Electrophilic Addition Reactions of Alkenylidenecyclopropanes. Formation of Highly Substituted, Nonplanar Butadienes[1]

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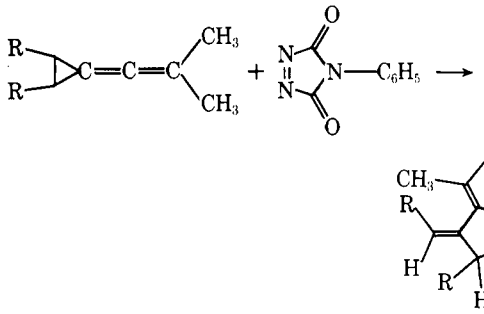
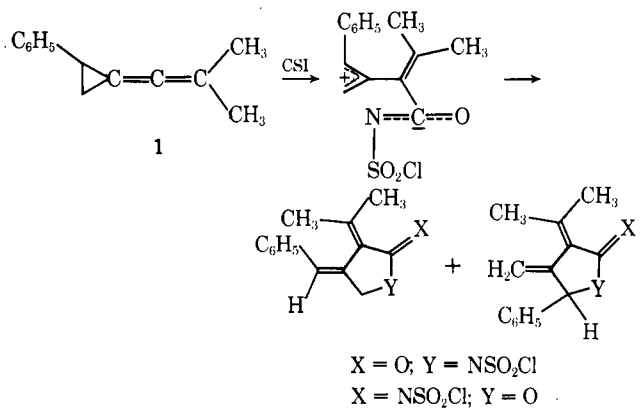
The reactions of 2-phenyl- (1) and 2,2,3,3-tetramethylisobutenylidenecyclopropane (2) with selected electrophilic reagents has been investigated. Electrophilic attack by proton, acetoxymercuri cation, and benzenesulfenyl cation occurs by highly selective attack on the C_1–C_4 (exocyclic) double bond leading to ring-opened products. Some attack on the three-membered ring of 1 occurs during acetoxymercuration, while benzenesulfenyl chloride undergoes some attack on the C_4–C_5 double bond. The ring-opened products derived from 1 are highly substituted 1,3-butadienes which must exist in nonplanar conformations separated by high energy barriers as evidenced by the appearance of the diastereotopic methylene hydrogens of **21** as AX doublets at 30°. The nature of the group interactions in **21** and the isomeric **20** in the transition state for enantiomerization of the diene is discussed. The acid-catalyzed and possible thermal rearrangements and isomerizations of these 1,3-butadienes have also been investigated. In contrast to the preference for electrophilic attack on the C_1–C_4 double bond of 1, electrophilic attack by proton and benzenesulfenyl cation occurs exclusively on the C_4–C_5 double bond of 2, while acetoxymercuration results in attack only on the C_1–C_4 double bond and the three-membered ring. The difference in position of electrophilic attack between 1 and 2 is discussed in terms of functional group interactions in transition states and intermediates, and of the nature of the electrophilic species.

Previous studies in our laboratories on the chemical properties of alkenylidenecyclopropanes have been focused in the area of cycloaddition reactions. Although alkenylidenecyclopropanes undergo cycloaddition with 4-phenyl-1,2,4-triazoline-3,5-dione only across the methylenecyclopropane system[2] with increased reactivity with increasing methyl substitution on the ring,[3] cycloaddition reactions

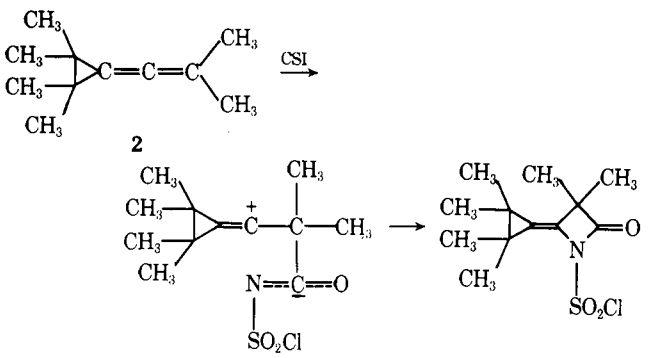


with chlorosulfonyl isocyanate (CSI) do not always display the same selectivity.[4] 2-Phenylisobutenylidenecyclopropane (1) reacts with CSI via electrophilic attack at the p orbital on C_4 of the C_1–C_4 double bond to produce a dipolar intermediate which collapses to products having structures similar to those derived with PTAD.[4] In contrast, 2,2,3,3-tetramethylisobutenylidenecyclopropane (2) undergoes attack at C_5 ultimately leading to the formation of a β-lactam derivative.[4a]

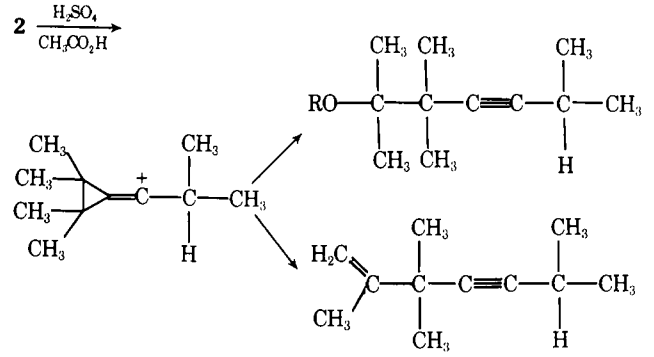


X = O; Y = NSO_2Cl

X = NSO_2Cl; Y = O



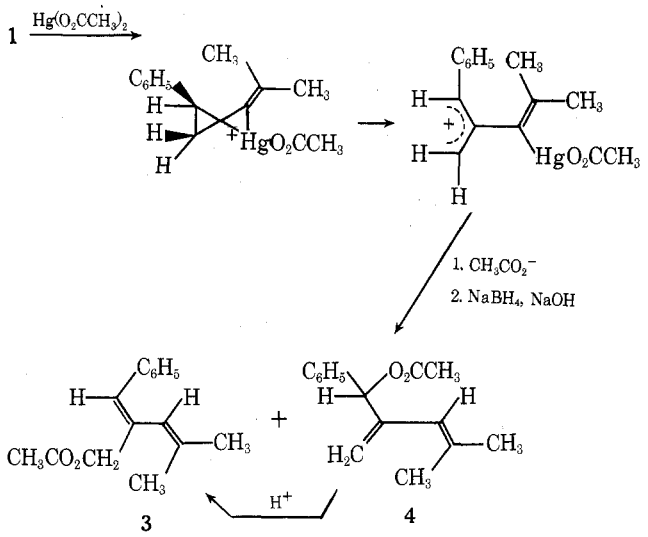
The dramatic difference in mode of reaction of 1 and 2 with CSI has prompted an investigation of the reactions of alkenylidenecyclopropanes with a variety of electrophilic species. The only previous reports of reactions of alkenylidenecyclopropanes with electrophilic reagents involve epoxidation[5] and protonation[5,6] of 2; reactions which involve electrophilic attack on the C_4–C_5 double bond, for example[5]



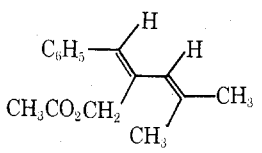
Results and Discussion

Solvomercuration. Acetoxymercuration of 1. Acetoxymercuration of 1 followed by reductive demercuration using a great excess of sodium borohydride[7] produces a complex mixture of the monomeric acetates 3 and 4 (60:40 ratio), dimeric diacetates, and bis(acetoxyalkyl)mercury compounds.[7] Acetates 3 and 4 were isolated in a pure state by chromatographic techniques and their structures were readily assigned from ir, NMR, and mass spectral data.

