toluene: ir (neat) 805, 890, and 925 cm^{-1} (-NF$_2$); nmr (CDCl$_3$) δ 4.58 (t, 2, J = 29 Hz, -CH$_2$NF$_2$) and 7.37 ppm (s, 5, C$_6$H$_5$-).

Anal. Calcd for $C_7H_7F_2N$: C, 58.74; H, 4.93; F, 26.54; N, 9.78. Found: C, 58.92; H, 5.19; F, 26.58; N, 9.59.

Photolysis of Cumene Solution.—The above photolysis procedure was repeated substituting cumene for toluene. Two photoproducts were detected by glpc analysis. The unreacted cumene was removed by vacuum distillation (15 mm, 50°) and the remaining residue was distilled at 1 mm and 50°. After the distillate was purified by preparative glpc only one of the original photoproducts could be detected. The photoproduct that decomposed showed difluoramino absorption at 885 cm^{-1} and the remaining photoproduct was passed through the preparative glpc to give an analytical sample of α-methylstyrene.

Anal. Calcd for C_9H_{10}: C, 91.46; H, 8.54. Found: C, 91.38; H, 8.51.

Photolysis of 3-Methylpentane Solution.—The photolysis procedure was repeated using 3-methylpentane as the solvent with an irradiation time of 4 hr. One major and several minor (total <5%) photoproducts were detected by glpc analysis. The major photoproduct was isolated by a similar distillation procedure (450 mm, 50°, then 1 mm, 50°) and purified by preparative glpc to give an analytical sample of 3-methyl-3-difluoraminopentane: ir (neat) 850 and 945 cm^{-1} (-NF$_2$); nmr (CDCl$_3$) δ 0.92 [t, 6, J = 7 Hz, (CH$_3$CH$_2$)$_2$CCH$_3$-], 1.17 [t, 3, J = 2 Hz, (CH$_3$CH$_2$)$_2$CCH$_3$-], and 1.67 ppm [m, 4, (CH$_3$CH$_2$)$_2$CCH$_3$-].

Anal. Calcd for $C_6H_{13}F_2N$: C, 52.54; H, 9.55; F, 27.70; N, 10.21. Found: C, 52.71; H, 9.61; F, 27.64; N, 10.04.

Photolysis of Cyclohexane Solution.—The photolysis procedure was repeated using cyclohexane as the solvent with an irradiation time of 325 min. Only one major and one minor volatile photoproduct were detected by glpc analysis. The photoproducts were concentrated by distillation. Because of the potentially hazardous nature of the products, only a small fraction of the concentrate was passed through the preparation glpc to give an analytical sample of difluoraminocyclohexane for the major product: ir (neat) 840, 910, and 960 cm^{-1} (NF$_2$); nmr (CDCl$_3$) δ 1.63 (m, 10, C$_6$H$_{10}$NF$_2$-) and 3.32 ppm (t, 1, J = 26 Hz).

Anal. Calcd for $C_6H_{11}F_2N$: C, 53.32; H, 8.20; F, 28.19; N, 10.27. Found: C, 53.50; H, 8.20; F, 28.19; N, 10.27.

A sample of the minor product was also isolated; however, the amount was too small for full characterization. This compound did not contain difluoramino groups, since no nitrogen was found by microchemical methods.

In a second experiment (uptake of tetrafluorohydrazine 440 ml, 0.0196 mol) the sequence of distillation was changed to elucidate the composition of the reaction residue. Both photoproduct and unreacted cyclohexane were vacuum distilled (1 mm, 25°) leaving undecomposed residue and trace amounts of cyclohexane and cyclohexane photoproduct. Infrared analysis of the pot residue showed peaks at 3500 (OH) and 885, 855 cm^{-1} (NF$_2$).

Hydrolysis of the residue was accomplished by adding aqueous acetic acid and excess potassium iodide, liberating iodine. The aqueous solution was extracted with methylene chloride and the resulting aqueous solution was diluted to 2 l. Twenty milliliters of standard arsenous acid (0.099 mol) was needed to titrate a 100-ml aliquot of the stock iodine solution using starch indicator. The total liberated iodine was calculated as 0.0398 mol which corresponds to 0.0199 mol of difluoraminodiphenylmethanol. The methylene chloride extract was evaporated under vacuum (1 mm) leaving 3.85 g (96% recovery) of benzophenone, which was identified by matching the infrared spectrum and melting point with those of an authentic sample.

Proper caution should be taken during distillation of potentially hazardous difluoramino compounds.

Acknowledgment.—This work was supported by the Naval Ordnance Systems Command under Task Assignment ORD-033-101/067-1/F009-06-01.

Registry No.—Tetrafluorohydrazine, 10036-47-2; benzophenone, 119-61-9; toluene, 108-88-3; α-difluoroaminotoluene, 23162-99-4; cumene, 98-82-8; α-methylstyrene, 98-83-9; 3-methylpentane, 96-14-0; 3-methyl-3-difluoraminopentane, 40715-62-6; cyclohexane, 110-82-7; difluoroaminocyclohexane, 14182-78-6.

