The Imino Lactone XX.—A mixture of 3.5 g (0.02 mole) of 2-hydroxy-1-naphthaldehyde (Eastman), 3.6 g (0.02 mole) of (phenylsulfonyl)acetonitrile, 20 ml of absolute ethanol, and 2 drops of piperidine was boiled for 0.5 hr (insolubles present), then diluted with 40 ml of toluene, and filtered to give 5.5 g of yellow solids, mp 226–227°; the melting point was unchanged after recrystallization from xylene. The infrared spectrum did not show a nitrile peak at *ca.* 4.4 μ but had bands at 3.1, 6.0, and 7.1 μ.

Anal. Calcd for $C_{19}H_{13}NO_2S$ (XX): N, 4.18; O, 14.3. Found: N, 4.10; O, 14.4.

Registry No.—I, 5219-61-4; II, 7605-24-5; III, 7605-25-6; IV, 7605-26-7; V, 7605-27-8; VI, 7605-28-9; VII, 5697-44-9; VIII, 7605-30-3; IX, 2850-19-3; X, 7605-32-5; XI, 7605-33-6; XII, 7605-34-7; XIII, 7605-35-8; XIV, 7605-36-9; XV, 7605-37-0; XVI, 7605-38-1; XVII, 7605-39-2; XVIII, 7605-40-5; α-phenylcinnamonitrile, 2510-95-4; α-cyanocinnamonitrile, 2700-22-3; *p*-methoxy-α-phenylcinnamonitrile, 5432-07-5; methyl *p*-methoxy-α-phenylcinnamate, 7605-44-9; methyl *m,p*-methylenedioxy α-methylcinnamate, 7605-45-0; α-cyano-*p*-methoxycinnamonitrile, 2826-26-8; α-cyano-*m,p*-methylenedioxycinnamonitrile, 2972-82-9; bis(4-*t*-butylphenyl) disulfide, 7605-48-3; XX, 7605-49-4.

Acknowledgments.—It is a pleasure to acknowledge the interest of Dr. W. C. Fernelius in this work, the assistance of the Chemical and Instrumental Analysis Group of these laboratories (particularly Mr. R. Mainier), and the invaluable help of Mr. H. E. Sobel in the synthetic part.

Reactions of Sulfenes with Ketene Acetals and Ketene Aminals

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Various ketene acetals cycloadd to "sulfenes" to give thietane dioxides. With benzoyl- and acetylketene diethylacetals, sulfenes undergo a Diels–Alder-like cycloaddition, yielding an unsaturated δ-sultone and a cyclic keto sulfone, respectively. Cyclic and/or acyclic products are obtained from the interaction between sulfene and a ketene aminal. The product distribution varies depending upon the nature of the substituent on the alkanesulfonyl chloride and the solvent used.

Earlier papers of this series[1] describe the reactions of alkanesulfonyl chlorides with ketene diethylacetal and with 1,1-bis(diethylamino)ethylene in the presence of triethylamine. The reactions were believed to proceed *via* sulfene intermediates, the intermediacy of which was subsequently verified through the alcoholysis of alkanesulfonyl chlorides with deuterated alcohols.[2]

In the course of a continuing investigation of the reactions of sulfenes with electron-rich olefins, we have found that various other ketene acetals also react readily with sulfene systems to afford the expected thietane dioxides (see **1** and Table I). The yields

$$RCH_2SO_2Cl + R_1CH{=}C(OR_2)_2 \xrightarrow{Et_3N} \underset{SO_2-CH-R_1}{\overset{|}{R-CH-C(OR_2)_2}}$$

1

ranged from 76 to 9%, depending upon the nature of the substituents on the β carbon of the ketene acetals. The yield of **1a** was improved by employing a dilution method in which an ethereal solution of phenylmethanesulfonyl chloride was added dropwise to a mixture of ketene diethylacetal and triethylamine in the same solvent (a total of 1 l. of ether was used for 0.1 mole scale). The resulting suspension was stirred overnight at room temperature. After the usual work-up, there was obtained a 76.3% yield of pure 2-phenyl-3,3-diethoxythietane 1,1-dioxide (**1a**). While methylketene diethylacetal (R_1 = CH_3) gave the sulfene cycloadduct in a fair yield (45%), bromoketene diethylacetal (R_1 = Br) afforded only 9.5% yield of the corresponding adduct (**1h**), and phenylketene dimethylacetal (R_1 = C_6H_5) yielded no adduct.[3] These data suggest that the most effective olefins, for trapping sulfene intermediates, are highly electron-donating, *e.g.*, ketene acetals,[1] ketene O,N-acetals,[4] and ketene aminals,[1c,4,5] and relatively unhindered.

The basicity of the tertiary amine and the acidity of the hydrogens α to the sulfone group are also important. Under the reaction conditions both methanesulfonyl and phenylmethanesulfonyl chlorides failed to give the sulfene adduct when pyridine was used as a base. On the other hand, bromomethanesulfonyl chloride did react in the absence of base with 1 equiv of ketene diethylacetal to give **1h** in 20.3% yield, compared with 20.7–34.0% using triethylamine and 27.7% in the presence of zinc.[6] Presumably the hydrogens on bromomethanesulfonyl chloride are sufficiently acidic[7] to be abstracted by ketene acetal, leading to the usual sulfene reaction.

In one instance, methanesulfonyl chloride plus ketene di-*sec*-butylacetal, a thiete dioxide (**2**) was formed.

$$\underset{SO_2-CH_2}{\overset{|}{CH{=}C-O\overset{CH_3}{\overset{|}{C}}HCH_2CH_3}}$$

2

(1) (a) W. E. Truce, *et al.*, *J. Am. Chem. Soc.*, **84**, 3030 (1962); (b) W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963); (c) W. E. Truce and P. Son, *J. Org. Chem.*, **30**, 71 (1965).

(2) (a) W. E. Truce, R. W. Campbell, and J. R. Norell, *J. Am. Chem. Soc.*, **86**, 288 (1964); **88**, 3599 (1966); (b) J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); **87**, 5684 (1965).

(3) The possibility that the formation of the four-membered ring adduct was followed by the rapid ring cleavage to give acyclic products was not entirely precluded.

(4) (a) R. H. Hasek, *et al.*, *J. Org. Chem.*, **28**, 2496 (1963); (b) R. H. Hasek, R. H. Meen, and J. C. Martin, *ibid.*, **30**, 1495 (1965).

(5) (a) G. Opitz and H. Schempp, *Z. Naturforsch.*, **19b**, 1 (1964); (b) G. Opitz and H. Schempp, *Ann. Chem.*, **684**, 103 (1965).

(6) The original objective of the usage of zinc, *i.e.*, to generate a sulfene through dehalogenation, was not achieved.

(7) (a) S. M. McElvain and D. Kundiger, *J. Am. Chem. Soc.*, **64**, 254 (1942); (b) L. Claisen and E. Hasse, *Ber.*, **33**, 1244 (1900).

TABLE I

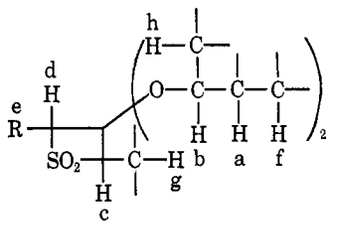
THIETANE 1,1-DIOXIDES (1)[a]

Compd	R	R_1	R_2	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % S	Calcd, % Br	Found % C	Found % H	Found % S	Found % Br
1a	C_6H_5	H	Et	90–91	76[b]	...	...	...	...	...	...	...	...
1b	C_6H_5	Me	Et	55–68	68[c]	59.15	7.04	11.27	...	59.01	7.26	11.44	...
1c	C_6H_5	H	*i*-Bu	70.5–72	61	62.58	7.98	9.82	...	62.33	8.24	9.73	...
1d	C_6H_5	H	Me	156–157	50	54.53	5.82	13.24	...	54.18	5.93	13.62	...
1e	H	Me	Et	53.5–54.5	45	46.15	7.70	15.39	...	46.45	7.78	15.19	...
1f	H	H	*i*-Bu	60–61.5	40	52.80	8.80	12.80	...	52.93	9.08	12.67	...
1g	H	H	Me	159.5–160.5	30	36.15	6.03	19.30	...	36.16	5.91	19.04	...
1h	H	Br	Et	69–70	9.5	30.77	4.76	11.72	29.30	31.01	4.96	11.91	29.09
1i	C_6H_5	H	*sec*-Bu	120–122	47	62.58	7.98	9.82	...	62.58	8.18	9.77	...