The stereochemistry of 3 has been assigned on the basis of mechanistic arguments. Disrotatory ring opening of an intermediate spiromercurinium ion (or possible cyclopropyl cation as a transition state) is expected to occur with outward rotation of the phenyl group, i.e., in the least sterically congested manner, to produce an allylic cation which then reacts with acetate to produce 3 and 4. Efforts to more



rigorously define the stereochemistry of 3 have met with failure. Attempted cycloaddition of 3 with maleic anhydride at 100° for 14 days resulted in no reaction. Various efforts to isomerize 3 to stereoisomer 5 for comparison of differences in chemical shifts of the isopropylidene methyls in 3 and 5 (arising from long-range shielding effects of the

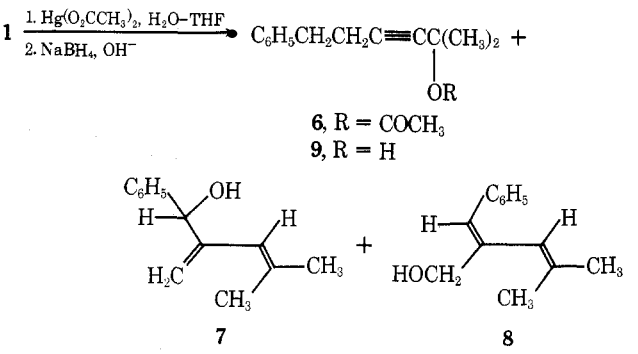


5

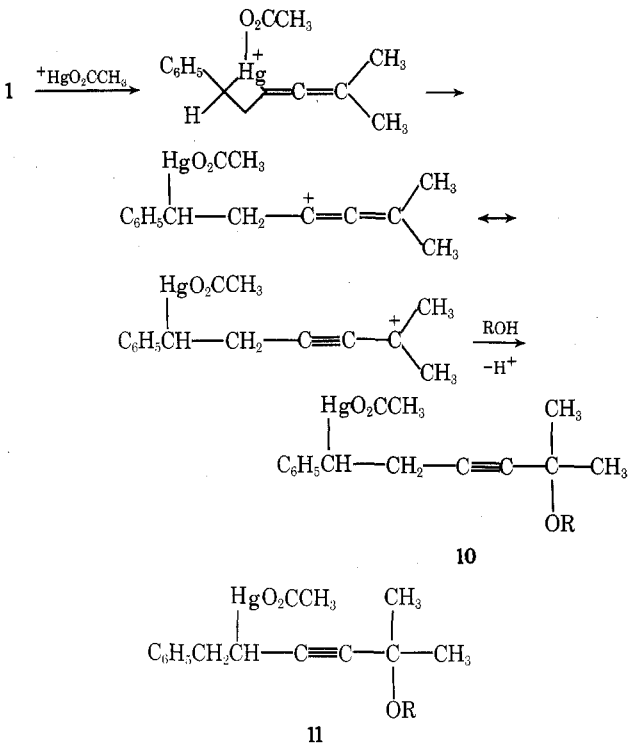
aromatic ring)[8] have failed. Attempted iodine-catalyzed thermal isomerization at 100° failed. Heating a benzene solution of 3 in a sealed tube at 300° for 5 days in an attempt to effect a reversible [3,3] sigmatropic rearrangement equilibrium[9] between 3 and 4 and hopefully 5 resulted only in partial polymerization. In the presence of strong protic acids, however, 4 cleanly rearranges to 3 (vide ante); no peaks are present in the NMR spectrum of the rearranged product which would suggest any formation of 5. The inability to thermally or chemically isomerize 3 to 5 and the acid-catalyzed rearrangement of 4 to 3 suggest that 3 is considerably more thermodynamically stable than 5. Inspection of models of various conformations of 3 and 5 suggests that 3 can in fact exist in a twisted conformation which possesses less steric strain than does any conformation of 5.

The three dimeric diacetates isolated from the acetoxymercuration of 1 (see Experimental Section for characterization and proposed structures) are formed by combination of the free radicals formed during the reductive demercuration.[9] NMR and mass spectral data indicate that the bis(acetoxyalkyl)mercury compounds contain acetoxyalkyl groups corresponding to 3 and 4 (see Experimental Section for characterization and partial structures).

Hydroxymercuration of 1. In addition to the formation of alcohols 7 and 8, which correspond to the acetates 3 and 4 formed in acetoxymercuration of 1, hydroxymercuration of 1 in 50% aqueous tetrahydrofuran also results in the formation of the acetylenic alcohol 9 (small amounts of ace-



tates 3, 4, and 6 are also formed). The acetate 6 and alcohol 9 must be formed by initial attack by acetoxymercuri cation on one of the ring bonds, either as shown to produce 10 or alternatively on the $-CH_2-C=$ bond to give 11, both of which would be reduced to 6 and 9. Attack by a mercuri

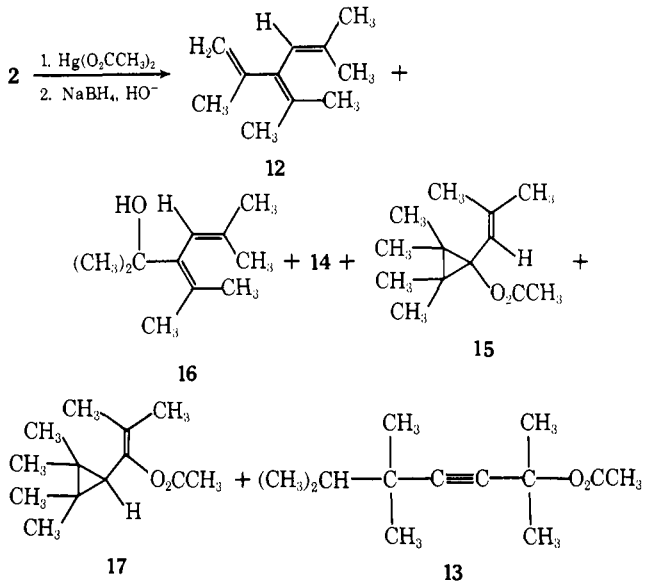


cation on a ring bond of a substituted cyclopropane has been observed previously by DePuy and co-workers[11] and in our laboratories with a bisalkylidenecyclopropane.[12] In aqueous THF electrophilic attack on the ring bond(s) of 1 accounts for 25% of the reactivity of 1, whereas in acetic acid no attack on the ring bonds is observed. We feel that this change in mode of reaction is primarily due to differences in the dielectric constants of the two solvent systems which affects the stabilization afforded transition states and/or intermediates, and not to changes in the nature of the electrophilic species.

Acetoxymercuration of 2. Acetoxymercuration–demercuration of 2 produces a complex mixture from which the five most abundant components were separated by preparative GLC. Identification of the two major components (12 and 16) has been achieved from ir, NMR, and mass spectral data, while the structures proposed for the minor components (13, 15, and 17) are based solely on proton Fourier transform NMR spectra. The fraction containing 13 also contained ~30% of another compound (14) which we have not been able to identify. The ratio of the products 12:16:13:14:15:17 is approximately 26:100:15:10:5:5.

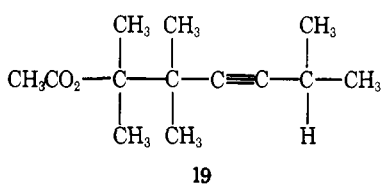
The triene 12 was easily identifiable by its characteristic NMR spectrum, which contains three vinyl hydrogen mul-

tiplets and five long-range coupled methyl resonances. Alcohol **16**, which is structurally identical with triene **12**, was similarly identified by its NMR spectrum, which showed one vinyl proton, four long-range coupled methyl doublets, a six-proton singlet, and an exchangeable OH resonance. The acetate of **16** must have been the primary product formed in the acetoxymercuration of **2** and must have undergone hydrolysis, or reduction, under the basic reductive demercuration conditions.



