by HCl occurs in this system, we believe the explanation resides in the relative rates of hydrogen abstraction from 2-propanol *vs.* electron abstraction from chloride ion by photoexcited nitrobenzene. Hurley and Testa[7] suggested that the excited state is short-lived ($\tau \sim 10^{-9}$ sec) and that direct hydrogen abstraction from 2-propanol ($k \sim 1 \times 10^6$ M^{-1} sec^{-1} by analogy to results with benzophenone[31]) competes poorly with deactivation. Electron transfer from chloride ion would be expected to occur much more rapidly (*vide supra*), causing interception of a greater proportion of excited molecules. Following electron transfer and protonation, the efficiency depends upon partitioning between the competing reactions shown in eq 9 and 10. This partitioning depends on the reactivity of the inorganic radical toward 2-propanol, toward the odd electron on the organic radical, and on the ability of the radical pair to dissipate energy. Each of these factors must be considered in predicting whether similar forms of catalysis would occur with other mineral acids or salts and other aromatic compounds.

(31) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

Reactions of π Sulfuranes (Ylides) with Aromatic Carbonium Ions

Barry M. Trost,*[1] Robert C. Atkins,[2] and (in part) L. Hoffman

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received August 30, 1972

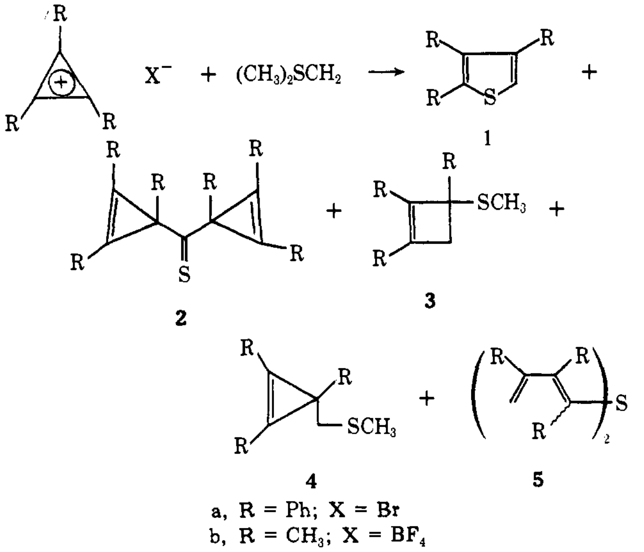
Abstract: The first observation of the use of sulfur ylides as a C–S transfer agent is reported. Reaction of triphenylcyclopropenium bromide with dimethylsulfonium methylide produced a 1.7:1.0 mixture of bis(1,2,3-triphenylcyclopropenyl) thioketone and 2,3,4-triphenylthiophene. The thioketone was characterized by its photolytic fragmentation to hexaphenylbenzene, presumably *via* hexaphenylquadricyclanthione. This reaction represents the first photochemical dethiocarbonylation. The reaction of trimethylcyclopropenium fluoroborate yielded 2,3,4-trimethylthiophene and ethane as the major products. These results suggest the intermediacy of a σ sulfurane—a species in which sulfur expanded its valence shell to ten electrons by formation of four σ bonds. The reaction is discussed in terms of the conversion of a π sulfurane into a σ sulfurane—a heterovinylcyclopropene rearrangement. σ sulfuranes similar to that postulated as intermediates in thiophene formation were generated by the treatment of triarylsulfonium salts with 2,2′-dilithiobiphenyl. Attempts to extend the C–S transfer reaction to tropylium fluoroborate led to heptafulvene instead.

The generation of nonclassical carbonium ions in strongly basic media as a potential route to strained hydrocarbons such as tetrahedrane prompted our investigation of the reaction of dimethylsulfonium methylide with cyclopropenium cations.[3] In the course of these studies, we discovered a novel new reaction indicative of π sulfurane intermediates.[4] The potential utility of σ sulfuranes in organic synthesis prompted our exploration of this reaction in detail and examination of related systems.[5]

Results and Discussion

The addition of triphenylcyclopropenium bromide[6] to a solution of dimethylsulfonium methylide[7] in THF led to a 1:1.7 mixture of two compounds, 2,3,4-triphenylthiophene (**1a**, mp 215–216°) and bis(1,2,3-triphenylcyclopropenyl) thioketone (**2a**, mp 198–200°), in 59% yield (see Scheme I). The structure of the thiophene was suggested by its mass spectrum with a molecular ion at *m/e* 312 and the appropriate M + 1 and M + 2 peaks for a single sulfur, its ultraviolet spectrum with

Scheme I. Reaction of Cyclopropenium Salts with Dimethylsulfonium Methylide



a, R = Ph; X = Br
b, R = CH_3; X = BF_4

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

(2) National Institutes of Health Predoctoral Fellow.

(3) The decompositions of *p*-toluenesulfonylhydrazones in basic alcoholic solvents represent examples of such reactions. See R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967); W. Kirmse, G. Arend, and R. Siegfried, *Angew. Chem.*, **82**, 174 (1970).

(4) A σ sulfurane is defined to be a decet sulfur species possessing four σ bonds. Such species have been postulated to be intermediates in a variety of reactions. See (a) V. Franzen and C. Mertz, *Angew. Chem.*, 72, 416 (1960); (b) V. Franzen, H. J. Schmidt, and C. Mertz. *Chem. Ber.*, 94, 2942 (1961); (c) J. Bornstein, J. E. Shields, and J. H. Supple, *J. Org. Chem.*, 32, 1499 (1967); (d) B. M. Trost, R. W. LaRochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, 91, 2175 (1969); (e) W. A. Sheppard, *ibid.*, 93, 5597 (1971); (f) B. M. Trost and R. W. LaRochelle, *ibid.*, 93, 6077 (1971); (g) G. Wittig and H. Fritz, *Justus Liebigs Ann. Chem.*, 577, 39 (1952).

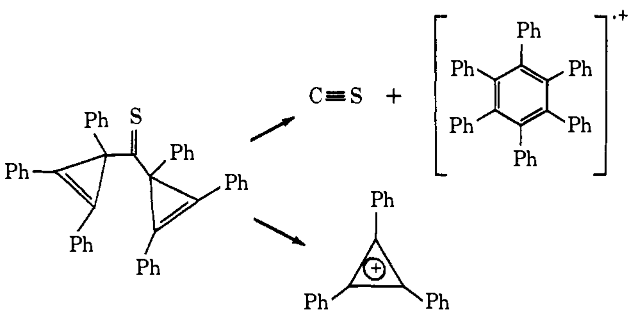
(5) For a preliminary communication of a portion of this work, see B. M. Trost and R. C. Atkins, *Tetrahedron Lett.*, 1225 (1968).

(6) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958).

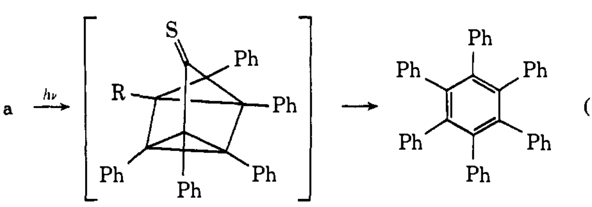
(7) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).

λ_{max} at 242 nm (log ϵ 4.41), and its nmr spectrum which exhibited only aromatic protons. Comparison of its properties with a known sample confirmed the assignment.[8]

The structure of the thioketone rests mainly on its spectroscopic properties. Elemental analysis combined with the parent ion at *m/e* 580 in its mass spectrum established the molecular formula of $C_{43}H_{30}S$. In addition to the molecular ion, the mass spectrum possesses only two additional peaks of moderate intensity, *m/e* 534 and 267 (base peak). The base peak indicated the presence of the triphenylcyclopropenyl unit. The unusual facile loss of 46 giving rise to the *m/e* 534 ion suggested the presence of a C=S unit. The infrared spectrum confirmed these deductions. Absorptions at 1072 and 1822 cm^{-1} can be assigned to the thiocarbonyl[9] and cyclopropene[10] groups, respectively. The similarity of the ultraviolet spectrum [nm (log ϵ) 225 (4.68), 302 (4.48), and 326 sh (4.26)] to the phenylated bicyclopropenyls supported the structural assignment.[10]



Chemical evidence for the structure derives from a consideration of its photochemistry. The correlation between reactions induced by electron bombardment (*i.e.*, mass spectral fragmentations) and photons suggested the extrusion of carbon monosulfide. In the event, irradiation of the thioketone with a medium-pressure Hanovia 450-W lamp produced a quantitative yield of hexaphenylbenzene—exactly as anticipated. Considering the facile conversions of bicyclopropenyls to benzenes (presumably *via* prismanes),[10] the photodimerization of 1,2,3-triphenylcyclopropene,[11] and the photodecarbonylation of quadricyclanone to benzene,[12] the rationale presented in eq 1 appears most reasonable

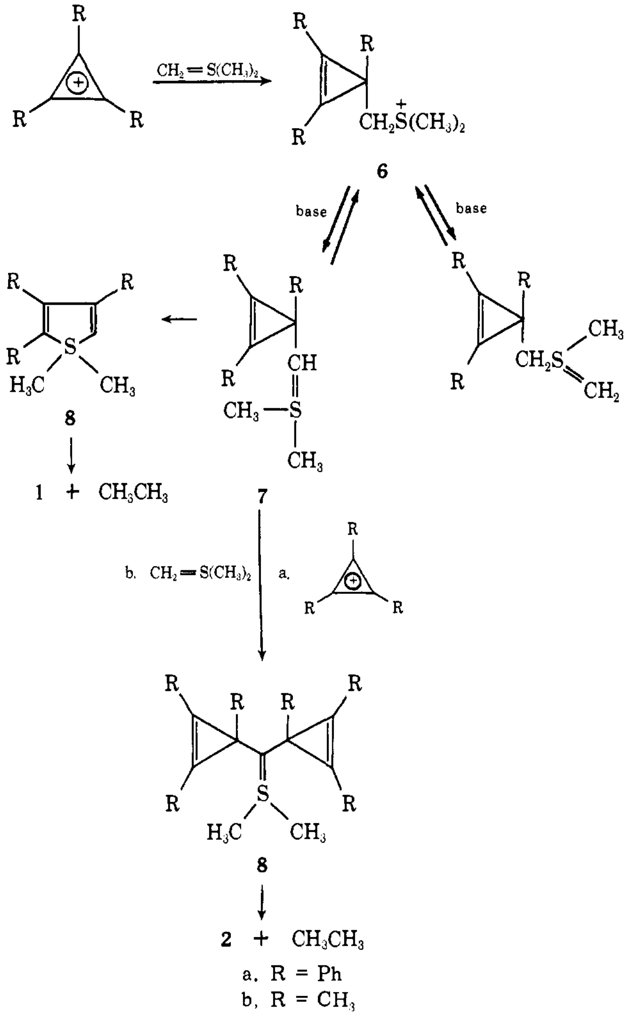


(1)

