in dry THF was added dropwise to the lithium salt. After the solution was stirred for 5 h the precipitate was removed by filtration and the solvent evaporated in vacuo. The pure product was obtained by chromatography and recrystallization.

Reaction 5: Sodium Hydride as Base. Indole (1 equiv) in dry ether was added to 1.5 equiv of sodium hydride and the mixture allowed to stir for 1 h to form a suspension of the sodium salt. The sulfenyl chloride (1.1 equiv) in dry THF was added dropwise. After stirring for 5 h, the reaction mixture was filtered and the solvent evaporated in vacuo. The product was obtained by chromatography and crystallization.

The other nitrophenylthioindoles **4** were prepared using reaction 1. The products were obtained by recrystallization from ethanol, except for **4ch** which was recrystallized from glacial acetic acid.

Registry No. **1a**, 7669-54-7; **1b**, 37692-14-1; **1c**, 937-32-6; **1d**, 528-76-7; **2g**, 120-72-9; **2h**, 6146-52-7; **4ag**, 72496-78-7; **4bg**, 72496-79-8; **4cg**, 72496-80-1; **4ah**, 72496-81-2; **4ch**, 72496-82-3; **4dh**, 72496-83-4; **4dg**, 72496-84-5.

Fragmentation Reactions of Ylides. 8. Reaction of 2-Alkyloxaziridines with Episulfide and Evidence for the Formation of Thionitrosoalkanes

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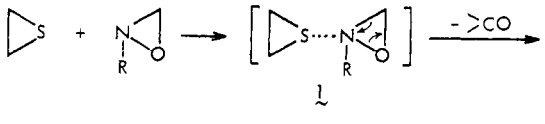
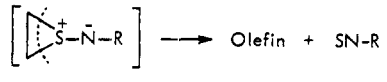
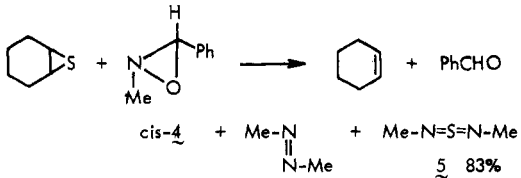
Recently, we found an interesting fragmentation reaction[1] of the oxaziridine ring with nucleophilic reagents in which these reagents exclusively attacked the nitrogen atom of the three-membered oxaziridine ring followed by a fragmentation reaction to form ylides. We also have reported previously on a cheletropic reaction of the ylide derived from the reaction of cyclohexene sulfide and carbene.[2] These findings taken together suggest the possibility that the reaction of episulfide and oxaziridine might occur by a cheletropic reaction to give olefin and the previously unknown thionitrosoalkane **3**.[3] With this in mind, we have studied the reaction of episulfides and 2-alkyloxaziridines and report here our results.

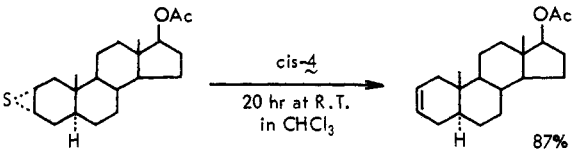


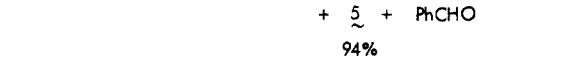


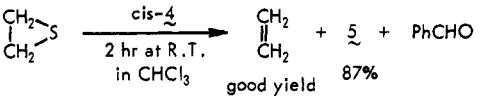
2 **3**

In chloroform solution, cyclohexene cis or trans smoothly in the reaction with a double molar amount of *cis*-2-methyl-3-phenyloxaziridine (*cis*-**4**) at room temperature and gave quantitative yields of cyclohexene and benzaldehyde, 83% of dimethylsulfur diimide (**5**), and a small amount of azomethane. Compound **5** was identified by comparison with an authentic sample.[4] Similar results were observed with ethylene sulfide and a steroidal episulfide.

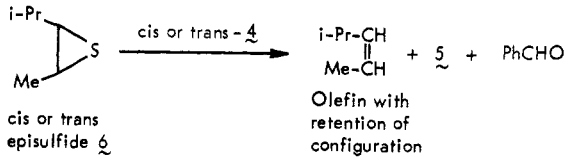




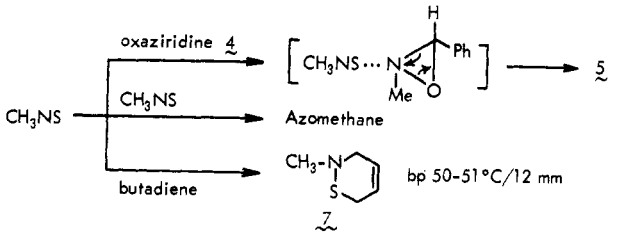




In the reaction of cis or trans isomers of 4-methyl-2-pentene sulfide **6** with *cis*- or *trans*-**4** in chloroform at room temperature, we observed the formation of cis or trans olefin having the same configuration as the starting episulfide in a yield of 80–50%[5] and found that the stereochemical reaction course was completely independent of the configuration of oxaziridines.



