The Reaction of Acetylenes with Chlorosulfonyl Isocyanate[1]

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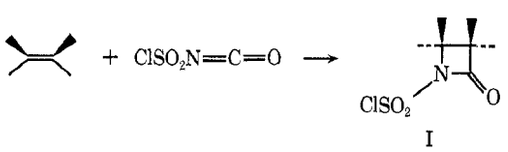
The addition of chlorosulfonyl isocyanate (CSI) to 2-butyne (**1a**), 3-hexyne (**1b**), 4-octyne (**1c**), methyl-*tert*-butylacetylene (**1e**), phenylmethylacetylene (**1f**), and phenylacetylene (**1g**) led to 1:1 rearranged 6-chloro-1,2,3-oxathiazine 2,2-dioxide cycloadducts, respectively, 4,5-dimethyl- (**2a**), 4,5-diethyl- (**2b**), 4,5-di-*n*-propyl- (**2c**), 4-*tert*-butyl-5-methyl- (**2e**), 5-methyl-4-phenyl- (**2f**), and 4-phenyl- (**2g**). Treatment of 2-hexyne (**1d**) with CSI gave a 73:27 mixture of 6-chloro-5-methyl-4-*n*-propyl- (**2d**) and 6-chloro-4-methyl-5-*n*-propyl-1,2,3-oxathiazine 2,2-dioxide (**2d'**). Orientation of 4,5 substituents on the oxathiazine ring system seems to be due both to steric (**2d**, **2e**) and electronic effects (**2f**, **2g**). The oxathiazine ring structure in **2** has been established by spectroscopic means (uv, ir, nmr, mass spectrometry, and X-ray) and chemically: (1) nucleophilic substitution of the 6-chloro group with thiophenol–pyridine afforded thiophenyl ethers **6a–c,e–g**; (2) reduction with 0.5 mol equiv of $LiAlH_4$ gave 3,4-dihydro derivatives **3a–c,e,f,l**; (3) reaction with nucleophiles H_2O, $^-OCH_3$, and CH_3OH led to ring-cleavage products, respectively, ketones **7a–h,l**, bis esters of unsaturated β-amino(*N*-sulfonic acid) carboxylic acid (**8a–c,e–h**), and β-keto ester **9**; catalytic hydrogenation of **8b** and **8g** afforded the corresponding saturated bis esters **10b** and **10g**, which were independently prepared by treatment of 1-chlorosulfonyl-3,4-diethyl- (**11b**) and 1-chlorosulfonyl-4-phenyl-2-azetidinone (**11g**) with $NaOCH_3$–CH_3OH; (4) oxidation (O_3 and $KMnO_4$) gave ring-cleavage products, 3,4-hexanedione (**14**), 3-hexanone (**7b**), and propionic acid (**15**), while reductions with excess $LiAlH_4$ led successively to 2-ethyl-2-pentenal (**12**) and 2-ethyl-2-penten-1-ol (**13**). Methylation of **3a–c,e,f** with CH_3I–K_2CO_3 afforded *N*-methyl derivatives **4a–c,e,f** some of which were dechlorinated with Li in *tert*-BuOH to **5a–c,f**. Diphenylacetylene (**1h**) and CSI gave two unstable products, the appropriate oxathiazine (**2h**) and the 1:2 cycloadduct bis(chlorosulfonyl)-5,6-diphenyluracil (**19**); hydrolysis and methanolysis of the former gave **7h** and **8h**, while **19** was converted to 5,6-diphenyluracil (**20**). 1-Hexyne (**1i**) and CSI led only to 2-heptynamide derivatives **21–23**. With CSI, 3-diethylamino-1-propyne (**1j**) gave the tertiary amine CSI salt while ynamine 1-diethylamino-1-propyne (**1k**) led to an unstable 1:1 adduct believed to have oxete structure **26**. CSI reacted only with the acetylene function in 1-octen-4-yne (**1l**) to form 6-chloro-4-*n*-propyl-5-(2-propenyl)-1,2,3-oxathiazine 2,2-dioxide (**2l**). In competitive rate studies with equimolar mixtures of **1d**-*trans*-2-hexene and **1d**-cyclohexene, CSI reacted solely with acetylene **1d**. With equimolar mixtures of **1f**-*trans*-β-methylstyrene and **1g**-styrene, CSI gave, respectively, 1:1 and 2:1 mixtures of azetidinone–oxathiazine adducts. The initial cycloaddition of CSI is proposed to occur in near-concerted fashion to **1a–e,l** and in a stepwise process to **1f–h**. CSI addition to benzyne precursor benzenediazonium carboxylate (**28**) afforded only 3-chlorosulfonyl-1,2,3-benzotriazin-4-one (**29**).

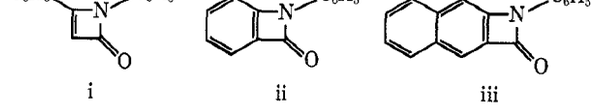
The ease with which chlorosulfonyl isocyanate (CSI) stereospecifically adds to carbon–carbon multiple bonds (alkenes, conjugated dienes, cumulenes, polyenes) affording 2-azetidinones (I)[3,4] raised the possibility of



I

similar reactivity toward carbon–carbon triple bonds. Thus cycloaddition of CSI to acetylenes proceeding by such limiting mechanisms as (1) a concerted $\pi^2a + \pi^2s$ process *via* a polar, unsymmetrical transition state (II)[5] and/or (2) a stepwise, electrophilic addition *via* an initially formed dipolar vinyl cation III[6] could lead to azetinones IV[7] and/or oxetes (V).[8,9]

We recently reported that addition of freshly distilled CSI in methylene chloride solution to an equimolar quantity of 3-hexyne (**1b**) at ambient temperature led to the 1:1 rearranged adduct 6-chloro-4,5-diethyl-1,2,3-



i ii iii

(1) This research was supported by Public Health Service Grants identified as RO1 AI08063-01-03 from the National Institute of Allergy and Infectious Diseases.

(2) Graduate Research Assistant (1967–1970) on a grant[1] supported by NIH; taken entirely from the Ph.D. Thesis of Y. Shimakawa, Fordham University, New York, 1971.

(3) R. Graf, *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968).

(4) E. J. Moriconi, "Mechanisms of Reaction of Sulfur Compounds," Vol. 3, Intra-Science Research Foundation, Santa Monica, Calif., 1968, p 131.

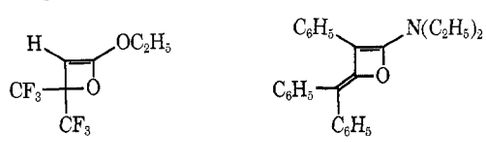
(5) We have recently suggested that CSI may play an antarafacial role as a π^2a component in concerted reactions with π^2s systems [E. J. Moriconi and W. C. Meyer, *J. Org. Chem.*, **36**, 2841 (1971)]. In this process the rate of formation of the second bond may lag behind the formation of the first. The formation of such as II in the rate-determining step permits the orientation, polar effect, and stereospecificity observed.

(6) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970), and references contained therein. There is the inevitable question of timing. If the reaction is stepwise, the vinyl cationic intermediate III should be of sufficient stability to be trapped by external reagents. This has occurred only with diphenylacetylene (**1h**).

(7) Only a few of which are known (i–iii).

(i) K. R. Henery-Logan and J. V. Rodricks, *J. Amer. Chem. Soc.*, **85**, 3524 (1963); (ii) E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1960); (iii) G. Ege and E. Beisiegal, *Angew. Chem., Int. Ed. Engl.*, **7**, 393 (1965).

(8) Examples of which include iv and v.



iv v

(iv) W. J. Middleton, *J. Org. Chem.*, **30**, 1307 (1965); (v) M. E. Kuehne and P. J. Sheeran, *ibid.*, **33**, 4406 (1968).

(9) However, the N- *vs.* O-cyclization rates would seem to be competitive. The factors which determine the preferred mode (to β lactams) have not been elucidated. To date, O-cyclized products have been obtained directly only on addition of CSI to cycloheptatriene[10] and a vinyldihydronaphthalene[11] and indirectly by rearrangement of the initial *N*-chlorosulfonyl-β-lactam cycloadducts obtained from CSI addition to olefin[12] and conjugated dienes.[5,13a,14]

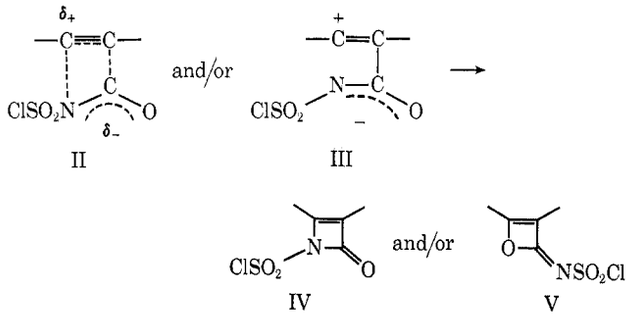
(10) E. J. Moriconi, C. F. Hummel, and J. F. Kelly, *Tetrahedron Lett.*, 5325 (1969).

(11) R. J. P. Barends, W. N. Speckamp, and H. O. Huisman, *ibid.*, 5301 (1970).

(12) T. W. Doyle and T. T. Conway, *ibid.*, 1889 (1969).

(13) (a) E. J. Moriconi and W. C. Meyer, *ibid.*, 3823 (1968); (b) E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **33**, 3036 (1968).

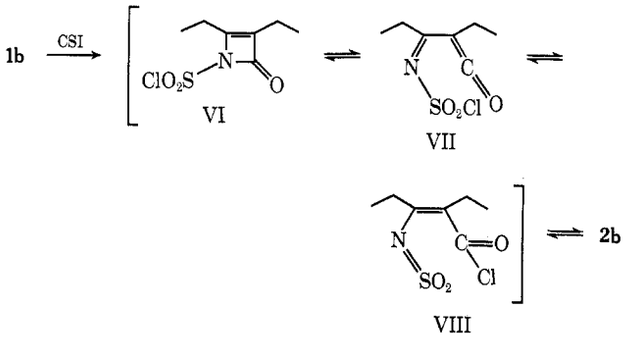
(14) Th. Haug, F. Lohse, K. Metzger, and H. Batzer, *Helv. Chim. Acta*, **51**, 2069 (1968); P. Goebel and K. Clauss, *Justus Liebigs Ann. Chem.*, **722**, 122 (1969).



II III IV V

oxathiazine 2,2-dioxide (**2b**, 96%).[15] The major chemical evidence provided in support of structure **2b** included (1) nucleophilic substitution of the 6-chloro group in **2b** to 4,5-diethyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (**6b**) using thiophenol–pyridine–acetone (this reagent normally reduces NSO_2Cl functions to NH while producing SO_2, pyridine hydrochloride, and diphenyl disulfide);[3] (2) reduction of **2b** with 0.5 mol equiv of $LiAlH_4$ to 6-chloro-4,5-diethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (**3b**, 81%) whose nmr revealed a new methine proton (δ 3.93, X portion of an ABX pattern) coupled to both NH and the CH_2 of an ethyl group.

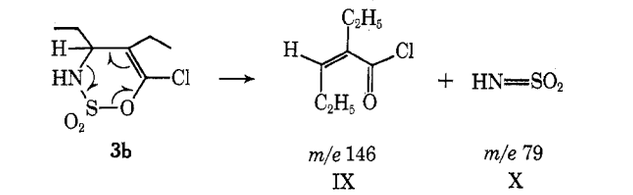
The structure of **2b** was confirmed by X-ray crystallographic analysis,[15,16] while its formation was rationalized by a sequence of cycloaddition (VI), electrocyclic ring opening to the ketene–imine–*N*-sulfonyl chloride (VII), 1,5-sigmatropic halogen shift (VIII), and elec-



VI VII VIII

trocyclic ring closure to oxathiazine **2b**. Rotation about the acyl carbon single bond of VIII must precede the final cyclization step.

The reversibility of steps VI ⇄ VII ⇄ VIII ⇄ **2b** would account for the appearance in the mass spectrum of **2b** of a fragment *m/e* 124 corresponding to the loss of SO_2Cl from the molecular ion. Under electron impact or thermal conditions in the mass spectrometer, **2b** reverted to VI. The mass spectrum of **3b** had no M − SO_2Cl fragment but did show two fragments (IX, X)

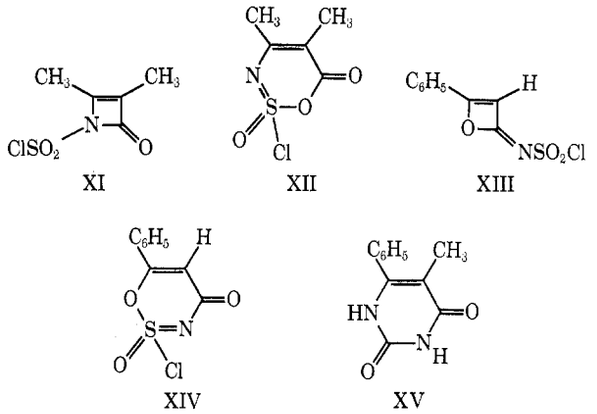


3b *m/e* 146 (IX) *m/e* 79 (X)

(15) E. J. Moriconi, J. G. White, R. W. Franck, J. Jansing, J. F. Kelly, R. A. Salomone, and Y. Shimakawa, *Tetrahedron Lett.*, 27 (1970).
(16) J. Jansing and J. G. White, unpublished results.

resulting from a retro-Diels–Alder rearrangement of **3b**.[17]

Shortly after the publication of our initial report, there appeared two communications[18] in which the structures of the CSI adducts with 2-butyne (**1a**), phenylacetylene (**1g**), and phenylmethylacetylene (**1f**) were variously considered to be XI–XV. All are incorrect.



