(10) The numbering system used for designating the atoms in **1** was retained for the purpose of simplification and ease of comparison.
(11) For example, 4-*N*-pyrrolidyl-3-penten-2-one, $CH_3COCH{=}C(CH_3)N\text{-}c\text{-}C_4H_8$, has uv max (EtOH) 312 nm (ε 32,000). β-Acetylvinyltrimethylammonium chloride, $CH_3COCH{=}CHN^+(CH_3)_3Cl^-$, has uv max (EtOH) 206.5 nm (ε 7300). On the other hand, ethyl(4-*N*-pyrrolidyl-3-penten-2-ylidene)oxonium iodide, $C_2H_5O^+{=}C(CH_3)CH{=}C(CH_3)N\text{-}c\text{-}C_4H_8\ I^-$, has uv max (EtOH) 302 nm (ε 24,600). See G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **30**, 1407 (1965).
(12) J. G. Roberts, *J. Chem. Soc.*, 176 (1964).
(13) N. J. Leonard and J. A. Adamcik, *J. Am. Chem. Soc.*, **81**, 595 (1959).
(14) R. Huisgen, K. Herbig, A. Siegel, and H. Huber, *Chem. Ber.*, **99**, 2526 (1966).
(15) Ehrlich's reagent, a solution of *p*-dimethylaminobenzaldehyde in acidic solution, is used to characterize two kinds of functional groups. The aldehyde reacts with active methylene groups, such as in barbituric acid [A. Weinschenk, *Ber.*, **34**, 1685 (1901)] and dimedone, to give colors ranging from orange to pink. It also reacts with amino and urea groups to give yellow colors: R. M. Fink, R. E. Cline, C. McGaughey, and K. Fink, *Anal. Chem.*, **28**, 4 (1956).
(16) B. Adcock, A. Lawson, and D. H. Miles [*J. Chem. Soc.*, 5120 (1961)] report mp 106–108° for this compound.
(17) F. Strauss and W. Voss [*Chem. Ber.*, **59**, 1681 (1926)] reported similar behavior for ethyl β-(diethylamino)acrylate, which they prepared by the addition of diethylamine to ethyl propiolate.
(18) P. R. Vagelos and J. M. Earl, *J. Biol. Chem.*, **234**, 2272 (1959).
(19) Ethyl β,β-dimethylacrylate has uv max (EtOH) 217 nm: H. E. Ungnade and I. Ortega, *J. Am. Chem. Soc.*, **73**, 1564 (1950). Ethyl β,β-dimethylthioacrylate has uv max (EtOH) 232 and 265.5 nm: L. B. Bos and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **82**, 157 (1963)].
(20) For cinnamamide, the uv max (EtOH) is 269 nm (ε 26,300) [G. Tsatsas, *Bull. Soc. Chim. Fr.*, 1011 (1947)], while for cinnamylurea uv max (EtOH) is 288 nm (ε 28,200) [R. E. Stuckey, *J. Chem. Soc.*, 207 (1949)].
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(25) These measurements are subject to considerable error because of the complexity of the reaction mixture.
(26) The extinction coefficients were estimated by assuming 100% conversion to enolate anion.
(27) The sample also contains tetramethylammonium cations, mesylate anions, and DMSO-h_6. Although it integrates correctly, this resonance may not be due to the NCH_3 group. This resonance could be hidden under one of the others.
(28) *N*-Methylimidazolidone was prepared from imidazolidone by reaction with sodium hydride and methyl iodide in dimethylformamide. It was crystallized from toluene, mp 112–113.5°. A. N. Smirnov and I. F. Spasskaya found mp 114° from CCl_4 [*Zh. Obshch. Khim.*, **35**, 178 (1965)] and A. M. Fusco, G. J. Del Franco, and E. J. Aranaff report mp 116–116.5° for a vacuum-sublimed sample [*J. Org. Chem.*, **31**, 313 (1966)].
(29) These latter two were probably present in the starting material, which had been exposed to air several times prior to use.
(30) This product consists of both **14a** and **14b** (^{1}H NMR). Apparently **14a** was produced by a facile exchange which took place when absolute ethanol was added to the crude reaction mixture.
(31) In all likelihood **5** was formed by the action of adventitiotious moisture on the reaction mixture. An alternative, however, is that this came about by the action of methoxide on **14b**, a reaction reported by S. Hünig, *Angew. Chem., Int. Ed. Engl.*, **3**, 548 (1964).
(32) The ^{1}H NMR spectrum was obtained on a mixture of the two products.

