which yields a value for $k_{1,obsd}$ that is invariant with time within experimental error. Then,

$$k_{3,obsd} = k_{1,obsd}/(DABCO)_0(ARSH)_0 \quad (19)$$

where $(DABCO)_0$ and $(ArSH)_0$ are the initial concentrations of base and thiol, respectively. The procedure is particularly successful for these rate data because both the base and thiol concentrations exceed the disulfide concentrations by a factor of at least 40, and therefore remain essentially constant throughout all runs.

The integrated rate expression was programmed in FORTRAN IV for an IBM 360-91 computer.

Acidity data were not available for the thiols in xylene solution; so rate constants for the anionic species were not determined. Rather comparisons were made of $k_{3,obsd}$ values for a single thiol on the various disulfides (**1**–**3**).

Registry No.—**1**, 22057-41-6; **2**, 955-59-9; **3**, 35740-31-9.

Acknowledgment.—The authors gratefully acknowledge the financial support of and helpful discussions with Dr. Paul D. Boyer. Mr. Darryl Benson provided excellent technical assistance.

Reactions of Sulfur Diimides with Ketenes

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The reaction products of sulfur diimides **1** with diphenylketene (**2a**) are temperature dependent. The reaction of diphenylsulfur diimide (**1a**) with **2a** at 6–8° gave the 1,2 cycloadduct **4** and at 80° the 1,1 cycloadduct **6a**. Refluxing **4** in benzene led to **6a** and **2a**. In contrast to **1a**, di-*tert*-butylsulfur diimide (**1b**) and **2a** at 0–2° gave 1,2 cycloadduct **3b**, which readily underwent rearrangement to **6b** under hexane reflux. The reaction of sulfur diimides **1** with alkylketenes gave no 1,2 or 1,3 cycloadducts but the thiobisamine derivatives **23** or **24** or their hydrolysis products. The reaction between diphenylsulfur diimide (**1a**) and dimethylketene (**2c**) gave rise to 2-phenylimino-3,3-dimethyl-1*H*-2,1-benzothiazin-4(3*H*)-one (**27a**) in addition to *N*,*N*′-diphenyl-*N*-(2-methylpropenoyl)-*N*′-isobutanoyl thiobisamine (**24b**).

Some studies on the reaction of sulfur diimides with diphenylketene have recently been reported. In our previous communication,[1] the structure of the product from diphenylsulfur diimide (**1a**) and diphenylketene (**2a**) was assumed to be 1-phenylimino-2,4,4-triphenyl-1,2-thiazetidin-3-one (**3a**) on the basis of ir, mass spectrum, and some chemical properties. An X-ray structure investigation,[2] however, showed that the structure is 2,4,4,5-tetraphenyl-1,2,5-thiadiazolidin-3-one (**6a**) instead of **3a**. The result is in accordance with the reported reaction of di-*p*-ethoxycarbonylphenylsulfur diimide with diphenylketene (**2a**).[3]

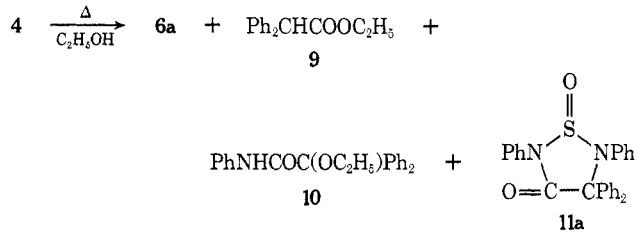
On the other hand, Kresze and Grill[4] isolated from the reaction of di-*p*-toluenesulfonylsulfur diimide with **2a** a 1-imino-1,2-thiazetidin-3-one derivative, which was easily isomerized to the 1,2,5-thiadiazolidin-3-one. Thus, variations in the sulfur diimide resulted in the formation of two types of 1,1 cycloadducts.

We have studied whether or not **6a** is formed *via* **3a** in analogy to Kresze's result.[4] Further, we report the reaction of various alkylketenes with sulfur diimides.

Part A

Results and Discussion

Reaction of Diphenylsulfur Diimide with Diphenylketene.—The reaction between diphenylsulfur diimide (**1a**) and diphenylketene (**2a**) in refluxing benzene gave the 1,3 cycloadduct, 2,4,4,5-tetraphenyl-1,2,5-thiadiazolidin-3-one (**6a**) in 67% yield. The reaction at lower temperature (6–8°), however, afforded only an unstable cycloadduct **4**. The yield of **4** was dependent on the molar ratio of **1a** to **2a** used in the reaction. The reaction using **1a** in double the molar quantity of **2a** gave **4** in 75% yield, while equimolar amounts produced **4** in 32% yield together with recovered **1a** (24%). On the other hand, refluxing an equimolar mixture of **4** and **1a** in benzene led to only **6a** (76%). With refluxing ethanol, **4** gave **6a** (44%), diphenylacetic acid ethyl ester (**9**) (38%), 1-ethoxy-1,1-diphenylacetanilide (**10**) (27%), and 2,4,4,5-tetraphenyl-1,2,5-thiadiazolidin-3-one 1-oxide (**11a**) (11%).



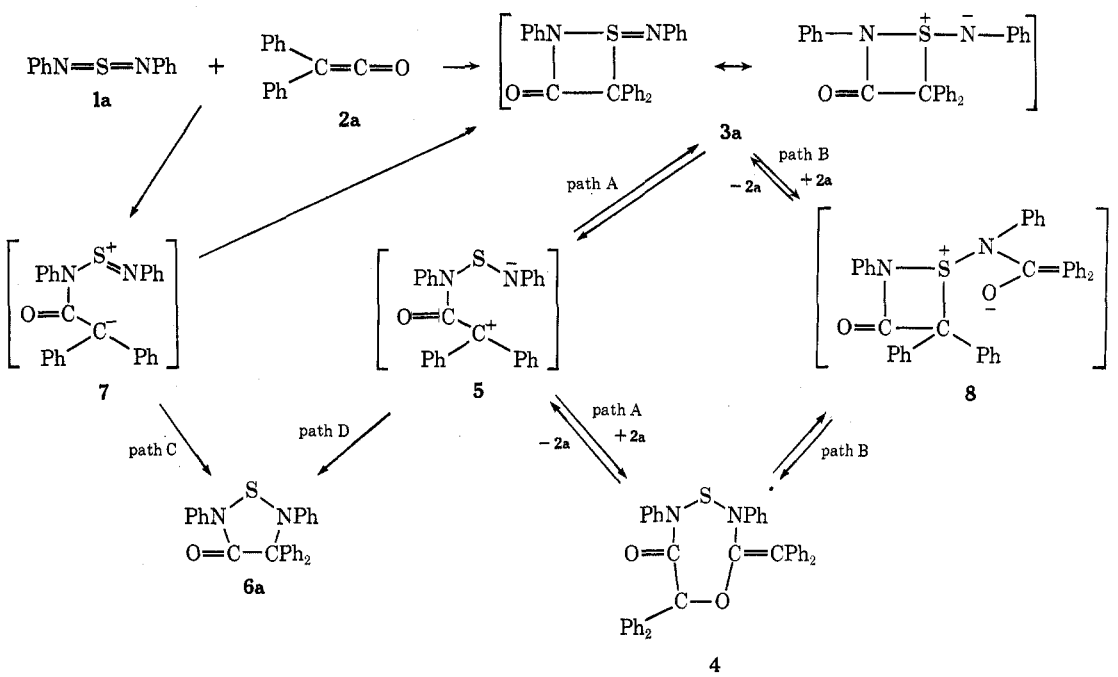
The unstable cycloadduct **4** contains 1 mol of **1a** and 2 mol of **2a** by elemental analysis, although the mass spectrum of **4** does not show any peak above the fragment ion peak at *m*/*e* 408 corresponding to the elimination of **2a** from the molecular ion. The ir spectrum of **4** exhibits carbonyl, carbon–carbon double bond, and ether absorptions at 1685, 1625, and 1275 cm^{-1}, respectively.

The chemical degradation and the physical data above do not clearly establish the structure of **4**. Accordingly, the structure was determined by X-ray analysis to be 2,3,4,6,7-pentahydro-2,4,4,7-tetraphenyl-3-oxo-1,5,2,7-thiaoxadiazepin-6-ylidenediphenylmethane. The molecular structure of **4** is shown in Figure 1.

Its formation would be rationalized in terms of one of two possible paths (path A and path B). As outlined in Scheme I, path A can be accounted for by a sequence of cycloaddition (**3a**), ring opening to the di-

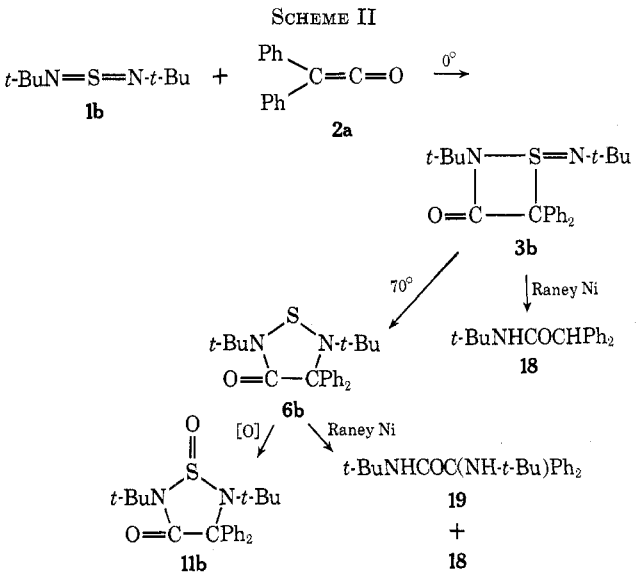
(1) T. Minami, O. Aoki, H. Miki, Y. Ohshiro, and T. Agawa, *Tetrahedron Lett.*, 447 (1969).
(2) N. Yasuoka, N. Kasai, T. Minami, Y. Ohshiro, T. Agawa, and M. Kakudo, *Bull. Chem. Soc. Jap.*, **43**, 1905 (1970).
(3) H. H. Hörhold and H. Eibisch, *Tetrahedron*, **25**, 4277 (1969).
(4) H. Grill and G. Kresze, *Tetrahedron Lett.*, 1427 (1970).