XI XII XIII XIV XV

In this concluding paper, we report (1) on the reaction of CSI with **1a**, **1b**, 4-octyne (**1c**), 2-hexyne (**1d**), methyl-*tert*-butylacetylene (**1e**), **1f**, and **1g**; (2) chemical degradation studies on oxathiazine adducts **2** and dihydro derivatives **3**; (3) the unique behavior of CSI on reaction with diphenylacetylene (**1h**), 1-hexyne (**1i**), 3-diethylamino-1-propyne (**1j**), 1-diethylamino-1-propyne (**1k**), 1-octen-4-yne (**1l**), and benzenediazonium carboxylate (**28**); and (4) competitive rate studies of CSI with acetylene–olefin mixtures which clarify to some extent the nature of the initial mode of addition (near concerted or stepwise).

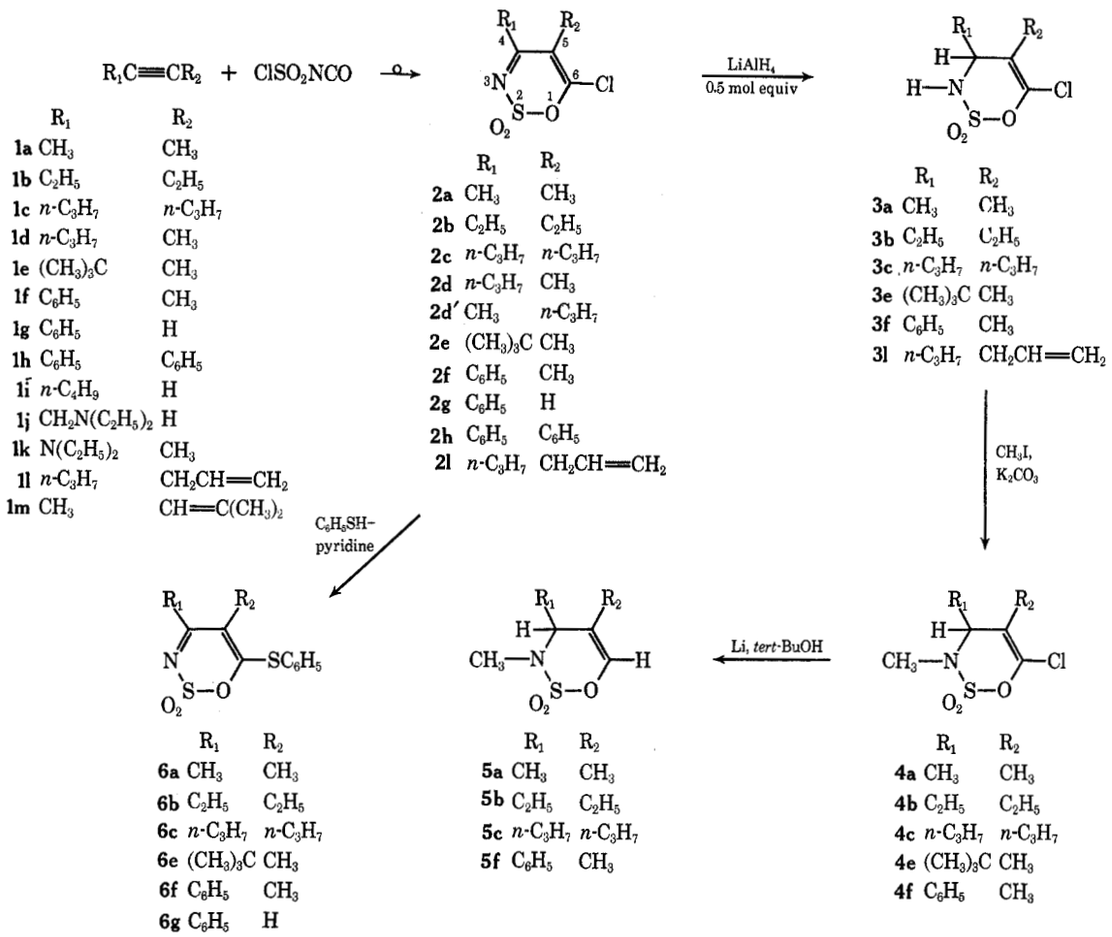
CSI Addition to Acetylenes (Scheme I)—Addition to CSI to equimolar amounts of **1a**, **1c**, **1e**, and **1f** in anhydrous methylene chloride at ambient temperatures afforded the following 6-chloro-1,2,3-oxathiazine 2,2-dioxides, respectively: 4,5-dimethyl- (**2a**, 42%), 4,5-di-*n*-propyl- (**2c**, 86%), 4-*tert*-butyl-5-methyl- (**2e**, 51%), and 5-methyl-4-phenyl- (**2f**, 86%). Similar treatment of **1d** with CSI led to a 73:27 mixture (92%) of 6-chloro-5-methyl-4-*n*-propyl- (**2d**) and 6-chloro-4-methyl-5-*n*-propyl-1,2,3-oxathiazine 2,2-dioxide (**2d′**). The reaction of **1g** with CSI at room temperature led mostly to polymers and no distinguishable products were isolated from the reaction mixture. Lowering the reaction temperature to −20–0° led, however, to the crude, unstable 6-chloro-4-phenyl-1,2,3-oxathiazine 2,2-dioxide (**2g**, ~50%) which could be separated by cooling to −78°, followed by rapid filtration. Since all attempts to purify this solid material were unsuccessful, the crude adduct was immediately converted to 4-phenyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (**6g**) with benzenethiol–pyridine in acetone. In all cases, no other products were isolated other than polymeric material.

The low yield of **2a** may be attributed to the volatility of **1a**. The orientation of 4,5 substituents on the

(17) The high-resolution mass spectra were run by Dr. R. A. Salomone while a NIH Postdoctoral Trainee, 1967–1969 (GM 015230), in the Department of Chemistry, Massachusetts Institute of Technology.
(18) (a) K. Clauss and H. Jensen, *Tetrahedron Lett.*, 119 (1970); (b) K-D. Kampe, *ibid.*, 123 (1970).

SCHEME I

PREPARATION OF 1,2,3-OXATHIAZINE 2,2-DIOXIDES AND THEIR DERIVATIVES



	R_1	R_2
1a	CH_3	CH_3
1b	C_2H_5	C_2H_5
1c	n-C_3H_7	n-C_3H_7
1d	n-C_3H_7	CH_3
1e	$(CH_3)_3C$	CH_3
1f	C_6H_5	CH_3
1g	C_6H_5	H
1h	C_6H_5	C_6H_5
1i	n-C_4H_9	H
1j	$CH_2N(C_2H_5)_2$	H
1k	$N(C_2H_5)_2$	CH_3
1l	n-C_3H_7	$CH_2CH{=}CH_2$
1m	CH_3	$CH{=}C(CH_3)_2$

	R_1	R_2
2a	CH_3	CH_3
2b	C_2H_5	C_2H_5
2c	n-C_3H_7	n-C_3H_7
2d	n-C_3H_7	CH_3
2d′	CH_3	n-C_3H_7
2e	$(CH_3)_3C$	CH_3
2f	C_6H_5	CH_3
2g	C_6H_5	H
2h	C_6H_5	C_6H_5
2l	n-C_3H_7	$CH_2CH{=}CH_2$

	R_1	R_2
3a	CH_3	CH_3
3b	C_2H_5	C_2H_5
3c	n-C_3H_7	n-C_3H_7
3e	$(CH_3)_3C$	CH_3
3f	C_6H_5	CH_3
3l	n-C_3H_7	$CH_2CH{=}CH_2$

	R_1	R_2
4a	CH_3	CH_3
4b	C_2H_5	C_2H_5
4c	n-C_3H_7	n-C_3H_7
4e	$(CH_3)_3C$	CH_3
4f	C_6H_5	CH_3

	R_1	R_2
5a	CH_3	CH_3
5b	C_2H_5	C_2H_5
5c	n-C_3H_7	n-C_3H_7
5f	C_6H_5	CH_3

	R_1	R_2
6a	CH_3	CH_3
6b	C_2H_5	C_2H_5
6c	n-C_3H_7	n-C_3H_7
6e	$(CH_3)_3C$	CH_3
6f	C_6H_5	CH_3
6g	C_6H_5	H

oxathiazine ring in **2e** and **2d** seems to be primarily due to the greater steric effects[19] of *tert*-butyl and *n*-propyl groups, respectively, in the cycloaddition step, while that in **2f**[20] and **2g** undoubtedly reflects the greater electronic stabilization of the incipient vinyl carbonium by the adjacent phenyl group either in transition state II or intermediate III.[6,21] In general, the rate of CSI addition to acetylenes was accelerated in more polar solvents, and the thermal stability of the oxathiazine products increased with increasing size of substituents at C-5.

In the infrared, adducts **2a–g** exhibited *no* carbonyl absorptions; the bands at 1626–1600 (6.15–6.25 μ) and 1500–1471 cm^{-1} (6.67–6.80 μ) in these oxathiazines are assigned to C=C and C=N absorptions. Adducts **2a–g** all showed the strong, sharp, split band patterns for SO_2 stretching modes in the 1399–1379- (7.15–7.25 μ) and 1212–1190-cm^{-1} (8.25–8.40 μ) regions.[22] In the ultraviolet, adducts **2a–e** displayed a chromophore with λ_{max} 292–295 nm (ϵ 3600–3800); phenyl group extension of the conjugated system in **2f** and **2g** shifted the λ_{max} to 297–302 nm (ϵ 12,000–12,700). The combined effect of spectral data alone (ir, uv, nmr, and X-ray) decisively preclude structures XI–XV or the acetylene–CSI cycloadducts.

Reaction of Oxathiazines (2) with Nucleophiles (Scheme II).—Methanolysis of **2b** led to the β-keto ester, methyl 2-ethyl-3-oxopentanoate (**9**, 60%); hydrolysis of **2b** afforded 3-hexanone (**7b**, 70%), the decarboxylation product of its β-keto acid precursor 2-ethyl-3-oxopentanoic acid. Similar hydrolysis of **2a**, **2c–g** with water or aqueous bicarbonate solution gave ketones **7a**, **7c–g** (31–81%), respectively. Treatment of **2a–c**, **2e–g** with 3 mol equiv of sodium methoxide in absolute methanol at 0° resulted in the formation of bis esters of β-amino(*N*-sulfonic acid)carboxylic acids **8a–c**, **8e–g** (30–98%), respectively. Catalytic hydrogenation of **8b** and **8g** afforded the corresponding saturated diesters **10b** and **10g**, which were independently prepared by treatment of 1-chlorosulfonyl-*cis*-3,4-diethyl- (**11b**)[13b] and 1-chlorosulfonyl-4-phenyl-2-azetidinone (**11g**)[13b] with sodium methoxide–methanol.[3] These results show that no rearrangement of the carbon skeleton had occurred during cycloaddition and rearrangement, and the carbon of CSI had become affixed to the acetylene function. As already noted with **2b** and **2g**, treatment of **2a**, **2c**, **2e**, and **2f** with thiophenol–

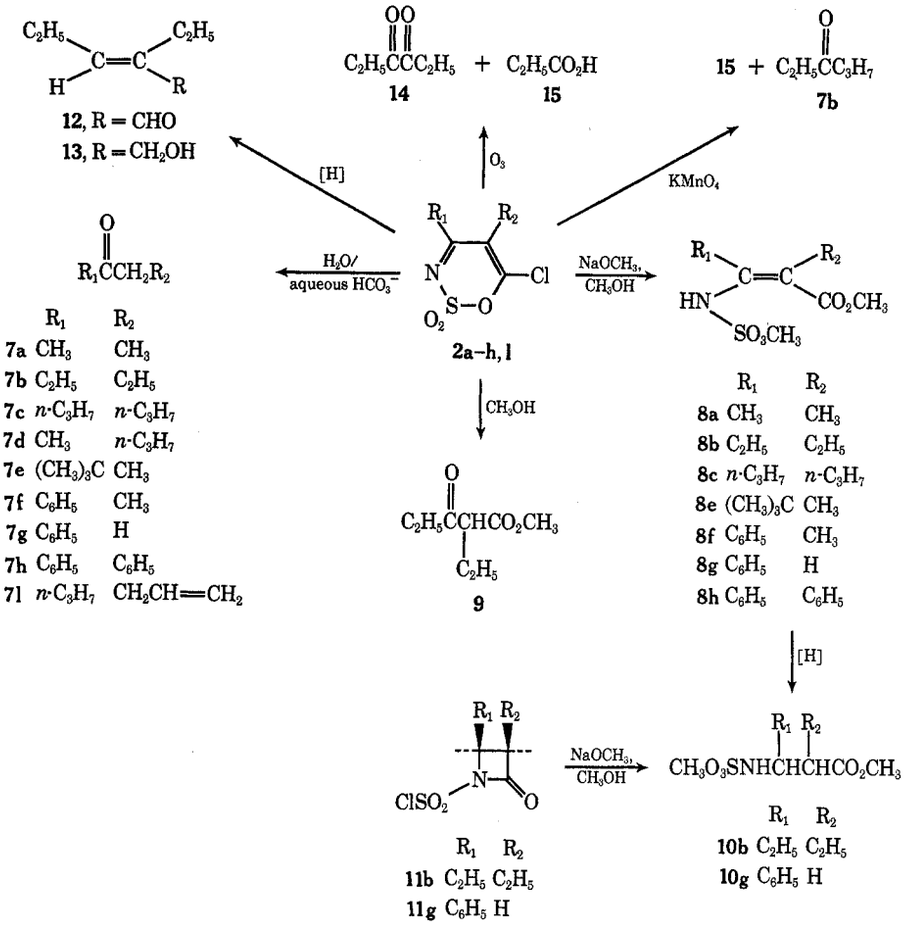
(19) On the basis of Taft's substituent constants, the difference between the inductive effects of a methyl and *tert*-butyl group is relatively small ($\Delta\sigma^* = 0.30$): J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, p 97.

(20) The rate for the CSI-**1e** cycloaddition was less than one-third as fast as the CSI-**1b** reaction whose rate was comparable to that for CSI-**1f**.

(21) A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Lett.*, 2939 (1969).

(22) Sulfones absorb in the 1350–1300 (7.41–7.69 μ) and 1160–1120-cm^{-1} (8.62–8.93 μ) regions. Attachment of two electronegative atoms (O, N) to S in cycloadducts **2** would be expected to result in frequency shifts of both characteristic bands toward higher frequencies: L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, pp 360–363.

