tricyclene product was produced. This material was isolated, after methylation, by g.l.c. using an Apiezon L column and identified by infrared and n.m.r. spectra.

Methylation of Triethoxysilylnorbornenes.—A sample of 3.70 g. (0.014 mole) of the triethoxysilylnorbornene was added to 50 ml. of 4.6% methyllithium in diethyl ether. The solution was stirred for 2 days at room temperature. The work-up was carried out in a fashion identical with that used in the methylations with methylmagnesium bromide. Vacuum distillation yielded 1.5 g. (63%) of the product.

The Stereoselective Reaction of Bicyclic Enamines with Sulfene

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The cycloaddition of sulfene to bicyclic enamines derived from 5-norbornene-2-carboxaldehyde and various secondary amines afforded in stereoselective fashion a single substituted thietane dioxide in all but one case. Evidence is presented which demonstrates the configurational features of the adducts. Brief mention is also made of the quaternization of the 3′-substituted spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxides.

This paper reports a study of the reactions of various enamines derived from 5-norbornene-2-carboxaldehyde (I) with methanesulfonyl chloride and triethylamine. Previous work has indicated that such a sulfonyl chloride–tertiary amine combination readily adds to appropriately activated olefins to afford substituted thietane dioxides.[2] More recently, such cycloaddition processes have been shown to proceed *via* sulfene intermediates.[3] The present research was undertaken because it appeared to offer the attractive opportunity to examine the stereoselectivity of sulfene addition to a bicyclic moiety.

5-Norbornene-2-carboxaldehyde (I)[4] readily condenses with a variety of secondary amines in refluxing toluene solution without added catalyst to produce in good yield the related enamines II (see Table I). The α,β-unsaturated amines were colorless liquids which could be stored without change for prolonged periods in a nitrogen atmosphere at 0° or below. Close scrutiny of the enamine structure II will reveal that two isomeric structures are possible in this system, the transoid form IIa and the cisoid counterpart IIb. Comparison of the n.m.r. spectra (in $CDCl_3$) of freshly distilled samples of several of the enamines listed in Table I with those reported by Slomp, MacKellar, and Umbreit[5] for the related *endo*- and *exo*-5-norbornene-2-carboxaldehydes (I) revealed that the transoid form predominated to the extent of 80 to 90% depending on the amine substituent. The ratio of the isomers could be readily determined by integration of the olefinic proton resonance peaks. The triplet pattern (characteristic of the *exo* aldehyde) was assigned to the cisoid form while the two sets of doublets of doublets (characteristic of the *endo* aldehyde) were assigned to the transoid isomer.

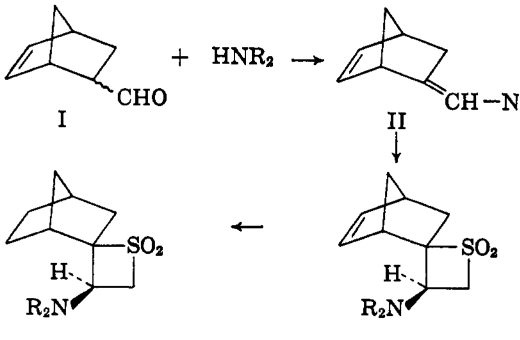
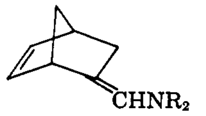
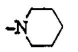
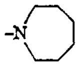
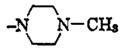
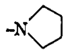
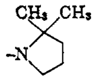
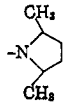
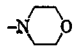
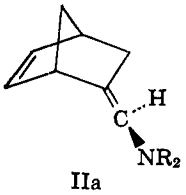


Table I

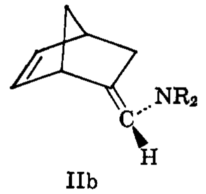
Enamines Derived from 5-Norbornene-2-carboxaldehyde