SCHEME I



polar acyclic adduct **5**, and the addition of a second molecule of **2a** to **5**, while path B is explicable by the addition of one more molecule of **2a** to **3a** to give **8**, followed by ring opening and cyclization. As shown in Scheme II, a 1,2 cycloadduct from **2a** and di-*tert*-

SCHEME II



butylsulfur diimide undergoes readily ring opening to a 1,3 cycloadduct but does not react with **2a**. The 1,2 cycloadduct from **2a** and di-*p*-toluenesulfonylsulfur diimide shows the similar chemical property.[4] These results suggest that ring opening is easier than the addition of **2a** to the 1,2 cycloadducts. Therefore, ring opening of **3a** would similarly take place rather than the addition of **2a** to **3a**. Since the formation of **4** cannot be explained by 1,5 cycloaddition of **7** across the C=O double bond of a second molecule of **2a**, ring opening of **3a** to **5**, followed by the addition of **2a**, must occur.

For the formation mechanism of **6a** from **1a** and **2a** at high temperature, two possible paths (path C and path D) are conceivable. Since it is reasonable to consider that products **4** and **6a** would be competitively formed *via* the same intermediate **5**, path D is more favorable. Likewise, the formation of **6a** by decomposition of **4** would be readily explained by closure of **5**, which would be generated by the elimination of **2a** from **4**.

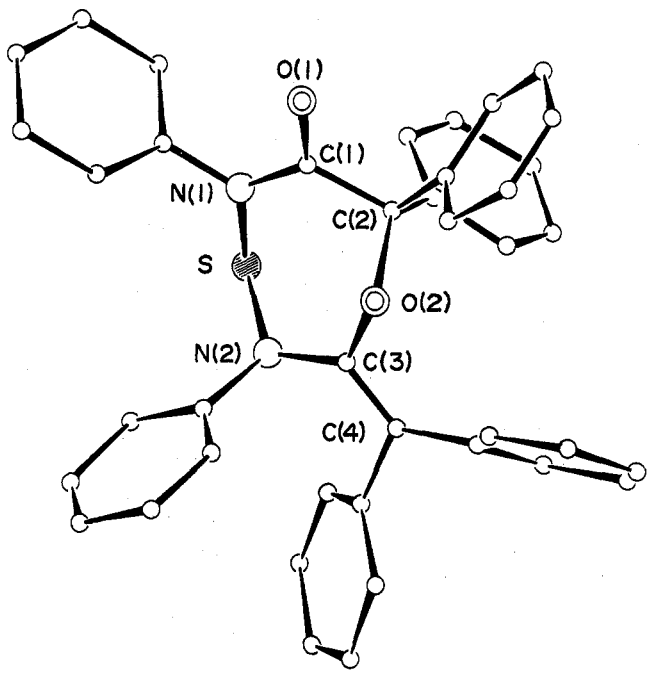
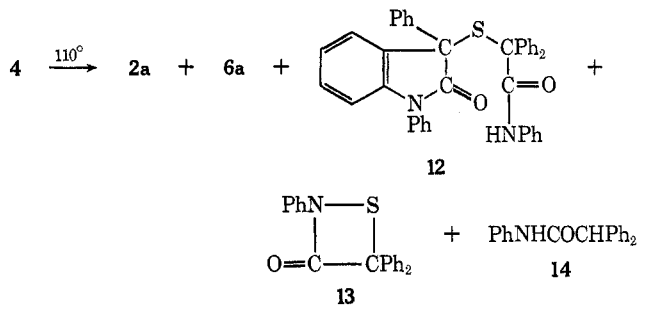
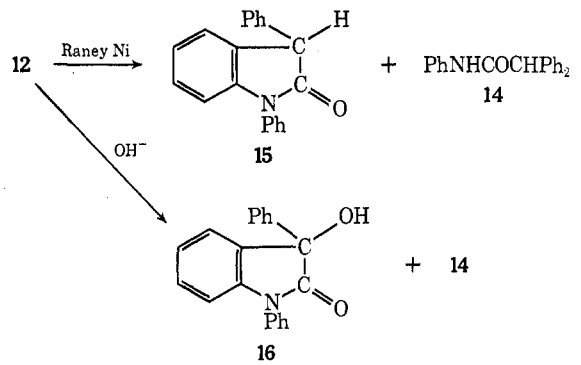


Figure 1.—X-Ray crystal structure of 2,3,4,6,7-pentahydro-2,4,4,7-tetraphenyl-3-oxo-1,5,2,7-thiaoxadiazepin-6-ylidenediphenylmethane (**4**).

Thermal Decomposition of Thiaoxadiazepine 4.—The thiaoxadiazepine derivative **4** on heating at 110° under reduced pressure decomposed to 2,3-dihydro-1,3-diphenyl-2-oxoindol-3-yl diphenyl(phenylcarbamoyl)methyl sulfide (**12**), 2,4,4-triphenyl-1,2-thiazetidin-3-one (**13**), and **6a**, all in 16–24% yield, and small amounts of diphenylacetanilide (**14**) and **2a**.

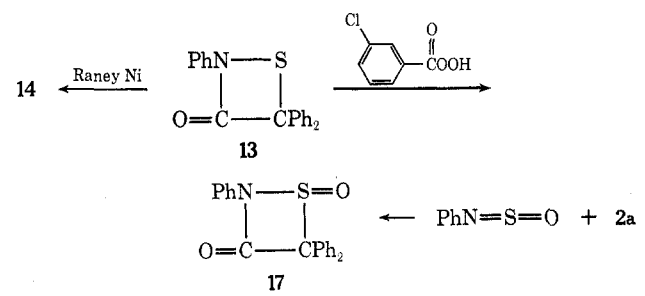


The reductive desulfurization of **12** by Raney Ni afforded 1,3-diphenyloxindole (**15**) and **14** in excellent yields. On basic hydrolysis, 1,3-diphenyldioxindole (**16**) and **14** were formed in 94 and 74% yields, respec-



tively. On the basis of this chemical evidence, the structure of **12** was assigned as 2,3-dihydro-1,3-diphenyl-2-oxoindol-3-yl diphenyl(phenylcarbamoyl)-methyl sulfide. The structure was confirmed by X-ray crystallographic analysis.[5]

The structure of **13** was determined as follows. The ir spectrum of **13** contains a strong carbonyl absorption at 1710 cm^{-1}, while **6a** has the corresponding absorption at 1670 cm^{-1}. This indicates that **13** has a ring smaller than **6a**. Reduction of **13** by Raney Ni gave **14** in good yield. Oxidation of **11** by *m*-chloroperbenzoic acid led to 2,4,4-triphenyl-1,2-thiazetidin-3-one 1-oxide (**17**), which was identical by melting point and ir spectrum with an authentic sample,[6] previously prepared from thionylaniline and diphenylketene (**2a**). These chemical properties and physical data are consistent with the structure **13**.



The thermal decomposition of **4** is too complicated to suggest the mechanism of the formation of oxindole **12**, which might be derived from **13** and α-lactam[7] formed by the elimination of **13** from **4**.

(5) Y. Kai, N. Yasuoka, N. Kasai, T. Minami, K. Yamataka, Y. Ohshiro, and T. Agawa, *Chem. Commun.*, 1532 (1971).

(6) H. Beecken and F. Korte, *Tetrahedron*, **18**, 1527 (1962).

(7) It is well known that 1,3,3-triphenylaziridinone gives 1,3-diphenyloxindole: J. C. Sheehan and J. W. Frankenfeld, *J. Amer. Chem. Soc.*, **83**, 4792 (1961).

Reaction of Di-*tert*-butylsulfur Diimide with Diphenylketene.—In contrast to **1a**, the reaction of di-*tert*-butylsulfur diimide (**1b**) with **2a** at 0° in ether afforded the 1,2 cycloadduct, 4,4-diphenyl-1-*tert*-butylimino-2-*tert*-butyl-1,2-thiazetidin-3-one (**3b**) in 74% yield. The product **3b**, when refluxed in hexane for 3 hr, was transformed quantitatively into the 1,3 cycloadduct, 4,4-diphenyl-2,5-di-*tert*-butyl-1,2,5-thiadiazolidin-3-one (**6b**). This observation is in agreement with Kresze's[4] result.

The structures of cycloadducts **3b** and **6b** were determined as follows. Cycloadduct **3b** has a strong ir band characteristic of the carbonyl group at 1720 cm^{-1} and two singlet *tert*-butyl signals at 1.15 and 1.53 ppm in the nmr spectrum, which were attributable to imino-*tert*-butyl and amino-*tert*-butyl protons, respectively. On the other hand, cycloadduct **6b** contains a carbonyl absorption at 1655 cm^{-1} in the ir spectrum and two singlet *tert*-butyl protons at 0.95 and 1.42 ppm due to two *tert*-butyls on N-5 and N-2 in the nmr spectrum, respectively.

Furthermore, the structures were clearly decided by hydrogenolysis of the products with Raney Ni. Hydrogenation of **3b** proceeded smoothly to afford *N*-*tert*-butyl-1,1-diphenylacetamide (**18**) in almost quantitative yield, while similar treatment of **6b** gave a mixture of **18** (28%) and *N*-*tert*-butyl-1-*tert*-butylamino-1,1-diphenylacetamide (**19**) (65%). Oxidation of **6b** with hydrogen peroxide gave the product **11b** (78%).