The Pyrolysis of Alkyl Sulfide Tosylhydrazone Salts. A Search for R$_2$S-4 Participation in Carbene Reactions. The Pyrolysis of Sodium Toluenesulfinate

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Received December 11, 1972

Sodium salts of alkyl sulfide tosylhydrazones **6**, **7**, and **8** have been pyrolyzed at several temperatures to see if sulfur-carbene interaction would lead to intramolecular sulfur ylide formation of the R$_2$S-4 type. Analysis of the results shows no evidence for sulfur ylide formation but rather α-insertion products typical of singlet carbene reactions producing olefins **9** and **10** and **13** and **15**, respectively. Sodium toluenesulfinate was pyrolyzed at 250 and 320° to establish products resulting from its thermal decomposition at these temperatures.

Recently, evidence for R$_2$S-4[1] participation in the photolytic reactions of keto sulfides **1**[2] and α-dione sulfides **2**[3] has been reported. Evidence for similar interaction in solvolytic **3**,[4,5] carbonium ion **4**,[6] and radical **5**[7] reactions has also been proposed. We wish to report here our initial search for R$_2$S-4 participation in sulfur-carbenoid species.[8]

While no exact proximity requirements for sulfur neighboring-group participation have emerged for the different R$_2$S-4 type transition states, careful solvolysis studies by Ireland[4] and later by Paquette[5] using caged alkyl thiatosylates have shown that sulfur can interact in ground-state reactions by stabilizing a developed reactive species, in these cases carbonium ions. Further, in those systems where conformational mobility is limited and stereochemical requirements are ideal, R$_2$S-4 effects can accelerate[5,7] the rate of formation of reactive species.

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[1] The symbolism R$_2$S-n is used here to denote the size of a bicyclic ring (n members) ultimately realizable if cyclization were to occur as a result of neighboring group participation. (See ref 5 for other examples of this useful nomenclature.)

[2] P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970).

[3] P. Y. Johnson, *Tetrahedron Lett.*, 1991 (1972).

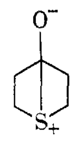
[4] R. E. Ireland and H. A. Smith, *Chem. Ind. (London)*, 1252 (1959).

[5] L. A. Paquette, G. V. Meehan, and L. D. Wise, *J. Amer. Chem. Soc.*, **91**, 3231 (1969).

[6] A. DeGroot, J. A. Boerma, and H. Wynberg, *Tetrahedron Lett.*, 2365 (1968).

[7] A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, 339 (1972).

[8] For a review on carbene chemistry, see W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, and references cited therein.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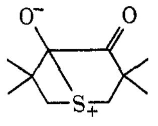
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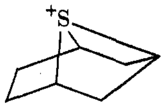
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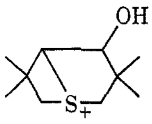
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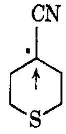
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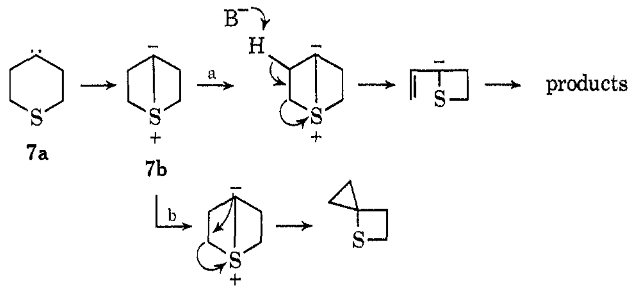
In photochemical studies[2,3] on a variety of keto sulfides, R_2S-4 transition states appear to be formed *via* charge-transfer mechanisms. In these high-energy excited species the added increment of energy required for formation of the unfavorable "boat" conformation which helps ensure close proximity between sulfur and the carbonyl in the uncaged systems does not seem to be as important a factor as it appears to be in the ground-state reactions. This could be due to the large size of the n,π^* orbitals of the excited carbonyl in the examples cited.

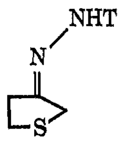
The stereochemical requirements for R_2S-4 sulfur carbene interaction seemed to lie between the fairly rigid solvolyses and less rigid excited-state requirements.

Monomeric products which might result from the decomposition of sulfur ylides[9] formed as a result of R_2S-4 sulfur carbene participation[10] (*e.g.*, ylide **7b** resulting from carbene **7a**) followed by either inter- or intramolecular β elimination (Scheme I, path a) or by a concerted or nonconcerted Stevens rearrangement[11] (Scheme I, path b) are shown in Scheme I.

