oxonium compounds was generally prepared for pmr observation. External capillary TMS was used for reference. A Varian Associates Model A-56/60A spectrometer with a variable temperature probe was used for all spectra.

Registry No.—XII, 27659-92-3; XIII, 27659-93-4; XIV, 27659-94-5; XXIV (*n* = 3), 27659-95-6; XXIV (*n* = 4), 27659-96-7; XXIV (*n* = 5), 27659-97-8; 2,5-dimethyltetrahydrothiophene, 1551-31-1.

Acknowledgment.—Support of this work by a grant from the National Institutes of Health is gratefully acknowledged.

Preparation and Chemistry of Vinyl Sulfonium Ylides. New Synthetic Intermediates[1]

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Diphenylsulfonium vinyl ylides are conveniently generated by treatment of allylsulfonium salts with an organolithium. Base treatment of allyldimethylsulfonium salts leads exclusively *via* [3,2]-sigmatropic rearrangement to homoallylmethyl sulfides. These ylides show no tendency to undergo α elimination thermally as evidenced by lack of cyclopropene formation. Alternatively, cyclopropene is produced upon photolytic decomposition at $-78°$. Accompanying such α elimination is 1,2- and 1,4-phenyl migration in the photolysis of diphenylsulfonium allylide. Detection of cyclopropene by formation of its Diels–Alder adduct with various dienes as well as some chemistry of these adducts is discussed. Vinyl ylides undergo epoxide formation with saturated ketones; with cyclohexanones, equatorial attack is preferred over axial attack. With Michael systems, reaction proceeds with exclusive generation of cyclopropanes.

Our initial investigations into the chemistry of vinyl sulfonium ylides were prompted by both mechanistic and synthetic considerations. From a mechanistic standpoint, it was desired to construct a system which would answer unambiguously the question of carbene formation in the thermal decomposition of sulfur ylides (eq 1).

$$\overset{-}{\mathrm{RCH}}\text{—}\overset{+}{\mathrm{S}}\mathrm{R_2'} \longrightarrow \mathrm{RCH{:}} + \mathrm{SR_2'} \longrightarrow \text{carbene-derived products} \quad (1)$$

Several authors have claimed carbene-derived products from the thermal decomposition of sulfonium ylides.[3] Notably, Johnson and coworkers[4] have reported the formation of *cis*- and *trans*-stilbene from diphenylsulfonium benzylide. These workers also claim that, when acenaphthylene is added to solutions of diphenylsulfonium benzylide or *n*-butylide, cyclopropanes are formed. However, there are other possible interpretations of the experimental data which is presented by the authors.

Franzen and coworkers[5] determined that, in the generation of diphenylsulfonium *n*-butylide with tritylsodium, triphenyl-*n*-butylmethane is produced, assertedly by insertion of *n*-propylcarbene into the C–H bond of triphenylmethane. Of greater significance, perhaps, is Franzen's claim that diphenylsulfonium isobutylide yields both 1-butene and methylcyclopropane. However, the authors present only vpc evidence for the formation of methylcyclopropane.

Although these results are all commensurate with carbene intermediacy, none of the products which have been proven to be produced demand a carbene mechanism. Other processes, among which may be nucleophilic substitution, can easily account for their formation. Moreover, it is significant that none of the researchers have reported the trapping of an ylide-derived carbene with an undisputed carbene trapping agent such as cyclohexene.

In contrast to the confusion that persists with regard to thermally induced elimination, the photolytic and metal cation induced α elimination of stable sulfur ylides is documented.[6] Recently, Corey has reported that ultraviolet irradiation of an α-ketosulfoxonium ylide leads to Wolff rearrangement products derived from an α-ketocarbene.[6b] We reported the formation of 7-benzoylnorcarane when dimethylsulfonium phenacylide, in the presence of cyclohexene, is photolyzed or reacted with the salts of transition metals.[6c] Johnson and Amel also reported photolytic decomposition of the same ylide.[6d] Kunieda and Witkop have demonstrated C–H bond insertion with a carbene generated from the photolysis of a sulfoxonium ylide.[6e]

One major source of ambiguity in the interpretation of the decomposition products of sulfur ylides is that if a carbene is formed, it may react almost exclusively with the very nucleophilic starting ylide. Even if an olefin is employed as solvent, the ylide, being much more nucleophilic, may react preferentially with the carbene. The product of such a process is usually an olefin, the formal carbene dimer. This reaction of the carbene with the ylide is thus indistinguishable from the product of nucleophilic substitution by the ylide on the sulfonium salt and from the more unlikely process, carbene dimerization.

We chose to study vinyl sulfonium ylides since trapping of the vinyl carbene would occur as an intramolec-

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[1] Preliminary accounts of portions of this work have appeared: B. M. Trost and R. LaRochelle, *Tetrahedron Lett.*, **29**, 3327 (1968); B. M. Trost and R. LaRochelle, *J. Amer. Chem. Soc.*, **92**, 5804 (1970).

[2] National Institutes of Health Predoctoral Fellow.

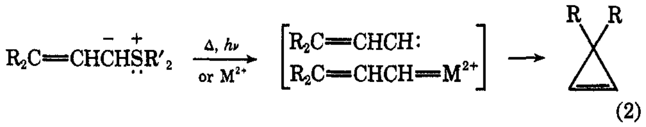
[3] A. W. Johnson, "Ylide Chemistry," Academic Press, New York, N. Y., 1966, pp 304–306.

[4] A. W. Johnson, V. J. Hruby, and J. L. Williams, *J. Amer. Chem. Soc.*, **86**, 918 (1964).

[5] V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1962).

[6] (a) L. Horner and E. Spetschka, *ibid.*, **85**, 225 (1952); (b) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1640 (1964); (c) B. M. Trost, *ibid.*, **89**, 138 (1967); (d) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969); (e) T. Kunieda and B. Witkop, *J. Amer. Chem. Soc.*, **91**, 7751 (1969).

ular process and thus would be the most facile reaction of the carbene (eq 2). Closs has clearly demonstrated


(2)

that the major reaction of a vinyl carbene is intramolecular insertion into the double bond to form a cyclopropene.[7]

It was also hoped that the reactions of such ylides would further illuminate the factors operative in ylide reactivity. It has been shown that the modes of ylide reactions are very sensitive to the changes in the electronic and conjugative stabilities of these species.[6c,8,9]

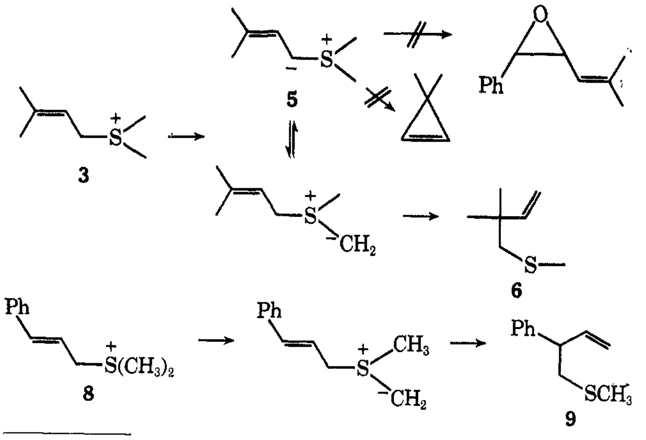
From a synthetic standpoint, the use of vinyl ylides promised to establish a convenient route to vinyl-substituted oxiranes and cyclopropanes, compounds quite difficult to prepare by other preparative methods. Furthermore, the reactions of such ylides were of interest because of their possible roles in C–C bond formation in the biosynthesis of squalene, chrysanthemic acid, stearolic acid, etc.

Initial Investigations.—Allyldimethylsulfonium bromide, **1**, was prepared in low yield in both ether and acetone solution using allyl bromide and dimethyl sulfide. The salt, though crystalline, was highly hygroscopic and thus unsuited for our purposes. The corresponding fluoroborate salt, compound **2**, was obtained as an oil; all attempts to crystallize the material failed.

Compund **3**, γ,γ-dimethylallyldimethylsulfonium fluoroborate, was prepared in 75% yield in acetonitrile using 1-bromo-3-methyl-2-butene (**4**), silver fluoroborate, and excess dimethyl sulfide. *n*-Butyllithium (1 equiv) was added to a −78° slurry of **5** in THF; benzaldehyde was then added to trap ylide **5**. However, none of the oxirane or of 3,3-dimethylcyclopropene could be detected. Instead, the homoallylic sulfide **6** was formed, as determined by vpc analysis (see Scheme I). Alkylation of dimethyl sulfide by cinnamyl bromide (**7**) generated the crystalline sulfonium salt **8**; *n*-butyllithium converted the salt exclusively to its corresponding homoallylic sulfide **9**.

SCHEME I

GENERATION AND REARRANGEMENT OF DIMETHYLSULFONIUM VINYL YLIDES



Bates[10] has independently carried out the same rearrangement. He reports an 80% yield of **6** when the bromide salt of **3** is simply reacted with *n*-butyllithium at −78° in THF. Subsequently, this reaction has been recognized as a specific example of a general class of [3,2]-sigmatropic rearrangements.[11,12]

To obviate this rearrangement, investigation was directed toward the preparation of an allylic diphenyl sulfonium salt. We attempted to prepare compound **10** using bromide **4**, diphenyl sulfide, and silver fluoroborate in various solvents and at several temperatures. All attempts to isolate the salt failed. However, allyldiphenylsulfonium fluoroborate (**11**) could be prepared easily in 86% yield by the rapid addition of allyl bromide to a 0° slurry of silver fluoroborate and excess diphenyl sulfide in acetone.

Generation and Reactions of Diphenylsulfonium Allylide 12.—Addition of *n*-butyllithium to a −78° THF slurry of **11** afforded a dark red-orange solution. Quenching of the solution with deuterioacetic acid led to the immediate disappearance of the color and to the precipitation of a while solid. The product was shown to be the deuterated salt **13**, isolated in 70–75% yield.

$$[R_2C{=}CHCH_2\overset{+}{\ddot{S}}Ph_2]\,[\overset{-}{B}F_4]$$

10, R = CH_3
11, R = H

$$CH_2{=}CH\overset{-}{C}H\overset{+}{\ddot{S}}Ph_2 \;\updownarrow\; \overset{-}{C}H_2{-}CH{=}CH\overset{+}{\ddot{S}}Ph_2$$

12

Nmr analysis ($CHCl_3$) revealed no signals attributable to the other possible deuterated salt **14**. The result of

$$[CH_2{=}CH{-}CHD\overset{+}{S}Ph_2]\,[\overset{-}{B}F_4] \qquad [CH_2D{-}CH{=}CH\overset{+}{S}Ph_2]\,[\overset{-}{B}F_4]$$

13 **14**

this experiment confirmed the generation of the desired ylide. Also, the site of deuteration demonstrated that the position of highest electron density in the conjugated ylide is the carbon α to the positively charged sulfur.