The structures of the cyclopropane ring containing products **15** and **17** are based solely on their FT spectra. The spectrum of acetate **15** contains a single vinyl proton resonance at δ 5.46 and two long-range coupled methyl doublets characteristic of a $-CH=C(CH_3)_2$ group. The methyl groups attached to the three-membered ring appear at high field as sharp singlets at δ 0.90 and 0.98, with the acetate methyl appearing at δ 1.91. In the NMR spectrum of acetate **17**, the low-field vinyl methyl groups appear as sharp singlets along with a single proton singlet. Also present are sharp, high-field methyl singlets at δ 1.04 and 1.21 for the ring methyls.

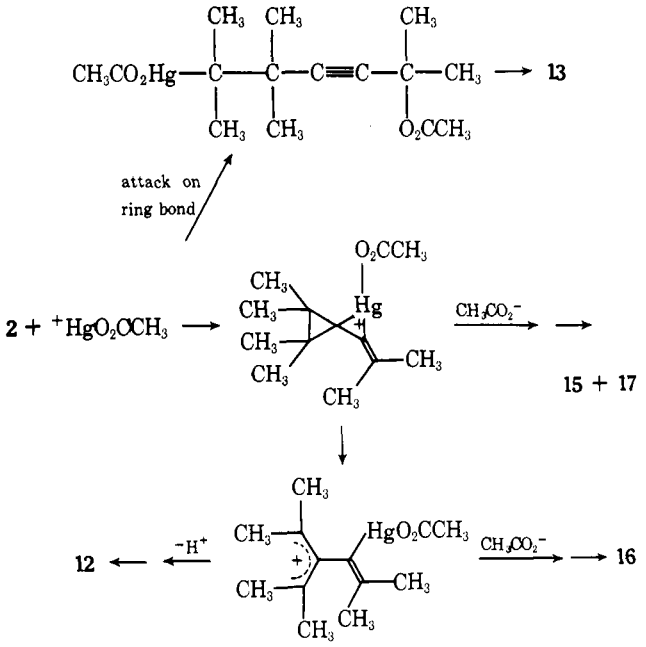
The structure of **13** is assigned on the basis of its NMR spectrum and by comparison of its spectral characteristics with those of **19**, which is the product formed in the acid-



19

catalyzed acetolysis of **2** (vide infra).[5] The isopropyl hydrogen of **13** appears as a multiplet at δ 1.40 characteristic of an isopropyl group attached to a saturated carbon atom. In contrast, the isopropyl hydrogen of **19** is deshielded by the triple bond and appears at δ 2.48. The isopropyl methyl doublet of **13** similarly appears at higher field than the isopropyl doublet of **19**.

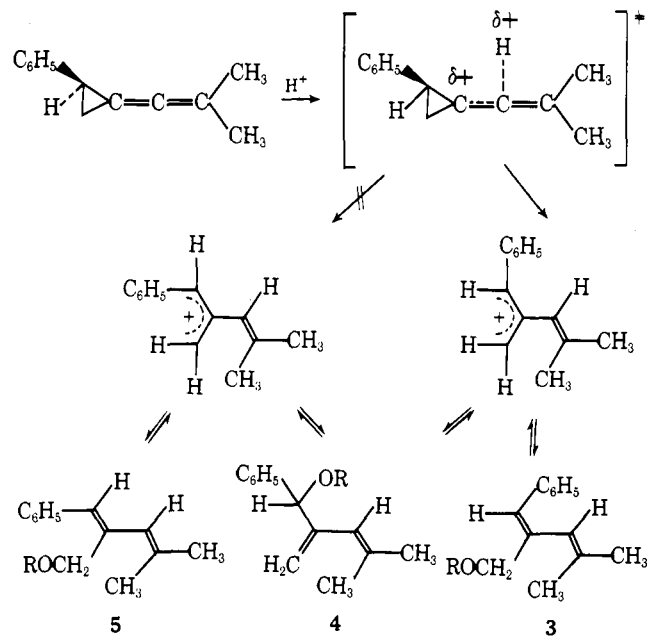
The formation of **12**, **16**, **15**, and **17** occurs via initial electrophilic attack on the C_1–C_4 double bond as illustrated in the following scheme. The formation of **13** must occur by attack on the three-membered ring as illustrated for the hydroxymercuration of **1**. No structures were isolated and characterized which would be formed via electropholic attack on the C_4–C_5 double bond (e.g., **18** and **19**).[13] This behavior is in contrast to that observed in the acid-catalyzed



acetolysis of **2**, which proceeds exclusively by attack of proton at C_5 (vide infra).

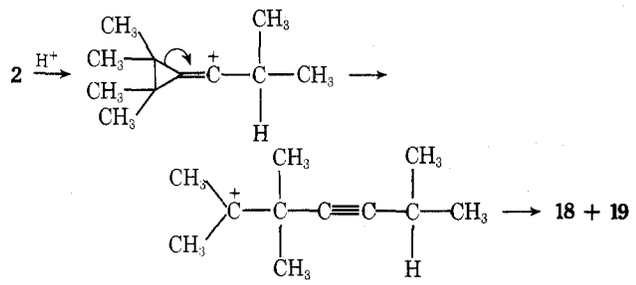
Acetolysis. Acetolysis of 1. **1** reacts very slowly with acetic acid at 115° to produce a 35:65 mixture of **3** and **4**. In order to avoid complications arising from thermal rearrangement of **1** at temperatures >100°, as well as polymerization, catalysis of the acetolysis by *p*-toluenesulfonic (pTS) acid was investigated. In the presence of catalytic quantities of pTS **1** reacts slowly at 70° to produce *only* **3**! Heating a sample of pure **4** in acetic acid in the presence of pTS at 105° results in quantitative rearrangement to **3**. Thus, **4** appears to be the kinetically favored product in the acetolysis of **1**, but **3** is the thermodynamically favored product.[14]

The exclusive rearrangement of **4** to **3**, and not to any extent to the stereoisomer **5**, at first appeared unusual. Although the stereochemistry in **3** is that expected in the product directly derived in the acetolysis of **1**, such stereochemical constraints are not present in the acid-catalyzed rearrangement; i.e., different rotomers of **4** can give rise to allylic cations of differing stereochemistry which should then react to give **3** and **5**, respectively. Inspection of mo-



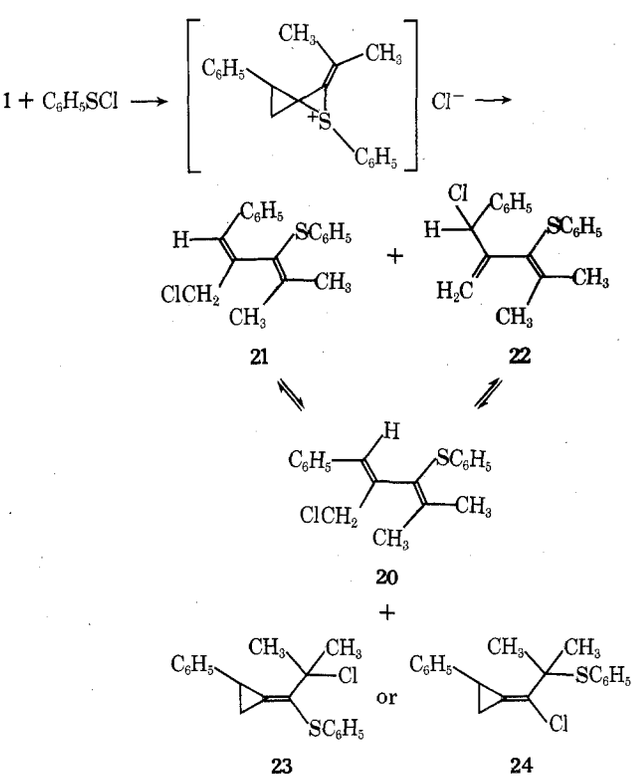
lecular models of **3** and **5** indicate that **5** is more sterically conjested than is **3** and, thus, should be less thermodynamically stable. As the rearrangements of **4** to **3** and **5** are reversible, the only observable rearrangement is to the most thermodynamically stable product **3**.