Compd.	R₂N-	Yield, %	B.p., °C. (mm.)	nD (°C.)
IIa		85.0	126–129 (11)	1.5318 (26.5)
IIb		52.0	138–144 (16)	1.5355 (25)
IIc		76.5	140–145 (16)	1.5322 (24)
IId		71.5	116–121 (15)	1.5378 (24)
IIe		59.1	94–98 (1)	1.5282 (25)
IIf		64.5	68–70 (0.4)	1.5068 (26)
IIg		81.2	132–135 (14)	1.5346 (23)



IIa



IIb

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[1] Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

[2] G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962); W. E. Truce, J. J. Breiter, D. J. Abraham, and J. R. Norell, *J. Am. Chem. Soc.*, **84**, 303 (1962); W. E. Truce and J. R. Norell, *ibid.*, **85**, 3231 (1963); W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetetrahedron Letters*, 1677 (1963); L. A. Paquette, *J. Org. Chem.*, **29**, 2854 (1964).

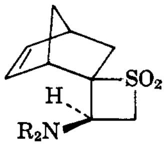
[3] I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964); see also J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

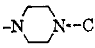
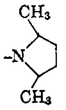
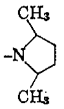
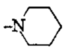
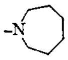
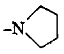
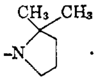
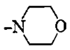
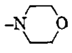
[4] Gas chromatographic analysis of this particular commercial sample demonstrated the presence of two major components of which 75% was the *endo* isomer and 25% the *exo* isomer. It is anticipated that either material would give rise to the same mixture of enamines, but we have not elucidated this point.

[5] G. Slomp, F. MacKellar, and G. R. Umbreit, to be published.

TABLE II

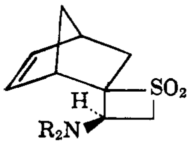
3′-SUBSTITUTED SPIRO[5-NORBORNENE-2,2′-THIETANE] 1′,1′-DIOXIDES



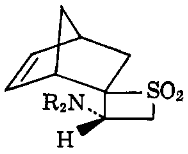
Compd.	R₂N-	Yield, %	M.p., °C.	Recrystn. solvent	Formula	Analyses, % Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
III		45.2	162–164	Ethanol	$C_{14}H_{22}N_2O_2S$	59.54	7.85	9.92	11.35	59.75	7.85	9.80	11.31
IV		45.7	102–104	Ethanol	$C_{15}H_{23}NO_2S$	64.02	8.24	4.98	11.40	63.77	8.06	4.97	11.34
V	 ·HCl	. . .	207–209 dec.	Ethanol-ether	$C_{15}H_{24}ClNO_2S$	56.67	7.61	4.41	10.09	56.76	7.62	4.61	10.01
VI	 ·HCl	44.5	243 dec.	Ethanol–ether	$C_{14}H_{22}ClNO_2S$	55.43	7.30	4.61	10.55	55.45	7.15	4.54	10.39
VII	 ·HCl	69.0	221 dec.	Ethanol–ether	$C_{15}H_{24}ClNO_2S$	56.67	7.61	4.41	10.09	56.96	7.55	4.28	9.91
VIII	 ·HCl	63.5	238 dec.	Ethanol–ether	$C_{13}H_{20}ClNO_2S$	53.87	6.95	4.83	11.06	53.77	7.03	4.51	11.13
IX	 ·HCl	59.8	234 dec.	Aq. ethanol–ether	$C_{15}H_{24}ClNO_2S$	56.67	7.61	4.41	10.09	56.39	7.45	4.56	9.95
X		76.6	128–129	Ethanol	$C_{13}H_{19}NO_3S$	57.96	7.11	5.20	11.90	57.73	7.18	5.23	11.90
XI	 ·HCl	. . .	225–226 dec.	Ethanol–ether	$C_{13}H_{20}ClNO_3S$	51.05	6.59	4.58	10.49	51.35	6.20	4.71	10.49

