136.5, 136, 135, 134.5, 128, 127, 126, 123.3, 120.5, 117.5, 108.6, 108, 95, 60; mass spectrum M+ 507, 479, 463, 333, 313, 285, 194, 178, 164, 165, 166, 152, 149, 119, 92, 83, 63.

5,5-Diphenyl-2-benzhydrylidene-*N*-(*o*-phenothioxide)-5*H*-[1,3]oxazonia-6-one (4b).—The title compound was prepared from **1b** according to ref 3: ir 1772 (s), 1640 (s), 1480, 1225, 1145, 1020, 760, and 710 cm^{-1}; pmr τ 3.82–4.02 (m, 1 H), 3.15 (s, 1 H), 2.5–3.52 (m, 23 H); ^{13}C nmr δ 166.9, 141.9, 140, 138.1, 137.9, 126.8, 127.0, 127.5, 128.0, 128.5, 129.5, 130.3, 124.9, 122.4, 121.3, 114.8, 112.8, 70.50, 62.54; mass spectrum M+ 523, 507, 495, 301, 195, 194, 163, 164, 165, 166, 167, 139, 135, 126, 115, 108, 97, 92, 77.

***o*-[*N*-(2,2-Diphenylacetyl)-2,2-diphenyl-2-carbomethoxy-*N*-acetiminium] Phenoxide (6).**—Oxazinone **4a** (0.3 g) was dissolved in hot dioxane (20 ml). Methanol (5 ml) containing sodium methoxide (0.3 g) was added to the solution, which turned yellowish. After heating on the steam bath for 5 min, the solution was filtered and the filtrate was diluted with water. The precipitated white solid was collected and treated with hot methanol. The dried white solid weighed 0.28 g, mp 174–176°. The analytical sample that melted at 180° was recrystallized from chloroform–methanol: ir 1738 (s), 1680 (2), 1490, 1265, 1235, 1215, 1180, 1160, 1100, 1025, 760, and 700 cm^{-1}; pmr τ 6.3 (s, 3 H), 4.3 (s, 1 H), 2.5–3.5 (m, 24 H), 2.1 (s, 1 H); mass spectrum M+ 539, 508, 480, 420, 314, 215, 197, 194, 165, 166, 167, 152, 119, 105, 85, 83, 77. *Anal.* Calcd for $C_{36}H_{29}O_4N$ (539.60): C, 80.13; H, 5.42; N, 2.60. Found: C, 80.14; H, 5.45; N, 2.75.

***o*-[*N*-(2,2-Diphenylacetyl)-2,2-diphenyl-2-(*N'*,*N'*-dimethylacylhydrazyl)-*N*-acetiminium] Phenoxide (6).**—Oxazinone **4a** (50 mg) was dissolved in excess *unsym*-dimethylhydrazine (3 ml) and the solution was heated on the steam bath until the solvent evaporated. The gummy residue was treated with ether and the resulting solid was collected (45 mg). The analytical sample was recrystallized from methanol–water and melted at 215°: ir 1680, 1650, 1485, 1260, 1220, 1150, 1030, 1020, 955, 770, and 710 cm^{-1}; pmr τ 7.6 (s, 6 H), 4.2 (s, 1 H), 2.5–3.6 (m, 24 H), 2.15 (s, 1 H); mass spectrum M+ 567, 508, 481, 448, 314, 287, 286, 255, 254, 225, 210, 194, 187, 167, 166, 165, 164, 152, 119, 77. *Anal.* Calcd for $C_{37}H_{33}O_3N_3$ (567.66): C, 78.28; H, 5.86; N, 7.40. Found: C, 78.36; H, 5.92; N, 7.14.

4,4-Diphenyl-5-pyrazolone (7) from 4a.—Oxazinone **4a** (1 g) was placed in hot methanol (15 ml). Hydrazine (95%, 5 ml) was added and the mixture was heated on the steam bath until all the solid (**4a**) dissolved. Water was added and the resulting white solid was collected by suction filtration, washed with water and methanol, and dried: 0.45 g; mp 207°; ir 3420, 1705, 1500, 1360, 840, 760, and 700 cm^{-1}; pmr τ 2.67 (s, 10 H), 2.05 (broad s, 1 H); mass spectrum M+ 236, 207, 194, 179, 166, 165, 152, 139, 102, 77.

Anal. Calcd for $C_{15}H_{12}ON_2$ (236.26): C, 76.25; H, 5.12; N, 11.86. Found: C, 76.06; H, 5.18; N, 11.76.

The mother liquor from the above reaction was left to stand overnight at room temperature. Diphenylacetylhydrazide precipitated, and was identified by comparison with an authentic sample: mp 134°; ir 3420, 1650, 1500, 1370, 1250, 1020, 1010, 750, 730, 700 cm^{-1}; nmr τ 2.6 (m, 2 H), 5.1 (s, 1 H), 3.7, (s, 10 H), 2.35 (m, 1 H).

Conversion of 6 into 4,4-Diphenyl-5-pyrazolone (7).—Product **6** [R = OCH_3 or $NHN(CH_3)_2$] (45 mg) was dissolved in hot methanol (10 ml). Hydrazine (95%, 2 ml) was added to the solution, which was left to stand at room temperature for 24 hr. Dilution with water and neutralization with hydrochloric acid resulted in the precipitation of 4,4-diphenyl-5-pyrazolone (10 mg), mp 207°.

The above procedure was also applied to the conversion of product **4b** into pyrazolone **7**.

Pyrolysis of Oxazinone 4a.—A sample of oxazinone **4a** was placed in a test tube and heated until it melted. The yellow liquid was shown (ir) to be a mixture of diphenylketene and benzoxazole by comparison with an authentic mixture. The identity of benzoxazole was confirmed by tlc on silica gel.

1-Methyl-5-benzhydrylidene-8,8-diphenyl-5*H*,8*H*-imidazo-[3,2-*c*]-1,3-oxazin-7-one (10).—The title compound was prepared from *N*-methylimidazole and diphenylketene according to ref 3. The product entraps solvent of crystallization (methanol): ir 1748 (s), 1600 (w), 1500, 1315, 1235, 1188, 1125 (s), 1050, 760, 750, and 710 cm^{-1}; pmr τ 6.9 (s, 3 H), 4.9 (s, 1 H), 3.35 (m, 1 H), 2.6–3.18 (m, 21 H); mass spectrum M+ 470, 276, 247, 194, 167, 165, 152, 83, 82.