Subsequent experiments showed that a much higher yield of the allylide resulted when *tert*-butyllithium was used as the base rather than the more nucleophilic *n*-butyllithium. The ylide solution so generated was golden yellow, rather than deep red as found with *n*-butyllithium.

The α elimination of the allylide **12** would be expected to yield the parent cyclopropene, an extremely sensitive hydrocarbon, one that is susceptible to polymerization in solution even at −78°. Consequently we decided to investigate the use of the Diels–Alder reaction to trap cyclopropene. Cyclopentadiene was

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[7] G. L. Closs in "Advances in Alicyclic Chemistry," Vol. I. H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N. Y., 1966, pp 63,64.

[8] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

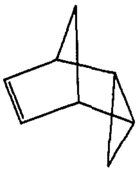
[9] J. Adams, L. Hoffman, Jr., and B. M. Trost, *J. Org. Chem.*, **35**, 1600 (1970).

[10] R. B. Bates and D. Feld, *Tetrahedron Lett.*, 417 (1968).

[11] (a) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 537, 538, 1083 (1968); (c) J. E. Baldwin and D. P. Kelly, *ibid.*, 899 (1968); (d) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *J. Amer. Chem. Soc.*, **90**, 4758 (1968); (e) R. B. Bates and D. Feld, *Tetrahedron Lett.*, 417 (1968); (f) G. M. Blackburn, W. D. Ollis, J. D. Plackett, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 186 (1968); (g) G. M. Blackburn and W. D. Ollis, *ibid.*, 1261 (1968); (h) G. M. Blackburn, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, **99** (1969); (i) R. W. C. Cose, A. M. Davis, W. D. Ollis, C. Smith, and I. O. Sutherland, *ibid.*, 293 (1969); (j) W. Kirmse and M. Kapps, *Chem. Ber.*, **101**, 994, 1004 (1968); (k) W. Antlo, K. Nakayama, K. Ichibori, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 5164 (1969).

[12] J. E. Baldwin and C. H. Armstrong, *Chem. Commun.*, 631 (1970), and references therein.

chosen as the diene with which to analyze for cyclopropene in the effluent gases from the reaction since the reaction of cyclopentadiene with cyclopropene had previously been shown to be quantitative, yielding the endo Diels–Alder adduct **15**.[13] Several base-stable dienes were also investigated as possible *in situ* traps of cyclopropene.



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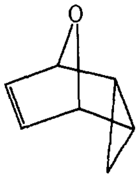

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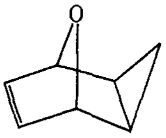
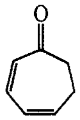


17

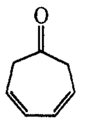
When we passed cyclopropene into neat furan at room temperature, two products were formed in approximately equal amounts, as determined by vpc analysis. The nmr spectrum of the first component was identical with that reported by Srinivasan for one of the compounds from the furan photolysis.[14] Although that author failed to use the nmr spectra to differentiate between the isomers, the nmr of the first component indicates that it is the exo isomer **17**. The nmr spectrum[15] consists of signals at 0.65–1.20 (3 H, m), 1.35–1.55 (1 H, m), 4.53 (2 H, br s), and 6.40 ppm (2 H, t, $J = 0.5$ Hz). The virtually nonexistent coupling of the bridgehead protons α to oxygen with the cyclopropylmethine protons is indicative that the latter protons are in the endo configuration.[16a] Furthermore, the abnormally low-field resonance of one cyclopropyl proton (1.35–1.55 ppm) suggests that it is syn to an oxygen atom.[16b]

The spectrum of the second component is in good agreement with that expected for the endo Diels–Alder adduct **16**. The nmr spectrum exhibits resonances at 0.60–0.72 (1 H, m), 0.90–1.05 (1 H, m), 1.60–1.85 (2 H, m), 4.75 (2 H, m, $W_H = 6.0$ Hz), and 5.93 ppm (2 H, t, $J = 0.5$ Hz). The relatively large coupling constants seen for the bridgehead protons α to oxygen implies that they are coupled with the cyclopropylmethine protons which are in the exo configuration.[16a] Also, the high degree of similarity of the nmr peak shapes of this compound with those of the endo Diels–Alder adduct **20** argues for the assignment given (see Experimental Section).

A third argument for the above assignment is the extreme ease of rearrangement of the compound. When samples of the endo adduct were isolated by vpc, the nmr spectrum exhibited, in addition to the data given above, broad resonances at 6.2 and 2.5 ppm. The ir spectrum showed a medium intensity band at 1660 cm^{-1}. When a sample of this mixture was repassed on vpc, none of the endo adduct could be detected. Instead another peak of longer retention time emerged. The nmr spectrum of this component consisted of broad resonances at 2.2–2.7 and 5.9–6.7 ppm which were of approximately equal intensity. The ir spectrum showed strong bands at 1710 and 1660 cm^{-1}; in addition, all of the ir data agreed in detail with the data reported for a crude mixture of compounds **18a** and **18b**.[17] The mass spectrun showed a molecular ion at m/e 108 ($C_7H_8O^+$). Mild hydrogenation of the ketones over 10% palladium on carbon gave one product, identical in vpc retention time and ir spectrum with cycloheptanone.



18a

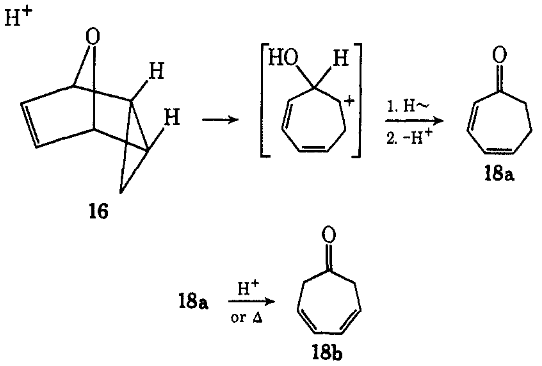


18b

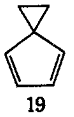
The above data is consistent with an acid- (or thermally) induced opening of the endo adduct **16** and facile hydride migration to yield the conjugated dienone **18a** (see Scheme II). In the endo compound the developing p orbital from the rupture of the C–O bond can overlap nicely with the exo cyclopropyl bond as it opens during the reorganization. This anchimeric assistance is sufficient to favor rearrangement of the endo isomer over the exo isomer; the exo compound was found to be stable to the vpc conditions. Unfortunately, even though furan appeared to be a reasonable trap for cyclopropene, when ylide generation was attempted using furan as solvent little or no allylide was formed. Consequently, furan was abandoned as a useful cyclopropene trap for our purposes.

SCHEME II

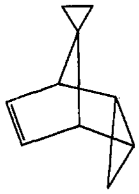
REARRANGEMENT OF DIELS–ALDER ADDUCT 16



We also investigated the spirocyclopentadiene **19** as a potential Diels–Alder diene. It was found that the Diels–Alder adduct **20** could be prepared easily by bubbling cyclopropene into a room temperature pentane solution of **19**. When cyclopropene was passed into a −78° THF solution of the diene, 1.3 mmol of adduct **20** was noted by vpc after work-up. A consecutively run reaction using a similar aliquot of cyclopropene and a cyclopentadiene trap yielded 3.4



19



20

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[13] K. B. Wiberg and W. J. Bartly, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

[14] R. Srinivasan, *ibid.*, **89**, 4813 (1967).

[15] Unless otherwise stated, all nmr and ir spectra were obtained in carbon tetrachloride solution.

[16] (a) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 3rd ed Pergamon Press, New York, N. Y., 1969, p 289; (b) R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970).

[17] J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *ibid.*, **77**, 4401 (1955).

mmol of **15**. This result indicated that **19** could be used to detect cyclopropene under the temperature conditions required. Furthermore, from the relative amounts of **15** and **20** formed in the control reaction, it was calculated that the spirodiene was approximately one-third as efficient as cyclopentadiene in trapping cyclopropene. In a subsequent control reaction, cyclopropene was added to a −78° THF solution of the allylide containing the diene **19**. Upon work-up, adduct **20** was noted. We were thus confident that cyclopropene could easily be detected if formed in our experiments.

To study the thermal decomposition of the allylide **12**, a solution of the ylide was generated at −78° and allowed to warm to room temperature. The deep red-orange color slowly faded yielding a bright yellow solution. No products of α elimination were observed; no cyclopropene-derived products could be noted. The effluent gases from the reaction were passed through a cyclopentadiene trap; none of adduct **15** could be detected.

In an analogous experiment, a solution of the ylide containing a large excess of **19** was allowed to thermally decompose. None of adduct **20** was apparent by vpc analysis.

The generation and thermal decomposition of the allylide, prepared from **11** and *n*-butyllithium, did result in the formation of several hydrocarbons and sulfides (see Table I). This study of the mechanism(s) of their formation is complex and tangential and is therefore reserved for separate consideration.

TABLE I

VOLATILE PRODUCTS IN GENERATION OF DIPHENYLSULFONIUM ALLYLIDE[a]

Compd	Relative %	Compd	Relative %
Propene	11.4	*n*-Butylbenzene	0.0
Benzene	48.8	Di-*n*-butyl sulfide	1.4
1-Heptene	0.0	Allyl phenyl sulfide	1.7
n-Octane	9.3	*n*-Butyl phenyl sulfide	22.1
Allylbenzene	0.0	Biphenyl	5.2

[a] Diphenyl sulfide produced in 62% yield.

In addition to these volatile products, the ylide's decomposition produced a considerable amount of a yellow intractable gum, presumably arising from polymerization of some sort. Nmr analysis of this material revealed many aryl and aliphatic absorptions but no absorptions indicative of polycyclopropene.

Closs has reported a simple synthesis of cyclopropene using allyl chloride and sodium amide in warm mineral oil.[18] It is thought that this transformation proceeds *via* the vinyl carbene. Because of the similarity of allyl chloride and allyldiphenylsulfonium fluoroborate, we reasoned that cyclopropene formation under Closs' conditions was favored by the unique chemical environment. Thus we tried a modification of Closs' procedure. The solid sulfonium salt was slowly added to a slurry of excess sodium amide in mineral oil at 80°. However, a cyclopentadiene monitor of the reaction gases revealed none of adduct **15**.