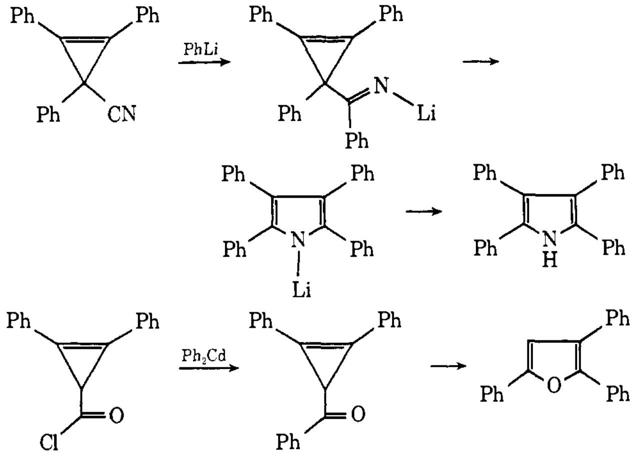
for this transformation. The photochemical event, therefore, clearly attests to the structural assignment of **2a** as presented. *This example represents the first observation of a thioketone analog of a photochemical decarbonylation.*

The formation of these products in the ylide reaction required the π sulfurane to be a thiocarbonyl transfer agent—an unprecedented reaction! Scheme II outlines

Scheme II. Proposed Pathways for Formation of **1** and **2**



a possible pathway for the reaction. Charge neutralization generates a cyclopropenylcarbinylsulfonium salt **6a**. Reversible ylide generation, in which dimethylsulfonium methylide may be serving as base, eventually generates the ylide **7a**. This ylide suffers unimolecular heterovinylcyclopropene rearrangement to the sulfurane **8** which aromatizes by dealkylation of sulfur. Precedent for such a rearrangement exists in the work of



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[8] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1483 (1965).

[9] (a) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 355; (b) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 311.

[10] R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965).

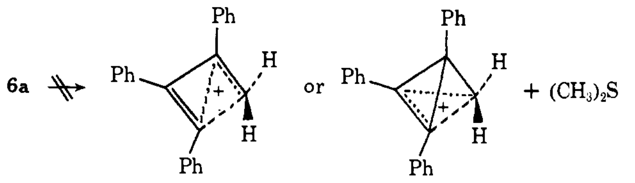
[11] (a) H. Durr, *Tetrahedron Lett.*, 1649 (1967); (b) C. DeBoer and R. Breslow, *ibid.*, 1033 (1967).

[12] D. M. Lemal, private communication.

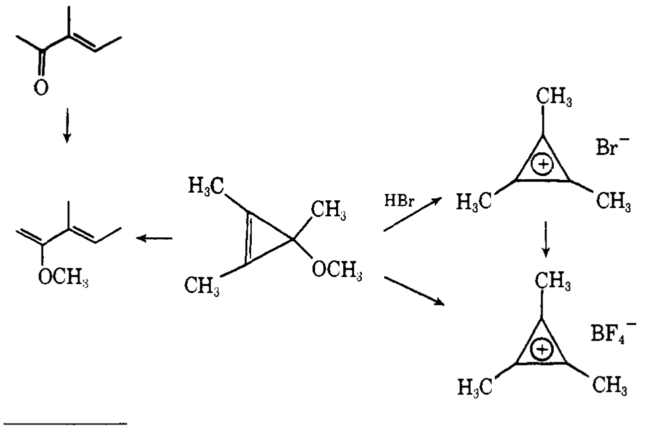
Table I. Yield Data for Reaction of Trimethylcyclopropenium Salt and Ylide

Ratio ylide : cyclopropenium salt	Compd 1b	3b	4b	5b	CH_4	CH_3CH_3	$CH_2{=}CH_2$
1:1	19.0	4.3	0.9	0.3	2.2	4.3	5.1
2:1	34.4	3.6			6.5	13.9	15.1

Breslow, who reported the generation of 2,3,4,5-tetraphenylpyrrole upon treatment of 1,2,3-triphenyl-1-cyanocyclopropene with phenyllithium and 2,3,5-triphenylfuran upon treatment of 1,2-diphenylcyclopropenecarboxylic acid chloride with diphenylcadmium.[13] Alternatively, the ylide **7a** may recombine with starting cyclopropenium salt to yield **8a** after proton abstraction. The tremendous steric hindrance at the ylidic carbon precludes any ylide reactions. Thus, conversion of decet sulfur of the π sulfurane to octet sulfur provides a driving force for sulfur dealkylation and generation of thioketone **2a**. No products attributable to the presence of a bicyclopropenyl or tetrahedranyl cation were detected. The facility of the ylide processes precluded even a supposedly facile solvolysis of the sulfonium salt **6**.[14,15]



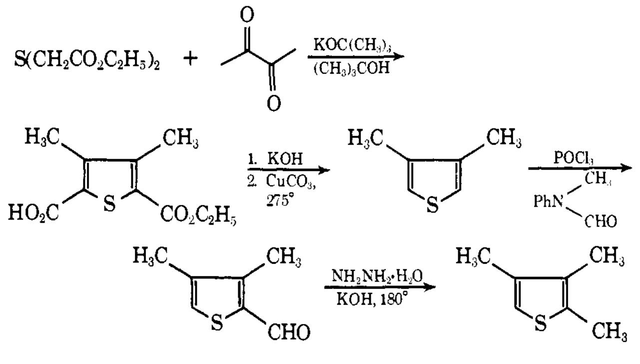
The unprecedented proposal of conversion of a π sulfurane into a σ sulfurane required more complete analysis of the reaction. The use of a trimethylcyclopropenium salt rather than the triphenyl derivative would greatly facilitate product isolation and analysis by the use of vpc. Furthermore, the methyl substitution should provide stabilization to any products formed while providing convenient nmr labels for their identification. Trimethylcyclopropenium fluoroborate was prepared from the corresponding bromide by treatment with silver fluoroborate or preferably by direct reaction of 1-methoxy-1,2,3-trimethylcyclopropene with anhydrous fluoroboric acid in the presence of acetic anhydride.[16] The greater stability of the fluoroborate compared with the bromide salt makes it the salt of choice. The sensitivity of the methoxycyclopropene to ring opening to 2-methoxy-3-methyl-1,3-pentadiene precluded its isolation. Thus, in all cases, it was converted directly to salt upon generation.



The reaction between trimethylcyclopropenium fluoroborate and dimethylsulfonium methylide, the latter generated by addition of a hexane solution of *n*-butyllithium to a stirred suspension of trimethylsulfonium fluorobrate in tetrahydrofuran at −78°, was conducted in an apparatus designed to allow the slow passage of nitrogen over the reaction and the collection of all volatile products in sand traps cooled to −78 and −196°. The products and their yields are summarized in Scheme I and Table I.

The major product was identified as 2,3,4-trimethylthiophene (**1b**) on the basis of its nmr and mass spectra (see Experimental Section). The labeling pattern was confirmed by unambiguous independent synthesis as outlined in Scheme III. The condensation of biacetyl with diethyl thiodiglycolate afforded, with saponification during work-up, 3,4-dimethylthiophene-2,5-dicarboxylic acid.[17] Heating the diacid with a catalytic amount of basic copper carbonate resulted in a double decarboxylation to yield 3,4-dimethylthiophene, the nmr of which had two singlets at δ 2.12 and 6.70 of intensity ratio 3:1. Treatment of the dimethylthiophene with the Vilsmeier reagent followed by Wolff–Kishner reduction afforded authentic 2,3,4-trimethylthiophene (**1b**). The material obtained in this way had spectral and gas chromatographic characteristics identical with those of the trimethylthiophene obtained from the ylide reaction.

Scheme III. Preparation of 2,3,4-Trimethylthiophene



The structures assigned to the three sulfide products are based on their spectral characteristics and on ele-

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[13] R. Breslow, R. Boikess, and M. Battiste, *Tetrahedron Lett.*, 42 (1960).

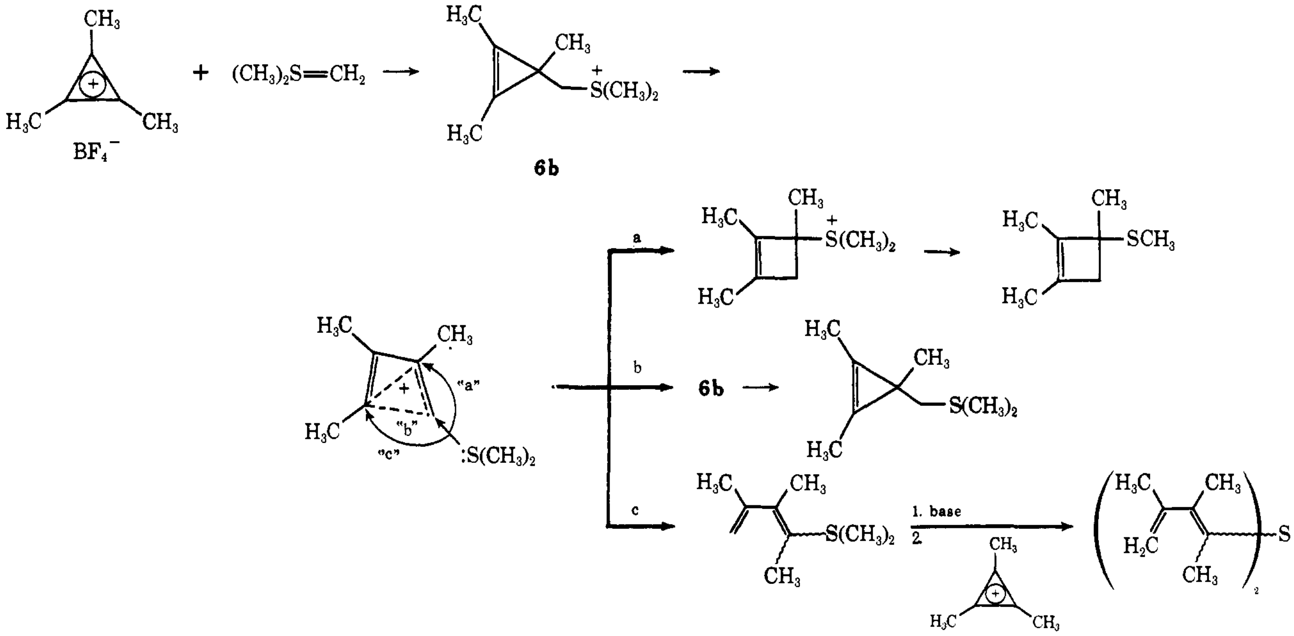
[14] For solvolysis of cyclopropenylcarbinyl systems, see R. Breslow, J. Lockhart, and A. Small, *J. Amer. Chem. Soc.*, **84**, 2793 (1962); R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966); R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963.

[15] For comparison of solvolysis of a sulfonium salt to a brosylate, see C. Chit and H. Felkin, *C. R. Acad. Sci., Ser. C*, **264**, 1412 (1967).