Registry No.—**1a**, 273-53-0; **1b**, 95-16-9; **1c**, 1632-83-3; **3c**, 40110-18-7; **4a**, 40110-19-8; **4b**, 40110-20-1; **6** (R = OMe), 40317-83-7; **6** (R = $NHNMe_2$), 40110-21-2; **7**, 40110-22-3; **10**, 40110-23-4; diphenylketene, 525-06-4; sodium methoxide, 124-41-4; *unsym*-dimethylhydrazine, 57-14-7; hydrazine, 302-01-2; diphenylacetylhydrazide, 6636-02-8; *N*-methylimidazole, 616-47-7.

Acknowledgment.—Support of this research by PHS Grant CA4474 from the National Cancer Institute is gratefully acknowledged.

The Chemistry of a Ketene–Sulfur Dioxide Adduct. II. Reactions with Heterocumulenes

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The reaction of ketenimines with ketene in anhydrous liquid sulfur dioxide gave substituted 1,2-oxathiane-4-one 2-oxides. The structures of these compounds were verified by both chemical and spectral methods. *p*-Tolylsulfonyl isocyanate reacted with ketene in liquid sulfur dioxide to yield *N*-(*p*-tolylsulfonyl)-3-thiazolidine-2,4-dione 1,1-dioxide. In addition, substituted 2,1,5-benzothiadiazepin-4-one 2-oxides were obtained from the corresponding *o*-phenylenediamine, ketene, and sulfur dioxide. The mechanisms of these reactions were believed to involve a ketene–sulfur dioxide adduct as a common intermediate. This reactive species was isolated and intercepted at low temperatures. During the course of this investigation, ketene was also found to react with *N*-sulfinylaniline to give *N*-phenyl-1,2-thiazetidin-3-one 1-oxide.

The cycloaddition of imines with ketene in liquid sulfur dioxide was described in earlier publications.[1,2] The mechanisms of the reactions discussed were believed to involve an intermediate formed from ketene and sulfur dioxide Although the isolation of the presumed adduct was not accomplished, its existence was detected by a low-temperature nmr study. Recently, we have observed other cycloadditions involving the ketene–sulfur dioxide adduct and certain heterocumulenes such as ketenimines. In addition, we offer further proof for the existence of such an adduct by its low-temperature isolation and interception with appropriate reagents.

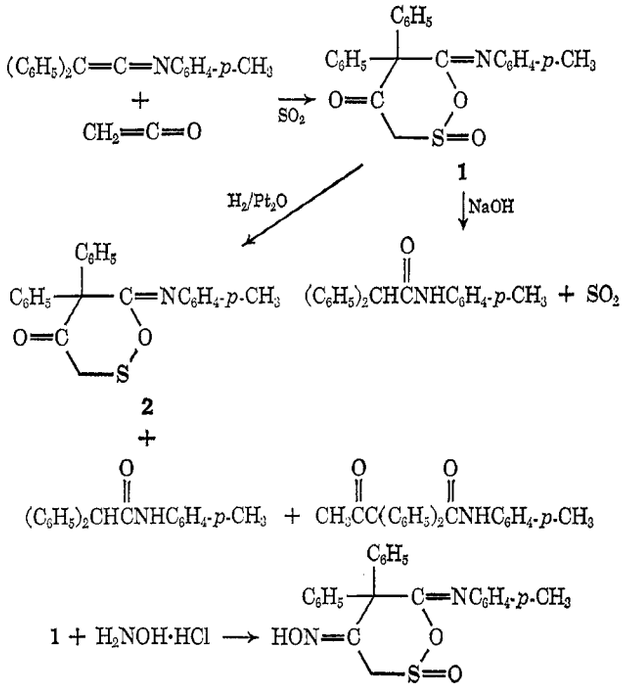
(1) A. S. Gomes and M. M. Joullié, *Chem. Commun.*, 935 (1967).
(2) A. S. Gomes and M. M. Joullié, *J. Heterocycl. Chem.*, **6**, 729 (1969).

Results and Discussion

The first investigation required the preparation of various ketenimines. These compounds were synthesized by the linear dehydration of substituted amides by either one of two methods. One procedure utilized a mixture of phosphorus pentoxide and alumina in pyridine[3] while the other employed triphenylphosphine dibromide and triethylamine in dichloromethane[4] as the dehydrating agents.

When diphenylketene-*N*-(*p*-tolyl)imine was treated with ketene in liquid sulfur dioxide, a white, crystalline product was obtained and postulated to be 5,5-diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one 2-oxide (**1**). This structure was established by both instrumental and chemical methods (Scheme I).[5]