In addition to studying the chemical transformations occurring during the thermal decomposition of the allylide, we documented the thermal stability of the ylide. Solutions of the ylide, generated as usual at −78°, were warmed to the desired temperatures and then stirred for the appropriate lengths of time. Cyclohexanone was then added to trap the ylide as the vinyl oxirane **26a**. As can be seen from Table II, the ylide is quite stable at −78° but decreases in stability rapidly as room temperature is approached.

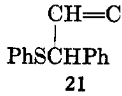
TABLE II

THERMAL STABILITY OF THE ALLYLIDE 12

Temp, °C	Time	Vinyl oxirane yield, %
−78	1.0 hr	56
−40	1.5 hr	56
−15	5 min	58
−15	50 min	16
0	5 min	5

When thermal conditions failed to induce α elimination from the allylide, other methods were attempted to effect carbene formation from the ylide. Since carbenoid reactions are often catalyzed by the salts of transition metals with filled or partially filled d orbitals,[6c] allylide solutions containing **19** were reacted with zinc iodide and anhydrous cupric sulfate. A cyclopentadiene trap monitored the effluent gases. Neither of the reactions produced any Diels-Adler products or any other apparent adducts with **19**.

We next investigated photolytic conditions. Because of ylide thermal instability, the vessel was cooled with a circulating flow of −78° methanol. With these precautions, the ylide could be maintained at or near −78° for a 1-hr photolysis. The ylide solution, containing diene **19**, was photolyzed for 1 hr with a high-pressure, 450-W Hanovia mercury-vapor lamp through a Pyrex filter. The colorless photolysate was allowed to slowly warm to room temperature. The usual vpc analysis revealed that the desired Diels-Alder adduct had been formed in 25% yield (based on ylide). Also, diphenyl sulfide was present in 29% yield. Using higher vpc column temperatures, a large, previously unnoted peak was observed, accounting for approximately 15% of the reaction products. A vpc-collected sample was examined by tlc analysis. The peak separated into three components on silica gel. Large-scale separation of the compounds led to their identification as photoproducts **21**, **22**, and **23**, in a ratio of 10:3:1. Each component



$$\mathrm{PhS\overset{\overset{\displaystyle CH=CH_2}{|}}{C}HPh}$$

21

$\mathrm{PhSCH{=}CHCH_2Ph}$

22

$\mathrm{PhSCH_2CH{=}CHPh}$

23

had the molecular formula $C_{15}H_{14}S$, as shown by exact mass determination. The nmr of spectrum of **21** showed peaks at 4.68 (1 H, br d, J = 7.5 Hz), 5.02 and 4.93 (2 H, two overlapping d, J = 9.0 and 17.0 Hz), 5.80–6.45 (1 H, m), and 7.23 ppm (10 H, br s).

Compund **22** had an nmr spectrum with signals at 3.43 and 3.57 (2 H, two overlapping d, J = 6.5 and 6.0 Hz), 5.95–6.42 (2 H, m), and 7.22 ppm (10 H, m). The two overlapping allylic doublets in the nmr spectrum of this band implied that both the cis and trans double bond isomers were present. In addition the ultraviolet spectrum showed absorptions at 248 nm

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[18] G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

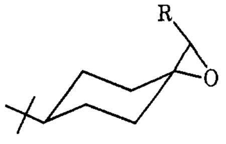
(ϵ 6500) and 264 (6700), a pattern characteristic of vinyl phenyl sulfides.[19]

The smallest component, compound **23**, had an nmr spectrum with resonance at 3.60 (2 H, a four-line pattern of intensity 2:1:1:2, consisting of two apparent doublets at 3.58 and 3.63 ppm, J = 1.5 Hz), 5.82–6.33 (2 H, m), and 7.23 ppm (10 H, Br s). The four-line pattern noted for the allylic protons is suggestive of virtual coupling of the allylic protons with two vinyl protons. It is unclear whether the sample, an off-white solid, is a mixture of isomers. The uv spectrum of this component exhibits one band at 252 nm (ϵ 5100). The appropriate control reactions showed that these compounds were not produced in the thermal decomposition of the allylide.

Synthetic Investigations with the Allylide.—Our synthetic investigations with the allylide were initiated to develop preparative routes to vinyl-substituted cyclopropanes and oxiranes and to help delineate the factors operative in ylide reactivity. Although there is still insufficient evidence to allow one to describe with certainty all the factors affecting ylide reactivity, two aspects of the problem now appear evident. The stability, and thus the modes of reaction, of ylides can be controlled by varying the ability of the substituent on the carbon to stabilize an adjacent carbanionic center.[9] Also, incorporation of ligands on sulfur such as aryl groups or oxygen atoms (sulfoxonium ylides), which can modulate the dispersal of charge, can further alter ylide reactivity.[8]

It is convenient to divide ylides into two main classes: reactive ylides, which are strongly nucleophilic and are generally unstable above 0°; and stabilized ylides, which usually react only with strong electrophiles and which are often stable (and sometimes unreactive) even at room temperature and above. Examples of the former group are dimethylsulfonium methylide[8] and diphenylsulfonium ethylide.[20] Examples of the latter class are myriad: dimethylsulfoxonium methylide,[8] dimethylsulfonium phenacylide,[6c] diphenylsulfonium benzylide,[4] dimethylsulfonium carbomethoxymethylide,[21] the dimethylthetin anion,[9] and many others.

Generally speaking, unstabilized ylides react with simple ketones to form oxiranes. With substituted cyclic ketones, such as 4-*tert*-butylcyclohexanone, these species react to give predominantly the product of axial attack, **24**. Dimethylsulfonium methylide, for example, yields **24a** and **25a** in a ratio of 83:17. When the same ylides are reacted with α,β-unsaturated ketones, the predominant or exclusive product is epoxide formation.



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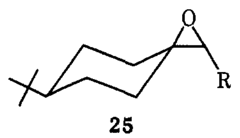
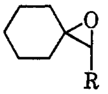


25

a, R = H
b, R = CO_2CH_3
c, R = $CH{=}CH_2$

The stabilized ylides, on the other hand, are oftentimes too stable to react with normal ketones. However, there are resonance-stabilized species which do react nicely with ketones. When these ylides are reacted with 4-*tert*-butylcyclohexanone, the predominant and often exclusive product is that of equatorial attack, **25**. Dimethylsulfoxonium methylide yields solely **25a**. The dimethylthetin anion gives almost exclusively the trans oxirane **25b** after esterification.

When allylide **12** was studied, it was found that the ylide was intermediate in reactivity between the two classes described above. When cyclohexanone was added to a −78° solution of the ylide generated with *tert*-butyllithium, an 80% yield of 2-vinyl-1-oxaspiro[5.2]octane (**26a**) was obtained, as determined by vpc analysis.[22] The vinyl oxirane exhibited ir absorptions at 1630, 995, 923, and 680 cm^{-1}. The nmr spectrum had resonances for the cyclohexyl ring in addition to peaks at 3.17 (1 H, d, J = 6.0 Hz) and 5.15–6.13 ppm (3 H, m).

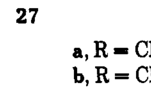


26

a, R = $CH{=}CH_2$
b, R = $CH_2CH_2CH_3$

When the ylide was generated using *n*-butyllithium, a 52–56% yield of **26a** was obtained. In addition, a 5–7% yield of the *n*-propyl oxirane **26b** was also isolated from the reaction. During the generation of the allylide some of the organolithium apparently attacks the positively charged sulfur displacing allyllithium. The *n*-butyldiphenylsulfonium salt thus formed is converted to an ylide which reacts with cyclohexanone.

When the allylide was reacted with 4-*tert*-butylcyclohexanone, two epimeric vinyl oxiranes, **24c** and **25c**, were formed in a ratio of 1:4, as determined by vpc analysis. Attempted large-scale vapor phase chromatography of the mixture resulted in considerable decomposition. Thick layer chromatography on alumina resulted in the isolation of the combined epimers. The nmr spectrum showed absorptions at 0.87 and 0.90 (9 H, two s), 0.90–2.10 (0 H, m), 3.07 (1 H, d, J = 5.5 Hz), and 5.10–5.90 ppm (3 H, m). Attempted combined hydrogenolysis–hydrogenation of the vinyl oxiranes over 10% palladium on carbon led to serious decomposition. Consequently, the mixtures were reduced with lithium aluminum hydride in ether at room temperature to a mixture of two epimeric allylic alcohols **27a** and **28a**. Vpc analysis showed two peaks in a ratio of 1:4.2. The alcohol mixture was then hydrogenated to a mixture of the cis and trans alcohols **27b**



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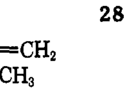

28

a, R = $CH_2CH{=}CH_2$
b, R = $CH_2CH_2CH_3$

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(19) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, p 47.

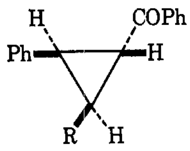
(20) E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964).

(21) W. A. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969).

(22) M. J. Hatch [*ibid.*, **34**, 2133 (1969)] reports low yields of vinyl oxiranes derived from simple ketones and allyldimethylsulfonium hydroxide in aqueous sodium hydroxide solution.

and **28b**. Vpc analysis revealed two components in a ratio of 1:3.8. The major component, **27b**, was shown to be identical with the major component formed in the reaction of *n*-propylmagnesium bromide with 4-*tert*-butylcyclohexanone.[23] The minor component, **28b**, was likewise identical in its properties with the minor component from the Grignard reaction.

The allylide reacted as a stabilized ylide with chalcone, giving exclusively the Michael addition products **29a** and **30a**. Separation of the two isomers by thick layer chromatography could not be accomplished. The ir spectrum of the mixture showed a strong absorption at 1670 cm^{-1} and other indicative absorptions at 1625, 905, 702, and 695 cm^{-1}. The nmr spectrum showed resonances at 2.4–2.9 (1.1 H, m), 3.19 (1.9 H, m), 5.12 (3 H, m), and 7.18 ppm (10 H, m).



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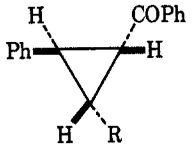


30

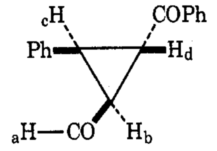
a, R = $CH{=}CH_2$
b, R = CHO
c, R = CO_2CH_3

Osmium tetroxide–sodium metaperiodate oxidation of the olefins gave an aldehyde mixture which could be separated by multiple thick layer chromatography. Prior to separation an nmr analysis of the aldehydes showed the aldehydic protons in a ratio of 2.5:1.0. This ratio was taken as a reflection of the isomer composition of the vinylcyclopropanes isolated from the reaction.