In these reactions, compound **5** and azomethane were presumed to arise by reactions of CH_3NS formed in an initial step of the reaction with the second mole of oxaziridine or thionitrosomethane. Evidence for the formation of thionitrosomethane was obtained by isolation of 2-methyl-3,6-dihydro-1,2-thiazine (**7**) when the reaction of



7

cyclohexene sulfide and *cis*- or *trans*-**4** was carried out in the presence of butadiene. The yields of thiazine **7**, sulfur diimide **5**, and azomethane depended on the rate ratio of the competition reaction of thionitrosomethane with butadiene, oxaziridines, and another molecule of thionitrosomethane, respectively. Generally, in the desulfurization reaction of episulfide, *trans*-**4** usually gave a better yield of thiazine **7** than *cis*-**4**. This suggested that thionitrosomethane reacted with another molecule of *cis*-**4** more favorably than with *trans*-**4** due to less steric hindrance.

In a similar reaction using *trans*-2-ethyl- or *trans*-2-isopropyl-3-phenyloxaziridine, we obtained 2-ethyl- or 2-isopropyl-3,6-dihydro-1,2-thiazine. Attempted preparation of the *tert*-butyl derivative of thiazine failed due to the very low reactivity of 2-*tert*-butyl-3-phenyl-

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(2) Y. Hata and M. Watanabe, *J. Am. Chem. Soc.*, **97**, 2553 (1975).
(3) Thionitrosobenzenes were assumed to be reactive intermediates in the decomposition of *N,N*-thiodianiline: P. Tavs, *Angew. Chem., Int. Ed. Engl.*, **5**, 1048 (1966); F. A. Davis and E. B. Skibo, *J. Org. Chem*, **41**, 1333 (1976).
(4) R. Appel and J. Kohnke, *Chem. Ber.*, **104**, 2648 (1971).
(5) Greater than 99% retention by VPC.

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oxaziridine. Unfortunately, our attempt to detect thionitrosomethane directly also failed.[6]

Experimental Section

2-Methyl-3,6-dihydro-1,2-thiazine (7). A mixture of 260 mg (1.93 mmol) of *trans*-2-methyl-3-phenyloxaziridine (4), 221 mg (1.93 mmol) of cyclohexene episulfide and 1 mL (12 mmol) of butadiene in 2 mL of chloroform gave a 69% yield of 2-methyl-3,6-dihydro-1,2-thiazine (7) after 2.5 h of reaction at room temperature: bp 50–51 °C (12 mm); IR 1435 (s), 1410 (m), 1195 (m), 1085 (s), 1010 (m), and 820 (m) cm^{-1}; NMR ($CDCl_3$) δ 6.07 (d, 1 H, =CH), 5.68 (d, 1 H, =CH), 3.47 (m, 2 H, CH_2), 3.20 (m, 2 H, CH_2), 2.85 (s, 3H, CH_3). Anal. Calcd for C_5H_9NS: C, 52.13; H, 7.88; N, 12.16. Found: C, 51.70; H, 7.97; N, 11.89. *cis*-Oxaziridine 4 gave 53% of thiazine 7 under the same reaction conditions.

In a similar procedure without butadiene, the mixture gave 57% of cyclohexene, 71% of benzaldehyde, 25% of azomethane, and 9% of sulfur diimide 5 accompanying 30% of the recovered *trans*-4 after 1 h of reaction at room temperature. The yields described here were determined by VPC or NMR by using undecane or dibenzyl ether as an internal reference. The isolation of thiazine 7 was accomplished by a large-scale experiment with approximately 40% yield. Methylthiazine 7 decomposed slowly during the repeated chromatography purification procedure. In a similar procedure, we obtained 2-ethyl- or 2-isopropyl-3,6-dihydro-1,2-thiazine as a liquid [bp 54–55 °C (9 mm) for the ethyl compoound Et and bp 56–57 °C (6 mm) for the isopropyl compound]. Reaction times, temperatures, and yields of each derivative were 12 h at room temperature and 26% for the ethyl compound and 12 h at 80 °C and 33% for the isopropyl thiazine, respectively.