Thus, diphenylsulfur diimide showed different behavior from di-*tert*-butylsulfur diimide in the reaction with diphenylketene. The S=N bond in **3a** and **3b** can be considered to contain the "ylide property" as known in iminosulfurane.[8] Positive charge on the sulfur atom in **3a** would be greater than in **3b**, since the phenyl group can delocalize negative charge on the adjacent nitrogen by resonance. Accordingly, ring opening to the acyclic adduct **5a**, followed by the interception by a second molecule of **2a**, would be easier in **3a**.

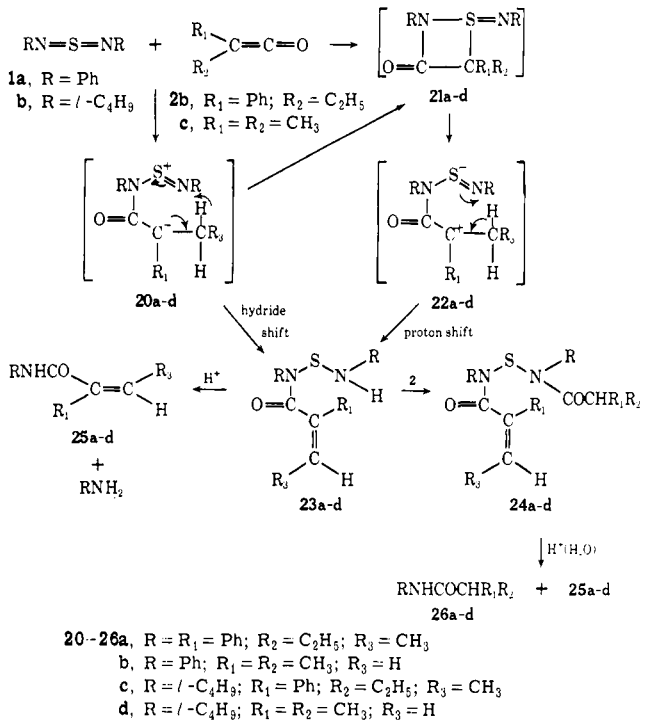
In conclusion, the difference of reactivities between **3a** and **3b** presumably dominates the reaction path.

Part B

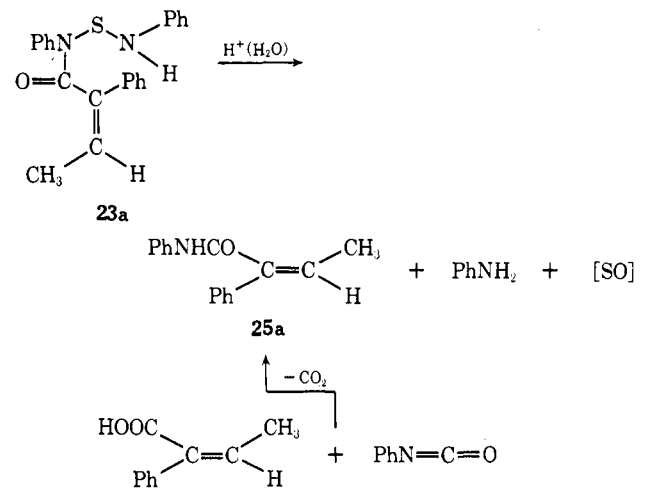
Reaction of Sulfur Diimides with Phenylethylketene.—The reaction of diphenylsulfur diimide (**1a**) with phenylethylketene (**2b**) at 0° gave a mixture of *N*,*N*'-diphenyl-*N*-(2-phenyl-*cis*-2-butenoyl)thiobisamine (**23a**) (17%) and its decomposition product, 2-phenyl-*cis*-2-butenoanilide (**25a**) (78%) (Scheme III). In the reaction of di-*tert*-sulfur diimide (**1b**) with **2b** under the same condition, the corresponding product *N*,*N*'-di-*tert*-butyl-*N*-(2-phenyl-*cis*-2-butenoyl)thiobisamine (**23c**) was isolated in 75% yield. Structural assignment to the product **23a** rests upon the following spectroscopic and chemical evidence. The ir spectrum shows the characteristic absorption bands at 3260, 1640, and 1630 cm^{-1} due to NH, amide carbonyl, and C=C bonds, respectively. The nmr spectrum ($CDCl_3$) indicates methyl (d, 3 H), vinyl and NH (m, 2 H), and phenyl protons (m, 15 H) at 1.80, 5.50–6.20, and 6.50–7.55 ppm. Acid-catalyzed hydrolysis led to 2-phenyl-

(8) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, p 356.

SCHEME III



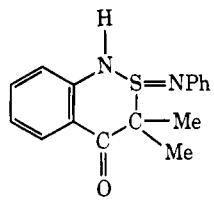
cis-2-butenoanilide (**25a**), which was confirmed by comparison of melting point, nmr, and ir with an authentic sample prepared from 2-phenyl-*cis*-2-butenoic acid, phenyl isocyanate, and aniline. Spectroscopic



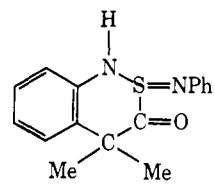
analysis and the chemical evidence, therefore, were consistent with *N*,*N*′-diphenyl-*N*-(2-phenyl-*cis*-2-butenoyl)thiobisamine (**23a**). Assignment of structure **23c** was similarly made.

Thus, no cycloadduct was obtained in the reaction of sulfur diimides with phenylethylketene (**2b**) in place of diphenylketene (**2a**). This result suggests that the thiobisamine derivative was formed either *via* an acyclic dipolar intermediate **20** followed by hydride shift or *via* an alternative dipolar intermediate **22**, followed by proton shift. However, we have no evidence to decide which path is more reasonable.

Reaction of Sulfur Diimides with Dimethylketene.—The reaction of **1a** with dimethylketene (**2c**) afforded a 1:1 adduct **27** (18%), *N*,*N*′-diphenyl-*N*-(2-methylpropenoyl)-*N*′-isobutanoylthiobisamine (**24b**) (3%), 2-methylacrylanilide (**25b**) (35%), and isobutyranilide (**26b**) (13%). The ir spectrum of the adduct **27** displayed characteristic bands at 3280 (NH) and 1635 cm^{-1} (carbonyl). The nmr spectrum showed absorptions at 2.00 (two methyls), 6.35 (NH), and 6.48–7.60 ppm (phenyl). There are two possible structures for the adduct **27** consistent with the spectral data: 2-phenylimino-3,3-dimethyl-1*H*-2,1-benzothiazin-4(3*H*)-one (**27a**) and 2-phenylimino-4,4-dimethyl-1*H*-2,1-benzothiazin-3(4*H*)-one (**27b**). Although the nmr spec-

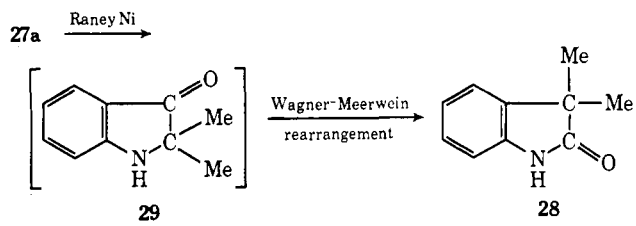


27a



27b

trum is compatible with both structures, the ir spectrum suggests that **27a** is the more probable structure on the basis of the low-frequency position of the carbonyl group. Reductive desulfurization of **27** with Raney Ni afforded 3,3-dimethyloxindole (**28**) (92%), which was identified by comparison of the ir spectrum and melting point with those of an authentic sample.[9] This chemical evidence seems to support the structure **27b**, since the formation of 2,2-dimethylindoxyl (**29**) is

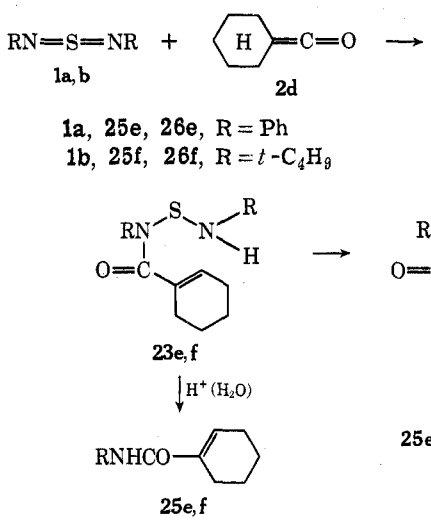


predicted from **27a**. However, it is well known that 2,2-disubstituted indoxyl is readily rearranged to 3,3-disubstituted oxindole.[10] Accordingly, it is reasonable to consider that the product **29**, which would be yielded by reduction of **27a**, underwent a Wagner–Meerwein rearrangement to lead to **28** under the experimental condition. On the basis of such spectral and chemical evidence, the 1:1 adduct was assigned the structure 2-phenylimino-3,3-dimethyl-1*H*-2,1-benzothiazin-4(3*H*)-one (**27a**).

In the reaction between **1b** and **2c**, no thiobisamine derivative (**23d** and/or **24d**) was obtained but *N*-*tert*-butyl-2-methylacrylamide (**25d**) and *N*-*tert*-butylisobutyramide (**26d**) were isolated in 69 and 9% yields, respectively.

Reaction of Sulfur Diimides with Pentamethyleneketene.—The reaction between **1a** and pentamethyleneketene (**2d**) yielded *N*,*N*′-diphenyl-*N*-(1-cyclohexenoyl)-*N*′-cyclohexanoylthiobisamine (**24e**) (55%), which would be provided by the addition of **2d** to *N*,*N*′-diphenyl-*N*-(1-cyclohexenoyl)thiobisamine (**23e**) initially formed, together with 1-cyclohexenoanilide (**25e**) (21%) and hexahydrobenzoanilide (**26e**) (5%). The difference in the yields between **25e** and **26e** evidently indicates the formation of **23e**, which might not be isolated for its instability, since only **25e** from **23e** and an

(9) K. Brunner, *Monatsh.*, **18**, 98 (1897).
(10) B. Witkop and A. Ek, *J. Amer. Chem. Soc.*, **73**, 5664 (1951).