SCHEME I



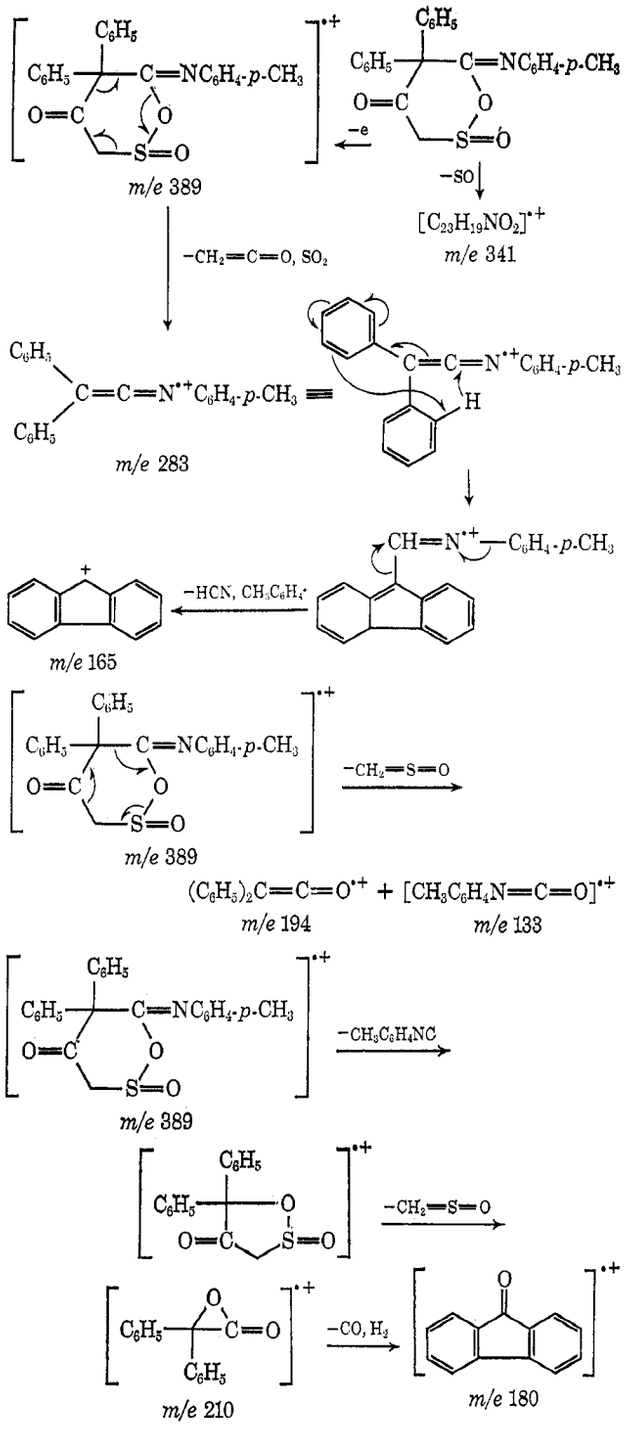
In addition to ir and nmr data, the mass spectral fragmentation of **1** was very useful in confirming the postulated structure (Scheme II).

The molecular ion (*m/e* 389), once generated, may undergo three modes of decomposition. The loss of both a molecule of ketene and a molecule of sulfur dioxide gives the ion radical (*m/e* 283) which undergoes further decomposition to form the fluorenyl cation (*m/e* 165). Both the diphenylketene (*m/e* 194) and the isocyanate (*m/e* 133) ion radicals may result from loss of a sulfene molecule from the molecular ion. Another fragmentation path may involve the loss of an isonitrile and subsequent elimination of sulfene to give the ion radical at *m/e* 210, which gives rise by further decomposition to the ion radical at *m/e* 180.

The mass spectrum of diphenylketene-*N*-(*p*-tolyl)-imine helped to elucidate the fragmentation pattern of **1**. The two major peaks in this spectrum appeared at the following *m/e* ratios: 283 (molecular ion) and 165

(3) C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1963).
(4) H. G. Bestmann, J. Lienert, and L. Mott, *Justus Liebigs Ann. Chem.*, **718**, 24 (1968).
(5) J. M. Bohen and M. M. Joullié, *Tetrahedron Lett.*, 1815 (1971).

SCHEME II



due to $C_{13}H_9$. This observation established the fragmentation of the ketenimine as a possible source of the fluorenyl cation. The proposed mechanism for the formation of this ion is similar to the one postulated for the fragmentation of the anil of benzophenone.[6]

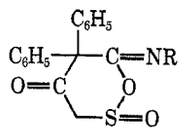
To further clarify the decomposition route of **1**, the mass spectrum of 5,5-diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one (**2**) was also investigated. The spectrum of **2** exhibited peaks at *m/e* 373 (molecular ion), 331 (loss of $CH_2{=}C{=}O$), 198 [$(C_6H_5)_2C{=}S\cdot^+$], and 194 [$(C_6H_5)_2C{=}C{=}O\cdot^+$]. However, a peak at *m/e*

(6) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

283 corresponding to $(C_6H_5)_2C{=}C{=}NC_6H_4$-*p*-$CH_3 \cdot^+$ was conspicuously missing from the spectrum. In the case of **1**, both ketene and sulfur dioxide can be lost to generate the *m/e* 283 peak. This type of fragmentation is not possible with **2**.

Additional reactions were performed with various ketenimines in order to establish the general nature of the ketene–sulfur dioxide cycloaddition. The results of these reactions are summarized in Table I.

TABLE I
SUBSTITUTED 1,2-OXATHIAN-4-ONE 2-OXIDES



Compd	R	Mp, °C[a]	Yield, %
1	C_6H_4-*p*-CH_3	207–208	57
3	C_6H_4-*p*-Br	206–207	64
4	C_6H_4-*p*-SCH_3	177–178	40
5	C_6H_4-*p*-SO_2CH_3	247–248	51
6	C_6H_5	212–213	37

[a] All compounds decomposed at their melting point.

Each of the synthesized 1,2-oxathianes (**3–6**) exhibited strong absorptions in the following regions of the infrared spectrum: 1736–1720 (>C=O), 1695–1675 (>C=N–), and 1070–1060 cm^{-1} (>S=O). The nmr spectra of the 1,2-oxathianes displayed the characteristic AB quartet for the nonequivalent methylene ring protons. Finally, the same fragmentation pattern (see Scheme II) was observed in the mass spectra of each of the synthesized compounds. Peak shifts were encountered owing to the difference of substituents on R.

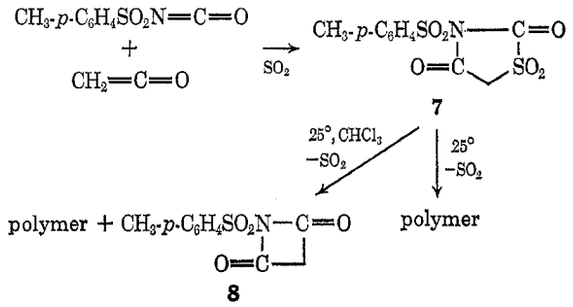
The reaction of ketenimines with the ketene–sulfur dioxide adduct was successful only when the heterocumulene was substituted with three aryl groups. Neither electron-donating nor electron-withdrawing groups on R seemed to have a pronounced effect on the cycloaddition. No 1,2-oxathianes were isolated from dimethylketene-*N*-phenylimine, diphenylketene-*N*-(*n*-butyl)imine, and isopropylketene-*N*-phenylimine, since these ketenimines resinified under the reaction conditions.