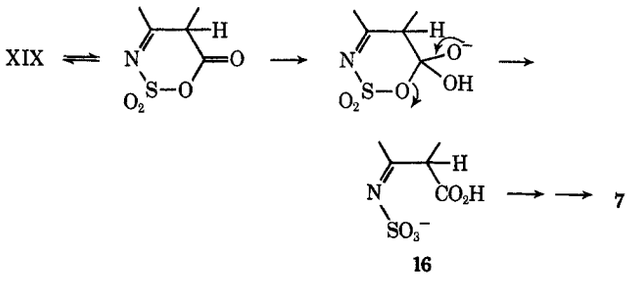
SCHEME II
RING DEGRADATION REACTIONS OF 1,2,3-OXATHIAZINE 2,2-DIOXIDES



pyridine in acetone afforded thioethers **6a**, **6c**, **6e**, and **6f** (27–44%), respectively. Nucleophilic substitution of the vinyl chloride in **2** finds its analogy in the pyridine ring system where the polarity of electrons toward nitrogen invites attack by nucleophiles at the γ position. In **2** the entering negative charge may reside not only on the C and N atoms but can be further delocalized into the adjacent SO_2 group *via* d–p_π bonding XVI ↔ XVII ↔ XVIII.

A general mechanism for the response of the 1,2,3-oxathiazine system to nucleophiles (H_2O, CH_3OH, $^-OCH_3$, C_6H_5SH) is proposed in Scheme III. Expulsion of chloride under the influence of the strong nucleophile thiophenol readily converts intermediate XVI ↔ XVII ↔ XVIII to the more stable conjugated thioethers **6**. Further attack by the appropriate nucleophile at the S site of the less stable substitution products XIX[23] and XX leads ultimately to cleavage products **7** and **9**. The bis esters **8**, structurally correspondent to proposed ring-cleaved intermediates XXI and XXII, have been isolated.

(23) An alternative hydrolysis mechanism might involve enolization of XIX followed by nucleophilic attack at the carbonyl carbon and ring opening to **16**.



Reduction and Oxidation.—Reduction of **2b** with 2 and 4 mol equiv of $LiAlH_4$ afforded 2-ethyl-2-pentenal (**12**, 30%) and 2-ethyl-2-penten-1-ol (**13**, 36%), respectively. The use of 0.5 mol equiv converted **2a–c**, **2e,f** and **2l** to the corresponding dihydro derivatives **3a–c**, **3e,f**, and **3l**, respectively. In all the latter, decreased conjugation was evidenced by the absence of any C=N stretching bands in the ir and a large hypsochromic shift in the uv [*e.g.*, *cf.* **2b**, λ_{max} 292 nm (ϵ 3600), and **3b**, λ_{max} 233 nm (ϵ 1500)]. A similar reduction of **2g** led only to polymeric material.

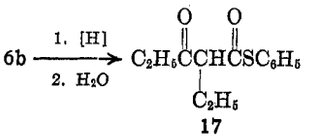
Methylation of **3a–c** and **3f** with CH_3I–K_2CO_3 in acetone afforded the *N*-methyl derivatives **4a–c** and **4f** (48–73%). With this reagent combination, **3e** reacted slowly and gave mostly ring-cleaved products. When the reaction was carried out in DMSO with a large excess of CH_3I and an equimolar amount of K_2CO_3, the desired 6-chloro-4-*tert*-butyl-3,5-dimethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (**4e**, 48%) was obtained. Although a large steric effect is expected between the neighboring *tert*-butyl and *N*-methyl groups in **4e**, nitrogen inversion was not observed in the nmr at room temperature.[24]

Dechlorination of **4a–c** and **4f**, unsuccessful with **3**,

(24) F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, **89**, 352, 357 (1968).

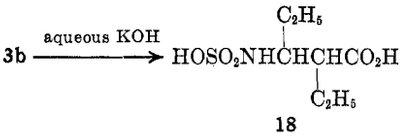
was achieved using Li in *tert*-BuOH[25] to give **5a–c** and **5f** (69–93%), respectively. The nmr of 4,5-diethyl-3-methyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (**5b**), for example, displayed a new vinyl proton (δ 6.30) coupled both to the methine C-4 proton and the methylene proton of the C-5 ethyl group.

Finally, catalytic hydrogenation of **2b** followed by hydrolytic work-up gave ketone **7b** (77%); similar reduction and hydrolysis of **6b** afforded phenyl 2-ethyl-3-oxothiopentanoate **17** (39%).



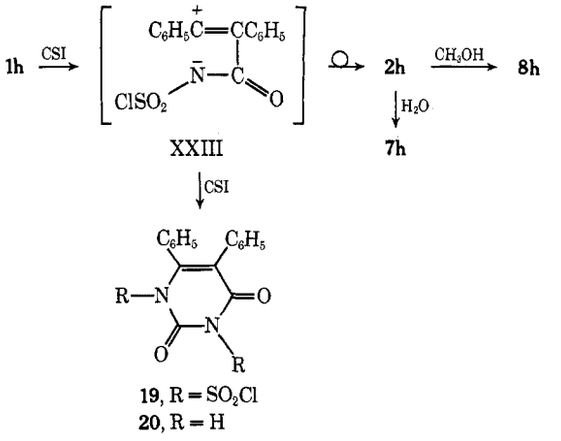
17

Ozonation of **2b** followed by oxidative work-up gave 3,4-hexanedione (**14**, 20%) and propionic acid (**15**, 14%). Potassium permanganate oxidation of **2b** afforded **15** (47%) and **7b** (20%). Alkaline hydrogen peroxide treatment of **3b** gave 2-ethyl-3-(aminosulfonic acid)pentanoic acid (**18**, 23%), identical with that formed directly (50%) *via* aqueous hydrolysis of **3b**.



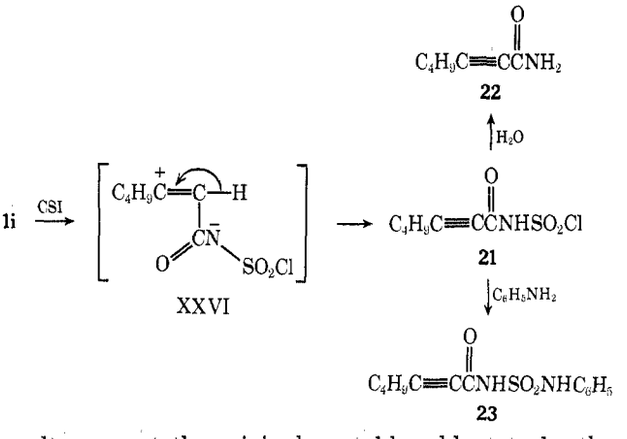
18

Miscellaneous Acetylenes.—Diphenylacetylene (**1h**) reacted slowly[26] with CSI (at least $^1/_{30}$ the rate of **1b**) to form two unstable products. The first, 1,3-bis(chlorosulfonyl)-5,6-diphenyluracil (**19**, 57%), was identified as its hydrolysis product 5,6-diphenyluracil (**20**).[27a] For the second, recrystallization from methanol gave methyl 2,3-diphenyl-3-(methoxysulfonylamino)propenoate (**8h**, 17%) while hydrolysis afforded deoxybenzoin (**7h**, 13%). Both **7h** and **8h** can be rationalized as methanolysis and hydrolysis products, respectively, of 6-chloro-4,5-diphenyl-1,2,3-oxathiazine 2,2-dioxide (**2h**). Mechanistically, the results suggest a slow,[6,26] stepwise addition of CSI to **1h**. The 1,4-dipolar intermediate XXIII can both cyclize to oxathiazine **2h**



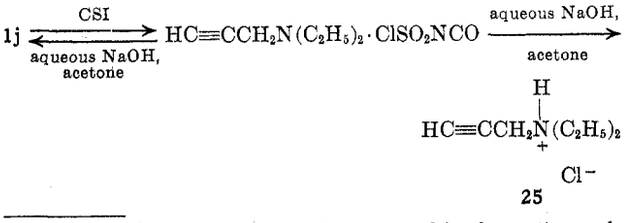
and be intercepted by a second molecule of CSI to form **19**.[27b,28]

1-Hexyne (**1i**) also reacted slowly with CSI. The initial adduct contained neither the oxathiazine nor uracil structures since the crude product displayed carbonyl (5.91 μ) and NH (3.1 μ) absorption bands in the ir and no vinyl proton in the nmr. Aqueous hydrolysis of this crude oil led to 2-heptynamide (**22**, 20%), while treatment with aniline afforded the *N*-sulfonylanilide of 2-heptynamide (**23**, 30%). These



results suggest the original unstable adduct to be the *N*-sulfonyl chloride of 2-heptynamide (**21**) whose formation must involve initial, stepwise attack by CSI at the terminal C atom of **1i** to intermediate XXVI followed by proton transfer to N.

Both 3-diethylamino-1-propyne (**1j**) and ynamine 1-diethylamino-1-propyne (**1k**) reacted with CSI rapidly and quantitatively in pentane (−78°) to yield unstable 1:1 adducts which decomposed under work-up conditions at room temperature. At low temperature, the unstable **1j**–CSI adduct could be isolated as a hygroscopic, white solid whose ir displayed isocyanate (2222 cm^{-1}, 4.50 μ) and acetylenic (2105 cm^{-1}, 4.75 μ) absorptions. Since careful hydrolysis of this material gave **1j** (70%), and its hydrochloride **25**, a reasonable structure for the initial adduct would be merely the *tert*-amine–CSI salt (**24**).[29]

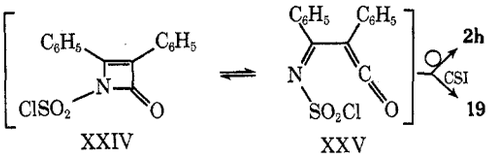


(25) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960).

(26) The low electron-withdrawing power of phenyl substituents in acetylenes is well documented; *e.g.*, in an approximate order of reactivity for tanyocyclophiles, **1h** failed to react [P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971)]. The steric effects of diphenyl substituents should also lower the reaction rate. See also ref 32.

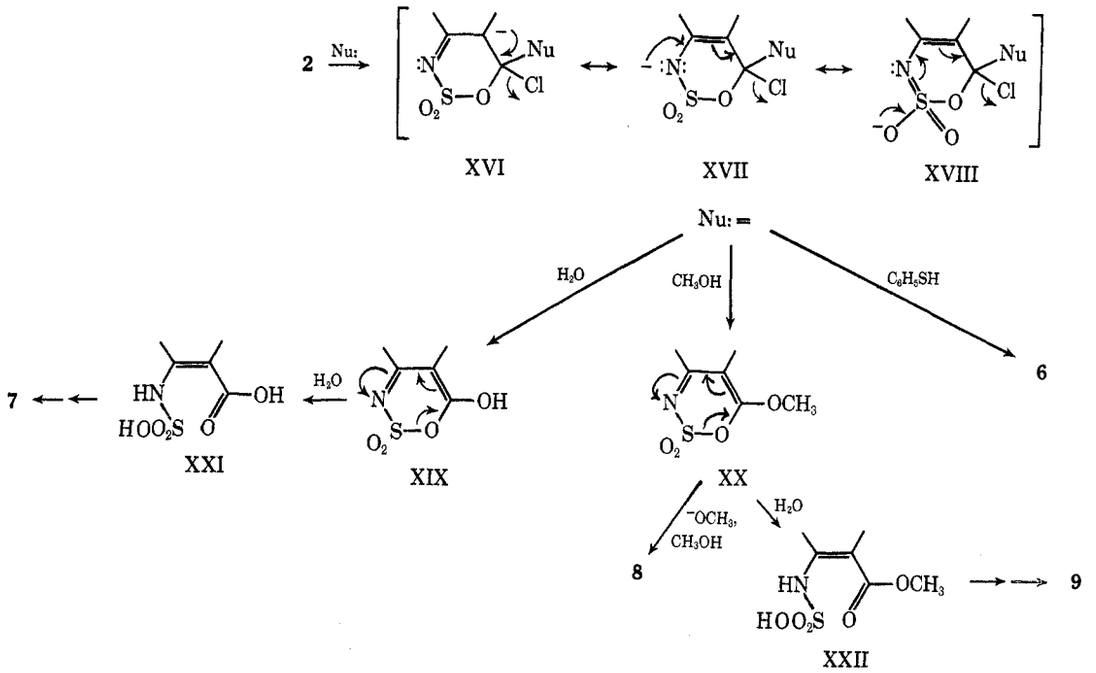
(27) (a) Uracil structures have also been proposed for the reaction products between fluorosulfonyl isocyanate (FSI) and both **1a** and **1f**.[18] (b) A bis(*N*-chlorosulfonyl)uracil intermediate was also proposed as one of the cycloaddition products of CSI and 3-methyl-1,2-butadiene: E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, **32**, 3036 (1968). A more recent precedent is the formation of 5-isopropenylhydantoin from the addition of CSI to 1-methylcyclopropene: T. J. Barton, R. Rogido, and J. C. Clardy, *Tetrahedron Lett.*, 2081 (1970).

(28) Oxathiazine **2h** and uracil **19** could also be formed *via* common intermediates XXIV ⇌ XXV.

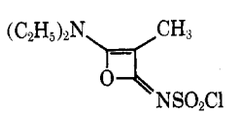


(29) R. Graf, German Patent 1,000,807 (1957); *Chem. Abstr.*, **54**, 1555*h* (1960).

SCHEME III



Similar isolation of the **1k**–CSI adduct afforded an unstable, yellow material whose ir showed C=C/C=N and SO_2 absorptions but no C=O band. Its nmr was also suggestive of an oxete-type structure **26**; hydrolysis, methanolysis, reduction, and oxidation of this material, however, led to no isolable products.