[16] G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968); G. L. Closs in "Advances in Alicyclic Chemistry," Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966.

[17] H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).

Scheme IV. Mechanism of Formation of Sulfides **3–5b**



mental analysis or high-resolution mass spectrometry data. In this way, the identity of **3b** has been established as 3-thiomethoxy-1,2,3-trimethylcyclobutene. The nmr showed an AB pattern at δ 2.44 and 2.20 (J = 12 Hz) due to the cyclobutene methylene. Two allylic methyl groups appeared as finely coupled singlets at δ 1.65 and 1.48. The *S*-methyl group absorbed at δ 1.82. The mass spectrum had a molecular ion at m/e 142 ($C_8H_{14}S$) and showed a peak at m/e 95 due to loss of S–CH$_3$.

The nmr spectrum of compound **4b** showed three singlets at δ 2.50 (2 H) due to the methylene adjacent to sulfur, δ 1.08 (3 H) due to the saturated methyl on the cyclopropene ring, and δ 1.94 (9 H). When the spectrum was recorded in benzene, the singlet at δ 1.94 split into two singlets of intensity ratio 1:2, due to the cyclopropene allylic methyls and the *S*-methyl. The mass spectrum showed a molecular ion at m/e 142 ($C_8H_{14}S$) and a base peak at m/e 81 (trimethylcyclopropenium). The molecular formula was confirmed by high-resolution mass spectrometry. These data establish the structure as methyl 1,2,3-trimethylcyclopropenylmethyl sulfide.

The spectral data for **5b** have led to its identification as bis(1,2,3-trimethyl-1,3-butadienyl) sulfide. The nmr spectrum showed a terminal methylene as two finely coupled singlets at δ 2.50, 1.95, and 1.80. The mass spectrum showed a molecular ion at m/e 222 ($C_{14}H_{22}S$), a peak at m/e 127 due to loss of $C_7H_{11}S$, and a peak at m/e 95 ($C_7H_{11}^+$). The ultraviolet spectrum indicated significant conjugation, having an absorption maximum at 227 nm with an ϵ of 22,000.

The gaseous products which were trapped at −196° were analyzed by gas chromatography. Identification was by retention time comparison with known samples. Use of a silica gel vpc column provided sufficient separation to make this a valid method of identification. The ethane was shown to arise from reaction of the ylide with the cyclopropenium salt by a control experiment in which dimethylsulfonium methylide was allowed to decompose in the absence of any cyclopropenium salt. Less than 0.1% (estimated limit of detection) ethane was produced, although ethylene was formed in substantial quantities, in agreement with the finding of Corey and Chaykovsky.[7]

In an effort to identify any nonvolatile components of the reaction mixture, extensive thin layer and column chromatographic analyses using various substrates and solvent systems were performed. The search failed to yield any additional identifiable compounds. Analysis of the aqueous phase from the reaction allowed recovery of 30–60% trimethylsulfonium salt but less than 10% trimethylcyclopropenium salt. Varying the ratio of ylide to cyclopropenium salt (Table I) resulted in substantial improvements in the yields of ethane and trimethylthiophene—these almost doubled when the ratio was 2:1.

In contrast to the reaction of the triphenyl salt, the trimethyl salt reaction led to detectable quantities of solvolysis products of the initially produced sulfonium salt **6b**. Thus, compounds **3–5b** arise by trapping of a cyclopropenylcarbinyl cation at each site bearing positive charge as outlined in Scheme IV. For simplicity the cation is drawn as a nonclassical ion; however, classical interconverting ions equally account for the products. Recombination of dimethyl sulfide followed by dealkylation at C-2 (path a) produces the cyclobutene derivative **3b**, at C-1 (path b) the cyclopropenylcarbinyl derivative **4b**, and at C-4 (path c) the bisbutadienyl sulfide **5b**.

The presence of solvolysis products prompted a detailed search for products of deprotonation of carbonium ions—in particular trimethyltetrahedrane and/or trimethylcyclobutadiene. The existence of trimethyltetrahedrane in the course of the reaction should be characterized by the anticipated decomposition products, propyne and 2-butyne.[18] Analysis of the sand traps failed to reveal either of these gases. Trimethylcyclobutadiene would be expected to dimerize to a tricyclo[2.2.0.0]octane[19] or undergo a Diels–Alder reaction

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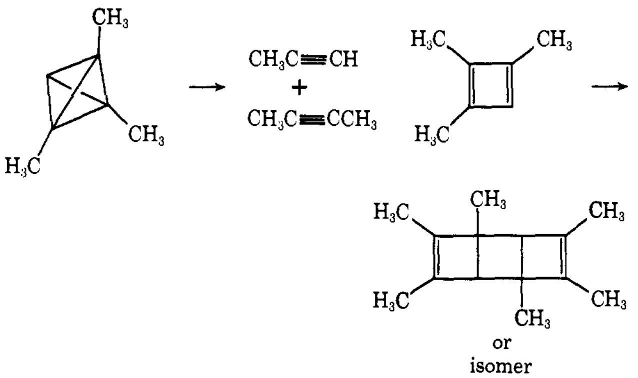
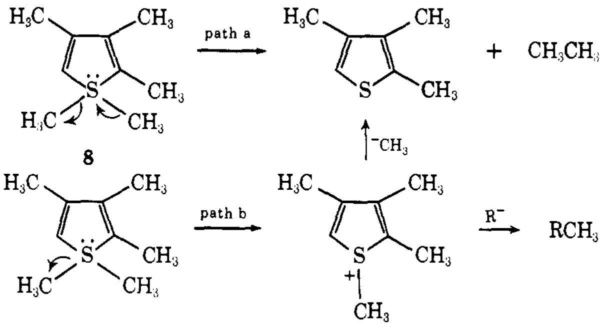
[18] (a) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, **92**, 406 (1970); (b) R. F. Peterson, R. T. K. Baker, and R. L. Wolfgang, *Tetrahedron Lett.*, 4749 (1969); (c) H. Ona, H. Yamaguchi, and S. Masamune, *J. Amer. Chem. Soc.*, **92**, 7495 (1970).



with the thiophene produced in the reaction. Again, no products attributable to such structures could be found. Attempts to enhance the solvolysis products by going to higher temperatures or more polar solvents only reduced the yields of all observed products with no formation of new ones.

Again, in contrast to the triphenyl salt, the major product of the trimethylcyclopropenium fluoroborate reaction was the thiophene with no detectable amounts of the thioketone. The formation of considerable quantities of ethane and the identical response of its yield as that of the thiophene with the variation in ratio of the two reactants ties these two products together as suggested in Scheme II. Thus, rationalization of formation of thiophene through an intermediate such as **8** appears vindicated.

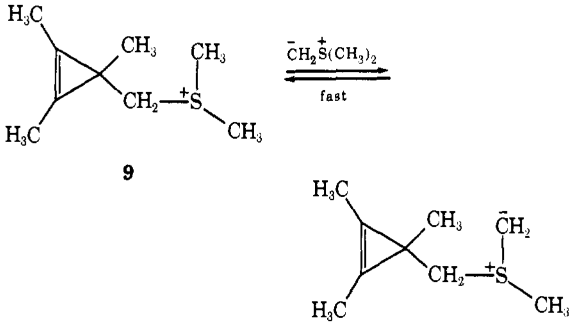
The fact that the yields of thiophene and ethane are not equal raises the question of the mechanism of dealkylation. Intramolecular ligand expulsion or ionization followed by S$_N$2 dealkylation of the thiophenium salt are the most likely possibilities. The occurrence of reasonable quantities of methane in all these reactions suggests that this latter pathway is operative at least to some extent.



Deuterium labeling potentially provides a more intimate probe into the mechanism of ethane formation. The reaction of a mixture of perdeuteriodimethylsulfonium methylide and perhydrodimethylsulfonium methylide with trimethylcyclopropenium salt would yield d_6- and d_0-ethane only if an intermediate such as **8** underwent intramolecular ligand expulsion. Disproportionation of **8** would lead to crossover and subsequent formation of substantial quantities of CH_3CD_3. It was shown that deuterium exchange between ylides prior to reaction with the cyclopropenium salt was not an important process by a control experiment in which an excess of cyclohexanone was added to a mixture of d_8-ylide and d_0-ylide. Only 7% d_1-oxirane was obtained, indicative of a minimal amount of crossover.

The ethane produced from the reaction of perdeuteriodimethylsulfonium methylide (prepared from 94% d_9-sulfonium salt) with trimethylcyclopropenium salt was shown mass spectrometrically to be 80% d_6. The thiophene produced was found to be at least 95% d_1 by$_2$ nmr analysis. Also isolated in the reaction was an 8% yield of 1,2,3-trimethylcyclopropenyl-*methyl*-d_3 methyl-*d* sulfide (**4**-d_5) as shown by its nmr spectrum which consisted of two singlets at δ 1.92 and 1.08 (intensity ratio 2:1) and its mass spectrum which had a molecular ion at *m/e* 147 ($C_8H_9D_5S$) and a base peak at 81 (trimethylcyclopropenium$^+$).

Mass spectral analysis of the ethane produced from the reaction of a mixture containing 1 equiv each of perdeuteriodimethylsulfonium methylide and perhydrodimethylsulfonium methylide with 1 equiv of trimethylcyclopropenium salt indicated that the deuterium content had been completely scrambled. Rapid ylide formation and subsequent protonation or deuteration, as shown in eq 2, would explain the loss of isotopic purity in the ethane produced.



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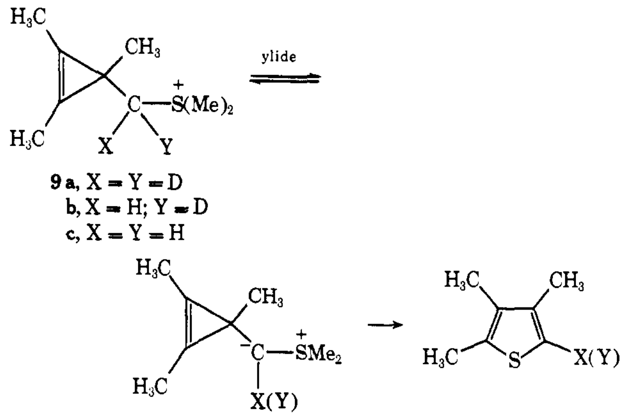
(2)

Having in hand isotopic distribution data for the mixture of perdeuterio- and perhydrosulfonium ylide (as measured by mass spectrometric analysis of the oxirane, 7-oxaspiro[5.2]octane) and the thiophene produced in the ylide reaction, examination of the relative kinetics of intermediate processes in the reaction becomes possible.