Acetolysis of 2. pTS-catalyzed acetolysis of **2** produces a 40:60 mixture of **18** and **19**[5] which were separated by column chromatography. The formation of **18** and **19** occurs via protonation at C_5 followed by ring opening as illustrated in the following scheme. No products were detected



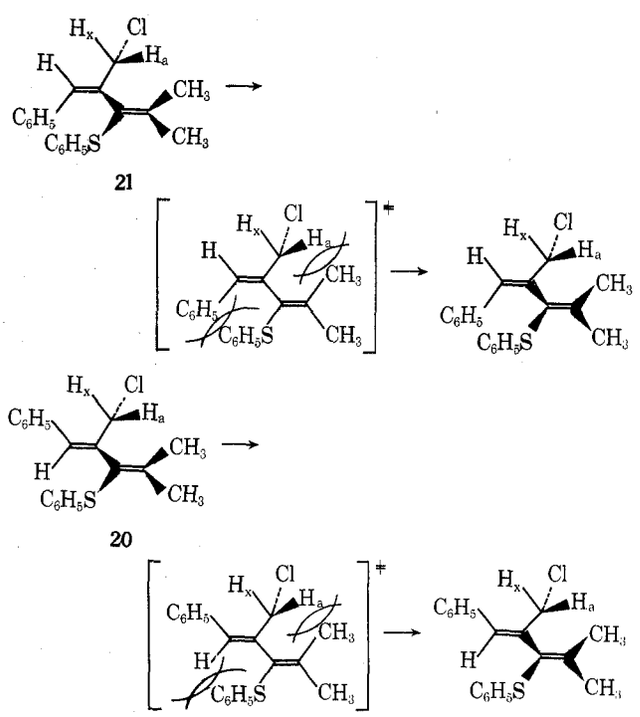
which would have been formed by electrophilic attack on the C_1–C_4 double bond (i.e., **12** or the acetate of **16**) or the three-membered ring (i.e., **13** or an enyne derived thereof). Qualitatively, **2** undergoes pTS-catalyzed acetolysis considerably more rapidly than does **1**.

Benzenesulfenyl Chloride. Reaction with 1. Benzenesulfenyl chloride reacts with **1** to produce a complex mixture of products which can be partially separated; extensive decomposition during chromatography, however, has precluded characterization of at least two minor products. Chromatography on silica gel resulted in the isolation of adducts **20**, **21**, and **22**, and a mixture of **21**, **22**, and a reactive adduct believed to possess structure **23**. Comparison of



the NMR spectrum of **20** with that of the original reaction mixture indicates that **20** is not a primary reaction product, but is an artifact of the chromatographic separation procedure. Integration of the NMR spectrum of the original reaction mixture indicates that **21**, **22**, and **23** are formed in a 29:57:14 ratio.

The structures of the adducts are assigned on the basis of NMR and mass spectral data. In the mass spectrometer the molecular ions of **20**, **21**, and **22** all undergo dominant fragmentation by loss of chlorine atom and hydrogen chloride characteristic of an allylic chloride, and not by dominant loss of phenylthio radical as observed with isomeric adducts in which the positions of the chlorine and phenylthio groups are interchanged.[15] The NMR spectrum of **22** is straightforward, displaying two broadened terminal methylene doublets and a broadened methine singlet. The NMR spectra of **20** and **21** at 30° are dramatically different and merit detailed discussion. The NMR spectrum of **20** shows a singlet for the $-CH_2Cl$ protons while the spectrum of **21** contains AX doublets with a geminal coupling constant of 12.7 Hz. The diastereotopicity of the $-CH_2Cl$ protons of **21** arises from slowed rotation about the central C–C bond of the butadiene chromophore which becomes a chiral diene on the NMR time scale.[16,17] On raising the temperature the AX doublets reversibly coalesce to produce a sharp singlet at 142°. (Coalesence occurs at approximately 95° resulting in a crude estimate for ΔG_{368} of ~18 kcal/mol.)[19] The assignments of the stereochemistry of **20** and **21** is based on mechanistic arguements (vide supra) and their NMR spectral behavior. Inspection of molecular models of **20** and **21** reveals that the barrier to rotation about the central C–C bond of **21**, via the lower energy transoid transition state,[20] must be higher than for **20**. In the transoid transition state for enantiomerization of the skewed diene system in **21** two severe "1,3-diaxial-type" interactions are present: one between phenyl and phenylthio, the other between chloromethyl and methyl. In the transition state for enantiomerization of **20** only one severe 1,3 interaction is present, that being between chloromethyl and methyl. Thus, the barrier

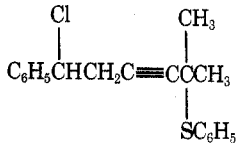


to rotation in **21** must be higher than that in **20** and is consistent with the stereochemistry of **21** assigned on the basis of mechanistic reasoning.

During the chromatographic separation **20** is formed by isomerization of **21** and/or rearrangement of **22**. That double bond isomerization is apparent in this system but does not occur in the acid-catalyzed isomerization of **4** to **3** is due to different substitution patterns on the butadiene frameworks. In the more stable twisted transoid conforma-

tion of **3** a 1,3 interaction exists between phenyl and hydrogen whereas in **21** a 1,3 interaction exists between phenyl and phenylthio. In both **5** and **20** substantial cis 1,2 interactions are present, in **5** between phenyl and acetoxymethyl and in **20** between phenyl and chloromethyl. Thus, the energy of **21** is higher relative to **20** than is the energy of **3** relative to **5**, and in a thermodynamically controlled situation **21** is more prone to isomerize to **20** than is **3** to **5**.

NMR evidence indicates that a ring-retained adduct is also formed. This adduct was isolated only as a mixture with **21** and **22**, and appears to undergo decomposition during chromatography. The NMR spectrum of this adduct shows distinct A and X resonance patterns of an AMX spin system (the M resonances are obscured by the methyl resonances of **21** and **22**). That the adduct is a methylenecyclopropane derivative and not a cyclopropane derivative is indicated by the chemical shift of the ring benzyl hydrogen (δ 2.76) while in **1** the benzyl hydrogen appears at δ 2.80. In addition, the methyl protons of the adduct appear as a singlet at δ 1.67 whereas in an isobutenylcyclopropane the two methyl groups would be expected to appear as two singlets at lower field. The positions of the chloro and phenylthio groups on the isobutylidenecyclopropane framework cannot be unambiguously specified. Both possible structures **23** and **24** are anticipated to be quite reactive; **23** being a tertiary halide and **24** being a halomethylenecyclopropane.[21] As no adducts were apparently formed that would be derived by electrophilic attack on the C_4–C_5 double bond followed by ring opening (e.g., **25** or its dehydrochlorination product), we believe that the structure of the ring-retained adduct is **23** which would be derived via the same episulfonium ion intermediate that would ultimately give rise to **21** and **22**. No adducts were observed that would be formed by electrophilic attack on the three-membered ring (e.g., **26**).