26

1-Octen-4-yne (11). Competitive Reaction Rates of Acetylenes and Olefins with CSI. Reaction Mechanisms.—1-Octen-4-yne (**11**) and CSI reacted at about $^1/_3$ the rate of the reaction of **1c** and CSI. On the basis of spectral data [ir 1640 cm^{-1} (6.10 μ) (C=C/C=N), no C=O absorption; nmr three vinyl protons], the adduct obtained in 75% yield was assigned the structure 6-chloro-4-*n*-propyl-5-(2-propenyl)-1,2,3-oxathiazine 2,2-dioxide (**21**). Reductions of **21** with 0.5 mol equiv of $LiAlH_4$ afforded the expected dihydro derivative (**31**, 70%) while reductive hydrolysis with aqueous sodium sulfite solution[30] gave 1-octen-5-one (**71**, 80%). It was unexpected that the electrophilic CSI preferred to react with the acetylenic function in **11** rather than the terminal double bond.

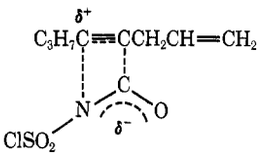
The addition of CSI to the conjugated enyne, 2-methyl-2-hexen-4-yne (**1m**), at low temperature always resulted in the formation of intractable polymers.

There is now considerable evidence which indicates that addition of electrophiles such as 2,4-dinitrobenzenesulfenyl chloride[31] and bromine,[32] *inter alia*, to olefins proceeds *via* a two-step process with the formation of a discrete ionic intermediate in the rate-determining step. While the intrinsic mechanism of addition of such electrophiles to acetylenes has not been firmly established,[33] it has long been suggested that the π electrons of acetylenes are more tightly held than are those of corresponding alkenes. Consequently, if the mechanism of electrophilic addition to corresponding acetylenes and alkenes is similar, then the rate for the former would be predictably slower. Comparison of the results for the addition of 2,4-dinitrobenzenesulfenyl chloride[31] and bromine[32] to acetylenes with those for the appropriate olefins show significantly lower reaction velocities for the acetylenes.

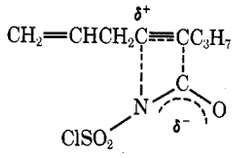
To determine relative reaction rates for the addition of CSI to acetylenes and olefins, equimolar mixtures of 2-hexyne (**1d**)–*trans*-2-hexene and **1d**–cyclohexene were treated with an insufficient amount of CSI. In each case, only acetylene **1d** reacted. Thus, on the basis of these relative rate studies, we suggest that, in the absence of any overwhelming electronic substituent effect (as in acetylenes **1a–e** and **1l**), addition of CSI to acetylenes proceeds *via* the near-concerted transition state II. The orientation in cycloadduct **21** may be rationalized by the greater stability of XXVII over XXVIII.[34] Homoallylic stabilization of XXVIII (*via* XXIX) was therefore not significant.

When a mixture of **1f**–*trans*-β-methylstyrene in methylene chloride was treated with 0.5 molar equiv of CSI, nmr analysis of the product indicated a nearly 1:1 mixture derived from cycloaddition of CSI to both acetylene and olefin. In the more polar solvent, the acetylene–CSI reaction rate increased the product mixture ratio to 1.4:1. Finally, an equimolar mixture of **1g**–styrene with CSI afforded a 2:1 mixture of the

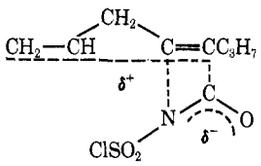
(30) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).
(31) N. Kharasch and C. N. Yiannios, *ibid.*, **29**, 1190 (1964).
(32) P. W. Robertson, W. E. Dasant, R. M. Milburn, and W. H. Oliver, *J. Chem. Soc.*, 1628 (1950).
(33) In electrophilic addition reactions (hydrolysis, hydrochlorination, reaction with trifluoroacetic acid) to acetylenes, vinyl cations have been proposed: P. E. Peterson and J. E. Duddy, *J. Amer. Chem. Soc.*, **88**, 4990 (1966), and references cited therein; R. C. Fahey and D. J. Lee, *ibid.*, **89**, 2780 (1967); D. S. Noyce, M. A. Matesich, and P. E. Peterson, *ibid.*, **89**, 6225 (1967); D. S. Noyce and M. D. Schiavelli, *ibid.*, **90**, 1020, 1023 (1968).
(34) The difference in inductive effect of the *n*-propyl and propenyl groups is small; *cf.* Taft's σ^* value for *n*-butyl (−0.13) and 2-butenyl (+0.13) groups.[19]



XXVII



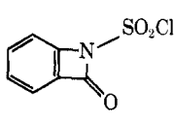
XXVIII



XXIX

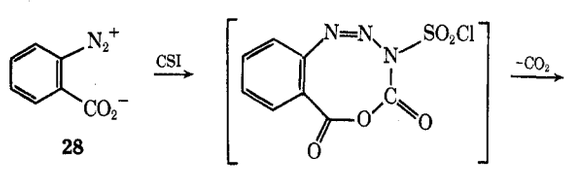
azetidinone–oxathiazine adducts. Thus in the reaction of CSI with acetylenes **1f** and **1g**, the mechanism of addition begins to change with increasing involvement of more stable vinyl cation intermediates, since the phenyl group can localize positive charge on the adjacent carbon. In the two-step addition of CSI to acetylene **1h**, the fully developed vinyl cation intermediate XXIII is trapped as the uracil **19**, while **1i** leads to unsaturated amide **21** *via* intermediate XXVI.

Benzenediazonium Carboxylate (28).—The propensity of benzyne to undergo cycloaddition reactions with olefins,[35] conjugated dienes,[36] and trienes[37] suggested the possibility that benzoazetinone **27** might be prepared by the cycloaddition of benzyne with CSI.[38]

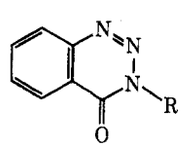


27

Thus benzyne precursor, benzenediazonium carboxylate (**28**), was prepared and treated with CSI at 70–80°. The sole product obtained was 3-chlorosulfonyl-1,2,3-benzotriazin-4-one (**29**, 80%) which was converted to 1,2,3-benzotriazin-4-one (**30**, 78%) on



28 XXX



29, R = SO_2Cl
30, R = H

recrystallization from methanol. Benzotriazinone formation can be rationalized by initial attack of CSI on **28** to intermediate XXX, decarboxylation of which afforded **29**. Benzotriazinone **30** was also obtained in 20% yield by the reaction of **28** with CSI–pyridine salt[29] and *N,N'*-bischlorosulfonylurea.[3] No reaction was observed on irradiation of **30** in THF under an Hanovia 450-W lamp for 10 hr at room temperature; **30** was quantitatively recovered.

(35) H. E. Simmons and R. W. Hoffmann in "Dehydrobenzene and Cycloalkynes," R. W. Hoffmann, Ed., Academic Press, New York, N. Y., 1967.

(36) M. Jones, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **91**, 6411 (1969); R. W. Atkin and C. W. Rees, *Chem. Commun.*, 152 (1969).

(37) I. Tabushi, H. Yamada, Z. Yoshida, and H. Kuroda, *Tetrahedron Lett.*, 1093 (1971).

(38) The reaction of benzyne with phenyl isocyanate afforded only 9-phenoxyphenanthridine: J. C. Sheehan and G. D. Daves, Jr., *J. Org. Chem.*, **30**, 3247 (1965).

Experimental Section[39]

Reaction of CSI with Acetylenes (1a–g).—The general procedure used was as follows. To a stirred solution (0°) of the acetylene in dry CH_2Cl_2 (0.3 mol, 50 ml) was added dropwise an equimolar amount of freshly distilled CSI in the same solvent (0.3 mol, 30 ml). Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and the reaction was continued until the ir spectrum showed the absence of the isocyanate peak at 4.4 μ (3–15 hr). The solvent was then evaporated *in vacuo* leaving a yellow oil which was extracted with seven 50-ml portions of boiling pentane. The solution was cooled to −20° to give the crude 1:1 adduct **2** which was purified *via* repeated recrystallizations from 1:3 ether–pentane. Concentration of the filtrate occasionally gave additional amounts of product. Variations in isolation procedure for **2** are noted under each acetylene.

2-Butyne (**1a**, 2.16 g, 0.040 mol, 9 hr) gave 3.25 g (42%) of **6-chloro-4,5-dimethyl-1,2,3-oxathiazine 2,2-dioxide** (**2a**): mp 47.0–48.5°; uv (isooctane) 295 nm (ϵ 3700); ir (KBr) 1625 and 1500 (C=C and C=N), 1389 and 1212 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.43 (s, 3, CH_3C=N) and 2.12 (s, 3, CH_3C=C).

Anal. Calcd for $C_5H_6NO_3SCl$: C, 30.79; H, 3.08; N, 7.18. Found: C, 30.73; H, 3.45; N, 7.38.

3-Hexyne (**1b**, 24.6 g, 0.30 mol, 6 hr) gave 63.8 g (95%) of **6-chloro-4,5-diethyl-1,2,3-oxathiazine 2,2-dioxide** (**2b**) as colorless needles: mp 54–55°; uv max (isooctane) 292 nm (ϵ 3600); ir (KBr) 1615 and 1490 (C=C and C=N), 1385 and 1209 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 3.05–2.40 (two quartets, 4, six equally spaced peaks, J = 7 Hz, CH_2CH_3), and 1.45–1.00 (two triplets, 6, CH_2CH_3).

Anal. Calcd for $C_7H_{10}NO_3SCl$: C, 37.59; H, 4.51; N, 6.26; mol wt, 224. Found: C, 37.78; H, 4.63; N, 6.02; mol wt, 229 (cryoscopic).

4-Octyne (**1c**, 8.8 g, 0.080 mol, 6 hr) gave 17.3 g (86%) of **6-chloro-4,5-di-*n*-propyl-1,2,3-oxathiazine 2,2-dioxide** (**2c**) as colorless needles: mp 26.0–27.0° (from hexane); uv (isooctane) 293 nm (ϵ 3700); ir (KBr) 1610 and 1490 (C=C and C=N), 1399 and 1212 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.80–2.35 (m, 4, $CH_2CH_2CH_3$), 1.91–1.28 (m, 4, $CH_2CH_2CH_3$), and 1.20–0.85 (two triplets, 6, $CH_2CH_2CH_3$).

Anal. Calcd for $C_9H_{14}NO_3SCl$: C, 43.10; H, 5.57; N, 5.57. Found: C, 42.84; H, 5.41; N, 5.52.

2-Hexyne (**1d**, 12.3 g, 0.15 mol, 6 hr) gave 30.5 g (92%) of a mixture of **6-chloro-5-methyl-4-*n*-propyl-1,2,3-oxathiazine 2,2-dioxide** (**2d**) and **6-chloro-4-methyl-5-*n*-propyl-1,2,3-oxathiazine**

(39) Melting points are corrected; boiling points are uncorrected. The infrared spectra were recorded on Perkin-Elmer 337 grating spectrophotometer. The ultraviolet spectra were taken on a Cary 15 spectrophotometer. Nmr spectra were obtained on Varian Associates A-60 and A-60A spectrometers; chemical shifts are expressed in parts per million (δ) downfield from TMS as an internal standard. Gas chromatographs were run on a Perkin-Elmer 880 with a flame ionization detector and using a column packed with 10% SE-30 on Chromosorb W. The mass spectra were obtained using the facilities of the National Institutes of Health sponsored (FR 00317) Mass Spectrometry Center at Massachusetts Institute of Technology. Microanalysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. CSI was obtained from the American Hoechst Corp.

2-Butyne (**1a**), 3-hexyne (**1b**), 2-hexyne (**1d**), 4,4-dimethyl-2-pentyne (**1e**), and 1-octen-4-yne (**1l**) were obtained from Chemical Samples Co.; phenylacetylene (**1g**) and diphenylacetylene (**1h**) were obtained from Aldrich Chemical Co.; phenylmethylacetylene (**1f**) and 1-hexyne (**1i**) were obtained from Farchan Research Lab.; 4-octyne (**1c**) was obtained from Pfaltz and Bauer Co.; 3-diethylamino-1-propyne (**1j**) was obtained from K & K Laboratories; 1-diethylamino-1-propyne (**1k**) was obtained from Fluka AG. 2-Methyl-2-hexen-4-yne (**1m**) was prepared from propargyl bromide and acetone by the sequence of a Reformatsky reaction, dehydration, and methylation.[40]

(40) H. B. Henbest, E. R. H. Jones, and H. M. S. Walls, *J. Chem. Soc.*, 2696 (1949); B. W. Nash, D. A. Thomas, W. K. Warburton, and T. D. Williams, *ibid.*, 2983 (1965); I. A. Favorskaya, E. M. Aiwinen, and Y. P. Artsybasheve, *Zh. Obshch. Khim.*, **28**, 1785 (1958) [*Chem. Abstr.*, **53**, 1097*i* (1959)].

2,2-dioxide (2d′). The mixture solidified upon cooling to −30° but all attempts to separate **2d** from **2d′** by fractional crystallization were unsuccessful. The nmr of this mixture indicated that the ratio of **2d** to **2d′** was 73:27:[41] ir (neat) 1625 and 1500 (C=C and C=N), 1390 and 1210 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.85–2.40 (m, 4, $CH_2CH_2CH_3$), 2.49 and 2.16 (two singlets, total 3, $CH_3C{=}N$, and $CH_3C{=}C$), 1.92–1.42 (m, 4, $CH_2CH_2CH_3$), and 1.15–0.91 (t, 6, $CH_2CH_2CH_3$).

4,4-Dimethyl-2-pentyne (1e, 3.84 g, 0.040 mol) was treated with an equimolar amount of CSI in 10 ml of CH_2Cl_2 for 15 hr at room temperature to give 4.85 g (51%) of **4-*tert*-butyl-6-chloro-5-methyl-1,2,3-oxathiazine 2,2-dioxide (2e)**: mp 65.0–66.0°; uv max (isooctane) 293 nm (ϵ 3800); ir (KBr) 1600 and 1470 (C=C and C=N), 1379 and 1200 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 2.30 (s, 3, $CH_3C{=}C$) and 1.40 (s, 9, *tert*-C_4H_9).