SCHEME I



To test this postulate and to examine the potential sulfur carbene interaction as a method of generating a synthesis for thietanes, we have pyrolyzed several alkylthiatosylhydrazone–sodium salts. In this study we have examined the thermal decomposition of dry sodium salts of the tosylhydrazones in order to avoid protic conditions which often lead to carbonium reactions instead of the desired carbene intermediates.[12] The molecules studied were sodium salts of **6**, **7**, and **8**.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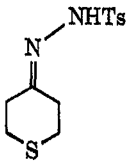
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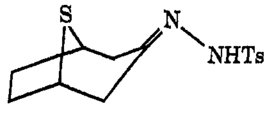
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Table I gives the results of these pyrolyses. Analysis of Table I shows that the major products from these pyrolyses are olefins which can best be accounted for by simple insertion of the generated carbene into the adjacent C–H bonds. The glyme found in runs A–D is the result of a 1:1 adduct (nmr) of the salt and glyme, the solvent used in the synthesis of these salts. Attempts to free the salts from the glyme using a high vacuum at 25° failed and heating the adduct at 70° under vacuum led to slow decomposition of the material, yielding a brown substance. The salt–glyme adduct was not observed in the case of **8**, perhaps because of increased steric factors in the bicyclo system.

TABLE I

CONDITIONS, PRODUCTS, AND YIELDS FOR PYROLYSIS OF **6**, **7**, AND **8**

Run[a]	Salt (g)	Temp, °C	Recovered, g	Products (ratio of material recovered)
A	**6** (1.57)	170-220	0.18	Glyme (39), **9** (39), **10** (11), **11** (trace)
B	**7** (1.5)	200	0.39	Glyme (30), **12** (0), **13** (70), **14** (trace)
C	**7**	270[b]		
D	**7** (1.0)	320	0.31	Glyme (19), **13** (63), **12** (0)
				Sodium sulfinate pyrolysis products
E	**8** (0.99)	160-200	0.09	**15** (75), **16** (25)
F	**8**	>320		**15** + others

[a] In most cases these reactions were run several times with fair repeatibility. [b] Results same as run B.


9


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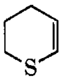
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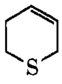
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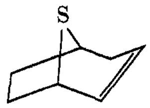
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The lack of observed isomerization of **13** to the conjugated isomer **12** under the reaction conditions (runs B, C, and D) leads us to believe that the 4:1 ratio of **9** to **10** in the pyrolysis of the salt of **6** (run A) is the result of preferential attack of the C–H bond adjacent to sulfur and not due to thermal isomerization of **10** to the conjugated isomer **9**.

While olefinic sulfides **9**,[13] **10**,[13] **12**,[14] and **13**[15] have been reported in the literature, the physical properties given did not enable us to unambiguously assign structures to these isomeric pairs. Hence, these molecules were synthesized, several by unreported routes owing to the availability of appropriate starting materials. Examination of the spectra of these olefins indicated that the best method for distinguishing isomers[16] and establishing purity was by analysis of the vinyl proton absorptions in the nmr spectra (Figure 1). Hence,

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[9] Intramolecular sulfur ylides (not of the R_2S-4 type) have been reported. See (a) K. Kondo and I. Ojimo, *Chem. Commun.*, 63 (1972); (b) S. S. Hixson and S. H. Hixson, *J. Org. Chem.*, **37**, 1279 (1972); (c) J. H. Robson and H. Schechter, *J. Amer. Chem. Soc.*, **89**, 7112 (1967).

[10] R_2S-4 carbene interaction in a noncyclic system has been postulated. See K. Kondo and I. Ojimo, *Chem. Commun.*, 62 (1972).

[11] A concerted Stevens rearrangement is symmetry forbidden if it occurs with retention, as would be the case with **7b**. See ref 21a, p 3871.

[12] (a) R. D. Allan and R. J. Wells, *Aust. J. Chem.*, **23**, 1625 (1970); (b) W. Kirmse and B. U. Bulow, *Chem. Ber.*, **96**, 3316 (1963); (c) C. H. DePuy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, **82**, 634 (1960); (d) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

[13] S. F. Brich and D. T. McAllan, *J. Chem. Soc.*, 2556 (1951).

[14] R. F. Naylor, *J. Chem. Soc.*, 2749 (1949).

[15] W. E. Parham, L. H. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

[16] While analysis of the M^+ and $M - 1$ peaks in the mass spectra can be used to establish isomers (see Experimental Section), we found it difficult to establish purity by this method.

