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OFFICE OF RESEARCH ADMINISTRATION
RESEARCH PROJECT INITIATION

Report
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Date: May 29, 1974

Project Title: **The Chemistry of N-Sulfonylamines**

Project No: **G-33-678**

Principal Investigator **Dr. Edward M. Burgess**

Sponsor: **Public Health Service**

Agreement Period: From June 1, 1974 Until May 31, 1976

Type Agreement: **Grant No. 2 R01 GM12672-07A1 MCHB**

Amount: **\$ 93,852 PHS**
10,332 GIT G-33-358
\$104,184 Total

Reports Required: **Annual Progress; to be submitted with renewal.**
Final Progress; if project is not renewed.

Sponsor Contact Person (s):
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Deputy Associate Director
for Program Activities
National Institute of General
Medical Sciences
National Institutes of Health
Bethesda, Maryland 20014

Assigned to: **Chemistry**

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Date: June 6, 1978

Project Title: The Chemistry of N-Sulfonylamines

Project No: G-33-678

Project Director: Dr. Edward M. Burgess

Sponsor: DHEW/PHS/NIH National Institute of General Medical Sciences

Effective Termination Date: 8/31/77 (Grant Expiration)

Clearance of Accounting Charges: n/a - account closed

Grant/Contract Closeout Actions Remaining: none

- Final Invoice and Closing Documents
- Final Fiscal Report
- Final Report of Inventions
- Govt. Property Inventory & Related Certificate
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- Other _____

Signed to: Chemistry (School/Laboratory)

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SECTION IV—SUMMARY PROGRESS REPORT		2 R01 GM 12672-07A1	
PRINCIPAL INVESTIGATOR OR PROGRAM DIRECTOR (Last, First, Initial)		PERIOD COVERED BY THIS REPORT	
Burgess, Edward M.		FROM	THROUGH
NAME OF ORGANIZATION		06-01-74	05-31-75
Georgia Institute of Technology			
TITLE (Repeat title shown in Item 1 on first page)			
THE CHEMISTRY OF N-SULFONYLAMINES			

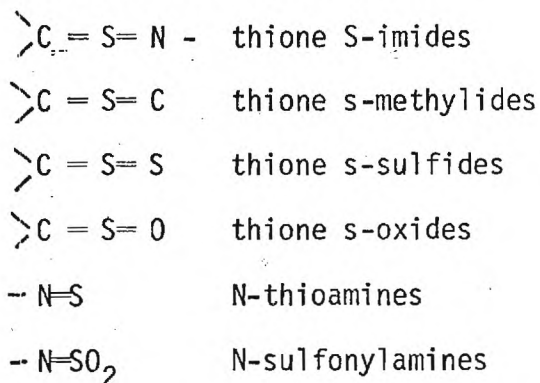
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1.(a) Synthesis and Cycloaddition Reactions of Fluorenothione S-Benzoylimide.
 E. M. Burgess and H. R. Penton, Jr., J. Org. Chem., 39, 2885 (1974)
 (Work done under grant 12672-06) (b). none, but a number in preparation.

2. none

3. Progress Report

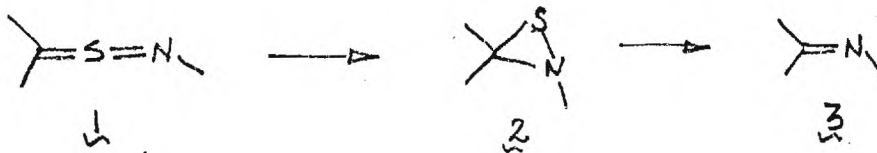
1a. The synthesis and reactions of new functional groups containing sulfur is the overall objective of this project. The number of new groups studied has expanded considerably over those proposed in the original application. Currently under investigation are:



and (b) studies on the above will continue.

2. Recent Developments:

1. Thiaziranes and Thione S-Imides. Our continued interest in the thione S-imide (1) ⇌ thiazirane (2) isomerization followed by thermal extrusion of sulfur to give an imine (3) has led us to search for derivatives of 1 which would possibly provide 2 by a photochemical process at such a low temperature that a least spectroscopic observation of this heterocycle might be realized. This



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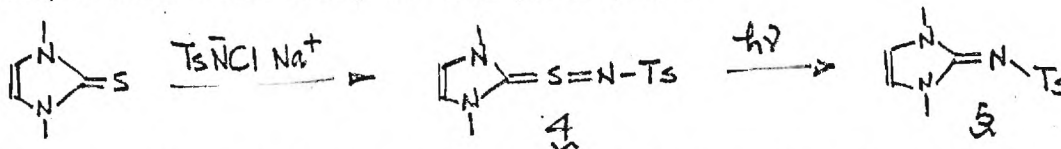
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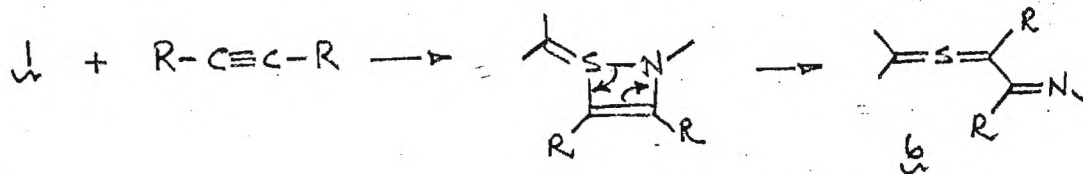
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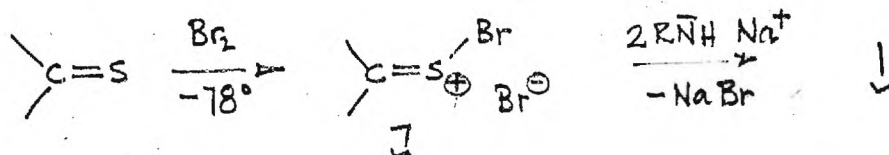
goal was achieved when 4, prepared by the reactions shown, was found to photochemically (also thermally at 100°) give 5 at -36°. We are currently involved in a low temperature H-nmr study of this photolysate.



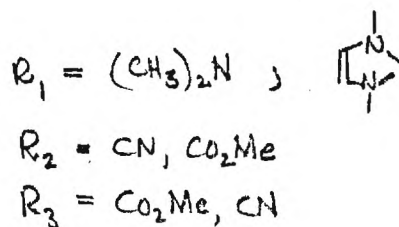
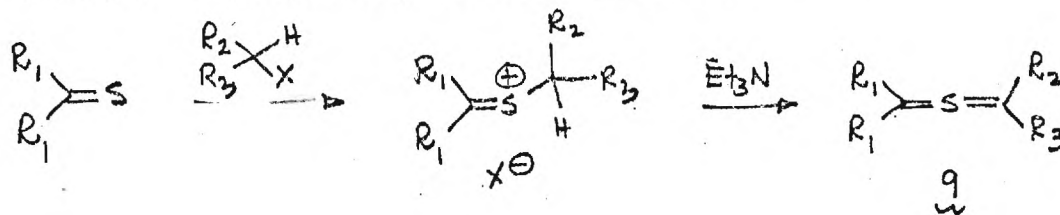
cycloaddition reactions of 1 with acetylene dicarboxyate derivatives give stable thione methylides of the type 6.



A new synthetic route to this functional group involving 7 as a key isolable intermediate has been developed.



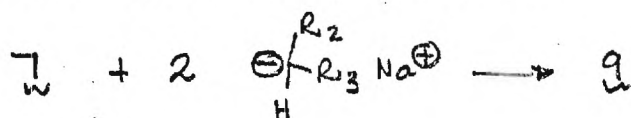
2. Thiocarbonyl Ylids. We have extended our synthetic schene (8→9) to produce a number of "push-pull" substituted ylids as shown below.



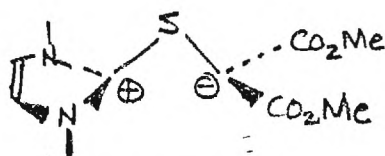
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Such ylides are also available via 7 in good yield.

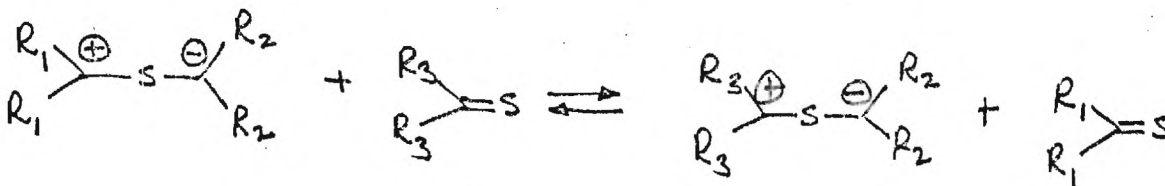
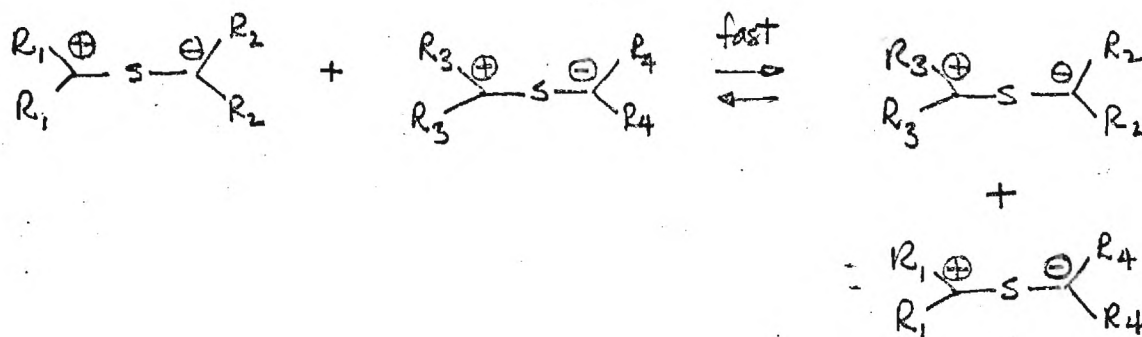


A x-ray crystallographic examination of 10 reveals the unusual structure below,



which is not in accord with the theoretically predicted "allyl anion" conjugated π -structure but represents a true 1,3-dipole electrostatically stabilized ylide of a type never observed before (but often proposed as a reactive intermediate).