If the assumption is made that proton exchange by the methinylide (derived from the cyclopropenylcarbinylsulfonium salt **9**) is slow relative to ring expansion to give thiophene, d_8-**9** (**9a**, equal to per cent d_2-oxirane) will give rise to d_1-thiophene, and d_0-**9** (**9c**, equal to per cent d_0-oxirane) will yield d_0-thiophene. Salt **9b** (equal to per cent d_1-oxirane) will be partitioned be-



9a, X = Y = D
b, X = H; Y = D
c, X = Y = H

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(19) For a recent generation of a cyclobutadiene by a cyclopropenylcarbinyl rearrangement, see G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, **88**, 4116 (1966).

tween d_1- and d_0-thiophene according to the value of k_H/k_D for proton abstraction. Applying reasonable values[20] for k_H/k_D of 1, 2, 3, 5, and 7, one arrives at predicted values for the isotopic distribution of thiophene, as given in Table II.

Table II. Isotope Data for the Reaction of Dimethylsulfonium Methylide with Trimethylcyclopropenium Salt[a]

Assumed k_H/k_D	Calcd deuterium distribution of thiophene, % Method A[b] d_0	d_1	Method B[c] d_0	d_1	Observed deuterium content of thiophene, %
1	64.0	36.0	64	36	78.1 d_0, 21.9 d_1
2	65.8	34.2	78	22	
3	66.7	33.3	84	16	
5	67.7	32.3	90	10	
7	68.1	31.9	93	7	

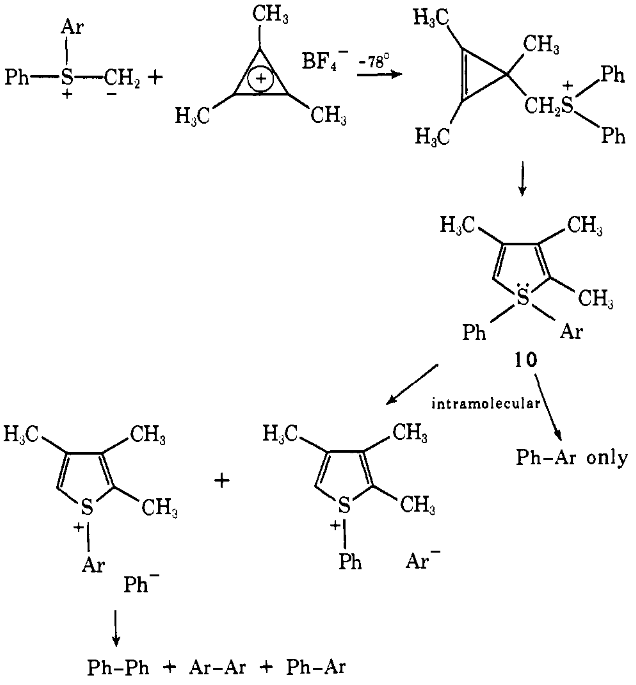
[a] Deuterium distribution of methylide was as follows: 58.5% d_0, 11.0% d_1, and 30.5% d_2. [b] Assuming proton exchange by the methinylide is slow relative to ring expansion. [c] Assuming complete scrambling of the methinylide; *i.e.*, proton exchange is rapid.

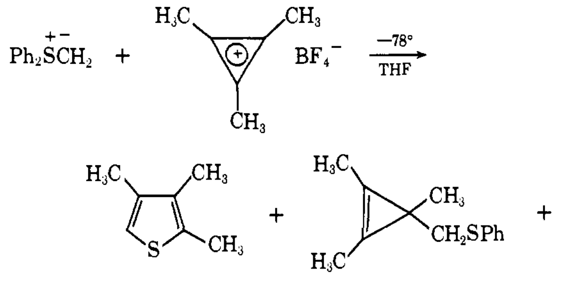
Assuming then that proton exchange by the methinylide is rapid relative to thiophene formation, the isotopic content of the carbinyl position in **9** will reflect the total deuterium content of the ylide solution (36% deuterium). Again, applying various values of k_H/k_D for proton abstraction, the isotopic content of the thiophene may be predicted.

As may be seen from Table II, the observed isotopic distribution of the thiophene is equal to that predicted assuming rapid exchange by **9** and a k_H/k_D value of 2. In systems where proton abstraction is not the rate-limiting step, values for k_H/k_D from 1.2 to 3 have been observed.[20b,c] When proton removal is the rate-limiting step, k_H/k_D values lie between 2.7 and 8.[20d] It therefore appears that proton exchange at the methylene group of the sulfonium salt **9** is rapid relative to ring expansion and the latter must be the rate-determining step of the reaction.

An alternative approach to the question of the existence of a pentacoordinated sulfur species may be had through the reaction of phenyl-*p*-tolylsulfonium methylide with trimethylcyclopropenium salt. As outlined in Scheme V, intramolecular ligand expulsion of a pentacoordinated intermediate such as **10** would yield only *p*-methylbiphenyl, whereas an intermolecular mechanism, such as disproportionation to yield a thiophenium salt, would give rise to biphenyl and bi-*p*-tolyl in addition to *p*-methylbiphenyl.

Scheme V. Phenyl-*p*-tolylsulfonium Methylide as a Probe of the Mechanism of Collapse of Pentacoordinate Sulfur

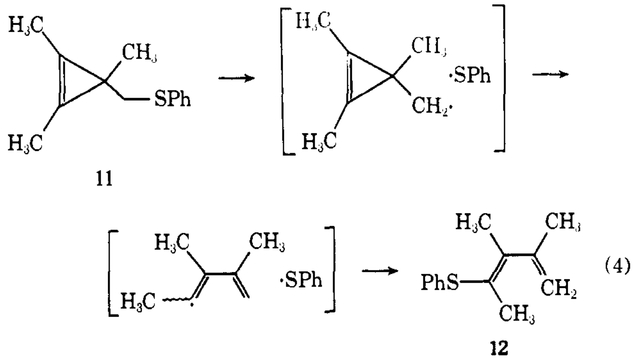




13 (0.38%) 11 (16%) (3)

$$n\text{-BuSPh} + \underset{(3\%)}{CH_3SPh} + \underset{(4.4\%)}{Ph\text{-}Ph} + \underset{(25\%)}{Ph_2S} + \underset{(43\%)}{Ph_2SCH_3}$$
$$(4.9\%)$$

The reaction of diphenylsulfonium methylide with trimethylcyclopropenium salt was studied as an initial probe into the problem. The products obtained (eq 3) indicate that thiophene formation is not a favorable process. The major product arising from reaction of the ylide with cyclopropenium salt was phenyl (1,2,3-trimethylcyclopropenyl)methyl sulfide (**11**). The nmr spectrum consisted of a broad singlet at δ 7.21 due to the phenyl group and three singlets at δ 3.00, 1.82, and 1.13 of intensity ratio 2:6:3, indicative of the trimethylcyclopropenylcarbinyl moiety. Gas chromatography of **11** resulted in a facile rearrangement (eq 4) to yield



phenyl (1,2,3-trimethylbutadienyl) sulfide (**12**) having nmr absorption at δ 7.19 due to the phenyl group, two broad singlets at δ 4.90 and 4.72 arising from the terminal methylene, and a finely coupled singlet at δ 1.89 from the three allylic methyl groups. Sulfide **12** presumably arises *via* cleavage of **11** to give a cyclopropenylcarbinyl thiophenoxide radical pair, which rapidly collapses to form the butadienylphenyl sulfide system. The alternative ion-pair mechanism seems less likely under such conditions.

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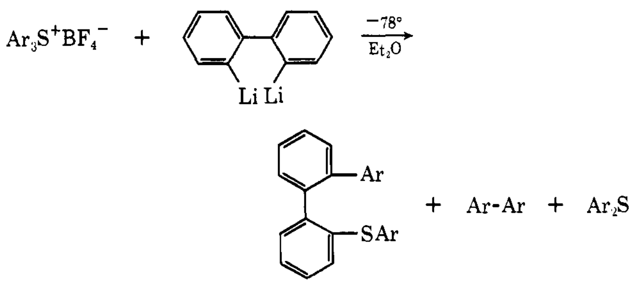
(20) (a) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955); (b) C. E. Boozer and E. S. Lewis, *J. Amer. Chem. Soc.*, **76**, 794 (1954); (c) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961; (d) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter 11.

The remaining products described in eq 3 all arise from thermal decomposition of the ylide.

The low yield of thiophene obtained was disappointing in terms of utilizing biphenyl formation as a probe into the possible existence of a pentacoordinated sulfur species. In an effort to explore the possibility that the lack of thiophene formation was due to an alternate mode of collapse of an initially formed pentacoordinated sulfur species, the study of a route which would lead to a related sulfurane was undertaken. The reaction of dilithiobiphenyl with a triarylsulfonium salt appeared to provide the means for generating such a species.[4] The reaction of 2,2′-dilithiobiphenyl with either triphenyl or tri-*p*-tolylsulfonium fluoroborate in ether at −78° was found to give a quantitative yield of the sulfides **13** and **14**, respectively. The structure assignment for **13** relies mainly on the mass spectrum which showed a molecular ion at *m/e* 338 ($C_{24}H_{18}S$) and a base peak resulting from loss of S–C_6H_5 at *m/e* 229. The molecular weight was confirmed by high-resolution mass spectrometry. The structure for **14** was assigned on the basis of its nmr spectrum which showed two complex multiplets at δ 7.25 and 6.86 due to the aromatic protons and two sharp singlets at δ 2.29 and 2.27 resulting from the two methyl groups. The molecular weight of **14** was also confirmed by high-resolution mass spectrometry to be 366.146 ($C_{26}H_{22}S$) and it possessed the appropriate fragments at *m/e* 243 for loss of S–C_7H_7. These products were subsequently confirmed by comparison to authentic samples prepared in an independent manner.[21]

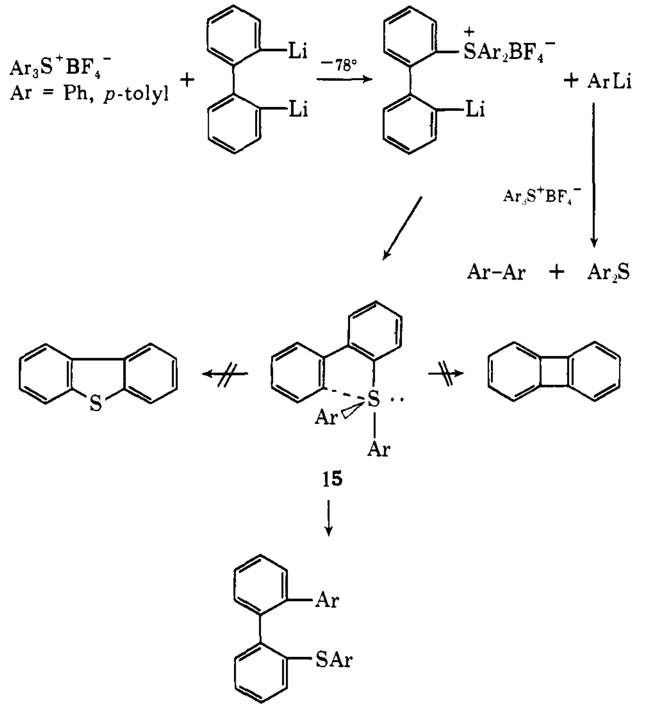


13, Ar = Ph
14, Ar = *p*-tolyl

Ar = Ph, *p*-tolyl

The products obtained are consistent with an initial addition of dilithiobiphenyl to the triarylsulfonium salt to give an intermediate sulfonium salt and 1 mol of aryllithium (Scheme VI). Intramolecular closure would give rise to the pentacoordinated sulfur species **15**. Representation of the intermediate as a trigonal bipyramid, with the free electron pair occupying an equatorial position, is in accordance with studies by Wittig[22] and Hellwinkel[23] of the pentacoordinated phosphorus analog and with what is known concerning the stereochemistry of pentacoordinated sulfur derivatives.[24] The axial–equatorial orientation of the dibenzothiophenium ring resulting from the ring closure is consistent with angular considerations and the work of Wittig.[22]