To extend our study of cycloadditions, we investigated the reaction of the isocyanates with the ketene–sulfur dioxide adduct. Both aryl and alkyl isocyanates were found to be unreactive. However, when the highly active *p*-tolylsulfonyl isocyanate was treated with ketene in anhydrous liquid sulfur dioxide at −10°, a white solid (**7**) resulted. This product was found to be unstable at room temperature and slowly decomposed to polymeric material with evolution of sulfur dioxide. When the decomposition was allowed to occur in chloroform, *N*-(*p*-tolylsulfonyl)malonimide (**8**) was isolated (Scheme III).

The ir spectrum ($CHCl_3$) of **7** exhibited a strong carbonyl absorption at 1705 cm^{-1}. This absorption is consistent with the value of 1700 cm^{-1} reported for the carbonyls of five-membered cyclic imides.[7] As **7** decomposed, the peak at 1705 cm^{-1} disappeared with the concurrent formation of a small peak at 1770 cm^{-1} (characteristic of the carbonyls of **8**).

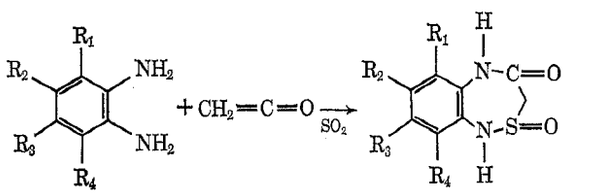
(7) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965.

SCHEME III



The reactions of the ketene–sulfur dioxide adduct with aromatic amines were extended to substituted *o*-phenylenediamines. When 3,6-dimethoxy-*o*-phenylenediamine and 4,5-dimethyl-*o*-phenylenediamine were treated with ketene in liquid dioxide, the corresponding 2,1,5-benzothiadiazepin-4-one 2-oxides resulted (Scheme IV).

SCHEME IV



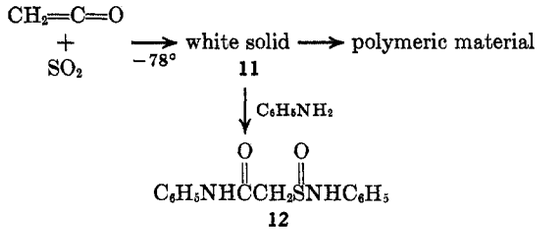
9, $R_1 = R_4 = H$; $R_2 = R_3 = CH_3$
10, $R_1 = R_4 = OCH_3$; $R_2 = R_3 = H$

Compounds **9** and **10** are both derivatives of a new ring system, 2,1,5-benzothiadiazepine, first synthesized in our laboratory.[2] The structures assigned to **9** and **10** were supported by analytical and spectral data. The ir spectra of both compounds showed the characteristic absorptions of an amide, 3200–3190 (>NH) and 1670–1664 cm^{-1} (>C=O), in addition to the strong absorption of a sulfinamide at 1075–1063 cm^{-1} (>S=O). The nmr spectra of both compounds exhibited an AB quartet for the nonequivalent methylene ring protons.

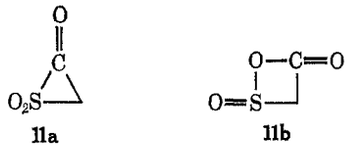
Since the cycloadditions discussed were believed to involve a ketene–sulfur dioxide adduct, the isolation of this adduct was attempted. When sulfur dioxide was mixed with an excess of ketene at −78° *in vacuo*, a white solid (**11**) formed. The excess ketene was removed by distillation, leaving only **11** in the reaction cell. When the solid was warmed to room temperature, decomposition occurred with evolution of sulfur dioxide. When **11** was treated with aniline in acetone at −78°, 2-(phenylsulfinamoyl)acetanilide (**12**) was formed (Scheme V).

The nmr spectrum of **11** in liquid sulfur dioxide at −67° exhibited a singlet at δ 2.30. This value was in agreement with the one observed in our first nmr study.[2] When the sample was allowed to decompose at higher temperatures, this peak disappeared. The chemical shift of the protons of **11** is more consistent with a three-

SCHEME V



rather than a four-membered ring structure (**11a** or **11b**).

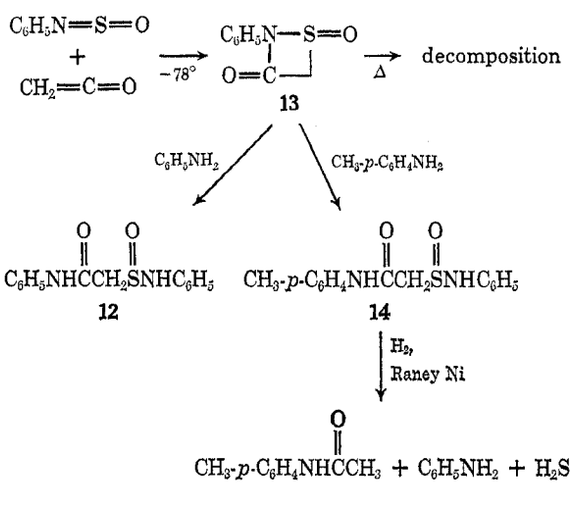


11a **11b**

This is supported by a low-temperature (−77°) nmr study of the nitrogen analog (**13**) of **11b**. The methylene protons of *N*-phenyl-1,2-thiazetidin-3-one 1-oxide (**13**) appeared as a singlet at δ 4.58. As the temperature was decreased slowly, this singlet began to broaden into a multiplet. The singlet observed for the ketene–sulfur dioxide adduct was not affected by a temperature decrease.

Although the cycloaddition of aromatic ketenes with both aliphatic and aromatic *N*-sulfinylamines and *N*-sulfinylsulfonamides has been previously described,[8-10] no products have been isolated from the reaction of these compounds with ketene. We have prepared **13** by the reaction of *N*-sulfinylaniline and ketene at −78° (Scheme VI).