[a] The cycloadduct (**1e**) was recrystallized from pentane; **1d** and **1g** were recrystallized from hexane and ethyl acetate, followed by sublimation; the rest were recrystallized from hexane. [b] Dilution method was used. The same cycloadduct was reported in ref 1. [c] Geometrical isomers (*cis* and *trans*) were not separated.

TABLE II

NMR DATA (δ) FOR THE THIETANE DIOXIDES[a]



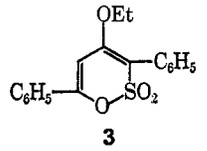
Compd	a	b	c	d	e	f	g or h	Relative areas a:b:c:d:e:f:g:h	Solvent
1a	1.10 *3d*	3.45 *4*	4.12 *1*	5.37 *1*	7.34 *c*	...	...	6:4:2:1:5	CCl_4
1b	1.10 *c*	3.40 *5*	4.45 *4d*	5.45 *3*	7.40 *c*	...	1.55 *2*	6:4:1:1:5:3	$CDCl_3$
1c	1.80 *6*	3.15 *2d*	4.25 *1*	5.45 *1*	7.40 *c*	0.90 *2d*	...	2:4:2:1:5:12	$CDCl_3$
1d	...	3.17 *2*	4.21 *1*	5.45 *1*	7.41 *c*	...	...	6:2:1:5	$CDCl_3$
1e	1.30 *3d*	3.50 *c*	4.30 *4d*	4.05 *1*	...	...	1.42 *2*	6:4:1:2:3	CCl_4
1f	1.85 *6*	3.15 *2*	4.18 *1*	...	...	0.95 *2*	...	2:4:4:12	$CDCl_3$
1g	...	3.13 *1*	4.39 *1*	...	...	...	...	6:4	Pyridine
1h	1.25 *3d*	3.55 *4d*	4.15 *1*	5.60 *1*	...	...	...	6:4:2:1	CCl_4
1i[b]	1.57 *c*	3.82 *6d*	4.35 *3*	5.50 *1*	7.39 *c*	0.82 *3d*	1.15 *2*	4:2:2:1:5:6:6	CCl_4

[a] The multiplicity is expressed as *1*, singlet; *2*, doublet; *c*, multiple peaks; *2d*, double doublets; *3d*, double triplets, and so on. When both c and d protons are equivalent, the data are entered in column c. [b] The spectrum of **1i** had a peak (area equivalent to about one proton) at δ 4.69 which was inexplicable.

Inasmuch as phenylmethanesulfonyl chloride with this ketene acetal produces the thietane dioxide (**1i**), the isolation of **2**, formed *via* β elimination of alcohol, is attributable to the modes of work-up.

The infrared spectra[8] ($CHCl_3$ or Nujol mull) of the thietane dioxides **1a–i** showed strong bands at 7.4–7.6, 8.4–8.6 (SO_2 group), and at 9.0–9.2 μ (RO group). The nmr[8] data are summarized in Table II.

Sulfenes are not restricted to 1,2 addition, but can add to a conjugated system in a Diels–Alder fashion. For instance, treatment of phenylmethanesulfonyl chloride in ether with benzoylketene diethylacetal and triethylamine at ice-bath temperatures gave rise to an unsaturated δ-sultone (**3**) in 20% yield. This yellow compound was found to be unstable and on standing it gradually turned into a dirty brown, amorphous solid.



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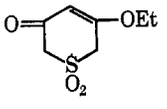
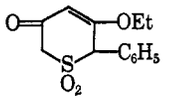


4

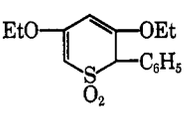


5

(8) The infrared spectra were run on a Perkin-Elmer Infracord or Perkin-Elmer Model 21 spectrometer. The nmr spectra were obtained using a Varian A-60 spectrometer at a sweep width of 500 cps with TMS as an internal standard.

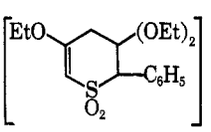
However, acetylketene diethylacetal behaves quite differently, *i.e.*; it forms cyclic keto sulfones **4** and **5** with methanesulfonyl and phenylmethanesulfonyl chlorides, respectively. The spectral assignments of structures **4** and **5** were confirmed by an alternative synthesis or by comparison with an authentic sample. Compound **5** was synthesized by following essentially the same procedures developed in this laboratory,[9] *i.e.*, treatment of phenylmethanesulfonyl chloride with excess ketene diethylacetal in benzene gave compound **5**, plus several others as listed below. The structure of adduct **7**

$$C_6H_5CH_2SO_2Cl + 3CH_2{=}C(OEt)_2 \rightarrow \mathbf{1a} + \mathbf{5} +$$



6

+

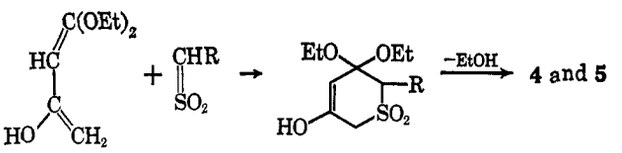


7

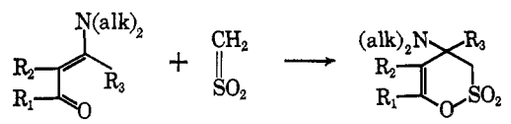
(impure owing to its instability) was inferred by its nmr spectrum, which showed essentially the same nmr signals as did **6** as well as the peaks owing to ethanol (see the Experimental Section). Compound **5** can also be obtained in 68.8% yield by hydrolysis of **6**.

(9) W. E. Truce, D. J. Abraham, and P. S. Radhakrishnamurti, *Tetrahedron Letters*, 1051 (1963).

In the absence of detectable enol in acetylketene diethylacetal (investigated by nmr up to −25°), the possibility that **4** and **5** were produced by 1,4 addition of sulfene in the following fashion is reduced.



During the progress of this work, Opitz and Tempel[10] published on the transformation of acylenamines with sulfene into β-amino-δ-sultones (**8**). Repeating one of their examples we have confirmed the assigned structure.

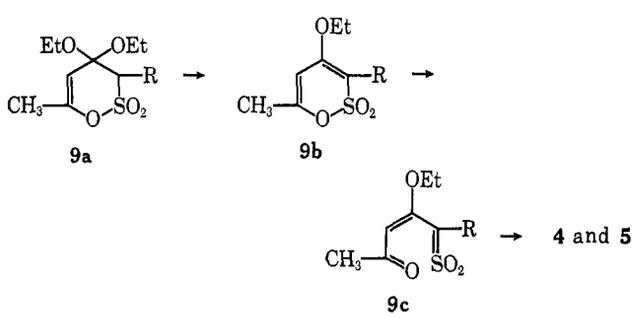


8

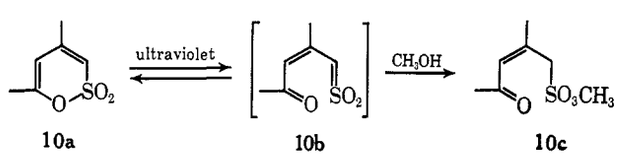
8a, $R_1=R_2=CH_3$; $R_3=H$; $N(alk)_2=N$⟨ ⟩

b, $R_1=Et$; $R_2=R_3=H$; $N(alk)_2=N$⟨ ⟩

In view of the ready formation of the unsaturated β-alkoxy-δ-sultone (**3**) from benzoylketene diethylacetal and of β-amino-δ-sultones (**8**) from acylenamines, cyclic keto sulfones **4** and **5** may result from rearrangement of the corresponding δ-sultone (**9b**) *via* the conjugated sulfene **9c**. A similar sulfene intermediate



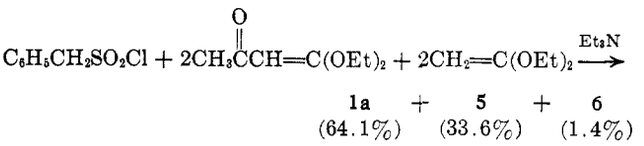
was postulated in the photolytic methanolysis of the unsaturated sultone (**10a**) and supported by isolation of the corresponding sulfonate ester **10c**.[11] On this



10a **10b** **10c**

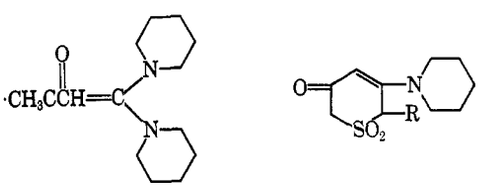
basis, absence of a rearrangement product (sulfone) in the case of acyleneamines results from their structural incapability to form such doubly unsaturated sultones (**9b**).