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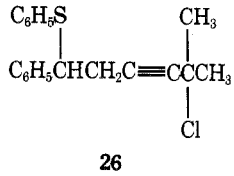

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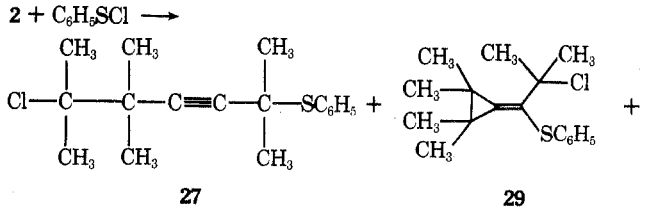
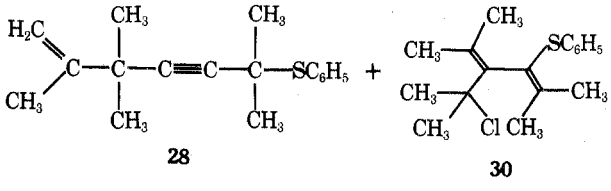
Reaction of Benzenesulfenyl Chloride with 2. Benzenesulfenyl chloride reacts with **2** to produce a mixture of apparently two major, very reactive adducts along with a dehydrochlorination product of one adduct and smaller amounts of unidentified products. The NMR spectrum of the product mixture shows only two low-field methyl resonances, a vinyl methyl double doublet belonging to **28** and a low-field singlet believed to belong to **29**. All other methyl resonances appear as singlets and fall in the δ 1.61–0.97 region characteristic of methyl groups attached to quaternary carbon atoms. The lack of low-field methyl resonances precludes the presence of structures related to **30** which would be formed by attack on the C_1–C_4 double bond as is observed with **1**. The products characterized are formed by electrophilic attack on the C_4–C_5 double bond.



27 **29**

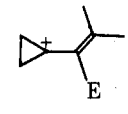


28 **30**

Storing the reaction mixture at 5° for short periods of time resulted in extensive change. Attempted chromatographic separation on silica gel resulted in extensive decomposition, although a substantial fraction was obtained which we believe contained **28** along with an unidentified compound. The structure of **28** is assigned by comparison of peak intensities and chemical shifts with those of **18**, the correspondence for the $H_2C{=}C(CH_3)C(CH_3)_2$– portions of **18** and **28** being within 0.03 ppm. The peaks of **28** are present in the NMR spectrum of the original sample and account for approximately 10% of the mixture. The formation of **28** during attempted chromatographic separation occurs by dehydrochlorination of **27**, whose NMR peaks in the original mixture are assigned by comparison of chemical shifts of **27** and **28** with **18** and **19**. **27** accounts for approximately 35% of the original product mixture. The presence of **29** is indicated by intense methyl singlets in the NMR spectrum of the original mixture at δ 0.97, 1.15, and 1.78. No decomposition products of **29** could be identified.

Discussion of Factors Affecting Selectivity of Electrophilic Attack. The results outlined in the forgoing portion show that the selectivity of attack by an electrophile on the alkenylidenecyclopropane system is greatly dependent on the nature of the substituents attached to the three-membered ring and, to some extent, the nature of the electrophilic species. Attack by proton occurs on the p orbital on C_4 of the C_1–C_4 double bond of the phenyl substituted system **1**, while with the tetramethyl substituted compound **2** attack occurs only at C_5. The benzenesulfenyl cation, which like the proton may be considered a "hard", irreversible, but bridging, electrophile, undergoes exclusive attack on the C_1–C_4 double bond of **1** while with **2** attack occurs on the C_4–C_5 double bond to form intermediate episulfonium ions. To gain an understanding of the difference in mode of reaction of **1** and **2** one must consider the nature of the bonding interactions in the cationic intermediates, or contributing structures to the episulfonium ion intermediates, formed in both processes and the interaction of groups attached to the three-membered ring with the molecular orbitals of the ring system.

Electrophilic attack on the p orbital of C_4 of the C_1–C_4 double bond produces a cyclopropyl cation (**31**) which derives little stabilization from groups attached to the three-membered ring. Although the p_z orbital on C_1 interacts strongly with the p_z orbitals on C_2 and C_3 to generate a set of bonding, degenerate group orbitals, the latter do not overlap strongly with the orbitals of carbon atoms attached to C_2 and C_3[22] and thus little stabilization is afforded carbonium ion formation at C_1 by alkyl groups attached to C_2 and C_3. Development of charge at C_1 does result in ultimate ring opening and release of ring strain but from the above reasoning this process should be little affected by groups attached to C_2 and C_3. Electrophilic attack at C_5 results in the formation of cation **32** in which the in-plane,



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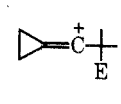

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vacant p orbital on C_4 interacts strongly with the Walsh-type orbitals[23] of the three-membered ring.[22] Although un-

saturated groups attached to the three-membered ring do not interact strongly with the Walsh orbitals of the three-membered ring owing to the small coefficients on the requisite p orbital on the atom attached to the ring,[24,25] alkyl groups interact to a much greater degree owing to the substantial coefficients of the appropriate atomic orbitals on both C_2 (or C_3) and the attached carbon atom.[22,25] Therefore, alkyl groups attached to the three-membered ring stabilize positive charge formation at C_4 to a greater degree than at C_1, and unsaturated groups (e.g., phenyl) do not lead to stabilization of charge formation at either center.[26]

The selectivity of attack by the acetoxymercuri cation on **2**, and in part on **1** in aqueous tetrahydrofuran differs from that observed in protonation and in attack by benzenesulfenyl cation. In contrast to the proton and the benzenesulfenyl cation, the acetoxymercuri ion is a soft electrophile and reacts reversibly with π bonds to form mercurinium ions.[27] The acetoxymercuri cation apparently is not as strong an electrophile and on attack on the π system does not polarize the C_1–C_4 or the C_4–C_5 double bonds sufficiently to induce ring opening or attack by a nucleophile, and by default undergoes electrophilic attack on a strained ring bond.

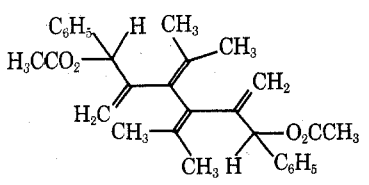
Experimental Section

Acetoxymercuration of 1. To a stirred solution of 3.18 g (10 mmol) of mercuric acetate in 10 ml of acetic acid at 25° was slowly added 1.70 g (10 mmol) of **1**. After stirring for 30 min the reaction mixture was cooled to 0° in an ice bath and a 12-fold excess of sodium borohydride[7] (4.96 g) in 60 ml of 10% sodium hydroxide was added as rapidly as possible, maintaining the temperature of the reaction mixture below 20°. Saturated aqueous sodium chloride (25 ml) was added and the mixture was extracted with two 40-ml portions of ether. The ether extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure, leaving 2.43 g of a colorless liquid of which approximately one-half was soluble in hexane.

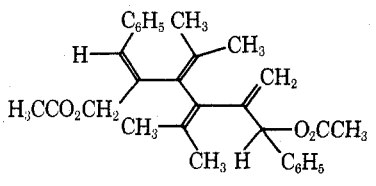
The hexane-soluble portion of the above product was chromatographed on a 2 × 25 cm column of silica gel. Elution with 20–25% benzene in hexane produced 96 mg of pure **4**: bp ~40° (0.08 mm in a microstill); ir (cap film) 1735 ($\nu_{C=O}$) and 905 cm^{-1} ($\nu_{=CH_2}$); NMR ($CDCl_3$) δ 1.68 (bs, 3 H), 1.70 (bs, 3 H), 2.08 (s, 3 H), 5.03 (bs, 1 H), 5.34 (bs, 1 H), 5.47 (bs, 1 H), 6.18 (bs, 1 H), 7.31 (s, 5 H); mass spectrum $M^{\cdot+}$ 230.129 (calcd for $C_{15}H_{18}O_2$, 230.131), major peaks at *m/e* 215, 188, 173, 170, 155 (base peak), 143, 141, 129, 115, and 91.