Thione methylides have been found to undergo a number of unusual and facile exchange reactions:



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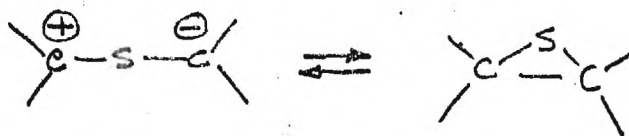
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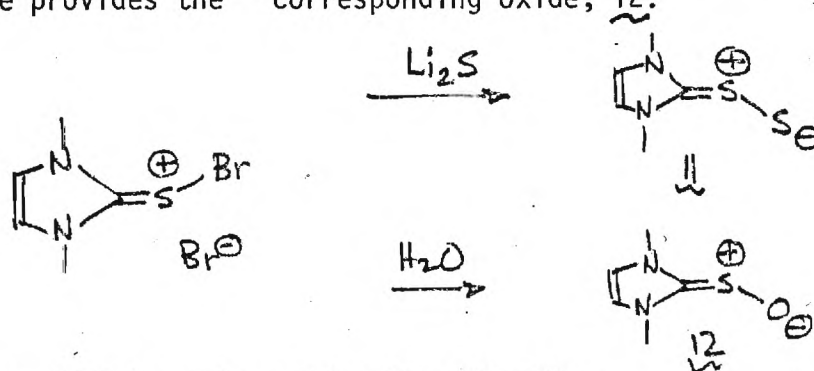
and utilizing the latter as a synthetic route to new ylides unobtainable via other methods we have been able to prepare

a thione ylide which is in valence tautomeric equilibrium with a thiirane:



3. Thione S-sulfides and oxides.

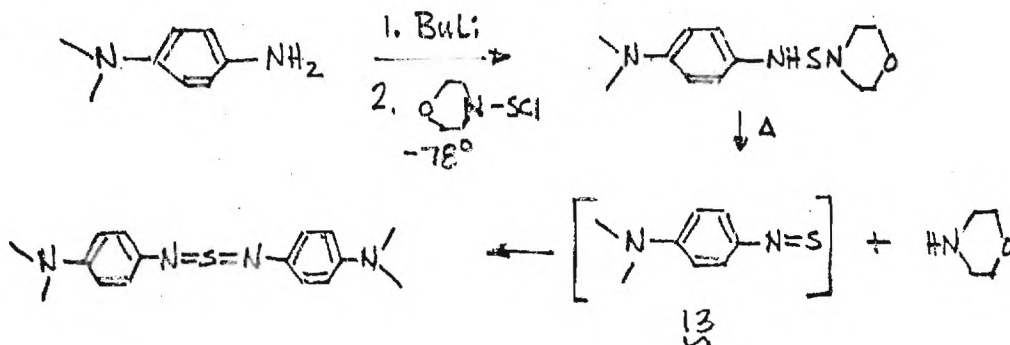
Treatment of 10 with Li_2S gives this new functional group as 11 and hydrolysis likewise provides the corresponding oxide, 12.



The chemistry of 11 is under active investigation.

4. N-Thioamines.

The following sequence has been demonstrated and attempts to isolate the intermediate N-thioamine, 13, is being pursued.

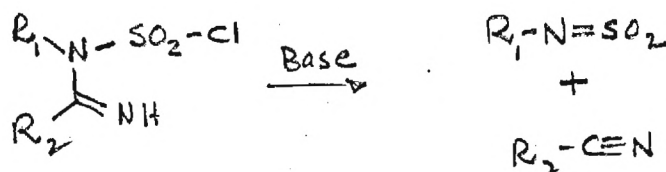


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4. N-Sulfonylamines.

Studies of the fragmentation reaction,



are underway and it is hoped that this reaction will provide a usable synthetic route to N-Sulfonylamines incapable of preparation by other routes.

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Burgess, Edward M.		FROM	THROUGH
NAME OF ORGANIZATION		06-1-75	02-29-76
Georgia Institute of Technology			
TITLE (Repeat title shown in Item 1 on first page)			
The Chemistry of N-Sulfonylamines			

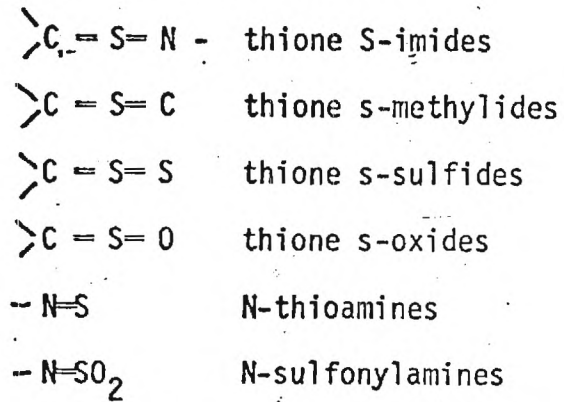
1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

1. Two communications submitted to J. Amer. Chem. Soc. but not yet in press.

2. none

3. Progress Report

1a. The synthesis and reactions of new functional groups containing sulfur is the overall objective of this project. The number of new groups studied has expanded considerably over those proposed in the original application. Currently under investigation are:



and (b) studies on the above will continue.

2. Recent Developments:

Our completed studies on thione S-methylides are summarized in the following two preprints.

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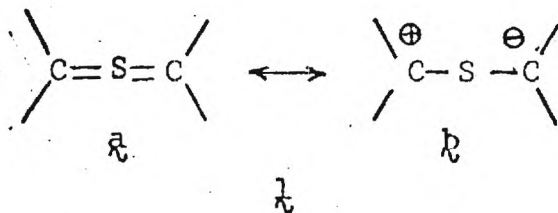
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Syntheses and Reactions of
Substituent Stabilized Thione Methylides

Theoretical consideration of adjacent charge stabilization by sulfur d-orbital conjugation or polarization¹ and the mode of electronic transmission in π -systems containing sulfur has stimulated recent efforts to synthesize various thione ylides (λ) in order to answer some of these questions.² From earlier work unperturbed noncyclic thione ylides appear to be unstable with respect to an electrocyclization to their thiirane valence tautomers^{2a} whereas substitution by a combination of π -electron donating and accepting groups ("push-pull") provides sufficient charge stabilization of contributor λb to allow isolation of some representatives of this ylide system.³ In this communication we wish to report on some stable thione methylene general synthetic routes and chemical reactions.



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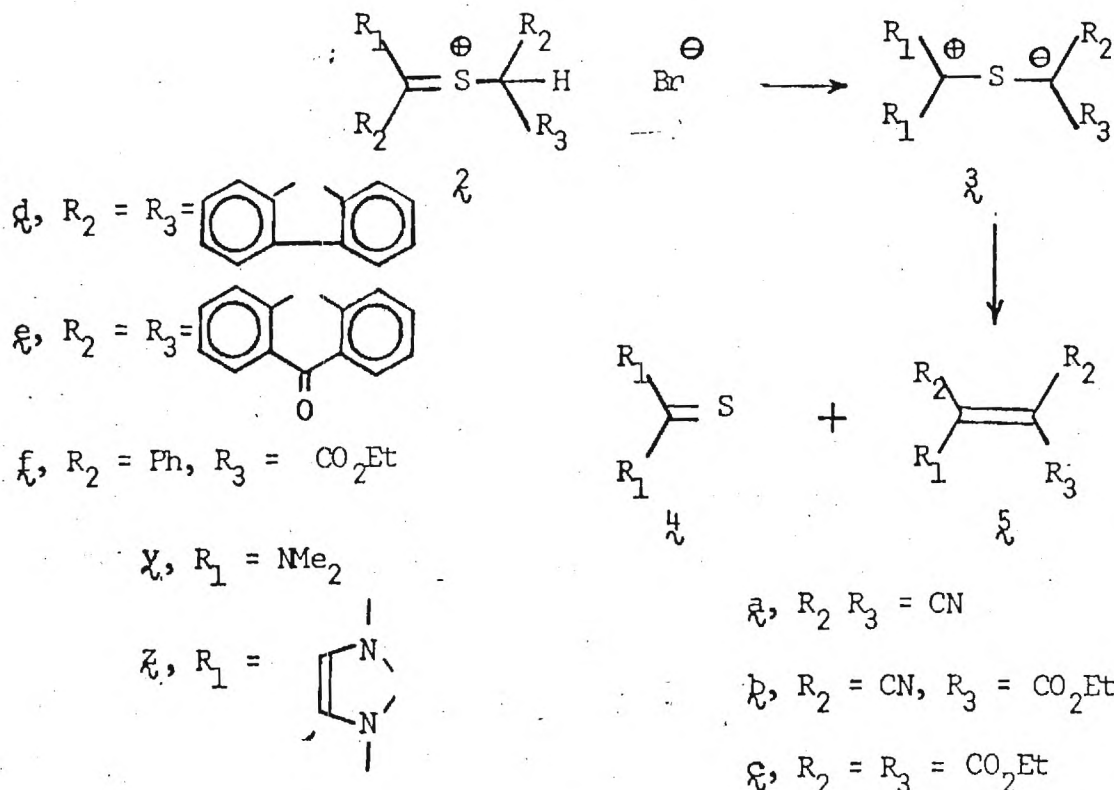
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The Chemistry of N-Sulfonyl Thioureas