Trapping of Thiaziridinimines with Heterocumulenes[1]

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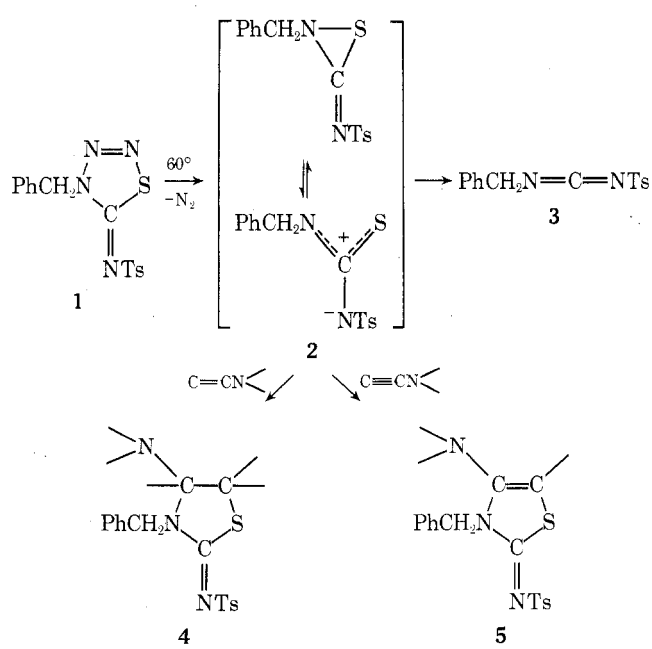
N-Sulfonyliminothiaziridines (e.g., **2**), generated by thermolysis of 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (e.g., **1**) react with ketenes, isocyanates, carbodiimides, and isothiocyanates to give five-membered heterocyclic compounds (**6**, **7**, **8**, and **9**) in good yields. Structure assignment was essentially based on independent synthesis and on comparison of the ^{13}C NMR data with those of pertinent model compounds from the chemical literature.

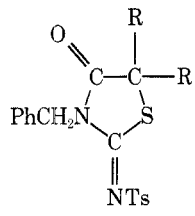
Recently, we reported that thiaziridinimines or their ring-opened dipolar species are formed as intermediates in the synthesis of sulfonylcarbodiimides by thermal decomposition of 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines (e.g., **1** → **2** → **3**).[2] Although **2** was too unstable to be isolated, it could be efficiently trapped with unsaturated systems. Thus, enamines and ynamines produced 4-aminothiazolidines (e.g., **4**) and 4-aminothiazolines (e.g., **5**), respectively. Keto-stabilized phosphorus ylides also trapped the thiaziridinimines to give thiazolines by loss of tertiary phosphine oxides.[2]

Since 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines are readily obtained in good yields from the reaction of sulfonyl isothiocyanates with alkyl azides at room temperature,[2] their decomposition in the presence of unsaturated systems provides a new entry into synthetic heterocyclic chemistry. The present phase of our work involves the use of heterocumulenes as trapping reagents for **2**.

Reaction Products. When 1-benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**) was decomposed at 60–80° in the presence of ketenes, isocyanates, carbodiimides, and isothiocyanates, compounds **6**, **7**, **8**, and **9** were obtained in reasonably good yields. The results are summarized in Table I.