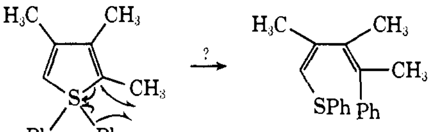
Scheme VI. Mechanism of the Reaction of Dilithiobiphenyl with Triarylsulfonium Salts



13, Ar = Ph
14, Ar = *p*-tolyl

Consideration of the orbitals involved in ligand expulsion will show that axial–equatorial coupling in which the ligand is capable of free rotation provides the opportunity for maximum overlap.[4] Vpc analysis of the reaction mixtures failed to show the presence of any biphenylene or dibenzothiophene that would have resulted from other modes of collapse. Formation of diaryl sulfide and biaryl in the reaction is readily explainable from the reaction of the initially formed aryllithium with additional triarylsulfonium salt.[4]

If the reaction of diarylsulfonium methylide with trimethylcyclopropenium salt is viewed in terms of a pentacoordinate intermediate such as **15** undergoing a similar form of ligand expulsion, the possibility of formation of a diarylbutadienyl sulfide (**16**) becomes evident. However, analysis of the reaction mixtures failed to indicate the presence of any products resembling **16**. The low yields of thiophene upon using diarylsulfonium methylides remains unexplicable.



16

It should be pointed out that the sulfuranes proposed as intermediates may be transition states. Although rigorous exclusion of the latter is impossible, the nature of the processes involved makes us favor the former.

Extension of the thiocarbonyl insertion reaction to the tropylium system was investigated as a route to the potential aromatic 1-thiacyclononatetraene in which there is a reduction in the steric crowding of the 10π-electron system in the mono-trans isomer. However, treatment of tropylium fluoroborate[25] with a tetrahydro-

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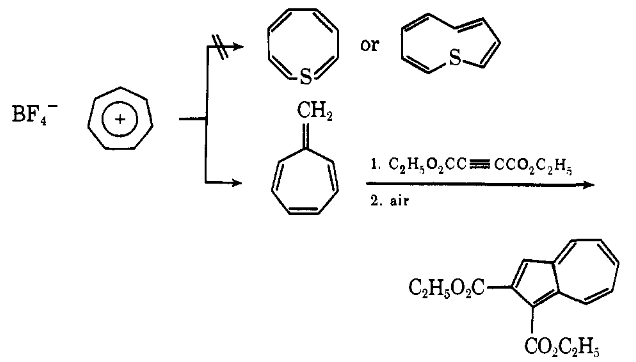
(21) B. M. Trost and H. C. Arndt, unpublished results.

(22) G. Wittig, *Bull. Soc. Chim. Fr.*, 1162 (1966).

(23) D. Hellwinkel, *Chem. Ber.*, **99**, 3642 (1966).

(24) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, p 535; (b) R. J. Arhart and J. C. Martin, *J. Amer. Chem. Soc.*, **94**, 4997, 5003 (1972); I. C. Paul, J. C. Martin, and E. F. Perozzi, *ibid.*, **94**, 5010 (1972).

(25) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).



furan solution of dimethylsulfonium methylide led to the very reactive heptafulvene in 90% yield. Addition of diethyl acetylenedicarboxylate followed by air oxidation which generated diethyl 1,2-azulenedicarboxylate allowed characterization of this unstable hydrocarbon.[26] This method constitutes a useful synthesis of the fascinating heptafulvene. No products attributable to the 10π heterocycle were present.

Experimental Section[27]

Reaction of Triphenylcyclopropenium Bromide with Dimethylsulfonium Methylide. A suspension of 510 mg (2.50 mmol) of powdered trimethylsulfonium iodide in 100 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride) was cooled to −78° under a nitrogen atmosphere. With vigorous stirring, 1.65 ml (2.48 mmol) of 1.5 *M* *n*-butyllithium in hexane was added dropwise. After the mixture was stirred for 15 min, 1.12 g (3.23 mmol) of triphenylcyclopropenium bromide[28] was added in one portion. The solution turned deep red instantaneously. Stirring continued at −78° for 3 hr during which time it turned pale orange and at room temperature for 1 hr during which time it turned yellow. The solution was diluted with 250 ml of ether and was washed with saturated aqueous ammonium chloride and aqueous potassium carbonate. After drying and evaporation *in vacuo*, the residue partially solidified. This residue was chromatographed on silica gel utilizing pentane–10% benzene as eluting solvent. The first eluted compound was recrystallized from ethanol to give 103 mg (32% yield) of white needles, mp 211–212° (lit.[8] mp 216°), and identified as 2,3,4-triphenylthiophene (**1a**). For its spectroscopic properties, see the section on Results and Discussion. Further elution with 20% benzene in pentane provided 210 mg (20%) of a second solid, mp 70–74°, tentatively assigned as 1,2,3-triphenyl-1-*n*-butylcyclopropene on the basis of its spectroscopic properties. Its infrared spectrum ($CHCl_3$) showed in addition to aliphatic and aromatic C–H stretch bands at 2850–3080 cm^{-1}, a cyclopropene double bond at 1820 cm^{-1}, and aromatic absorptions at 1495 and 1600 cm^{-1}. Its ultraviolet spectrum (C_2H_5OH) showed maxima at nm (ε) 333 (23,100), 317 (27,500), 310 sh (23,000), and 228 (28,900). Its nmr spectrum showed the aromatic multiplet at δ 7.08–7.85 (15 H), multiplets at δ 2.37 (2 H) and 1.32 (4 H), and a distorted triplet at δ 0.81 (3 H). Its mass spectrum showed a molecular ion at *m/e* 324 and a base peak at *m/e* 267. Continued elution with 20% benzene in pentane provided 160 mg (27% yield) of a third solid, mp 198–200°, which was identified as bis(1,2,3-triphenylcyclopropenyl) thioketone (**2a**). For spectroscopic properties, see the section on Results and Discussion.

Anal. Calcd for $C_{43}H_{30}S$: C, 89.23; H, 5.23. Found: C, 89.49; H, 5.46.

Photolysis of Bis(1,2,3-triphenylcyclopropenyl) Thioketone. A solution of 36.8 mg (0.064 mmol) of thioketone was dissolved in 250 ml of freshly distilled deaerated benzene. It was placed in a photolysis well fitted with a Pyrex filter and irradiated 4 hr with a medium-pressure 450-W Hanovia lamp. Tlc analysis indicated the absence of starting material. Rotoevaporation *in vacuo* yielded a crude solid which was chromatographed on 35 g of silica gel eluting with benzene. There was obtained 33.6 mg (99%) of a pale yellow solid which was obtained colorless after recrystallization from pentane–cyclohexane (31.4 mg, 94% recovery), mp >310°. Comparison of its infrared spectrum with an authentic sample confirmed its identity as hexaphenylbenzene.

Preparation of 3,4,5-Trimethyl-3-methoxy-3*H*-pyrazole. 3-Methylpentane-2,4-dione [124 mg, bp 58–58° (11 mm)] was prepared in 83% yield as described[29] from 168 g (1.21 mol) of anhydrous potassium carbonate, 131.3 g (1.31 mol) of acetylacetone, and 226 g (1.59 mol) of freshly distilled methyl iodide in 250 ml of dry acetone.

Treatment of 32.45 g (0.284 mol) of 3-methylpentane-2,4-dione in 50 ml of methanol with 20.97 g (0.420 mol) of hydrazine hydrate as described by Rothenberg[30] produced 28.42 g (91%, mp 134.5–135.5°) of 3,4,5-trimethylpyrazole.

3,4,5-Trimethyl-3-methoxy-3*H*-pyrazole [2.77 g (44%), bp 52–53° (2.8 mm)] was obtained as a bright yellow liquid from 7.90 g (0.044 mol) of *N*-bromosuccinimide and 4.88 g (0.044 mol) of 3,4,5-trimethylpyrazole in methanolic potassium hydroxide as previously described.[31]

Preparation of Trimethylcyclopropenium Salts. 1,2,3-Trimethyl-1-methoxycyclopropane. All photolyses were run employing a Pyrex filter and a 450-W Hanovia high-pressure mercury vapor lamp. In a typical run, 6.70 g (47.9 mmol) of freshly distilled 3,4,5-trimethyl-3-methoxy-3*H*-pyrazole was dissolved in 500 ml of freshly distilled and dried pentane. The yellow solution was cooled to *ca.* 15° with tap water and photolyzed for 1–2 hr. Upon completion of the reaction as monitored by N_2 evolution, the solution was colorless. Later photolysis runs were made at 0° in an ice bath. Interruption of the photolysis prior to completion showed the intense red color described by Closs.[32]

Bromide Salt. All work was performed in a dry bag under a nitrogen atmosphere. Dry hydrogen bromide gas was passed through the crude pentane photolysis solution until a white solid began to appear (1–2 min). The precipitate was immediately filtered with suction through a sintered glass funnel. The resulting tan solid was then put in a vial and stored under nitrogen at 0°. Moisture (exposure to air) quickly turned the salt into a colored oil. In a typical run, 6.15 g (43.9 mmol) of methoxypyrazole yielded 2.58 g (36%) of the salt. An nmr spectrum (CF_3COOH) showed one sharp singlet at δ 2.97.

Anal. Calcd for C_6H_9Br: C, 44.75; H, 5.63; Br, 49.62. Found: C, 44.63; H, 5.83; Br, 49.51.

Fluoroborate Salt. The colorless photolysis solution (obtained as described above) was transferred to a 2-l. three-neck flask. In a run using 6.70 g (0.48 mol) of methoxypyrazole as photolysis precursor, 17.8 g (0.096 mol) of 48% fluoroboric acid and 98 g (0.70 mol) of acetic anhydride were mixed dropwise at 0°. This yellow liquid was then added dropwise over 0.5 hr to the photolysis solution being held at −20°. After an additional 0.5 hr at −20°, the mixture was warmed to 0°, 500 ml of ether was added, and the stirring was continued at 0° for 1 hr. The supernatant liquid was then decanted from the red solid product which, upon the addition of 1 l. of ether and shaking, produced tan crystals. Filtration, dissolving in a minimum amount of acetone, and reprecipitation by the slow addition of 1 l. of ether produced 4.64 g (58%) of a white solid: mp 130–132° (lit.[32] 132–134°); nmr (D_2O) δ 2.81 (singlet); ir (CH_2Cl_2) 3050, 2930, 1440, 1260, 1050 cm^{-1} (broad).