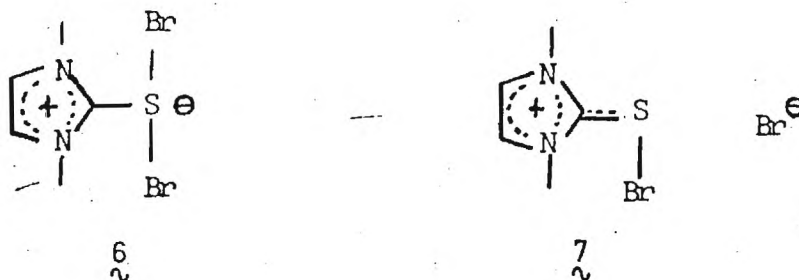
One synthetic approach was derived from consideration of the requirement for stabilizing substituents and led to selection of thiouronium salts as central intermediates whose base catalyzed deprotonation would provide 1 .⁴ Tetramethylthiourea and *N,N'*-dimethylimidazolethione⁵ were converted to the corresponding *S*-alkylthiouronium salts 2 , by reaction with the appropriate alkyl bromide in $MeCl_2$ solution at 30° . Treatment of these salts with an equivalent of triethylamine in $MeCl_2$ or THF solution at temperatures between -78° to 30° led to the immediate formation of the thione methylides, 3 , and triethylamine hydrobromide. Only ylides $3ya-c$ and $3za-c$ could be isolated at room temperature as crystalline solids which were characterized by



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their absorption in the ir (CHCl_3) at $1650\text{--}1700\text{ cm}^{-1}$ ($\text{C}=\text{O}$) or $2120\text{--}2140\text{ cm}^{-1}$ ($\text{C}\equiv\text{N}$) and consistent mass spectra.⁶ Deprotonation of salts 2y,z-d,f with triethylamine in THF at -78° produced solutions of transient ylides which upon warming to ca. -30° led to the formation of 4 and 5.⁷ The decomposition reaction observed for unstable thione methylides is analogous to those reported for many simple 1,2-sulfonium methylides.⁸ No products derived from electrocyclic closure to a thiirane were apparent in such ylide decompositions.

As an alternative approach to the general construction of such "push-pull" substituted ylides we have investigated the possibility of displacement at sulfur by carbon bases on the sulfurane 6.⁹ Our



original expectations as to the potential substitution site were realized when, for example, 6 underwent reaction with two equivalents of sodio-diethylmalonate in THF solution at 0° to provide 3zc.⁷ Such a sulfur ligand exchange reaction parallels those reported for other sulfuranes and probably involves the intermediacy of cation 7 which accepts a nucleophile at sulfur and not carbon.¹⁰

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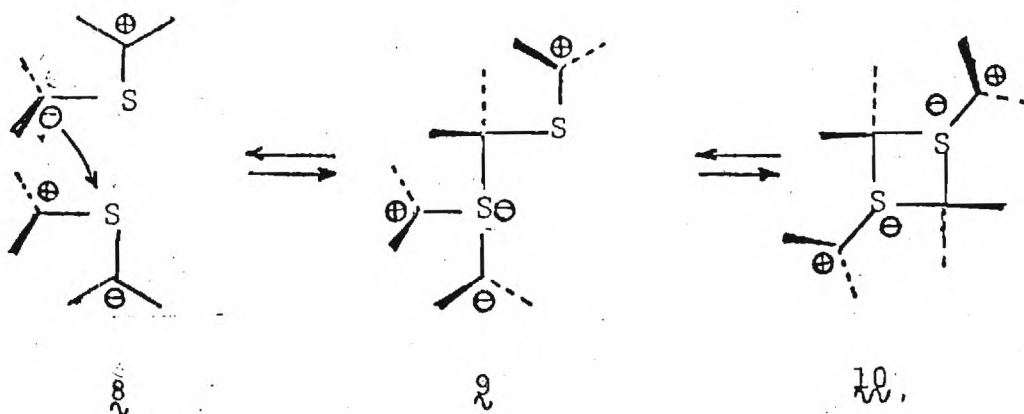
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The Chemistry of N-Sulfonylamines

Upon admixture in MeCl_2 solution at 30° a pair of thione methylides which are differentiated by nonidentical sets of π -donor and acceptor substituents undergo rapid ($t_x < 5$ min) exchange of the latter substituent. For example, $3za$ reacts with $3vc$ to afford $3ya$ and $3zc$, furthermore, the direction of this exchange reaction is enforced by the ready decomposition of $3ya$ to $4y$ and $5a$.¹¹ Similar ligand exchange reactions have been reported for sulfonium methylides and a degenerate ligand exchange mechanism has been suggested to account for the facile racemization of chiral sulfur in certain of these ylides.¹² The mechanism of substituents stabilized thione methylene multiple ligand exchange may be rationalized by a sequence ($8 \rightarrow 10$) whose critical first step requires hypervalent bonding at sulfur rather than attack at the π -donor substituted carbon atom.¹³ The

intermediate 10 which resembles a bisulfurane stabilized by equatorial π -acceptor substituents but with considerable angle deviation in the apical CSC bonding system can fragment in two possible modes to effect the overall exchange observed. The proposed CS bonding established in 8 is supported by an inspection of the frontier HOMO and



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and LUMO eigenvectors for a model ylide as determined by a SCF-CNDO2 calculation.¹⁴ The HOMO is primarily the carbanion P_x orbital while the LUMO has a greater sulfur P_y contribution than the carbocation P_y (Fig. 1)¹⁵ which suggests initial CS union to form sulfurane \mathfrak{g} is the controlling frontier orbital interaction and the same argument

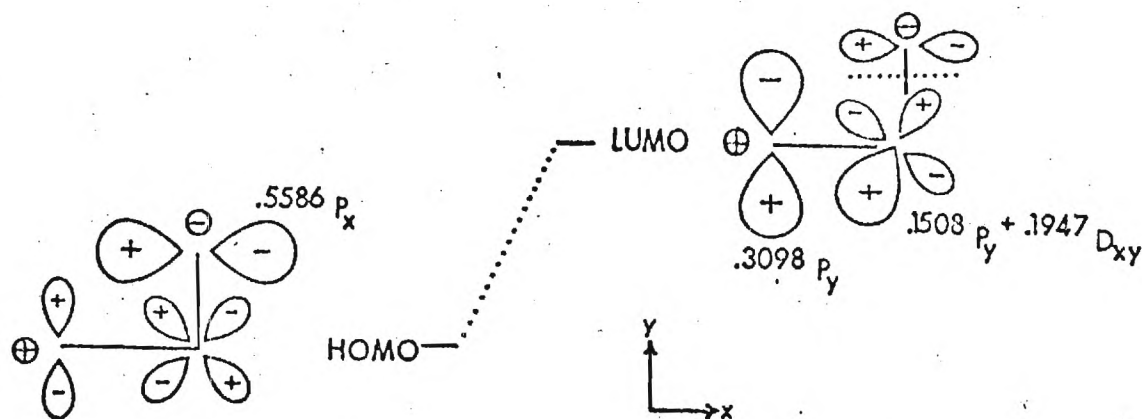


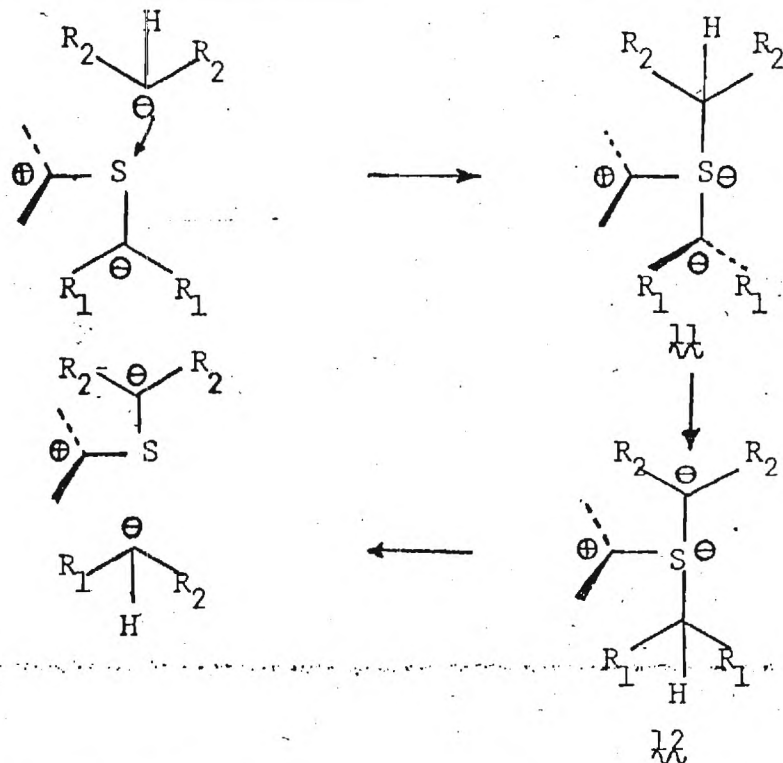
Figure 1. Representation of the HOMO and LUMO of \mathfrak{g} with calculated coefficients. The energy separation is ~ 11 eV.

