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SYNTHESIS AND PYROLYSIS OF CYCLIC SULFONIUM YLIDES

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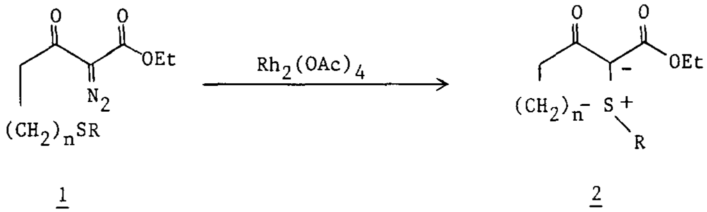
Abstract: Intramolecular capture of carbenoid intermediates by sulfides results in the formation of a series of stable cyclic sulfonium ylides.

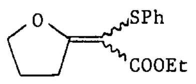
We have initiated a study to examine the chemistry of stable sulfonium ylides of general structure 2, in order to determine their utility as reagents in organic synthesis. In this paper we describe the facile synthesis of a series of such compounds by intramolecular capture of carbenoid intermediates by sulfides[1] . We have also examined the thermolysis of these ylides and have found that the observed rearrangements are highly dependent on ring size.



It is well known that carbenes react with sulfides to form sulfonium ylides and these are readily isolable when stabilized by two electron withdrawing groups[2]. Several unstable cyclic ylides have also been generated by intramolecular capture of carbenes by sulfides[2a,3] and the rearrangement of related sulfur ylides has been developed into a useful ring expansion procedure[3]. Examples of stable cyclic ylides, however, are limited to 3,4-dihydro-2-thianaphthalene[4] and 10-thiaanthracene[5] derivatives, and these compounds were prepared by an alternative method involving alkylation at sulfur followed by deprotonation. In order to extend the carbenoid approach to the synthesis of stable cyclic ylides, prepared a series of suitable precursors 1[6-8] and examined their rhodium(II) acetate catalyzed decomposition.

In a typical procedure 1a (5 mmol) in dichloromethane (20 ml) was added over 8 h by means of a Sage syringe pump to a stirred suspension of rhodium(II) acetate (0.05 mmol) in dichloromethane (100 ml), heated under reflux in an argon atmosphere. After heating for a further 8 h, the solvent was evaporated and the residue was recrystallized from ethyl acetate to give pure 2a (67% yield). The five and seven membered ring ylides, 2b and 2c were similarily prepared, but attempts to form larger rings by decomposition of 1d and 1e resulted only in C-H insertion[1b,9] to give the cyclopentanones 3b and 3c, respectively. Although decomposition of the ethyl sulfide 1f resulted in the formation of the four-membered ring ylide 2f, the phenyl sulfide 1g failed to give a clean reaction and the only isolable product was assigned structure 4. The mechanism for the formation of 4 will be discussed later, but this result clearly shows that the sulfur group plays an important role in stabilizing this ylide system.

Even though 2a-c are quite stable at room temperature, they all undergo smooth rearrangement on heating to 160°C. However, none of the susbstrates form the usual products derived from a Stevens type 1,2-rearrangement[2,10]. The six-membered ring ylide 2a rearranged to an E/Z mixture of 5, the product of an overall 1,4-rearrangement[11]. In contrast, the five and seven-membered ring ylides 2b and 2c underwent fragmentation to the alkenes 6 and 7, respectively. Presumably, the acidic beta hydrogen in 2b facilitates the elimination reaction, while in 2c the ring is sufficiently flexible to allow a concerted intramolecular fragmentation to occur. Indeed, this is the predominant reaction with acyclic ylides containing beta hydrogens[2], and a similar reaction involving an eight-membered ring ylide has been described[12]. Finally, the four-membered ring ylide 2f decomposed under milder conditions (80°C) to give 8, which is analogous to the product formed from the rhodium(II) acetate catalyzed decomposition of the phenyl sulfide 1g. This product arises from a 1,4-rearrangement involving the ester carbonyl, and this is presumably favored over the other possible 1,4-rearrangement, which would result in the formation of a highly unstable allene oxide.