Anal. Calcd for $C_6H_9BF_4$: C, 42.90; H, 5.40; F, 45.25. Found: C, 43.11; H, 5.47; F, 45.21.

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(26) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

(27) Melting points were taken on a Thomas–Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Models 11 and 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A or HA-100 spectrometer fitted with a variable temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Analyses were performed by Spang Microanalytical Laboratory and Micro-Tech Laboratories, Inc. Unless otherwise indicated, extractions were performed with chloroform and magnesium sulfate was employed as a drying agent. Vpc analyses were performed on an Aerograph Model 90P instrument equipped with a thermal conductivity detector or a Hewlett-Packard Model 5750 equipped with a flame ionization detector. All columns were prepared from base washed support in 0.25 in. o.d. copper or stainless steel tubing.

(28) R. Breslow and H. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

(29) A. W. Johnson, *Org. Syn.*, **42**, 75 (1962).

(30) V. Rothenberg, *J. Prakt. Chem.*, **160**, 51 (1895).

(31) G. L. Closs and H. Heyn, *Tetrahedron*, **22**, 463 (1966).

(32) (a) G. L. Closs and V. N. M. Rao, *J. Amer. Chem. Soc.*, **88**, 4116 (1966); (b) G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968).

Perdeuteriotrimethylsulfonium Iodide.[33] Trimethylsulfonium iodide (1.22 g, 6.0 mmol) was dissolved in 10.0 ml of D_2O (99.7% D) containing 0.61 g of 40% sodium deuterioxide (to give a 0.6 *N* solution). The solution was stirred in a 25-ml three-neck flask for 3 hr at 62°. After cooling, 0.5 ml of concentrated hydriodic acid (57%) was added to neutralize the solution. The mixture was then evaporated to dryness on a rotary evaporator connected to a vacuum pump. The orange solid was leached with acetone to remove the sodium iodide. The remaining white solid was dissolved in absolute ethanol and precipitated with ether. Filtration gave 1.02 g (84%) of a white solid, mp 192–194° dec (lit.[33] mp 193–194° dec). Isotopic purity was determined to be 96% by nmr integration as compared with a known amount of dimethyl sulfoxide (determined in D_2O).

Perdeuteriotrimethylsulfonium Fluoroborate. Following the procedure described above for the perhydro compound, 1.02 g (0.48 mol) of perdeuteriotrimethylsulfonium iodide gave 0.764 g (93%) of the fluoroborate salt, with an isotopic purity of 94%.

Standard Procedure for Reaction of Dimethylsulfonium Methylide with 1,2,3-Trimethylcyclopropenium Salt. In a typical run, 8 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was placed in a 25-ml three-neck flask cooled to −78° and connected to two sand traps cooled to −78 and −196°. Trimethylsulfonium fluoroborate (0.614 g, 2.74 mmol) was added and the mixture was stirred for 15 min. *n*-Butyllithium (2.52 ml, 2.74 mmol, 1.60 *N* in hexane) was then added from a syringe, and the solution was stirred 15 min at −78°. With a steady flow of nitrogen, 1,2,3-trimethylcyclopropenium fluoroborate (0.312 g, 1.87 mmol) was added in one portion from a solid addition funnel. The solution turned yellow almost immediately. After 0.5 hr at −78°, the cooling bath was removed and the reaction stirred at room temperature for 3 hr. Upon warming the yellow color disappeared, and the mixture became grey. After quenching with 4 ml of water, the reaction was extracted with ether, dried over potassium carbonate, and filtered. Careful distillation of solvent (bath temperature 50°) left a yellow liquid.

The identity and yields of the reaction products were determined by vpc analysis.[34] All collected samples were repassed for further purification prior to spectral analysis. Yields were determined by the response factor method using *o*-methylanisole as an internal standard (relative retention time, $t_R = 1.00$).

The major product isolated from the reaction was found to be 2,3,4-trimethylthiophene (**1b**), rel $t_R = 0.774$ (34.4%). The material isolated was identical in every respect (ir, nmr, and mass spectrum) with that prepared by independent synthesis.

Anal. Calcd for $C_7H_{10}S$: C, 66.61; H, 7.99; S, 25.40. Found: C, 66.79; H, 8.11; S, 25.31.

The minor component with rel $t_R = 0.326$ (4.3%) has been identified as 3-thiomethoxy-1,2,3-trimethylcyclobutene (**3b**): ir (CCl_4) 2920, 1430, 1370, 1290 cm^{-1}; nmr (100-MHz, CCl_4) δ 2.44, 2.20 (AB pattern, two broad doublets, $J = 12$ Hz, 2 H, cyclobutene CH_2), 1.82 (singlet, 3 H, SCH_3), 1.65 (finely coupled singlet, $J = 1$ Hz, 3 H), 1.48 (finely coupled singlet, $J = 1$ Hz, 3 H), 1.34 (singlet, 3 H); mass spectrum *m/e* (rel intensity) 142 (2), 127 (48), 95 (19), 39 (100).

Anal. Calcd for $C_8H_{14}S$: C, 67.54; H, 9.92; S, 22.54. Found: C, 57.62; H, 9.86; S, 22.39.

The third component, rel $t_R = 0.358$ (0.85%), has been characterized as methyl 1,2,3-trimethylcyclopropenylmethyl sulfide (**4b**): ir (CCl_4) 2920, 1860, 1430, 1370, 1240, 1070, 1050 cm^{-1}; nmr (CCl_4) δ 2.50 (singlet, 2 H), 1.94 (singlet, 9 H), 1.08 (singlet, 3 H). When recorded in benzene, the singlet at δ 1.94 split into two singlets of intensity ratio 1:2. Mass spectrum: *m/e* (rel intensity) 142 (4), 127 (57), 81 (100, trimethylcyclopropenium$^+$). The structural formula was established by high-resolution mass spectrometry (calcd for $C_8H_{14}S$, 142.0816; found, 142.0819 ± 0.001).

The minor component with rel $t_R = 0.458$ (0.3%) has been identified as bis(1,2,3-trimethyl-1,3-butadienyl) sulfide (**5b**): ir (CCl_4) 3100, 1630, 1430, 1370, 1280, 1050, 900 cm^{-1}; nmr (100-MHz, CCl_4) δ 4.88, 4.68 (finely coupled singlets, 2 H, $=CH_2$), 2.50, 1.95, 1.80 (finely coupled singlets, 3 H each); uv (EtOH) λ_{max} 227 nm (ϵ 22,000); mass spectrum *m/e* (rel intensity) 222 (6), 161 (1), 127 (4), 95 (28), 41 (100).

An additional minor product was isolated in quantities too small to permit identification. Trap distillation of the reaction mixture (0.05 mm, bath temperature 100°) left a dark viscous oil. Various attempts at column and thin-layer chromatography failed to produce any identifiable products. Vpc analysis[35] also failed to yield any additional products.

Nmr analysis of the aqueous phase (using DMSO as an internal standard) showed 30–60% recovery of sulfonium salt and less than 10% recovery of cyclopropenium salt.

Independent Synthesis of 2,3,4-Trimethylthiophene. Preparation of 3,4-Dimethylthiophene-2,5-dicarboxylic Acid.[36] *tert*-Butyl alcohol (250 ml) was distilled from calcium hydride into a 500-ml three-neck flask fitted with a dropping funnel, condenser, and mechanical stirrer. Potassium metal (15.6 g, 0.398 g-atom, cut under xylene) was then added in small pieces. After the mixture was stirred at room temperature for 0.5 hr, the reaction was refluxed for 2 hr. Diethyl thiodiacetate[37] (40 g, 0.19 mol) and biacetyl (25 g, 0.29 mol) were mixed and put in a dropping funnel. After cooling the butoxide slurry to room temperature the reagents were added dropwise over 15 min. The mixture turned black immediately. After the mixture was stirred at room temperature for 1 hr, 100 ml of 1:1 hydrochloric acid in water was added slowly with ice cooling. After solvent removal on a rotary evaporator, the brown solid which had appeared was dissolved in ether and washed with 1 l. of 2% potassium hydroxide. Acidification of the black aqueous phase gave a tan solid which was filtered and dried under vacuum. The crude yield was 24.3 g (62%).

The infrared spectrum (KBr pellet) of the crude material showed only one carbonyl band at 1650 cm^{-1}. Broad absorption at 2900 cm^{-1} (acid OH) was present. A small sample of the desired half acid–half ester prepared previously showed two distinct carbonyl bands at 1700 and 1650 cm^{-1}. The crude material showed nmr absorption (DMSO-d_6) at δ 7.36 (broad singlet) and 2.41 (singlet). The product was presumed to be 3,4-dimethylthiophene-2,5-dicarboxylic acid, obtained as a result of saponification during the potassium hydroxide base extraction. The diacid was characterized as its methyl ester derivative. A 0.5-g portion of the diacid was purified by extraction with sodium bicarbonate, acidification, and extraction with ether to yield 0.4 g of a light tan solid. To a solution of 24 mg of the purified diacid in 2 ml of ether was added an excess of diazomethane (in ether). Addition of glacial acetic acid followed by washing the ethereal solution with sodium bicarbonate, drying over magnesium sulfate, and evaporation of the solvent on a rotary evaporator yielded a white solid, mp 168–169° (lit.[36] 170–171°), nmr ($CDCl_3$) δ 3.88 and 2.46 (two singlets of equal intensity), in agreement with that reported[36] for dimethyl 3,4-dimethylthiophene-2,5-dicarboxylate.

3,4-Dimethylthiophene. Copper carbonate (1.00 g) was mixed well with crude diacid (9.50 g, 0.0475 mol) and placed in a 50-ml flask connected to a distillation apparatus. Heating the flask to 275° for 1 hr caused a yellow liquid to distill. Extraction with ether, drying, and trap distillation yielded 2.35 g (44%) of the product as a clear liquid. Spectral samples were purified by vpc;[34] ir (CCl_4) 3000, 2940, 1440, 1130, 860 cm^{-1}; nmr (CCl_4) δ 6.70 (singlet, 2 H), 2.12 (singlet, 6 H).

3,4-Dimethylthiophene-2-aldehyde.[38,39] 3,4-Dimethylthiophene (2.30 g, 0.020 mol), freshly distilled phosphorus oxychloride (3.84 g, 0.025 mol), and freshly distilled *N*-methylformanilide (3.38 g, 0.025 mol) were mixed in a 25-ml flask fitted with a reflux condenser and heated briefly on a steam bath. After the reaction had begun (gas evolution and darkening of the solution), the mixture was cooled briefly and then heated on a steam bath for 0.5 hr. After subsequent cooling, aqueous sodium acetate was added. Steam distillation afforded a white solid which was extracted with ether, dried, and evaporated to give 2.06 g (72%) of pure product: mp 68.5–69.5° (lit.[39] 69–70°); ir (CCl_4) 2940, 2750, 1670, 1440, 1240, 860 cm^{-1}; nmr (CCl_4) δ 9.84 (singlet, 1 H), 7.20 (singlet, 1 H), 2.44 (singlet, 3 H), 2.20 (singlet, 3 H).