Analysis of the nmr coupling constants and chemical shifts of the two aldehydes led to the stereochemical assignments shown. The major isomer was identified as **29b**, the minor as **30b**.

H-H coupling constants, Hz

$J_{ab} = 5.0$
$J_{bc} = 10.0$
$J_{bd} = 4.5$
$J_{cd} = 6.0$



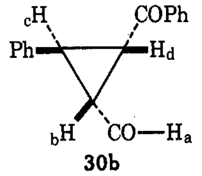
29b

Chemical shifts, ppm

$H_a = 9.20$
$H_b = 2.93$
$H_c = 3.45$
$H_d = 3.98$

H-H coupling constants, Hz

$J_{ab} = 6.0$
$J_{bc} = 6.0$
$J_{bd} = 9.0$
$J_{cd} = 5.5$



30b

Chemical shifts, ppm

$H_a = 9.57$
$H_b = 2.69$
$H_c = 3.53$
$H_d = 3.53$

The aldehyde mixture was further oxidized with silver oxide to the corresponding acids, which were then esterified with diazomethane and separated by thick layer chromatography. The nmr spectra of the esters, **29c** and **30c**, proved to be identical with those derived from addition of dimethylthetin anion to chalcone, followed by esterification.[9]

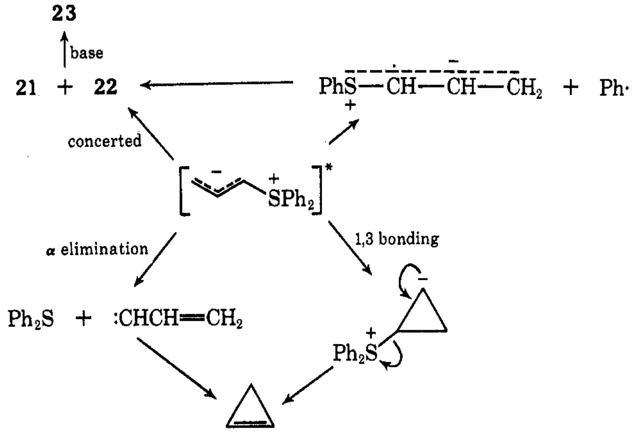
Corey has reported the facile alkylation of diphenylsulfonium ethylide with methyl iodide.[24] Allylide **12** is not sufficiently nucleophilic to react with either methyl iodide or dimethyl sulfate. No apparent reaction with these methylating agents takes place at −78° or upon warming to room temperature.

Discussion

To date there is no concrete evidence that sulfur ylides of any type undergo thermal α elimination to yield carbenes. The thermal decomposition of diphenylsulfonium allylide has been shown not to yield vinyl carbene. The failure of α elimination in sulfur ylides compared to diazo compounds relates to a higher C–S π bond order compared to the C–N case and/or lower heat of formation of the resultant sulfide compared to molecular nitrogen. On the other hand, the photolytic decomposition provides an intriguing result. At first glance, formation of the cyclopropene Diels–Alder adduct might be taken as evidence for α elimination. Alternatively, the ylide may be considered simply as a perturbed allyl carbanion; overlap of the orbitals at C_1 and C_3 would form a cyclopropyl carbanion (see Scheme III). Subsequent β elimination of the closed species generates cyclopropene. The great endothermicity associated with such a ring closure in the present case (going from a highly stabilized anion to a highly localized charge separated species) requires 1,3 bonding to occur during internal conversion (*i.e.*, as a mechanism to dissipate excited state energy by a nonradiative process). An electrocyclic reaction of this sort is attractive and intriguing to consider. To our knowledge, it would be the first example of the closure of an allyl anion to a cyclopropyl anion. The intermediacy of such a process is difficult to rule out. However, since other sulfur ylides have been shown to undergo α elimination to carbenes during photolysis, it is most likely that cyclopropene formation occurs by a similar process.

SCHEME III

INTERPRETATIONS OF PHOTOLYTIC YLIDE DECOMPOSITION



The origin of the phenyl migration products provides additional insight into the photochemistry of sulfur ylides. Conceivably, a concerted 1,2 or 1,4 migration could account for the sulfides **21**, **22**, and **23**. Simple orbital symmetry concepts cannot be utilized to predict the preferred pathway. In considering such factors, we can treat our system as a butadiene occupied by five electrons and a phenyl radical (see Scheme III). De-

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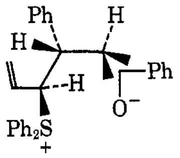
[23] H. Felkin and C. Frajerman, *Tetrahedron Lett.*, **13**, 1045 (1970).
[24] E. J. Corey, M. Jautelot, and W. Oppolzer, *ibid.*, 2325 (1967).

pending on the electronic configuration of the excited state either 1,2 or 1,4 migration would be a symmetry allowed process. Furthermore, since d orbitals are undoubtedly involved in bonding in such species their rôle in determining the preferred pathway obscure interpretations based on orbital symmetry. Scheme III also outlines a nonconcerted route. Simple homolysis of the phenyl sulfur bond followed by recombination would generate the observed products. Preferential coupling would be expected to occur at the α carbon since it is the site of highest odd-electron density. The formation of cinnamylphenyl sulfide (**23**) in addition to 1-phenylthio-3-phenylpropene was not unexpected since base-catalyzed double bond isomerization proceed facilely in such systems. Radical pathways have been found to compete with the [3,2]-sigmatropic rearrangement of allylsulfonium alkylides.[11a]

In the condensation reactions diphenylsulfonium allylide behaves more like a stabilized ylide. It attacks cyclohexanones preferentially equatorially although the specificity is considerably less than observed with more highly stabilized ylides.[9] With α,β-unsaturated ketones, it reacts by Michael addition exclusively.

The stereochemistry of the cyclopropanes reflects both steric and electronic factors. Structures **31** and **32** represent the zwitterion intermediates formed upon addition of ylide to chalcone; **31** leads to cyclopropane **29** and **32** to cyclopropane **30**. Intermediate **32** involves eclipsing the bulky phenyl ring and the diphenyl sulfur moiety as well as maximum charge separation. On the other hand, zwitterion **31** possesses a much less severe eclipsing of the vinyl group with the bulky phenyl as well as internal stabilization of charge. Thus, **31** should be preferred and cyclopropane **29** should be the major product as is observed. These preferences can be explained on the basis of the factors previously discussed for stabilized ylides.[6c,9] The vinyl ylide provides a convenient synthetic route to both vinyl epoxides and vinylcyclopropanes in good yields. It is interesting to note that *tert*-butyllithium gave substantially higher yields of ylide than *n*-butyllithium. In the latter case, we have found that appreciable reaction occurs at sulfur to produce sulfuranes.[25] Such species are a new class of intermediates in organic chemistry and undergo interesting new reactions. Other publications from our laboratories will detail the chemistry of tetrasubstituted sulfuranes.



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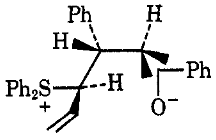

32

Experimental Section

General.—Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Unless otherwise stated, infrared spectra were determined in carbon tetrachloride solution on a Beckman IR-8 spectrophotometer; ultraviolet spectra were determined in 95% ethanol on a Cary Model 15 spectrometer. Nmr spectra were determined in carbon tetrachloride solution on a Varian Associates Model A-60A spectrometer. Chemical shifts are given in ppm relative to TMS as internal standard. Mass spectra were taken on either a CEC 103 C mass spectrometer or an AEI MS-902 mass spectrometer at an ionizing current of 50 mA and an ionizing voltage of 70 V All exact mass determinations were obtained on the MS-902 instrument. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Vpc analyses were performed on an Aerograph Model 90P instrument.

Synthesis of Allyldimethylsulfonium Bromide. Method A.—To 15 ml of ethyl ether under nitrogen were added 2.42 g (20.0 mmol) of allyl bromide and 1.37 g (22.0 mmol) of dimethyl sulfide. After stirring at room temperature for 62 hr, an oil had separated from the reaction solution. The flask was immersed in a −78° bath, and the oil quickly solidified. The solid was filtered under nitrogen to give 0.02 g (0.54%) of a white, crystalline salt which proved to be highly hygroscopic when exposed to the atmosphere: ir ($CHCl_3$) 1640, 995, 947 cm^{-1}; nmr (D_2O) 2.82 (6 H, s), 3.94 (2 H, br d, J = 6.0 Hz), 5.69 (2 H, d, J = 1.0 Hz), 5.80 ppm (1 H, br d, J = 6.0 Hz).

Method B.—The salt was prepared as in method A above, using 2.42 g (20.0 mmol) of allyl bromide and 1.37 g (22.0 mmol) of dimethyl sulfide in 15 ml of acetone. After 44 hr, the yield was 0.70 g (19%).

Synthesis of Allyldimethylsulfonium Fluoroborate.—To 0.500 g (2.57 mmol) of silver fluoroborate in the flask under nitrogen were added 3 ml of acetonitrile and 0.640 g (10.2 mmol) of dimethyl sulfide. To the stirring suspension, 0.311 g (2.57 mmol) of allyl bromide was added dropwise. After stirring for 8 hr, the solution was filtered. The filtered silver bromide precipitate was washed several times with acetonitrile, and the washings were combined with the filtrate. The acetonitrile solution was concentrated *in vacuo* to give 0.430 g (88%) of a partly crystalline, colorless oil. All attempts to further solidify the material failed: ir (film) 1640, 1433, 1055, 953 cm^{-1}; nmr (DMSO-d_6) 2.82 (6 H, s), 4.03 (2 H, d, J = 7.0 Hz), 5.69 (2 H, s), 5.87 ppm (1 H, d, J = 7.0 Hz).

Synthesis of γ,γ-Dimethylallyldimethylsulfonium Fluoroborate.—Under nitrogen, 4.47 g (22.9 mmol) of silver fluoroborate was slowly added to 50 ml of rigorously dried acetonitrile. The flask was immersed in an ice–water bath and wrapped in aluminum foil. The 5.70 g (91.5 mmol) of dimethyl sulfide was added to the stirring suspension. A solution of 3.42 g (22.9 mmol) of the bromo olefin in 10 ml of acetonitrile was added dropwise. When the addition was complete, the cooling bath was removed, and the reaction was stirred at room temperature for 3 hr. The reaction mixture was filtered, and the silver bromide precipitate was washed with acetonitrile. The combined acetonitrile solutions were concentrated *in vacuo* to give 4.91 g (98.1%) of a gray solid. The crude material was dissolved in a minimum amount of absolute ethanol and filtered through sintered glass to remove a black contaminant. The filtrate was triturated with ethyl ether to yield white crystals. Recrystallization from ethanol–ether afforded 3.77 g (75.3%) of a white crystalline solid (mp 67–68°): ir ($CHCl_3$) 1665, 1064, 928 cm^{-1}; nmr (DMSO-d_6) 1.78 (3 H, br s), 1.84 (3 H, br s), 2.78 (6 H, s), 4.03 (2 H, br d, J = 9.0 Hz), 5.27 ppm (1 H, br t, J = 9.0 Hz).

