

The Chemistry of a Ketene-Sulfur Dioxide Adduct (1)

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Dedicated to Professor Allan R. Day

We have demonstrated the formation of a reactive species from ketene and sulfur dioxide and have investigated some of its reactions. The $3 + 2 \rightarrow 5$ cycloaddition reactions of this intermediate with benzylideneaniline and its derivatives gave the corresponding 2,3-diphenylthiazolidin-4-one 1,1-dioxides. The reduction of 2,3-diphenylthiazolidin-4-one 1,1-dioxide with lithium aluminum hydride yielded the corresponding thiazolidine. Aniline and its derivatives reacted with the ketene-sulfur dioxide adduct to give thioaceto-1,3-dianilide 3-oxide. *o*-Phenylenediamine gave [2,1,5]benzothiadiazepin-4-one 2-oxide, a derivative of a new ring system, [2,1,5]benzothiadiazepine. *o*-Aminophenol yielded [1,2,5]benzothiazepin-4-one 2-oxide.

Sulfur dioxide has long been used as a solvent for reactions involving carbonium ions. Although this compound has a comparatively low dielectric constant ($D = 14$), it is a good solvent in such reactions because of its ionizing power and because it does not undergo irreversible reactions with carbonium ions (2). The use of liquid sulfur dioxide as an outstanding solvent for the reactions of ketene with activated acid chlorides is well documented (3,4). During the course of an investigation designed to lead to β -lactams, a previously unreported reaction between ketene and sulfur dioxide was observed (5). Although the isolation of an actual adduct could not be accomplished, its formation was detected by interception with appropriate reagents and its existence was supported by a low temperature nmr study.

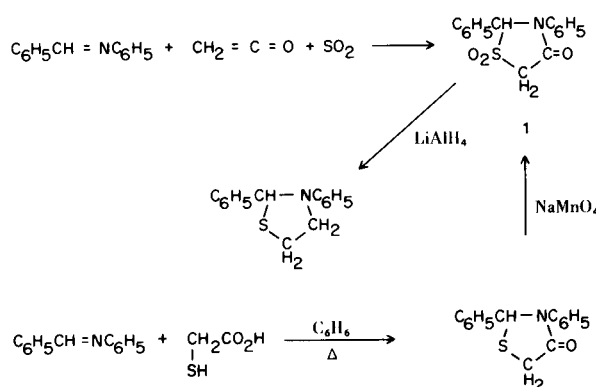
RESULTS

1,3-Dipolar Additions.

The first experiment which revealed the existence of a ketene-sulfur dioxide adduct was the reaction of ketene and benzylideneaniline in liquid sulfur dioxide at -70° . The expected β -lactam was not formed. A white crystalline product was obtained instead and postulated to be 2,3-diphenylthiazolidin-4-one 1,1-dioxide (1) (5). This structure was confirmed by an independent synthesis and its reduction to a thiazolidine with lithium aluminum hydride (see Scheme I).

In order to establish the scope of this cycloaddition, other reactions were carried out with derivatives of benzylideneaniline. The results of these reactions are summarized in Table I.

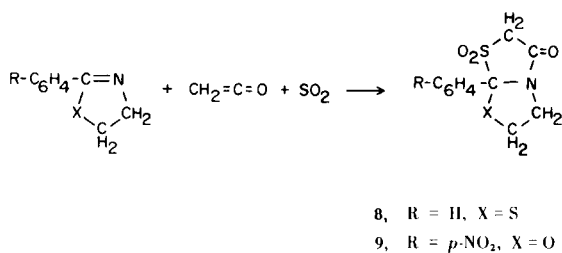
SCHEME I



The infrared bands of the main functional groups and chemical shifts of the protons are shown in Table II. The reaction appeared to be sensitive to electronic effects in the anticipated direction. Electron-withdrawing groups in the benzylidene ring favored the reaction while the same groups in the aniline ring of the Schiff's base hindered the reaction. For instance, benzylidene *p*-nitroaniline did not react and benzylidene *p*-bromoaniline gave a poor yield of product. Similar substituent effects have been observed in the cycloaddition of Schiff's bases with both ketene (6) and diphenylketene (7).