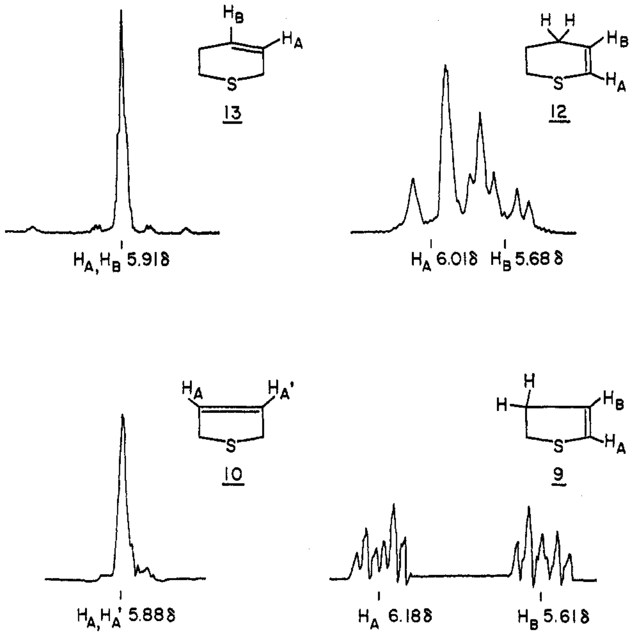
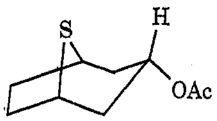


Figure 1.—60-MHz proton nmr absorption in the vinyl region of sulfides **9**, **10**, **12**, and **13**, taken in CCl_4 with TMS as internal reference.

integration of the distinctive, nonoverlapping peaks attributable to the vinyl protons of **9** and **10** provided the best method for isomer ratio analysis in the pyrolysis of the salt of **6**. The lack of **12** (runs B, C, and D) was ascertained by the lack of absorption attributable to it in the nmr of the recovered pyrolysis mixture of **7**.

The bicyclo olefinic sulfide **15** was the major product in the pyrolysis of the salt of **8**; however, the yield of recovered material was never high in this reaction. High-temperature pyrolysis (run F) provided shorter contact times and appeared to increase the yield of **15**; however, this procedure also dramatically increased the number of side products, making isolation of **15** impossible and product ratio analysis extremely difficult (see below).

8-Thiabicyclo[3.2.1]oct-2-ene (**15**) is a low-melting solid which decomposed in the presence of air or light but which was stable when stored at 0° in the dark. It was identified by its spectral properties and by comparison to an authentic sample prepared by pyrolysis of acetate **17**.



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Interestingly, **17**, a single peak by vpc, tlc, and nmr (single $CH_3C{=}O$, δ 1.94), was obtained from a 80:20 mixture (vpc) of epimeric alcohols,[4] by treating them at reflux in acetic acid–acetic anhydride. It seems clear that an R_2S-4 intermediate such as **3** was involved at some stage of this reaction, accounting for its stereoselectivity.[4]

The mass spectrum of **15** shows major ions at *m/e* 126 (M^+, one sulfur indicated by the M + 2 peak) and supporting ions at *m/e* 91 (tropilium ion) and 84 (thiophene ion).

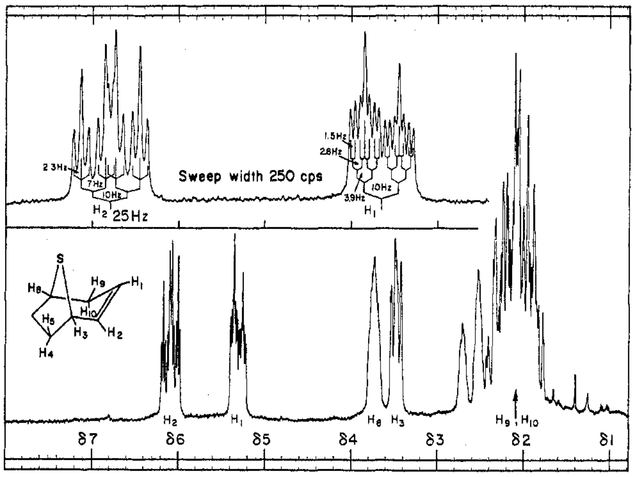


Figure 2.—100-MHz proton nmr spectra of sulfide **15**, taken in CCl_4 with TMS as internal reference.

Since **15** was generated both times by pyrolysis reactions,[17] a 100-megacycle nmr spectrum with 250-cps sweep width expansion of the vinyl absorptions was obtained for this olefin in order to ensure that no thermal rearrangements common to both reactions had occurred. Extensive decoupling experiments allowed complete assignment and interpretation of the downfield absorptions (Figure 2). Important coupling constants obtained from the decoupling experiments are given in Table II and were found to be in excellent agreement with those predicted from studies of models of **15** using the Karplus relationship.[18] Decoupling experiments also showed that allylic protons H_9 and H_{10} were centered at δ 2.1.

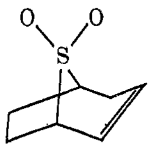
TABLE II

COUPLING CONSTANTS DETERMINED FOR OLEFIN **15**[a]

$J_{H_1H_2}$ = 10 Hz[b]	$J_{H_2H_3}$ = 7 Hz
$J_{H_1H_8}$ = 1.5 Hz	$J_{H_2H_9}$ = 2.3 Hz
$J_{H_1H_9}$ = 2.8 Hz	$J_{H_2H_{10}}$ = 2.3 Hz
$J_{H_1H_{10}}$ = 3.9 Hz	$J_{H_3H_4}$ = ~0.0 Hz
	$J_{H_3H_5}$ = 4 Hz

[a] Proton numbers can be found on Figure 2. [b] All values ±0.2 Hz.

