assigned a lower value of k (0.8) to take into account the unusual length of these bonds[6] is seen to improve the agreement between the calculations and experiment. It is important to note that the spin density of 0.178 on C_1 indicates that 70% of the total odd electron density resides at these four positions.[7]

Further information concerning the spin distribution of the odd electron in III can be obtained from the g factor. Semiquinone radical anions containing no halogen usually have g factors in the narrow range 2.0044 ± 0.0004, while hydrocarbon radical anions have g values in the range 2.0026 ± 0.0001.[8,9] The g factor of dibenzopentalenosemiquinone radical anion (2.0035) is unusually low, suggesting that the spin density on the oxygen atoms is unusually low. Reference to the previously derived relationship among half-wave potential, g factor, and oxygen spin density[10] suggests each oxygen atom in dibenzopentalenosemiquinone radical anion bears a spin density of only 0.0791, in good agreement with McLachlan calculations. Calculations indicate that the remaining 14% of the odd electron density should mainly be distributed between the two carbonyl carbons. Thus, little, if any, excess spin density may reside on the vinyl cross-link. These results strongly support the view that dibenzopentalenosemiquinone radical anion closely resembles a [12]-annulene semiquinone radical anion.[11]

The polarographic characteristics of the quinone and the esr spectral properties of the semiquinone anion radical support the description of this perturbed planar [12]annulene as an antiaromatic. Thus, the unusually high spin density in the hydrocarbon framework suggests a strong electronic demand by the [12]annulene system. Furthermore, the substantially more negative reduction potential compared to pyracyloquinone and anthraquinone reflects a thermodynamic instability in the dibenzopentalene system compared to the pyracylene or anthracene system. The magnitude of the differences (0.157 and 0.111, respectively) provides support for the contention that electronic destabilization accompanies a planar [12]annulene.

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(6) The corresponding bonds in dihydrodibenzopentalene are found to be exceptionally long.[1a] This large deviation from normal bond lengths is associated with the high degree of stain in the molecule. Dibenzopentalenoquinone should be even more highly strained as a result of the sp^2–sp^2 hybridization of the bonds α to the carbonyl *vs.* sp^2–sp^3 hybridization of the corresponding bonds in dihydrodibenzopentalene.

(7) Calculations indicate that the spin density at C_2 is negative.

(8) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, **43**, 4191 (1965).

(9) A. J. Stone, *Mol. Phys.*, 3, 233 (1960).

(10) S. F. Nelsen, B. M. Trost, and D. H. Evans, *J. Amer. Chem. Soc.*, **89**, 3034 (1967).

(11) For the semiquinone anion of 1,7-[12]annulenoquinone, the spin density corresponding to C_1 of I and oxygen is 0.137 and 0.083, respectively.

(12) National Institutes of Health Predoctoral Fellow, 1968–1970.

(13) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Recipient.

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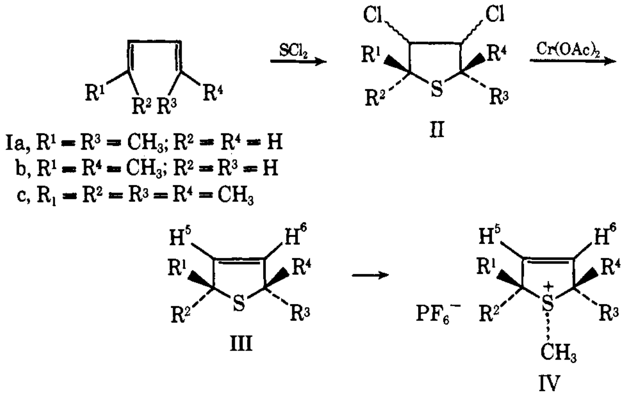
Stereochemistry of *n*-Butyllithium-Induced Fragmentation of Dihydrothiophenium Hexafluorophosphates. A Novel Sulfurane Reaction

Sir:

The question of sulfurane intermediates has led us to explore the reactions of cyclic sulfur compounds with organolithiums.[1] In this communication, we wish to report that the stereochemistry of organolithium-induced fragmentations of dihydrothiophenium salts provides strong evidence for the existence of such species.[2]