Anal. Calcd for $C_8H_{12}NO_3SCl$: C, 40.50; H, 5.07; N, 5.92. Found: C, 40.39; H, 5.02; N, 5.82.

Phenylmethylacetylene (1f, 4.64 g, 0.040 mol, 6 hr) gave 8.85 g (86%) of **6-chloro-5-methyl-4-phenyl-1,2,3-oxathiazine 2,2-dioxide (2f)** after extraction with three 20-ml portions of boiling hexane: mp 58.0–59.0°; uv max ($CHCl_3$) 297 nm (ϵ 12,700); ir (KBr) 1600 and 1475 (C=C and C=N), 1389 and 1190 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.58 (s, 5, C_6H_5) and 2.08 (s, 3, $CH_3C{=}C$).

Anal. Calcd for $C_{10}H_8NO_3SCl$: C, 46.70; H, 3.11; N, 5.45. Found: C, 36.53; H, 3.09; N, 5.52.

Phenylacetylene (1g, 10 g, 0.10 mol) gave 11.5 g (48%) of **6-chloro-4-phenyl-1,2,3-oxathiazine 2,2-dioxide (2g)**. After addition of **1g** to CSI, the mixture was stirred for 3 hr at 0° (the solution darkened), after which an equal volume of pentane was added and cooled to −60°. The dark solid which precipitated was filtered quickly and washed with three 5-ml portions of cold ether to give crude **2g** which was unstable at room temperature. All attempts to further purify this adduct led to decomposition: mp 106–108° dec; uv max (CH_2Cl_2) 302 nm (ϵ 12,000); ir (KBr) seven bonds in 1720–1440-cm^{-1} region (C=C and C=N), 1379 and 1198 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 8.10–7.75 (m, 5, C_6H_5) and 6.97 (s, 1, HC=C).

Crude **2g** (1.22 g, 5.0 mmol) was treated with benzenethiol–pyridine in acetone to give 0.6 g (38%) of **4-phenyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6g)** after the same work-up as **6f**: mp 91.0–93.5° (from pentane–CH_2Cl_2); ir (KBr) five bands in 1585–1425-cm^{-1} region (C=C and C=N), 1379 and 1198 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.92–7.47 (m, 10, C_6H_5) and 6.37 (s, 1, C=CH).

Anal. Calcd for $C_{15}H_{11}NO_3S_2$: C, 56.78; H, 3.47; N, 4.42. Found: C, 56.82; H, 3.78; N, 4.64.

Reaction of Oxathiazines (2) with Nucleophiles. Thiophenol–Pyridine.—The general procedure used was as follows. A solution of pyridine in acetone (0.1 mol, 15 ml) was added dropwise (30 min) to a stirred solution (−30°) of 0.1 mol of oxathiazine (**2**) and 2 mol equiv of C_6H_5SH in 25 ml of acetone. After the mixture was stirred for an additional 30 min, an amount of water equal to the volume of solvent acetone was added slowly with stirring. The oil which separated was extracted with six 20-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and evaporated to dryness, and the residue was recrystallized to give the phenyl thioether **6**. Any variations in isolation procedures for **6** are noted under each oxathiazine.

Compound **2a** (0.59 g, 3.0 mmol) gave 0.35 g (44%) of **4,5-dimethyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6a)**: mp 120–122° (from ether–pentane); ir (KBr) 1600 and 1481 (C=C and C=N), 1370 and 1205 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.52 (s, 5, C_6H_5), 2.35 (s, 3, $N{=}CCH_3$), and 2.11 (s, 3, $C{=}CCH_3$).

Anal. Calcd for $C_{11}H_{11}NO_3S_2$: C, 49.10; H, 4.09; N, 5.20. Found: C, 48.92; H, 3.87; N, 5.33.

Compound **2b** (11.2 g, 0.050 mol) gave 5.2 g (35%) of **4,5-diethyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6b)**: mp 92.0–93.0° (from ether–pentane); uv max (C_2H_5OH) 321 nm (ϵ 6200); ir (KBr) 1575 and 1471 (C=C and C=N), 1370 and 1190 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.43 (s, 5, C_6H_5), 2.80–2.30 (two quartets, 4, CH_2CH_3), and 1.35–0.95 (two triplets, 6, CH_2CH_3).

Anal. Calcd for $C_{13}H_{15}NO_3S_2$: C, 52.50; H, 5.09; N, 4.71. Found: C, 52.48; H, 5.09; N, 4.83.

Compound **2c** (3.75 g, 0.015 mol) gave 1.30 g (27%) of **4,5-dipropyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6c)**: mp 73.0–74.5° (from ether–pentane); ir (KBr) 1575 and 1450 (C=C and C=N), 1379 and 1205 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.42 (s, 5, C_6H_5), 2.73–2.25 (m, 4, $CH_2CH_2CH_3$), 1.92–1.30 (m, 4, $CH_2CH_2CH_3$), and 1.15–0.78 (two triplets, 6, $CH_2CH_2CH_3$).

Anal. Calcd for $C_{15}H_{19}NO_3S_2$: C, 55.40; H, 5.84; N, 4.31. Found: C, 55.47; H, 6.07; N, 4.36.

Compound **2e** (0.50 g, 2.1 mmol) gave 0.2 g (31%) of **4-*tert*-butyl-5-methyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6e)**: mp 87.0–89.0° (from ether–pentane); ir (KBr) 1563 and 1460 (C=C and C=N), 1379, and 1198 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.50 (s, 5, C_6H_5), 2.30 (s, 3, $C{=}CCH_3$), and 1.40 (s, 9, *tert*-C_4H_9).

Anal. Calcd for $C_{14}H_{17}NO_3S_2$: C, 54.01; H, 5.47; N, 4.52. Found: C, 53.81; H, 5.62; N, 4.72.

Compound **2f** gave **5-methyl-4-phenyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6f)**. To a stirred solution of 2.57 g (0.010 mol) of **2f** and 2 mol equiv of C_6H_5SH in 25 ml of acetone cooled to −60° was added dropwise a solution of 0.79 g (0.01 mol) of pyridine in 5 ml of acetone and the solution was stirred for 30 min. Pentane (50 ml) was then added with stirring at −60°. The precipitate was filtered while it was still cold, and the filtrate was evaporated *in vacuo* to dryness. The residual oil was deposited on a 1.0 × 20 cm column packed with silica gel and successively eluted with 50 ml of pentane, 50 ml of ether, and 50 ml of CH_2Cl_2. Evaporation of the CH_2Cl_2 fraction gave a yellow solid which was recrystallized from 1:3 CH_2Cl_2–pentane to afford 1.60 g (48%) of **5-methyl-4-phenyl-6-thiophenyl-1,2,3-oxathiazine 2,2-dioxide (6f)**: mp 166.0–167.5°; ir (KBr) 1585, 1550, and 1455 (C=C and C=N), 1379 and 1190 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.59–7.53 (two doublets, 10, C_6H_5) and 2.12 (s, 3, $C{=}CCH_3$).

Anal. Calcd for $C_{16}H_{13}NO_3S_2$: C, 58.10; H, 3.93; N, 4.23. Found: C, 57.97; H, 3.87; N, 4.53.

Methanol.—To 75 ml of CH_3OH cooled in an ice bath was added 22.4 g (0.10 mol) of oxathiazine (**2b**) and the solution was stirred for 30 min at room temperature. After the CH_3OH was evaporated *in vacuo*, the residual oil was distilled to give 9.5 g (50%) of **methyl 2-ethyl-3-oxopentanoate (9)**: bp 51–52° (0.6 mm) [lit.[42] bp 81–85° (11 mm)]; ir (neat) 1739 and 1709 cm^{-1} (C=O); nmr (neat) δ 3.72 (s, 3, CO_2CH_3), 3.48 (t, J = 7.5 Hz, 1, CH next to ethyl group), 2.58 (1, J = 7.5 Hz, 2, $COCH_2CH_3$), 2.12–1.60 (m, 2, CH_2CH_3), and 1.17–0.90 (t, 6, CH_2CH_3).

A second product, bp 110° (0.3 mm), was obtained in 2.5-g yield but could not be identified.

Water.—The general procedure used was as follows. To 50 ml of water was added 10 g (0.040 mol) of **2** and the mixture was heated to 50–60° at which reflux temperature **2** began to decompose rapidly. The solution was refluxed gently for 2 hr after which it was cooled slowly and extracted with three 30-ml portions of *n*-pentane. The combined pentane extracts were dried ($MgSO_4$), filtered, and distilled to give the ketone **7** identified where possible by comparison with an authentic sample.

Compound **2a** (1.0 g, 5.0 mmol) gave 0.3 g (81%) of **2-butanone (7a)**, bp 79.0°.

Compound **2b** (10 g, 0.045 mol) gave 3.1 g (70%) of **3-hexanone (7b)**, bp 124–125°.

Compound **2c** (2.5 g, 0.010 mol) gave 1.0 g (80%) of **4-octanone (7c)**, bp 52–53° (7 mm).

A mixture of **2d** and **2d′** (prepared from a 1:1 mixture of 2-hexyne and CSI) afforded a mixture of **3-hexanone (7b)** and **2-hexanone (7d)**. To 10 g (0.045 mol) of mixture **2d** and **2d′** was added 50 ml of water and the solution was refluxed for 1 hr after which it was allowed to cool to room temperature and extracted with three 20-ml portions of CH_2Cl_2. The aqueous layer was saturated with NaCl and then extracted with three 20-ml portions of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The residue was distilled to give 2.55 g (58%) of a mixture of **7b** and **7d**, bp 122–125°.

A vpc of this mixture demonstrated that the **7b**:**7d** ratio was 75:25, while the nmr showed a 77:23 ratio: ir (CCl_4) 1725 cm^{-1} (C=O); nmr (neat) δ 2.70–2.27 (m, $COCH_2$), 2.13 (s, $COCH_3$), 1.85–1.28 (m, CH_2CH_3), and 1.20–0.85 (two triplets, CH_2CH_3). The integral ratio of these peaks were 4.3:1.0:3.3:6.8.

Compound **2e** (0.75 g, 3.2 mmol) gave 0.15 g (41%) of **2,2-dimethyl-3-pentanone (7e)**. To a solution of **2e** in 5 ml of

(41) The integral ratio of the methyl protons linked to C=C and C=N bonds were compared. The methyl protons linked to a C=N bond were always found to be more deshielded than those linked to a C=C bond.

(42) J. Buchi, P. Schneeberger, and R. Lieberherr, *Helv. Chem. Acta*, **36**, 1402 (1953).

acetone was added 20 ml of H_2O and the solution was refluxed gently for 4 hr, after which it was extracted with three 10-ml portions of CH_2Cl_2. The CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and evaporated. The residue was distilled to give pure **7e**: bp 123–124° (lit.[43] bp 125–126°); ir (CCl_4) 1709 cm^{-1} (C=O); nmr ($CDCl_3$) δ 2.50 (q, 2, CH_2CH_3), 1.15 (s, 9, *tert*-C_4H_9), and 1.00 (t, 3, CH_2CH_3).

Compound **2f** (2.0 g, 8.0 mmol) gave 0.80 g (77%) of **propiophenone** (**7f**), bp 217°.

Compound **2g** (3.0 g, 0.012 mol) gave 0.5 g (52%) of **acetophenone** (**7g**) after the reaction (30 min at 65°) was followed by extraction with three 10-ml portions of ether.

Hydrolysis of **2g** (2.0 g, 8.2 mmol) with 10 ml of saturated aqueous $NaHCO_3$ solution at 0° for 1 hr also afforded 0.3 g (31%) of **7g**.

Sodium Methoxide–Methanol.—The general procedure used was as follows. To a cooled (0°) solution of oxathiazine **2** in absolute CH_3OH (1 mmol/2 ml) was added slowly a solution of $NaOCH_3$ (3 mol equiv) prepared by the inverse Tishler procedure[44] in 10 ml of CH_3OH, and the solution was stirred for 30 min at 0°.

The reaction mixture was neutralized with 4 *N* HCl solution and after the solvent was evaporated *in vacuo* the residual oil was extracted with three 40-ml portions of 1:1 CH_2Cl_2–H_2O. The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and evaporated. In the case of **2b**, the residual oil was distilled to give **9**. The combined water extracts were acidified with 4 *N* HCl and then extracted with three 20-ml portions of CH_2Cl_2. These combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and evaporated to give crude **8**.

Compound **2a** (0.4 g, 2.0 mmol) gave 0.15 g (33%) of **methyl 2-methyl-3-methoxysulfonylamino-*trans*-2-butenoate** (**8a**): ir (neat) 3280 (NH), 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.80–5.37 (broad singlet, 1, NH), 3.88 (s, 3, SO_2CH_3), 3.74 (s, 3, CO_2CH_3), 2.22 (s, 3, C=CCH_3), and 1.36 (s, 3, C=CCH_3).

Compound **2b** (2.24 g, 0.010 mol) gave 0.31 g (20%) of **9** and 1.26 g (50%) of **methyl 2-ethyl-3-methoxysulfonylamino-*trans*-2-pentenoate** (**8b**). Compound **8b** was purified by chromatography (a 1.0 × 20 cm column packed with silica gel) using ether as eluent: ir (neat) 3200 (NH), 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.80–7.00 (broad, 1, NH), 3.89 and 3.70 (two singlets, 6, CO_2CH_3 and SO_2CH_3), 2.90–2.20 (m, 4, CH_2CH_3), and 1.30–0.90 (two triplets, 6, CH_2CH_3).

Compound **2c** (2.0 g, 8.0 mmol) gave 0,90 g (40%) of **methyl 2-*n*-propyl-3-methoxysulfonylamino-*trans*-2-hexenoate** (**8c**): bp 128–130° (0.3 mm); ir (neat) 3430 (NH), 1740 cm^{-1} (C=O) nmr ($CDCl_3$) δ 5.66–5.32 (broad singlet, 1, NH) 3.85 (s, 3; SO_2CH_3), 3.72 (s, 3, CO_2CH_3), 2.62–2.05 (m, 4, $CH_2CH_2CH_3$), 1.86 (m, 4, $CH_2CH_2CH_3$), and 1.12–0.78 (two triplets, 6, $CH_2CH_2CH_3$).