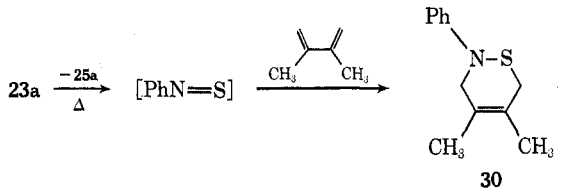
1a, **25e**, **26e**, R = Ph
1b, **25f**, **26f**, R = *t*-C_4H_9

equimolar amount of **25e** and **26e** from **24e** should be obtained.

In the reaction using **1b**, no thiobisamine derivative (**23f** and/or **24f**) was isolated, but its decomposition product, *N-tert*-butyl-1-cyclohexenylcarboxamide (**25f**), was obtained in 87% yield.

Reaction of Thiobisamine 23a with 2,3-Dimethylbutadiene.—Treatment of **23a** with 2,3-dimethylbutadiene at 140° in a sealed tube gave 2-phenyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine (**30**) (35%) and **25a** (80%).

The formation of the thiazine derivative **30** suggests



similarly the presence of thioaniline as a dienophile, as proposed by Tavs.[11] In the reaction using tetraphenylcyclopentadienone in place of 2,3-dimethylbutadiene, no 1,2-thiazine derivative was formed but azobenzene was obtained in 65% yield.

In conclusion, ketenes containing hydrogen on the α carbon atom react with sulfur diimide to give thiobisamine derivatives, regardless of the substituents on the sulfur diimide.

Experimental Section

General.—All melting points of products obtained (Table I) were determined with a Yanagimoto micro melting apparatus and uncorrected. The nmr spectra were obtained on a Joellmm 3H-60 spectrometer with tetramethylsilane as an internal standard. The ir spectra were recorded with a Jasco-IR-E spectrometer. The mass spectra were taken with a Hitachi RMU-6E spectrometer.

Materials.—Diphenylsulfur diimide[12] and di-*tert*-butylsulfur diimide[13] were prepared according to the established procedures.

Phenylethylketene was synthesized from 2-phenylbutanoyl chloride and triethylamine, bp 48° (2 mm), ir (neat) 2300 cm^{-1} (C=C=O).

2,3,4,6,7-Pentahydro-2,4,4,7-tetraphenyl-3-oxo-1,5,2,7-thiaoxadiazepin-6-ylidenediphenylmethane (**4**).—Diphenylsulfur diimide (**1a**) (2.14 g, 0.01 mol) dissolved in 50 ml of benzene was added dropwise to a stirred solution of diphenylketene (**2a**) (3.88 g, 0.02 mol) in 50 ml of benzene at 6–8° under an atmosphere of nitrogen. After stirring for 0.5 hr, the solution was allowed to warm to ambient temperature and stirring was continued for 0.5 hr. Benzene was then removed under reduced pressure. The residue immediately crystallized to give 4.5 g (75%) of **4**, which was washed with anhydrous ether to afford pure **4**: mp 101–110° dec; ir (Nujol) 1685 (C=O), 1625 (C=C), and 1275 cm^{-1} (COC); nmr ($CDCl_3$) δ 6.60–7.60 (m, phenyl protons); mass spectrum (70 eV) no molecular ion, *m/e* 408 ($M^+ - Ph_2CCO$), 317 ($M^+ - Ph_2CCONPh$), 285 (Ph_2CCOPh^+), 256 ($PhNCPh_2^+$).

Anal. Calcd for $C_{40}H_{30}N_2O_2S$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.69; H, 5.08; N, 4.60.

In the reaction using an equimolar amount of **1a** to **2a** under the same condition, **4** was obtained in 32% yield together with unreacted **1a** (24%).

2,4,4,5-Tetraphenyl-1,2,5-thiadiazolidin-3-one (**6a**). **Procedure A.**—A mixture of 4.81 g (8 mmol) of **4** and 1.48 g (6.9 mmol) of **1a** in 50 ml of benzene was refluxed for 3 hr. The solvent was removed *in vacuo* and the resulting solid residue was recrystallized from benzene–ethanol to give 4.60 g (76%) of **6a**: mp 167° (lit.[2] mp 167°); ir (Nujol) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.75–7.75 (m, phenyl protons); mass spectrum (70 eV) *m/e* 408 (M^+), 288 ($M^+ - PhNHCO$), 257 ($M^+ - PhNCO - S$), 214 ($PhNSNPh^+$), and 194 (Ph_2CCO^+).

Anal. Calcd for $C_{26}H_{20}N_2OS$: C, 76.45; H, 4.94; N, 6.86. Found: C, 76.29; H, 4.99; N, 6.80.

Procedure B.—A solution of 3.70 g (0.0173 mol) of **1a** in 50 ml of benzene was added dropwise to a solution of 3.9 g (0.02 mol) of **2a** in 50 ml of benzene at ambient temperature under a nitrogen atmosphere. After stirring at ambient temperature for 0.5 hr, the solution was refluxed for 3 hr. After work-up similar to above, **6a** was obtained in a yield of 4.70 g (67%).

Ethanolysis of 4.—A solution of 2.0 g (3.32 mmol) of **4** in 50 ml of 99% ethanol was refluxed for 3 hr. The solvent was removed *in vacuo* and the residue was recrystallized from benzene–ethanol to afford 0.60 g (44%) of **6a**. The filtrate was chromatographed on neutral alumina using benzene as eluent. The first fraction was concentrated and the residue was recrystallized from benzene–hexane to give 0.30 g (38%) of **diphenylacetic acid ethyl ester** (**9**), mp 56–58° (lit.[14] mp 57–58°). Similar treatment of the second fraction gave 0.30 g (27%) of **1-ethoxy-1,1-diphenylacetanilide** (**10**), mp 134° (lit.[1] mp 133.5–134.5°). Similar treatment of the third fraction afforded 0.15 g (11%) of **2,4,4,5-tetraphenyl-1,2,5-thiadiazolidin-3-one 1-oxide** (**11a**): mp 179–180.5° (hexane–benzene); ir (Nujol) 1720 (C=O) and 1160 cm^{-1} (S=O); nmr ($CDCl_3$) δ 6.80–8.00 (m, phenyl protons); mass spectrum (70 eV) *m/e* 424 (M^+), 305 ($M^+ - PhNCO$), 257 ($M^+ - PhNCO - SO$), and 180 (Ph_2CN^+).

TABLE I
SOME PHYSICAL DATA OF THE REACTION PRODUCTS OF SULFUR DIIMIDES WITH DIPHENYLKETENE AND THEIR DECOMPOSITION PRODUCTS

Product	Ir (Nujol), cm^{-1}	Nmr ($CDCl_3$), δ ppm	Mp, °C
6a	1670	6.75–7.75 (m, phenyl protons)	167
4	1685	6.60–7.60 (m, phenyl protons)	101–110 dec
11a	1720	6.80–8.80 (m, phenyl protons)	179–180.5
13	1710	6.95–7.60 (m, phenyl protons)	156–158
17	1740	7.80–7.83 (m, phenyl protons)	117–118 (lit.[6] 116–117.5)
3b	1720	1.15 (s, 9 H, S=N-*t*-Bu) 1.53 (s, 9 H, >N-*t*-Bu)	96–98 dec
6b	1655	0.95 (s, 9 H, >N-*t*-Bu) 1.42 (s, 9 H, CON-*t*-Bu)	103–104.5
11b	1705	1.17 (s, 9 H, >N-*t*-Bu) 1.58 (s, 9 H, CON-*t*-Bu)	180–181

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Anal. Calcd for $C_{26}H_{20}N_2O_2S$: C, 73.64; H, 4.67; N, 6.68. Found: C, 73.57; H, 4.75; N, 6.60.

11a from 6a and Hydrogen Peroxide.—A mixture of **6a** (2.40 g, 5 mmol) and 35% concentrated hydrogen peroxide (1 ml) in 50 ml of tetrahydrofuran was allowed to stir at 0° for 1.5 hr. After removal of solvent *in vacuo*, the resulting residue was extracted with benzene, followed by washing with water, drying over sodium sulfate, and evaporation of benzene. The residue was recrystallized from hexane–benzene to give **11a** (1.52 g, 36%).

Pyrolysis of 4.—The compound **4** (5.60 g, 9.3 mmol) was pyrolyzed at 110° under reduced pressure (1 mm) for 0.5 hr. The distillate (trace) was identified as diphenylketene. The residue was triturated with ether (10 ml) and then filtration gave the mixture of **2,3-dihydro-1,3-diphenyl-2-oxoindol-3-yl diphenyl(phenylcarbamoyl)methyl sulfide** (**12**) (1.24 g, 22%), **2,4,4-triphenyl-1,2-thiazetidin-3-one** (**13**) (0.70 g, 24%), and **6a** (0.28 g), which was separated by recrystallization from benzene–hexane. The crude compound **12** was recrystallized from benzene–ethanol, giving a pure sample, mp 208–209°, as a white, granular crystal: ir (Nujol) 3280, 3200 (NH), 1700 (indole ring C=O), 1690 (amide C=O), and 1550 cm^{-1} (NH); nmr ($CDCl_3$) δ 6.60–7.75 (m, 29 H, phenyl protons) and 9.82 (broad, 1 H, amide proton); mass spectrum (70 eV) *m/e* 602 (M^+), 317 ($M^+ - PhNCOCPh_2$), 285 ($M^+ - PhNCOCPh_2 - S$), and 194 (Ph_2CCO^+).