also applies to $\mathfrak{7}$. In a related reaction equivalents of $\mathfrak{3va}$ and sodio-diethylmalonate in THF solution at 30° gives $\mathfrak{3vc}$ and malononitrile.⁷ Again, we visualize this ligand displacement process as proceeding through hypervalent intermediates $\mathfrak{11}$ and $\mathfrak{12}$.¹⁶ Finally, the thione

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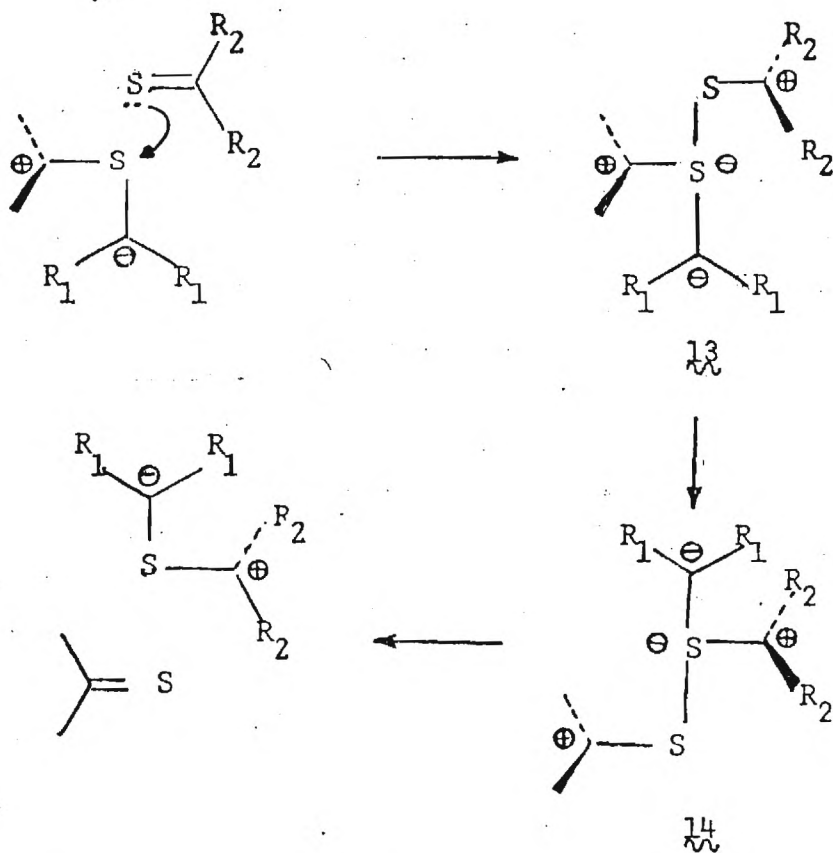
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methylides derived from N,N'-dimethylimidazolethione as a precursor undergo a facile reaction with tetramethylthiourea in MeCl₂ solution at 0-30° to afford this bis (dimethylamino)-substituted ylides.⁷ This process, which is equivalent to ligand transfer between ylide and thione, appears to proceed in a direction to provide the ylide with the less effective π-electron donor substituents. Rationalizing this behavior in a manner consistent with the other observed multiple ligand exchange and displacement reactions requires an intermediate 13 in which the equivalent of a 1,2-shift of the π-electron rich group occurs to give 14. The driving force for the shift being the formation of the most stable sulfurane as determined by the electron withdrawing ability of the equatorial substituent. In conclusion, the general features of the chemistry of highly perturbed thione methylides

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closely resemble those of sulfuranes and are certainly unlike those of the unperturbed congeners.

REFERENCES AND NOTES

- (1) For an excellent discussion, see C.A. Coulson, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XVI. Theoretical Chemistry, 1973, pp. 61-117.
- (2) Especially noteworthy are the studies of (a) R.M. Kellogg, S. Wassenaar, and J. Butler, *J. Org. Chem.*, 37, 4045 (1972); (b) M. P. Cava and G.E.M. Husbands, *J. Amer. Chem. Soc.*, 91, 3952 (1969). See also E. M. Burgess and H. R. Penton, Jr., *J. Org. Chem.*, 39, 2885 (1974).

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- (3) Thione methylides have been isolated from the reaction of trithiones with electrophilic diazo compounds [S. Tamagaki and S. Oae, Tetrahedron Letts., 1159 (1972)] and from thioureas and 2,2-dicyano-3,3-bis(trifluoromethyl) oxirane [W.J. Middleton, J. Org. Chem., 31, 3731 (1966)].
- (4) This approach was reported to be unsuccessful by earlier workers. M. Takaku, S. Mitamura, and H. Nozaki, Tetrahedron Letts., 3651 (1969).
- (5) R. Grigg, T. J. King and G. Shelton, Chem. Comm., 56 (1970).
- (6) Satisfactory ($\pm 0.3\%$) elemental analyses (C,H,N,S) have been obtained for all new isolated compounds.
- (7) Identified by mixture melting point and/or ir spectral comparison with authentic samples.
- (8) E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 84, 3782 (1962), 87, 1353 (1965); A. W. Johnson, V. J. Hruby, and J. L. Williams, ibid., 86, 918 (1964); V. Franzen and H. E. Driessen, Chem. Ber., 96, 1881 (1963); C. G. Swain and E. R. Thornton, J. Amer. Chem. Soc., 83, 4033 (1961).
- (9) A. J. Arduengo and E. M. Burgess, unpublished results.
- (10) J. C. Martin and L. J. Kaplan, ibid., 95, 793 (1973); J. C. Martin and R. J. Arhart, ibid., 93, 2339 (1971).
- (11) We exclude an ylide to carbene dissociative mechanism by our failure to obtain trapped carbene products with added thioethers or alkenes.
- (12) H. Nozaki et.al., Tetrahedron, 23, 4279 (1967).
- (13) This proposal has certain features in common with the proposed mechanisms for ciral sulfoxide and sulfimide interconversions. D. J. Cram, F. G. Yamagishi, D. R. Rayner and E. T. Zwicker, J. Amer. Chem. Soc., 95, 1916 (1973); D. J. Cram, D. C. Garwood and M. R. Jones, ibid., 95, 1925 (1973).
- (14) The geometrical parameters used were those of $\lambda\lambda C$ as determined by x-ray crystallography. A. J. Arduengo and E. M. Burgess, ibid., 97, 0000 (1976).
- (15) The calculated composition of π -LUMO at sulfur is $.1508P_x - .1947d_{xy} - .0567P_x$ and the resultant hybrid is shown in Fig. 1.
- (16) An analogous mechanism has been used for ligand displacements at selenium in ylides. S. Tamagaki and H. Nozaki, Tetrahedron Letts.