The NMR spectra of the crude reaction mixtures indicated that single products were formed in all cases, except for the reaction of diphenylketene with **1**, which gave **10** (9%, mp 221–223°, C=N at 1525 cm^{-1}) and **11** (16%, mp 234–238°, C=N at 1535 cm^{-1}) in addition to **6a** (major product). Compound **10** results from cycloaddition of **2** with **3** (formed as side product) and compound **11** is formally the cycloaddition product of **2** with tosyl isothiocyanate. We assume that tosyl isothiocyanate is formed in this

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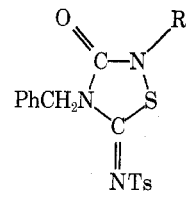
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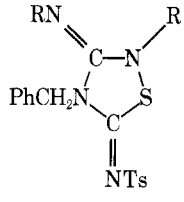
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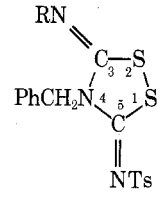
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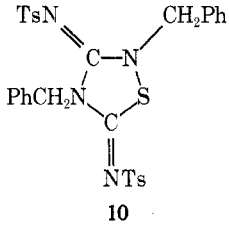
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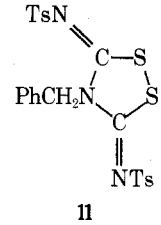
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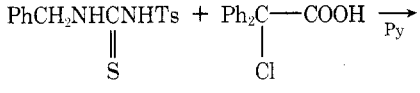
particular case by cycloreversion of 1 during the reaction conditions.

$$1 \xrightarrow[-PhCH_2N_3]{} TsN{=}C{=}S \xrightarrow{2} 11$$

The structures of the adducts were fully supported by elemental analyses, spectral data, and independent syntheses (see below). The presence of an exocyclic C=NTs bond in all the adducts is apparent from the broad and strong ir absorptions at ca. 1530 cm^{-1} (see Table I)[3] and also from the ^{13}C NMR spectra (see below).

Independent Syntheses. Since in principle the thiaziridinimine **2** can add to heterocumulenes in 12 different ways, we have focused on the regiochemistry of the addition products. An independent synthesis of **6a** was realized by treating *N*-benzyl-*N'*-tosylthiourea (**12**) with α-chlorodiphenylacetic acid (**13**) in the presence of pyridine as catalyst.[4]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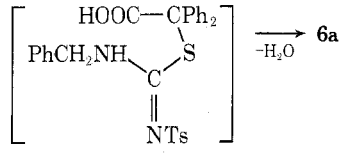
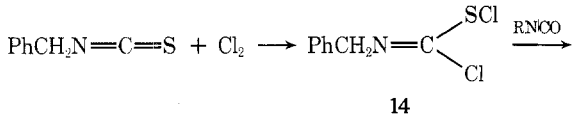

6a

In the thiadiazolidinone series **7**, the three-step procedure of Ottmann and Hooks[5] was utilized to prepare **7b**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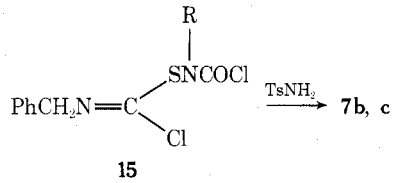
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Table I
Synthesis of Heterocycles from 1 and Heterocumulenes[d]

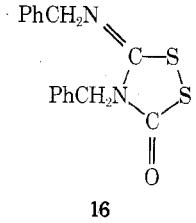
Compd	R	Yield, Method A[a]	Yield, Method B[b]	Mp, °C	Ir, C=N, cm^{-1}
6a	Ph		32–54	142–143	1540
6b	*t*-Bu and CN		40[c]	156–157	1565
7a	Et		66	112–115	1535
7b	*n*-Bu	77	50	117–119	1535
7c	Ph	63	25	160–161	1540
7d	*p*-$MeOC_6H_4$	81		141.5–142.5	1550
7e	*p*-ClC_6H_4	69	17	140–141.5	1540
8a	c-C_6H_{11}	90		103–105	1540, 1655
8b	$PhCH_2$	82		146–147	1525, 1675
8c	Ph	86		147.5–149	1528, 1649
9a	Me	72		168–170	1500, 1645
9b	*n*-Bu	93		101–102.5	1500, 1645
9c	$PhCH_2$	88	40	161–162	1510, 1642
9d	Ph	84		137–138.5	1503, 1627, 1640
9e	*p*-MeC_6H_4	92		144–146	1510, 1628
9f	*p*-ClC_6H_4	50		162–164	1510, 1638