Anal. Calcd for $C_{40}H_{30}N_2O_2S$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.91; H, 4.91; N, 4.60.

The crude product **13** was recrystallized from benzene–hexane, giving a pure sample, mp 156–158°, as pale yellow plates: ir (Nujol) 1710 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.95–7.60 (m, phenyl protons); mass spectrum (70 eV) *m/e* 317 (M^+), 285 ($M^+ - S$), 256 ($M^+ - S - CO - H$), and 198 (Ph_2CS^+).

Anal. Calcd for $C_{20}H_{15}NOS$: C, 75.69; H, 4.67; N, 4.41. Found: C, 75.75; H, 4.68; N, 4.40.

The filtrate was chromatographed over neutral alumina using hexane, benzene, and ethanol as eluent to give **6a** (0.32 g) and **diphenylacetanilide** (**14**) (0.20 g, 8%), mp 184–185° (lit.[15] mp 180°). The combined yield of **6a** was 0.60 g (16%).

Oxidation of 13.—A solution of 0.70 g (2.23 mmol) of **13** and 1.0 g of *m*-chloroperbenzoic acid in 50 ml of chloroform was allowed to stir at room temperature for 24 hr. The solution was washed with 50 ml of 10% aqueous sodium sulfite, followed by washing with 50 ml of 5% aqueous sodium bicarbonate and 3 × 50 ml of water, and dried over sodium sulfate. After removal of solvent *in vacuo*, the residue was recrystallized from ether–benzene (9:1) to give 0.02 g (27%) of pure **2,4,4-triphenyl-1,2-thiazetidin-3-one 1-oxide** (**17**): mp 117–118° (lit.[6] mp 116–117.5°); ir (Nujol) 1740 (C=O), 1126 (S=O), and 1141 cm^{-1} (S=O); nmr ($CDCl_3$) δ 7.08–7.83 (m, phenyl protons); mass spectrum (70 eV) no molecular ion, *m/e* 285 ($M^+ - SO$), 256 ($M^+ - 1 - SO - CO$), and 194 (Ph_2CCO^+).

Anal. Calcd for $C_{20}H_{15}NO_2S$: C, 72.06; H, 4.54; N, 4.20. Found: C, 72.07; H, 4.54; N, 4.26.

The filtrate was chromatographed on neutral alumina. Elution with benzene–ethanol gave 0.25 g (41%) of **14**.

Reduction of 13.—A solution of 0.50 g (1.58 mmol) of **13** in 50 ml of tetrahydrofuran containing 1 g of Raney Ni was allowed to stir under reflux for 5 hr. The organic layer was separated and concentrated. Recrystallization of the residue from benzene gave 0.37 g (82%) of **14**.

Reduction of 12.—Reduction of **12** (1.70 g, 2.8 mmol) with Raney Ni (2 g) in tetrahydrofuran (50 ml) was similarly carried out. After removal of solvent *in vacuo*, the residue was chromatographed on alumina to give 1.10 g (92%) of **14** and 1.00 g (85%) of **1,3-diphenyloxindole** (**15**): mp 114–115° (lit.[7] mp 113–114°); ir (Nujol) 1720 (C=O) and 1610 cm^{-1} (C=C); nmr ($CDCl_3$) δ 4.77 (broad, 1 H, >CHPh) and 6.55–7.65 (m, 14 H, phenyl protons); mass spectrum (70 eV) *m/e* 285 (M^+) and 256 ($M^+ - 1 - CO$).

Anal. Calcd for $C_{20}H_{15}NO$: C, 84.18; H, 5.36; N, 4.91. Found: C, 84.12; H, 5.57; N, 4.82.

Base-Catalyzed Hydrolysis of 12.—A solution of **12** (1.70 g, 2.8 mmol) in tetrahydrofuran (100 ml) was refluxed with aqueous sodium hydroxide (10 ml, 20%) for 20 hr. After removal of solvent, the residue was extracted with benzene, followed by washing with water and drying over sodium sulfate. The benzene layer gave 0.60 g (74%) of **14**. The water layer was neutralized with hydrochloric acid and extracted with benzene. The benzene extract afforded 0.80 g (94%) of **1,3-diphenyldioxindole** (**16**): mp 172–173°; ir (Nujol) 3420 (OH), 1710 (C=O), and 1175 cm^{-1} (CO); nmr ($CDCl_3$) δ 4.13 (s, 1 H, OH) and 6.72–7.62 (m, 14 H, phenyl protons); mass spectrum (70 eV)-*m/e* 301 (M^+), 285 ($M^+ - O$), 272 ($M^+ - 1 - CO$), and 256 ($M^+ - CO - OH$).

Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.73; H, 4.80; N, 4.57.

4,4-Diphenyl-1-*tert*-butylimino-2-*tert*-butyl-1,2-thiazetidin-3-one (**3b**).—A solution of di-*tert*-butylsulfur diimide (**1b**) (3.0 g, 0.02 mol) in 30 ml of ether was added dropwise to a stirred solution of **2a** (3.88 g, 0.02 mol) in 30 ml of ether at 0–2° under a nitrogen atmosphere. After stirring for 0.5 hr, the solvent was removed *in vacuo* at room temperature. The residue was crystallized from cold hexane, and standing at −20° gave 5.42 g (74%) of **3b**: mp 96–98° dec; ir (Nujol) 1720 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.15 (s, 9 H, >S=N-*t*-Bu), 1.53 (s, 9 H, CON-*t*-Bu), and 7.02–7.55 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 368 (M^+), 312 ($M^+ + 1 - t$-Bu), 256 [$M^+ + 2 - 2(t$-Bu)], 213 (Ph_2CHNS^+), 194 (Ph_2CCO^+), and 180 (Ph_2CN^+).

Anal. Calcd for $C_{22}H_{28}N_2OS$: C, 71.71; H, 7.66; N, 7.60. Found: C, 71.99; H, 7.59; N, 7.64.

4,4-Diphenyl-2,5-di-*tert*-butyl-1,2,5-thiadiazolidin-3-one (**6b**).—A solution of 0.48 g (1.34 mmol) of **3b** in 50 ml of hexane was allowed to reflux for 4 hr. The solution was concentrated to one fifth of its original volume and allowed to stand at −20° to give 0.46 g (96%) of **6b**: mp 103–104.5°; ir (Nujol) 1655 cm^{-1} (CO); nmr ($CDCl_3$) δ 0.95 (s, 9 H, >N-*t*-Bu), 1.42 (s, 9 H, CON-*t*-Bu) and 7.03–7.68 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 368 (M^+), 312 ($M^+ + 1 - t$-Bu), 256 [$M^+ + 2 - 2(t$-Bu)], 213 (Ph_2CHNS^+), 194 (Ph_2CCO^+), and 180 (Ph_2CN^+).

Anal. Calcd for $C_{22}H_{28}N_2OS$: C, 71.71; H, 7.66; N, 7.60. Found: C, 71.40; H, 7.65; N, 7.57.

Reduction of 3b.—**3b** (0.45 g, 1.22 mmol) with Raney Ni (1 g) in THF was hydrogenated at room temperature for 3 hr in the same manner as **13**. After similar treatment, *N-tert*-butyl-1,1-diphenylacetamide (**18**) was obtained in a yield of 0.3 g (92%): mp 182–189° subl (lit.[16] mp 201–202°); ir (Nujol) 3300 (NH), 1635 (C=O), and 1550 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.30 (s, 9 H, *t*-Bu), 4.82 (s, 1 H, –CH<), 5.47 (broad, 1 H, NH), and 3.07–3.53 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 267 (M^+).

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.49; H, 7.86; N, 5.30.

Reduction of 6b.—A mixture of **6b** (1.0 g, 2.7 mmol) and Raney Ni (1 g) in 50 ml of ethanol was heated at reflux for 6 hr. After similar work-up the residue was crystallized from benzene–hexane to give 0.02 g (28%) of **18**.

The filtrate was evaporated and the residue was crystallized from hexane to give 0.59 g (65%) of *N-tert*-**butyl-1-*tert*-butylamino-1,1-diphenylacetamide** (**19**): mp 132–133.5°; ir (Nujol) 3320 (NH) and 1660 cm^{-1} (C=O); nmr ($CDCl_3$) δ 0.90 (s, 9 H, >N-*t*-Bu), 1.20 (s, 9 H, CON-*t*-Bu), 1.90 (broad, 1 H, amine proton), 7.02–7.35 [m, 6 H, amide proton (1 H) and phenyl protons (5 H)], and 7.35–7.77 (m, 5 H, phenyl protons); mass spectrum (70 eV) *m/e* 338 (M^+).

Anal. Calcd for $C_{22}H_{30}N_2O$: C, 78.06; H, 8.93; N, 8.28. Found: C, 78.14; H, 9.15; N, 8.29.

4,4-Diphenyl-2,5-di-*tert*-butyl-1,2,5-thiadiazolidin-3-one 1-Oxide (**11b**).—This derivative was prepared in the same way as **11a**, from the oxidation of 4.05 g (0.011 mol) of **6b** with 35% concentrated hydrogen peroxide (2 ml). The yield of **11b** was 3.30 g (78%) (after recrystallization from benzene–hexane): mp 180–181°; ir (Nujol) 1705 (C=O) and 1120 cm^{-1} (S=O); nmr ($CDCl_3$) δ 1.15 (s, 9 H, >N-*t*-Bu), 1.57 (s, 9 H, CON-*t*-Bu), and 7.15–7.85 (m, 10 H, phenyl protons); mass spectrum (70 eV) *m/e* 384 (M^+), 313 ($M^+ - t$-BuN), and 285 ($M^+ - t$-BuNCO).

Anal. Calcd for $C_{22}H_{28}N_2O_2S$: C, 68.72; H, 7.34; N, 7.29. Found: C, 68.45; H, 7.32; N, 6.97.