2,3,4-Trimethylthiophene (1a).[39,40] 3,4-Dimethylthiophene-2-aldehyde (2.06 g, 0.014 mol) was dissolved in 50 ml of diethylene glycol in a 100-ml three-neck flask fitted with an internal thermometer and distillation apparatus. Hydrazine hydrate (5 ml) was added

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[33] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **77**, 521 (1955).

[34] An 8 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column was employed.

[35] An 11 ft × 0.25 in. 20% SE-30 on Chromosorb W column was employed.

[36] H. Wynberg and D. J. Zwanenburg, *J. Org. Chem.*, **29**, 1919 (1964).

[37] R. Seka, *Chem. Ber.*, **58**, 1786 (1925).

[38] W. J. King and F. F. Nord, *J. Org. Chem.*, **13**, 635 (1948).

[39] B. F. Crowe and F. F. Nord, *ibid.*, **15**, 1177 (1950).

[40] W. J. King and F. F. Nord, *ibid.*, **14**, 638 (1949).

and the mixture was heated to 160° for 0.5 hr. A small amount of liquid distilled (100–105°). After cooling to approximately 70°, potassium hydroxide (5 g) was added. A reflux condenser replaced the distillation apparatus, and the reaction was heated to 180° (bath temperature) for 1 hr. The internal temperature remained at 140° with vigorous refluxing.

After cooling, the product was trap distilled from the ethylene glycol, extracted with ether, dried, and evaporated on a rotary evaporator to give 1.25 g (68%) of pure product: ir (CCl_4) 2920, 1440, 860 cm^{-1}; nmr (CCl_4) δ 6.49 (broad singlet, 1 H), 2.27 (singlet, 3 H), 2.04 (doublet, J = 1 Hz, 3 H), 1.96 (singlet, 3 H); uv (EtOH) λ_{max} 238 nm (ϵ 5920); mass spectrum m/e (rel intensity) 126 (72), 125 (66), 111 (100).

Gas Analysis. General Procedure. The −196° liquid nitrogen trap, after completion of the reaction, was evacuated and warmed to room temperature. A known amount of propane was then added as internal standard. Yields were determined by the response factor technique using gas densities obtained from a standard source.[41] Vpc analysis was done on a silica gel column (8 ft × 0.25 in.) at 82°. Retention times (relative to propane) were as follows: methane, 0.080; ethane, 0.30; ethylene, 0.57. Samples to be used for mass spectral analysis were trap distilled into a small U tube and then vpc collected in a sand trap, cooled to −196°, fitted with vacuum stopcocks. Control experiments demonstrate that by this technique 93–100% of ethane generated is recoverable.

Ylide Decomposition Control Experiment. Following the general procedure previously described, 0.502 g (3.00 mmol) of sulfonium salt and 2.02 ml (3.00 mmol) of *n*-butyllithium were used to generate the ylide. The addition of cyclopropenium salt was omitted, but otherwise the reaction was run as usual. Gas analysis showed that the yield of ethane (relative to ethylene) was less than 0.1%. Analysis of the aqueous phase showed that less than 4% sulfonium salt was present.

Reaction of Perdeuteriodimethylsulfonium Methylide with Cyclopropenium Salt. Following the procedure described in the general description above, 1.00 g (5.80 mmol) of perdeuteriosulfonium fluoroborate and 3.60 ml (5.80 mmol) of *n*-butyllithium were allowed to react with 0.486 g (2.90 mmol) of cyclopropenium salt. Quenching the ylide with an excess of cyclohexanone in a control experiment determined the ylide yield to be 57%. Mass spectral analysis of the deuteriooxirane showed it to be 83% d_2, 11% d_1, and 6% d_0. The thiophene produced (22% yield, by vpc analysis) was shown by nmr to be at least 95% d_1. Also isolated was an 8.6% yield of 1,2,3-trimethylcyclopropenyl-*methyl-d*$_3$ methyl-d_2 sulfide (**4b**-d_5): ir (CCl_4) 2860, 1440, 1375, 1060 cm^{-1}; nmr (100 MHz, CCl_4) δ 1.92, 1.08 (singlets, intensity ratio 2:1); mass spectrum m/e (rel intensity) 147 (1), 146 (1), 129 (29, $M^+ - CD_3$), 81 (100, trimethylcyclopropenium). Mass spectral analysis of the ethane produced gave the peak distribution for C_2D_6 (12.5 eV); m/e (rel intensity) 30 (2), 31 (23), 32 (100), 33 (3), 35 (9), 36 (19).

Reaction of a 1:1:1 Mixture of Perhydromethylide, Perdeuteriomethylide, and Cyclopropenium Salt. Following the general procedure described above, 0.541 g (3.12 mmol) of perdeuteriosulfonium salt, 0.512 g (3.12 mmol) of perhydrosulfonium salt, and 3.90 ml (6.24 mmol) of *n*-butyllithium were allowed to react with 0.524 g (3.12 mmol) of cyclopropenium salt. Just prior to the addition of cyclopropenium salt, a 0.25-ml aliquot of the ylide solution was withdrawn and quenched in cyclohexanone at −78°. Mass spectral analysis of the oxirane showed it to be 58.5% d_0, 11.0% d_1, and 30.5% d_2. Using the isotopic distribution found above for pure perdeuterio ylide, it was found that 7% of the d_1-oxirane was due to crossover. Mass spectral analysis of the thiophene produced (8 eV) showed it to be 21.9% d_1 and 78.1% d_0. Analysis of the ethane produced showed it to have the following mass spectrum: m/e (rel intensity) 28 (68), 29 (100), 30 (90), 31 (57), 32 (35), 33 (15), 34 (5), 35 (2), 36 (1).

Reaction of Dimethylsulfonium Methylide with Cyclopropenium Salt under Solvolysis Conditions. Using the apparatus described above in the general procedure, 0.800 g (4.88 mmol) of trimethylsulfonium fluoroborate was added to 10 ml of THF and cooled to −78°. *n*-Butyllithium (3.05 ml, 4.88 mmol) was added and the solution was stirred for 15 min at −78°. The reaction was then warmed to −5° for 5 min and the cyclopropenium salt (0.410 g, 2.44 mmol) was added. After 3 min of warming, cloudiness had been noted. The usual yellow color appeared upon addition of the cyclopropenium salt but disappeared after 2–3 min. After the mixture was stirred at room temperature for 3 hr, the reaction was worked up as usual. The usual product analysis showed the yields to be as follows: thiophene, 14%; ethane, 2.9%; ethylene, 1.6%; methane, 2.7%. Generating the ylide under the conditions just described and quenching with cyclohexanone showed the yield to be 46.5%.

Reaction of Dimethylsulfonium Methylide with Cyclopropenium Salt in Hexamethylphosphoramide. Following the general procedure described above, 0.725 g (4.42 mmol) of sulfonium salt and 3.00 ml (4.42 mmol) of *n*-butyllithium were allowed to react with 0.728 g (4.34 mmol) of cyclopropenium salt at −25° in 2:1 hexamethylphosphoramide–tetrahydrofuran. After the mixture was stirred for 0.5 hr at −25° and 4.5 hr at room temperature, the reaction mixture was worked up as usual using pentane as solvent. The yields were as follows: thiophene, 13.0%; cyclobutene, 1.75%; ethane, 5.25%; ethylene, 0.20%; methane, <0.01%. Analysis of the aqueous phase showed a 67% recovery of sulfonium salt.

Control Reaction of Diphenylsulfonium Methylide with Cyclohexanone. To a 10-ml side arm flask containing 5 ml of freshly distilled tetrahydrofuran was added 100 mg (0.348 mmol) of diphenylmethylsulfonium fluoroborate. After cooling to −78°, 0.218 ml (0.348 mmol, 1.60 *N*) of *n*-butyllithium was added and the mixture was stirred for 15 min at −78°. An excess of distilled cyclohexanone (49 mg, 0.50 mmol) was added to the yellow solution and the mixture was stirred for 15 min at −78° and 1 hr at room temperature. After quenching with water and extraction with ether, the reaction was analyzed by vpc.[35] The yield of 7-oxaspiro[5.2]octane (using cycloheptanone as an internal standard) was determined to be 31.1 mg (80%).

Reaction of Diphenylsulfonium Methylide with 1,2,3-Trimethylcyclopropenium Fluoroborate. In a typical run, 1.087 g (3.77 mmol) of diphenylmethylsulfonium fluoroborate was added to 10 ml of freshly distilled tetrahydrofuran in a 25-ml flask and cooled to −78°. To the stirred mixture was added 2.36 ml (3.77 mmol, 1.60 *N*) of *n*-butyllithium, giving rise to a yellow solution. After 15 min, 0.317 g (1.89 mmol) of trimethylcyclopropenium fluoroborate was added (the mixture turned orange immediately) and the mixture was stirred for 2 hr at −78°. After the mixture was stirred for 3 hr at room temperature, the reaction was quenched with water, and the mixture was extracted with ether and dried over potassium carbonate. After solvent removal by careful distillation through a Vigreux column, the residue (volume *ca.* 8 ml) was analyzed by vpc.[42] Yields were determined by the use of *p*-methylphenetole and phenyl-*p*-tolyl sulfide as internal standards. The products identified (retention time, yield, mg (%)) were as follows: 2,3,4-trimethylthiophene (identical with previously identified samples by ir and mixed injection) t_R = 37 min, 0.91 mg (0.38%); methyl phenyl sulfide (identical with a known sample) t_R = 42 min, 10.8 mg (3%); *n*-butyl phenyl sulfide (identical with a known sample) t_R = 85 min, 30.6 mg (4.9%); biphenyl, t_R = 90 min, 25.2 mg (4.4%); phenyl (1,2,3-trimethylcyclopropenylmethyl) sulfide (**11**) (see below for structural identification) t_R = 112 min, 61.2 mg (16%); diphenyl sulfide, t_R = 130 min, 200 mg (25%). Analysis of the aqueous phase of the reaction by nmr (using DMSO as an internal standard) showed the recovery of diphenylmethylsulfonium salt to be 43%.

The following spectral properties were exhibited by sulfide **11**: ir (CCl_4) 3040, 1580, 1490, 1370, 690 cm^{-1}; nmr (CCl_4) δ 7.21 (broadened singlet, 5 H), 3.00 (singlet, 2 H), 1.82 (singlet, 6 H), 1.13 (singlet, 3 H). The mass spectrum was identical with that obtained for the thermal rearrangement product discussed below.

Anal. Calcd for $C_{13}H_{16}S$: C, 76.40; H, 7.91; S, 15.69. Found: C, 76.26; H, 7.95; S, 15.80.