To date, however, there is no evidence to support the intermediacy of **9c** in the formation of sulfones **4** and **5**. An experiment designed to trap the sulfene **9c** with ketene diethylacetal has been unfruitful, *i.e.*, 2 equiv of acetylketene diethylacetal were treated with phenylmethanesulfonyl chloride and ketene diethylacetal in the presence of triethylamine at −5°. After stirring the mixture for 2 hr, additional ketene diethylacetal was added and stirred overnight. After the usual



work-up, the crude products were chromatographed on alumina. From 56 fractions there were obtained only those compounds which involved phenylsulfene ($C_6H_5CH{=}SO_2$) presumably more reactive than the postulated sulfene (**9c**).

In another experiment, acetylketene dipiperidinoaminal (**11**) was treated with phenylmethanesulfonyl chloride and triethylamine, hoping to isolate the re-

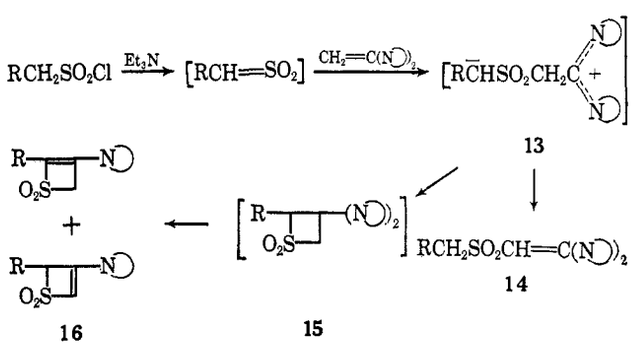


11 **12**

arranged product (**12**). In addition to the starting material, there was obtained only resinous material which resisted characterization even after careful chromatography on alumina. Likewise, we failed to isolate an adduct from benzoylketene dipiperidinoaminal and phenylmethanesulfonyl chloride.

The enhanced reactivity of ketene acetals obtained by replacing the alkoxyl group(s) by one or two dialkylamino group(s) has been predicted by Gates[12a] and McElvain[12b] and was observed in reactions with sulfenes. Both ketene O,N- and N,N-acetals (aminals) readily yielded the sulfene adducts; however, spontaneous β elimination occurred to produce the 3-dialkylaminothiete 1,1-dioxides (**16**).[4,5] With ketene aminals, both cyclic and acyclic products are usually formed.[13] The ratio of cyclic to acyclic products varies, depending upon the polarity of the solvent used, the nature of the alkyl group of the sulfonyl chloride, and of the substituent on the ketene aminal. Based on these considerations, a mechanism involving a zwitterion (**13**) has generally been assumed[1c,4,5] (Scheme I). Some sup-

SCHEME I



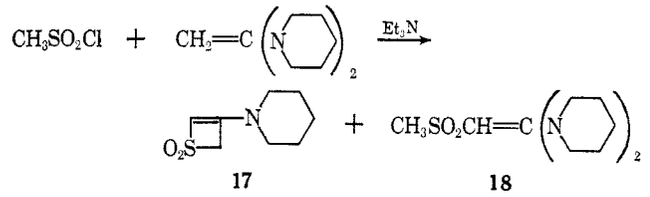
(10) G. Opitz and E. Tempel, *Angew. Chem. Intern. Ed. Engl.*, **4**, 786 (1965).

(11) J. F. King, P. de Mayo, E. Morkved, A. B. M. A. Sattar, and A. Stoessl, *Can. J. Chem.*, **41**, 100 (1963).

(12) (a) M. Gates, *J. Am. Chem. Soc.*, **66**, 124 (1944); (b) S. M. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(13) The >C=C< bands, in the infrared spectrum, appear at 6.10–6.25 μ for the cyclic products and 6.45–6.57 μ for the acyclic products.

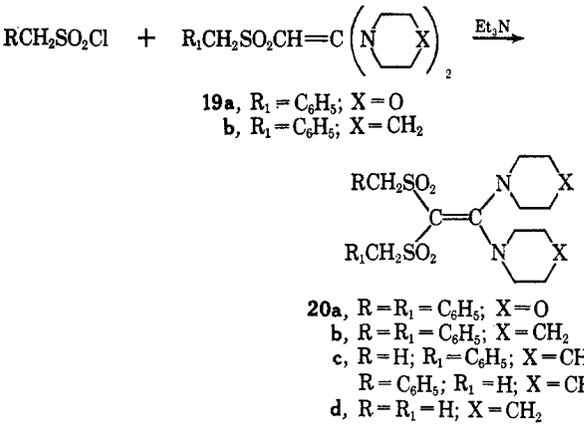
port for this mechanism is as follows. (a) While methanesulfonyl chloride reacts with 1,1-di(4-morpholino)-ethylene and triethylamine in aprotic solvents (ether, benzene, or tetrahydrofuran) to give a 69–92% yield of the thiete dioxide (**16**), those alkanesulfonyl chlorides in which R is CH_3, CH_3CH_2, $CH_3CH_2CH_2$, and $C_6H_5CH_2$ afforded under similar conditions both **14** and **16**, the former compound being the major product (52–76% *vs.* 3–15%).[5] These data reflect the steric retardation by R of the process of collapsing the zwitterion (**13**) to produce cycloadduct. (b) The stabilization of both negative and positive charges on the zwitterion would be expected to favor the formation of the acyclic products (**14**). Except in one case,[5] no acyclic product has been observed under similar conditions with ketene acetals and enamines. The fact that a positive charge is stabilized more effectively by two amino groups in the ketene aminal system is self-explanatory. The stabilization of the negative charge next to the sulfone group by such electron-attracting groups as Cl and C_6H_5 would also favor the formation of **14**. Indeed, the sole product isolated from the reaction of phenylmethanesulfonyl or chloromethanesulfonyl chloride with ketene aminals was found to be acyclic product in 60–78% yields.[1c,5] (c) In general, highly polar solvents also favor the formation of acyclic product. Hasek and his co-workers[4b] found that the interaction of 1,1-di-(morpholino)ethylene with sulfene ($CH_2{=}SO_2$) in benzene or tetrahydrofuran gave rise to the cycloadduct in good yield. On the other hand, in acetonitrile or *N*,*N*-dimethylformamide the acyclic product was isolated as a major product and only a trace of the cycloadduct was detectable in the infrared spectrum. The study of the solvent effect upon the product distribution in the 1,1-di(1-piperidino)ethylene systems by taking nmr spectra of the crude products, however, revealed a more complex picture. The approximate



17 **18**

ratios of cyclic to acyclic products (**17**:**18**) were 1:1.6–1.7 in benzene,[14a] 1:0.14 in ether, 1:2.0 in chloroform,[14b] and 1:3.0 in acetonitrile. Except for benzene, there is an expected trend in which a polar solvent favors the formation of the acyclic product **18**. It is not immediately clear what causes the anomaly with benzene, but one may rationalize it in terms of two competing reaction paths. The previous findings lend some support to this explanation. From the ratios of mono- and undeuterated alkanesulfonates, which were obtained by alcoholysis of alkanesulfonyl chlorides with deuterated alcohols (ROD) in the presence of base, Truce and Campbell[15] proposed that there are two competing reactions (E2 and SN2) and that the less polar solvent would favor the substitution reaction at the expense of the elimination reaction. Secondly, benzenesulfonyl chloride (where no sulfene formation is possible) readily forms the substitution product, 2-benzenesulfonyl-1,1-di(4-morpholino)ethylene with the appropriate ketene aminal in the presence of base.[4b] That the substitution process may involve a sulfonyl quarternary ammonium halide is supported by the observations made by Opitz and Fischer[16] and by the isolation of methanesulfonyltriethylammonium chloride.[17]