Anal. Calcd for $C_7H_{15}SBF_4$: C, 38.55; H, 6.93; S, 14.71. Found: C, 38.67; H, 7.03; S, 14.70.

Reaction of 3 with *n*-Butyllithium.—A reaction flask was set up with the exit gases passing through two liquid nitrogen traps. To 80 ml of THF under nitrogen were added 2.17 g (9.96 mmol) of the sulfonium salt. The reaction was immersed in a −78° bath and stirred at that temperature for 30 min. Then 7.48 ml (9.96 mmol) of a 1.33 *N* solution of *n*-butyllithium in hexane was added dropwise to the reaction mixture over a 30-min period. The light yellow solution was stirred for 30 min; then a solution of 0.975 g (9.20 mmol) of benzaldehyde in 20 ml of THF was added dropwise over a 20-min period. The reaction solution was stirred for an additional 30 min at −78°. The bath was then removed to allow the solution to warm to room temperature. The reaction solution was poured onto 50 g of crushed ice and extracted with three 80-ml portions of ether. The ethereal extracts were dried (K_2CO_3), filtered, and distilled at low temperature.

The residue was analyzed by vpc on an 8 ft × 0.25 in. 20% Carbowax on Chromosorb P column at 187°. Anisole was added as internal standard. There were four prominent peaks in the chromatogram: retention time (compound) 5.5 min (THF), 10.0 min (3,3-dimethyl-4-thiomethoxy-1-butene, **7**, 20.3%),

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[25] B. M. Trost, R. La Rochelle, and R. C. Atkins, *J. Amer. Chem. Soc.*, **91**, 2175 (1969), and references therein.

25.4 min (anisole), 49.5 min (benzaldehyde). The structure of the sulfide was assigned on the strength of its spectral data: ir 1640, 1382, 1367, 918, 674 cm^{-1}; nmr 1.08 (6 H, s), 2.07 (3 H, s), 2.42 (2 H, s), 4.90 (1 H, d of d, J = 10.0, 1.5 Hz), 4.92 (1 H, d of d, J = 18.0, 1.5 Hz), 5.83 ppm (1 H, d of d, J = 18.0, 10.0 Hz). The spectra were identical with the published data.[9]

The pot residue was analyzed by vpc at higher temperatures and by column chromatography; however, none of the desired oxirane could be detected.

Analysis of the liquid nitrogen trap showed some dimethyl sulfide (by vpc retention), but no 3,3-dimethylcyclopropene.

Preparation of Cinnamyldimethylsulfonium Bromide.—A solution of 19.7 g (0.10 mol) of cinnamyl bromide and 32 g (0.50 mol) of dimethyl sulfide was allowed to stand in acetone 24 hr. The resultant solid was collected by filtration to generate a quantitative yield of product. It was highly hygroscopic and thus precluded elemental analysis. Its infrared spectrum ($CHCl_3$) showed absorptions at 1645 and 975 (trans disubstituted double bond) and 1600, 1585, and 1495 cm^{-1} (phenyl ring). The nmr spectrum ($CDCl_3$) exhibited a singlet (6 H) at δ 3.33, a broad doublet (2 H, J = 7.5 Hz) at δ 4.89, a doublet of triplets (1 H, J = 15.5, 7.5 Hz) at δ 6.24, a doublet (1 H, J = 15.5 Hz) at δ 7.09, and a multiplet (5 H) centered at δ 7.32.

***n*-Butyllithium Treatment of Cinnamyldimethylsulfonium Bromide.**—A suspension of 261 mg (1.0 mmol) of cinnamyldimethylsulfonium bromide in 10 ml of dry tetrahydrofuran (freshly distilled from lithium aluminum hydride) was treated with 1.0 ml of a 1.2 M (1.2 mmol) *n*-butyllithium solution in hexane at −78°. After stirring at that temperature for 1 hr, the reaction mixture was allowed to warm to room temperature. Pouring the resultant solution into water quenched the reaction. After extracting with ether and drying over magnesium sulfate, the mixture was analyzed by vpc. A single product was formed whose mass spectrum indicated a molecular formula of $C_{11}H_{14}S$. Based on that formula, the yield was calculated to be 86%. The infrared spectrum showed absorptions at 1640, 985, and 918 (monosubstituted vinyl group) and 1600 and 1500 cm^{-1} (phenyl absorptions). The nmr spectrum exhibited a singlet (3 H) at δ 1.95, a doublet (2 H, J = 7.0 Hz) at δ 2.78, a broadened quartet (1 H, J = 7.0 Hz) at δ 3.48, a doublet of triplets (1 H, J = 17.0, 1.2 Hz) at δ 5.01, a doublet of triplets (1 H, J = 10.4, 1.1 Hz) at δ 5.09, a multiplet (1 H) centered at δ 6.05, and a pseudosinglet (5 H) at δ 7.21. The mass spectrum had a molecular ion at m/e 178 and abundant peaks at 130, 117 (base peak), 115, 103, 91, 85, 83, 77, and 61. This data clearly identifies the product as 4-methylthio-3-phenyl-1-butene (Calcd for $C_{11}H_{14}S$: 178.08162. Found: 178.08413).

Synthesis of Allyldiphenylsulfonium Fluoroborate.—Under nitrogen 24.8 g (0.127 mol) of silver fluoroborate was slowly dissolved in 40 ml of dry acetone. Then 157 g of diphenyl sulfide was added to the solution. The flask was wrapped in aluminum foil and immersed in a 0° bath. To the stirring brown slurry 17.0 g (0.140 mol) of allyl bromide was rapidly added *via* syringe. The bath was removed after 5 min. Soon a yellow-green solid formed in the colorless solution. After approximately 2 hr, the solution began to turn light yellow. (The yellow color accompanies decomposition of the salt. The reaction was therefore terminated when the color change was noted.) The reaction was filtered, and the silver bromide was washed with methylene chloride. The organic fractions were combined, and the volume was reduced *in vacuo* to yield a dark red oil. Ether (200 ml) was added to the oil, and the mixture was vigorously shaken to induce solidification. The solid mass was broken up with a stirring rod, a few milliliters of methylene chloride added, and the mixture shaken. After a few minutes of shaking, the solid material was an off-white color. The solid was filtered and recrystallized by dissolving in methylene chloride and triturating with ether to yield 34.4 g (85%) of the desired salt (mp 70–72°): ir ($CHCl_3$) 1640, 1055, 875, 682 cm^{-1}; nmr ($CDCl_3$) 4.80 (2 H, d, J = 6.0 Hz), 5.28–5.95 (3 H, m), 7.5–7.8 ppm (10 H, m); λ_{max} 235 nm (sh) (ϵ 9530), 259 (1400), 267 (1680), 273 (1300).

Anal. Calcd for $C_{15}H_{15}SBF_4$: C, 75.30; H, 4.81; S, 10.21. Found: C, 75.39; H, 4.94; S, 10.16.

Preparation of Diphenylsulfonium Allylide (12) in THF at −78°.—In a typical reaction, to 50 ml of dry THF in the flask under nitrogen was added 1.0 g (3.18 mmol) of the sulfonium salt. The slurry was stirred at −78° for 30 min, whereupon 2.37 ml (3.50 mmol) of a 1.48 N solution of *n*-butyllithium in hexane was added *via* syringe over a 4-min period. The reaction mixture gradually became a deep red-orange solution during the addition.

Quenching of the Allylide with Deuterioacetic Acid.—The ylide solution (from 3.18 mmol of the salt) was stirred at −78° for 30 min; 0.25 ml of deuterioacetic acid was then added to the solution. The red color immediately disappeared yielding a white slurry. The slurry was warmed to room temperature, and 0.25 ml of water was added. The reaction mixture was poured into 5 ml of methylene chloride, and ether was added to induce crystallization. The yield of white solid was 0.70 g (70%): nmr ($CDCl_3$) 4.80 (1 H, d, J = 6.0 Hz), 5.25–5.95 (3 H, m), 7.50–8.10 ppm (10 H, m). The nmr spectrum was scanned at 100 Mc also; however, no resonances attributable to the d_1-3-deuterio-1-propenylsulfonium salt **14** could be detected. The limit of detection was estimated to be 5%.

Diels–Alder Addition of Cyclopropene to Furan.—Cyclopropene was prepared by the method of Closs.[18] The effluent gases, generated using 2.65 g (0.035 mol) of allyl chloride and 1.36 g (0.035 mol) of sodium amide in 10 ml of mineral oil, were bubbled into a test tube containing 25 g of freshly distilled furan. The addition of the allyl chloride solution to the sodium amide slurry was carried out over a 30-min period. A slow stream of nitrogen was then passed through the apparatus for an additional 30 min.

The furan solution was carefully distilled (pot temperature 50°); the residue was examined by vpc[26] at 87°. Small, analytical injections revealed two components at 21 min and 50 min. Large-scale, preparative injections revealed another peak with a retention time of 32 min. The first product was identified as the exo Diels–Alder adduct **17**: ir 990, 953, 900, 858, 669 cm^{-1}; nmr 0.65–1.20 (3 H, m), 1.35–1.55 (1 H, m), 4.53 (2 H, br s), 6.40 ppm (2 H, t, J = 0.5 Hz). The nmr spectrum was identical with that reported by Srinivasan for one of his isomers.[14]

The second component was identified as the endo Diels–Alder adduct **16** contaminated with 2,4-cycloheptadienone (**18a**): ir 1660, 982, 910, 857, 690 cm^{-1}; nmr 0.60–0.72 (1 H, m), 0.90–1.05 (1 H, m), 1.60–1.85 (2 H, m), 4.75 (2 H, m), 5.93 ppm (2 H, t, J = 0.5 Hz). The nmr spectrum also showed broad resonances from contaminants at 2.2–2.7 and 5.9–6.7 ppm.

The third component was isolated both from the original reaction mixture and from a repassed sample of the endo adduct. This product was identified as a mixture of 2,4- and 3,5-cycloheptadienone: ir 1710, 1660, 1605, 1590, 1580, 1420, 1345, 1315, 1270, 1220, 1190, 1143, 1032, 986, 960, 905, 865, 685 cm^{-1} (the ir spectrum was identical with that reported for a mixture of the dienones[17]); nmr 2.2–2.7 (4 H, m), 5.9–6.7 ppm (4 H, m); mass spectrum m/e (% of base peak) 108 (25), 91 (10), 80 (60), 79 (100).

