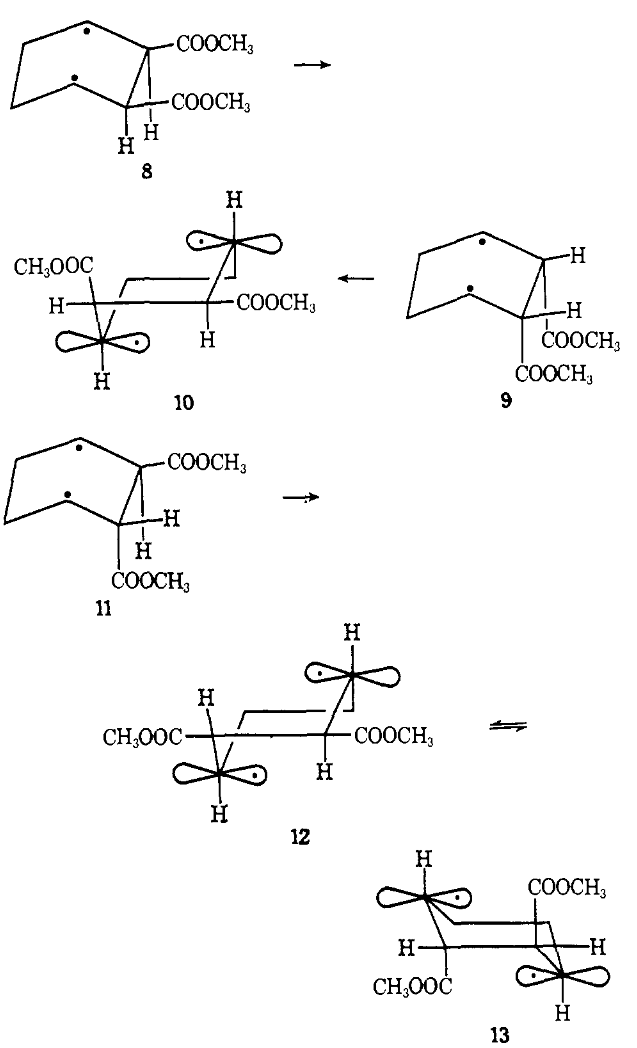

would reasonably afford chiefly *cis–trans*-diene **4**. Rearrangement of **3** in a comparable stepwise fashion would result in conversion of initially formed **11** to diradicals **12** and **13**.[12]

From the fact that the thermal rearrangements of **1–3** require highly elevated temperatures, explicit recognition of a second stepwise mechanism must be made. Estimates based upon known rates of Cope rearrangement of model compounds suggested that *meso-* and *dl*-**7** should undergo [3,3]-sigmatropic shift at least as fast, if not much faster, than pyrolysis of **1–3**. Therefore, the isomers of **7** become permissible kinetic intermediates. Furthermore, since *meso*-**7** is connected to *cis–trans*-dienedioate **4** by the usual chair-like Cope transition state,[13] whereas *dl*-**7** is similarly linked to the *trans–trans-* (**5**) and *cis–cis-* (**6**) diesters, these substances are also permissible stereochemical intermediates. In actuality, these changes are realized in near-quantitative yield upon resubmission of **7** to the pyrolysis conditions (410°).

Although a specific answer to the question of relative involvement of these two pathways is not available at the present time, the stereochemical results appear to rule out the interpretation[14] that passage of intermediates such as **8**, **9**, and **11** to the corresponding dienes is a synchronous process involving only "electronic reorganization." In the final analysis, it is amusing but pedagogically useful that the high level of antarafaciality attained by one of the double bonds during the pyrolysis of bicyclo[2.2.0]hexane derivatives, although predicted from orbital symmetry considerations, is actually the result of a two-step process.

Acknowledgment. We wish to thank Badische Anilin und Soda Fabrik for their generous gift of cyclooctatetraene which was required in the cyclobutadiene synthesis.