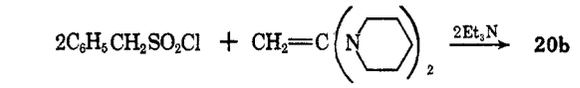
Attempted transformation of 3-dialkylaminothiete 1,1-dioxide or of β-sulfonylenamines[18] into sulfene adducts has been unsuccessful. In contrast, β-sulfonylketene aminals (**19**) do react with alkanesulfonyl chlorides under the normal sulfene-generating conditions to yield interesting tetrasubstituted ethylenes (**20**) in 30–40% yields. The accompanying scheme illustrates the results. Compound **20b** can also be ob-



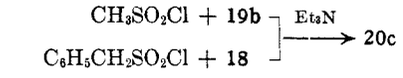
19a, $R_1 = C_6H_5$; X = O
b, $R_1 = C_6H_5$; X = CH_2

20a, R = $R_1 = C_6H_5$; X = O
b, R = $R_1 = C_6H_5$; X = CH_2
c, R = H; $R_1 = C_6H_5$; X = CH_2 or R = C_6H_5; R_1 = H; X = CH_2
d, R = R_1 = H; X = CH_2

tained directly from ketene dipiperidinoaminal and 2 equiv of phenylmethanesulfonyl chloride and triethylamine in benzene in a 29.7% yield, which is only slightly higher than the over-all yield (28.2%) obtained by involving two steps. The fact that compound **20c**



can be made either by the interaction of methanesulfonyl chloride with **19b** or by treatment of **18** with phenylmethanesulfonyl chloride, corraborates the assigned structure (**20c**). In addition to elemental



analyses and molecular weight determinations, the spectral data are in accord with the assigned structures (**20**). The infrared spectra (Nujol mull) showed an olefinic band at 6.53–6.62 and sulfone bands at 7.56–7.60 and 8.59–8.76 μ. The nmr spectra ($CDCl_3$) were relatively simple. The benzylic and methyl protons appeared as singlets at δ 4.63–4.66 and 3.20–3.22, respectively (see the Experimental Section).

These high-melting ethylenes (**20**) are quite stable and failed to react further with sulfene even at refluxing benzene temperature.

In summary, various ketene acetals afforded sulfene cycloadducts in good to poor yields. Reactivity of the

(14) (a) Two runs gave similar results. (b) The solubility of triethylammonium chloride (by-product of the sulfene reaction) in chloroform is another factor which would increase the formation of the acyclic product.

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(16) G. Opitz and K. Fischer, *Z. Naturforsch*, **18b**, 775 (1963).

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(18) W. E. Truce and D. G. Brady, unpublished observations.

electron-rich olefins toward a sulfene intermediate appeared to be affected by introducing a substituent at the β carbon atom. Both electronic and steric effects seem to determine the reactivity of the sulfene-accepting olefins. The remarkable reactivity of ketene aminals was demonstrated by transforming β-alkanesulfonylketene aminals into the corresponding 1,1-di(dialkylamino)-2,2-di(alkanesulfonyl)ethylenes.

Experimental Section[19]

Materials.—Ketene diethylacetal was prepared from bromoacetaldehyde diethylacetal[20] following the procedure described by McElvain and Kundinger.[21] Triethylamine (Matheson Coleman and Bell, bp 88–90°) was used as obtained or distilled from potassium hydroxide when required. Phenylmethanesulfonyl chloride and methanesulfonyl chloride were Eastman Kodak White Label grade and were used without further purification. Anhydrous diethyl ether (Mallinckrodt) and benzene (Baker Analyzed reagent) were used as obtained. Reagent chloroform (J. T. Baker Chemical Co.) was purified by shaking with concentrated sulfuric acid, washing with water, drying, and distilling. Acetonitrile was purified by heating to reflux with, and then distilling from phosphorus pentoxide. Tetrahydrofuran (Fisher certified reagent) was used as obtained or purified by distilling it from lithium aluminum hydride. The ketene acetals and aminals were prepared according to the references cited below and the physical constants agreed closely with those recorded in the literature. These included bromoketene diethylacetal,[22] bp 52–54° (2 mm), n^{25}D 1.4605; methylketene diethylacetal,[23] bp 85° (100 mm), n^{25}D 1.4241; ketene diisobutylacetal,[24] bp 75–80° (15 mm), n^{25}D 1.4238; phenylketene dimethylacetal,[25] bp 97–101° (2 mm), n^{25}D 1.5550; ketene dimethylacetal,[26] bp 89–92°, n^{25}D 1.4017; acetylketene diethylacetal,[26] bp 147–149° (20 mm), n^{25}D 1.4710; benzoylketene diethylacetal,[27] mp 44–46°; benzoylketene dipiperidinoaminal,[27] mp 89.5–91.5°; α-methyl-α-(piperidinomethylene)acetone,[28] bp 159–160° (8 mm), n^{19}D 1.5628; 1,1-di(4-morpholino)ethylene,[29] bp 120–121° (4.7 mm); and 1,1-di(1-dipiperidino)ethylene,[29] bp 112.5–114.0° (8.5 mm), n^{29}D 1.5057. N,N′-Bis-3-oxapentamethylene formamidiniumdithiocarboxylate was prepared by the method of Clemens, *et al.*,[30] mp 235–238°.

Preparation of Bromomethanesulfonyl Chloride.—A mixture of dibromomethane (186.0 g, 1 mole) and a saturated solution of sodium sulfite (126.1 g, 1 mole) was refluxed with stirring for 4 days. Water was removed from the resulting cloudy solution on a hot plate to leave colorless crystals, which were recrystallized from water and dried, giving a total of 182.6 g (0.93 mole) of crude sodium bromomethanesulfonate, mp 272–278°. The sulfonate was placed in a 500-ml, three-necked flask, equipped with a stirrer, a glass stopper, and a reflux condenser capped with a drying tube, and cooled with an ice bath. Phosphorus pentachloride (198.6 g, 0.95 mole) was added cautiously to the sulfonate with vigorous stirring. It liquified immediately and the reddish brown solution was heated for 4 hr. The solution was then poured into 500 ml of ice–water and allowed to stand for 1 hr in order to hydrolyze the phosphorus oxychloride. The desired sulfonyl chloride was extracted with three 150-ml portions of methylene chloride. The combined methylene chloride extracts were washed with 200 ml of water, two 200-ml portions of 5% sodium bicarbonate, and finally with 150 ml of water. The solvent was evaporated to leave a brown residue, which was distilled giving bromomethanesulfonyl chloride (28.0 g), bp 87–89° (15 mm), n^{18}D 1.5262.

Anal. Calcd for CH_2BrClO_2S: C, 6.21; H, 1.04; Br, 41.31; Cl, 18.33; S, 16.58. Found: C, 5.90; H, 0.75; Br, 41.50; Cl, 18.40; S, 16.33.

The infrared spectrum (neat) had absorptions at 7.24 (s), 7.35 (s), 8.30 (s), 8.61 (s), 9.08 (m), 12.09 (s), 13.38 (s) and 14.83 (s) μ. The nmr spectrum (CCl_4) had a singlet at δ 4.98.

Ketene Di-*sec*-butylacetal.[24]—In a 1-l. flask were placed 86.0 g (1.0 mole) of vinyl acetate and 465 ml (5.0 moles) of *sec*-butyl alochol. To the above solution, cooled to −10°, was added 160 g (1.0 mole) of bromine and the mixture was stirred for 2 days. After the reaction mixture was poured over ice, an organic layer separated; this was dried over calcium chloride, and fractionated (glass wool overcame foaming problem) from potassium carbonate. Crude α-bromo di-*sec*-butylacetal distilled at 80–110° (8 mm). Dehydrohalogenation of this bromo acetal was effected by the same method described in the literature.[21] Ketene di-*sec*-butylacetal boiled at 70–75° (9–10 mm), n^{25}D 1.4191, and was used without further purification.