Other compounds containing the imine function were reacted with ketene in liquid sulfur dioxide. 2-Phenylthiazoline and 2-(*p*-nitrophenyl)oxazoline gave excellent yields of 8 and 9 (Scheme II).

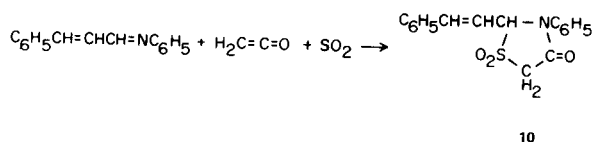
SCHEME II



These compounds were unstable at room temperature and decomposed within a week to the starting materials. This method of preparation for these new compounds is significant since both compounds are heat sensitive and would be difficult to synthesize otherwise.

The expected formation of a five-membered ring in competition with a seven-membered ring compound is illustrated by the reaction of cinnamylideneaniline with ketene in anhydrous liquid sulfur dioxide (Scheme III).

SCHEME III



The analytical data and spectroscopic data supported the formation of the five-membered ring, **10**. The nuclear magnetic resonance and infrared spectra of this compound were also in excellent agreement with the reported spectroscopic values for a similar compound (see Experimental) (**8**).

Before proceeding to discuss the nature of the adduct formed between ketene and sulfur dioxide, a number of known facts must be kept in mind:

1) The reaction of ketene with benzylideneaniline to form a β -lactam has only been accomplished at high temperatures (180-200°) (**6,9**).

2) Sulfene (H₂C=SO₂), the sulfur analog of ketene, does not react with benzylideneaniline (**10,11**).

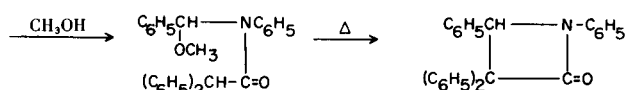
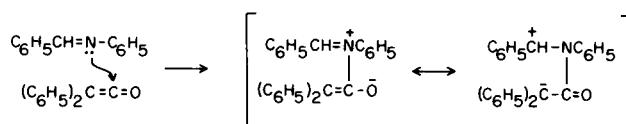
3) Only strongly nucleophilic double bonds were attacked by the sulfur dioxide adduct to give stable cycloadducts. Unsaturated esters, azo compounds, aldehydes, ketones and nitriles do not react. Compounds which are decomposed by sulfur dioxide cannot be used.

4) Other ketenes such as dimethylketene, ethylbutylketene and diphenylketene do not form an adduct with sulfur dioxide. This is not in itself surprising since ketene and substituted ketenes are known to differ in chemical reactivity.

Diphenylketene reacts with benzylideneaniline in liquid sulfur dioxide to give the corresponding β -lactam in good

yields. The lack of reactivity of diphenylketene towards sulfur dioxide could be explained as the result of steric hindrance or delocalization of the negative charge.

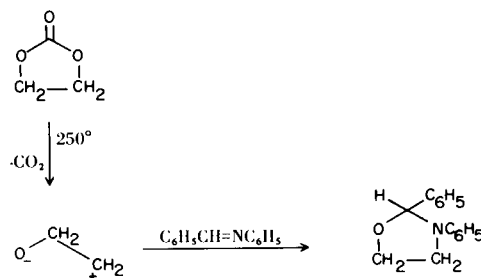
The cycloaddition of diphenylketene and benzylideneaniline was studied by Kagan and Luche who advocated a two-step ionic mechanism involving a slow zwitterion formation followed by ring closure. In addition to the influence of substituents on the cycloaddition, which was clearly demonstrated from competitive rate studies, further evidence was provided by the interception of an intermediate with methanol. This compound yielded the corresponding β -lactam when heated (**6**).



Although it is tempting to regard the formation of **1** as the result of a similar reaction, attack of a zwitterionic intermediate on the solvent (sulfur dioxide), an important difference must be noted. Compound **1** does not react to form β -lactam but rather decomposes into the starting material when heated.