Dihydrothiophenes are generated by the two-step procedure outlined in Scheme I. Admixture of dilute hexane solutions of a diene (Ia,b,c) with sulfur dichloride generates an isomeric mixture of dichlorides II.[3] The crude dichlorides are directly reduced with the ethylenediamine complex of chromous acetate[4] to produce the desired dihydrothiophenes. Starting from *cis,trans*-2,4-hexadiene (Ia), a 9:1 mixture of *trans*-(IIIa) and *cis*-2,5-dimethyl-2,5-dihydrothiophenes (IIIb) was obtained. Alternatively, the *trans,trans*-2,4-hexadiene (Ib) produced a 3:2 mixture of the dihydrothiophenes IIIa and IIIb.[5] The overall yield for the two-step process is 12–13%. Utilizing 2,5-dimethyl-2,4-hexadiene (Ic) this sequence generated 2,2,5,5-tetramethyl-2,5-dihydrothiophene (IIIc) in 8% yield.

Scheme I. Preparation of Dihydrothiophenes and Their Salts



Ia, $R^1 = R^3 = CH_3$; $R^2 = R^4 = H$
b, $R^1 = R^4 = CH_3$; $R^2 = R^3 = H$
c, $R_1 = R^2 = R^3 = R^4 = CH_3$

Alkylation of each pure dihydrothiophene with trimethyloxonium tetrafluoroborate in methylene chloride at −40° produced the corresponding sulfonium salt in 90% yields. Due to the hygroscopicity of the fluoroborates, metathesis to the hexafluorophosphate was performed.[6,7] The structures of the sulfonium salts were fully confirmed by their nmr spectral data (see Table I) which also provided the stereochemical assign-

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(1) (a) B. M. Trost, W. L. Schinski, I. B. Mantz, and F. Chen, *J. Amer. Chem. Soc.*, **93**, 680 (1971), and references therein; (b) B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, 91, 4320 (1969); (c) B. M. Trost and S. D. Ziman, *Chem. Commun.*, 181 (1969).

(2) For a related case see J. Bornstein, J. E. Shields, and J. H. Supple, *J. Org. Chem.*, 32, 1499 (1967).

(3) H. J. Baker and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **154**, 52 (1935); F. Lautenschlaeger, *J. Org. Chem.*, 31, 1669 (1966).

(4) J. K. Kochi, D. M. Singleton, and L. J. Andrews, *Tetrahedron*, **24**, 3503 (1968).

(5) In the analogous reaction, methyl phosphorous dichloride has been shown to add stereospecifically to the *trans,trans*-2,4-hexadiene: A. Bond, M. Green, and S. C. Pearson, *J. Chem. Soc. B*, 929 (1968).

(6) G. C. Brumlik, A. I. Kosak, and R. Pitcher, *J. Amer. Chem. Soc.*, 85, 5360 (1964).

(7) All new compounds gave satisfactory elemental analyses and were further characterized by infrared and nmr spectroscopy. Spectral data were consistent with the structure.

Table I. Nmr Data of Dihydrothiophenes and Their Salts[a]

Compd	R_1	R_2	R_3	R_4	H_5	H_6	S–CH_3	$J_{1,2}$	$J_{5,6}$
IIIa[b]	1.34	4.29	1.34	4.29	5.58	5.58		6.5	
IIIb[b]	1.39	4.20	4.20	1.39	5.58	5.58		6.5	
IIIc[b]	1.47	1.47	1.47	1.47	5.36	5.36			
IVa[c,d]	1.60	4.80	1.65	5.25	5.96	6.15	2.88	7.0	8.0
IVb[c]	1.70	4.82	4.82	1.70	6.20	6.20	3.05	7.0	
IVc[c]	1.95	1.70	1.70	1.95	6.03	6.03	3.08		

[a] All chemical shifts are expressed in parts per million downfield from internal TMS. [b] Carbon tetrachloride solvent. [c] Acetone-d_6 solvent. [d] Methine–vinyl coupling not interpretable.

ments. It is interesting to note that the spectrum taken upon heating the trans salt IVa up to 120° in the nmr probe shows no evidence for inversion at sulfur.