SCHEME VI



N-Phenyl-1,2-thiazetidin-3-one 1-oxide (**13**) decomposed when warmed to room temperature. However, when it was treated with aniline at −78°, 2-(phenylsulfinamoyl)acetaniline (**12**) was obtained. The reaction of **13** with *p*-toluidine gave 2-(phenylsulfinamoyl)-*p*-acetotoluidide (**14**) exclusively. The structure of **14** was supported by its reduction with Raney nickel, which yielded only *N*-(*p*-tolyl)acetamide and aniline.

(8) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede, *Angew. Chem., Int. Ed., Engl.*, **1**, 89 (1962).

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

(10) G. Kresze and W. Wucherpfennig, *Angew. Chem., Int. Ed. Engl.*, **6**, 149 (1969).

Experimental Section

All microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Midwest Microlab, Ltd., Indianapolis, Ind. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were taken on a Perkin-Elmer 521 double beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60A spectrometer. Chemical shifts are expressed in δ (parts per million) downfield from TMS. Mass spectra were obtained on a Consolidated Electrodynamics Corp. CEC-110 (double focusing) mass spectrometer. Brinkmann aluminum oxide F-254 (1.5 mm) and silica gel F-254 (2.0 mm) precoated 20 × 20 mm glass plates were employed for preparative thin layer chromatography.

Materials.—Ketene was prepared by the pyrolysis of acetone in a ketene generator. When necessary, samples of ketene were purified on a vacuum system by the following method. Both stopcocks on a gas collection trap were closed. The exit port was connected to a calcium chloride drying tube and the inlet to the generator. The stopcocks were opened and ketene was allowed to pass through the trap for a few minutes. The trap was then immersed into a dewar flask containing a Dry Ice–acetone mixture (−78°). When a sample of ketene had been collected, the stopcocks were closed and the trap was disconnected from the generator. The sample was cooled to −195° in a liquid nitrogen bath and evacuated on the vacuum system to a pressure of less than 10^{-3} mm. The collection trap was slowly warmed to −78° and the gas was distilled through a trap cooled to −78° and collected in a second trap at −195°. The distillation was repeated. The pure sample of ketene was stored at −195° *in vacuo* until it was used.

The cell used for low-temperature reactions consisted of a 28 × 180 mm Pyrex tube joined to a stopcock. A 18/7 ball joint was attached to the stopcock in order to connect the vessel to the vacuum system.

All low-temperature nmr studies were performed on samples sealed in evacuated nmr tubes.

Synthesis of Ketenimines.—The yields, principal ir absorptions (>C=C=N–),[11] and melting or boiling points of the cumulenes are indicated in parentheses. The following ketenimines were synthesized by the method of Stevens and Singhal:[3] diphenylketene-*N*-(*p*-tolyl)imine (86.5%, 1990 cm^{-1}, mp 82–83°), diphenylketene-*N*-(*p*-bromophenyl)imine (71.5%, 2000 cm^{-1}, mp 79–80.5°), and diphenylketene-*N*-(*p*-methylthiophenyl)-imine (83.5%, 1960 cm^{-1}, mp 79–81°). Diphenylketene-*N*-(*p*-methylsulfonylphenyl)imine (66.7%, 1980 cm^{-1}, mp 138.5–139.5°), diphenylketene-*N*-phenylimine (80.5%, 2005 cm^{-1}, mp 54–56°), diphenylketene-*N*-*n*-butylimine [25.0%, 2015 cm^{-1}, bp 136–140° (0.1 mm)], dimethylketene-*N*-phenylimine [27.3%, 2010 cm^{-1}, 47–48° (0.1 mm)], and isopropylketene-*N*-phenylimine [66.1%, 2010 cm^{-1}, bp 47–48° (0.1 mm)] were prepared by the method of Bestmann, *et al.*[4]

5,5-Diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one 2-Oxide (1).—The general procedure for the reaction of ketene with ketenimines in anhydrous sulfur dioxide is described in the preparation of this compound.

Diphenylketene-*N*-(*p*-tolyl)imine (2.8 g, 0.01 mol) was placed in a 50-ml, two-necked, round-bottomed flask fitted with a gas inlet tube, Dry Ice condenser, and a calcium chloride drying tube. Anhydrous sulfur dioxide (25 ml) was condensed into the reaction flask. The reaction mixture was cooled to −78°. Ketene was generated and bubbled through the solution at a rate of 0.408 mol per 1 hr for 20 min. At the end of the ketene addition, the delivery tube was replaced with a stopper. The amber solution was stirred for 45 min without the use of the Dry Ice–acetone bath. The excess sulfur dioxide was removed *in vacuo* and the resulting brown tar was dissolved in 75 ml of methanol. The solution was allowed to stand overnight at room temperature. The solid that formed was collected by filtration, washed with cold methanol, and then recrystallized from absolute methanol. The yield of **I** was 1.6 g (57.2%): mp 207–208° dec; ir (KBr) 1720 (>C=O), 1675 (>C=N–), and 1063 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 2.38 (s, 3 H), 3.57 (d, 1 H, J = 17.0 Hz), 4.08 (d, 1 H, J = 17.0 Hz), and 7.34 (m, 14 H); mass spectrum *m/e* 389, 341, 283, 210, 194, 180, 165, and 133.

Anal. Calcd for $C_{23}H_{19}NSO_3$: C, 70.93; H, 4.92; N, 3.60; S, 8.24. Found: C, 70.72; H, 4.96; N, 3.72; S, 8.40.

(11) Spectra were determined as solutions in $CHCl_3$.

Reduction of 5,5-Diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one 2-Oxide.—A catalytic amount of platinum oxide was added to a solution of 0.5 g (1.2×10^{-3} mol) of **1** dissolved in 250 ml of ethanol. The suspension was shaken for 4 hr under 60 psi of hydrogen on a Parr hydrogenator. The ethanolic solution was filtered to remove the catalyst and then concentrated. The solution was allowed to stand overnight at room temperature. The solid that formed was collected by filtration, washed with cold methanol, and then recrystallized from absolute methanol. The yield of 5,5-diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one (**2**) was 385 mg (82.5%): mp 208–209° dec; ir (KBr) 1725 (>C=O) and 1690 cm^{-1} (>C=N–); nmr ($CDCl_3$) δ 2.36 (s, 3 H), 3.55 (s, 2 H), and 7.17 (m, 14 H); mass spectrum *m/e* 373, 331, 198, and 194.