The Nature of the Intermediate.

The reaction of the ketene-sulfur dioxide adduct and imines appears to be a typical 1,3-dipolar cycloaddition. However, 1,3-dipolar systems without a double bond are rare. Huisgen postulates such an intermediate in the thermolysis of ethylene carbonate in *N*-benzylideneaniline to yield 2,3-diphenyloxazine (**12**).



A similar 1,3-dipole (**12**) could be postulated for the reaction of ketene and sulfur dioxide, although in this case the conditions for its formation are much less drastic. However, the possibility of an equilibrium between an open 1,3-dipolar ion and a cyclic structure such as 2-oxo-thiirane 1,1-dioxide (**11**) is conceivable.



A similar equilibrium has been postulated for cyclopropanones (13). In an attempt to elucidate the structure of the adduct formed between ketene and sulfur dioxide, we examined the nmr spectrum of ketene in liquid sulfur dioxide at -60° . The spectrum of pure ketene (neat) was studied at -60° . The methylene protons were observed at δ 2.47. Anhydrous sulfur dioxide was then added until a 50% solution was obtained. The time elapsed between the addition of the sulfur dioxide and the recording of the first spectrum (15 minutes) was sufficient for the appearance of several small peaks in the regions δ 2.22-2.68 and δ 3.5-6.5. The resonance at δ 2.68 was shown to be due to the methylene protons of ketene in sulfur dioxide. Another spectrum recorded twenty minutes later showed a relative increase in the new peaks observed but showed a decrease in the ketene peak at δ 2.68. A careful analysis of these spectra was undertaken by comparing these peaks with those obtained from the decomposition of ketene (diketene and higher molecular weight products) and ketene itself. The only peak that could be attributed to the reaction of ketene and sulfur dioxide was a sharp singlet at δ 2.30 which increased as the ketene peak decreased. Although the peak observed at δ 2.30 suggests the existence of an intermediate resulting from the addition of sulfur dioxide to ketene, more chemical and physical data are needed before the nature of this product can be established.

Reactions with Aromatic Amines.

To further explore the reactivity of the ketene-sulfur dioxide adduct, we reacted aniline with ketene in sulfur dioxide. Instead of the expected acetanilide, thioacetamide, 1,3-dianilide 3-oxide was obtained (Scheme IV).

SCHEME IV



- 13, R = H
14, R = *p*-OCH₃

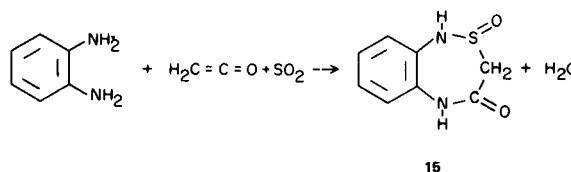
The analytical and spectroscopic data for **13** were in agreement with the postulated structure. The infrared spectrum of **13** showed the presence of a typical amide carbonyl (1650 cm^{-1}) and a strong S=O absorption at 1050 cm^{-1} . The nmr spectrum showed peaks at δ 4.09, 7.15, 8.80 and 10.0 in the ratio 2:10:1:1, respectively.

p-Methoxyaniline gave a similar compound (**14**).

The nmr spectra of **13** and **14** were of interest since they presented two different -NH peaks, both broad, at δ 10.00 and δ 8.80. The peak at δ 10.00 was assigned to the amide NH and the peak at δ 8.80 was assigned to the sulfinamide peak, by comparing these values to those of known compounds containing these groups.

The reaction of *o*-phenylenediamine with ketene in liquid sulfur dioxide (Scheme V) gave the derivative of the unreported ring system [2,1,5]benzothiadiazepin-4-one 2-oxide.