It was found that vpc analysis of **11** led to a rearrangement, giving rise to phenyl (1,2,3-trimethylbutadienyl) sulfide (**13**): nmr (CCl_4) δ 7.19 (broadened singlet, 5 H), 4.90, 4.72 (broad singlets, 2 H), 1.89 (finely coupled singlet, 9 H); mass spectrum m/e (rel intensity) 204 (9), 189 (2), 171 (4), 127 (100). The structural identification was hampered by the difficulty in obtaining one isomer uncontaminated by the other.

In one run the previously described gas traps were connected to the reaction flask in the usual manner. As expected, the yield of methane, ethane, and ethylene was found to be 0%.

Decomposition of Diphenylsulfonium Methylide. Control Experiment. Diphenylmethylsulfonium fluoroborate (0.576 g, 2.0 mmol) was added to 12 ml of freshly distilled tetrahydrofuran in a 25-ml flask and cooled to −78°. *n*-Butyllithium (1.25 ml, 2.0 mmol)

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(41) N. A. Lange, "Handbook of Chemistry," 10th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1961, p 822.

(42) A 17 ft × 0.25 in. 25% SE-30 on Chromosorb P column was employed.

was added and the mixture was stirred for 1 hr at −78° followed by 3 hr at room temperature. The initially yellow solution became dark grey upon warming. After the usual work-up, the reaction was analyzed by vpc using *o*-methylanisole as an internal standard. The following products were identified: methyl phenyl sulfide, 45.8 mg (18.5%); *n*-butyl phenyl sulfide, 1.2 mg (0.37%); biphenyl, 6.5 mg (2.1%); diphenyl sulfide, 170 mg (46%).

Methylphenyl-*p*-tolylsulfonium Fluoroborate. Silver tetrafluoroborate (4.90 g, 0.025 mol) was added to 5.60 g (0.028 mol) of freshly distilled phenyl-*p*-tolylsulfide[43] cooled to −20° in 10 ml of dry methylene chloride. Methyl iodide (3.55 g, 0.025 mol) was added over 5 min from a syringe. After 15 min at −20° and 5 min at room temperature, the yellow suspension was filtered twice through sintered glass. The organic phase was washed with water, dried over potassium carbonate, and concentrated. Considerable effort failed to effect crystallization of the yellow oil. Purification was achieved by cooling to −78° in ether and rapidly decanting the solvent from the white crystals which formed at the low temperature. Warming to room temperature gave the product as a clear white oil: ir ($CHCl_3$) 2940, 1600, 1050, 910 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.3 (complex multiplet, 9 H), 3.58 (singlet, 3 H), 2.37 (singlet, 3 H).

Anal. Calcd for $C_{14}H_{15}SBF_4$: C, 55.65; H, 5.00; S, 10.61. Found: C, 55.43; H, 4.97; S, 10.50.

Reaction of Methylphenyl-*p*-tolylsulfonium Fluoroborate with 1,2,3-Trimethylcyclopropenium Fluoroborate. The sulfonium salt (0.262 g, 0.873 mmol) was cooled with rapid stirring to −78° in 5 ml of tetrahydrofuran (distilled from $LiAlH_4$) producing an oily suspension. *n*-Butyllithium (0.545 ml, 0.873 mmol) was added, producing a brown color after *ca.* 15 sec. After the mixture was stirred for 15 min, cyclopropenium salt (0.073 g, 0.437 mmol) was added in one portion. After the mixture was stirred at −78° for 2 hr and 0.5 hr at 25°, the clear yellow solution was quenched with water and extracted with ether. After drying, the products were analyzed by vpc[42] using dibenzothiophene as an internal standard. Identification was primarily through the use of an integrated gas chromatograph–mass spectrometer. The major products were as follows: methyl-*p*-tolyl sulfide, t_R = 8 min, 5.24 mg (4.4%); *n*-butyl-*p*-tolyl sulfide, t_R = 15 min, 13.9 mg (8.8%); *p*-methylbiphenyl, t_R = 23 min, 2.96 mg (2.0%); phenyl-*p*-tolyl sulfide, t_R = 30 min, 129 mg (74%). Trace quantities of methyl phenyl sulfide, *n*-butyl phenyl sulfide, diphenyl sulfide, and di-*p*-tolyl sulfide were also detected.

Careful vpc[42] analysis failed to indicate the presence of any 2,3,4-trimethylthiophene. No other products resulting from reaction of the ylide with cyclopropenium salt were detected.

2,2′-Dilithiobiphenyl.[44] In a dry 25-ml flask under argon was put 8 ml of ether (distilled from $LiAlH_4$), 0.10 g (14 mg-atom) of high purity lithium wire, and 0.375 g (1.2 mmol) of 2,2′-dibromobiphenyl. After refluxing for 3 hr the orange solution was filtered under Ar and stored at 0°. Quenching of a 0.50-ml aliquot with water and vpc analysis of the biphenyl produced showed the concentration to be 0.109 mol/l.

Reaction of 2,2′-Dilithiobiphenyl with Triphenylsulfonium Fluoroborate. A 2.50-ml (0.272 mmol) aliquot of the dilithiobiphenyl solution was cooled to −78° in a 10-ml flask. Triphenylsulfonium fluoroborate[45] (0.095 g, 0.272 mmol) was added in one portion, resulting in a yellow color almost immediately. After 1 hr of stirring at −78° the reaction was warmed to room temperature. The reaction was quenched with deuterium oxide and extracted with ether. Vpc analysis[42,46] yielded the following products: biphenyl (58%), diphenyl sulfide (57%), (2′-phenylbiphenyl)phenyl sulfide (**13**) (44%). The spectral data for sulfide **13** were as follows: ir (CCl_4) 1590, 1460, 700, 690 cm^{-1}; nmr (100 MHz, CCl_4) δ 7.5–6.9 (complex); uv (EtOH) λ_{max} 249 nm (ϵ 23,500), 283 (1430); mass spectrum *m/e* (rel intensity) 340 (8), 338 (98), 229 (100). The molecular weight was determined by high-resolution mass spectrometry (calcd for $C_{24}H_{18}S$, 338.1129; found, 338.1133).

Mass spectral analysis of the biphenyl yielded the following isotopic distribution: 82% d_0, 0.5% d_1, 17.5% d_2. The d_2-biphenyl presumably arises from the reaction of unreacted 2,2′-dilithiobiphenyl with deuterium oxide during work-up. The yields given above are corrected for unreacted dilithiobiphenyl.

The use of known samples allowed the determination that no dibenzothiophene or biphenylene had been produced in the reaction.

Reaction of 2,2′-Dilithiobiphenyl with Tri-*p*-tolylsulfonium Fluoroborate. A 1.00-ml (0.109 mmol) aliquot of the dilithiobiphenyl solution was cooled to −78° in a 10-ml flask. Tri-*p*-tolylsulfonium fluoroborate[45] (43 mg, 0.109 mmol) was added and the mixture stirred 1 hr at −78° and 1 hr at room temperature. The reaction was quenched with water and extracted with ether. Vpc analysis,[35,46] using *p*-methylbiphenyl as an internal standard, allowed determination of the following yields: biphenyl, 47%; bi-*p*-tolyl, 33%; di-*p*-tolyl sulfide, 43%; (2′-*p*-tolylbiphenyl)-*p*-tolyl sulfide (**14**), 49%. The sulfide **14** has the following spectral properties: ir (CCl_4) 2920, 1500, 1470, 700 cm^{-1}; nmr (100 MHz, CCl_4) δ 7.25 (multiplet, 4 H), 6.86 (multiplet with superimposed singlet, 12 H), 2.29 (singlet, 3 H), 2.27 (singlet, 3 H); mass spectrum *m/e* (rel intensity) 368 (11), 366 (100), 228 (65), 184 (66). The molecular weight was determined by high-resolution mass spectrometry (calcd for $C_{26}H_{22}S$, 366.14421; found, 366.14605). The absence of dibenzothiophene and biphenylene in the reaction mixture was confirmed by vpc analysis using known samples.

Reaction of Dimethylsulfonium Methylide with Tropylium Fluoroborate. Dimethylsulfonium methylide was prepared at −78° from 2.1 g (12.9 mmol) of trimethylsulfonium fluorobroate and 7 ml (11.2 mmol) of 1.6 *M* *n*-butyllithium in hexane in 60 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride). After the mixture was stirred at −78° for 1 hr, 1.0 g (5.6 mmol) of tropylium fluoroborate[47] was added all at once. The reaction mixture, which turned red immediately, was stirred 1 hr at −80° and then allowed to warm to room temperature over a period of 1.5 hr. During this period the reaction became dark green at between −20 and +15° and red again above +15°. Aqueous work-up, followed by extraction with ether, drying over potassium carbonate, and concentration *in vacuo* at −45° revealed the presence of two volatile components in the ratio of approximately 2:1 by vpc analysis.[48] The major component t_R = 9.2 min was tentatively identified as 7-*n*-butylcycloheptatriene arising as a result of incomplete ylide generation. The minor component t_R = 16 min showed only weak double bond absorption at 1610 cm^{-1} in its infrared spectrum (CCl_4). Its nmr spectrum (CCl_4) showed a 3 H singlet at δ 2.02 overlapping a 1 H multiplet at 1.95, a 2 H doublet (J = 7.7 Hz) at δ 3.77, a 2 H broadened doublet of doublets (J = 9.4, 5.2 Hz) at δ 5.19, a 2 H multiplet at δ 6.1, and a 2 H broadened triplet (J = 3 Hz) at δ 6.56. Its mass spectrum shows in addition to a molecular ion at *m/e* 152 abundant ions at 104 (heptafulvene radical cation), 91 (tropylium ion), and 61 ($CH_3S^+{=}CH_2$). These data allow a tentative structural assignment as 7-methylthiomethylcycloheptatriene.

Alternatively, 0.80 g (5.6 mmol) of dimethyl acetylenedicarboxylate was added to the reaction mixture prior to work-up. After the mixture was stirred for 3 days at 0°, the red solution turned to yellow. Concentration of the solution to 5 ml at −45° *in vacuo* was followed by addition of 50 ml of benzene. To the resultant solution under nitrogen was added 1.25 g (5.6 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone in one portion. The reaction was stirred for 1 hr, concentrated *in vacuo*, and filtered through a short (1 × 3 cm) column of alumina with ether as the eluting solvent to give 110 mg (8%) of purple dimethyl azulene-1,2-dicarboxylate.[49] Its infrared spectrum (CCl_4) showed carbonyl absorption at 1710 and 1725 cm^{-1} and double bond absorption at 1585 cm^{-1}. Its nmr spectrum (CCl_4) showed a singlet (6 H) at δ 3.83, a singlet (1 H) at δ 7.3 superimposed on a multiplet (3 H) centered at δ 7.5, a broadened doublet (J = 9.4 Hz) at δ 8.30, and a broadened doublet (J = 9.6 Hz) at δ 9.30.

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