Elution with 30% benzene in hexane produced pure **3**: bp ~40° (0.08 mm in a microstill); ir (cap film) 1742 cm^{-1}; NMR ($CDCl_3$) δ 1.43 (d, J = 0.9 Hz, 3 H), 1.76 (d, J = 1.6 Hz, 3 H), 2.06 (s, 3 H), 4.66 (m, 2 H), 5.75 (bm, 1 H), 6.46 (bm, 1 H), and 7.25 (m, 5 H); mass spectrum $M^{\cdot+}$ 230.129 (calcd for $C_{15}H_{18}O_2$, 230.131) (the mass spectrum of **3** was identical in all respects with that of **4**).

Elution with 45–50% benzene in hexane produced fractions containing a mixture of dimers [40 mg, mp (from hexane) 118–125°, $M^{\cdot+}$ *m/e* 458] i and ii: ir (CCl_4) 1744 and 1731 cm^{-1}; NMR of i



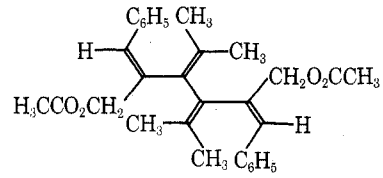
i



ii

($CDCl_3$) δ 1.69 (bs, 3 H), 1.92 (bs, 3 H), 2.11 (s, 3 H), 4.86 (m, 1 H), 5.38 (m, 1 H), 6.14 (bs, 1 H), 7.33 (s, 5 H); NMR of ii ($CDCl_3$) δ 1.69 (s, 3 H), 1.70 (s, 3 H), 1.93 (s, 3 H), 2.01 (s, 3 H), 2.02 (s, 3 H), 2.04 (s, 3 H), 5.08 (bs, 1 H), 5.31 (bs, 1 H), 6.18 (bs, 1 H), 6.75 (bs, 1 H), 7.25 (m, 10 H).

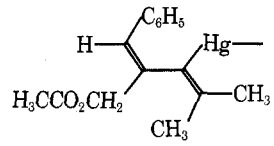
Further elution with 50% benzene in hexane gave 35 mg of unidentified material. Elution with 55% benzene in hexane gave iii as



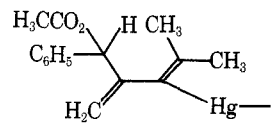
iii

a viscous liquid: ir (CCl_4) 1733 cm^{-1}; NMR ($CDCl_3$) δ 1.70 (s, 6 H), 2.04 (s, 6 H), 2.12 (s, 6 H), 4.66 (bs, 4 H), 6.46 (bs, 2 H), and 7.33 (m, 10 H).

The NMR and mass spectra ($M^{\cdot+}$ series of peaks at *m/e* 656–662) of the hexane insoluble fraction indicate the presence of a mixture of bis(acetoxyalkyl)mercury compounds with partial structures iv and v: NMR ($CDCl_3$) of iv δ 1.70 (s), 2.02 (s), 2.07 (s),



iv



v

4.64 (m), 6.40 (bs), and ~7.2 (m); NMR of v δ 1.62 (s), 1.72 (s), 2.10 (s), 4.87 (m), 5.36 (m), 6.15 (m), and 7.31 (s).

Hydroxymercuration of 1. To a bright yellow solution of 3.5 g (11.4 mmol) of mercuric acetate in 22 ml of 50% aqueous tetrahydrofuran was added 1.87 g (11.1 mmol) of **1**. The yellow color was rapidly discharged. After stirring for 30 min at 25° a solution of 0.5 *M* sodium borohydride in 10% sodium hydroxide (22 ml) was rapidly added with stirring. The reaction mixture was added to 100 ml of water and was extracted with two 40-ml portions of ether. The combined extract was washed with water and dried ($MgSO_4$), and the solvent was removed under reduced pressure, giving 2.79 g (135% based on 1 plus H_2O) of residue. The residue was chromatographed on a 2 × 25 cm column of silica gel. Elution with benzene gave 0.15 g of a mixture of **3** and **4**. Further elution with benzene gave 50 mg of a mixture containing some **3** and **4** along with mostly a compound assigned structure **6** (structure is assigned by comparison of NMR spectral properties with those of alcohol **9** below): NMR ($CDCl_3$) δ 1.44 (s), A_2X_2 multiplets at 2.52 and 2.74 (J = 5.8 Hz), and ~7.3 (s).

Still further elution with benzene gave 150 mg of pure **7** (purified by molecular distillation at 40°, 1.0 mm): ir (cap film) ν_{OH} 3430, $\nu_{=CH_2}$ 904 cm^{-1}; NMR ($CDCl_3$) δ 1.72 (overlapping doublets, $J \simeq 1$ Hz, 6 H), 5.02 (m, 1 H), 5.15 (bs, 1 H), 5.41 (m, 1 H), 5.47 (very broad m, 1 H), and 7.33 (s, 5 H); mass spectrum $M^{\cdot+}$ 188.119 (calcd for $C_{13}H_{16}O$, 188.120), major peaks at *m/e* 170 ($M^{\cdot+} - H_2O$), 107 ($C_6H_5CHOH^+$, base peak), 105 ($C_6H_5CO^+$).

Elution with 50% chloroform in benzene gave 350 mg of pure **8** (purified by molecular distillation at 40–43°, ~0.07 mm): ir ν_{OH} 3390 cm^{-1}; NMR ($CDCl_3$) δ 1.43 (d, J = 1.1 Hz, 3 H), 1.74 (d, J = 1.3 Hz, 3 H), 3.60 (bs, 1 H), 4.16 (d, J = 1.2 Hz, 2 H), 5.77 (bm, 1 H), 6.54 (t, J = 1.2 Hz, 1 H), 7.28 (m, 5 H); mass spectrum $M^{\cdot+}$ 188.119 (calcd for $C_{13}H_{16}O$, 188.120), major peaks at *m/e* 173 ($M^{\cdot+} - CH_3$), 170 ($M^{\cdot+} - H_2O$), 157 ($M^{\cdot+} - CH_2OH$), 155, 143, 115, and 91 (base peak).

Following the elution of **8**, fractions containing **8** and **9** (0.47 g, ~50:50 ratio of **8**:**9**) were eluted and rechromatographed on a similar column to give pure **9**: ir (5% in CCl_4) ν_{OH} 3608 and $\nu_{C\equiv C}$ 2258 cm^{-1}; NMR ($CDCl_3$) δ 1.45 (s, 6 H), 1.79 (s, 1 H, δ is concentration dependent), 2.44 (X_2 portion of an A_2X_2 system, J = 5.7 Hz, 2 H), 2.79 (A_2 portion of an A_2X_2 system, J = 5.7 Hz, 2 H), and 7.25 (s, 5 H); mass spectrum $M^{\cdot+}$ 188.119 (calcd for $C_{13}H_{16}O$, 188.120), major peaks at *m/e* 173 ($M^{\cdot+} - CH_3$), 170 ($M^{\cdot+} - H_2O$), and 91 (base peak).

Acetoxymercuration of 2. To a solution of 1.21 g (3.8 mmol) of mercuric acetate in 20 ml of acetic acid at 0° was added 0.57 g (3.8 mmol) of **2**. The reaction mixture was stirred for 15 min at 0° and was then allowed to warm to 25° for 1.75 hr. Sodium borohydride (10 ml of 0.5 *M* in 10% sodium hydroxide) was added and the resulting reaction mixture was stirred for 2 hr. The reaction mixture

was transferred to a separatory funnel and 15 ml of saturated sodium chloride was added followed by extraction with three 15-ml portions of ether. The ether extract was washed with aqueous sodium bicarbonate and was dried ($MgSO_4$). The solvent was carefully removed by distillation, leaving 0.49 g of a colorless, viscous oil containing some white solid material: ir ($CHCl_3$) 3680, 3470 (broad), 1737, 1725 (shoulder), 1665, 1635, and 914 cm^{-1}; NMR ($CDCl_3$) indicated a complex mixture. Analysis by GLC on an 8-ft Carbowax 20M column programmed from 85 to 145° at 2°/min indicated the presence of up to 12 components. Preparative GLC using the above conditions yielded sufficient sample for identification of the five major (total >85%) components (in order of elution).