[a] Reactions carried out with a tenfold excess of heterocumulene in the absence of solvent. [b] Reactions carried out with 1 equiv of heterocumulene (0.01 mol) in CCl_4 or benzene (50 ml) as solvent. [c] The yield of **6b** was 70% when 3 equiv of *tert*-butyl cyanoketene was used. [d] Satisfactory analytical values (±0.3% for C, H, N) were reported for all compounds tabulated except **8b,c** and **9a**, for which *m/e* values for the parent ion (±0.3 millimass units) were given. Ed.

and **7c**. Thus, the *S*-chloroisothiocarbamoyl chloride **14**, obtained by chlorination of benzyl isothiocyanate, was treated with *n*-butyl isocyanate or phenyl isocyanate to give the corresponding *S*-(chlorocarbonylamino)isothiocarbamoyl chloride **15**. Upon treatment with tosylamide, **15** was converted into **7b** and **7c**, respectively.

Finally, the structure of **8** was easily proven by acid hydrolysis of **8c**, giving **7c** in 94% yield.

^{13}C NMR Analysis. For convenience in discussing the ^{13}C NMR data, the atoms comprising the five-membered rings are all numbered in the same manner as shown in structure **9**. The absorption values are summarized in Table II. Since the chemical shift value of the C_3 atom of adduct **9** would provide diagnostic proof for the assigned structure, we have prepared three model compounds (**16, 17,** and **18**) whose structures have been unambiguously set-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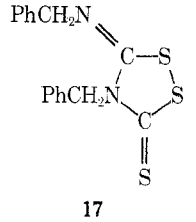
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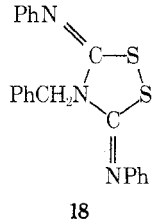
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tled. 3-Benzylimino-4-benzyl-1,2,4-dithiazolidin-5-one (**16**, mp 93–94°) and 3-benzylimino-4-benzyl-1,2,4-dithiazolidine-5-thione (**17**, mp 68–69°) were prepared by the methods of Freund,[6,7] whereas 3,5-bis(phenylimino)-4-benzyl-1,2,4-dithiazolidine (**18**) was obtained during our research on the reaction of benzyl azide with phenyl isothiocyanate. Its symmetric structure is apparent from the ^{13}C NMR data and also from an X-ray analysis reported by Revitt.[9]

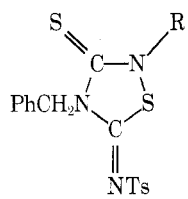
The C_3 atom absorptions of **9** at ca. δ 150 correspond with those of the model compounds **16–18** (see Table II). If addition of **2** would have occurred onto the C=N bond of the isothiocyanate to give **19**,[10] the C_3 atoms would reso-

Table II
^{13}C NMR Data of the New Heterocycles[a]

Compd	C_3	C_5	$PhCH_2N<$	Other shift values
6a	174.4	165.8	47.4	C_2 at 67.2
6b	167.2[b]	163.6[b]	48.2	C_2 at 59, C≡N at 114.5, $(CH_3)_3C$ at 25.2 and 41.3
7a	152.1	164.6	48.3[c]	CH_3CH_2 at 40.1
7b	152.4	164.5	48.4	$C_3H_7CH_2$ at 44.8
7c	150.5	163.8	48.5	
8a	144.5	167.3	48.5	
8b	147.9	167.2	48.8[c]	$PhCH_2N=$ at 51.8,[d] $PhCH_2$ in position 2 at 57.1[c]
8c	142.1	166	49.1	
9b	148.6	166.1	51.9	$C_3H_7CH_2$ at 53.6
9c	150.5	166.1	52.2[c]	$PhCH_2N=$ at 57.1[d]
9d	152.5	166.4	52.2[c]	
10	147.6	164.9	49.9[c]	$PhCH_2$ in position 2 at 55.1[c]
11	167.3	167.3	52.1	
16	148.5	169.2	50.15	$PhCH_2N=$ at 54.3[d]
17	154.6	193.9	53.1	$PhCH_2N=$ at 56.2[d]
18	153.5	153.5	51.1	