Acetylketene Dipiperidinoaminal (11).—Acetyl chloride (13.3 g, 0.17 mole) was added dropwise to ketene dipiperidinoaminal (131.4 g, 0.68 mole) for 30 min. The reaction mixture was allowed to stir for 1 hr then the excess ketene dipiperidinoaminal was decanted away. The residual solid was dissolved in chloroform, concentrated, and distilled. The fractions collected in the range of bp 134–157° (0.6 mm) solidified on standing. Recrystallization from hexane afforded a pale yellow solid, mp 80–81° (4.5 g, 11.3% yield). The title compound **11** is hygroscopic, but can be stored in a desiccator up to a period of 1 month.

Anal. Calcd for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.23; N, 11.86; mol wt, 236.4. Found: C, 70.86; H, 10.15; N, 11.68; mol wt, 231.

The infrared spectrum (Nujol) had bands at 6.16 and 6.59 μ [C(=O)C=C<] and the nmr spectrum ($CDCl_3$) showed two broad doublets at δ 1.60 and 3.19 (12:8 area ratio) which were ascribed to the protons of the two piperidino groups. Two singlets at δ 1.98 and 4.41 (3:1 area ratio) were assigned to the three protons of the acetyl group and one olefinic proton, respectively.

General Procedure for Reaction of Sulfonyl Chlorides with Ketene Acetals and Ketene Aminals.—In order to avoid repetition, the procedures for these reactions have been generalized. The results of the reactions which yielded 3,3-dialkoxythietane 1,1-dioxides are summarized in Tables I and II. The detailed procedures for the preparation of 2-phenyl-3,3-diethoxythietane 1,1-dioxide (**1a**) are given however, for they illustrate the optimum conditions for this particular sulfene cycloadduct. To a stirred solution of 0.1 mole of the olefin and 0.10–0.12 mole of triethylamine in 150–200 ml of solvent under a nitrogen atmosphere, a solution of 0.1 mole of the sulfonyl chloride in 50 ml of the same solvent was added in 0.5–1 hr at room temperature. Triethylammonium chloride precipitated immediately, and the resulting suspension was allowed to stir for 4–18 hr. The salt was removed by filtration and washed with small portions of solvent. The filtrate and the washings were evaporated to a yellow to brown oil or solid; the residue was recrystallized from the appropriate solvents usually giving a white, crystalline material.

2-Phenyl-3,3-diethoxythietane 1,1-Dioxide (1a).—To a stirred solution of ketene diethylacetal (11.8 g, 0.10 mole) and triethylamine (10.1 g, 0.10 mole) in 600 ml of anhydrous diethyl ether was slowly added phenylmethanesulfonyl chloride (19.1 g, 0.10 mole) in 400 ml of ether over a 40-min period (the prolonged addition up to 7 hr did not raise the yield). A white precipitate formed immediately. The resulting suspension was allowed to stir overnight, filtered, and then washed with two 30-ml portions of acetone, after which 12.7 g (92% yield) of triethylammonium chloride, mp 254–256° dec, was isolated. Removal of acetone from the above filtrate gave a pale yellow oil, which was crystallized from ethyl acetate. Two recrystallizations from ethyl acetate yielded 0.20 g (*ca.* 0.7%) of triethylammonium benzylsulfonate, mp 114–115°. From the original filtrate, ether was evaporated *in vacuo* and the resulting semisolid was recrystallized three times from hexane, giving a total of 20.6 g (76.3% yield) of **1a**, mp 90–91°. The mixture melting point with an authentic sample showed no depression.

3-*sec*-Butoxythiete 1,1-Dioxide (2).—Under the general procedure with anhydrous ethyl ether as solvent, methanesulfonyl

(19) All melting points and boiling points are uncorrected. The molecular weights were determined by a Mechrolab vapor pressure osmometer. Ultraviolet spectra were recorded on the Bausch and Lomb Model 505 spectrophotometer.

(20) Obtained from Aldrich Chemical Co., Milwaukee, Wis.

(21) S. M. McElvain, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 506.

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(27) H. D. Stachel, *Arch. Pharm.*, **296**, 89 (1963).

(28) (a) E. Benary, *Ber.*, **63**, 1573 (1930); (b) G. Opitz and F. Zimmermann, *Ann.*, **662**, 178 (1963).

(29) H. Baganz and L. Domaschke, *Chem. Ber.*, **95**, 2095 (1962).

(30) D. H. Clemens, *et al.*, *Tetrahedron Letters*, 3257 (1965).

chloride and ketene di-*sec*-butylacetal gave a 24.3% yield of **2**, mp 70–72° (from hexane), after work-up with solvents and evaporation on the steam bath. Infrared absorptions ($CHCl_3$) were at 6.21, 7.70, 8.50, and 9.20 μ. The nmr spectrum ($CDCl_3$) showed two singlets at δ 4.40 (CH_2SO_2) and 5.60 (olefinic proton), a doublet at 1.30 (methyl group), a quartet at 4.11 (OCH), a triplet and a quintet at 0.96 and 1.65 (ethyl group).

Anal. Calcd for $C_7H_{12}O_3S$: C, 47.67; H, 6.82; S, 18.18. Found: C, 47.73; H, 7.09; S, 17.90.

1,4-Diphenyl-2-ethoxy-4-hydroxy-1,3-butadiene-1-sulfonic Acid Sultone (3).—Phenylmethanesulfonyl chloride (7.63 g, 0.04 mole) in 70 ml of tetrahydrofuran was added over a period of 1 hr to a stirred mixture of benzoylketene diethylacetal (8.81 g, 0.04 mole) and trimethylamine (5.06 g, 0.05 mole) in 300 ml of ether at ice-bath temperature. The mixture was stirred at room temperature overnight, filtered and washed with acetone to give crude triethylammonium chloride, mp 249–254° dec, 5.17 g (75.1%). The acetone filtrate yielded 1.88 g (17.1%) of triethylammonium phenylmethanesulfonate after the usual work-up. Concentration of the mother liquor resulted in a yellow oil (13.5 g), from which *trans*-stilbene (0.6 g, mp 123–124.5°) was isolated after cooling and filtration followed by two sublimations. Addition of a trace of methanol to the filtrate resulted in a yellow solid which was recrystallized from methanol to afford 2.57 g (19.6% yield) of solid which melts at 113–116°. An analytical sample was prepared by chromatography on alumina (acid washed) using ether as eluent, and then by recrystallization from a 2:1 mixture of hexane and benzene. The yellow solid had mp 115–116.5°. The infrared spectrum (Nujol) showed absorption bands at 6.09 and 6.45 (>C=C<) and 7.38 and 8.42 SO_2O μ. The nmr spectrum ($CDCl_3$) consisted of a singlet (δ 6.57, olefinic proton), a triplet (δ 1.26, methyl group), a quartet (δ 4.05, OCH_2CH_3), and multiplet (δ 7.28–7.92 two phenyl groups).

Anal. Calcd for $C_{18}H_{16}O_4S$: C, 65.83; H, 4.91; S, 9.77; mol wt, 328.4. Found: C, 65.48; H, 4.91; S, 9.50; mol wt, 341.

3-Ethoxy-Δ^3-thiacyclohexen-5-one 1,1-Dioxide (4).—Following essentially the same procedures as described above acetylketene diethylacetal (8.70 g, 0.055 mole) was treated with methanesulfonyl chloride (6.30 g, 0.055 mole) in the presence of triethylamine (6.07 g, 0.060 mole) with ether as solvent. The concentrated mother liquor was placed on a column of alumina (neutral) and successive elution with pentane, benzene, ether, ethyl acetate, methanol, and chloroform gave a white solid. Two recrystallizations from ethyl acetate–hexane afforded 1.64 g (15.7% yield) of **4**, mp 116–117°. The mixture melting point with the authentic sample showed no depression. Also the nmr and infrared spectra were identical with those of an authentic sample.