Reaction of the sulfonium salts with *n*-butyllithium at −78° produces two types of products—elimination and fragmentation (see Scheme II). The ratio of these two processes is a function of steric hindrance to approach of the nucleophile at sulfur; thus fragmentation increases (at the expense of elimination) in the order IVc < IVa < IVb. Presumably, the elimination product from IVc arises by an E2 process, whereas the elimination product VI from IVa or b arises *via* the intermediacy of the ylide V (route C, Scheme II). Preferential attack at sulfur for the dihydrothiophenium salts compared to preferential proton abstraction in their acyclic counterparts[8] suggests a facilitation of sulfur attack by constraining the sulfur in a five-membered ring. Most remarkable is the complete stereospecificity associated with the fragmentation reaction. Trans salt IVa produces *cis,trans*-2,4-hexadiene (VII) exclusively, whereas, cis salt IVb produces only *trans,trans*-VIII and *cis,cis*-2,4-hexadiene (IX) (see Table II).

Scheme II. Reactions of 2,5-Dihydrothiophenium Salts with *n*-Butyllithium

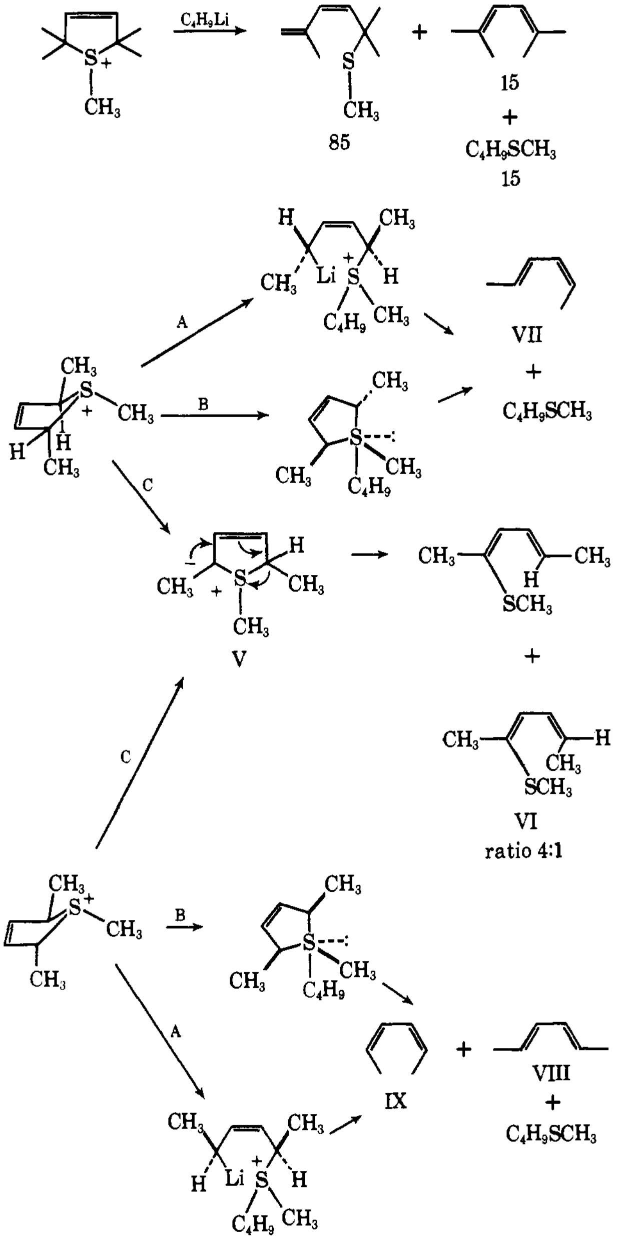

Table II. Decomposition of Sulfonium Salts with *n*-Butyllithium[a]

		Absolute yields				
Salt	Temp, °C	VII	VIII	IX	$C_4H_9SCH_3$	VI
IVa	−78	62.0	0	0	59.0	39.5
IVa	−22	69.0	0	0	69.0	34.0
IVb	−78	0	33.5	58.5	84.5	9.5

[a] All data are the results of two runs.