Compound **2e** (0.50 g, 2.1 mmol) gave 0.6 g (98%) of **methyl 2,4,4-trimethyl-3-methoxysulfonylamino-*trans*-2-pentenoate** (**8e**) which could not be distilled without decomposition. The crude **8e** was purified by chromatography (0.5 × 20 cm column packed with silica gel using 1:1 pentane–ether mixture as an eluent): ir (neat) 3280 (NH), 1724 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.31 (s, 1, NH), 3.97 (s, 3, SO_2CH_3), 3.78 (s, 3, CO_2CH_3), 2.02 (s, 3, C=CCH_3), and 1.20 (s, 9, *tert*-C_4H_9).

Compound **2f** (2.0 g, 7.8 mmol) gave 1.65 g (79%) of **methyl 2-methyl-3-methoxysulfonylamino-*trans*-cinnamate** (**8f**) which could not be distilled without decomposition. The crude **8f** was purified by chromatography (0.5 × 20 cm column packed with silica gel using ether as an eluent): ir (neat) 3226 (NH) 1739 cm^{-1} (C=O); nmr ($CDCl_3$) δ 8.10–7.90 (broad singlet, 1, NH), 7.40 (s, 5, C_6H_5), 3.80 (s, 3, SO_2CH_3), 3.68 (s, 3, CO_2CH_3), and 1.65 (s, 3, C=CCH_3).

Compound **2g** (1.5 g, 6.2 mmol) gave 0.5 g (30%) of **methyl 3-methoxysulfonylamino-*trans*-cinnamate** (**8g**) as colorless needles: mp 80.5–81.0° (from CH_3OH–pentane); uv max (CH_3OH) 273.5 nm (ϵ 5400); ir (KBr) 3150 (NH), 1681 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.52 (m, 6, NH and C_6H_5), 5.42 (s, 2, C=CH), 3.88 and 3.83 (two singlets, 6, SO_2CH_3 and CO_2CH_3).

Anal. Calcd for $C_{11}H_{13}NO_5S$: C, 48.70; H, 4.80; N, 5.27. Found: C, 48.54; H, 4.80; N, 5.23.

Catalytic Hydrogenation of 8b and 8g.—A mixture of 1.0 g (4.0 mmol) of **8b** in 100 ml of C_2H_5OH and 0.2 g of 5% Pd/C was hydrogenated in Paar apparatus under 50 psi for 20 hr. The catalyst was filtered and the solvent evaporated to dryness. The residual oil was purified by chromatography (0.5 × 15 cm column packed with silica gel; ether as eluent) to give 0.80 g (80%) of **methyl 2-ethyl-3-methoxysulfonylaminovalerate** (**10b**). Compound **10b** is a viscous oil which could not be distilled without decomposition: ir (neat) 3250 (NH), 1730 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.90 (broad singlet, 1, NH), 3.89 and 3.70 (two singlets, 6, OCH_3), 3.60–3.40 (m, 1, CH next to CH_2 and NH), 2.95–2.60 (m, 1, CHCO), 2.05–1.60 (m, 4, CH_2CH_3), and 1.30–1.00 (t, 6, CH_2CH_3).

Hydrogenation (5% Pd/C) of **8g** (1.0 g, 3.7 mmol) gave 0.75 g (75%) of **methyl 3-methoxysulfonylamino-3-phenylpropanoate** (**10g**). Compound **10g** was stable at room temperature but unstable to distillation. Vpc indicated the presence of only a single component: ir (neat) 3226 (NH), 1709 (C=O), 1342 and 1163 cm^{-1} (SO_2); uv max (C_2H_5OH) 206.5 nm (ϵ 8450), 263.5 (790); nmr ($CDCl_3$) δ 7.40 (s, 5, C_6H_5), 6.25 (d, J = 8.5 Hz, 1, NH), 5.10–4.70 (m, 1, CH next to NH and CH_2, J = 6.5 Hz), 3.60 and 3.55 (two singlets, 6, OCH_3), and 2.90 (d, J = 6.5 Hz, 2, CH_2CO).

Anal. Calcd for $C_{11}H_{15}NO_5S$: C, 48.35; H, 5.49; N, 5.13. Found: C, 48.18; H, 5.58; N, 5.06.

Reaction of 1-Chlorosulfonyl-*cis*-3,4-dimethyl- (11b) and 1-Chlorosulfonyl-4-phenyl-2-azetidinone (11g) with Sodium Methoxide–Methanol.—To a solution of 2.2 g (0.010 mol) of **11b**[13b] in 10 ml of CH_3OH cooled to 0° was added slowly a solution of $NaOCH_3$ (0.03 mol equiv) in CH_3OH, and the solution was stirred for 24 hr at room temperature. The solution was neutralized with 4 *N* HCl and the solvent then was removed *in vacuo*. The residue was extracted with three 10-ml portions of CH_2Cl_2. The solution was dried ($MgSO_4$) and purified by chromatography (10 × 20 cm column packed with silica gel; ether as eluent) to give 2.3 g (80%) of **10b**.[13b] Similar treatment of **11g**[13b] afforded **10g** in 50% yield.

Reduction of 2b with $LiAlH_4$ (2 Mol Equiv).—A slurry of 3.8 g (0.10 mol) of $LiAlH_4$ in 250 ml of anhydrous ether was added slowly to a stirred solution of 11.2 g (0.50 mol) of **2b** in 50 ml of anhydrous ether. The mixture was stirred at room temperature for 30 min and then decomposed with 30% NH_4Cl solution. The solid was filtered and washed with five 10-ml portions of ether. The combined filtrates were dried ($MgSO_4$), filtered, and evaporated. The residue was added to 50 ml of a saturated solution of 2,4-DNPH in CH_3OH and the solution was allowed to stand for 2 hr. Concentration of this solution gave an orange solid which was recrystallized twice from C_2H_5OH to give 0.5 g (30%) of the DNPH derivative of **2-ethyl-2-pentenal** (**12**): mp 170.5–171.5° (lit.[45] mp 173°); ir (KBr) 1613 cm^{-1} (C=C); nmr ($CDCl_3$) δ 11.06 (s, 1, NH), 9.10 (d, 1, CH=N), 8.40–7.26 (m, 3, aromatic), 5.90 (t, J = 4 Hz, 1, C=CH), 2.66–2.10 (m, 4, CH_2CH_3), and 1.30–0.90 (two triplets, 6, CH_2CH_3).

Reaction of 2b with $LiAlH_4$ (4 Mol Equiv).—To a slurry of 16.2 g (0.43 mol) of $LiAlH_4$ in 300 ml of anhydrous ether cooled to 0° was added a solution of 22.4 g (0.10 mol) of **2b** in 100 ml of anhydrous ether. The mixture was stirred overnight at room temperature and then decomposed in the cold with 30% NH_4Cl. The solid was filtered and washed with 50 ml of ether. The combined filtrates were dried ($MgSO_4$), filtered, and evaporated. The residual yellow oil was distilled to give 4.1 g (36%) of **2-ethyl-2-penten-1-ol** (**13**): bp 76–77° (30 mm) [lit.[46] bp 66–67° (25 mm)]; ir (neat) 3226 cm^{-1} (OH); nmr (neat) δ 5.40 (t, J = 5 Hz, 1, C=CH), 4.47 (broad singlet, 1, OH), 4.05 (d, J = 7.5 Hz, 2, CH_2OH), 2.32–1.82 (m, 4, CH_2CH_3), and 1.2–0.85 (two triplets, 6, CH_2CH_3).

Reduction of Oxathiazines (2) with $LiAlH_4$ (0.5 Mol Equiv).—The general procedure used was as follows. To a solution of **2** in anhydrous ether (0.050 mol/75 ml) was added slowly (20 min) a slurry of $LiAlH_4$ (0.5 mol equiv) in ahydrous ether (0.025 mol/100 ml) with vigorous stirring. The mixture was stirred for 30 min at room temperature and then a saturated solution (30%) of NH_4Cl was added until any reaction ceased. The mixture was filtered through filter cell and the solid was washed with 50 ml of ether. The combined filtrates were dried ($MgSO_4$), filtered, and evaporated. The residual yellow oil was chromatographed on silica gel (1 × 20 cm column) with ether as eluent to give the pure dihydro derivative of oxathiazine (**3**). Variations in isolation procedure of **3** are noted under each oxathiazine.

(43) F. C. Whitmore, C. I. Noll, and V. C. Meunier, *J. Amer. Chem. Soc.*, **61**, 683 (1939).

(44) H. E. Baumgarten and J. M. Peterson, *Org. Syn.*, **41**, 82 (1961).

(45) H. Bouget, *Bull. Soc. Chim. Fr.*, 2059 (1965).

(46) H. B. Green and W. J. Hickinbottom, *J. Chem. Soc.*, 3262 (1957).

Compound **2a** (0.97 g, 5.0 mmol) gave 0.60 g (62%) of **6-chloro-4,5-dimethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (3a)**. After the reaction, crude **3a** was deposited on a 0.5 × 10 cm silica gel column and eluted successively with 20 ml of pentane and 20 ml of ether. Evaporation of both fractions afforded **3a** as a viscous oil. Neither crystallization nor distillation of **3a** was successful but tlc indicated the presence of only a single component: ir (neat) 3226 (NH), 1653 (C=C), 1370 and 1198 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 5.24–4.98 (broad doublet, 1, NH), 4.33–3.88 (m, 1, $CHCH_3$), 1.82 (s, 3, $C=CCH_3$), and 1.52–1.40 (d, 3, $CHCH_3$).

Anal. Calcd for $C_5H_8NO_3SCl$: C, 30.45; H, 4.06; N, 7.12. Found: C, 30.68; H, 4.06; N, 7.11.

Compound **2b** (11.2 g, 0.050 mol) gave 9.0 g (81%) of **6-chloro-4,5-diethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (3b)**: mp 58.0–59.0° (from pentane): uv max (*n*-hexane) 233 nm (ϵ 1500); ir (KBr) 3195 (NH), 1642 (C=C), 1364 and 1202 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 5.00 (d, J = 7 Hz, 1, NH), 3.93 (X portion of an ABX pattern, J_{BX} = 5.5, J_{AX} = 7.5 Hz, further split by NH, J = 7 Hz, 1, CH next to ethyl group), 2.50–1.60 (m, 4, CH_2CH_3), and 1.30–0.85 (m, 6, CH_2CH_3).

Anal. Calcd for $C_7H_{12}NO_3SCl$: C, 37.25; H, 5.36; N, 6.26; mol wt, 226. Found: C, 37.11; H, 5.26; N, 6.06; mol wt, 225 (from mass spec).

Compound **3b** can be recrystallized from hot water without decomposition.

Compound **2c** (5.10 g, 0.020 mol) gave 3.35 g (66%) of **6-chloro-4,5-di-*n*-propyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (3c)**: mp 34.5–35.0° (from 1:1 pentane–ether); ir (KBr) 3226 (NH), 1639 (C=C), 1370 and 1198 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 5.20–5.00 (broad doublet, 1, NH), 4.27–3.88 (m, 1, CH next to *n*-propyl group), 2.38–2.07 (m, 2, $C=CCH_2CH_2CH_3$), 1.86–1.30 (m, 6, CH_2 of *n*-propyl groups), and 1.17–0.85 (two triplets, 6, $CH_2CH_2CH_3$).

Anal. Calcd for $C_9H_{16}NO_3SCl$: C, 42.71; H, 6.33; N, 5.54. Found: C, 42.63; H, 6.48; N, 5.41.

Compound **2e** (0.80 g, 3.3 mmol) gave 0.4 g (50%) of **4-*tert*-butyl-6-chloro-5-methyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (3e)**: mp 74.0–75.0° (from 1:1 ether–pentane); ir (KBr) 3226 (NH), 1626 (C=C), 1399 and 1205 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 5.67 (d, J = 5.5 Hz, 1, NH), 3.79 (d, J = 5.5 Hz, 1, CH next to NH), 1.95 (s, 3, $C=CCH_3$), and 1.10 (s, 9, *tert*-C_4H_9).

Anal. Calcd for $C_8H_{14}NO_3SCl$: C, 40.17; H, 5.85; N, 5.85. Found: C, 40.20; H, 5.77; N, 5.98.

Compound **2f** (2.10 g, 8.2 mmol) gave 1.10 g (52%) of **6-chloro-5-methyl-4-phenyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (3f)**: colorless needles; mp 83.0–84.5° (from 1:3 ether–pentane); ir (KBr) 3226 (NH), 1653 (C=C), 1408 and 1205 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.40 (s, 5, C_6H_5), 5.10 (broad singlet, 1, CH), 4.90–4.70 (broad singlet, 1, NH), and 1.57 (s, 3, C=C-CH_3).

Anal. Calcd for $C_{10}H_{10}NO_3SCl$: C, 46.33; H, 3.86; N, 5.40. Found: C, 46.19; H, 4.10; N, 4.99.

Methylation of 3.—The general procedure used was as follows. To a stirred solution of **3** and an excess of CH_3I (3–5 mol equiv) in acetone (15 ml/0.01 mol) was added slowly an equimolar amount of K_2CO_3 and the mixture was stirred for 20 hr at room temperature. The mixture was then filtered and the filtrate evaporated *in vacuo* leaving a yellow oil which was dissolved in ether. Addition of pentane and cooling to −30° precipitated the *N*-methyl derivative **4**. Any variation in reaction and isolation procedures for **4** are noted under each dihydro derivative.

Compound **3a** (0.5 g, 3.0 mmol) gave 0.35 g (65%) of **6-chloro-3,4,5-trimethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (4a)**: mp 29.0–30.0° (from hexane); ir (KBr) 1653 (C=C), 1399 and 1212 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 4.10 (q, J = 7.5 Hz, 1, $CHCH_3$), 2.92 (s, 3, NCH_3), 1.81 (s, 3, $C=CCH_3$), and 1.52 (d, J = 7.5 Hz, 3, $CHCH_3$).