2-Phenyl-3-ethoxy-Δ^3-thiacyclohexen-5-one 1,1-Dioxide (5).—Under the same method as described above, acetylketene diethylacetal (7.23 g, 0.045 mole) and triethylamine (5.60 g, 0.050 mole) in 200 ml of ether were treated with phenylmethanesulfonyl chloride (9.54 g, 0.050 mole) in 100 ml of benzene. After the usual work-up, crude triethylammonium chloride (6.08 g) and triethylammonium benzylsulfonate (0.41 g) were isolated. Removal of the solvents from the mother liquor left 14.39 g of yellow oil, which was chromatographed on alumina (acid washed), using benzene, ether, chloroform, and methanol as successive eluents. The first fraction gave *trans*-stilbene, which was followed by a fraction which contained the desired product as well as *trans*-stilbene. The latter compound was separated by sublimation (total 0.56 g, 13.3%) and the white solid which did not sublime was recrystallized three times from methanol giving 4.88 g (40.8% yield) of **5**, mp 149.5–151°. Infrared absorptions (Nujol) were at 5.98 (s), 6.18 (s), 7.58 (s), 8.20 (s), 8.48 (m), and 8.80 (s) μ. The nmr spectrum ($CDCl_3$) revealed four singlets at δ 7.38 (aromatic protons), 5.91 (olefinic proton), 4.96 ($C_6H_5CHSO_2$), and 3.84 ($C(=O)CH_2SO_2$). Five protons of the ethoxy group had a triplet at δ 1.29 and a quartet at 4.03. The ultraviolet spectrum (MeOH) showed λ_{max} 254 mμ (ϵ *ca.* 9500) and 210 mμ (ϵ *ca.* 7400). For the elemental analysis, see the following experiment.

Reaction of Phenylmethanesulfonyl Chloride with Excess Ketene Diethylacetal.—To a solution of ketene diethylacetal (29.5 g, 0.254 mole) in 400 ml of benzene was added in one portion 9.68 g (0.08 mole) of phenylmethanesulfonyl chloride. The solution turned yellow and was allowed to stir overnight. Evaporation of benzene from the solution left an oil, which was cooled in a refrigerator to form a semisolid. Fractional crystallization afforded 0.23 g (1.1%) of **1a**, 0.50 g (2.1%) of 3,5-diethoxy-6-phenyl-Δ^2-Δ^4-thiacyclohexadiene 1,1-dioxide (**6**), mp 132–133° (from hexane–ethyl acetate), and 1.45 g (6.1%) of **5** mp 151–152° (from hexane–ethyl acetate). Compound **6** gave the following elemental analysis.

Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16; S, 10.89; mol wt, 294.4. Found: C, 61.20; H, 6.39; S, 10.98; mol wt, 292.5.

The infrared spectrum (Nujol) of **6** had bands at 6.06 and 6.34 (>C=C<) and 7.68 and 8.61 (SO_2) μ. Two olefinic protons had signals in the nmr spectrum ($CDCl_3$) at δ 5.22 (quartet) and 5.37 (doublet). Five aromatic protons appeared as a singlet at δ 7.28. A doublet at δ 4.56 was assigned to the proton α to the phenyl group. Protons of the two ethoxy groups had signals at δ 1.31 (quartet or two overlapping triplets) and 3.88 (multiplet) with area ratio of 6:4.

Compound **5** gave the following elemental analysis. (For spectral data see above experiment.)

Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30; S, 12.04; mol wt, 266.3. Found: C, 58.50; H, 5.14; S, 12.03; mol wt, 267.

In addition to the above three compounds there was obtained 4.32 g (15.5% yield) of white solid **7**, mp 113–120°, after four recrystallizations from methanol and 1.52 g (6.4% yield) of yellow solid, mp 167–170° (two recrystallizations from methanol). The former compound was found to be unstable. Although both gave poor elemental analysis, based on the spectral data, structure **7** was tentatively assigned to the white solid, while the yellow solid was thought to be a mixture of **6** and its isomer (possibly diene conjugates with phenyl group). Compound **7** had the following elemental analysis and spectral data.

Anal. Calcd for $C_{17}H_{24}O_5S$: C, 59.99; H, 7.35; S, 9.43; mol wt, 340.4. Found: C, 61.13; H, 6.52; S, 10.17; mol wt, 301.5.

The infrared spectrum (Nujol) showed strong bands at 6.04 (>C=C<) and 7.58 and 8.68 (SO_2) μ. The nmr spectrum ($CDCl_3$) had signals at δ 1.03–1.44 (multiplet), 2.37 (singlet), 3.42–4.00 (multiplet), 4.60 (doublet), 5.24 (doublet), 5.40 (doublet), and 7.29 (singlet) in a ratio of roughly 9:1:6:1:1:1:5, respectively.

The yellow solid had the following elemental analysis and spectral data.

Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16; S, 10.89; mol wt, 294.4. Found: C, 62.39; H, 6.91; S, 10.84; mol wt, 287.5.

Infrared absorptions were at 6.15, 6.26, 6.38, 7.65 and 8.67 μ. The nmr spectrum ($CDCl_3$) showed multiplets at δ 1.33 and 3.90, doublets at 4.60 and 5.40, a quartet at 5.25, and a singlet at 7.32 with relative area ratio of approximately 6:4.5:1:1:1:5, respectively.

Hydrolysis of 6.—To compound **6** (0.18 g, 0.61 mmole) in 20 ml of 95% ethanol, was added 6 drops of 1 *N* hydrochloric acid and the mixture was warmed until solution occurred. The solution was allowed to stand for 10 min, then extracted with 30 ml of chloroform and washed with 30 ml of water. Evaporation of chloroform left a semisolid, which was recrystallized from methanol to give 0.11 g (68.8% yield) of **5**. The mixture melting point with authentic sample showed no depression (mp 151–153°). The infrared spectrum (Nujol) was identical with that of the authentic sample.

Reaction of Phenylmethanesulfonyl Chloride with Acetylketene Diethylacetal in the Presence of Ketene Diethylacetal and Triethylamine.—In a 500-ml, three-necked flask, fitted with a stirrer, a reflux condenser, and two dropping funnels were placed 31.2 g (0.197 mole) of acetylketene diethylacetal and 9.98 g (0.099 mole) of triethylamine in 200 ml of anhydrous ether and cooled in an ice–salt bath. To the above stirred mixture was added dropwise 18.8 g (0.099 mole) of phenylmethanesulfonyl chloride in 130 ml of tetrahydrofuran over a period of 1 hr. At the same time, 11.46 g (0.099 mole) of ketene diethylacetal in 70 ml of ether was added for 1.5 hr. After the completion of the addition of phenylmethanesulfonyl chloride the ice bath was removed. The mixture gradually turned yellow. Two hours later additional ketene diethylacetal (11.46 g, 0.099 mole) in 70 ml of ether was added for 0.5 hr. After stirring overnight triethylammonium chloride was removed by filtration. Evaporation of the solvents from the filtrate left a brown oil (69.4 g), part of which was chromatographed over alumina, using hexane, carbon tetrachloride, benzene, ethyl acetate, absolute ethanol, and methanol as eluents. From the 56 fractions three compounds were isolated: **1a** (64.1%), **5** (33.6%), and **6** (1.4%). They were

identified by taking mixture melting points and by comparing the infrared spectra with those of authentic samples.

Reaction of Methanesulfonyl Chloride with 1-Piperidino-2-methyl-1-buten-3-one.—Following the same method as described for the preparation of **3**, 1-piperidino-2-methyl-1-buten-3-one (24.1 g, 0.144 mole) was treated in ether with methanesulfonyl chloride (16.5 g, 0.144 mole) in the presence of triethylamine (14.6 g, 0.144 mole). After the usual work-up, the mother liquor was dried over anhydrous magnesium sulfate, filtered, and concentrated to a brown oil, which solidified on cooling. Recrystallization from methanol gave 14.7 g (41.6% yield) of crude 3,4-dimethyl-2-piperidino-4-hydroxy-3-butene-1-sulfonic acid sultone (**8a**). A pure sample was obtained by sublimation, mp 107–108° (lit.[10] 108–109°). The infrared spectrum (Nujol) showed bands at 5.92, 7.37, 8.44, and 8.62 μ. The nmr spectrum ($CDCl_3$) revealed two broad peaks at δ 1.50 and 2.41 (piperidine group) and two singlets at 1.72 and 1.93 (two methyl groups). Two protons α to sulfone group and an allylic proton were tentatively assigned to a triplet (unsymmetrical) at δ 3.27 and a multiplet at 3.60, respectively.

A brown solid which was separated by filtration was washed with acetone and recrystallization from methanol–ether gave 17.3 g of triethylammonium chloride. Work-up of the acetone filtrate afforded 0.54 g of the hydrochloride of **8b**, mp 200–209° (from ethanol).

Anal. Calcd for $C_{11}H_{20}ClNO_3S$: C, 46.88; H, 7.15; Cl, 12.58; N, 4.97; S, 11.38. Found: C, 46.56; H, 7.34; Cl, 12.66; N, 5.20; S, 11.17.