Scheme II presents the two most reasonable mechanisms for consideration—(1) a stepwise fragmentation through a zwitterion (route A) or (2) a concerted fragmentation through a sulfurane (route B). Associated with route A are the assumptions that 1,4 elimination from the zwitterion is stereospecifically syn and that inversion of the metal–carbon bond is slow relative to elimination.[9] Although no experimental evidence exists relating to stereochemistry of 1,4 eliminations, other studies suggest that inversion of organometallics is generally competitive with elimination.[1] Substantial evidence against the stepwise pathway arises from the fragmentation of IVb. On the basis of the zwitterion intermediate, the major, if not exclusive, product should be the trans,trans diene VIII—a prediction not in accord with the experimental evidence.[10]

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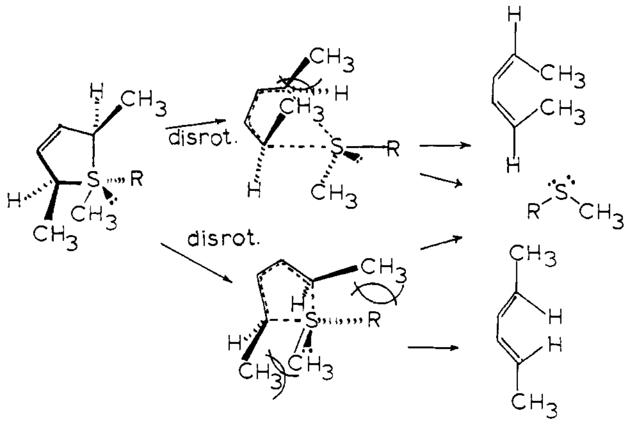
(8) R. W. LaRochelle, B. M. Trost, and L. Krepski, *J. Org. Chem.*, **36**, 1126 (1971).

(9) In Scheme II, the stereochemistry of the organolithium in the zwitterion is obtained assuming ring cleavage proceeds with retention of configuration. Similar arguments apply if inversion of configuration is assumed. The stereospecificity of the fragmentation requires this ring opening to be stereospecific if route A is valid.

(10) Without providing a special role for the butylmethyl sulfide in determining the stereochemical course of elimination, it is difficult to rationalize the observed results. The zwitterion mechanism does not provide such a role. Other eliminations involving loss of a small fragment have generated only *trans,trans*-2,4-hexadiene. See D. M. Lemal and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 1335, 2858 (1966); W. L. Mock, *ibid.*, **88**, 2857 (1966); J. A. Berson and S. J. Olin, *ibid.*, **91**, 777 (1969).

Path B accommodates all the experimental evidence. Assuming that the five-membered ring occupies an apical-basal orientation about sulfur, with the remaining basal ligands being the electron pair and the methyl group,[11] a disrotatory fragmentation to generate the cis,cis diene requires only that the methyl groups in the 2,5 positions be eclipsed as the carbon-sulfur bonds break (Scheme III).[12] However, the forming butyl methyl sulfide experiences very little steric hindrance. On the other hand, in a disrotatory elimination leading to the all-trans isomer, the butyl methyl sulfide experiences a large interaction with both of the pseudoequatorial ring methyl groups as bond breaking commences.

Scheme III. Proposed Stereochemistry of Sulfurane Decomposition



It appears that this second interaction is slightly stronger, a fact which leads to a slight preponderance of cis,cis diene IX.

Acknowledgment. We wish to express our thanks to the National Institutes of Health and the National Science Foundation for their generous support of our program.

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(11) (a) K. Mislow, *et al.*, *J. Amer. Chem. Soc.*, **91**, 7031 (1969); **91**, 564 (1969); (b) K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970), and references therein.

(12) It is difficult to visualize the developing eclipsing interactions depicted in Scheme III for each mode of disrotation without the aid of molecular models.

(13) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient.

(14) National Institutes of Health Predoctoral Fellow.