Olefin **15** was converted into its sulfone, **15b**, in high yield by treating **15** with hydrogen peroxide in acetic acid, further substantiating its structure.



15b

The other products observed in this study were all dimeric in nature. In the pyrolysis of the salt of **6**, the carbene dimer **11** of unknown stereochemistry about the double bond was isolated by vpc and identified by its mass spectrum. In the pyrolysis of salts of **7** and **8** the dimeric products were isolated by vpc and were identi-

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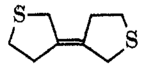
(17) Other standard approaches such as reaction of the alcohols with $SOCl_2$ in pyridine failed to give **15** in our hands.

(18) M. K. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).



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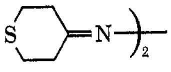

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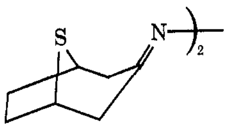

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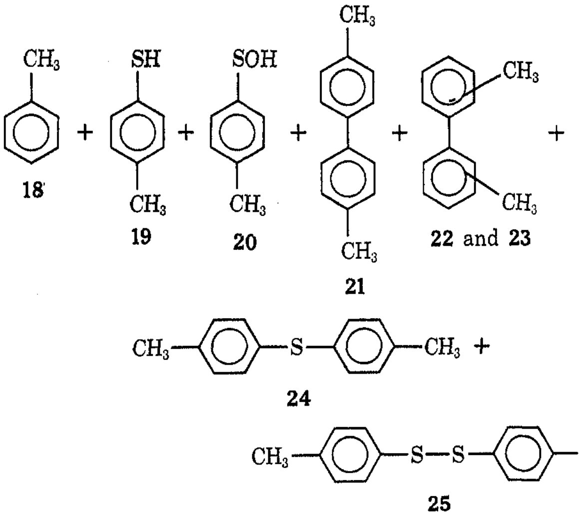
fied as the corresponding azines **14** and **16** by comparison with authentic samples synthesized by reaction of 2 mol of the appropriate ketone with hydrazine. Mechanisms for dimer and azine formation have been discussed.[19] While there is ample precedent for carbene addition to either the sulfur[20] or the olefin[21] part of olefinic sulfides, we found no evidence for dimeric products resulting from ylide–dimer or cyclopropyl-dimer rearrangements.

As noted above (Table I, runs D and F), we found that the bicyclotosylhydrazone salt **8** gave low recovery of material at minimum pyrolysis temperatures, 150–250°. It was decided to use higher temperatures, which would allow shorter contact times, in hopes of increasing the yield of **15**. This goal was partially realized; however, the number of side products increased dramatically as pyrolysis temperatures of 300° were approached. Analysis of some of the products led us to believe that they must have resulted from pyrolysis of the sodium toluenesulfinate at these temperatures.

A search of the literature revealed that, while many authors had noted "extra" products when pyrolyzing tosylhydrazone salts at various temperatures, only toluene was consistently identified. In order to facilitate the interpretation of tosylhydrazone pyrolyses, at higher temperatures in particular, we have identified the products resulting from the pyrolysis of sodium toluenesulfinate[22] below.



We found the products and their yields to be dependent on the temperature, experimental conditions, and time lapse between reaction and analysis.

Toluene (**18**) and toluenethiol (**19**)[23] were the only products observed at pyrolysis temperatures under 300°. If the pyrolysis mixtures was allowed to stand in the presence of air, **19** would dimerize to **25**.

At pyrolysis temperatures of 320–340°, **18**, **19**, **21**, **24**, and **25** became major products.

Sulfenic acid (**20**) was not isolated but was identified from mass spectral data after separation from the reaction mixture by vpc (SE-30 column). This acid disappeared within 30 min after warming the reaction mixture to room temperature.

4,4′-Dimethylbiphenyl (**21**)[24] was identified by comparison to an authentic sample. Biphenyls **22** and **23** were not conclusively identified but are believed to be the 4,3′- and 4,2′-dimethylbiphenyl isomers on the basis of mass spectral similarities to the 4,4′-biphenyl isomer. Several other possibilities, such as 1,2-diphenylethane and benzyl methyl benzenes, were ruled out after comparison of their mass spectra[25] to those of **22** and **23**.

Toluenesulfide **24**[26] and disulfide **25**[27] are white solids easily identifiable by their spectra. The amount of these higher boiling products, which coated the pyrolysis vessel, depended on whether they were "chased" into the collection flask with a low flame or not. We were not able to observe **25** when vpc analysis was performed on a Carbowax column; however, this column gave better separation of the other products.

The identified products can generally be accounted for by intermolecular oxidation–reduction and free-radical processes. The formation of **21**, **22**, and **23** is less clear.