Addition of methanesulfonyl chloride to a dioxane solution of equimolar amounts of an enamine from Table I and triethylamine was carried out as outlined earlier. It was found most efficacious to purify the crude, and usually dark, reaction mixtures by rapid passage through a column of Woelm basic alumina. Elution with ether gave the spiro[5-norbornene-2,2′-thietane] 1,1′-dioxides in yields of 45 to 77%. In most cases the resulting bases were converted directly to their hydrochloride salts (for purposes of water solubility) and characterized in that state. In contrast to the six other examples where a single thietane dioxide was isolated, the reaction of the morpholine enamine IIg under similar conditions gave rise in 77% yield to a product which contained somewhat less than 5% of a second isomer as determined from n.m.r. data. The two components could not be separated by fractional crystallization but the major isomer could be obtained in a pure state by conversion of the base to its *p*-toluenesulfonic acid salt and subsequent regeneration of the base with sodium hydroxide. The fact that a second isomer was in evidence in this particular example is probably due to the very high yield observed with the morpholine enamine; that is, in the other cases where the yields of cycloaddition product were lower, the second isomer could have precipitated as its hydrochloride salt along with the triethylamine hydrochloride, or could have been lost during the single crystallization involved (if it were formed initially).

Examination of the n.m.r. spectra of the spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxides revealed that the olefinic region consisted solely of two sets of doublets of doublets as in the *endo* aldehyde and transoid enamines. If the basic assumption is made that sulfene reagent of necessity must approach the bicyclic system from the *exo* face,[6] then the resulting spiro compound must be represented by XIX or XX. The n.m.r. data can thereafter only be accommodated by structures of the type III–XI which offer perturbation at a single olefinic proton by the heterocyclic amine moiety. Examination of molecular models of the isomeric structure XX reveals that the amine substituent is located at a point roughly equidistant to the two vinyl protons, an arrangement which would not be expected to give rise to the unsymmetrical perturbation that is in evidence. In addition, a structure such as XX, with the bulky heterocyclic moiety (especially in the case of the 2,2-dimethylpyrrolidinyl radical) embedded under the bicyclic superstructure, would be expected, from steric considerations alone, to be extremely resistant to formation. On the basis of this reasoning we have assigned the stereochemistry indicated by structure XIX to the thietane dioxides.



XIX



XX

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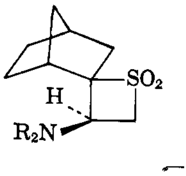
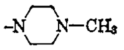
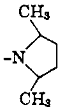
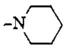
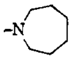
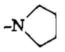
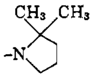
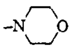
[6] For a comprehensive discussion of *endo* and *exo* addition to various norbornane derivatives, see J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

Table III

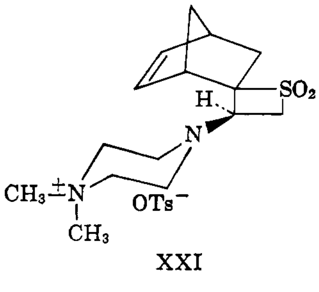
3′-Substituted Spiro[5-norbornane-2,2′-thietane] 1′,1′-Dioxides



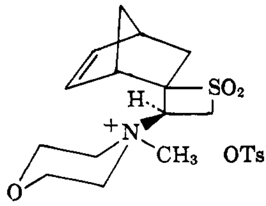
Compd.	R_2N-		Yield, %	M.p., °C.	Recrystn. solvent	Formula	Analyses, %							
							Calcd.				Found			
							C	H	N	S	C	H	N	S
XII		·HCl	100	273 dec.	Ethanol–ether	$C_{14}H_{25}ClN_2O_2S$	52.40	7.85	8.73	9.99	52.20	7.82	8.71	9.87
XIII		·HCl	100	235–236 dec.	Ethanol–ether	$C_{15}H_{26}ClNO_2S$	56.31	8.19	4.38	10.02	56.68	8.41	4.05	9.91
XIV		·HCl	100	245 dec.	Aq. ethanol–ether	$C_{14}H_{24}ClNO_2S$	54.97	7.91	4.58	10.48	54.43	7.97	4.35	9.85
XV		·HCl	100	241 dec.	Aq. ethanol–ether	$C_{15}H_{26}ClNO_2S$	56.31	8.19	4.38	10.02	56.36	8.27	4.30	10.11
XVI		·HCl	88.0	233–234	Ethanol–ether	$C_{13}H_{22}ClNO_2S$	53.50	7.60	4.80	10.99	53.02	7.57	4.79	11.05
XVII		·HCl	100	235 dec.	Aq. ethanol–ether	$C_{15}H_{26}ClNO_2S$	56.31	8.19	4.38	10.02	56.40	8.11	4.24	9.90
XVIII		·HCl	98.3	241–242 dec.	Ethanol–ether	$C_{13}H_{22}ClNO_3S$	50.72	7.20	4.55	10.42	50.87	7.28	4.60	10.45