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TITLE (Repeat title shown in Item 1 on first page)			
The Chemistry of N-Sulfonylamines			

1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

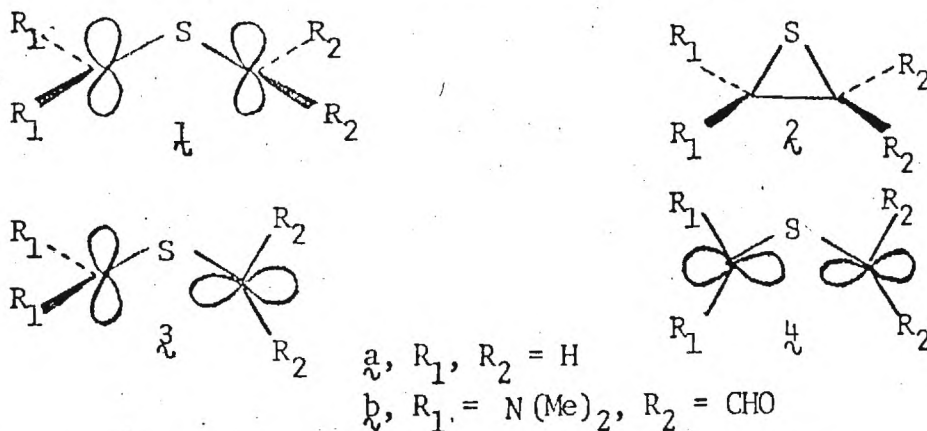
The Structure of a Substituent Stabilized
Thione Methylide

The pericyclic chemistry observed for 1,3-dipolar ylides $(R_2C=X-CR_2)$ containing certain first row central atoms ($X=N,O$) has correlated using the occupied π -molecular orbitals associated with an "allyl anion" bonding model requiring a planar geometry for the substituted ylide.¹ Extension of this model to define the stereochemistry of second row ($X=S$) symmetrically substituted thione methylide electrocyclic closures to thiiranes has been successful.² The potential surface for conrotation of a thione methylide (1) to thiirane (2) is to the first approximation dependent upon the energetic behavior of key high-lying molecular orbitals as determined by symmetry conservation (Woodward-Hoffman).³ The alteration of this surface by a large deviation from symmetry could possibly provide intermediates of lower energy than either end-point reactant as well as change the preference for a particular ring closure mode as indicated by a recent theoretical investigation.⁴ Snyder has calculated the shape of the one dimensional

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surface (Fig. 1) for the conversion of an unperturbed symmetric planar thione methylide, $1a$, to the corresponding thirane $2a$, using a conrotatory motion (the forbidden disrotatory transition state lines >7 kcal/mole above the allowed one) in agreement with the observed stereochemistry.³ We have examined this analogous surface for the closure of an asymmetric thione methylide $1b$ perturbed with π -donor (R_1) and acceptor (R_2) substituents using an energy-geometry optimized SCF-MINDO3 procedure.⁵ The results (Fig. 1) reveal a striking departure from the unperturbed system with both end-point structures of higher energy than a non-planar intermediate, $3b$. The local surface in the vicinity of $3b$ is reasonably flat with rotamers such as $4b$ lying only 1.4 kcal/mole above $3b$ and configuration interaction with the first doubly excited state lowered but failed to reorder these energies.⁶

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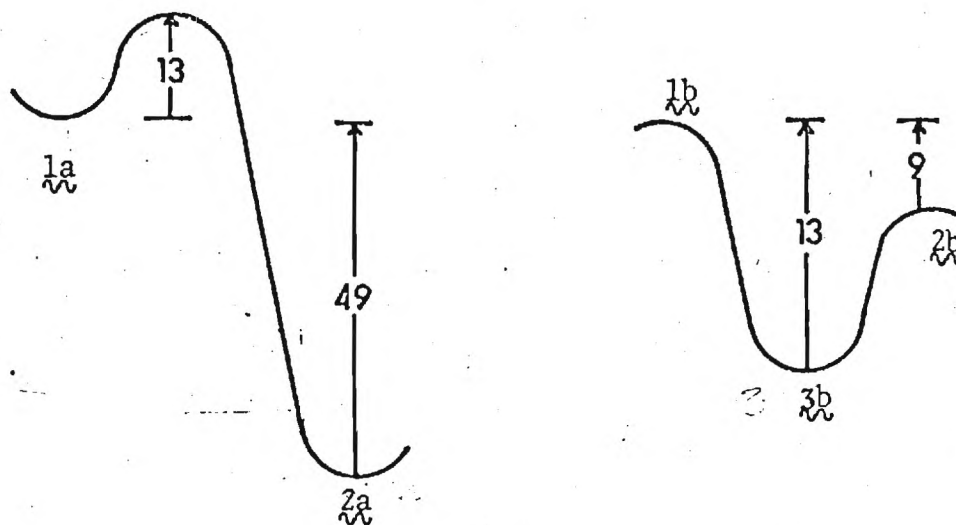


Figure 1. Potential Surfaces for the conversion of unperturbed (right) and perturbed (left) thione methylides to thiiranes. The energy differences are shown in kcal/mole.

The critical molecular orbital whose energy contributes most to re-ordering the total calculated energy of the planar ylides, $1a$ and $1b$ relative to their respective nonplanar conrotated transition state or intermediate structures is the highest occupied molecular orbital, π_2 . The substituent perturbation on this orbital shifts the node toward the π -acceptor substituted carbon thus increases the electron density on sulfur and raises in π_2 the antibonding character relative to the symmetric structure. The small total energy separation of 3 and 4 is derived from the difference that the π -donor substituted carbon p_{π} -orbital experiences upon interaction with either the in or out-of-plane sulfur lone pair orbital. With the above theoretical analysis in mind

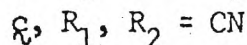
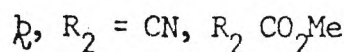
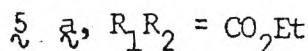
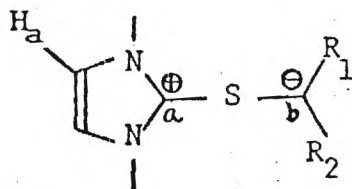
SECTION IV

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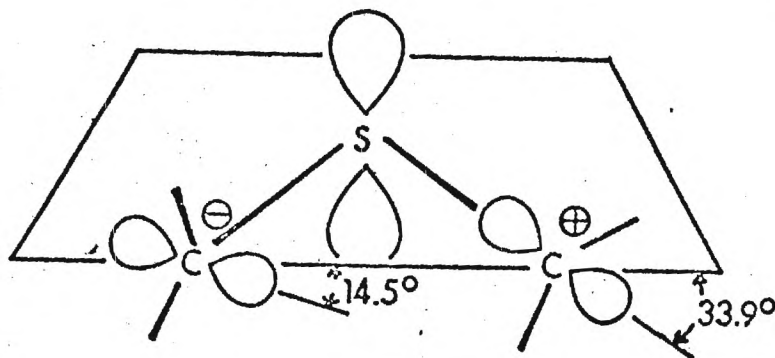
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The Chemistry of N-Sulfonylamines

it would be of interest to examine the structure of a substituent-perturbed thione methylene available from previous synthetic efforts,⁷ and we now wish to report the details of such a study. Due to its high thermal stability ylide 5a was selected for an x-ray crystallographic analysis.⁸ The C_aSC_b angle is an unexceptional 104.26° while the C_aS and C_bS lengths are both 1.7 \AA and thus intermediate between



a CS double and single bond has been observed for 1,2-sulfonium methylenes.⁹ However, the most extraordinary feature is the inclination of the C_a and C_b substituent planes to the C_aSC_b plane which results in a carbon p_π -orbital topology as shown in Fig. 2 and the close correspondence to the theoretically derived structures 3-4 is notable.



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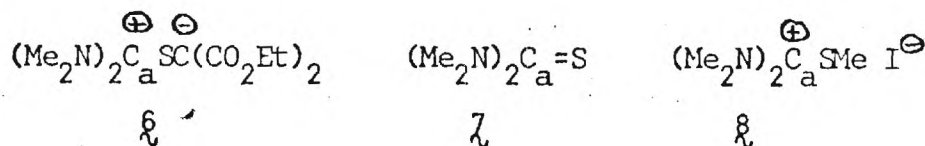
The Chemistry of N-Sulfonylamines

Some conclusions as to the role of a central second row atom in conjugative interaction between the carbon termini in 1,3-dipolar ylides may be drawn from magnetic resonance spectroscopy studies. The efficiency of charge transmission across the methylene sulfur atom is evident from the effect of various combinations of electrons withdrawing substituents at C_b on selected C^{13} and H^1 nmr chemical shifts in the system δ (Table I).

Table I. NMR Chemical Shifts in δ Relative to TMS in DMSO- d_6

Compound	H_a	Chemical Shift (δ) C_a	C_b
δ	7.81	144.2	9.9
δb	7.69	144.1	34.5
δa	7.51	146.1	59.1

A correlation appears to exist between the ring current induced diamagnetic anisotropic deshielding of H_a with the degree of total shielding of C_b while the relative shifts of C_a remain small and consistent with the view that ring current variations have little effect on C^{13} shifts.¹⁰ To further identify the mode (σ vs π) of charge transmission in perturbed thione methylides the C_a^{13} shift of δ was compared with some reference compounds, λ and δ (Table II).



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The Chemistry of N-Sulfonylamines

The calculated values shown in Table II were based upon the following assumptions, (a) the dominant contribution to the differences in chemical shift were nearest neighbor dependent and derived from variations in the second-order paramagnetic shielding tensor, $\sigma_{xyz}^{(2)}$, for the 2p orbitals of C_a , (b) the mean excitation energy, ΔE , was localized at C_a -S and could be approximated by the calculated n_s, π^* transition¹¹, and (c) the largest variation in the rotationally averaged second-order term arose essentially from $\sigma_z^{(2)}$ of the carbon p_π -orbital. Using the Karplus-Pople relationship¹², $\sigma_z^{(2)} \approx [-e^2 h^2 / 48 m^2 c^2 a_0^3] [3.25 - .35 (P_{ii} - 1)]^3 [P_{ii} + \sum_j P_{ij}] / \Delta E$, and the diagonal (P_{ii}) and off-diagonal (P_{ij}) density matrix elements as well as ΔE from a SCF-CND02 calculation¹³ on C_a in λ , μ , and δ ; the calculated values were fitted to a line, $\sigma_{xyz}^{(2)} = 1.0383 \sigma_z^{(2)} - 1.6$ ppm. A planar geometry was assumed

Table II. Observed C_a^{13} Chemical Shifts (relative to TMS) and Calculated Parameters.