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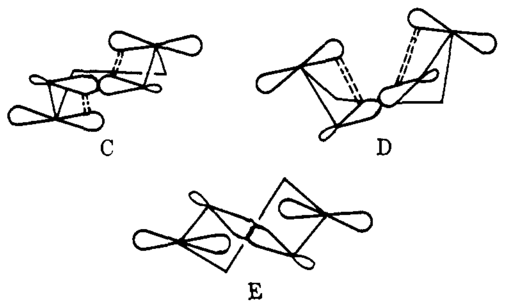
position from twist-boat form D does not account for the stereochemical observations; therefore, if twist-boat forms are involved, bond cleavage is restricted to E. The second consideration arises from the lower relative energy of C (R. Hoffmann, private communication) and the significantly more favorable alignment of the development p orbitals in C relative to D and E.



(13) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(14) For a review of bicyclo[2.2.0]hexane chemistry, see K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 238 (1968).

(15) National Science Foundation Undergraduate Research Participant, Summer 1969.

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Nucleophilic Substitution at Bivalent Sulfur. Reaction of Alkyllithium with Cyclic Sulfides

Sir:

Epoxides and higher heterocyclics containing oxygen are known to react with alkyllithium by nucleophilic attack at the carbon adjacent to oxygen and subsequent ring opening with formation of the corresponding lithium alkoxides.[1,2] It has been suggested[3] that heterocyclics containing sulfur may behave differently in that carbanions may attack the heterocyclic at the sulfur atom, rather than at an adjacent carbon atom, by analogy to the action of trivalent phosphorus compounds. However, no experimental evidence has been forthcoming to substantiate this view. An unusual attack of nucleophiles on the sulfonium sulfur in the specific case of cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate has recently been demonstrated,[4] but no attempt has been made to generalize this behavior. This communication reports experimental evidence that, under stringent experimental conditions, alkyllithiums attack sulfur-containing heterocyclics *exclusively* at the sulfur atom if severe bond angle distortions are forced upon the atom by the geometry of the molecule.

2-Methylthiacyclopropane, II, was added to an equimolar amount of ethyllithium, I, in tetrahydrofuran

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(1) S. Searles, *J. Amer. Chem. Soc.*, **73**, 124 (1951).

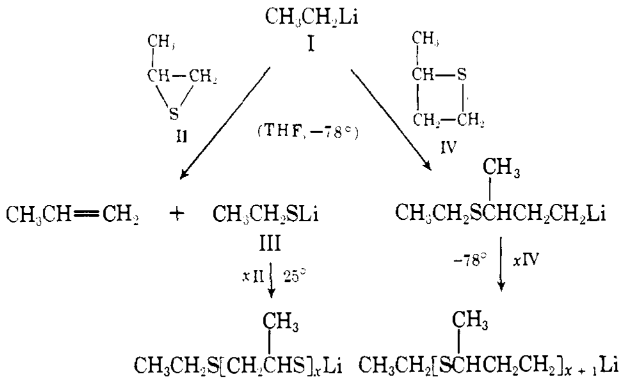
(2) E. C. Steiner, R. R. Pelletier, and R. O. Trucks, *ibid.*, **86**, 4678 (1964).

(3) N. P. Neureiter and F. G. Bordwell, *ibid.*, **81**, 578 (1959).

(4) D. C. Owsley, G. K. Helmkamp, and S. N. Spurlock, *ibid.*, **91**, 3606 (1969).

solution, and maintained at a temperature of −78°. In order to assure the absence of oxygen and moisture, all operations were carried out under high vacuum conditions. The resultant reaction products, after acid hydrolysis, were analyzed by gas-vapor chromatography and were found to be exclusively propylene and ethanethiol. The fact that the sulfur atom of the heterocyclic was found with the organic moiety of the alkyllithium leads to the conclusion that the sulfur atom was the site of attack by the carbanion. Lithium ethanethiolate, III, formed in this reaction, is capable of reacting with excess II at room temperature to a quantitative yield of a linear polymer possessing a carbon–carbon–sulfur backbone.

The reaction products of four-membered heterocyclic sulfur compounds with ethyllithium were analyzed *in situ* by high-resolution nmr. Under reaction conditions identical with those employed for the three-membered ring compound, 2-methylthiacyclobutane,[5] IV, and thiacyclobutane, V, yielded products which would be expected from an attack of a carbanion at the sulfur atom and subsequent ring opening with formation of a new carbanion species.