[a] All the spectra (δ values in parts per million from Me_4Si) were recorded in $CDCl_3$ except those of **6a** (C_6D_6) and **11** (DMSO-d_6). [b] The reversed assignment is possible. [c] $^1J_{C-H}$ = 142–144 Hz. [d] $^1J_{C-H}$ = 133–135 Hz.

nate at ca. δ 171–175 ppm. This is calculated from the C_3 absorption values of **7a–c** by use of the empirical relationship of Kalinowski and Kessler:[11] $\delta_{C=S} = 1.45\ \delta_{C=O} - 46.5$ ppm.



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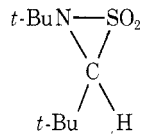
Measurement of the coupling constant $^1J_{C-H}$ for the benzyl methylene groups in **9c** further substantiates its structure. Indeed, the value of $^1J_{C-H}$ is known to be related to the extent of charge localization on the nitrogen atom.[12] In structure **9c**, the imine CH_2 group in position 3 (δ 57.1 ppm) exhibits a coupling constant of 133 Hz whereas the CH_2 group at the 4 position has $^1J_{C-H}$ = 143 Hz. This criterion was further used to assign structure **10** to one of the side-products from **1** and diphenylketene, $^1J_{C-H}$ being 143 Hz for both CH_2 groups.

From the viewpoint of ^{13}C NMR spectroscopy, it is interesting to compare the C=NTs, C=O, and C=S carbon absorptions at the 5 position of **9c, 16,** and **17.** Whereas the chemical shift value of C=NTs (δ 166 ppm) is comparable with that of C=O (δ 169 ppm) in this homologous series, the C=S absorption in **17** is found at lower field (δ 193.9 ppm). This value, however, is in good agreement with the estimated value (δ 198.5 ppm) obtained by applying the empirical equation of Kalinowski and Kessler.[11]

After our work had been completed, Neidlein and Salzmann[13] also reported on this topic, apparently without knowledge of our previous work.[2]

It is also interesting to note that the first thiaziridine derivative **20** has been isolated recently in 43% yield by Quast and Kees[14] from the reaction of *N*-sulfonyl-*tert*-butylamine and *tert*-butyldiazomethane.



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Experimental Section

The ir spectra were taken on a Perkin-Elmer Model 157G spectrometer. Proton NMR spectra were recorded with a Jeol MH-100 or Varian XL-100 spectrometer using Me_4Si as an internal reference. For ^{13}C NMR spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation.

1-Benzyl-5-tosylimino-1,2,3,4-thiatriazoline (**1**) was prepared as reported[2] by the reaction of benzyl azide with 1 equiv of tosyl isothiocyanate in CCl_4 at room temperature.

General Procedure for the Preparation of 6, 7, 8, and 9. Compound **1** (0.01 mol) was thermolyzed at 60° in the presence of a tenfold excess of heterocumulene for 2 hr and then heated at 80° for another 1 hr. The excess of heterocumulene was distilled off in vacuo and the residue was crystallized from ether (**7** and **8**) or from MeOH (**9**).