The 3′-substituted spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxides were readily catalytically hydrogenated to their dihydro derivatives (see Tables II and III).

The thietane dioxide III on reaction with methyl *p*-toluenesulfonate in refluxing ethanol resulted in the formation of the quaternary salt XXI while the thietane dioxide X under similar conditions afforded instead the *p*-toluenesulfonic acid salt of the base (X·TsOH). This phenomenon is undoubtedly due to the increased steric hindrance in the environment of the nitrogen electron pair in X which allows removal of a proton from a solvent molecule but prohibits an SN2 displacement on the methyl *p*-toluenesulfonate molecule. The methyl *p*-toluenesulfonate salt (XXII) of X could, however, be isolated in moderate yield when the solvent was omitted.



XXI



XXII

Experimental[7]

General Procedure for Enamine Formation.—A solution of 61 g. (0.50 mole) of 5-norbornene-2-carboxaldehyde (I)[4] and 43 g. (0.50 mole) of piperidine in 150 ml. of toluene was refluxed for 3 hr. under a water separator in an atmosphere of nitrogen. The toluene was removed under reduced pressure and the residue was distilled under nitrogen to give 80.3 g. (85.0%) of colorless liquid, b.p. 126–129° (11 mm.), $n^{26.5}\mathrm{D}$ 1.5318.

General Procedure for the Cycloaddition Reaction. A. Direct Crystallization of the Crude Product.—A solution of 102 g. (0.50 mole) of the enamine IIc and 50.6 g. (0.50 mole) of triethylamine in 400 ml. of dioxane was treated dropwise with a solution of 57.3 g. (0.50 mole) of methanesulfonyl chloride in 50 ml. of dioxane. When the addition was completed, the mixture was allowed to stand overnight at room temperature. The precipitated triethylamine hydrochloride was separated by filtration and rinsed with a small amount of cold dioxane. The combined filtrates were evaporated under reduced pressure and the dark oil thus obtained was dissolved in hot ethanol, filtered to remove some dark brown insoluble gum, and cooled. There was obtained 63.7 g. (45.2%) of product, m.p. 160–164°. Several additional recrystallizations of this material from ethanol gave pure 3′-(4-methyl-1-piperazinyl)spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxide as large white prisms, m.p. 162–164°.

B. Purification of the Crude Product by Passage through Alumina.—A solution of 50 g. (0.29 mole) of the enamine IIf and 29.3 g. (0.29 mole) of triethylamine in 125 ml. of dioxane was treated with a solution of 33.1 g. (0.29 mole) of methanesulfonyl chloride in 30 ml. of dioxane as described above. The resulting dark brown oil was purified by chromatography on Woelm basic alumina (elution with ether). The crystalline solid then obtained was recrystallized from ethanol to give 42.0 g. (45.7%) of product, m.p. 102–105°. Pure 3′-(2,5-dimethyl-1-pyrrolidinyl)-spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxide was obtained as flaky white prisms from ethanol, m.p. 102–104°.

General Procedure for Catalytic Hydrogenation.—A solution of 0.02–0.04 mole of 3′-substituted spiro[5-norbornene-2,2′-thietane] 1′,1′-dioxide hydrochloride in 150 ml. of ethanol containing 100 mg. of Adams catalyst was hydrogenated in a Parr apparatus at an initial pressure of 50 p.s.i. Hydrogen uptake ceased after the consumption of 1 molar equiv. The catalyst was removed by filtration and the solvent was evaporated under reduced pressure. The residual solid was purified by recrystallization from ethanol–ether.