The infrared spectrum (Nujol) had bands at 4.07, 5.88, 7.36, 7.60, 8.45, 8.78, 10.27, and 10.92 μ. The nmr spectrum (D_2O) revealed two broad peaks at δ 1.79 and 3.37 (piperidine group) and a doublet at 5.40 (olefinic proton). Two singlets at δ 2.80 and 4.67 appeared to be due to an impurity and H_2O, respectively. Two doublets at δ 4.03 and 4.14 and a multiplet at 4.54 were due to two protons α to the sulfone group and an allylic proton. No attempts were made to distinguish these two different types of protons.

Reaction of 8a with 3 *N* Hydrochloric Acid.—A solution of compound **8a** (2 g, 8.15 mmoles) and 40 ml of 3 *N* hydrochloric acid was refluxed for 14 hr. Evaporation of the solution followed by sublimation of the resulting solid yielded 2.12 g (92.2% yield) of the hydrochloride of **8a**, mp 203–205°.

Anal. Calcd for $C_{11}H_{20}ClNO_3S$: C, 46.88; H, 7.15; N, 4.97; Cl, 12.58; S, 11.38. Found: C, 46.54; H, 6.86; N, 4.98; Cl, 12.38; S, 11.54.

The infrared spectrum (Nujol) showed bands at 3.97 (N^+H stretching), 5.93 (>C=C<), and 7.46 and 8.43 (SO_2O) μ. The nmr spectrum (D_2O) revealed two broad singlets at δ 1.83 and 3.37 (piperidine group), two singlets at 1.93 and 2.09 (two methyl groups), a multiplet at 4.59 (>CHN^+), and a singlet and a doublet at 4.31 and 4.19 (CH_2SO_2O).

Reaction of Methanesulfonyl Chloride with 1,1-Di(1-piperidino)ethylene.—Under the general procedure with benzene as solvent, 1,1-di(1-piperidino)ethylene (ketene dipiperidinoaminal, 37.9 g, 0.195 mole) was treated with methanesulfonyl chloride (22.35 g, 0.195 mole) in the presence of triethylamine (20.2 g, 0.20 mole). After the usual work-up, benzene was removed from the filtrate to leave a pale orange semisolid. The nmr spectrum ($CDCl_3$) of this crude product showed olefinic protons at δ 4.10 and 5.17 in ratio of 1.7:1, the cycloadduct **17** being the minor product. Recrystallization from hexane–ethyl acetate–ethanol gave 30.3 g (33.8% yield based on the above ratio of **18**:**17**) of a mixture of both isomers, mp 83–90°. They were separated by fractional recrystallizations. Four recrystallizations from ethanol afforded 3-piperidinothiete 1,1-dioxide (**17**), mp 142–143.5°.

Anal. Calcd for $C_9H_{15}NO_2S$: C, 51.31; H, 7.00; N, 7.48; S, 17.13; mol wt, 187.3. Found: C, 51.76; H, 7.22; N, 7.32; S, 17.12; mol wt, 187.8.

The infrared spectrum (Nujol) showed bands at 6.14, 7.80, 8.27, 8.67, and 8.76 μ. The nmr spectrum ($CDCl_3$) had singlets at δ 1.65, 3.16, 4.34, and 5.18 with a ratio of 6:4:2:1.

Three recrystallizations from ethyl acetate–methanol (trace) gave an analytically pure 1,1-di(1-piperidino)-2-(methanesulfonyl)ethylene (**18**), mp 112–113°.

Anal. Calcd for $C_{13}H_{24}N_2O_2S$: C, 57.34; H, 8.88; N, 10.29; S, 11.78; mol wt, 272.3. Found: C, 57.18; H, 8.83; N, 10.28; S, 11.77; mol wt, 272.

The infrared spectrum (Nujol) had bands at 6.56, 7.56, 7.80, 8.21, 8.52, 8.60, and 8.78 μ. The nmr spectrum revealed four singlets at δ 1.60, 2.95, 3.23, and 4.10 in a ratio of 12:3:8:1.

Reaction of Methanesulfonyl Chloride with 1,1-Di(1-piperidino)ethylene in Various Solvents.—Employing the same procedures as described above, 1,1-di(1-piperidino)ethylene (4.5 g, 0.023 mole) was treated with methanesulfonyl chloride (2.64 g, 0.023 mole) in the presence of triethylamine (3.04 g, 0.030 mole) in an appropriate solvent. The solution was stirred for about 4 hr after the completion of the addition of methanesulfonyl chloride (over the period of 20 min), filtered, and washed with acetone when triethylammonium chloride was not soluble in the solvent used. Solvents were removed from the combined filtrate and washings to give a yellow-to-orange semisolid. The ratio of **17**:**18** was estimated by measuring the integrations of the olefinic protons at δ 5.2 and 4.1 in the nmr spectrum ($CDCl_3$). The results are listed in Table III.

TABLE III

Solvent	Wt of crude products, g	17:18
Benzene	3.7	1:1.6
Et_2O	2.3	1:0.14
$CHCl_3$	2.2	1:2
CH_3CN	2.4	1:3

1,1-Di(4-morpholino)-2-(phenylmethanesulfonyl)ethylene (19a).—Under the general procedure with benzene as solvent 1,1-di(4-morpholino)ethylene (ketenedimorpholinoaminal) and phenylmethanesulfonyl chloride (0.11-mole scale) gave a 68.8% yield of **19a** (from ethanol), mp 165–166° (lit.[5b] 164°). From ethanol filtrate a 4.2% yield of benzylsulfonyl-N-acetylmorpholine (from hexane–ethyl acetate), mp 132.5–133.5° (lit.[5b] 129–131°), was also obtained.

Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.12; H, 6.05; N, 4.95; S, 11.30; mol wt, 283.4. Found: C, 55.20; H, 5.97; N, 4.93; S, 11.32; mol wt, 286.5.

1,1-Di(1-piperidino)-2-(phenylmethanesulfonyl)ethylene (19b).—Under the general procedure with benzene as solvent (0.195-mole scale) 1,1-di(1-piperidino)ethylene (ketene dipiperidinoaminal) and phenylmethanesulfonyl chloride gave a 70.2% yield of crude **19b** (from ethanol), mp 96–101°. An analytical sample was obtained by further recrystallization from ethanol, mp 102–103°.

Anal. Calcd for $C_{19}H_{28}N_2O_2S$: C, 65.48; H, 8.09; N, 8.04; S, 9.20; mol wt, 348.5. Found: C, 65.80; H, 8.16; N, 7.89; S, 9.19; mol wt, 354.

The infrared spectrum (Nujol) had bands at 6.57, 7.46, 7.79, 8.23, and 8.68 μ. The nmr spectrum ($CDCl_3$) showed singlets at δ 1.57, 3.79, 4.22, and 7.32 and a doublet at 3.12 in ratio of 12:1:2:5:8, respectively.

1,1-Di(4-morpholino)-2,2-di(phenylmethanesulfonyl)ethylene (20a).—To a stirred benzene solution (10 ml) of triethylamine (0.61 g, 0.006 mole) were added concurrently phenylmethanesulfonyl chloride (1.14 g, 0.006 mole) in 20 ml of benzene and **19a** (1.20 g, 0.0034 mole) in 60 ml of benzene over a period of 20 min. The mixture was allowed to stir overnight and then filtered, isolating a pale yellow solid, which was washed with two 40-ml portions of water. Recrystallization from chloroform–acetone afforded 0.40 g (23.3% yield) of **20a**, mp 281.5–282.5° dec.

Anal. Calcd for $C_{24}H_{30}N_2O_6S_2$: C, 56.90; H, 5.97; N, 5.54; S, 12.61; mol wt, 506.6. Found: C, 56.95; H, 6.10; N, 5.45; S, 12.71; mol wt, 502.

The infrared spectrum (Nujol) showed bands at 6.56, 7.56, 7.72, 8.59, and 8.68 μ. The nmr spectrum ($CDCl_3$) had a multiplet at δ 3.17–3.61, a poorly resolved (owing to solubility difficulty) singlet at 4.63, and a multiplet at 7.25–7.50 with an area ratio of roughly 16:4:10.