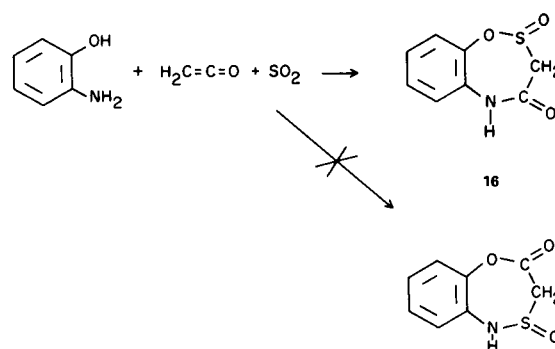
SCHEME V



The structure assigned to **15** was supported by analytical data and spectroscopic data. The nmr spectrum showed absorptions at δ 4.10 (CH₂), 7.2 (multiplet), 8.80 (-NH) and 9.82 (-NH), in the ratio of 2:4:1:1, respectively.

The reaction of *o*-aminophenol with ketene in liquid sulfur dioxide (Scheme VI) was of interest since two cyclic products could be predicted.

SCHEME VI



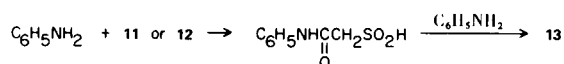
The analytical and spectroscopic data support structure **16**. The nmr spectrum of **16** showed the following peaks at δ 3.90 (CH₂), 7.36 (multiplet) and 10.4 (-NH), in the ratio of 2:4:1, respectively. The infrared spectrum did not show the absorption at $1050 \pm 20\text{ cm}^{-1}$ which would be expected for the -NHS=O group in the alternate structure.

In the nmr spectra of **15** and **16**, methylene protons appeared as a quartet. These results are due to the non-equivalence of the two protons which resulted in geminal

coupling. The measured $J_{HH'}$ value for compounds **15** and **16** were equal to 10 cps and 14 cps, respectively.

A reasonable path for the reaction of an amino group with ketene in liquid sulfur dioxide could involve the reaction of this group with a ketene-sulfur dioxide intermediate (either the dipolar form or one of the covalent cyclic forms) to give a sulfinic acid which would react further under the dehydrating conditions to yield the sulfinamide (Scheme VII).

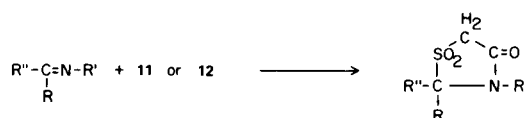
SCHEME VII



The last step is supported by the fact that the condensation of benzene-sulfinic acid with aniline is known to produce the corresponding sulfinamide (**14**). The path shown in Scheme VII can also account for the formation of products **15** and **16**.

We believe that the mechanistic path for the reactions of imines with ketene in liquid sulfur dioxide can also be explained by the formation of the same intermediate and subsequent attack of this intermediate over the active nucleophilic double bond (Scheme VIII).

SCHEME VIII



EXPERIMENTAL

All microanalyses were performed by Alfred Bernhardt Micro-analytical Laboratories, Mulheim, West Germany. Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were determined on a Perkin-Elmer 521 double beam recording spectrophotometer as potassium bromide disks. Absorptions are given in cm^{-1} . Nmr spectra were determined on a Varian A-60A, in DMSO unless otherwise noted. Chemical shifts are given in ppm (δ) (TMS=O). Abbreviations are: s, singlet; d, doublet; q, quartet and m, multiplet. Ketene was prepared by the pyrolysis of acetone in a ketene generator. All products were recrystallized from methanol unless otherwise noted.

Preparation of 2,3-Diphenylthiazolidin-4-one 1,1-Dioxide (**1**).