Compounds	$\delta(\text{obs})$	$\sigma_{xyz}^{(2)}$	$\sigma_z^{(2)}$	P_{ii}	$\sum_j P_{ij}$	$P_{ij} S_{ij}$
λ	-193.9	-190.9	-185.4	.6822	1.4542	.1446
μ	-180.8	-182.5	-177.3	.7509	1.1554	.1076
δ	-174.5	-175.6	-170.7	.6811	1.4294	.0684

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for δ but δ was allowed to adopt the three-dimensional structure found for δ_a . With inclusion of sulfur d-orbitals in the basis the order of calculated C^{13} shifts is the same as the observed values, no correspondence between the C_a orbital electron population (P_{ii}) or the bond orders (P_{ij}) and this observable are apparent. However, the C-S bond order when scaled by the overlaps (S_{ij}) to represent its contribution to the total Mulliken population¹⁴ does correlate with the observed shifts. Although such a population analysis is at best approximate it does seem to qualitatively indicate a CS partial double bond providing the stabilizing conjugative link between the two charged centers through sulfur. The inclusion of higher-order d-orbitals of proper symmetry in the sulfur basis for the orbital description no doubt leads to more favorable charge distribution (increased electron density at the electropositive sulfur) due primarily to modification of the non-bonding π -orbitals. The bonding contribution of d-orbitals to the actual total energy of such sulfur compounds is controversial. The net lowering of the calculated SCF energy with a d-orbital inclusive basis may not be due to a net decrease in the occupied orbital energies but a result of altered coulomb and exchange terms.¹⁵

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- (6). The optimized CSC angles found for 1a, 3a, and 4a were 1.37.3° 126.3°, and 123.3°. Forced rotation in 4a of the π -acceptor substituted carbon p-orbital out of the CSC plane resulted in a rapid increase in the heat of formation accompanied by an equal (optimized) conrotation of the π -donor substituted carbon p-orbital. This would seem to indicate that the stereomode of conversion of 1→2 follows the Woodward-Hoffmann Rules even in a highly perturbed system.
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- (14). R. S. Mulliken, ibid., 23, 1833 (1955).
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1. List publications: (a) published and not previously reported; (b) in press. Provide five reprints if not previously submitted.
2. List all additions and deletions in professional personnel and any changes in effort.
3. Progress Report. (See Instructions)

The undersigned agrees to accept responsibility for the scientific and technical conduct of the project and for provision of required progress reports if a grant is awarded as the result of this application.

March 3, 1976

Date

Edward M. Burgess

Principal Investigator or
Program Director

FINAL PROGRESS REPORT

G-33678

Report submitted

5/22/78,

Title: The Chemistry of N-Sulfonylamines

Grant Number: 2 R01 GM 12672-08

Period: June 1, 1974 - August 31, 1977

Principle Investigator: Edward M. Burgess
School of Chemistry
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Atlanta, Georgia 30332

1. Summary Statement of Progress

Isolable substituent stabilized thione S-methylides have been produced from the base catalyzed deprotonation of tetramethylthiouronium and N,N'-dimethylimidazolthionium salts. The crystallographic structure has been determined for a representative of this class of ylides and the bonding a sulfur has been related to ^{13}C nmr data. A facile disproportionation reaction has been observed for these thione S-methylides and some mechanistic conclusions reached. Other ylide chemistry, such as ligand exchange and fragmentation to thiones and alkenes, has also been studied.

A new class of tricoordinate sulfur hypervalent molecules has been investigated and the structures evaluated by x-ray crystallography.

N,N'-Dimethylimidazole-2-thione S-carbomethoxy methylid, generated in situ, reacts with aldehydes to give predominately the Z-substituted acrylic ester. The mechanism is visualized in terms of a hypervalent tricoordinate sulfur intermediate whose stereochemistry is reflected in the product. The effect of added lithium ions and changes in substituents at either terminus of

the reactive 1,3-dipolar ylide in product composition and stereochemistry has been studied.

The thermal decomposition of di-t-butylthione S-oxide to di-t-butylthione and di-t-butylketone has been investigated. The kinetic parameters and product ratios suggest this decomposition is autocatalytic and products are derived from two distinct mechanistic pathways. Experiments on determining the nature of the catalytic species present have been done.

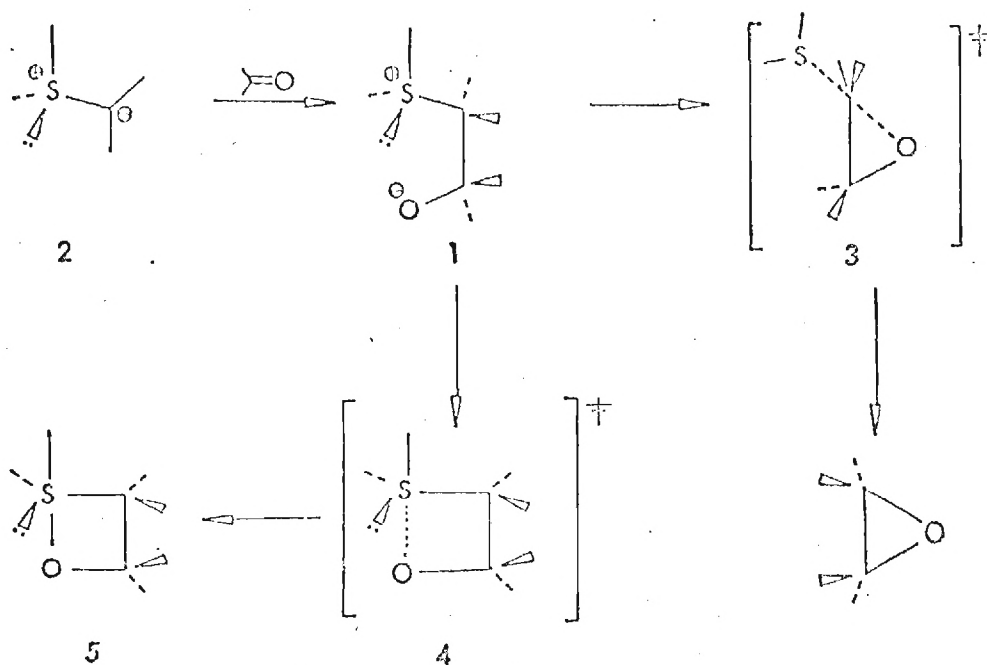
2. List of Results.

The attached reprints describe our results in the area of the structure, synthesis, and reactions of thione S-methylides as well as tricoordinate hypervalent sulfur compounds.

Recent unpublished results in the chemistry of sulfur functional groups is outlined in the following two sections.

a. Thione S-Methylides as Quasi-Wittig Reagents. ~~~~~

Betaines (1) derived from reaction of carbonyl functions with alkylidenesulfuranes (2) undergo an intramolecular displacement reaction leading to oxiranes¹ while alkylidenephosphoranes (Wittig Reagents) select the alternate closure to a hypervalent phosphorous intermediate which is penultimate to the alkene product.² The partition of 1 between two potential surfaces



whose maxima are described by transition states $\bar{3}$ or $\bar{4}$ electronically³ depends upon the magnitude of the first-order frontier interaction⁴ (E) between the overlapping oxygen p-orbital (p_o) and the terminus of the high lying σ^* -orbital involved (S in $\bar{4}$, C in $\bar{3}$; Fig. 1).

Sulfonium ylid derived betaines might be encouraged to undergo

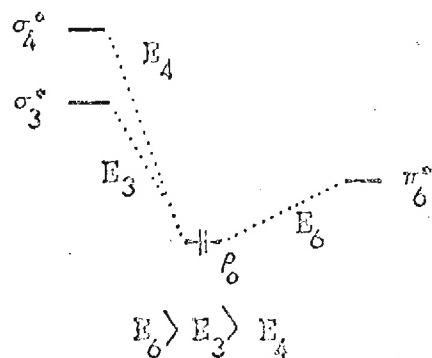
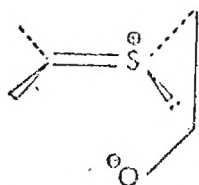


Figure 1. Frontier Molecular Orbitals involved in Betaine Decompositions.