The new carbanion species appears in the nmr spectrum as a triplet (τ 10.95, $J = 8.5$ cps) which is clearly distinguishable from the quartet (τ 11.05, $J = 8.4$ cps) originating from ethyllithium. No elimination products such as cyclopropane or methylcyclopropane were observed. The newly formed carbanion species is capable of reacting in a repetitive process with excess IV or V to a quantitative yield of a linear polymer. This polymer–lithium species readily initiates the polymerization of vinyl compounds such as styrene, which is further evidence for the carbanionic nature of the propagating chain end. In contrast to thiacyclopropanes, the four-membered cyclic sulfides did not react with authentic III under comparable experimental conditions.

The higher rings, thiacyclopentane and thiacycloheptane, failed to undergo reaction with either I or III at −78 or 25°, respectively. From thermodynamic considerations[6] thiacyclopentane is not expected to polymerize, while thiacycloheptane should undergo ring opening. The ring strain in the seven-membered ring compound, however, arises mainly from hydrogen atom crowding brought about by eclipsed conformations, rather than bond angle distortions as is the case in rings of smaller size. Nucleophilic attack at bivalent sulfur, flanked by two carbon atoms, appears therefore to be restricted to valence states arising from severe bond angle distortions around the sulfur atom.

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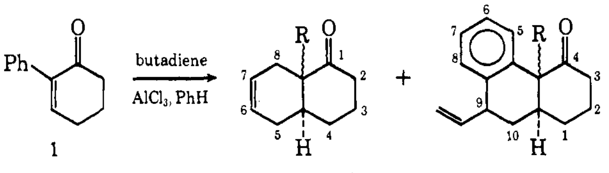
[5] Synthesized according to the procedure of S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, 27, 2828 (1962).

[6] F. S. Dainton and K. J. Ivin, *Quart. Rev.*, 12, 61 (1958).

The Mechanism of the Catalyzed Diels–Alder Reaction

Sir:

Evidence has long been available that in Diels–Alder reactions employing strongly electrophilic dienophiles rates may be increased by addition of proton[1] and Lewis acids.[2] Recently additional findings concerning isomer distribution,[3] reaction rates,[3b,c] and spectra of presumed intermediates[4] have prompted the postulation of mechanisms for the Lewis acid catalyzed version which incorporate initial coordination of the catalyst with the dienophile's electron-withdrawing function[3a,c,4] and a two-step ring formation with a very short-lived zwitterionic intermediate.[3c] We have succeeded in trapping internally an intermediate of the postulated type by a catalyzed reaction between butadiene and 2-phenyl-2-cyclohexen-1-one (**1**). This is the first instance of which we are aware of the isolation of isomeric products derived from such intermediates in a catalyzed Diels–Alder reaction, and our results, as well as strongly supporting the suggested mechanism, demonstrate that the intermediates may have appreciable lifetimes.



3, R = ---Ph
5, R = —Ph
4a, R = —H
4b, R = ---H

Although the uncatalyzed reaction failed to proceed even at 200°, when the reaction was carried out by bubbling butadiene through a solution of **1** and *ca.* 0.5 equiv of aluminum chloride in benzene at 50–60°, loss of starting material was complete in about 1.5 hr. The product was a complex mixture containing components with a wide range of vpc retention times; however when the nonpolar polymers and solvent–condensation products were removed by column chromatography, the remaining material contained only four compounds whose vpc retention values were consistent with 1:1 adduct structures. These compounds, **3**, **4a**, **4b**, and **5**, were present in a ratio of 13:6 (both **4a** and **4b**):1 and in a combined absolute yield of about 65%. They

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[1] A. Wasserman, *J. Chem. Soc.*, 828 (1935); A. Wasserman, *ibid.*, 3046 (1949); A. Rodgman and G. F. Wright, *J. Org. Chem.*, 18, 465 (1953).

[2] P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, 82, 4436 (1960); G. I. Fray and R. Robinson, *ibid.*, 83, 249 (1961).

[3] (a) E. F. Lutz and G. M. Bailey, *ibid.*, 86, 3899 (1964); (b) J. Sauer, D. Lang, and H. Wiest, *Ber.*, 97, 3208 (1964); (c) T. Inukai and T. Kojima, *J. Org. Chem.*, 31, 1121, 2032 (1966).

[4] J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966).