In conclusion, in these pyrolysis studies the main products isolated seem to have resulted from singlet carbene insertion reactions. By contrast, generation of carbene **7a** in ether at 25° using alkyllithiums or by photolysis of the salt **7** appears to give different products, possibly by the desired R_2S-4 pathway. A report on this latter work will be forthcoming.

Experimental Section

Melting points were taken on a calibrated Mel-Temp apparatus. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on Varian A-60 and HA-100 spectrometers using TMS as an internal standard. Mass spectra were obtained on a Hitachi RMU6D mass spectrometer. Vpc analyses were performed using program temperature control on a Hewlett-Packard 5750 gas chromatograph equipped with 8 ft × 0.25 in. 10% Carbowax on Chromosorb P and 8 ft × 0.25 in. 10% SE-30 on Chromosorb P stainless steel columns. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

General Procedure for Pyrolyses.—The distilling flask of an evacuated (0.05 mm) short-path distillation apparatus containing the tosylhydrazone salt with a plug of glass wool over it was immersed into a preheated oil or sand bath, depending on the temperature required, for 15–30 min. The collection flask was cooled with liquid nitrogen.

Synthesis of Thiacyclohexan-4-one Tosylhydrazone (7).—Thiacyclohexan-4-one[2] (2.3 g) was refluxed with 1 equiv (3.7 g) of toluenesulfonyl hydrazide for 1 hr in 50 ml of ethanol. Benzene, 50 ml, was added and over one half of the total solvent was removed by azeotrope from the reaction flask. The resulting mixture was cooled overnight and the tosylhydrazone crystals that had formed were collected by filtration. Recrystallization from ethanol gave 3.8 g (76%) of **7** as a white solid: mp 151–153°; ir ($CHCl_3$) 3005, 1510, 1430, 1390, 1280, and 1175 cm^{-1};

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[19] See ref 8, pp 26–28.

[20] (a) See ref 8, pp 437–442; (b) W. Ando, *et al.*, *J. Org. Chem.*, **37**, 1721 (1972), and references cited therein.

[21] (a) W. Ando, *et al.*, *J. Amer. Chem. Soc.*, **94**, 3870 (1972); (b) W. E. Parham and E. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961).

[22] "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1944, p 492.

[23] Aldrich Chemical Co.

[24] We wish to thank George Gurria of The Johns Hopkins University for providing us with spectra of this biphenyl.

[25] American Petroleum Institute, Research Project 44, Catalogue of Mass Spectral Data.

[26] Beilstein, "Handbuch der Organische Chemie," **6**,^{2} 395.

[27] Reference 26, **6**,^{2} 400.

nmr ($CDCl_3$) δ 2.43 (s, 3), 2.66 (m, 8), 7.56 (d, 2), 7.91 (d, 2); mass spectrum (70 eV) *m/e* (rel intensity) 284 (18, M^+), 171 (5), 157 (32), 140 (30), 139 (37), 129 (84, $C_5H_8S{=}NNH^+$), 128 (16), 124 (22), 100 (75), 99 (45), 92 (26), 91 (100), 85 (80).

Anal. Calcd for $C_{12}H_{16}N_2O_2S_2$: C, 50.70; H, 5.63; N, 9.86. Found: C, 50.85; H, 5.49; N, 10.03.

Synthesis of Thiacyclopentan-3-one Tosylhydrazone (**6**).—Tosylhydrazone **6** was synthesized according to the above procedure from thiacyclopentan-3-one:[28] mp 165° dec;[29] mass spectrum (70 eV) important or major peaks at *m/e* 270 (M^+), 157, 155, 139, 115 ($C_4H_6S{=}NNH^+$), 91

Anal. Calcd for $C_{11}H_{14}N_2O_2S_2$: C, 48.87; H, 5.22; N, 10.36. Found: C, 48.81; H, 5.17; N, 10.33.

Synthesis of 8-Thiabicyclo[3.2.1]octan-3 one Tosylhydrazone (**8**).—Tosylhydrazone **8** was synthesized according to the above procedure from 8-thiabicyclo[3.2.1]octan-3-one:[2,4] mp 185–186°; mass spectrum (70 eV) important or major peaks at *m/e* 310 (M^+), 155 ($C_7H_8S{=}NNH^+$), 139, 126, 97, 91.

Anal. Calcd for $C_{14}H_{18}N_2O_2S_2$: C, 54.19; H, 5.81; N, 9.03. Found: C, 54.16; H, 5.90; N, 9.03.

General Procedure for the Synthesis of Sodium Salts of 6, 7, and 8.—Salts of **6**, **7**, and **8** were obtained by adding 1 equiv of NaH to 1 equiv of tosylhydrazone in freshly distilled glyme. After stirring for 24 hr under N_2 the resulting suspensions were filtered, washed with glyme, and dried for 24 hr under high vacuum. The salts, nonhydroscopic white solids, were used without further purification.