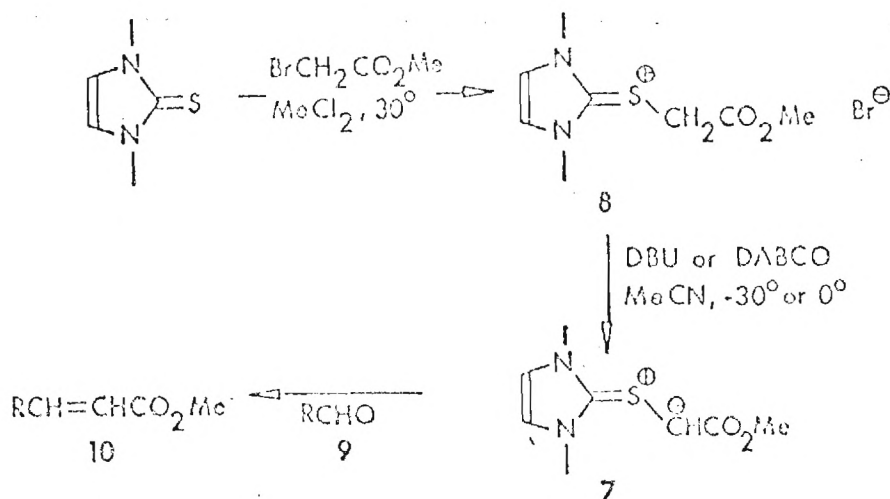
intramolecular closure to yield a "Wittig" reaction if a low lying π^* -orbital was available at sulfur (Fig. 1). This requirement would be met by betaines (6) generated from thione methylides⁵ and appropriate carbonyl substrates. We now wish to report that



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thione methylids can undergo Wittig-type reactions and stereochemically complement the Wadsworth-Emmons phosphonate modification of the Wittig Reaction in substituted acrylic ester syntheses.

The quasi-Wittig reagent, N,N'-dimethylimidazole-2-thione S-carbomethoxy methylid (7) is easily generated *in situ* from the corresponding salt 8. Specifically, to a solution of an equivalent of 8 in dry acetonitrile at 0° is added an equivalent of base and after 5 min. the carbonyl reagent is introduced. The resulting mixture



is stirred for 10 min. at 0° to complete the reaction. Table I summarizes the results including overall isolated yield of pure product and the isomer distribution for some representative aldehydes (\mathfrak{g}).⁶ Improvement of the overall yield of acrylic

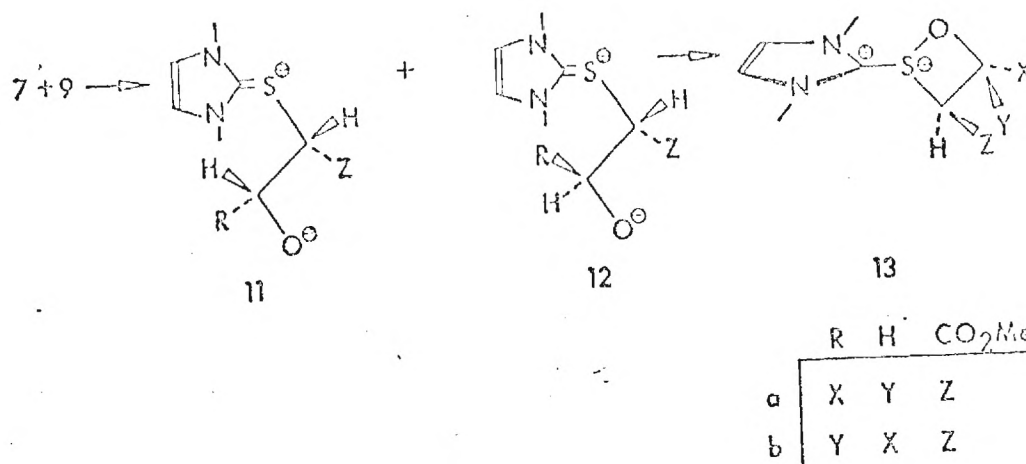
Table I. Products from Quasi-Wittig Reaction.

\mathfrak{g} , R=	Z-isomer	E-isomer	% yield
Ph	75	25	60
CH ₃ CH ₂ CH ₂	71	29	31*
(CH ₃) ₂ C:CHCH ₂ CH ₂ CH ₂	75	25	42*
CH ₃ CH:CHCH:CH	35	65	12

*Molar ratio of aldehyde to \mathfrak{g} was 2:1

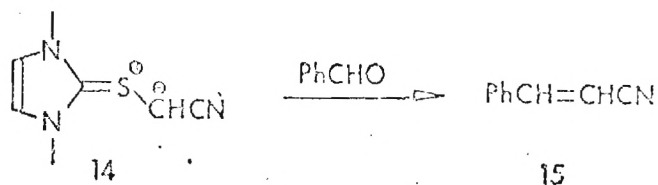
ester from enolizable substrates was effected by increasing the ratio of \mathfrak{g} to substrate present in the reaction mixture.

The stabilized thione S-methylid differs from its Wittig counterparts in that the former produces primarily the Z-isomer (Table I). With this difference in mind, two pathways via $\mathfrak{11}$ or $\mathfrak{12}$ may be involved in the formation of the observed products.

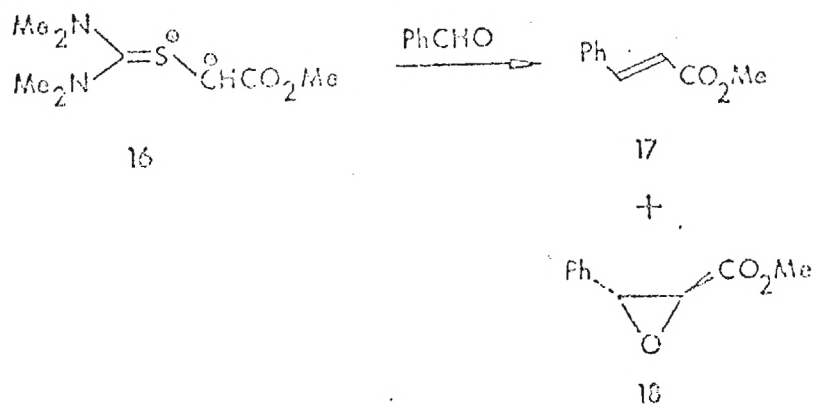


Considering the most favorable conformation, the erythro-betaine, 11 , experiences less steric repulsion than the alternative threo-isomer, 12 , but at the same time cannot enjoy without severe congestion the intramolecular electrostatic interaction between the charged centers possible in 12 . If steps 11 , $12 \rightarrow 13 \rightarrow 10$ are considered irreversible or faster than betaine dissociation the isomer distribution of 10 is determined by the ratio of 11 to 12 (erythro- \rightarrow Z-isomer, threo- \rightarrow E-isomer). This must be the case as the predominant Z-isomer arises from the sterically most encumbered hypervalent sulfuranium $13a$.⁷ Addition of a metal cation to the reaction should lower the energy of 10 relative to 11 by ion-pairing at the alkoxide site and increase the proportion of betaine 11 available for Z-alkene production. In fact, addition of LiI (3 equivalents) to the ylid reaction with benzaldehyde raised the Z- to E- isomer distribution of the methyl cinnamate

product to 92:8.⁸ Thione S-methylids with sterically less-demanding groups at the carbanionic center yield a more nearly equal distribution of product stereoisomers. For example, 14 provides (50% isolated yield) a ratio of E- to Z-cinnamonitriles



of 59:41. It should be noted also that the electron donating ability of the thione substituents is critical in determining both the partition of the reaction paths and the distribution of geometrical isomers.⁹ The ylid (11) derived from tetramethylthiourea gave a 90:10 ratio of E- to Z- 17 along with 18 in a overall ratio of 1:1.

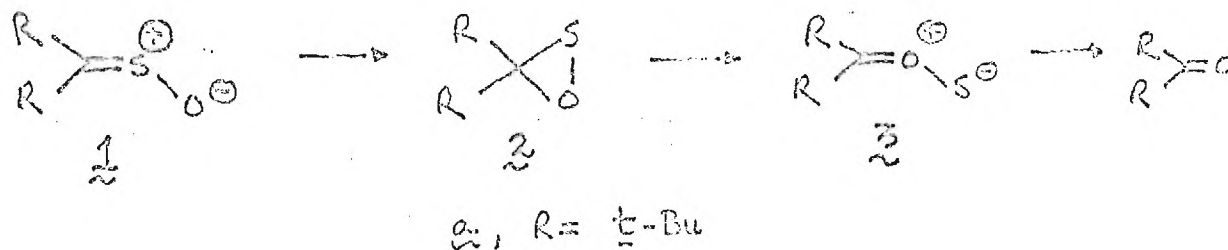


References and Notes

- (1) In one reported instance the reaction of an oxosulphonium ylide with an aldehyde gave a mixture of oxirane and alkene. This was a result of the large steric demand imposed on the transition state 3 by substituents about the C-C bond which lead to the appearance of a competitive pathway (4). Y. Tamura, T. Miyamoto, and Y. Kita, J. Chem. Soc., Chem. Commun., 531 (1974).
- (2) An excellent review of both reactions may be found in H. O. House, Modern Synthetic Reactions, W. A. Benjamin, New York, 1972, pp. 682-733.
- (3) Unlike 3 transition state 4 suffers a sulfur-oxygen lone pair closed-shell destabilizing interaction.
- (4) The magnitude of E is directly dependent upon the resonance intergal developed between the reacting centers and inversely dependent upon the orbital energy difference.
- (5) E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 98, 5020, 5021 (1976).
- (6) The results were interpreted by comparing the IR, NMR (as well as GC retention times in some cases) of the products with those of independently synthesized authentic samples.
- (7) The stabilizing electronic features and geometry of tri-coordinate hypervalent sulfuranes have been delineated. E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 99, 2376 (1977).
- (8) The opposite effect occurs in the stereochemistry of Wittig Reactions.
- (9) The energetic placement of the acceptor orbital of the equatorial substituent governs the bond energy of the hypervalent system (see ref. 5).