12: colorless oil; NMR ($CDCl_3$) δ 1.56 (d, J = 1.2 Hz, 3 H), 1.59 (d, J = 0.9 Hz, 3 H), 1.73, 1.75, 1.77 (overlapping broad singlets, 9 H total), 4.62 (m, 1 H), 4.90 (m, 1 H), and 5.59 (m, 1 H).

13 (also contains ~30% of an unknown structure **14**): colorless oil; NMR ($CDCl_3$, ^1H FT) δ 0.94 (d, J = 6.7 Hz), 1.33 (s), 1.40 (m), 1.63 (s), 1.99 (s). **14:** NMR ($CDCl_3$) δ 1.10, 1.12, 1.17, 1.25 (s).

15: NMR ($CDCl_3$, ^1H FT) δ 0.90 (s), 0.98 (s), 1.60 (d, J = 0.9 Hz), 1.66 (d, J = 1.2 Hz), 1.91 (s), 5.46 (m); mass spectrum $M^{\cdot+}$ 210.1620 (calcd for $C_{13}H_{22}O_2$, 210.1620).

16: colorless crystals from hexane (colorless plates), mp 67.5–69°; ir ($CHCl_3$) ν_{OH} 3660 and $\nu_{=CH_2}$ 907 or 917 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (s, 6 H), 1.51 (d, J = 1.2 Hz, 3 H), 1.58 (d, J = 1.3 Hz, 3 H), 1.64 (s, peak disappears on addition of deuterium oxide, 1 H), 1.76 (d, J = 1.4 Hz, 3 H), 1.96 (d, J = 1.8 Hz, 3 H), 5.67 (m, 1 H); mass spectrum $M^{\cdot+}$ 168.1514 (calcd for $C_{11}H_{20}O$, 168.1514), major peaks at m/e 153, 150, 135 (base peak), 119, 110, 107, 95, and 59. **16** could be isolated from the original reaction mixture by precipitation with hexane.

17: NMR ($CDCl_3$, ^1H FT) δ 1.04, 1.21, 1.26, 1.69, 1.72, and 2.11 (all singlets with approximate relative intensities of 6:6:1:3:3:3); mass spectrum $M^{\cdot+}$ 210.1620 (calcd for $C_{13}H_{22}O_2$, 210.1620).

The GLC analysis and the NMR spectrum of the original reaction mixture indicate that the relative ratio of the products **12:13:14:15:16:17** is 26:15:10:5:100:5. Insufficient quantities of the other fractions prevented obtaining good NMR spectra for identification purposes. No significant dialkylmercury formation was indicated or observed with **2**.

***p*-Toluenesulfonic Acid Catalyzed Acetolysis of 1.** A solution of 65 mg of **1** in 1 ml of acetic acid containing one small crystal of *p*-toluenesulfonic acid was sealed in an NMR tube and heated in a sand bath at 70°. After 2 hr analysis by NMR indicated that no **1** remained and that **3** was formed as the only product. The tube was opened and its contents were poured into 15 ml of water. The mixture was extracted twice with 15-ml portions of ether. The combined ether extract was washed with 5% sodium bicarbonate until free from acetic acid. The extract was dried ($MgSO_4$) and the solvent was removed, giving 50 mg of pure **3** (by NMR).

Acetolysis of 1. A solution of 65 mg of **1** in 1 ml of glacial acetic acid was sealed in an NMR tube and was heated in a sand bath at 115°. The reaction was periodically monitored by NMR. After 20 hr at 115° peaks corresponding to **3** and **4** were observed (~25% reaction producing a ~35:65 ratio of **3** to **4** along with some apparent polymerization and/or isomerization of **1** also occurring).

Acid-Catalyzed Isomerization of 4 to 3. A solution of 37 mg of **4** in 1 ml of acetic acid containing one small crystal of *p*-toluenesulfonic acid was sealed in an NMR tube and was heated at 105° in a sand bath. Analysis by NMR indicated that **4** was essentially completely rearranged to **3** within 45 min.

Acetolysis of 2. In an NMR tube was sealed 126 mg of **2** in 1 ml of acetic acid with one small crystal of *p*-toluenesulfonic acid. After standing at 25° for 24 hr NMR analysis indicated that **2** had completely reacted. The contents of the tube were dissolved in 20 ml of ether and the ether solution was washed repeatedly with saturated sodium bicarbonate until free of acetic acid. The solution was dried ($MgSO_4$) and the solvent was carefully removed under reduced pressure, leaving 143 mg of a 40:60 mixture of **18** and **19**[5] which were separated by chromatography on a 1 × 45 cm column of silica gel. Elution with hexane gave **18:** NMR ($CDCl_3$) δ 1.13 (d, J = 6.4 Hz, 6 H), 1.30 (s, 6 H), 1.84 (m, 3 H), 2.48 (septet, J = 6.4 Hz, 1 H), 4.74 and 5.00 (m's, 1 H each). Elution with 30% benzene–hexane gave **19:** NMR ($CDCl_3$) δ 1.12 (d, J = 6.4 Hz, 6 H), 1.21 (s, 6 H), 1.61 (s, 6 H), 1.97 (s, 3 H), and 2.48 (septet, J = 6.4 Hz, 1 H).

Reaction of 1 with Benzenesulfenyl Chloride. To 365 mg (2.1 mmol) of **1** in 3 ml of dichloromethane containing 50 mg of calcium carbonate was slowly added 295 mg (2.0 mmol) of benzenesulfenyl chloride dissolved in 2 ml of dichloromethane at 0° under a nitrogen atmosphere, the red color of the benzenesulfenyl chloride being discharged immediately. The reaction mixture was allowed to warm to room temperature and was stirred for 20 min. The reaction mixture was dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure, leaving a pale yellow oil. The residue was dissolved in hexane and was applied to a 2 × 27.5 cm column of silica gel. Extensive decomposition occurred at the top of the column. Elution with 5% benzene–hexane gave 42 mg of **1**. Elution with 10% benzene–hexane produced 14 mg of **20:** NMR ($CDCl_3$) δ 2.10 (s, 3 H), 2.17 (s, 3 H), 4.41 (s, 2 H), 6.39 (s, 1 H), and 7.3 (m, 10 H); mass spectrum $M^{\cdot+}$ 314.0892 (calcd for $C_{19}H_{19}S^{35}Cl$, 314.0896), major peaks at m/e 316, 314, 278 (base peak, $M^{\cdot+}$ − HCl), 263, 248, 219, 205 (rel intensity 11.5), 201, and 185.