Reactions of 16 and 17 with Boron Fluoride Etherate.—The nmr of the endo adduct was recorded as usual. The nmr signals were identical with those mentioned above. Then 5 μl of boron fluoride etherate were added to the solution. The solution immediately turned oily and brown. The nmr spectrum exhibited resonances only at 2.2–2.7 and 5.9–6.7 ppm, characteristic of the cycloheptadienone mixture.

A similar reaction was run with the exo isomer. Addition of the boron fluoride etherate afforded a dark brown oily residue. The nmr spectrum revealed only resonances attributable to the exo isomer (*vide supra*), though these signals were significantly reduced in intensity relative to those obtained for the sample before addition of the boron fluoride etherate. However, after standing for 20 hr at room temperature, vpc analysis revealed three peaks. The retention times of the first two components agreed with those of the exo adduct and of the dienone mixture. In addition, a third peak was noted with a retention time somewhat longer than that of the dienones. Another nmr spectrum showed resonances attributable to the exo compound and to the dienones. In addition, there was a rather intense crude singlet at 7.33 ppm. Evidently the acid-catalyzed rearrangement of the exo isomer proceeds to the cycloheptadienones, but at a rate far slower than that of the endo compound. In addition, the exo adduct yields another, as yet unidentified, product.

Hydrogenation of 18a and 18b to Cycloheptanone.—The dienone mixture (3.0 mg, 2.78 × 10^{-5} mol) and 50 mg of 10% Pd/C were added to 5 ml of diethyl ether. The mixture was hydrogenated at room temperature at 1 atm for 1 hr. The reaction mixture was then filtered through Filter Cel and the ether

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[26] The analysis was performed on a 11 ft × 0.25 in. 20% SE-30 on Chromosorb W column.

carefully removed by distillation. Vpc analysis[26] at 120° revealed one product, identical in retention time and ir spectrum with a known sample of cycloheptanone.

Synthesis of Spiro-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene-8,1′-cyclopropane.—Cyclopropene (from 11.5 g, 0.15 mol of allyl chloride) was passed through a room-temperature trap containing 13.8 g (0.15 mol) of spiro[4.2]hepta-1,3-diene in 20 ml of pentane.

Upon completion of the reaction, the pentane solution was distilled at atmospheric pressure to remove the pentane. The residue was examined by vpc at 112°.[27] There were two prominent peaks: 10 min (spirodiene), 41 min (Diels–Alder adduct, 2.5%). The Diels–Alder adduct is a liquid (bp *ca.* 170°): ir 1620, 910, 900, 857, 714, 657 cm^{-1}; nmr 0.42 (4 H, s), 0.52 (2 H, m), 1.38 (2 H, m), 2.13 (2 H, m), 5.72 ppm (2 H, d of d, J = 2.0, 2.0 Hz); mass spectrum m/e (% of base peak) 132 (5), 131 (18), 118 (66), 104 (47), 91 (91), 73 (74), 51 (47), 39 (100).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.69; H, 9.17.

Control Reactions for Trapping Cyclopropene with Diene 19.—Cyclopropene, generated from 4.9 g (64 mmol) of allyl chloride and 2.5 g (64 mmol) of sodium amide, was passed into a solution consisting of 5.0 g (54 mmol) of diene **19** in 80 ml of THF at −78°. Work-up and vpc analysis[27] indicated 1.3 mmol of the Diels–Alder product **20**. A similar aliquot of cyclopropene was passed through a 0° pentane solution containing 14 g of freshly cracked cyclopentadiene. Vpc analysis showed that 3.4 mmol of Diels–Alder adduct **15** had been produced.

In another experiment, cyclopropene, generated from 2.65 g (35 mmol) of allyl chloride and 1.34 g (35 mmol) of sodium amide, was bubbled into a −78° solution of the allylide containing 1.0 g (11 mmol) of diene **19**. The ylide was generated from 0.30 g (0.96 mmol) of allyl salt **11** and 0.60 ml (0.97 mmol) of a 1.6 N solution of *tert*-butyllithium in pentane. Upon work-up, Diels–Alder adduct **20** was noted by vpc.

Thermal Decomposition of the Allylide.—The ylide solution (from 6.37 mmol of the salt and 6.4 mmol of *n*-butyllithium) was generated in a flask that led to two traps in series. The first trap, consisting of a gas dispersion tube in a test tube at 0°, contained 15 g of freshly cracked cyclopentadiene in 35 ml of pentane. The second trap, a similar apparatus at 0°, contained 3 g of bromine in 50 ml of carbon tetrachloride.

After the ylide solution had stirred at −78° for 30 min, the bath was removed to allow the reaction to warm to room temperature. The color of the solution gradually changed from red-orange to light yellow. The solution was stirred at room temperature for 30 min and then at 50° for an additional 30 min. The solution was cooled to room temperature, and 20 ml of water were added *via* syringe. The reaction was stirred for 5 min and then thoroughly extracted with ether. The ethereal extracts were dried (K_2CO_3), filtered, and distilled. Fractions were taken with the pot temperature at 50° and at 50° (20 mm). The atmospheric pressure fraction was examined by vpc at 90° on a 15 ft × $^3/_8$ in. column packed with 20% Carbowax on Chromosorb P. The chromatogram showed significant peaks at 4 min (ether), 6–7 min (hexane), and 23–25 min (THF). The aspirator distillate was similarly examined. Besides the peaks for solvent, there were peaks at 16 min (*n*-octane, 20%), and 38 min (benzene, 10%). Both products were identified by comparison of their vpc retention times and ir spectra with those of authentic samples. Toluene was used as internal standard.

The pot residue was analyzed by vpc[27] at 185°. Several peaks were prominent on the chromatogram: 4 min (allylbenzene, 0.5%), 6 min (di-*n*-butyl sulfide, 3.6%), 17 min (allyl phenyl sulfide, 0.50%), 27 min (*n*-butyl phenyl sulfide, 8%), 38 min (biphenyl, 2%), 111 min (diphenyl sulfide, 62%). All compounds were identified by comparison of their vpc retention times and ir spectra with those of authentic samples. Acenaphthene was used as internal standard.

The cyclopentadiene trap was distilled at low temperature, and the pot residue analyzed by vpc[27] at 82°. Using toluene as internal standard (retention time, 23 min), none of the Diels–Alder product from cyclopropene could be detected at the retention time for the compound (40 min).

The bromine trap was treated with aqueous sodium bisulfite and extracted with ether. The ethereal extracts were dried and distilled at low temperature. Vpc analysis of the residue showed peaks at 23 min (propylene bromide, 4.7%) and 36 min (anisole, internal standard).

Thermal Decomposition of the Allylide in the Presence of Diene 19.—A solution of the ylide was prepared as usual in −78° THF solution from 0.250 g (0.80 mmol) of the salt and 0.55 ml (8.8 mmol) of a 1.6 N solution of *n*-butyllithium in hexane. After the ylide had been stirred at −78° for 30 min, 1.0 g (11 mmol) of diene **19** was added to the solution. The mixture was stirred at −78° for an additional 30 min and then was allowed to slowly warm to room temperature. The mixture was quenched with water and ether extracted. The ethereal extracts were dried (K_2CO_3) and distilled (pot temperature 60°). The residue was examined by vpc; none of Diels–Alder adduct **20** could be detected.

Reaction of Allyldiphenylsulfonium Fluoroborate with Sodium Amide in Mineral Oil.—In a variation of Closs' synthesis of cyclopropene, to 6 ml of mineral oil in the flask under nitrogen was added 0.294 g (7.55 mmol) of sodium amide. The flask was heated to 70°, and 2.37 g (7.55 mmol) of the sulfonium salt was added over a 2.5-hr period *via* a solid addition funnel. The reaction mixture was heated at 70° for an additional 1.5 hr and then heated at 110° for 1.5 hr. The cyclopentadiene trap was distilled, and the residue analyzed by vpc. None of the Diels–Alder adduct could be detected.

Thermal Stability of the Allylide.—In a study of the thermal stability of the ylide, the ylide solution was generated as usual at −78° and then warmed to the desired temperature for the specified time. The concentration of the ylide was determined by quenching the reaction mixture, or an aliquot, with cyclohexanone.

In a typical run, the ylide solution (from 0.8 mmol of the salt) was stirred at −78° for 30 min. The reaction vessel was then immersed in a −40° bath (Dry Ice–chlorobenzene) for 1.5 hr. A 4-ml aliquot was removed *via* syringe and quenched in 6 ml of cyclohexanone at −20°. Then 0.150 g of cyclohexanone was added to the main vessel. Both reactions were stirred at −20° for 15 min, the baths removed, and both mixtures (now colorless) stirred at room temperature for 1 hr. Each reaction was worked up as usual and analyzed by vpc.[28] The yield of vinyl oxirane from the aliquot was 53.5%, from the main pot 54.6%.

Reaction of Allylide 12 with Anhydrous Cupric Sulfate.—The ylide solution (from 3.18 mmol of the salt) was generated in the usual apparatus, which was also fitted with a condenser which led to a cyclopentadiene trap.

After the ylide solution had stirred at −78° for 20 min, 2.5 g of diene **19** were added. Then 1.01 g (6.36 mmol) of anhydrous cupric sulfate were rapidly added to the ylide. The mixture turned from deep red to orange; after 1 hr, the mixture was a golden slurry. After 2.5 hr, the reaction had turned to a grayish-white slurry. The reaction was warmed to room temperature, heated to reflux for 1 hr, and cooled to 0°. Hydrolysis with 3 ml of water gave a blue solution and precipitate. The mixture was filtered and distilled (pot temperature 70°). The residue was examined by vpc[27] at 112°. None of the cyclopropene adduct could be detected. Vpc analysis of the cyclopentadiene trap revealed no bicyclooctene. Repetition of the experiment utilizing zinc iodide gave similar results.

Photolysis of Allylide 12 in the Presence of Diene 19.—A thin, flexible rubber collar was placed between the standard taper joints of the photolysis flask and the quartz insert. To the flask under nitrogen were added 80 ml of dry THF and 0.60 g (1.91 mmol) of the salt. The slurry was stirred at −78° for 15 min whereupon 1.2 ml (1.94 mmol) of a 1.6 N solution of *tert*-butyllithium in pentane was added dropwise to the slurry. The golden-yellow solution was stirred for an additional 15 min; then 6.0 g (66 mmol) of diene **19** was added to the ylide solution. Cold (−78°) methanol was circulated through the jacket of the quartz insert. The cold insert was lowered into the ylide solution by carefully slipping the rubber collar over the male joint of the insert. With the insert in the normal position, the ylide solution filled approximately three-fourths of the photolysis flask.