Synthesis of Δ^2-Dihydrothiophene (**9**) **and Δ^2-Dihydrothiapyran** (**12**).—These olefins were synthesized in good yields from tetramethylene sulfoxide[30] and pentamethylene sulfoxide[31] using the standard Pummerer[32] reaction (1 hr reflux in acetic anhydride): **9**—nmr, see ref 33; mass spectrum (70 eV) *m/e* (rel intensity) *86 (50, M^+), 85 (100)*, 71 (7), 60 (4), 59 (6), 58 (12), 57 (6), 53 (9), 51 (5), 47 (3), 46 (5), 45 (35), 44 (8); **12**—nmr, see ref 33; mass spectrum (70 eV) *m/e* (rel intensity) *100 (96, M^+), 99 (49)*, 87 (5), 86 (5), *85 (100)*, 74 (4), 73 (6), 72 (76), 71 (37), 53 (7), 47 (6), 46 (8), 45 (37).

Synthesis of Δ^3-Dihydrothiophene (**10**).—Olefin **10** was obtained in moderate yield by reduction of Δ^3-sulfolene with excess $LiAlH_4$ in ether: nmr, see ref 33; mass spectrum (70 eV) *m/e* (rel intensity) *86 (92, M^+), 85 (100)*, 71 (7), 60 (3), 59 (7), 58 (11), 57 (5), 53 (12), 51 (9), 50 (7), 47 (4), 46 (5), 45 (40), 44 (11).

Synthesis of Δ^3-Dihydrothiapyran (**13**).—4-Acetoxytetrahydrothiapyran,[34] 1.5 g in 25 ml of hexane, was dripped through an 8-in. glass helix packed column preheated to 500° under N_2. Olefin **13** was isolated in moderate, but varying yields after short-path distillation of the pyrolysis residue: nmr, see ref 33; mass spectrum (70 eV) *m/e* (rel intensity) *100 (100, M^+), 99 (95)*, 97 (5), 87 (3), 86 (4), *85 (47)*, 72 (19), 71 (9), 69 (4), 67 (23), 66 (6), 65 (16), 59 (6), 58 (5), 55 (5), 54 (35), 53 (9), 51 (4), 50 (4), 47 (3), 46 (10), 45 (19).

Synthesis of 8-Thiabicyclo[3.2.1]-3-acetoxyoctane (**17**).—Acetate **17** was obtained from a 80:20 mixture of epimeric alcohols which were obtained from the $NaBH_4$ reduction of 8-thiabicyclo[3.2.1]octan-3-one.[4] The alcohols, 0.76 g, were refluxed in a mixture of 0.5 g of acetic anhydride and 10 ml of acetic acid for 2 hr. The cooled mixture was extracted with ether–water and the ether was washed with aqueous K_2CO_3 until no reaction occurred. Short-path distillation of the residue after evaporation of the ether gave 0.65 g of an oil which appeared to be a single epimer (vpc, tlc, nmr), probably the endo[4,5] acetate: ir (CCl_4) 2950, 2900, 2855, 1758, 1451, 1370, 1262, 1245, 1188, and 1085 cm^{-1}; nmr (CCl_4) δ 1.5–2.5 (m, 8), 1.94 (s, 3), 3.58 (m, 2), 4.97 (m, 1); mass spectrum (70 eV) *m/e* (rel intensity) 186 (22, M^+), 126 (84), 98 (17), 97 (27), 93 (32), 92 (25), 85 (27), 84 (13), 79 (11), 67 (20), 45 (13), 43 (100).

Anal. Calcd for $C_9H_{14}O_2S$: C, 58.00; H, 7.58. Found: C, 58.20; H, 7.73.

Synthesis of 8-Thiabicyclo[3.2.1]oct-2-ene (**15**)—Pyrolysis of 0.75 g of acetate **17**, as noted above in the synthesis of **13**, gave 0.3 g (59%) of a yellow oil. Elution of this oil on a silicic acid column with hexane gave, after short-path distillation, 200 mg of **15** as a low-melting solid: nmr, see Figure 2; ir (CCl_4) 3010, 2950, 2880, 2805, 1640, 1420, 1305, 1280, 1240, 1190, 1060, and 1010 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 128 (5), 127 (8), *126 (100, M^+)*, 111 (8), 99 (7), 98 (23), 97 (67), 94 (5), 93 (53), 92 (35), 91 (41), 85 (26), 84 (17), 80 (5), 79 (26), 78 (9), 77 (39), 71 (7), 67 (23), 66 (12), 65 (18), 59 (6), 58 (7), 53 (10), 51 (9).

Anal. Calcd for $C_7H_{10}S$: C, 66.66; H, 7.99. Found: C, 64.67; H, 7.51.

