of pentalenolactone as its benzylamine salt (see ref 19) were provided by the Pfizer Laboratories through the courtesy of Drs. Arthur Nagel and Robert Volkmann and by Professor David Cane of Brown University. The authors also acknowledge the help and advice of Dr. Milan Uskokovic of the Hoffmann-La Roche Laboratories in dealing with the Brederick reagent.

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(4) The structure assignment is supported by its infrared, NMR, and mass measurements. Carbon hydrogen combustion analyses within 0.4% of theory were obtained for all crystalline compounds (see melting points in flow sheets).

(5) Attempts to use the anhydride related to **2**[8] as the dienophile toward **4** were equally successful. However, in this series, the basic unraveling of the enone could not be disengaged from retro-Diels–Alder cleavage with the formation of 3-hydroxyphthalic acid.

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Received June 30, 1978

Thione *S*-Methylides as Quasi-Wittig Reagents

Sir:

Betaines (**1**) derived from reaction of carbonyl functions with alkylidenesulfuranes (**2**) undergo an intramolecular displacement reaction leading to oxiranes,[1] while alkylidenephosphoranes (Wittig reagents) select the alternate closure to a hypervalent phosphorus intermediate which is penultimate to the alkene product.[2] The partition of **1** between two potential surfaces whose maxima are described by transition states **3** or **4** electronically[3] depends upon the magnitude of the first-order frontier interaction[4] (*E*) between the overlapping oxygen p orbital (p_O) and the terminus of the high lying σ^* orbital involved (S in **4**, C in **3**; Figure 1). Sulfonium ylide derived betaines might be encouraged to undergo intramolecular closure to yield a "Wittig" reaction if a low-lying π^* orbital was available at sulfur (Figure 1). This requirement would be met by betaines (**6**) generated from thione methylides[5] and appropriate carbonyl substrates. We now report that thione methylides can undergo Wittig-type reactions and stereochemically complement the Wadsworth–Emmons phosphonate modification of the Wittig reaction in substituted acrylic ester syntheses.

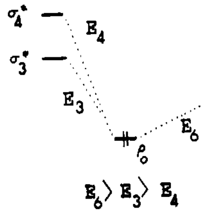
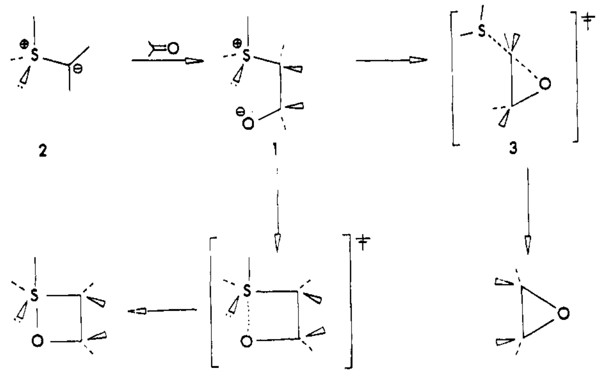
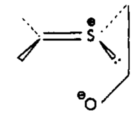


Figure 1. Frontier molecular orbitals involved in betaine decompositions.





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The quasi-Wittig reagent, *N,N'*-dimethylimidazole-2-thione *S*-carbomethoxymethylide (**7**), is easily generated in situ from the corresponding salt **8**. Specifically, to a solution of 1 equiv of **8** in dry acetonitrile at 0 °C is added 1 equiv of base and after 5 min the carbonyl reagent is introduced. The resulting mixture is stirred for 10 min at 0 °C to complete the reaction. Table I summarizes the results including overall isolated yield of pure product and the isomer distribution for some representative

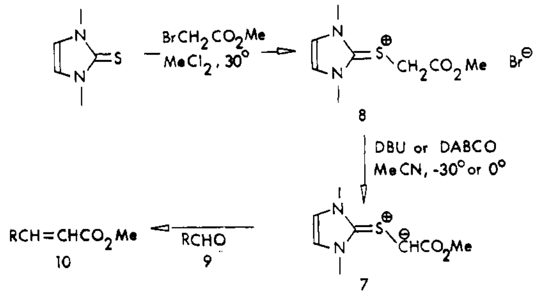

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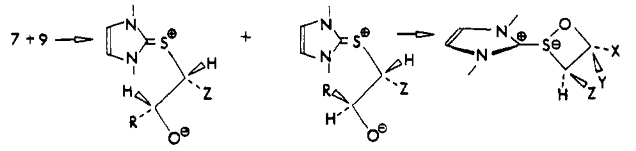
Table I. Products from Quasi-Wittig Reaction

9, R	Z isomer	E isomer	% yield
Ph	75	25	60
$CH_3CH_2CH_2$	71	29	31[a]
$(CH_3)_2C{=}CHCH_2CH_2CH_2$	75	25	42[a]
$CH_3CH{=}CHCH{=}CH$	35	65	12

[a] Molar ratio of aldehyde to **8** was 2:1.