Anal. Calcd for $C_6H_{10}NO_3SCl$: C, 34.12; H, 4.74; N, 6.65. Found: C, 34.38; H, 5.01; N, 6.81.

Compound **3b** (5.0 g, 0.022 mol) gave 3.2 g (64%) of **6-chloro-4,5-diethyl-3-methyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (4b)**: mp 31.5–32.0° (from hexane); ir (KBr) 1653 (C=C), 1399 and 1176 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 3.80–3.47 (two doublets, J_{AX} = 10.0, J_{BX} = 5.5 Hz, 1, CH next to ethyl group), 2.92 (s, 3, NCH_3), 2.50–1.70 (m, 4, CH_2CH_3), and 1.3–0.9 (two triplets, 6, CH_2CH_3).

Anal. Calcd for $C_8H_{14}NO_3SCl$: C, 40.10; H, 5.85; N, 5.85. Found: C, 39.98; H, 5.98; N, 5.73.

Compound **3c** (1.5 g, 6.0 mmol) gave 1.15 g (73%) of **6-chloro-3-methyl-4,5-di-*n*-propyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (4c)**. The crude **4c** was chromatographed on silica gel (0.5 × 15 cm column) with 2:1 ether–pentane as eluent to afford pure **4c** as a viscous oil, which could not be distilled without decomposition: ir (neat) 1653 (C=C), 1399 and 1212 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 3.90–3.60 (two doublets, J_{AX} = 10.0, J_{BX} = 4.0 Hz, 1, CH next to *n*-propyl group), 2.90 (s, 3, NCH_3), 2.37–1.93 (m, 2, $=CCH_2CH_2CH_3$), 1.83–1.22 (m, 6, $=CCH_2CH_2CH_3$ and $CHCH_2CH_2CH_3$), and 1.10–0.80 (two triplets, 6, $CH_2CH_2CH_3$).

Anal. Calcd for $C_{10}H_{18}NO_3SCl$: C, 45.00; H, 6.74; N, 5.24. Found: C, 45.30; H, 6.78; N, 5.25.

Compound **3e** (0.20 g, 0.80 mmol) gave 0.10 g (48%) of **6-chloro-3,5-dimethyl-4-*tert*-butyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (4e)**. To a solution of **3e** in 5 ml of DMSO was added large excess of CH_3I (5 g, 0.04 mol) and K_2CO_3 (0.1 g, 1 mmol). The mixture was stirred for 10 hr at room temperature after which 10 ml of CH_2Cl_2 was added. The mixture was then filtered, and the filtrate was extracted with ten 10-ml portions of water to remove DMSO. The solution was dried ($MgSO_4$), filtered, and evaporated *in vacuo* to leave a viscous oil which was crystallized from pentane to give **4e**: mp 50.0–51.0°; ir (KBr) 1667 (C=C), 1351 and 1176 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 3.28 (s, 1, CH next to *tert*-butyl group), 3.00 (s, 3, NCH_3), 1.98 (s, 3, $C=CCH_3$), and 1.07 (s, 9, *tert*-C_4H_9).

Anal. Calcd for $C_9H_{16}NO_3SCl$: C, 42.70; H, 6.32; N, 5.53. Found: C, 42.71; H, 6.25; N, 5.45.

Compound **3e** (2.55 g, 0.010 mol) gave 1.95 g (73%) of **6-chloro-3,5-dimethyl-4-phenyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (4f)**. The crude **4f** was deposited on a 0.5 × 20 cm column packed with silica gel and eluted successively with 40 ml each of pentane, ether, and CH_2Cl_2. Evaporation of the first two fractions gave **4b** as a viscous oil, which could not be distilled without decomposition. Tlc indicated the presence of only a single component: ir (neat) 1667 (C=C), 1370 and 1207 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.40 (s, 5, C_6H_5), 4.70 (s, 1, CH next to phenyl group), 2.70 (s, 3, NCH_3), and 1.58 (s, 3, $C=CCH_3$).

Anal. Calcd for $C_{11}H_{12}NO_3SCl$: C, 48.40; H, 4.39; N, 5.13. Found: C, 48.26; H, 4.46; N, 5.33.

Dechlorination of 4 with Li-*tert*-BuOH.—To a stirred solution of 0.50 g (2.0 mmol) of **4b** and 1.0 g (0.014 mol) of *tert*-BuOH in 20 ml of dry THF cooled in an ice bath was slowly added 0.20 g (0.029 mol) of finely chopped Li wire under nitrogen. After 20 min, a vigorous exothermic reaction began which was maintained at steady reflux for 2 hr. As the exothermic reaction subsided the reaction mixture was heated externally to continue refluxing for an additional 2 hr and then stirred finally at room temperature for 1 hr. The mixture was poured onto 20 ml of ice and extracted with six 10-ml portions of ether. The combined ether extracts were washed with three 20-ml portions of water and two 10-ml portions of saturated NaCl solution. The ethereal solution was dried ($MgSO_4$), filtered, and evaporated *in vacuo* leaving a white solid which was recrystallized three times from ether–pentane to give 0.4 g (93%) of **4,5-diethyl-3-methyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (5b)** as colorless needles: mp 35.5–36.0°; ir ($CHCl_3$) 1660 (C=C), 1389 and 1176 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 6.30 (m, 1, C=CH), 3.92–3.57 (two doublets, J_{AX} = 10, J_{BX} = 5 Hz, 1, CH next to ethyl group), 2.90 (s, 3, NCH_3), 2.32–1.72 (m, 4, CH_2CH_3), and 1.17–0.92 (two triplets, 6, CH_2CH_3).

Anal. Calcd for $C_8H_{15}NO_3S$: C, 46.82; H, 7.32; N, 6.82. Found: C, 46.64; H, 7.42; N, 6.58.

Compound **4a** (0.50 g, 2.3 mmol) gave 0.35 g (86%) of **3,4,5-trimethyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (5a)** after similar work-up as **5b**: mp 32.0–33.0°; ir ($CHCl_3$) 1653 (C=C), 1379 and 1190 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 6.34–6.20 (broad singlet, 1, C=CH), 3.98 (q, J = 7 Hz, 1, $CHCH_3$), 2.90 (s, 3, NCH_3), 1.72 (s, 3, $C=CCH_3$), and 1.51 (d, 3, $CHCH_3$, J = 7 Hz).

Compound **4c** (0.50 g, 1.9 mmol) gave 0.3 g (69%) of **3-methyl-4,5-di-*n*-propyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (5c)** as a viscous oil after a similar work-up as **5b** followed by chromatography on a 0.5 × 20 cm silica gel column using ether as eluent. Compound **5b** could not be distilled without decomposition: ir (neat) 1653 (C=C), 1380 and 1189 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 6.27 (d, J = 1.5 Hz, 1, C=CH), 3.90–3.65 (two broad peaks, 1, CH next to propyl group), 2.90 (s, 3, NCH_3), 2.25–1.80 (m, 2, $C=CCH_2CH_2CH_3$), 1.80–1.15 (m, 6, $CHCH_2$-

CH_2CH_3 and $C{=}CCH_2CH_2CH_3$), and 1.10–0.78 (two triplets, 6, $CH_2CH_2CH_3$).

Compound **4f** (1.0 g, 3.6 mmol) gave 0.6 g (69%) of **3,5-dimethyl-4-phenyl-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide (5f)** after a similar work-up as **5b**. The product was a pale yellow viscous oil which could not be distilled without decomposition, but tlc indicated the presence of only a single component: ir (neat) 1613 (C=C), 1408 and 1335 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.42–7.15 (m, 5, C_6H_5), 6.02–5.90 (m, 1, C=CH), 4.72–4.55 (broad singlet, 1, CHC_6H_5), 2.98 (s, 3, NCH_3), and 2.05 (s, 3, $C{=}CCH_3$).

Catalytic Hydrogenation of 2b and 6b.—A mixture of 3.5 g (1.56×10^{-2} mol) of **2b** in 30 ml of ethyl acetate and 0.2 g of 5% Pd–$BaSO_4$ was hydrogenated in a Paar apparatus under 50 psi of hydrogen for 20 hr. The catalyst was filtered and the solvent evaporated to dryness. Chromatographic purification of the residue led to decomposition. This residual oil was dissolved in 10 ml of CH_2Cl_2 and 4 *N* KOH solution was added with stirring until it was neutral to litmus paper. The CH_2Cl_2 layer was separated, dried ($MgSO_4$), and distilled to give 1.56 g (77%) of **3-hexanone (7b)**.

Catalytic hydrogenation (30% Pd/C) of **6b** followed by similar hydrolytic work-up gave 0.78 g (39%) of **phenyl 2-ethyl-3-oxothiopentanoate (17)** as a yellow oil which could not be distilled without decomposition: ir (neat) 1720 and 1690 cm^{-1} (C=O); nmr (CCl_4) δ 7.35–7.00 (m, 5, C_6H_5), 3.50 (t, J = 6.0 Hz, 1, CH next to CH_2), 2.70–2.40 (q, 2, CH_2CO), 1.90–1.60 (m, 1, CH_2CH_3), and 1.02 (t, 6, CH_2CH_3, J = 8 Hz).

Ozonation of 2b.—Excess ozone (3.4×10^{-2} mol) was bubbled through a solution of 3.0 g (1.3×10^{-2} mol) of **2b** in 150 ml of CH_2Cl_2 at 0°. The solution was then flushed with nitrogen and warmed to room temperature. Upon addition of 100 ml of 1:1 10% NaOH–30% H_2O_2 solution, the mixture was agitated with nitrogen bubbling for 1 hr and then refluxed for 18 hr. The CH_2Cl_2 layer was separated from water, washed with two 50-ml portions of 5% NaOH solution, and dried ($MgSO_4$). Removal of the solvent *in vacuo* afforded 0.3 g (20%) of **3,4-hexanedione (14)**, bp 127–129° (lit.[47] bp 130°). The aqueous layer was concentrated to 1/3 of the initial volume, acidified with concentrated HCl, saturated with NaCl, and then extracted with three 30-ml portions of ether. The solvent was evaporated to dryness leaving the residue from which was obtained 0.2 g (14%) of **propionic acid (15)**.

Permanganate Oxidation of 2b.—To a solution of 2.29 g (0.010 mol) of **2b** in 20 ml of acetone was added an oxidation mixture composed of 1.26 g of $KMnO_4$ and 0.96 g of $MgSO_4$ in 30 ml of water. The mixture was stirred for 2 hr at room temperature after which 10 g of $NaHSO_3$ was added to destroy excess oxidant. The mixture was filtered, the acetone was evaporated, and the remaining aqueous layer was extracted with six 20-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and the solvent was evaporated to leave an oil which was distilled to give 0.7 g (47%) of **propionic acid (15)** and 0.2 g (20%) of **3-hexanone (7b)**.

Alkaline Peroxide Oxidation of 3b.—To a solution of 1.0 g (0.040 mol) of **3b** and 5 ml of 30% H_2O_2 in 20 ml of CH_3OH was added slowly 5 ml of 10% NaOH solution. The solution was warmed on a steam bath for 30 min and 20 ml of water added. The resulting aqueous solution was acidified with 0.1 *N* HCl and extracted with four 10-ml portions of ether. The combined ether extracts were dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The residual oil was purified by chromatography using a 0.5 × 15 cm column packed with silica gel and ether as eluent to give **2-ethyl-3-(aminosulfonic acid)pentanoic acid (18)** as a single component on tlc. Compound **18** was unstable to distillation and could not be induced to crystallize: ir (neat) 3250 (NH), 1710 cm^{-1} (C=O); nmr (D_2O) δ 3.72–3.40 (m, 1, CH next to CH_2, CH and NH), 3.00–2.65 (m, 1, CH next to CH_2 and CO_2H), 2.05–1.60 (m, 4, CH_2CH_3), and 1.30–0.98 (t, 6, CH_2CH_3).

Compound **3b** (2.4 g, 0.010 mol) was treated with 25 ml of 10% KOH solution for 18 hr at room temperature, followed by acidification with concentrated HCl and evaporation to dryness. The residue was extracted with three 20-ml portions of CH_2Cl_2 and the combined extracts were dried ($MgSO_4$). Evaporation of the solvent *in vacuo* afforded an oil which was chromatographed using 1 × 20 cm silica gel column and ether as eluent to give 1.2 g (50%) of **18** as a single component on tlc.

Reaction of Diphenylacetylene (1h) with CSI.—A solution of 3.6 g (0.020 mol) of **1h** and 3.50 g (0.025 mol) of CSI in 30 ml of CH_2Cl_2 was stirred for 10 days at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted with four 10-ml portions of *n*-pentane to remove unreacted **1h**. The residual oil was then extracted with five 20-ml portions of ether. The combined ether extracts were evaporated *in vacuo* leaving a dark solid which was recrystallized several times from CH_3OH to give 1.20 g (17%) of **methyl 2,3-diphenyl-3-(methoxysulfonylamino)propenoate (8h)**: mp 131.0–133.5°; ir (KBr) 3279 (NH), 1653 (C=O), 1389 and 1176 (SO_2), 1266 cm^{-1} (OCH_3); uv max (CH_3OH) 290 nm (ϵ 15,000); nmr ($CDCl_3$) δ 11.80 (s, 1, NH), 7.20–7.00 (two peaks, 10, C_6H_5), and 3.75 and 3.70 (two singlets, 6, OCH_3).

Anal. Calcd for $C_{17}H_{17}NO_5S$: C, 58.80; H, 4.90; N, 4.03. Found: C, 59.20; H, 5.06; N, 4.03.

To a solution of the ether extract in 20 ml of CH_2Cl_2 was added 20 ml of H_2O and the whole mixture was refluxed for 1 hr. The CH_2Cl_2 layer was separated, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was recrystallized several times from ethanol to give 0.5 g (13%) of **deoxybenzoin (7h)**: mp 55–57° (lit.[48] mp 55–56°).