Pure benzylidene aniline (18.1 g., 0.01 mole) was dissolved in 20 ml. of benzene in a 250 ml. one-necked, round-bottomed flask fitted with a Dean-Stark tube. A 70% aqueous solution of thioacetic acid (15 ml.) was added to the initial solution and the mixture refluxed overnight. The solution was concentrated, treated with 20 ml. of diethyl ether and the solid formed collected by filtration. A 90% yield of 2,3-diphenylthiazolidin-4-one was obtained, m.p. 132-133° (lit. (**15**) m.p. 131.6-132.2°). This

solid was dissolved in 600 ml. of dioxane and added to 30 g. of sodium permanganate dissolved in 70 ml. of water and 400 ml. of acetic acid. The mixture was allowed to stand for one hour. A solution of 50 g. of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 400 ml. of water was added to the brown solution and water was added until a white precipitate formed. The mixture was allowed to stand for half an hour in the refrigerator. The solid formed was collected by filtration to give a 95% yield of **1**. The physical constants, ir and nmr spectra of this product were identical to those of **1** prepared by the cycloaddition of benzylideneaniline and ketene in liquid sulfur dioxide.

General Procedure for the Reactions of Ketene with Imines in Anhydrous Liquid Sulfur Dioxide.

The imine (0.1 mole) was dissolved in 50 ml. of anhydrous liquid sulfur dioxide in a 250 ml. three-necked, round-bottomed flask, immersed in a dry-ice/acetone bath, and adapted to a Dewar condenser filled with dry-ice and acetone. Ketene was bubbled through the solution at a rate of 0.48 moles/hour for one hour. During this period, the reaction mixture was magnetically stirred and kept at the lowest possible temperature (-70°). At the end of the one-hour period, the ketene delivery tube was removed and the light yellow solution was stirred for another hour without using the dry-ice/acetone bath. The excess of sulfur dioxide was evaporated at room temperature, in a hood, by substituting the Dewar condenser for the calcium chloride tube. The solid was collected and washed with cold methanol. The physical and spectroscopic data for the substituted 2,3-diphenylthiazolidin-4-one 1,1-dioxides are reported in Tables I and II.

Dihydro-7a-phenyl-7aH-thiazolo[2,3-b]thiazol-3 (2H)-one 1,1-Dioxide (**8**).

This compound was prepared in 80% yield, m.p. 116.5° dec. It was washed with cold acetone and stored in the refrigerator to avoid decomposition. The ir spectrum of **8** showed bands at 1700 (C=O), 1350, 1320 and 1150 (SO_2) cm^{-1} . The nmr spectrum (in deuterated acetone) showed absorptions at δ 4.25 m, 4.62 m and 7.45 m, in the ratio 2:4:5, respectively.

Anal. Calcd. for $C_{11}H_{11}NO_3S_2$: C, 49.05; H, 4.14; N, 5.16; S, 23.81. Found: C, 49.20; H, 4.22; N, 5.17; S, 23.89.

Dihydro-7a-p-nitrophenyl-7aH-oxazolo[2,3-b]thiazol-3 (2H)-one 1,1-Dioxide (**9**).

This compound was obtained in 90% yield, m.p. 115° dec. It was collected *in vacuo*, washed with cold acetone and dried. It was stored in the refrigerator to avoid decomposition. The ir spectrum of **9** showed bands at 1720 (C=O), 1350, 1330 and 1130 (SO_2) cm^{-1} . The nmr spectrum showed absorptions at δ 4.28 m, 4.68 m, and 8.35 m, in the ratio of 4:2:4, respectively.

Anal. Calcd. for $C_{11}H_{10}N_2O_6S$: C, 44.39; H, 3.32; N, 9.39; S, 10.73. Found: C, 44.38; H, 3.55; N, 9.60; S, 10.73.

2-Styryl-3-phenylthiazolidin-4-one 1,1-Dioxide (**10**).

This compound was obtained in 51% yield, m.p. 140-141° dec. The ir spectrum of this compound showed bands at 1685 (C=O), 1370, 1340, 1130 (SO_2) and 970 (*trans* C=C) cm^{-1} . The nmr spectrum showed absorptions at δ 4.60 s, 6.16 d, 6.40 d, 6.86 d and 7.42 m in the ratio of 2:1:1:1:10, respectively.

Anal. Calcd. for $C_{17}H_{15}NO_3S$: C, 65.15; H, 4.82; N, 4.47; S, 10.23. Found: C, 65.37; H, 4.90; N, 4.65; S, 10.61.