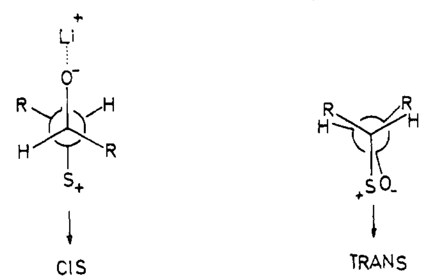
aldehydes (**9**).[6] Improvement of the overall yield of acrylic ester from enolizable substrates was effected by increasing the ratio of **8** to substrate present in the reaction mixture.

The stabilized thione *S*-methylide differs from its Wittig counterparts in that the former produces primarily the *Z* isomer (Table I). With this difference in mind, two pathways via **11** or **12** may be involved in the formation of the observed products. Considering the most favorable conformation, the *erythro*-betaine, **11**, arises from addition of the ylide to the carbonyl function with the changed centers diametrically opposed while the opposite is true for the development of the *threo*-betaine, **12.** If steps **11** + **12** → **13** → **10** are considered irreversible or faster than betaine dissociation the isomer distribution of **10** is determined by the ratio of **11** to **12** which, in turn, is a result of this conformational preference, i.e.,

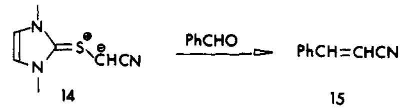


11 12 13

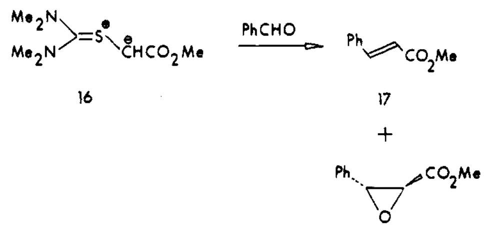
	R	H	CO_2Me
a	X	Y	Z
b	Y	X	Z



This must be the case as the predominant *Z* isomer arises from the sterically most encumbered hypervalent sulfurane **13b.**[7] Addition of a metal cation to the reaction should lower the transition state energy leading to **11** relative to **12** 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 equiv) to the ylide reaction with benzaldehyde raised the *Z* to *E* isomer distribution of the methyl cinnamate product to 92:8.[8] Thione *S*-methylides with sterically less-demanding groups at the carbonionic 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 ylide **16** derived from tetramethylthiourea gave a 90:10 ratio of *E*- to *Z*-**17** along with **18** in an overall ratio of 1:1.



14 15



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Acknowledgments. We sincerely thank the National Science Foundation and the National Institutes of Health for research grants and Professors Kent Barefield and Charles Liotta for stimulating discussions.

References and Notes

(1) In one reported instance the reaction of an oxosulfonium 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 led to the appearance of a competitive pathway (**4**): Y. Tamura, T. Miyamoto, and Y. Kita, *J. Chem. Soc., Chem. Commun.*, 531 (1974).

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(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 integral developed between the reacting centers and inversely dependent upon the orbital energy difference.

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(6) The results were interpreted by comparing the IR and NMR (as well as GC retention times in some cases) of the products with those of independently synthesized authentic samples. An equivalent amount of 1,3-dimethylimidazole-2-thione was also isolated in all reactions.

(7) The stabilizing electronic features and geometry of tricoordinate hypervalent sulfuranes have been delineated: E. M. Burgess and A. J. Arduengo, *J. Am. 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).

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Received February 2, 1978

Isolation and Characterization of Two $C_{11}H_{11}$ Cationic Rearrangements

Sir:

Unsaturated substrates rearrange by some mechanisms that are cationic and by others that are not. The distinction is easier to recognize in principle than to resolve in practice. How can one isolate the rearrangement of an ionic intermediate from the competitive rearrangement of its covalent precursor or product?

We encountered this problem, as one might have expected, in trying to generate the bicyclo[4.3.2]undecatetraenyl cation[1] (**1**, Figure 1) from its covalent precursor under classic S_N1 conditions (2,6-lutidine-buffered 70% aqueous acetone hydrolysis of the 9-*syn*-*p*-nitrobenzoate (**2**)[2] at 80 °C). The problem was previously recognized in studies of apparently cationic C_9H_9 rearrangements.[3] Within the $C_{11}H_{11}$ series, some ten different rearrangements have already been reported.[4,5] Most of them appear to be cationic, but some clearly are not.[5a,b,d,e]

The S_N1 conditions which we selected generated only two products of kinetic control,[6] both rearranged: the anti-tetracyclic alcohol (**4**)[7a,b] and anti-pentacyclic alcohol (**5**).[7a,c] We