Reaction between Diphenylsulfur Diimide (**1a**) **and Phenylethylketene** (**2b**).—The reaction between **1a** (1.73 g, 8.08 mmol) and phenylethylketene (**2b**) (2.20 g, 15 mmol) was carried out in a similar manner as previously described for the reaction of **1b** with **2a**. The ethereal solution was concentrated *in vacuo* to one-third of its original volume and allowed to stand at 0° overnight. Filtration gave 0.50 g (17%) of *N,N'*-**diphenyl-*N*-(2-phenyl-*cis*-**

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2-butenoyl)thiobisamine (**23a**). The thiobisamine derivative **23a** was recrystallized from ether: mp 123–124.5°; ir (Nujol) 3260 (NH), 1640 (C=O), and 1630 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.80 (d, J = 6.7 Hz, 3 H, =CHCH_3), 5.50–6.20 (m, 2 H, =C**H**CH_3 and NH), and 6.50–7.55 (m, 15 H, phenyl protons); mass spectrum (70 eV) m/e 360 (M^+), 237 (M^+ − PhNS), 145 (M^+ − PhNSNHPh), and 117 (M^+ − PhCONSNHPh).

Anal. Calcd for $C_{22}H_{20}N_2OS$: C, 73.31; H, 5.59; N, 7.77. Found: C, 73.39; H, 5.72; N, 7.69.

The filtrate was chromatographed on alumina using benzene–ethanol (95:5) as eluent to give **2-phenyl-*cis*-2-butenoanilide** (**25a**) (1.5 g, 78%). Recrystallization from benzene–hexene afforded the analytical sample: mp 154–155°; ir (Nujol) 3280 (NH), 1650 (C=O), 1630 (C=C), and 1550 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.97 (d, J = 7.2 Hz, 3 H, =CHCH_3), 6.13 (d, J = 7.2 Hz, 1 H, =C**H**CH_3), and 7.00–7.85 (m, 11 H, phenyl protons and NH); mass spectrum (70 eV) m/e 237 (M^+), 145 (M^+ − PhNH), and 117 (M^+ − PhNHCO).

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.21; H, 6.22; N, 6.02.

Preparation of Authentic 2-Phenyl-*cis*-2-butenoanilide.—A mixture of 2-phenyl-*cis*-2-butenoic acid[17] (2.0 g, 0.0123 mol), phenyl isocyanate (1.50 g, 0.0126 mol), and triethyamine (2 ml) in 50 ml of toluene was refluxed for 10 hr. The solvent was removed under reduced pressure and the residue was crystallized from benzene–hexane to give 1.90 g (65%) of **2-phenyl-*cis*-2-butenoanilide**, mp 154°, which was consistent with **25a** obtained in the above experiment.

Acid-Catalyzed Hydrolysis of 23a.—A solution of **23a** (2.0 g, 5.56 mmol) in THF (50 ml) containing 48% aqueous HBr (4 ml) was refluxed for 5 hr. After removal of solvent, the residue was extracted with benzene, followed by washing with water and drying over sodium sulfate. The benzene layer gave 1.0 g (76%) of **25a**.

Reaction between Diphenylsulfur Diimide (1a) and Pentamethyleneketene (2d).—Hexahydrobenzoic acid chloride (7.35 g, 0.05 mol) in 50 ml of benzene was added dropwise to a stirred solution containing triethylamine (6.06 g, 0.06 mol) and diphenylsulfur diimide (3.57 g, 0.0167 mol) in 50 ml of benzene at room temperature under a nitrogen atmosphere. After the solution was stirred for 20 hr, the resulting amine salt was removed by filtration. The filtrate was evaporated under reduced pressure and the residue was crystallized from benzene to give 4.0 g (55%) of **N,N'-diphenyl-N-(1-cyclohexenoyl)-N'-cyclohexanoylthiobisamine** (**24e**): mp 195–196°; ir (Nujol) 1690 (C=O), 1680 (C=O), and 1645 cm^{-1} (C=C); nmr ($CDCl_3$) δ 0.72–2.12 (m, 18 H), 2.63 (broad, 1 H, cyclohexanoyl 1-proton), 5.60 (broad, 1 H, olefinic proton), and 6.95–7.55 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 434 (M^+), 324 ($M^+ + 1 -$ $C_6H_{11}CO$), 231 ($M^+ + 1 - C_6H_{11}CONPh$), 201 ($C_6H_{11}CONPh -$ $1)^+$, 123 ($PhNS^+$), and 110 ($C_6H_{12}CO + 1)^+$.

Anal. Calcd for $C_{26}H_{30}N_2O_2S$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.54; H, 6.85; N, 6.31.

The filtrate was chromatographed on neutral alumina using benzene–hexane as eluent to give a mixture of **1-cyclohexenoanilide** (**25e**) (0.72 g, 21%) and hexahydrobenzoanilide (**26e**) (0.18 g, 5%), whose ratio was determined with its nmr spectrum. The mixture was recrystallized from benzene–hexane to give pure **25e**: mp 125–127°; ir (Nujol) 3280 (NH), 1650 (C=O), 1625 (C=C), and 1540 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.05–2.55 (m, 8 H), 6.65 (broad, 1 H, olefinic proton), 6.85–7.80 (m, 5 H, phenyl protons), and 7.90 (broad, 1 H, NH); mass spectrum (70 eV) m/e 201 (M^+) and 109 (M^+ − PhNH).

Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.31; H, 7.80; N, 7.02.

The filtrate was concentrated and the residue was recrystallized from benzene–hexane to give pure **26e**: mp 137–138° (lit.[18] mp 130–131°); ir (Nujol) 3260 (NH), 1655 (C=O), and 1545 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.90–2.50 (m, 11 H), 6.85–7.65 (m, 5 H, phenyl protons), and 7.80 (broad, 1 H, amide proton); mass spectrum (70 eV) m/e 203 (M^+).

Anal. Calcd for $C_{13}H_{17}NO$: C, 76.78; H, 8.43; N, 6.89. Found: C, 76.94; H, 8.48; N, 6.94.

Acid-Catalyzed Hydrolysis of 24e.—A solution of **24e** (2.0 g, 4.61 mmol) in THF was treated under the same condition as **23a**. After similar work-up, a mixture of **25e** (0.52 g, 93%) and **26e** (0.50 g, 91%), whose ratio was determined with the nmr spectrum, was given.

Reaction between Diphenylsulfur Diimide (1a) and Dimethylketene (2c).—The reaction was carried out at 6–8° for 1 hr using the procedure described above with isobutyric acid chloride (21.3 g, 0.20 mol), triethylamine (24.2 g, 0.24 mol), and **1a** (20 g, 0.0805 mol) in dry benzene. After removal of amine salt by filtration, the filtrate was concentrated under reduced pressure. The resulting residue was crystallized from benzene to afford a mixture of **2-phenylimino-3,3-dimethyl-1*H*-2,1-benzothiazin-4-(3*H*)-one** (**27a**) and **N,N'-diphenyl-N-(2-methylpropenoyl)-N'-isobutanoylthiobisamine** (**24b**). Pure samples of individual **27a** (4.2 g, 18%) and **24b** (0.8 g, 3%) were isolated by repeated recrystallization of the mixture from benzene.

27a had mp 173–175°; ir (Nujol) 3280 (NH) and 1635 cm^{-1} (CO); nmr ($CDCl_3$) δ 2.00 (broad, 6 H, >C(CH_3)$_2$), 6.35 (broad, 1 H, NH), and 6.48–7.60 (m, 9 H, phenyl protons); mass spectrum (70 eV) m/e 284 (M^+), 161 (M^+ − PhNS), 146 (M^+ − PhNSNH), and 123 ($PhNS^+$).

Anal. Calcd for $C_{16}H_{16}N_2OS$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.71; H, 5.79; N, 9.69.

24b had mp 183–185.5°; ir (Nujol) 1695 (CO), 1675 (CO), and 1630 cm^{-1} (C=C); nmr ($CDCl_3$) δ 0.87 (d, 6 H, J = 6.3 Hz, −CH(CH_3)$_2$), 1.58 (broad, 3 H, CH_3C=CH_2), 3.13 (m, 1 H, −C**H**<), 4.85 [broad, 1 H, COC=CH (*trans*)], 5.03 [broad, 1 H, COC=CH (*cis*)], and 6.98–7.56 (m, 10 H, phenyl protons); mass spectrum (70 eV) m/e 354 (M^+), 284 (M^+ − (CH_3)$_2$CCO), 191 (M^+ − PhNHCOCHC(CH_3)$_2$), 161 (M^+ − PhNSCOC(CH_3)$_2$), and 123 ($PhNS^+$).

Anal. Calcd for $C_{20}H_{22}N_2O_2S$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.66; H, 6.00; N, 7.72.

The filtrate was chromatographed on alumina using benzene as eluent to afford a mixture of 4.47 g (35%) of **2-methylacrylanilide** (**25b**) and 1.68 g (13%) of **isobutyranilide** (**26b**), whose ratio was determined with its nmr spectrum. Pure samples of individual **25b** and **26b** were isolated by recrystallization of the mixture from benzene–hexane.

25b had mp 86–87° (lit.[19] mp 87°); ir (Nujol) 3300 (NH), 1650 (CO), 1615 (C=C), and 1525 cm^{-1} (NH); nmr ($CDCl_3$) δ 2.00 (broad, 3 H, CH_3C=CH_2), 5.38 (broad, 1 H, CH_3C=C**H**), 5.72 (broad, 1 H, COC=C**H**), 6.88–7.65 (m, 5 H, phenyl protons), and 8.00 (broad, 1 H, NH); mass spectrum (70 eV) m/e 161 (M^+) and 146 (M^+ − CH_3).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.67. Found: C, 74.64; H, 6.89; N, 8.67.