b. Thermal Decomposition of Thione S-Oxides.
 ~~~~~

A thermal (and photochemical) reaction reported for thione S-oxides<sup>1</sup> (1) (sulfines) and S-imides<sup>2</sup> is the extrusion of sulfur and the formation of the corresponding carbonyl or imine derivative and cyclooctasulfur. A theoretical investigation of the S-oxide decomposition suggests that the thermal reaction proceeds initially by electrocyclization of the ylide to a lower energy intermediate oxathirane (2) from which sulfur extrusion occurs directly or which may undergo subsequent valence isomerization to a carbonyl (or imine) ylide (3) which is penultimate to the extrusion step.<sup>3</sup> Although derivatives of 2 or 3 have never been isolated this hypothesis has received support from the recent spectroscopic observation that 1,1-



diphenyloxathirane ( $\lambda_{\text{max}}$  390 nm ( $\epsilon$  200)), generated photochemically from the corresponding S-oxide at  $-213^\circ$ , decomposes at  $-158^\circ$  to give a quantitative yield of benzophenone.<sup>4</sup> The curious feature of some mechanistic proposals is that they suggest the spin-forbidden highly endothermic formation of ground state  $^3P_2$  atomic sulfur, a

process which we consider unlikely. In this communication we wish to present our findings on some of the aspects of this "extrusion" step as exemplified by the thermal decomposition of the relatively stable sulfine, di-t-butylthione S-oxide<sup>5</sup> (1a).

Table I. Kinetic Parameters and Product Data on the Thermolysis of 1a.

| Substrate               | Conc<br>(M) | T+2<br>(°C) | $k_{int} \cdot 10^{-3}$<br>(min <sup>-1</sup> ) <sup>a</sup> | Thione:Ketone<br>Ratio |
|-------------------------|-------------|-------------|--------------------------------------------------------------|------------------------|
| <u>1a</u>               | .4          | 125         | --                                                           | 0.8:99.2 final         |
|                         | .053        | 150         | 2.0                                                          | 9:91 final             |
|                         | .27         | 150         | 4.0                                                          | 9:91 final             |
|                         | 1.04        | 150         | 3.6                                                          | 11:88 final            |
|                         | .11         | 210         | 2.0                                                          | 25:75 final            |
|                         | .54         | 210         | 2.0                                                          | 43:57 final            |
| <u>1a</u><br>+ <u>6</u> | .39         | 210         | 20.3                                                         | 25:75 initial          |
|                         | .38         |             |                                                              | 75:25                  |

(a) The regression coefficient (r) for all plots were within .938-.99 with  $r_{avg} = .974$ .

The thermolysis of 1a in solvent diphenylmethane at 125-210° gave, in addition to cyclooctasulfur, di-t-butylketone (4) and di-t-butylthione (5) in a ratio which was time and temperature dependent (Table I).<sup>6</sup> At high temperatures (210°) and high concentrations (1.04 M) of 1a the kinetic profiles exhibited a

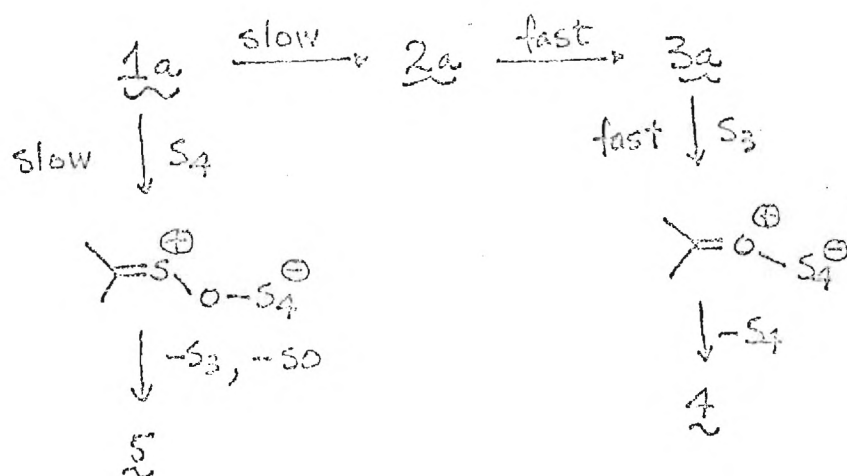
typical autocatalytic sigmoid curvature with a linear first order process and a steady product development of ratio  $\sim 1:3$  observed over the first quarter-life followed by non-linear rate acceleration to a final (over one half-life) ratio of  $\sim 1:1$ . At low temperatures ( $150^\circ$ ) and low concentrations of  $\text{I}_a$  the reaction appeared to be first order over three half-lives with a constant product ratio while at all concentrations and the higher temperatures the autocatalytic reaction produces initially ketone in a first-order process followed by thione in a higher-order. For this S-oxide decomposition the following conclusions emerge: (a) at the minimum reaction temperature  $\text{I}_a$  is converted in a slow unimolecular process to a species (probably  $\text{Z}_a$ ) which is catalytically desulfurized to give only ketone, and (b) at a higher temperature  $\text{I}_a$  is directly deoxygenated by the catalyst (resulting in loss of this species) to thione in a competitive process.

Some information on the nature of the catalytic intermediate responsible for the observed processes, (a) and (b), was obtained from the following experiments. The reaction is not product catalyzed as either added 4, 5, or cyclooctasulfur had no effect on  $k_{\text{int}}$  at  $150^\circ$ . Tetramethylthiourea S-p-toluene sulfonimide ( $\text{Q}$ ) decomposes at  $210^\circ$  in diphenylmethane with a half-life of  $< 5$  sec. to give N-[bis-(dimethylamino)]methylene-p-toluenesulfonamide and cyclooctasulfur as isolated products in  $> 98\%$  yield.<sup>7</sup> When  $\text{I}_a$  and  $\text{Q}$  were codecomposed at  $210^\circ$  (Table I) the disappearance of  $\text{I}_a$  increased by an order of magnitude, demonstrated first order kinetics

over three half-lives, and a constant ratio of product development. We must conclude that in this reaction a high concentration of a catalytic reagent,  $S_{8-x}$ , derived from  $\text{O}$  and having a long life-time has enforced a pseudo first-order reactant dependence on both processes. Furthermore, when  $\text{I}_a$  is decomposed in the presence of nucleophiles such as triphenylphosphine, diphenylsulfide, or dimethylsulfoxide the rate decreases by an order of magnitude while the product ratio is unaltered.<sup>8</sup> This suggests the allotropic species,  $S_{8-x}$ , is an electrophile. Since each desulfurization step contributes only a single sulfur atom to move the reacting allotrope ( $S_{8-x}$ ) to a higher order ( $S_{9-x}$ ) product the catalytic activity can only be maintained by considering a number of allotropes to be reactive and after the same number of desulfurization events;

a regeneration step, for example:  $S_3 \xrightarrow[\text{4}]{-5} S_4 \xrightarrow[\text{4}]{-5} S_5 \xrightarrow[\text{4}]{-5} S_6 \longrightarrow 2S_3$ .

These mechanistic features may be summarized in the multistep process shown below (illustrated for  $S_3$ ).



Finally the photolysis of  $\mathbf{1a}$  at  $30^\circ$  in  $\text{CHCl}_3$  gave only  $\mathbf{4}$  which may indicate that all of the thione product observed thermally arises from the direct deoxygenation of  $\mathbf{1a}$ .

### References and Notes.

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- (6) Product development and reactant disappearance were monitored by  $\text{H}^1$  nmr spectroscopy over a minimum of one half-life.
- (7) H. K. Penton, Ph.D. Thesis, Georgia Institute of Technology, Atlanta, Georgia, 1973.
- (8) Addition of a equivalent amount of chloroacetic acid to the decomposition of  $\mathbf{5}$  at  $150^\circ$  also diminished  $k_{int}$  to  $5 \times 10^{-3} \text{ min}^{-1}$ . It has been proposed that the opposite effect of Bronstead acids should be observed (ref. 3).



3. List of Publications.

## a. Publications in Print.

Syntheses and Reactions of Substituent Stabilized Thione Methylides. E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 98, 5020 (1976).

The Structure of a Substituent Stabilized Thione Methylide. E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 98, 5021 (1976).

Tricoordinate Hypervalent Sulfur Compounds. E. M. Burgess and A. J. Arduengo, J. Amer. Chem. Soc., 99, 2376 (1977).

## b. Publications submitted.

Thione S-Methylides as Quasi-Wittig Reagents. E. M. Burgess and M. C. Pulcrano, J. Amer. Chem. Soc. (1978).

Thermal Decomposition of Thione S-oxides. E. M. Burgess and A. L. Mauer, J. Amer. Chem. Soc. (1978).

## c. Publications contemplated.

The Reactions of Substituent Stabilized Thione S-imides. E. M. Burgess and M. C. Pulcrano.

The Reactions of an Electrophilic Disulfide. E. M. Burgess and M. C. Pulcrano.

Hypervalent Carbon. E. M. Burgess and D. C. Campbell.

Nitrones as Oxenoids. E. M. Burgess and A. L. Mauer.