfone, 49639-05-6; 2,2-dimethyl-3-(phenylsulfonyl)propanenitrile, 87279-54-7; 2,2-dimethyl-3-(phenylsulfonyl)propanoic acid, 38435-02-8.

Synthesis of Thione *S*-Imides by Alkylidenation of Sulfinylanilines and Imination of Sulfines

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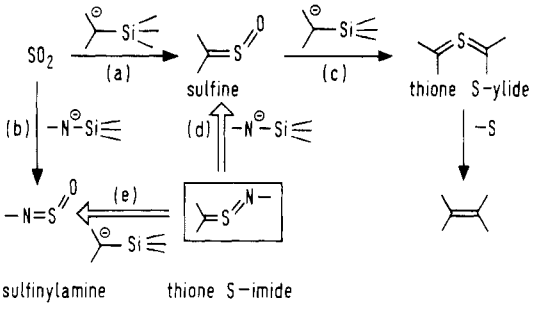
Thione *S*-imides **3** have been synthesized by alkylidenation of sulfinylamines **1** using α-trimethylsilyl carbanions **2**. Imination of sulfines **4** by means of anions of (trimethylsilyl)amines **5** also led to thione *S*-imides **3**. It was found to be essential that in these syntheses the thione *S*-imides are substituted with sterically filled groups.

Alkylidenation of sulfur dioxide by using α-silyl carbanions constitutes a new and convenient route to sulfines[1,2] (thione *S*-oxides; Scheme I, reaction a). Sulfinylamines can be prepared in an analogous manner by imination of sulfur dioxide with anions of silylamines (Scheme I, reaction b).[3] During the synthesis of sulfines by following this modified Peterson reaction, it was found to be essential that the α-silyl carbanion is added to an excess of sulfur dioxide in order to avoid the formation of an olefin as a byproduct;[2,4] e.g., the preparation of fluorenethione *S*-oxide is accompanied by the formation of some bifluorenylidene.[2,4] This side reaction probably involves the reaction of the α-silyl carbanion with already formed sulfine to give a thione *S*-ylide. This heterocumulene is known to be very unstable and loses sulfur readily to give an olefin (Scheme I, reaction c).[2,4] In fact, this alkylidenation of sulfines represents a new entry to thione *S*-ylides.

Extrapolation of these findings leads to the proposal that imination of sulfines with anions of silylamines potentially forms a route to thione *S*-imides. Alternatively, the formation of these thione *S*-imides can be envisaged via alkylidenation of sulfinylamines by means of α-silyl carbanions. Both suggested methods of preparation of thione *S*-imides are incorporated in Scheme I in a retrosynthetic

Scheme I



fashion (reaction d and e, respectively). This paper deals with the results obtained by using both these approaches.

The synthesis of thione *S*-imides has attracted considerable attention in the recent literature. Oae et al.[5] reported for the first time the isolation of these sulfur-centered heterocumulenes. These authors obtained remarkably stable thione *S*-tosylimides by treatment of 1,2-dithiole-3-thiones with chloramine T.[6] As shown by Wentrup et al.,[7] reaction of these thiones with *N*-chlorobenzamide followed by base leads to the corresponding

(1) Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 1.
(2) van der Leij, M.; Porskamp, P. A. T. W.; Lammerink, B.H.M.; Zwanenburg, B. *Tetrahedron Lett.* **1978**, 811.
(3) Porskamp, P. A. T. W.; Zwanenburg, B. *Synthesis* **1981**, 368.
(4) van der Leij, M. Thesis, University of Nijmegen, 1979.
(5) Tamagaki, S.; Oae, S. *Tetrahedron Lett.* **1972**, 1159. Tamagaki, S.; Sakaki, K.; Oae, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2608; **1974**, *47*, 3084; *Heterocycles* **1974**, *2*, 39.
(6) A modified procedure using tosylamides and bromine was reported by: Koide, A.; Saito, T.; Kawasaki, M.; Motoki, S. *Synthesis* **1981**, 486.
(7) Wentrup, G. J.; Boberg, F. *Justus Liebigs Ann. Chem.* **1978**, 387. Boberg, F.; Puttins, U.; Wentrup, G. J. *Ibid.* **1979**, 689.

0022-3263/83/1948-4582$01.50/0