26b had mp 106–108° (lit.[20] mp 105°); ir (Nujol) 3280 (NH), 1655 (CO), and 1545 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.12 (d, 6 H, two methyl protons), 2.55 (m, 1 H, >CH–), 6.75–7.60 (m, 5 H, phenyl protons), and 9.08 (broad, 1 H, NH); mass spectrum (70 eV) m/e 163 (M^+).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.78; H, 8.21; N, 8.87.

Reduction of 27a.—A solution containing **27a** (2.5 g, 8.8 mmol) and Raney Ni (2 g) in 50 ml of THF was refluxed for 5 hr. The organic layer was separated and concentrated under reduced pressure. The residue was chromatographed on alumina to give 1.30 g (92%) of **3,3-dimethyloxindole** (**28**): mp 157–158° (lit.[9] mp 152–153°); ir (Nujol) 3160 (NH), 1715 (C=O), 1675 (C=O), and 1620 cm^{-1} (C=C); nmr ($CDCl_3$) δ 1.40 (s, 6 H, >C(CH_3)$_2$), 6.85–7.25 (m, 4 H, phenyl protons), and 9.85 (broad, 1 H, NH); mass spectrum (70 eV) m/e 161 (M^+) and 146 (M^+ − CH_3).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.86; H, 6.71; N, 8.80.

Reaction between Di-*tert*-butylsulfur Diimide (1b) and Phenylethylketene (2b).—The reaction was carried out at 0° using the procedure described above with **1b** (3.48 g, 0.02 mol) and **2b** (2.92 g, 0.02 mol) in petroleum ether (bp 30–60°). The reaction mixture was concentrated to one fifth of its original volume and allowed to stand at −20° to give 4.8 g (75%) of **N,N'-di-*tert*-butyl-N-(2-phenyl-*cis*-2-butenoyl)thiobisamine** (**23c**): mp 72.5–74°; ir (Nujol) 3320 (NH) and 1635 cm^{-1} (CO); nmr ($CDCl_3$) δ 1.40 (s, 9 H, NH-*t*-Bu), 1.59 (s, 9 H, CON-*t*-Bu), 1.88 (d, J = 6.6 Hz, 3 H, =CHC**H**$_3$), 3.45 (broad, 1 H, NH), 5.98 (q, J = 6.6 Hz, 1 H, =C**H**CH$_3$), and 7.18–7.35 (m, 5 H, phenyl protons); mass spectrum (70 eV) m/e 320 (M^+), 249 (M^+ −

(17) L. A. Carpino, *J. Amer. Chem. Soc.*, **80**, 601 (1958).
(18) W. Scharvin, *Chem. Ber.*, **30**, 2863 (1897).
(19) W. Autenrieth and C. Pretzell, *ibid.*, **36**, 1269 (1903).
(20) W. Crossley and W. H. Perkin, *J. Chem. Soc.*, **73**, 34 (1898).

N-*t*-Bu), 217 (M^+ − SN-*t*-Bu), 145 ($PhC(CO)=CHCH_3)^+$, and 117 ($PhC=CHCH_3^+$).

Anal. Calcd for $C_{18}H_{28}N_2OS$: C, 67.47; H, 8.81; N, 8.74. Found: C, 67.47; H, 9.01; N, 8.51.

Reduction of 23c.—Reduction of **23c** (1.60 g, 5 mmol) with Raney Ni (1 g) in 50 ml of ethanol was similarly carried out. After removal of solvent, the resulting residue was crystallized from benzene–hexane to give 0.76 g (69%) of ***N*-tert-butyl-2-phenylbutyramide (26c)**: mp 111.5–112.5°; ir (Nujol) 3320 (NH), 1635 (CO), and 1545 cm^{-1} (NH); nmr ($CDCl_3$) δ 0.87 (t, 3 H, CH_2CH_3), 1.28 (s, 9 H, *t*-Bu), 1.95 (m, 2 H, $CHCH_2CH_3$), 3.15 (t, 1 H, $CHCH_2$–), 5.35 (broad, 1 H, NHCO), and 7.28 (s, 5 H, phenyl protons); mass spectrum (70 eV) *m/e* 219 (M^+) and 120 (M^+ − *t*-BuNCO).

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.76; H, 9.81; N, 6.19.

The filtrate was concentrated and the crystallization of the residue from hexane afforded 0.21 g (19%) of ***N*-tert-butyl-2-phenyl-*cis*-2-butenoamide (25c)**: mp 108–109°; ir (Nujol) 3240 (NH), 1640 (CO), 1625 (C=C), and 1545 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.43 (s, 9 H, *t*-Bu), 1.93 (d, J = 6.6 Hz, 3 H, $=CHCH_3$), 5.51 (broad, 1 H, NH), 6.02 (q, 1 H, J = 6.6 Hz, $=CHCH_3$), and 7.12–7.45 (m, 5 H, phenyl protons); mass spectrum (70 eV) *m/e* 217 (M^+), 161 (M^+ − *t*-Bu), 145 (M^+ − NH-*t*-Bu), and 117 (M^+ − *t*-BuNHCO).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.18; H, 9.02; N, 6.48.

Preparation of Authentic *N*-tert-Butyl-2-phenyl-*cis*-2-butenoamide.—*tert*-Butylamine (0.34 g, 5 mmol) in 20 ml of benzene was added dropwise to a stirred solution of 2-phenyl-*cis*-2-butenoyl chloride (0.5 g, 2.76 mmol) and triethylamine (0.51 g, 5 mmol) in 20 ml of benzene at room temperature over a period of 0.5 hr. After removal of amine salt by filtration, the filtrate was concentrated under reduced pressure. The resulting residue was crystallized from hexane to give 0.4 g (68%) of ***N*-tert-butyl-2-phenyl-*cis*-2-butenoamide**, mp 106–108°, which was consistent with **25c** obtained in the above experiment.

Acid-Catalyzed Hydrolysis of 23c.—A solution of **23c** (2.0 g, 6.25 mmol) in 50 ml of ethanol containing 48% aqueous hydrobromic acid (4 ml) was refluxed for 5 hr. After similar work-up, as described above, the yield of **25c** was 0.68 g (65%).

Reaction between Di-*tert*-butylsulfur Diimide (1b) and Pentamethyleneketene (2d).—The reaction was carried out at room temperature for 20 hr as described above using hexahydrobenzoic acid chloride (7.35 g, 0.05 mol), **1b** (3.48 g, 0.02 mol), and triethylamine (6.06 g, 0.06 mol). After similar work-up, the residue obtained was crystallized from hexane to give 1.75 g of ***N*-tert-butyl-1-cyclohexenylcarboxamide (25f)**: mp 111–112.5°; ir (Nujol) 3320 (NH), 1650 (CO), 1615 (C=C), and 1525 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.40 (s, 9 H, *t*-Bu), 1.45–2.30 (m, 8 H), 5.55 (broad, 1 H, NHCO), and 6.50 (broad, 1 H, olefinic proton); mass spectrum (70 eV) *m/e* 181 (M^+).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.88; H, 10.57; N, 7.33. Found: C, 72.97; H, 10.87; N, 7.61.

The filtrate was chromatographed on alumina using benzene–hexane as eluent to give 1.5 g of **25f**. The combined yield of **25f** was 3.25 g (89%).

Reaction between Di-*tert*-butylsulfur Diimide (1b) and Dimethylketene (2c).—The reaction was carried out at room temperature for 1 hr as described above using isobutyric acid chloride (4.5 g, 0.04 mol), **1b** (3.48 g, 0.02 mol), and triethylamine (4.50 g, 0.0445 mol). After similar work-up, the residue obtained was chromatographed on alumina using benzene–hexane as eluent to give a mixture of ***N*-tert-butyl-2-methylacrylamide (25d)** (1.94 g, 69%) and ***N*-tert-butylisobutyramide (26d)** (0.26 g, 9%), whose ratio was determined with its nmr spectrum. Recrystallization of the mixture from hexane afforded pure **25d**: mp 50–57° subl; ir (Nujol) 3300 (NH), 1650 (C=O), 1615 (C=C), and 1525 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.40 (s, 9 H, *t*-Bu), 1.92 (broad, 3 H, $CH_3C=C<$), 5.23 [broad, 1 H, –(CO)C=C(H)– (trans)] and 5.55 [broad, 2 H, –(CO)C=C(**H**)– (cis) and amide proton]; mass spectrum (70 eV) *m/e* 141 (M^+).

Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 67.80; H, 11.01; N, 9.91.

The filtrate was concentrated and the residue was recrystallized from hexane to give pure **26d**: mp 50–70 subl; ir (Nujol) 3320 (NH), 1640 (CO), and 1545 cm^{-1} (NH); nmr ($CDCl_3$) δ 1.13 (d, 6 H, $CH(CH_3)_2$), 1.85 (s, 9 H, *t*-Bu), 2.23 (m, 1 H, –CH<), and 5.53 (broad, 1 H, NHCO); mass spectrum (70 eV) *m/e* 143 (M^+).

Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 66.76; H, 12.35; N, 9.55.

Reaction of 23a with 2,3-Dimethylbutadiene.—A mixture of **23a** (3.40 g, 9.4 mmol) and 2,3-dimethylbutadiene (4.4 ml) in benzene (15 ml) was heated at 140° in a sealed tube for 6 hr. After removal of the resulting **2-phenyl-2-butenoanilide (25a)** (1.80 g, 80%) by filtration, the filtrate was evaporated *in vacuo* to yield a brown oil (1.50 g). The oil was distilled to give 0.67 g (35%) of a pale yellow oil, whose structure was identified as **2-phenyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine (30)** by comparison of its nmr spectrum with that of an authentic sample:[11] bp 83–85° (0.03 mm) [lit.[11] bp 103–105° (0.1 Torr)]; nmr ($CDCl_3$) δ 1.70 (s, 6 H, $-CH_3$), 2.90 (s, 2 H, $-NCH_2$), 3.90 (s, 2 H, SCH_2), 7.0–7.3 (m, 5 H, phenyl protons); mass spectrum (70 eV) *m/e* 205 (M^+), 123 ($PhN=S^+$).