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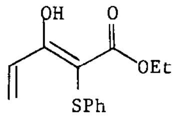

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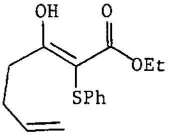

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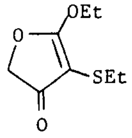

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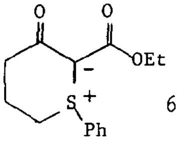
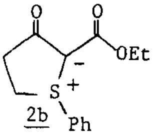
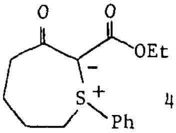
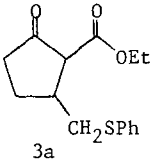
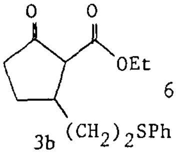
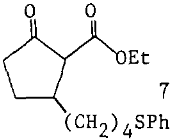
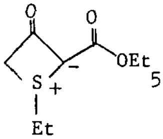
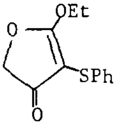
In summary, a new class of stable cyclic sulfonium ylides are readily

Table: Rhodium(II) Acetate Catalyzed Decomposition of 1

Entry	Substrate	Product(s) Yield (%)^a	
1	1a n=2, R=Ph	 67% 2a	
2	1b n=1, R=Ph	 69% 2b	
3	1c n=3, R=Ph	 45% 2c	 16% 3a
4	1d n=4, R=Ph		 64% 3b
5	1e n=6, R=Ph		 71% 3c
6	1f n=0, R=Et	 53% 2f	
7	1g n=0, R=Ph		 50% 4

a) Isolated yield

obtained by intramolecular capture of carbenoid intermediates by sulfides. Their susceptibility to both nucleophilic and electrophilic attack is now under study and will be reported in due course.

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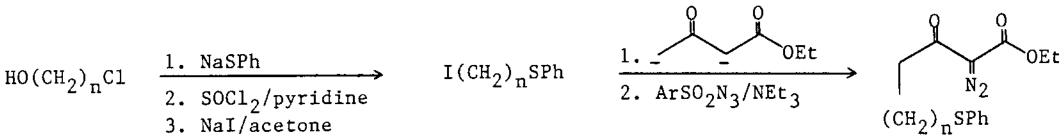
References and Notes

1. For recent examples of heterocyclic synthesis by intramolecular capture of carbenoids by sulfur, oxygen or nitrogen, see: a) Moyer, M.P.; Feldman, P.L.; Rapoport, H. *J. Org. Chem.* *1985*, *50*, 5223 and references cited therein; b) Heslin, J.C.; Moody, C.J.; Slawin, A.M.Z.; Williams, D.J. *Tetrahedron Lett.* *1986*, *27*, 1403.
2. a) Ando, W. *Acc. Chem. Res.* *1977*, *10*, 179; b) Ando, W.; Yagihara, T.; Tozune, S.; Imai, I.; Suzuki, J.; Toyama, T.; Nakaido, S.; Migita, T. *J. Org. Chem.* *1972*, *37*, 1721.
3. Vedejs, E. *Acc. Chem. Res.* *1984*, *17*, 358.
4. a) Hori, M.; Kataoka, T.; Shimizu, H.; Kataoka, M.; Tomoto, A.; Kishida, M. *Tetrahedron Lett.* *1983*, *26*, 3733; b) Hori, M.; Kataoka, T.; Shimizu, H.; Imai, E.; Tomoto, A. *Tetrahedron Lett.* *1982*, *25*, 2597; c) Hori, M.; Kataoka, T.; Shimizu, H.; Tomoto, A. *Tetrahedron Lett.* *1981*, *24*, 3629.
5. Hori., M.; Kataoka, T.; Shimizu, H.; Ohno, S. *J. Org. Chem.* *1980*, *45*, 2468.
6. Compounds *1a*, *1c-e* were prepared according to the following scheme:



7. Compound *1b* was prepared by reacting the dianion of ethyl acetoacetate with chloromethyl phenyl sulfide followed by diazotization with n-dodecylbenzene sulfonyl azide with triethylamine as base.
8. Compound *1f* and *1g* were prepared by treating the dianion of ethyl acetoacetate with the appropriate sodium thiolate followed by diazotization with n-dodecylbenzenesulfonyl azide and triethylamine as base.
9. Taber, D.F.; Petty, E.H. *J. Org. Chem.* *1982*, *47*, 4808.
10. Trost, B.M.; Melvin, L.S., "Sulfur Ylides", Academic Press, New York, N.Y., 1975.
11. For examples of 1,4-rearrangements of sulfur ylides see Ref. 4c and 5.
12. Vedejs, E.; Arnost, M.J.; Hagen, J.P. *J. Org. Chem.* *1979*, *44*, 3230.

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