1,1-Dimethyl-4-{spiro[5-norbornene-2,2′-thietane]-3′-yl}piperazinium *p*-Toluenesulfonate 1′,1′-Dioxide Monohydrate (XXI·H_2O).—A solution of 5.6 g. (0.02 mole) of III and 4.1 g. (0.022 mole) of methyl *p*-toluenesulfonate in 50 ml. of ethanol was refluxed for 3 hr. The solvent was removed under reduced pressure and the residue was crystallized on trituration with ethanol–ether. After drying the solid, there was obtained 9.3 g. (96.0%)

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[7] Melting points are corrected while boiling points are uncorrected. The microanalytical and spectral determinations were obtained in the Physical and Analytical Chemistry Department under the direction of Dr. D. R. Myers.

of white powder, m.p. 132–134°. The pure hydrated quaternary salt was obtained as small, shiny platelets from ethanol–ether, m.p. 136° dec.

Anal. Calcd. for $C_{22}H_{34}N_2O_6S_2$: C, 54.29; H, 7.04; N, 5.76; S, 13.18. Found: C, 54.24; H, 6.94; N, 5.69; S, 13.13.

Attempted Quaternization of X. 3′-Morpholinospiro[5-norbornene-2,2′-thietane] 1′,1′-Dioxide *p*-Toluenesulfonate (X·*p*-TsOH).—A solution of 5.4 g. (0.02 mole) of purified X (containing about 5% of an isomeric substance, m.p. 118–121°) and 4.1 g. (0.022 mole) of methyl *p*-toluenesulfonate in 50 ml. of ethanol was refluxed for 4 hr. After cooling, ether was added to the cloud point and the contents were cooled. There was obtained 6.6 g. (75.0 %) of a white solid, m.p. 204–209°. Two recrystallizations of this material from ethanol–ether gave the pure *p*-toluenesulfonic acid salt, m.p. 217–218°.

Anal. Calcd. for $C_{20}H_{27}NO_6S_2$: C, 54.40; H, 6.16; N, 3.17; S, 14.52. Found: C, 54.40; H, 6.08; N, 3.35; S, 14.60.

A 1.0-g. sample of this salt was dissolved in water and the aqueous solution was treated with a slight excess of sodium hydroxide solution. The cloudy suspension was extracted several times with 10-ml. portions of methylene chloride. The combined organic layers were washed with water, dried, filtered, and evaporated. The resulting white solid was recrystallized from ethanol to give 550 mg. of pure X, m.p. 128–129°.

4-Methyl-4-{spiro[5-norbornene-2,2′-thietane]-3′-yl}morpholinium *p*-Toluenesulfonate 1′,1′-Dioxide (XXII).—A mixture of 13.5 g. (0.05 mole) of X (m.p. 118–121°) and 13.0 g. (0.07 mole) of methyl *p*-toluenesulfonate was heated on a steam bath for 4 hr. The solution which first formed slowly deposited a crystalline solid. The resulting solid mass was recrystallized from ethanol–ether and dried to give 8.7 g. (39.7%) of white solid, m.p. 241–242° dec. The pure quaternary salt was obtained as small white platelets from 95% ethanol–ether, m.p. 244° dec.

Anal. Calcd. for $C_{21}H_{29}NO_6S_2$: C, 55.36; H, 6.41; N, 3.08; S, 14.08. Found: C, 55.34; H, 6.41; N, 2.98; S, 14.19.

Acknowledgment.—The author wishes to acknowledge helpful discussions with Dr. G. Slomp concerning certain aspects of the n.m.r. spectra.

α-Halosulfones. III. The Steric Course of the Cycloaddition of Chlorosulfene to Enamines[1]

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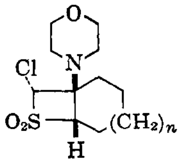
The cycloaddition of chlorosulfene to various morpholine enamines has been studied. The assignment of stereochemistry to the resulting chloro morpholino thietane dioxides has been deduced from their n.m.r. spectra.