Anal. Calcd for $C_{23}H_{19}NSO_2$: C, 73.97; H, 5.15; N, 3.75; S, 8.58. Found: C, 73.97; H, 5.28; N, 3.71; S, 8.66.

A second sample of 0.5 g was reduced under the conditions described above for 9 hr. Concentration of the ethanolic solution yielded 230 mg (63.7%) of *N*-(*p*-tolyl)diphenylacetamide, which was collected by filtration: mp 178–179° (lit.[3] mp 178–179°); ir (KBr) 3300, 3260 (>NH), and 1660 cm^{-1} (>C=O); nmr (DMSO-d_6) δ 2.18 (s, 3 H), 5.15 (s, 1 H), 7.28 (m, 14 H), and 10.3 (s, 1 H). The ethanol filtrate was chromatographed on a preparative alumina thin layer plate with benzene. A white solid (8 mg) was isolated and identified as *N*-(*p*-tolyl)-α,α-diphenylacetoacetamide: ir (KBr) 3318, 3200 (>NH), 1690 (>C=O), and 1671 cm^{-1} (>C=O amide); nmr (DMSO-d_6) δ 2.37 (s, 3 H), 2.39 (s, 3 H), 7.00 (m, 14 H), and 7.92 (s, 1 H).

Hydrolysis of 5,5-Diphenyl-6-(*p*-tolylimino)-1,2-oxathian-4-one 2-Oxide (1).—A solution of 0.5 g (0.014 mol) of sodium hydroxide in 5 ml of water was added slowly to a stirred solution of 1.0 g (2.4×10^{-3} mol) of **1** dissolved in 150 ml of methanol. The reaction mixture turned yellow with evolution of sulfur dioxide. The solution was stirred for 20 min at room temperature. The reaction mixture was concentrated *in vacuo* and the resulting solid was collected by filtration. The solid was washed with water until the washings were neutral to litmus. The crude solid was recrystallized from methanol. The yield of *N*-(*p*-tolyl)-diphenylacetamide was 450 mg (62.3%): mp 178–179° (lit.[3] mp 178–179°); ir (KBr) 3300, 3260 (>NH), and 1660 cm^{-1} (>C=O); nmr (DMSO-d_6) δ 2.18 (s, 3 H), 5.15 (s, 1 H), 7.28 (m, 14 H), and 10.3 (s, 1 H).

5,5-Diphenyl-6-(*p*-bromophenylimino)-1,2-oxathian-4-one 2-Oxide (3).—Compound **3** was obtained in 63.7% yield: mp 206–207° dec; ir (KBr) 1726 (>C=O), 1683 (>C=N–), and 1070 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 3.56 (d, 1 H, J = 17.0 Hz), 4.05 (d, 1 H, J = 17.0 Hz), and 7.38 (m, 14 H); mass spectrum *m/e* 455, 453, 407, 405, 349, 347, 210, 194, 180, and 165.

Anal. Calcd for $C_{22}H_{16}NSO_3Br$: C, 58.16; H, 3.55; N, 3.09; S, 7.06; Br, 17.59. Found: C, 57.91; H, 3.42; N, 3.20; S, 7.16; Br, 17.80.

5,5-Diphenyl-6-(*p*-methylthiophenylimino)-1,2-oxathian-4-one 2-Oxide (4).—Compound **4** was obtained in 40.4% yield: mp 177–178° dec; ir (KBr) 1725 (>C=O), 1684 (>C=N–), and 1063 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 2.48 (s, 3 H), 3.62 (d, 1 H, J = 17.0 Hz), 4.10 (d, 1 H, J = 17.0 Hz), and 7.81 (m, 14 H); mass spectrum *m/e* 421, 373, 315, 210, 194, 180, and 165.

Anal. Calcd for $C_{23}H_{19}NS_2O_3$: C, 65.53; H, 4.54; N, 3.32; S, 15.21. Found: C, 65.34; H, 4.58; N, 3.25; S, 15.46.

5,5-Diphenyl-6-(*p*-methylsulfonylphenylimino)-1,2-oxathian-4-one 2-Oxide (5).—Compound **5** was obtained in 50.6% yield: mp 247–248° dec; ir (KBr) 1736 (>C=O), 1693 (>C=N–), and 1068 cm^{-1} (>S=O); nmr (DMSO-d_6) δ 3.27 (s, 3 H), 3.84 (d, 1 H, J = 17.0 Hz), 4.52 (d, 1 H, J = 17.0 Hz), and 7.81 (m, 14 H); mass spectrum *m/e* 453, 405, 347, 210, 194, 180, and 165.

Anal. Calcd for $C_{23}H_{19}NS_2O_5$: C, 60.91; H, 4.22; N, 3.09; S, 14.14. Found: C, 61.19; H, 4.27; N, 2.96; S, 14.18.

5,5-Diphenyl-6-phenylimino-1,2-oxathian-4-one 2-Oxide (6).—Compound **6** was obtained in 37.4% yield: mp 212–213° dec; ir (KBr) 1729 (>C=O), 1687 (>C=N–), and 1068 cm^{-1} (>S=O); nmr ($CDCl_3$) δ 3.57 (d, 1 H, J = 17.0 Hz), 4.05 (d, 1 H, J = 17.0 Hz), and 7.35 (m, 15 H); mass spectrum *m/e* 375, 327, 269, 210, 194, 180, and 165.

Anal. Calcd for $C_{22}H_{17}NSO_3$: C, 70.38; H, 4.56; N, 3.73; S, 8.54. Found: C, 70.10; H, 4.72; N, 3.75; S, 8.38.