For the reaction of **1** with diphenylketene, the residue, after evaporation of the solvent, was fractionally crystallized from MeOH to give **6a, 10,** and **11.**

In the case of **6b**, *tert*-butyl cyanoketene was first generated in situ by thermolysis of 2,5-di-*tert*-butyl-3,6-diazidobenzoquinone (1 g) in dry benzene (30 ml) as reported by Moore and Weyler.[15] After cooling to room temperature, the thiaziridinimine precursor **1** (2.3 g) was added and the solution was heated at 70° for 2 hr. The solvent was removed in vacuo, and the residue was dissolved in ether or methanol (30–40 ml) and then cooled to give **6b.**

Independent Synthesis of 6a. Equimolar amounts (0.006 mol) of **12** and **13** were dissolved in CCl_4 (10 ml) containing 0.5 ml of pyridine. The solution was heated to reflux for 72 hr. After cooling to room temperature, 20 ml of CCl_4 was added to the heterogeneous mixture and the CCl_4 layer was separated and dried over $MgSO_4$. After removal of the solvent, the residue was crystallized from MeOH to give white crystals of **6a** in 72% yield.

Independent Synthesis of 7b and 7c. Nearly 1 equiv of chlorine was added to a solution of benzyl isothiocyanate (0.03 mol) in dry pentane (20 ml) at ca. −10°. After the excess of chlorine was removed in vacuo at 0°, the residue (**14**) was dissolved in dry pentane. To this solution phenyl isocyanate (0.03 mol) in pentane was added dropwise at ca. 10° during a period of 30 min. The mixture was allowed to react for another 1.5 hr and the slurry (containing **15**) was then dissolved in THF (100 ml). To this solution tosylamide (0.03 mol) in THF (25 ml) containing 6 g of NEt_3 was added with stirring at room temperature. After a reaction time of 2 hr, the precipitate (NEt_3·HCl) was removed by filtration and the mother liquor was evaporated in vacuo to give a yellow oil (**7b**) which was crystallized from MeOH (10 ml), overall yield 56%.

Compound **7b** (overall yield 35%) was obtained in a similar manner by using *n*-butyl isocyanate instead of phenyl isocyanate.

Acid Hydrolysis of 7c. A solution of **7c** in ethanol (0.5 g in 20 ml) containing 5 ml of H_2SO_4 was heated at reflux for 1 hr. The precipitate was filtered off, washed with water, dried, and crystallized from MeOH–$CHCl_3$, yield 94%.

Synthesis of 18. A mixture of phenyl isothiocyanate (0.1 mol)

and benzyl azide (0.2 mol) was heated at 100° until gas evolution ceased (72 hr). Addition of ether furnished **18** (55%) which was crystallized from ether–petroleum ether, mp 151–153°, ir (KBr) 1610 cm^{-1}.

Acknowledgment. We thank Dr. E. Van Loock for having carried out some preliminary experiments in this field. We are also indebted to the F. K. F. O. (Belgium) for financial support.

Registry No.—**1**, 42770-61-6; **6a**, 54999-84-7; **6b**, 54999-85-8; **7a**, 54999-86-9; **7b**, 54999-87-0; **7c**, 54999-88-1; **7d**, 54999-89-2; **7e**, 54999-90-5; **8a**, 54999-91-6; **8b**, 54999-92-7; **8c**, 54999-93-8; **9a**, 54999-94-9; **9b**, 54999-95-0; **9c**, 54999-96-1; **9d**, 54999-97-2; **9e**, 54999-98-3; **9f**, 54999-99-4; **10**, 55000-00-5; **11**, 55000-01-6; **12**, 53016-96-9; **13**, 7475-56-1; **14**, 55000-02-7; **15** (R = *n*-Bu), 55000-03-8; **15** (R = Ph), 55000-04-9; **16**, 55000-05-0; **17**, 21494-82-6; **18**, 55000-06-1; diphenylketene, 525-06-4; *tert*-butyl cyanoketene, 29342-22-1; ethyl isocyanate, 109-90-0; *n*-butyl isocyanate, 111-36-4; phenyl isocyanate, 103-71-9; *p*-methoxyphenyl isocyanate, 5416-93-3; *p*-chlorophenyl isocyanate, 104-12-1; dicyclohexylcarbodiimide, 538-75-0; dibenzylcarbodiimide, 6721-03-5; diphenylcarbodiimide, 622-16-2; methyl isothiocyanate, 556-61-6; *n*-butyl isothiocyanate, 592-82-5; benzyl isothiocyanate, 622-78-6; phenyl isothiocyanate, 103-72-0; *p*-tolyl isothiocyanate, 622-59-3; *p*-chlorophenyl isothiocyanate, 2131-55-7; benzyl azide, 622-79-7.