The bright yellow solution was photolyzed at −78° for 1 hr through a Pyrex filter with a 450-W Hanovia mercury vapor lamp. Upon completion of the photolysis, the cooling was discontinued, and the mixture was allowed to warm to room temperature. After being stirred at room temperature for 3 hr, the

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(27) The analysis was performed on a 8 ft × 0.25 in. 20% Dow Corning silicone oil 710 on Chromosorb P column.

(28) The analysis was performed on a 8 ft × 0.25 in. 20% SE-30 on Chromosorb W column.

mixture was hydrolyzed and ether extracted. The combined ethereal layers were dried (K_2CO_3) and distilled at low temperature. Vpc analysis at 135° revealed the Diels–Alder adduct **20** in 15% yield; diphenyl sulfide was also present in 29% yield. Acenaphthene was used as internal standard. On the same column at 200° another peak emerged at 50 min (15% of the reaction mixture). Attempted large-scale separation of this last component by high temperature vpc resulted in considerable decomposition. Consequently, the mixture was distilled at 40° (15 mm), the distillate collecting in a cold receiver. It was found that the components of the pot residue could be separated by preparative thick layer chromatography on plates of 1.0 mm PF 254 silica gel in multiple developments with hexane: R_f (compound) 0.27 (sulfide **23**), 0.39 (sulfide **21**), 0.54 (sulfide **22**), 0.59 (diphenyl sulfide), 0.85 (acenaphthene). The three photoproducts were isolated in a ratio of **23**:**21**:**22** of 1:10:3.

The structures were determined by their spectral properties. Compound **23** gave the following: ir 1570, 1470, 1022, 956, 688 cm^{-1}; nmr 3.60 (2 H, four-line pattern of intensity 2:1:1:2, consisting of two apparent doublets at 3.58 and 3.63 ppm, J = 1.5 Hz), 5.82–6.33 (2 H, m), 7.23 ppm (10 H, br s); uv λ_{max} 252 nm (ϵ 5100); mass spectrum m/e (% of base peak) 266 (23), 149 (16), 118 (38), 117 (43), 116 (43), 115 (100), 110 (24), 109 (32), 90 (64) (Calcd for $C_{15}H_{14}S$: 226.081. Found: 226.081 ± 0.002).

Compound **21** gave the following: ir 1620, 1525, 1475, 1430, 1024, 915, 693 cm^{-1}; nmr 4.68 (1 H, br d, J = 7.5 Hz), 4.83 and 5.02 (2 H, two overlapping d, J = 9.0 and 17.0 Hz), 5.80–6.45 (1 H, m), 7.23 ppm (10 H, br s); uv λ_{max} 252 nm (ϵ 4240); mass spectrum m/e (% of base peak), 226 (5), 117 (100), 115 (31), 109 (10), 91 (16) (Calcd for $C_{15}H_{14}S$: 226.081. Found: 226.081 ± 0.003).

Compound **22** gave the following: ir 1680, 1480, 1024, 686 cm^{-1}; 3.43 and 3.57 (2 H, ovelapping d, J = 6.5 and 6.0 Hz), 5.95–6.42 (2 H, m), 7.22 ppm (10 H, m); uv λ_{max} nm 248 (ϵ 6500), 264 (6700); mass spectrum m/e 226 (20), 131 (47), 117 (87), 115 (40), 110 (65), 109 (35), 103 (41), 91 (77), 77 (82), 65 (42), 57 (100), 51 (72) (Calcd for $C_{15}H_{14}S$: 226.081. Found: 226.081 ± 0.002).

Reaction of Cyclohexanone with the Allylide. Synthesis of 2-Vinyl- and 2-*n*-Propyl-1-oxaspiro[5.2]octane (26a and 26b).—The ylide solution (from 0.8 mmol of the salt and 0.81 mmol of *n*-butyllithium) was stirred at −78° for 30 min. Then 0.078 g (0.8 mmol) of cyclohexanone was added to the solution. The reaction mixture was stirred at −78° for 30 min. The cooling bath was removed, and the solution was allowed to warm to room temperature. The red color gradually changed to light yellow. After stirring at room temperature for 45 min, 5 ml of water was added to the solution, and the mixture was thoroughly extracted with ether. The organic extracts were dried (K_2CO_3) and filtered, and the volume was reduced by low-temperature distillation. The residue was analyzed by vpc[28] at 120°. Several peaks were prominent on the chromatogram: 6.0 min (cyclohexanone), 10.0 min (cycloheptanone, internal standard), 14.0 min (compound **26a**, 52–56%), 31.5 min (compound **26b**, 5–7%). At higher temperatures, *n*-butyl phenyl sulfide, biphenyl, and diphenyl sulfide could be detected also. The two oxiranes were identified by analysis of their spectral data. 2-Vinyl-1-oxaspiro[5.2]octane (**26a**) gave the following: ir 1630, 995, 923, 905, 680 cm^{-1}; nmr ($CDCl_3$) 1.57 (10 H, br s), 3.17 (1 H, d, J = 6.0 Hz), 5.15–6.16 ppm (3 H, m).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.20; H, 10.15.

2-*n*-Propyl-1-oxaspiro[5.2]octane gave the following: 1200, 915 cm^{-1}; nmr ($CDCl_3$) 0.99 (3 H, t, J = 6.0 Hz), 1.57 (14 H, m), 2.68 ppm (1 H, t, J = 5.5 Hz).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.66; H, 11.60.

Generation of Allylide 12 Using *tert*-Butyllithium. Synthesis of Oxirane 26a.—A solution of the allylide was prepared at −78° in 5 ml of THF using 0.100 g (0.319 mmol) of the salt and 0.200 ml (0.325 mmol) of a 1.6 *N* solution of *tert*-butyllithium in pentane. After the golden yellow solution had stirred for 15 min, 0.05 g (0.5 mmol) of cyclohexanone was added. The mixture was stirred for an additional 15 min at −78° and was then allowed to warm to room temperature. The reaction was worked up as usual and analyzed by vpc[26] at 135°. There were four prominent peaks in the chromatogram: 9 min (cyclohexanone), 16 min (cycloheptanone, internal standard), 22 min (oxirane **26a**, 77% yield), and at 200°, 48 min (diphenyl sulfide, 99% yield).

Synthesis of *cis*- and *trans*-5-*tert*-Butyl-2-vinyl-1-oxaspiro[5.2]octane.—A solution of the allylide was prepared in 25 ml of −78° THF using 0.500 g (1.59 mmol) of the salt and 0.94 ml (1.75 mmol) of a 1.94 *N* solution of *n*-butyllithium in hexane. The ylide solution was stirred at −78° for 25 min whereupon a solution of 0.248 g (1.6 mmol) of 4-*tert*-butylcyclohexanone in 2 ml of dry THF was added to the ylide. The cooling bath was removed and the reaction was allowed to warm to room temperature. After the usual work-up, vpc analysis[26] at 165° revealed three main components: 6 min (4-*tert*-butylcyclohexanone), 18 min and 20 min (oxiranes **24c** and **25c**, in a ratio of 1:4, respectively); at 200°, 32 min (diphenyl sulfide). Attempted large-scale isolation of the isomers by vpc resulted in unacceptable decomposition. The oxiranes were isolated with negligible decomposition by thick layer chromatography on alumina, R_f (compound): 0.07 (4-*tert*-butylcyclohexanone), 0.27 (**24c** and **25c** mixture, 151 mg, 49% yield), 0.55 (diphenyl sulfide).

The mixture of the oxiranes was identified by its spectra: ir 1640, 1360, 993, 980, 923, 893, 694, 684 cm^{-1}; nmr 0.87 and 0.90 (9 H, two s), 0.90–2.10 (9 H, m), 3.03 (1 H, d, J = 5.5 Hz), 5.10–5.91 ppm (3 H, m).

Conversion of the Epoxide Mixture (24c and 25c) to Saturated Alcohols (27b and 28b).—To the flask under nitrogen were added 10 ml of diethyl ether, 6 mg (0.23 mmol) of lithium aluminum hydride, and 40 mg (0.206 mmol) of the oxirane mixture. The reaction was refluxed for 2 hr, cooled to room temperature, and carefully hydrolyzed with 4 ml of water. The layers were separated, and the aqueous layer was washed with four 20-ml portions of ether. The combined organic phases were reduced in volume *in vacuo* and analyzed by vpc[29] at 140°. Two peaks were noted at 26 min and 28 min in a ratio of 4.3:1.0, respectively. The ir spectrum of each of the components was similar: 3650, 3500, 1625, 1355, 915, 872 cm^{-1}.

A solution of 40 mg (0.205 mmol) of the allylic alcohol mixture in 5 ml of ether was prepared. The mixture was hydrogenated at room temperature and 1 atm over 10% Pd/C for 45 min. The mixture was then filtered through Filter Cel and the filtrate concentrated *in vacuo*. Vpc analysis[29] of the mixture at 140° showed two components at 22 min (**28b**) and 24 min (**27b**) in a ratio of 3.8:1.0, respectively. The ir spectrum of the major isomer was identical with that of the major product from the addition of *n*-propylmagnesium bromide to 4-*tert*-butylcyclohexanone. The ir of the minor isomer was identical with that of the minor product of the Grignard reaction (*vide infra*).

Preparation of *cis*- and *trans*-1-*n*-Propyl-4-*tert*-butylcyclohexanol (27b and 28b).—The reaction was carried out in a manner analogous to that used for the addition of methylmagnesium bromide to 4-*tert*-butylcyclohexanone;[30] the results are analogous. Vpc analysis[29] at 130° revealed two components at 32 min (the trans alcohol **28b**) and 34 min (the cis alcohol **27b**) in a ratio of 4.4:1.0, respectively.

The ir of **28b** showed absorptions at 3630, 3490, 1364, 958, 940, 885 cm^{-1}. The ir of **27b** showed absorptions at 3610, 3500, 1360, 1020, 980, 854 cm^{-1}.

Anal. Calcd for $C_{13}H_{26}O$: C, 78.79; H, 13.13. Found for **27b**: C, 78.51; H, 13.33. Found for **28b**: C, 78.89; H, 13.19.