The ether insoluble part was crystallized from the 1:1 MEK–pentane mixture to give 5.2 g (57%) of **1,3-bis(chlorosulfonyl)-5,6-diphenyluracil (19)** as a pale yellow solid: mp 186–188° dec; ir (KBr) 1745 and 1700 (C=O), 1375 and 1200 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 7.40–7.00 (aromatic).

Compound **19** is unstable at room temperature and all attempts to recrystallize it from hot CH_3OH quantitatively converted it to **5,6-diphenyluracil (20)**: mp 302–303°; ir (KBr) 3333 (NH), 1725 and 1650 cm^{-1} (C=O); uv max (CH_3OH) 292 nm (ϵ 10,500); nmr (DMSO-d_6) 8.10–7.80 (two peaks, 2, CONH) and 7.35–7.00 (two peaks, 10, C_6H_5).

Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.56; N, 10.60. Found: C, 72.48; H, 4.86; N, 10.40.

Reaction of 1-Hexyne (1i) with CSI.—A solution of 4.92 g (0.060 mol) of **1i** in 10 ml of dry CH_3NO_2 was added to a solution of 8.52 g (0.060 mol) of CSI in 10 ml of dry CH_3NO_2 and the whole mixture was stirred for 24 hr at ambient temperature. The solvent was evaporated *in vacuo* to dryness; the residual oil was extracted with three 10-ml portions of *n*-pentane to give ***N*-chlorosulfonyl-2-heptynamide (21)** which could not be further purified by distillation or chromatography without decomposition.

To a stirred solution of 2.4 g (0.010 mol) of crude **21** in 10 ml of CH_2Cl_2 was added dropwise excess aniline (0.03 mol) at 0° and stirring was continued for 2 hr. Addition of 10 ml of pentane to the reaction mixture precipitated a yellow solid which was filtered and the filtrate was extracted with ten 10-ml portions of H_2O to remove unreacted aniline. The CH_2Cl_2 layer was dried ($MgSO_4$), filtered, and evaporated *in vacuo* leaving an oil which was purified by chromatography (1.0 × 20 cm column packed with silica gel; a 1:1 pentane–ether mixture as eluent) to give the ***N*-sulfonylanilide of 2-heptynamide (23**, 30%) as a single component on tlc: mp 142–144°; ir ($CHCl_3$) 3200 (NH), 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 11.80 (s, 2, CONH), 8.65–7.90 (m, 5, C_6H_5), 5.90 (s, 1, NH), 2.90–2.30 (m, 2, CCH_2), 1.85–1.20 (m, 4, CH_2CH_3), and 1.00 (t, 3, CH_2CH_3, J = 6 Hz).

Hydrolysis of the crude **21** with 4 *N* NaOH in acetone led to **2-heptynamide (22**, 20%): bp 130–132° (15 mm); ir ($CHCl_3$) 3550 (NH_2), 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.70–7.50 (s, 2, $CONH_2$), 2.65–2.40 (m, 2, $\equiv CCH_2$), 1.75–1.50 (m, 4, $CH_2CH_2CH_3$), and 0.95 (t, J = 6 Hz, 3, CH_2CH_3).

Reaction of 3-Diethylamino-1-propyne (1j) and 1-Diethylamino-1-propyne (1k) with CSI.—To a cooled solution (−78°) of 1.68 g (0.015 mol) of **1j** in 15 ml of *n*-pentane was added dropwise a solution of 2.13 g (0.015 mol) of CSI in 10 ml of the same solvent and the whole mixture was stirred for 1 hr. The white precipitate obtained was filtered and rinsed with five 20-ml portions of cold (−78°) pentane and dried *in vacuo* to give 3.6 g (95%) of **3-diethylamino-1-propyne–CSI salt (24)**: mp 112° dec; ir (KBr) 3226 (≡C—H), 2222 (N=C=O), 2105 cm^{-1} (C≡C); nmr (D_2O) δ 4.10 (d, J = 2.5 Hz, 2, CH_2C), 3.38 (q, J = 7.5 Hz, 4, CH_2CH_3), 3.11 (d, 1, C≡CH), and 1.23 (t, 6, CH_2CH_3, J = 7.5 Hz).

(47) J. Wegmann and H. Dahn, *Helv. Chim. Acta*, **29**, 101 (1946); I. Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, London, 1965, p 1607.

(48) C. F. H. Allen and W. E. Barker, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1957, p 156.

Salt **24** was too unstable to analyze. Hydrolysis of **24** (1.0 g, 1.4 mmol) with 4 *N* NaOH aqueous solution in acetone at ambient temperature afforded 0.3 g (70%) of **1j** and 0.2 g (20%) of **3-diethylamino-1-propyne hydrochloride** (**25**): mp 197–199° dec; ir (KBr) 3175 (≡CH), 2564 (N^+H), 2105 cm^{-1} (C≡C); nmr (D_2O) δ 4.10 (d, J = 2.5 Hz, 2, CH_2C), 3.38 (q, 4, CH_2CH_3), 3.11 (d, 1, CH, J = 2.5 Hz), and 1.32 (t, 6, CH_2CH_3, J = 7.5 Hz).

Addition of CSI to a pentane solution of an equimolar amount of **1k** at −78° resulted in the immediate precipitation of a yellow solid. The solution was decanted, and the yellow solid was rinsed several times with cold (−78°) pentane and dried *in vacuo* to give quantitatively a 1:1 adduct structured as **26**: mp 47° dec; ir (KBr) 1630 (C=C), 1420 and 1160 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 4.0–3.2 (broad, 4, NCH_2), 2.2–2.0 (m, *ca.* 1.5, CCH_3), and 1.5–1.2 (m, *ca.* 7.5, CH_2CH_3).

Hydrolysis, methanolysis, reduction, and oxidation of **26** resulted in the formation of polymers in all cases.

Reaction of 1-Octen-4-yne (1l) with CSI.—To a stirred solution of 7.10 g (0.050 mol) of CSI in 15 ml of CH_2Cl_2 was added slowly 5.40 g (0.050 mol) of **1l** in 10 ml of CH_2Cl_2 and the solution was stirred for 24 hr at ambient temperature. The solvent was then evaporated *in vacuo* leaving an oil which was extracted with three 5-ml portions of pentane to remove unreacted **1l**. The residue was purified by chromatography (1.0 × 20 cm column packed with silica gel; CCl_4 as eluent) to give 11.00 g (90%) of **6-chloro-4-*n*-propyl-5-(2-propenyl)-1,2,3-oxathiazine 2,2-dioxide** (**2l**): ir (CCl_4) 1640 (C=C), 1410 and 1200 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 6.25–5.00 (m, ABC pattern, 3, $CH{=}CH_2$), 3.30 (d, J = 5.0 Hz, 2, CH_2 next to vinyl group), 2.85–2.60 (t, 2, CH_2-C=C), 2.00–1.35 (m, 2, CH_2CH_3), and 1.03 (t, 3, CH_2CH_3, J = 6.5 Hz).

Reduction of **2l** (6.00 g, 0.024 mol) with 0.5 mol equiv of $LiAlH_4$ in anhydrous ether gave 4.2 g (70%) of **6-chloro-4-*n*-propyl-5-(2-propenyl)-3,4-dihydro-1,2,3-oxathiazine 2,2-dioxide** (**3l**): ir (CCl_4) 3350 (NH) and 1625 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.10–5.15 (m, 3, ABC pattern. $HC{=}CH_2$), 5.00 (s, 1, NH), 4.20–3.80 (m, 1, $CHCH_2$), 2.89 (d, J = 5.5 Hz, 2, CH_2C=C), 1.85–1.20 (m, 4, $CH_2CH_2CH_3$), and 1.10–0.80 (t, 3, $CH_2CH_2CH_3$).

Reduction of **2l** (3.0 g, 0.012 mol) in 20 ml of ether with 25% aqueous Na_2SO_3 at 0° gave 1.2 g (80%) of **1-octen-5-one** (**7l**): bp 94–95° (68–70 mm); ir (CCl_4) 1725 (C=O), 1635 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.25–4.85 (m, ABC pattern, 3, $CH{=}CH_2$), 2.60–2.30 (m, 6, $CH_2CH_2COCH_2$), 1.90–1.35 (m, 2, CH_2CH_3), and 0.92 (t, 3, CH_2CH_3, J = 7.0 Hz).

Competitive Reactions of 1:1 Acetylene–Olefin Mixtures with CSI.—The general procedure used was as follows. To a 1:1 molar equiv mixture of acetylene and olefin in CH_2Cl_2 (10 ml, 0.01 mol) was added dropwise 0.5 molar equiv of CSI in the same solvent at ambient temperature and the solution was stirred for 4–6 hr. Aliquot quantities of the reaction mixtures were taken after 2 and 4 hr, whereupon the solvent and unreacted starting materials were evaporated *in vacuo*. The residual oil was extracted with five 20-ml portions of cold pentane (−20°) to remove unreacted acetylenes, and the residual components were analyzed by nmr. Mixtures of **2-hexyne** (**1d**)–*trans*-**2-hexene** and **1d**–**cyclohexene** so treated with CSI gave, in each case, only the **1d**–CSI oxathiazine adduct.

A 1:1 mixture of **1f**–*trans*-β-**methylstyrene** in methylene chloride gave a nearly 1:1 mixture of **2f** and **1-chlorosulfonyl-3-methyl-4-phenyl-2-azetidinone** adducts based on nmr integration of the methyl groups in each adduct: nmr ($CDCl_3$) δ 7.55 (s, 5, C_6H_5), 7.40 (s, 5, C_6H_5), 4.88–4.80 (d, 1, H at C-4), 3.50–3.20 (m, 1, H at C-3), 2.02 (s, 3, CH_3C=C), and 1.40 (d, J = 7.5 Hz, 3, $CHCH_3$).

The same mixture in anhydrous ether gave a 1.4:1 oxathiazine:azetidinone product ratio.

Finally a 1:1 mixture of **1g**–**styrene** in CH_2Cl_2 gave a 2:1 mixture of azetidinone–oxathiazine adducts based on nmr integration of vinyl and β-lactam protons: nmr ($CDCl_3$) δ 7.45 (s, 15, C_6H_5), 6.88 (s, 1, C=CH), 5.50–5.20 (m, 2, H at C-4), and 3.90–3.28 (m, 4, H at C-3).

Reaction of Benzenediazonium Carboxylate (28) with CSI.—To a slurry of **28**[49] prepared from 3.0 g (0.022 mol) of anthranilic acid in 30 ml of ethylene chloride was added a solution of 5.35 g (0.022 mol) of CSI in 10 ml of the same solvent at 0° with stirring. The mixture was stirred for an additional 30 min at 0° after which it was gradually warmed to 70–80°, whereupon the stirring was continued until gas evolution stopped (*ca.* 2.5 hr). The resulting precipitate was filtered and washed with three 10-ml portions of ethylene chloride to give crude **3-chlorosulfonyl-1,2,3-benzotriazin-4-one** (**29**, 80%): mp 113–116° dec; ir (KBr) 1695 (C=O), 1325 and 1149 cm^{-1} (SO_2).

Compound **29** was too unstable to analyze. Recrystallization of **29** from CH_3OH resulted in the formation of 1.5 g (78%) of **1,2,3-benzotriazin-4-one** (**30**): mp 210–211° dec; ir (KBr) 1681 cm^{-1} (C=O); uv max (C_2H_5OH) 278 nm (ε 6500); nmr (DMSO-d_6) 11.00 (s, 1, CONH) and 8.10–7.60 (m, 4, aromatic).

Anal. Calcd for $C_7H_5N_3O$: C, 57.00; H, 3.40; N, 28.70. Found: C, 56.81; H, 3.35; N, 29.02.

Reaction of **28** with CSI–pyridine salt[29] and *N*,*N*-bischlorosulfonylurea[3] at 40–50° also ultimately gave **30** in 20% yield in each case.

A solution of 0.35 g (2.4 mmol) of **30** in 120 ml of dry THF was irradiated under an Hanovia 450-V lamp for 10 hr at room temperature. No reaction was observed and **30** was quantitatively recovered.

Registry No.—CSI, 1189-71-5; **1l**, 24612-83-7; **2a**, 32544-41-5; **2b**, 26261-67-6; **2c**, 32493-88-2; **2d**, 32544-42-6; **2d′**, 32493-89-3; **2e**, 32544-43-7; **2f**, 32493-90-6; **2g**, 32493-91-7; **2l**, 32493-92-8; **3a**, 32493-93-9; **3b**, 26261-69-8; **3c**, 32493-06-4; **3e**, 32493-07-5; **3f**, 32493-08-6; **3l**, 32493-09-7; **4a**, 32493-10-0; **4b**, 26261-70-1; **4c**, 32493-12-2; **4e**, 32493-13-3; **4f**, 32493-14-4; **5a**, 32493-15-5; **5b**, 26928-79-0; **5c**, 32493-17-7; **5f**, 32493-18-8; **6a**, 32493-19-9; **6b**, 26261-68-7; **6c**, 32493-21-3; **6e**, 32493-22-4; **6f**, 32493-23-5; **6g**, 32493-24-6; **7a**, 78-93-3; **7b**, 589-38-8; **7c**, 589-63-9; **7d**, 591-78-6; **7e**, 564-04-5; **7f**, 93-55-0; **7g**, 98-86-2; **7l**, 30503-12-9; **8a**, 32500-23-5; **8b**, 32500-24-6; **8c**, 32500-25-7; **8e**, 32500-26-8; **8f**, 32500-27-9; **8g**, 32605-75-7; **8h**, 32493-31-5; **9**, 32493-32-6; **10b**, 32493-33-7; **10g**, 32493-34-8; **12**, 3491-57-4; **13**, 32493-36-0; **17**, 32493-37-1; **18**, 32493-38-2; **19**, 32493-39-3; **20**, 32493-40-6; **22**, 32493-41-7; **23**, 32493-42-8; **24**, 32493-43-9; **25**, 23123-80-0; **26**, 32493-45-1; **29**, 32493-46-2; **30**, 90-16-4; 1-chlorosulfonyl-3-methyl-4-phenyl-2-azetidinone, 32493-48-4.

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