From the aqueous solution, 0.35 g (36.5% yield) of crude benzylsulfonyl-N-acetylmorpholine as well as triethylammonium chloride (0.17 g), was isolated. The amide showed no depressed mixture melting point with an authentic sample.

1,1-Di(1-piperidino)-2,2-di(phenylmethanesulfonyl)ethylene (20b). Method A.—A solution of phenylmethanesulfonyl chloride (7.63 g, 0.04 mole) in 50 ml of benzene was added dropwise for 45 min to a mixture of **19b** (12.9 g, 0.04 mole) and triethylamine (5.06 g, 0.05 mole) in 200 ml of benzene. The reaction mixture was stirred overnight. Triethylammonium chloride was removed by filtration. The filtrate was evaporated to a semisolid. Crystallization from benzene gave 8.2 g (40.8% yield) of crude **20b**, mp 212–222°. An analytical sample was

prepared by recrystallization from chloroform–methanol (2:3), mp 227–229°.

Anal. Calcd for $C_{26}H_{34}N_2O_4S_2$: C, 62.12; H, 6.82; N, 5.57; S, 12.76; mol wt, 502.7. Found: C, 62.48; H, 6.90; N, 5.86; S, 13.06; mol wt, 493.

Infrared absorptions (Nujol) were at 6.61 (>C=C<), 7.58, and 8.72 (SO_2) μ. The nmr spectrum ($CDCl_3$) showed broad singlets at δ 1.58 and 3.13 (piperidine groups), a singlet at 4.66 (four benzylic protons), and a multiplet at 7.40 (aromatic protons).

Method B.—Employing procedures as described above, 1,1-di(1-piperidino)ethylene (13.0 g, 0.067 mole) was treated with excess phenylmethanesulfonyl chloride (25.6 g, 0.134 mole) in the presence of triethylamine (15.2 g, 0.150 mole). After the usual work-up, 2.2 g of **20b** was isolated from the filtered solid. The major portion of the desired product, however, was obtained from the mother liquor after removal of the benzene giving rise to a brown semisolid. Recrystallization from methanol–chloroform afforded **20b**. A total of 10.0 g (29.7% yield) was isolated. The mixture melting point with an authentic sample showed no depression.

In addition there was obtained 2.3 g of brown oil which resisted characterization. Its infrared spectrum (neat) showed bands at 5.76, 6.10, 6.24, 6.70, 6.93, 7.60, 8.03, 8.45, 8.61, 8.80, and 9.65 μ.

1,1-Di(1-piperidino)-2-(methanesulfonyl)-2-phenyl(methanesulfonyl)ethylene (20c). Method A.—Employing similar procedures as described above, methanesulfonyl chloride (4.93 g, 0.043 mole) was treated with **19b** (15.1 g, 0.043 mole) in benzene in the presence of triethylamine (5.06 g, 0.05 mole). After the usual work-up, benzene was removed from the mother liquor to leave a yellow solid which was recrystallized from ethyl acetate–methanol (trace) to give 12.3 g (67.2% yield) of crude **20c**. An analytical sample was prepared by recrystallizations (thrice) from methanol and chloroform, mp 176.5–178.5°.

Anal. Calcd for $C_{20}H_{30}N_2O_4S_2$: C, 56.31; H, 7.09; N, 6.57; S, 15.03, mol wt, 426.6. Found: C, 56.22; H, 7.32; N, 6.81; S, 14.90; mol wt, 426.

The infrared spectrum (Nujol) had bands at 6.53 (s), 7.60 (s), 7.76 (s), 8.60 (m), and 8.76 (s) μ. The nmr spectrum ($CDCl_3$) showed a broad singlet and a broad doublet at δ 1.63 and 3.30 (piperidino groups), a multiplet at 7.25 (aromatic protons), and two singlets at 3.20 (methyl protons) and 4.63 (benzylic protons).

Method B.—In a 50-ml erlenmeyer flask were placed 0.54 g (2 mmoles) of **18** and 0.22 g (2.2 mmoles) of triethylamine in 25 ml of benzene. To the above stirred mixture was slowly added 0.38 g (2 mmoles) of phenylmethanesulfonyl chloride in 15 ml of benzene over a 10-min period. The mixture was stirred overnight and filtered. Benzene was removed from the filtrate leaving a yellow oil which solidified after cooling. Recrystallizations from ethyl acetate and then from methanol afforded 0.29 g (34.1% yield) of white, crystalline material, mp 176.5–178.0°. The mixture melting point with **20c** showed no depression. Its infrared spectrum (Nujol) was identical with that of **20c**.

1,1-Di(1-piperidino)-2,2-di(methanesulfonyl)ethylene (20d).—Following the method described above, methanesulfonyl chloride (0.28 g, 2.4 mmoles) was treated with **18** (0.65 g, 2.4 mmoles) in the presence of triethylamine (0.26 g, 2.6 mmoles). After the usual work-up benzene was evaporated from the filtrate to a yellow oil. Work-up with solvents such as ethyl acetate, ethanol, methanol, and hexane followed by cooling gave a yellow solid. Two recrystallizations from ethyl acetate–methanol (trace) afforded 0.32 g (38.1% yield) of **20d**, mp 196.0–197.5°.

Anal. Calcd for $C_{14}H_{26}N_2O_4S_2$: C, 47.97; H, 7.48; N, 7.99; S, 18.30. Found: C, 48.04; H, 7.75; N, 7.93; S, 18.06.

The infrared spectrum (Nujol) showed bands at 6.62 (s), 7.56 (s), 7.77 (s), 8.56 (w), and 8.74 (m) μ. The nmr spectrum ($CDCl_3$) revealed a broad singlet and a broad doublet at δ 1.75 and 3.50 (piperidine groups), a singlet at 3.22 (six methyl protons).

Registry No.—**1a**, 1950-82-9; **1b**, 10099-00-0; **1c**, 10099-01-1; **1d**, 10099-02-2; **1e**, 10099-03-3; **1f**, 10099-04-4; **1g**, 10099-05-5; **1h**, 10099-06-6; **1i**, 10099-07-7; bromomethanesulfonyl chloride, 10099-08-8; **2**, 10099-10-2; **3**, 10099-11-3; **4**, 10099-13-5; **5**, 10099-12-4; **6**, 10099-14-6; **7**, 10084-33-0; **8a**, 1433-29-0; hydrochloride of **8b**, 10099-16-8; **11**, 10099-09-9; **17**, 1623-62-7; **18**, 10076-45-6; **19a**, 1599-17-3; **19b**, 10099-19-1; **20a**, 10084-34-1; **20b**, 10099-20-4; **20c**, 10099-21-5; **20d**, 10076-46-7; benzylsulfonyl-N-acetylmorpholine, 1709-88-2.

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Mass Spectrometry in Structural and Stereochemical Problems. CXXIV.[1] Mass Spectral Fragmentation of Alkylquinolines and Isoquinolines[2]

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The mass spectra of alkylquinolines and isoquinolines were examined. Evidence was obtained for an azatropylium ion intermediate in the pathway leading to the M − (H + HCN) ion from methylquinolines and isoquinolines. The predominant fragmentation modes of alkylquinolines and isoquinolines having more than three carbon atoms in the chain are β cleavage and McLafferty rearrangement. The relative amounts of these cleavages can be correlated with the electron density at the position of substitution. Alkyl chains at C-4 and C-8 undergo facile γ and δ cleavage, probably because the resulting radicals can be stabilized by cyclization to the *peri* position.

Compounds containing quinoline and isoquinoline ring systems are prevalent in nature. Since structure elucidation of such compounds may be limited by the small quantities of material available, application of mass spectrometry to these systems is frequently required. However, aside from Clugston and McLean's[5] study of the behavior of oxygenated quinolines upon electron impact, no systematic investigation of the characteristic cleavages of substituted quinolines or isoquinolines has been undertaken.

The only important fragment in the mass spectra of quinoline (Σ_{40} = 9.2%) and isoquinoline (Σ_{40} = 9.1%)

(1) For paper CXXII, see S. Huneck, C. Djerassi, D. Becher, M. Barber, M. v. Ardenne, K. Steinfelder, and R. Tümmler, *Tetrahedron*, in press.

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(5) D. M. Clugston and D. B. McLean, *Can. J. Chem.*, **44**, 781 (1966).