Synthesis of Sulfone 15b.—Sulfide **15** (20 mg) was stirred in 1 ml of acetic acid containing 20 drops of 30% H_2O_2 for 3 days at 25°, at which time 5 ml of H_2O was added. The aqueous layer was extracted with methylene chloride, which was washed well with aqueous K_2CO_3 and H_2O, dried with K_2CO_3, filtered, and evaporated to give 30 mg of crude solid. Recrystallization from hexane with a trace of benzene gave pure sulfone: mp 178–180°; mass spectrum (70 eV) *m/e* (rel intensity) 158 (8, M^+), 94 (38), 93 (21), 91 (11), 79 (100), 77 (24), 66 (19), with a metastable peak at 66.4 ($79^2/94$).

Anal. Calcd for $C_7H_{10}SO_2$: C, 53.17; H, 6.37. Found: C, 52.96; H, 6.31.

Identification of Dimer 11.—Thiatetramethylidene dimer, **11**, was identified *via* its mass spectrum (70 eV): *m/e* (rel intensity) 174 (9, M + 2 peak indicates two sulfur atoms per molecule), 173 (10), *172 (100*, M^+), 144 (17), 139 (12), 138 (16), 126 (10), 125 (39), 124 (22), 112 (25), 111 (47), 105 (10), 99 (12), 98 (10), 97 (36), 93 (19), 65 (12), 61 (10), 58 (10).

Synthesis of Azines 14 and 16.—Azines **14** and **16** were synthesized from the appropriate ketones by the same general procedure given here for **14**. Thiacyclohexan-4-one, 2.55 g (2 equiv), and 0.66 g (1 equiv) of 98% hydrazine were refluxed for 6 hr in 50 ml of ethanol. The mixture was allowed to cool and the resulting crystals were collected by vacuum filtration. Recrystallization from ethanol gave 2.8 g (56%) of **14**: mp 139–141°; ir ($CHCl_3$) 3000, 2970, 2920, 2840, 1650, 1450, 1350, 1300, 1280, and 1215 cm^{-1}; nmr ($CDCl_3$) δ 2.77 (m, 16); mass spectrum (70 eV) *m/e* (rel intensity) 228 (82, M^+), 116 (32), 115 (13), 114 (49), 113 (100).

Anal. Calcd for $C_{10}H_{16}N_2S_2$: C, 52.57; H, 7.06; N, 12.27. Found: C, 52.85; H, 7.13; N, 12.35.

Azine **16** had mp 188° (yellows), 204–206°; mass spectrum (70 eV) *m/e* (rel intensity) 280 (66, M^+), 247 (29), 142 (28), 141 (25), 140 (36), 139 (61), 106 (19), 99 (100), 98 (19), 97 (33), 85 (47), 81 (20), 79 (25), 77 (10), 71 (28), 69 (24), 67 (36), 65 (43).

Anal. Calcd for $C_{14}H_{20}N_2S_2$: C, 59.94; H, 7.19; N, 10.00. Found: C, 59.96; H, 7.04; N, 9.44.

Toluenesulfenic Acid (**20**).—Toluenesulfenic acid was identified by its lifetime and mass spectrum (70 eV, rel intensity): *m/e* 140 (5, M^+), 139 (11), 138 (100), 137 (17), 123 (35), 121 (10), 92 (14), 91 (21), 79 (16), 77 (13), 65 (12), 63 (10).

Acknowledgment.—P. Y. Johnson wishes to thank the National Institutes of Health for partial support of this work.

Registry No.—**6**, 1708-23-2; **6** Na salt, 40697-90-3; **7**, 40697-91-4; **7** Na salt, 40697-92-5; **8**, 40697-93-6; **8** Na salt, 40697-94-7; **9**, 1120-59-8; **10**, 1708-32-3; **11**, 40697-97-0; **12**, 13042-80-3; **13**, 40697-99-2; **14**, 40698-00-8; **15**, 40698-01-9; **15b**, 40697-28-7; **16**, 40697-29-8; **17**, 40698-02-0; **20**, 17671-92-0; thiacyclohexan-4-one, 1072-72-6; toluenesulfonylhydrazide, 1576-35-8; thiacyclopentan-3-one, 1003-04-9; 8-thiabicyclo[3.2.1]-octan-3-one, 16892-50-5; Δ^3-sulfolene, 77-79-2; 4-acetoxytetrahydrothiapyran, 40697-32-3; *endo*-8-thiabicyclo[3.2.1]octan-3-ol, 40698-03-1; *exo*-8-thiabicyclo[3.2.1]octan-3-ol, 40698-04-2; hydrazine, 302-01-2; sodium toluenesulfinate, 824-79-3.

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(28) M. A. Giantirco, *Tetrahedron*, **20**, 1772 (1964).

(29) No attempt was made to distinguish syn and anti isomers and data is given for the mixture.

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(31) T. Cairns, G. Eglinton, and D. T. Gibson, *Spectrochim. Acta*, **20**, 31 (1964).

(32) For typical procedure see W. E. Parham and L. D. Edwards, *J. Org. Chem.*, **33**, 4150 (1968).

(33) See Figure 1 for nmr data of **9**, **10**, **12**, and **13**.

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