Reaction of 23a with Tetraphenylcyclopentadienone.—The reaction was carried out as described above using **23a** (3.60 g, 0.01 mol) and tetraphenylcyclopentadienone (3.85 g, 0.01 mol). After removal of solvent, the resulting residue was extracted with hexane, ethanol, and benzene. The hexane extract afforded azobenzene (1.18 g, 65%) and small amounts of oil which were comprised of several components by vpc. The ethanol extract gave 2.1 g (89%) of 2-phenyl-2-butenoanilide. The benzene extract afforded 3.1 g (80%) of starting diene.

Results of X-Ray Analysis of 4.—The structure of **4** was unambiguously established through a single-crystal X-ray analysis. The product **4** is unstable and attempts at recrystallization were unsuccessful. Therefore the crystals isolated by adding ether to a concentrated reaction mixture were used for the present X-ray work.

Crystal data follows: $C_{40}H_{30}O_2N_2S \cdot 0.5C_6H_6$, mol wt, 641.9, monoclinic, space group $I2/c$ (No. 15); a = 25.965 (8), b = 10.927 (6), c = 23.932 (9) Å and β = 94.83 (3)°, U = 6766 Å^3; D_m = 1.25 g/cm^3 (flotation method), D_c = 1.26 g/cm^3 for Z = 8.

TABLE II

SELECTED BOND LENGTHS (Å) AND ANGLES (DEGREE) IN THE MOLECULE 2,3,4,6,7-PENTAHYDRO-2,4,4,7-TETRAPHENYL-3-OXO-1,5,2,7-THIAOXADIAZEPIN-6-YLIDENEDIPHENYLMETHANE[a]

Bond	Length, Å	Angle	Degree
S–N(1)	1.718 (8)	N(1)–S–N(2)	104.6 (4)
S–N(2)	1.664 (8)	S–N(1)–C(1)	123.3 (6)
N(1)–C(1)	1.38 (1)	N(1)–C(1)–O(1)	120.3 (8)
C(1)–O(1)	1.22 (1)	C(2)–C(1)–O(1)	120.9 (8)
C(1)–C(2)	1.55 (1)	N(1)–C(1)–C(2)	118.7 (8)
C(2)–O(2)	1.46 (1)	C(1)–C(2)–O(2)	109.9 (7)
C(3)–O(2)	1.38 (1)	C(2)–O(2)–C(3)	125.1 (7)
C(3)–C(4)	1.34 (1)	O(2)–C(3)–C(4)	120.9 (8)
N(2)–C(3)	1.41 (1)	N(2)–C(3)–C(4)	122.7 (8)
		N(2)–C(3)–O(2)	115.9 (7)
		S–N(2)–C(3)	115.1 (6)

[a] Estimated standard deviations are shown in parentheses.

The three-dimensional intensity data were collected on an automated single-crystal diffractometer. The structure was solved by the parallel use of the direct method and of the heavy atom method, and then refined by the block-diagonal least-squares procedure (R = 0.080 for 2785 observed reflections). Anisotropic temperature factors were assigned for nonhydrogen atoms except those in benzene, for which isotropic temperature factors were used. Isotropic hydrogen atoms were included in the refinement.

The molecule crystallizes with 0.5 mol of benzene. The latter lies on a twofold axis, with a long axis of the molecule parallel to it. The electron density distribution around the benzene molecule is smeared out, probably because of the orientational disorder and/or the low occupancy. Although the refinement might be necessary in this connection, the chemical structure of the product has been well established in view of the low R value. The molecular structure of the molecule viewed along the b axis is shown in Figure 1. The important bond lengths and angles along with estimated standard deviations are listed in Table II.

Other pertinent crystallographic data and parameters may be found in the microfilm edition.[21]

Registry No.—**3b**, 36146-94-8; **4**, 36146-93-7; **6a**, 29376-74-7; **6b**, 36146-96-0; **11a**, 36146-97-1; **11b**, 36146-98-2; **12**, 35133-13-2; **13**, 36147-00-9; **15**, 23210-25-5; **16**, 36147-01-0; **17**, 10572-61-9; **18**, 36147-03-2; **19**, 36147-04-3; **23a**, 36138-85-9; **23c**, 36138-86-0; **24b**, 36147-05-4; **24e**, 36147-06-5; **25a**, 36138-87-1; **25b**, 1611-83-2; **25c**, 36138-88-2; **25d**, 6554-73-0; **25e**, 32119-42-9; **25f**, 36147-10-1; **26b**, 4406-41-1; **26c**, 36146-78-8; **26d**, 7472-49-3; **26e**, 2719-26-8; **27a**, 36146-81-3; **28**, 19155-24-9; **31**, 13616-67-6; phenylethylketene, 20452-67-9.

(21) The observed and calculated structure factors, atomic coordinates, and temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-72-3810. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Carbamoyl Chlorosulfines

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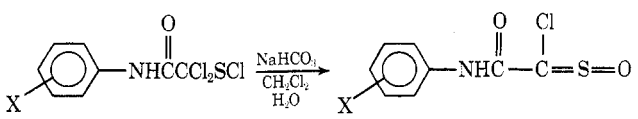
The synthesis of novel carbamoyl chlorosulfines *via* two different pathways is described. In some cases these reagents slowly convert to a geometrical isomer at room temperature. An assignment of structure to the geometrical isomers is proposed on the basis of physical and spectra data. These sulfines yield α-chloroacetamides upon strong base hydrolysis.

In previous papers we reported that carbamoyldichlorosulfenyl chlorides can be conveniently synthesized[1,2] and that these substances undergo a wide range of reactions.[2] We now wish to report that mild basic hydrolysis of these reagents conveniently yields novel carbamoylchlorosulfines in moderate yield.

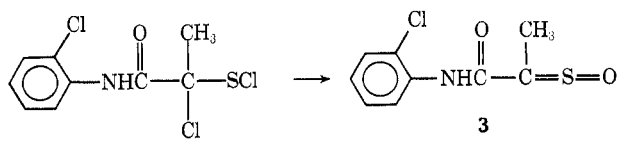
Treatment of **1** with aqueous sodium bicarbonate in a two-phase system employing methylene dichloride as a cosolvent yields carbamoyl chlorosulfines (**2**) in



1 **2**

a, X = 4-Cl
b, X = 3-CF_3
c, X = 3-Br
d, X = 4-OCH_3
e, X = 4-CH_3
f, X = 2,6-di-CH_3
g, X = 2-CH_3, 6-*t*-C_4H_9

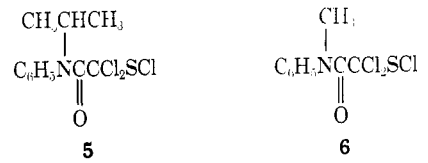
24–57% yield after purification. The reaction is general in that a variety of aromatic substituents may be employed. Water may be substituted for the aqueous bicarbonate although the reaction appears to be slower. In one instance a carbamoyl alkyl sulfine (**3**) was prepared in low yield by hydrolysis of the corresponding sulfenyl chloride (**4**). The only previous



4 **3**

example of the preparation of a sulfine *via* hydrolysis of a sulfenyl chloride is that of Silhanek and Zbirovsky[3] who reported that dichloromethylene sulfoxide may be prepared by hydrolysis of trichloromethanesulfenyl chloride.

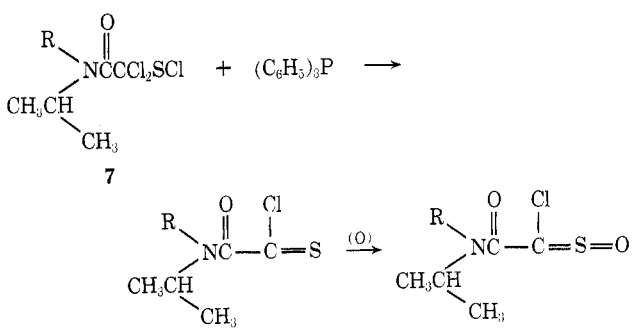
The sequence is not applicable to N,N-disubstituted carbamoyl sulfenyl chlorides. Treatment of **5** with aqueous sodium bicarbonate for 3 days resulted in a high recovery of starting material while **6** slowly yielded



5 **6**

a mixture of unidentified products from which no sulfine could be isolated.[4]

N,N-Disubstituted carbamoyl chlorosulfines may be prepared by another route. Treatment of N,N-disubstituted carbamoyldichlorosulfenyl chlorides (**7**) with triphenylphosphine yields the corresponding 2-chloro-2-thioxo-*N*,*N*-(disubstituted)acetamide (**8**).[2] Oxidation of these substances with *m*-chloroperbenzoic acid yields the sulfines in moderate yield.



7

8 **9**

a, R = C_6H_5
b, R = *i*-C_3H_7

In some cases the sulfines formed *via* the hydrolysis route were thermodynamically unstable. For ex-

(1) W. G. Phillips and K. W. Ratts, *J. Org. Chem.*, **36**, 3145 (1971).
(2) W. G. Phillips and K. W. Ratts, *ibid.*, **37**, 1526 (1972).
(3) J. Silhanek and M. Zbirovsky, *Chem. Commun.*, 878 (1969).
(4) Attempts to extend this synthetic route to other sulfenyl chlorides failed; hydrolysis of phenylsulfonyldichloromethylsulfenyl chloride with weak base yielded no reaction while hydrolysis of cyanodichloromethylsulfenyl chloride yielded α-chloroacetonitrile.