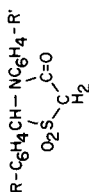
General Procedure for the Reactions of Aromatic Amines with Ketene in Anhydrous Liquid Sulfur Dioxide.

The aromatic amine (0.1 mole) was mixed with 100 ml. of liquid sulfur dioxide in a 250 ml. three-necked flask, immersed in

TABLE I
Substituted 2,3-Diphenylthiazolidin-4-one 1,1-Dioxides

Compound No.	R	R'	M.p., °C (a)	Yield	Formula	Calcd.			Analysis, %			Found		
						C	H	N	S	C	H	N	S	
1	H	H	181-182	52	C ₁₅ H ₁₃ NSO ₃	62.69	4.52	4.87	11.14	62.51	4.63	4.99	11.31	
2	<i>p</i> -CH ₃	H	187-188	49	C ₁₆ H ₁₅ NSO ₃	63.78	4.98	4.65	10.64	63.71	5.00	4.69	10.67	
3	<i>p</i> -Cl	H	178-179	55	C ₁₅ H ₁₂ NSClO ₃ (b)	55.98	3.72	4.35	9.95	55.81	3.74	4.49	10.07	
4	<i>m</i> -CH ₃ O	H	155	41	C ₁₆ H ₁₅ NSO ₄	60.56	4.73	4.41	10.09	60.74	4.86	4.55	10.08	
5	<i>p</i> -NO ₂	H	115	60	C ₁₅ H ₁₂ N ₂ SO ₅	54.21	3.61	8.43	9.66	54.15	3.70	8.51	9.83	
6	H	<i>p</i> -CH ₃	181-182	51	C ₁₆ H ₁₅ NSO ₃	63.78	4.98	4.65	10.64	63.68	5.05	4.66	10.41	
7	H	<i>p</i> -Br	203-204	36	C ₁₅ H ₁₂ NSBrO ₃ (c)	49.17	3.27	3.86	8.74	49.03	3.42	3.97	8.85	

(a) All compounds decompose at their melting point. (b) % Cl, Calcd., 11.40; Found, 11.39. (c) % Br, Calcd., 21.85; Found, 21.84.



a dry-ice/acetone bath and adapted to a Dewar condenser. The yellow solid formed was the 1:1 adduct reported to be formed between sulfur dioxide and the amine (16). Ketene was added to this suspension for one hour (0.48 mole) with magnetic stirring and a change in color of the solution occurred, from yellow to green to gray. After the addition of ketene was completed, the mixture was magnetically stirred for 40 minutes without any use of a dry-ice/acetone bath. After that period, the solid was collected by filtration and washed with cold methanol. All products were recrystallized from methanol.

Thioaceto-1,3-dianilide 3-Oxide (13).

This compound was obtained in 67% yield, m.p. 167° dec. The ir spectrum of this compound showed bands at 3280, 3250 and 3190 (NH stretch), 1650 (C=O stretch) cm⁻¹. The nmr spectrum showed absorptions at δ 4.09 s, 7.15 m, 8.80 m and 10.0 m, in the ratio of 2:10:1:1, respectively.

Anal. Calcd. for C₁₄H₁₄NO₂S: C, 61.31; H, 5.10; N, 10.20; S, 11.68. Found: C, 61.11; H, 4.95; N, 10.12; S, 11.16.

Thioaceto-1,3-di(*p*-methoxyanilide) 3-Oxide (14).

This compound was obtained in 34% yield, m.p. 164°. The ir spectrum of this compound showed bands at 3280, 3250 and 3140 (NH stretch), 1650 (C=O), 1060 (S=O) and 1030 cm⁻¹. The nmr spectrum showed absorptions at δ 3.80 s, 4.00 s, 7.00 m, 8.70 m, and 10.2 m, in the ratio of 6:2:8:1:1, respectively.

Anal. Calcd. for C₁₆H₁₈N₂O₄S: C, 57.48; H, 5.38; N, 8.32; S, 9.58. Found: C, 57.30; H, 5.33; N, 8.48; S, 9.58.