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Competing Intramolecular Nucleophilic and General Base Catalysis in the Hydrolysis of Catechol Monosuccinates

Sir:

A recent communication[1] describing a possible case of intramolecular bifunctional catalysis (nucleophilic and general acid catalysis) in the hydrolysis of hexachlorophene monosuccinate (**1**) prompts us to report some results obtained from the hydrolysis of compounds belonging to a structurally similar system, the catechol monosuccinates (**2**). Here we find evidence for *competing* intramolecular nucleophilic and general base catalysis instead of cooperating bifunctional catalysis.

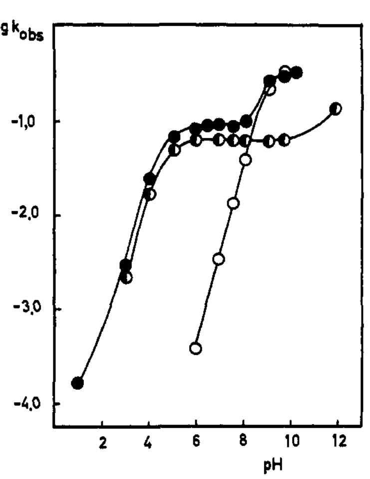
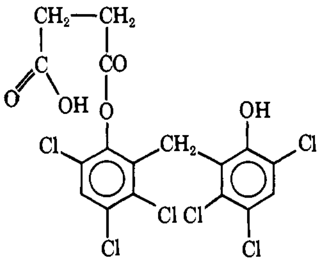


Figure 1. pH-rate profiles for catechol monosuccinate (**2a**, filled circles), *o*-methoxyphenyl hydrogen succinate (semifilled circles), and catechol monoacetate (**3**, open circles) at 25.0° in water containing 11% (by volume) acetonitrile.



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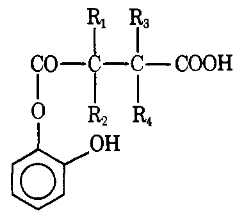

2a, $R_{1-4} = H$
b, $R_{1,3} = H$; $R_{2,4} = Me(dl)$
c, $R_{1-4} = Me$

It is well established that aryl hydrogen succinates hydrolyze *via* an intramolecular nucleophilic attack by the carboxylate group on the ester carbonyl carbon atom with formation of succinic anhydride and the corresponding phenolate ion.[2,3] We have now investigated the hydrolysis of a series of catechol monosuccinates[4] (**2a–c**) which also hydrolyze *via* intramolecular carboxylate ion attack in the pH interval where only the carboxyl group is ionized. However, in the pH region where the phenolic hydroxyl group begins to ionize, one can also recognize a second mechanism, in which the phenolate group appears to act as a general base in competition with the nucleophilic attack by carboxylate ion. Thus, the pH-rate profile for **2a** shows an increase in rate at pH values above 7 (Figure 1) and a second plateau at pH > 9, which coincides with the plateau found in the pH-rate profile of catechol monoacetate (**3**) (Figure 1). The kinetic pK_{app} values for **2a** and **3** are identical within the limits of experi-

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(1) T. Higuchi, H. Takechi, I. H. Pitman, and H. L. Fung, *J. Amer. Chem. Soc.*, **93**, 539 (1971).

(2) (a) E. Gaetjens and H. Morawetz, *ibid.*, **82**, 5328 (1960); (b) T. C. Bruice and U. K. Pandit, *ibid.*, **82**, 5858 (1960); (c) T. C. Bruice and U. K. Pandit, *Proc. Nat. Acad. Sci. U. S.*, **46**, 402 (1960); (d) T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, **87**, 4846 (1965).

(3) It has been shown (J. W. Thanassi and T. C. Bruice, *ibid.*, **88**, 747 (1966); L. Eberson, *Acta Chem. Scand.*, **18**, 2015 (1964); G. H. Hurst and M. L. Bender, *J. Amer. Chem. Soc.*, **93**, 704 (1971)) that the choice between participation of neighboring carboxylate or carboxyl group is governed by leaving group tendencies, good leaving groups being hydrolyzed *via* carboxylate group participation.

(4) Intermediates in the hydrolysis of cyclic succinoylcatechols; L. Eberson and L. Å. Svensson, work to be published.