References and Notes

(1) Part of this work has been communicated at the VI International Symposium on Organic Sulphur Chemistry, Bangor, July 1974, and presented in a plenary lecture at the congress on Aziridines in Nice, Dec 1974.
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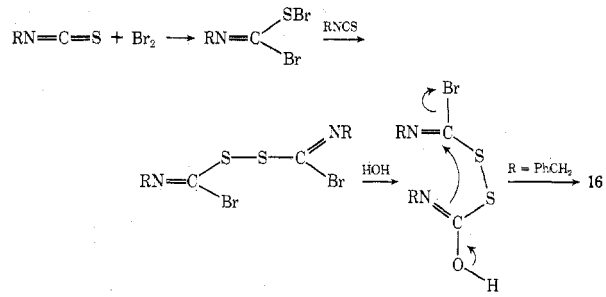
(7) Over 80 years ago, Freund[6] reported the reaction of isothiocyanates with bromine in the presence of some water to give a product of empirical formula $(RNCS)_2O$. Only very recently its correct structure (e.g., **16**) was elucidated,[8] but the mechanism of this unusual reaction remains to be resolved. Based on the work of Ottmann and Hooks,[5] we propose the following mechanism.



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2-Dialkylphosphonyl- and 2-Alkylidene-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines

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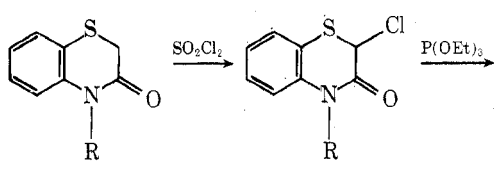
2-Chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines have been shown to react with triethyl phosphite in a Michaelis–Arbuzov manner to give the 2-phosphonates. These latter compounds react readily with aldehydes and ketones to give the 2-alkylidene derivatives. The olefins from aldehydes are assigned the *Z* stereochemistry on the basis of NMR data.

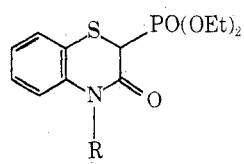
The reaction of various α-halocarbonyl systems with phosphorus nucleophiles has been well investigated. α-Haloamides normally react with trialkyl phosphites in a Michaelis–Arbuzov fashion to give phosphonates unless special structural requirements are met.[1-6] Although the possible influence of an α-thioether group in this reaction has not been reported previously, an α-thioether group generally is believed to enhance SN2 reactivity,[7] which is the usual mechanism of the Michaelis–Arbuzov reaction.

We now wish to report on the reaction of triethyl phosphite with 2-chloro-3,4-dihydro-3-oxo-2*H*-1,4-benzothiazines (**2**), a cyclic α-haloamide system bearing an α-thioether linkage, and on the utility of the products of this reaction in a new general route to alkylidene benzothiazines.



1 **2**

a, R = H
b, R = Me
c, R = CH_2CO_2Et



3

Results and Discussion

Reaction of 2 with Triethyl Phosphite. The three chlorobenzothiazinones **2a–c** were obtained from treatment of the corresponding **1** with 1 equiv of sulfuryl chloride. Reaction of **2** with neat, excess, refluxing triethyl phosphite gave the analogous phosphonate (Michaelis–Arbuzov product) in good yield. The structure of **3** is confirmed in each case by the observation of an infrared band for the amide carbonyl group at 1660–1675 cm^{-1} and a ^1H NMR signal for the 2-H as a doublet at δ 4.57–4.35 with J_{H-P} = 21.2–22.6 Hz.

Thus, in this case the presence of an α-thioether group