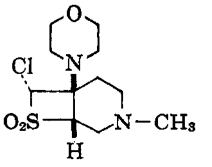
Although chloroketene is not yet known, we were prompted to study the possibility of preparing chlorosulfene (I) and to examine the steric course of its addition to certain enamines.[3,4] Addition of chloromethanesulfonyl chloride to an equimolar mixture of triethylamine and the morpholine enamines of cyclopentanone, cyclohexanone, and cycloheptanone in dioxane solution gave rise to single crystalline substances which have been formulated as the chloro morpholino thietane dioxides IIa–c on the basis of elemental analysis, and infrared and nuclear magnetic resonance spectra (see Table I). A similar reaction with 1-methyl-4-morpholino-1,2,5,6-tetrahydropyridine, however, gave both of the possible isomeric cycloadducts, III and IV. In another example, treatment of the morpholine enamine of 5-norbornene-2-carboxaldehyde with chlorosulfene yielded a mixture of the two isomers V and VI.

$$\mathrm{ClCH{=}SO_2 \longleftrightarrow Cl\bar{C}H{-}SO_2^{+}}$$

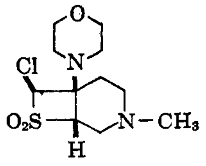
I



IIa, *n* = 0
b, *n* = 1
c, *n* = 2



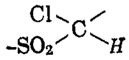
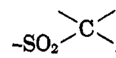
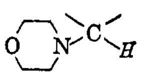
III



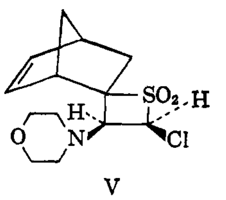
IV

TABLE I

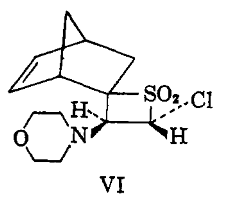
PARAMETERS OF N.M.R. SPECTRA IN DEUTERIOCHLOROFORM SOLUTION (δ-UNITS)

Compd.			
IIa	5.71 (J = 2.5)[a]	4.54[b]	...
IIb	5.49 (J = 1.5)[a]	4.27[b]	...
IIc[c]	...	...	...
III	5.58 (J = 2.0)[a]	4.35[b]	...
IV	5.22 (J = 2.0)[a]	4.50[b]	...
V	5.80 (J = 9)[d]	...	3.42 (J = 9)[d]
VI	5.50 (J = 5)[d]	...	3.04 (J = 5)[d]

[a] Triplet; the appearance of this proton as a triplet in all the compounds reported herein is most fascinating. The first impulse is to attribute the splitting to a 1,3-transannular interaction with the proton at that position. However, in similar systems wherein the relation of these two protons may be considered roughly identical, an unsplit signal in the δ 5.29–5.48 region is reported for this hydrogen.[4] Whatever the causative agent, more specific examples of related systems must be studied before definite claims can be made. [b] Broad doublet with small additional splitting. [c] Spectrum could only be obtained in dimethyl sulfoxide. [d] Doublet.



V



VI

Consideration of the n.m.r. spectra of compounds IIa–c and III (Table I) has led to the conclusion that

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(1) For parts I and II, see L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085, 4089 (1964).

(2) Department of Chemistry, The Ohio State University, Columbus 10, Ohio.

(3) For recent evidence regarding the intermediacy of sulfenes, see I. J. Borowitz, *J. Am. Chem. Soc.*, **86**, 1146 (1964); J. F. King and T. Durst, *ibid.*, **86**, 287 (1964); W. E. Truce, R. W. Campbell, and J. R. Norell, *ibid.*, **86**, 288 (1964).

(4) After the completion of this work, Truce and Norell [*ibid.*, **85**, 3231 (1963)] independently reported the cycloaddition of chlorosulfene to ketene diethyl acetal.