***N*-(*p*-Tolylsulfonyl)-thiazolidine-2,4-dione 1,1-Dioxide (7).**—*p*-Tolylsulfonyl isocyanate (10.0 g, 0.05 mol) was placed in a 250-ml, two-necked, round-bottomed flask fitted with a gas inlet tube, Dry Ice condenser, and a calcium chloride drying tube. Sulfur dioxide (100 ml) was condensed into the reaction flask and the resulting solution was cooled to −78°. Ketene was generated and bubbled through the reaction mixture at a rate of 0.408 mol per 1 hr for 30 min. When the addition was completed, the delivery tube was replaced with a stopper. The solution was stirred for 1 hr at −78°. The reaction mixture was slowly warmed to −10° and stirred at this temperature for an additional 20 min. The solution was concentrated and the resulting white solid was collected by filtration. The dry solid started to decompose with evolution of sulfur dioxide. When a portion of the solid was dissolved in chloroform, decomposition continued. When gas evolution ceased, the chloroform was evaporated under reduced pressure and a white solid was isolated. The solid was recrystallized from ethyl acetate and identified as *N*-(*p*-tolylsulfonyl)malonimide (**8**): mp 139–141° dec (lit.[12] mp 144–147° dec); ir (KBr) 1780 (>C=O), 1300, and 1170 cm^{-1} (–SO_2–); nmr (acetone-d_6) δ 2.62 (s, 3 H), 4.14 (s, 2 H), 7.92 (d, 2 H, J = 9.2 Hz), and 8.36 (d, 2 H, J = 9.2 Hz).

2,1,5-(4,5-Dimethyl)benzothiadiazepin-4-one 2-Oxide (9).—The apparatus and procedure used were the same as those described for the preparation of compound **8**. Pure 4,5-dimethyl-*o*-phenylenediamine (5.0 g, 0.036 mol) was mixed with 100 ml of liquid sulfur dioxide. The yellow solid that resulted was attributed to an adduct formed from the amine and sulfur dioxide. Ketene was generated and bubbled through the suspension at a rate of 0.408 mol per 1 hr for 45 min. When the addition was completed, the delivery tube was replaced with a stopper. The suspension was stirred for 45 min without the use of the Dry Ice–acetone bath. The excess sulfur dioxide was removed *in vacuo* and the resulting brown residue was dissolved in 100 ml of methanol. The solid that formed was collected by filtration, washed with cold methanol, and recrystallized from absolute methanol. The yield of **9** was 4.1 g (50.8%): mp 226–227° dec; ir (KBr) 3190 (>NH), 1670 (>C=O), and 1060 cm^{-1} (>S=O); nmr (DMSO-d_6) δ 2.17 (s, 6 H), 3.17 (d, 1 H, J = 12.0 Hz), 3.90 (d, 1 H, J = 12.0 Hz), 6.93 (m, 2 H), 8.62 (s, 1 H), and 9.43 (s, 1 H).

Anal. Calcd for $C_{10}H_{12}N_2SO_2$: C, 53.55; H, 5.39; N, 12.49; S, 14.30. Found: C, 53.77; H, 5.44; N, 12.64; S, 14.20.

2,1,5-(3,6-Dimethoxy)benzothiadiazepin-4-one 2-Oxide (10).—The apparatus and procedure used were the same as those described for the preparation of compound **8**. Pure 3,6-dimethoxy-*o*-phenylenediamine (5.0 g, 0.037 mol) yielded 3.6 g (51.6%) of **10**: mp 230–231° dec; ir (KBr) 3200, 3120 (>NH), 1664 (>C=O), and 1063 cm^{-1} (>S=O); nmr (DMSO-d_6) δ 3.17 (d, 1 H, J = 12.2 Hz), 3.77 (s, 6 H), 3.90 (d, 1 H, J = 12.2 Hz), 6.90 (s, 2 H), 8.40 (s, 1 H), and 9.30 (s, 1 H).

Anal. Calcd for $C_{10}H_{12}N_2SO_4$: C, 46.86; H, 4.72; N, 10.93; S, 12.51. Found: C, 46.96; H, 4.68; N, 10.83; S, 12.31.

Isolation and Interception of the Ketene–Sulfur Dioxide Adduct (11).—On a vacuum system, a pure sample of anhydrous sulfur dioxide was distilled into an evacuated reaction cell cooled to −195°. Ketene was generated, collected, and purified as previously described. The pure sample of ketene was distilled into the reaction vessel in excess. The stopcock on the cell was closed when the addition of the ketene was completed. The temperature of the mixture was slowly raised to −78°. The solution was maintained at this temperature for 1 hr. During this period, a white solid formed in the vessel. The excess ketene was removed by distillation. The stopcock was closed and the cell was removed from the vacuum system. The temperature of the cell was slowly raised to 25°. The white solid decomposed with evolution of gases and formation of a brown tar.

A second sample of the ketene–sulfur dioxide adduct was prepared as described above. Freshly distilled aniline (1.0 g) was dissolved in 10 ml of anhydrous acetone and the resulting solution was cooled to −78°. The aniline solution was slowly added to the adduct. The reaction mixture was maintained at −78° for 1 hr, when the addition of the aniline was completed. The solution was then warmed to room temperature. Methanol was added and the resulting white solid was collected by filtration. The solid was recrystallized from absolute methanol. The yield of 2-(phenylsulfinamoyl)acetanilide (**12**) was 127 mg: mp 172–173° dec (lit.[2] mp 167–168° dec); ir (KBr) 3280, 3250 (>NH), 1655 (>C=O), and 1062 cm^{-1} (>S=O); nmr (DMSO-

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d_6) δ 4.55 (s, 2 H), 7.28 (m, 10 H), 9.08 (s, 1 H), and 10.3 (s 1 H).

N-**Phenyl-1,2-thiazetidin-3-one 1-Oxide (13).**—In a reaction cell, 0.5 g (3.7×10^{-3} mol) of pure sulfinylaniline was dissolved in 25 ml of dry acetone. The mixture was cooled to −195° and the vessel was evacuated to a pressure of less than 10^{-3} mm on the vacuum system. Ketene was generated, collected, and purified as previously described. The pure ketene was distilled into the reaction cell. The temperature of the mixture was slowly raised to −78°. The solution was stirred at this temperature for 2 hr. During this period, the orange solution became colorless and a white solid formed. The reaction mixture was slowly warmed to room temperature. The solid decomposed with evolution of ketene. The acetone was evaporated under reduced pressure and the resulting oil was chromatographed on a dry column of silica gel with benzene. Only sulfinylaniline and polymeric materials were isolated.