Further elution with 10% benzene–hexane gave 110 mg of a mixture of **21, 22,** and **23** or **24** from which pure fractions of **21** and **22** were obtained by careful rechromatography on a 2 × 25 cm column of silica gel using pure hexane as eluent. **21:** NMR ($CDCl_3$) δ 1.72 (s, 3 H), 2.00 (s, 3 H), 4.14 (d, J = 12.7 Hz, 1 H), 4.50 (d, J = 12.7 Hz, 1 H), 6.47 (bs, 1 H), and 7.3 (m, 10 H); mass spectrum $M^{\cdot+}$ 314.0889 (calcd for $C_{19}H_{19}S^{35}Cl$, 314.0896), spectrum essentially identical with that of **20. 22:** NMR ($CDCl_3$) δ 1.73 (s, 3 H), 1.75 (s, 3 H), 4.78 (bs, 1 H), 4.97 (broadened d, J = 1.7 Hz, 1 H), 5.43 (broadened d, J = 1.7 Hz, 1 H), and 7.2 (m, 10 H); mass spectrum $M^{\cdot+}$ 314.0876 (calcd for $C_{19}H_{19}S^{35}Cl$, 314.0896), spectrum essentially identical with that of **20** and **21**. Unknown structure **23** or **24:** NMR (from $CDCl_3$ solution of mixture with **21** and **22**) δ 0.72 (dd, J = 5.2 and 10.2 Hz, 1 H), 1.67 (s, 6 H), ~1.7 (dd, J = 5.2 and 7.9 Hz, 1 H), 2.76 (dd, J = 7.9 and 10.2 Hz, 1 H), ~7.2 (m, 10 H).

Further elution with more polar solvent systems produced continuous fractions, the NMR spectra of which did not correspond to peaks appearing in the NMR spectrum of the crude reaction mixture. These fractions represent decomposition products formed on the silica gel column. As no clean separation of these decomposition products could be achieved, further characterization was not attempted.

Careful inspection of the NMR spectrum of the crude reaction mixture does not show the presence of peaks corresponding to **20.** Integration of the peaks corresponding to **21, 22,** and **23** or **24** indicate they were formed in a ratio of 29:57:14 and account for at least 75% of the product. Peaks appearing in the NMR spectrum which were not identified with an isolable product appear at δ 1.85 (bs), 3.21 (an apparent triplet), and weak multiplets at 4.65 and 5.85.

Reaction of 2 with Benzenesulfenyl Chloride. Benzenesulfenyl chloride (283 mg, 2.0 mmol) and 300 mg (2.0 mmol) of **2** were allowed to react following the procedure outlined above for the reaction with **1**. Peaks in the NMR spectrum of the reaction mixture assigned to **27, 28,** and **29** are as follows. **27:** NMR ($CDCl_3$) δ 1.21, 1.47, and 1.61 (all singlets of equal intensity). **28:** δ 1.28 (s, 6 H), 1.53 (s, 6 H), 1.86 (dd, $J \doteq$ 1.4 and 0.7 Hz, 3 H), 4.75 and 4.97 (m's, 1 H each) (the relative intensities are assigned from the NMR spectrum of a chromatography fraction rich in **28**. **29:** δ 0.97 (s, 6 H), 1.15 (s, 6 H), and 1.78 (s, 6 H). Attempted chromatographic separation of the mixture on a 2 × 16 cm column of silica gel resulted in extensive decomposition. Elution with benzene gave one fraction rich in **28.**

Registry No.—i, 57443-31-9; ii, 57443-32-0; iii, 57443-33-1; **1,** 4544-23-4; **2,** 13303-30-5; **3,** 57443-34-2; **4,** 57443-35-3; **6,** 57443-36-4; **7,** 57443-37-5; **8,** 57443-38-6; **9,** 57443-39-7; **12,** 25914-11-8; **13,** 57443-40-0; **15,** 57443-41-1; **16,** 30762-44-8; **17,** 57484-05-6; **18,** 21860-12-8; **19,** 21860-14-0; **20,** 57443-42-2; **21,** 57443-43-3; **22,** 57443-44-4; **23,** 57443-45-5; **27,** 57443-46-6; **28,** 57443-47-7; **29,** 57443-48-8; mercuric acetate, 1600-27-7; benzenesulfenyl chloride, 931-59-9.

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(14) Similar behavior has been observed in preliminary kinetic studies of the trichloroacetolysis of **1** in carbon tetrachloride (D. J. Pasto, unpublished observations).
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Electrophilic and Radical Addition Reactions of a Bisalkylidenecyclopropane[1]

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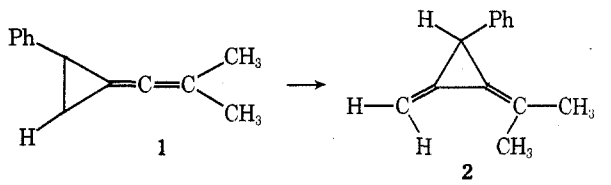
The reactions of 2-isopropylidene-3-phenylmethylenecyclopropane (**2**) with the electrophilic reagents acetic acid, mercuric acetate in acetic acid, benzenesulfenyl chloride (BSC), chlorosulfonyl isocyanate (CSI), and borane in tetrahydrofuran, and thiophenol have been investigated. The acetolysis of **2** and reactions with BSC and CSI occur by electrophilic attack on the methylene double bond giving ring-opened, butadiene-type products. The acetoxymercuration of **2** appears to occur by attack on the isopropylidene double bond. In the hydroboration of **2** attack occurs on both double bonds ultimately giving both ring-retained and ring-opened products. The addition of thiophenol to **2** occurs solely by attack of the thiophenoxy radical on the methylene group giving a ring-retained product of cis stereochemistry.

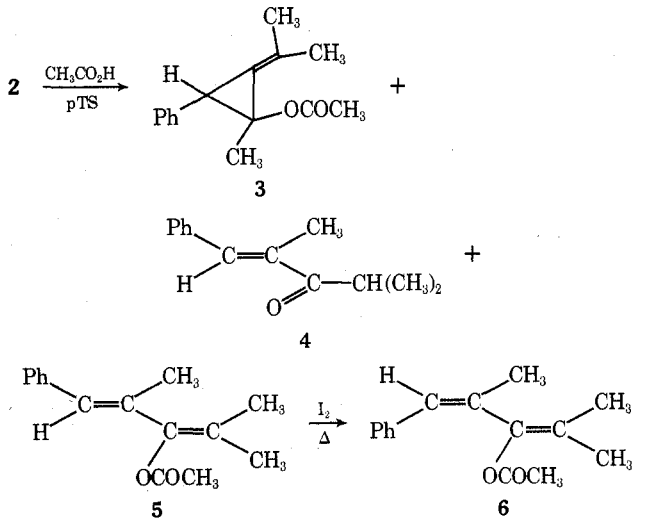
In conjunction with other chemical and physical studies of alkenylidenecyclopropanes carried out in our laboratories we initiated a stereochemical study of the thermal rearrangement of alkenylidenecyclopropanes to bisalkylidenecyclopropanes;[2] for example, the rearrangement of **1** to **2**. However, the high reactivity of **1** and **2** and the similarities in their physical properties have made separation of the mixtures of **1** and **2** very difficult. In an attempt to circumvent these problems we have investigated various reactions of **1** and **2** which could conceivably prove useful for converting **1** and **2** to more tractable and easily separated compounds still containing the chiral center present in **1** and **2**. In the foregoing article we have described some of the more interesting reactions of **1**;[3] in the present article we wish to report the results of similar studies with **2**.



1 **2**

Results and Discussion

Acetolysis of 2. Heating **2** in acetic acid at 115°C for prolonged periods of time did not result in acetolysis. The addition of a catalytic amount of *p*-toluenesulfonic acid, however, resulted in complete reaction at 115°C in 23 hr. Chromatographic separation on silica gel resulted in the isolation of small amounts of **3**[4] and **4**, with the major product being **5**. The structures of the products were identified



3 **4** **5** **6**

by their ir and NMR spectral properties. The ir spectrum of **3** shows a typical alkyl acetate band at 1736 cm^{-1}. In the NMR spectrum of **3** the isolated methyl appears as a singlet at δ 1.56 while the isopropylidene methyls appear as doublets at δ 1.96 and 2.06 ($J \simeq 1.1$ Hz). The cyclopropyl hydrogen appears as a multiplet at δ 2.17. The phenyl hy-