Reaction of the Allylide with Chalcone. Synthesis of 1-Benzoyl-2-phenyl-3-vinylcyclopropane (29a).—The ylide solution (from 3.18 mmol of the salt) was stirred at −78° for 30 min. Then 0.662 g (3.18 mmol) of chalcone, dissolved in 5 ml of THF, was rapidly added *via* syringe to the red ylide solution. The color immediately changed to yellow. After stirring at −78° for 30 min, the solution was warmed to room temperature and stirred for 1 hr. Water (10 ml) was added, and the mixture was extracted with ether. The ethereal extracts were dried (K_2CO_3), filtered, and concentrated *in vacuo* to yield 1.40 g of a light yellow oil. It was found that the components of the residue could be separated by preparative thick layer chromatography on plates of 1.0 mm PF 254 silica gel in benzene: R_f (compound) 0.32 (chalcone), 0.50 [1-benzoyl-2-phenyl-3-vinylcyclopropane (**27a**)], 0.78 (diphenyl sulfide). The cyclopropyl product was dissolved away from the silica gel with chloroform; the solution was reduced *in vacuo* to yield a partly solidified yellow oil. The oil was then solidified by freezing in Dry Ice. The material was crushed and washed with cold cyclohexane to yield 0.062 g (53%) of a white solid (mp 67–71°): ir 1670, 1625, 905, 720, 695 cm^{-1};

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(29) The analysis was performed on a 8 ft × 0.25 in. 20% DEGS on Chromosorb P column.

(30) W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962).

nmr ($CDCl_3$) 2.4–2.9 (1.1 H, m), 3.19 (1.9 H, d further split, J = 6.0 Hz), 5.12 (3 H, m), 7.10–8.10 ppm (10 H, m including a singlet at 7.18); uv λ_{max} 250 nm (ϵ 18,500).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.12; H, 6.47.

The 100-Mc nmr of the compound showed a high degree of complexity which implied that the solid was a mixture of isomers. Attempts to further separate the material failed.

Oxidation of 29a with Osmium Tetroxide and Sodium Metaperiodate to 1-Benzoyl-2-phenyl-3-carboxaldehyde cyclopropane.—To 20 ml of 75% aqueous dioxane in the flask under nitrogen was added 0.495 g (2.0 mmol) of the vinyl cyclopropane mixture. A trace amount (5 mg) of osmium tetroxide was added to the stirring reaction at room temperature; the mixture immediately turned a deep black. Over a 30-min period, 0.856 g (4.0 mmol) of powdered sodium metaperiodate was added to the reaction. The yellow-tan slurry was stirred for an additional 1.5 hr. The mixture was then extracted with ether, and the ethereal solution dried ($MgSO_4$). The volume of the solution was reduced *in vacuo* to yield 0.573 g of a black oil: nmr ($CDCl_3$) 2.57–3.08 (1.1 H, m), 3.46 (1.3 H, m), 3.95 (0.6 H, m), 7.10–8.20 (10 H, m, including singlet at 7.26), 9.20 (0.72 H, d, J = 5.0 Hz), 9.57 ppm (0.28 H, d, J = 6.0 Hz). The ratio of the aldehyde proton resonances was taken as the ratio of the two isomers present (2.5:1.0). The black oil was separated by preparative thick layer chromatography on 1.5 mm PF 254 silica gel with two developments with benzene. The spot with R_f 0.33 was collected. This aldehyde mixture was rechromatographed on a similar plate with four developments with benzene. The aldehyde isomers separated, the minor isomer at R_f 0.38, the major at R_f 0.50.

Isolation of the major isomer afforded a yellow oil which solidified upon freezing in Dry Ice. The yellow solid was crushed and washed with cold cyclohexane to yield a white solid (mp 62–63°): ir 2830, 2740, 1710, 1660, 725, 695 cm^{-1}; nmr ($CDCl_3$) 2.93 (1 H, quintuplet, J = 5.0 Hz), 3.45 (1 H, d of d, J = 10.0, 6.0 Hz), 3.98 (1 H, d of d, J = 6.0, 4.5 Hz), 7.20–8.20 (10 H, m, including singlet at 7.47), 9.20 ppm (1 H, d, J = 5.0 Hz); uv λ_{max} 257 nm (ϵ 18,400).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.78. Found: C, 81.29; H, 5.78.

The minor isomer was isolated in a similar manner (however, all attempts to solidify the compound failed): ir 2830, 2740, 1710, 1660, 728, 693 cm^{-1}; nmr ($CDCl_3$) 2.69 (1 H, m), 3.53 (2 H, m), 7.15–8.10 (10 H, m including singlet at 7.23), 9.57 ppm (1 H, d, J = 6.0 Hz). In benzene solvent the multiplet at 2.69 ppm resolved into a six-line pattern at 2.42 (1 H, d of t, J = 9.0, 6.0 Hz); the multiplet at 3.53 ppm resolved into two 1 H patterns at 2.90 (1 H, d of d, J = 9.0, 6.0 Hz), 3.28 (1 H, d of d, J = 6.0, 6.0 Hz). A 100-Mc nmr spectrum (CCl_4) revealed the same pattern as the 60-Mc benzene spectrum. The aldehyde proton appeared as a doublet at 9.60 ppm (J = 6.0 Hz). The uv spectrum gave λ_{max} 250 nm (ϵ 17,900).

Oxidation of 1-Benzoyl-2-phenyl-3-vinylcyclopropane with Osmium Tetroxide–Sodium Metaperiodate Followed by Oxidation with Silver Nitrate–Sodium Hydroxide.—To 10 ml of 75% aqueous dioxane in the flask under nitrogen were added 0.285 g (1.15 mmol) of the olefin and 3 mg of osmium tetroxide. The black solution was stirred at room temperature, and 0.492 g (2.30 mmol) of sodium metaperiodate was added over a 30-min period. The resultant tan slurry was stirred for an additional 1.5 hr to yield a heavy white slurry. The mixture was extracted with ether, and the ethereal extracts were dried ($MgSO_4$). The extracts were filtered and concentrated *in vacuo* to a dark brown oil.

To a 5:2 (v/v) solution of ethanol–water in the flask under nitrogen was added the brown oxidation residue and 0.205 g (1.20 mmol) of silver nitrate. A solution of 0.205 g (5.13 mmol) of sodium hydroxide in 10 ml of water was added to the stirring mixture to yield a gray solution and black precipitate. After stirring for 3 hr, the green solution was filtered and extracted with ether. The aqueous phase was neutralized and extracted with ether. The neutral product yielded 0.090 g (31%) of a yellow oil, an aldehyde mixture. The acidic product was 0.124 g (41%) of a gray oil, a carboxylic acid mixture.

Analysis of the aldehyde mixture indicated that it was composed of three isomers: ir 2850, 2730, 1710, 1670, 695, 660 cm^{-1}; nmr ($CDCl_3$) 2.57–3.10 (1 H, m), 3.45 (1.5 H, m), 3.97 (0.5 H, d of d, J = 6.0, 4.5 Hz), 7.10–8.20 (10 H, m including singlets at 7.13, 7.25, and 7.28), 9.22 (0.6 H, d, J = 5.0 Hz), 9.58 (0.25 H, d, J = 6.0 Hz), 9.77 ppm (0.15 H, d, J = 2.5 Hz). Attempts to cleanly separated the three isomers failed. Apparently the conditions of the silver nitrate–sodium hydroxide oxidation had caused isomerization of the two aldehydes previously isolated (*vide supra*).

Analysis of the acid mixture showed that it, too, was a mixture of isomers: ir 3600–2500, 1670, 1705, 873, 726, 710, 694 cm^{-1}; nmr ($CDCl_3$) 2.81 (0.7 H, d of d, J = 9.0, 5.0 Hz), 3.32 (1.5 H, m), 3.82 (0.7 H, d of d, J = 6.0, 5.5 Hz), 7.10–8.20 (10 H, m including singlets at 7.12 and 7.25), 10.85 ppm (1 H, br s). No attempt was made to separate the isomers. A diazomethane solution was added dropwise to a solution of 0.043 g (0.162 mmol) of the acid mixture in 70 ml of ether until the yellow color persisted for 10 min. The yellow color was discharged by addition of a few drops of glacial acetic acid. The ether solution was extracted with aqueous sodium bicarbonate and dried (K_2CO_3). Concentration yielded 0.042 g (92%) of brown oil: ir 1725, 1670, 874, 694 cm^{-1}; nmr ($CDCl_3$) 2.84 (0.75 H, d of d, J = 10.0, 5.0 Hz), 3.22 (1.1 H, m), 3.72 (4.1 H, m, including singlets at 3.53 and 3.75), 7.10–8.20 ppm (10 H, m, including singlets at 7.14 and 7.27). Attempts to separate the esters by preparative thick layer chromatography failed to yield the isomers cleanly separated. However, all the spectral data for the ester mixture were identical with those of a sample of an ester mixture prepared in an independent route in these laboratories.[7]

Attempted Alkylation of Allylide 12 with Methyl Iodide.—A solution of the ylide was generated as usual from 1.00 g (3.19 mmol) of the salt and 2.2 ml (3.50 mmol) of a 1.6 N solution of n-butyllithium in hexane. The ylide was stirred at −78° for 30 min whereupon 0.500 g (3.50 mmol) of methyl iodide were added to the reaction *via* syringe. No color change was noted, the cooling bath was removed, and the reaction was allowed to warm to room temperature. The color of the solution changed from red to light yellow but no white precipitate appeared. The volume of the solution was reduced *in vacuo* to yield an orange oil. Examination of the oil revealed the absence of any methylated salt.

Attempted Alkylation of Allylide 12 with Dimethyl Sulfate.—The reaction was run in a manner similar to the methyl iodide reaction above, substituting dimethyl sulfate for the iodide. Again, no sulfonium salt could be isolated from the reaction.

Registry No.—*endo*-**16**, 27557-50-2; **20**, 27557-61-5; **21**, 18740-08-4; *cis*-**22**, 27557-51-3; *trans*-**22**, 27557-52-4; **23**, 10276-14-9; **24c**, 27557-53-5; **25c**, 27557-54-6; **26a**, 27561-18-8; **26b**, 22959-22-4; **27b**, 27557-55-7; **28b**, 27557-56-8; **29a**, 27557-57-9; **29b**, 27557-62-6; **30a**, 27557-58-0; **30b**, 27557-63-7; allyldimethylsulfonium bromide, 3084-75-1; allyldimethylsulfonium fluoroborate, 27557-59-1; γ,γ-dimethylallyldimethylsulfonium fluoroborate, 27557-60-4; cinnamyldimethylsulfonium bromide, 23531-42-2; 4-methylthio-3-phenyl-1-butene, 20025-33-6; allyldiphenylsulfonium fluoroborate, 27617-88-5.

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