Dimethylsulfur Diimide (5). The use of 2-methyl-3-(*p*-nitrophenyl)oxaziridine and ethylene sulfide was convenient for the preparation of dimethylsulfur diimide due to its low boiling point. A mixture of 3.6 g (0.02 mol) of *cis*- or *trans*-methyl(*p*-nitrophenyl)oxaziridine and 0.8 g (0.013 mol) of ethylene sulfide was distilled by using a dry ice cooling trap under reduced pressure, and the fraction was redistilled to obtain 5 (bp 90–92 °C) in a yield which varied considerably with the initial mixing conditions. The physical properties coincided well with those of an authentic sample.[4]

Registry No. *trans*-4, 40264-03-7; *cis*-4, 39245-63-1; 5, 13849-02-0; 7, 72952-29-5; 2-ethyl-3,6-dihydro-1,2-thiazine, 72952-30-8; 2-isopropyl-3,6-dihydro-1,2-thiazine, 72952-31-9; cyclohexene episulfide, 286-28-2; cyclohexene, 110-83-8; benzaldehyde, 100-52-7; azomethane, 503-28-6; *trans*-2-isopropyl-3-phenyloxaziridine, 57527-58-9; *trans*-2-ethyl-3-phenyloxaziridine, 57527-57-8; *cis*-methyl(*p*-nitrophenyl)oxaziridine, 28944-73-2; *trans*-methyl(*p*-nitrophenyl)-oxaziridine, 28958-67-0; ethylene sulfide, 420-12-2.

(6) The solution of an equimoler mixture of cyclohexene sulfide and *trans*-4 in $CDCl_3$ at −20 °C did not show any other signal except one of starting materials, diimide 5, and azomethane in NMR. The formation of thiazine 7 was not observed when butadiene was added after the completion of the reaction between episulfide and oxaziridine in chloroform.

Reaction of Pyrroles with Diethyl Azodicarboxylate

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Diethyl azodicarboxylate (DADC) has been widely used as a dienophile, especially to synthesize pyridazine derivatives.[1] Among the diene systems examined, furfural diacetate was the only heterocyclic aromatic compound which reacted with DADC to give a Diels–Alder adduct.[2] The known reactivity of pyrroles as a diene system with dimethyl acetylenedicarboxylate (DMAD)[3] prompted us to determine if a similar type of addition reaction takes place with DADC.

In the present paper we report the reactions of pyrrole and some of its derivatives with DADC in protic and in aprotic solvents.

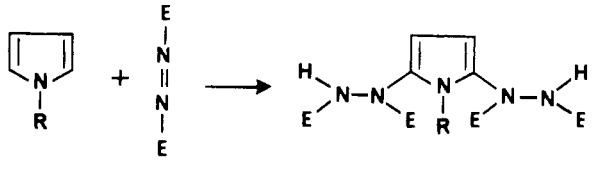
Table I. Yields and Reaction Conditions for Michael-Type Additions of DADC to Pyrroles

pyrrole	R	reflux, h (yield, %) ether	reflux, h (yield, %) ethanol	mp, °C
1a	H	24 (56)	12 (0)[a]	58–60
1b	CH_3	24 (66)	12 (86)	172–173
1c	n-C_4H_9	24 (33)	12 (59)	149
1d	C_6H_5	72 (0)[b]	12 (32)	80–80.5
1e	p-$CH_3OC_6H_4$	48 (9)	12 (52)	162
1f	p-$O_2NC_6H_4$	72 (0)[b]	12 (4)	158–159
1g	2,6-$(CH_3)_2C_6H_3$	72 (0)[b]	12 (17)	128–130

[a] Yellow gummy material was obtained which could not be characterized. [b] No adduct formed even after refluxing in benzene for 72 h.

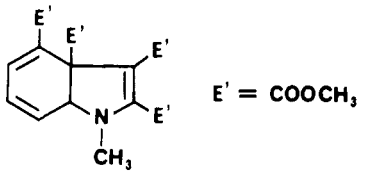
Results and Discussion

Most pyrroles examined in our laboratory gave 1:2 adducts (2) with DADC under the conditions specified in Table I. In contrast to the structure of the product (3) from the reaction with DMAD, adduct 2 was derived from Michael-type addition of DADC at both α positions of the pyrroles. The presence of a band at approximately 3300



1 2

E = $COOC_2H_5$



3

E' = $COOCH_3$

cm^{-1} in the IR spectra of the adducts strongly suggests the presence of a secondary amine. Two distinctive bands at approximately 1745 and 1700 cm^{-1} are consistent with two different carbonyl functions. Structure 2 shows that the ring and the side chains are not conjugated. This is supported by the low λ_{max} values which are between 220 and 235 nm for most of the adducts.

As shown in Table I, the yield of the 1:2 adduct varies depending upon the solvents employed and upon the substituents on the nitrogen of pyrrole. In general, the yields were greater in the protic solvent ethanol than in the aprotic solvents ether or benzene. It has been reported that Michael-type addition takes place when pyrroles react with DMAD.[4] Similarly, the initial addition of DADC to

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