2,1,5-Benzothiadiazepin-4-one 2-Oxide (15).

This compound was obtained in 51% yield, m.p. 195-196° dec. The ir spectrum of this compound showed peaks at 3190 (NH stretch), 1675 (C=O) and 1080 (S=O) cm⁻¹. The nmr spectrum showed absorptions at δ 4.1 q, 7.2 m, 8.80 m and 9.82 m, in the ratio of 2:4:1:1, respectively.

Anal. Calcd. for C₈H₈N₂O₂S: C, 48.97; H, 4.08; N, 14.28; S, 16.32. Found: C, 48.85; H, 4.22; N, 14.09; S, 16.49.

1,2,5-Benzoxathiazepin-4-one 2-Oxide (16).

This compound was obtained in 25% yield, m.p. 171-172° dec. The ir spectrum of this compound showed peaks at 3340, 3220, 3140 (NH stretch), 1675 (C=O), 1350, 1140 and 1100 (O-S=O) cm⁻¹. The nmr spectrum showed absorptions at δ 3.90 q, 7.36 s and 10.41 m, in the ratio of 2:4:1, respectively.

Anal. Calcd. for C₈H₇NO₃S: C, 48.73; H, 3.56; N, 7.12; S, 16.24. Found: C, 48.75; H, 3.56; N, 7.11; S, 16.45.

Reduction of 2,3-Diphenylthiazolidin-4-one 1,1-Dioxide.

A solution of 5.7 g. (0.02 mole) of **1** in 50 ml. of THF was added to a stirred solution of 2 g. (0.05 mole) of lithium aluminum hydride in 30 ml. of THF at room temperature. The mixture was refluxed for four hours, cooled and 10 ml. of water, 10 ml. of sodium hydroxide (10%) and 15 ml. of water were added successively. The yellow solid formed was collected by filtration and washed with 50 ml. of THF. The filtrate was dried (magnesium sulfate) and concentrated. The yellow oil which remained was allowed to stand overnight. The crystals formed were washed with cold petroleum ether (b.p. 30-60°) and dried to yield 2 g. of 2,3-diphenylthiazolidine, m.p. 85-86° (lit. (17) m.p. 86°).

Decomposition of Dihydro-7*a*-phenyl-7*aH*-thiazolo[2,3-*b*]thiazol-3-(2*H*)-one 1,1-Dioxide.

A solution of 6.7 g. (0.025 mole) of **8** in 50 ml. of acetone was refluxed in a steam bath for seven hours. The decomposition of **8** was followed with ir measurements of samples taken every hour by

TABLE II
IR and NMR Spectra of
Substituted 2,3-Diphenylthiazolidin-4-one 1,1-Dioxides

Compound No.	C=O	Ir bands, cm ⁻¹ (a)		-CH ₂	Chemical shift, ppm (b)	
		SO ₂			C-H	Aromatic Protons
1	1690	1340 1320	1140 1123	4.60 s	6.75	7.30 m
2	1705	1330 1315	1127 1119	4.60 s	6.69	7.32 m
3	1718	1335 1325	1138 1123	4.60 s	6.80	7.48 m
4	1685	1335 1315	1135 1120	4.60 s	6.70	7.31 m
5	1710	1345 1320	1120	4.65 s	—	7.40 m
6	1705	1318 1305	1125	4.60 s	6.70	7.32 m
7	1705	1320	1125	4.65	6.80	7.45 m

(a) Spectra were determined as potassium bromide disks. (b) Spectra were measured in DMSO, abbreviations are s, singlet; m, multiplet.

observing the disappearance of the sulfone absorptions at 1350 and 1150 cm⁻¹. At the end of that period, the solvent was evaporated and the remaining yellow liquid was distilled to yield 3.9 g. (98%) of 2-phenylthiazoline, b.p. 158-160° (10 mm Hg) (lit. (18) b.p. 276-277°). The nmr spectrum of this compound was identical to that of an authentic sample.

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