Interception of *N*-Phenyl-1,2-thiazetidin-3-one 1-Oxide (13) with Aniline and *p*-Toluidine.—A sample of *N*-phenyl-1,2-thiazetidin-3-one 1-oxide (13) was prepared as described above. A solution of aniline (1.0 g) in 10 ml of dry acetone was cooled to −78° and then added slowly to the reaction mixture. The solution was allowed to stand at −78° overnight. It was then warmed to room temperature and the white solid was collected by filtration. The solid was recrystallized from methanol. The yield of 2-(phenylsulfinamoyl)acetanilide was 463 mg (45.8%): mp 172–173° dec (lit.[2] mp 167–168° dec); ir (KBr) 3280, 3250 (>NH), 1655 (>C=O), and 1062 cm^{-1} (>S=O); nmr (DMSO-d_6) δ 4.55 (s, 2 H), 7.28 (m, 10 H), 9.08 (s, 1 H), and 10.3 (s, 1 H).

A second sample of **13** prepared as described above was treated with a solution of *p*-toluidine (1.0 g) dissolved in 10 ml of dry acetone. The yield of 2-(phenylsulfinamoyl)-*p*-acetotoluidide (**14**) was 1.45 g (58.3%): mp 181–182° dec; ir (KBr) 3225, 3185 (>NH), 1650 (>C=O), and 1049 cm^{-1} (>S=O); nmr (DMSO-d_6) δ 2.27 (s, 3 H), 4.12 (s, 2 H), 7.25 (m, 9 H), 9.23 (s, 1 H), and 10.3 (s, 1 H).

Anal. Calcd for $C_{15}H_{16}N_2SO_2$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.70; H, 5.82; N, 9.58; S, 11.05.

Reduction of 2-(Phenylsulfinamoyl)-*p*-acetotoluidide (14).—A solution of 70 mg (2.4×10^{-4} mol) of **14** dissolved in 30 ml of absolute ethanol was placed in a 50-ml, round-bottomed flask, fitted with a condenser. Raney nickel W-4 (500 mg) was added to the solution. The reaction mixture was heated under reflux overnight. The hot solution was filtered to remove the catalyst. The ethanol was evaporated under reduced pressure and the residue was chromatographed on a preparative alumina thin layer plate with ether. The major band (R_f 0.49) was isolated and the alumina was leached with acetone. The acetone was evaporated under reduced pressure and the resulting white solid was recrystallized from chloroform. The yield of *N*-(*p*-tolyl)-acetamide was 16 mg (44.5%): mp 155–156° (lit.[13] mp 155–156°); ir (KBr) 3215 (>NH) and 1660 cm^{-1} (>C=O); nmr ($CDCl_3$) δ 2.12 (s, 3 H), 2.30 (s, 3 H), 7.09 (d, 2 H, J = 8.0 Hz), 7.39 (d, 2 H, J = 8.0 Hz), and 8.05 (s, 1 H).

Registry No.—**1**, 32720-35-7; **2**, 32720-36-8; **3**, 40328-72-1; **4**, 40328-73-2; **5**, 40328-74-3; **6**, 40328-75-4; **7**, 40328-76-5; **8**, 1888-29-5; **9**, 40328-78-7; **10**, 40328-79-8; **11a**, 27393-94-8; **12**, 23990-58-1; **13**, 40328-82-3; **14**, 40328-83-4; ketene, 463-51-4; diphenylketene-*N*-(*p*-tolyl)imine, 5110-45-2; diphenylketene-*N*-(*p*-bromophenyl)imine, 29376-76-9; diphenylketene-*N*-(*p*-methylthiophenyl)imine, 40328-86-7; diphenylketene-*N*-(*p*-methylsulfonylphenyl)imine, 40328-87-8; diphenylketene-*N*-phenylimine, 14181-84-1; diphenylketene-*N*-*n*-butylimine, 21843-89-0; dimethylketene-*N*-phenylimine, 14016-34-3; isopropylketene-*N*-phenylimine, 34621-16-4; sulfur dioxide, 7446-09-5; *N*-(*p*-tolyl)diphenylacetamide, 4107-01-1; *N*-(*p*-tolyl)-α,α-diphenylacetoacetamide, 40328-93-6; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7; 3,6-dimethoxy-*o*-phenylenediamine, 40328-95-8; *N*-(*p*-tolyl)acetamide, 103-89-9.

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The Solvolysis of Pyridine Analogs of Cumyl Chloride. The Determination of the Brown Electrophilic Substituent Constants for Pyridine Derivatives[1a]

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Rates of solvolysis in 80% ethanol have been determined for 2-(2-pyridyl)-2-chloropropane, 2-(3-pyridyl)-2-chloropropane, and 2-(4-pyridyl)-2-chloropropane, and for 2-(2-pyridyl)-2-chloropropane *N*-oxide and 2-(4-pyridyl)-2-chloropropane *N*-oxide. From these rates and the rates of solvolysis of cumyl chlorides bearing electron-withdrawing substituents, σ^+ values appropriate for the replacement of the benzene ring by a pyridine moiety have been calculated.

There have been numerous studies in recent years aimed at relating pyridine derivatives to benzene derivatives. As a determination of the Hammett substituent constant, σ, appropriate for substitution of the aza =N for =CH in benzene by the primary defining reaction (ionization of an aromatic carboxylic acid) is fraught with some difficulty because of zwitterion formation, such σ values have generally been evaluated by secondary reactions. A summary by Blanch[2] evaluates a number of such reactions, and lists preferred σ values. A more recent study by Campbell, *et al.*,[3] derives similar though slightly modified values from ester saponification rates. Katritzky and Swinbourne[4] have derived substituent constants for the pyridine *N*-oxide moiety from spectroscopic studies. There has been less attention to determination of Brown's electrophilic substituent constants, σ^+.[5] An early study by Taylor[6] derives σ^+ values from the high-temperature pyrolysis of 1-(X-pyridyl)ethyl acetates. Extensive studies of the nitration, bromination, and hydrogen exchange reactions of pyridine derivatives

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