mercury formation even when using large quantities of reducing agent.
(8) As an example see D. J. Pasto, R. L. Smorada, B. L. Turini, and D. J. Wampfler, *J. Org. Chem.*, following paper in this issue.
(9) See D. J. Pasto and J. Gontarz, *J. Am. Chem. Soc.*, **91**, 719 (1969); G. A. Gray and W. R. Jackson, *ibid.*, **91**, 6205 (1969); G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970).
(10) The mass spectra of **3** and **4** were completely identical, suggesting that the radical cations derived from the two structures were identical. This further suggested the possibility that under thermal activation **3** and **4** could be interconverted.
(11) C. H. DePuy and R. J. Van Lanen, *J. Org. Chem.*, **39**, 3360 (1974).
(12) See references in ref 8.
(13) Comparison of GLC retention times of **18** and **19** with those of the components in the crude acetoxymercuration reaction mixture indicated possible identity with two of the very minor components.
(14) Similar behavior has been observed in preliminary kinetic studies of the trichloroacetolysis of **1** in carbon tetrachloride (D. J. Pasto, unpublished observations).
(15) See references in ref 8.
(16) Similar behavior with other highly substituted acyclic butadienes has been reported: A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *Tetrahedron Lett.*, 2153 (1974), and references cited therein; Professor E. F. Kiefer, University of Hawaii, private communication.
(17) The ease of synthesis of chiral alkenylidenecyclopropanes[18] presents the possibility of the direct formation of optically active acyclic, substituted butadienes. Efforts are underway along such lines.
(18) D. J. Pasto and J. K. Borchardt, *Tetrahedron Lett.*, 2517 (1973).
(19) Insufficient material has prevented obtaining high quality spectra of necessary for accurate determination of T_c or for full line-shape analyses for either **20** or **21** (see ref 15).
(20) Enantiomerization via the planar transoid transition state is of lower energy than via the planar cisoid conformation (see references by Mannschreck in ref 16).
(21) M. Hanack, T. Bassler, W. Eymann, W. E. Heyd, and R. Kopp, *J. Am. Chem. Soc.*, **96**, 6686 (1974).
(22) D. J. Pasto, T. P. Fehlner, M. E. Schwartz, and H. F. Baney, *J. Am. Chem. Soc.*, **98**, 530 (1976).
(23) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); *Nature (London)*, **159**, 167, 712 (1947).
(24) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 8193 (1975).
(25) See also discussion in ref 3.
(26) Other factors which might also contribute to preferential attack at C_5 of **2** relative to C_4 in **1** would be reduced steric inhibition to attack at the perpendicular p orbital at C_4 of the C_1–C_4 double bond, and steric inhibition to disrotatory ring opening in the cyclopropyl cation derived from **2**.
(27) D. J. Pasto and J. A. Gontarz, *J. Am. Chem. Soc.*, **93**, 6902, 6909 (1971).

Electrophilic and Radical Addition Reactions of a Bisalkylidenecyclopropane[1]

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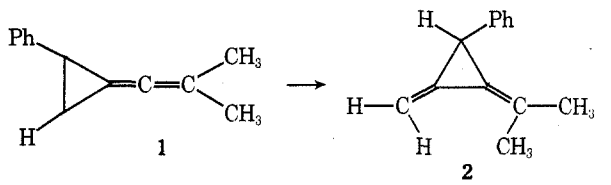
The reactions of 2-isopropylidene-3-phenylmethylenecyclopropane (**2**) with the electrophilic reagents acetic acid, mercuric acetate in acetic acid, benzenesulfenyl chloride (BSC), chlorosulfonyl isocyanate (CSI), and borane in tetrahydrofuran, and thiophenol have been investigated. The acetolysis of **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.

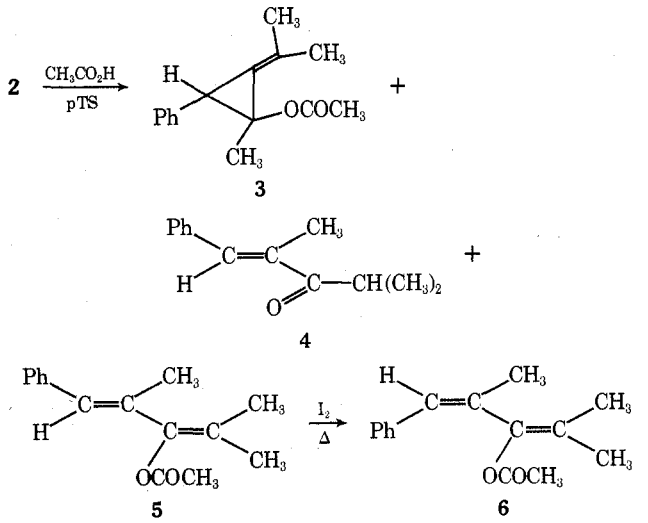
In conjunction with other chemical and physical studies of alkenylidenecyclopropanes carried out in our laboratories we initiated a stereochemical study of the thermal rearrangement of alkenylidenecyclopropanes to bisalkylidenecyclopropanes;[2] for example, the rearrangement of **1** to **2**. However, 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**

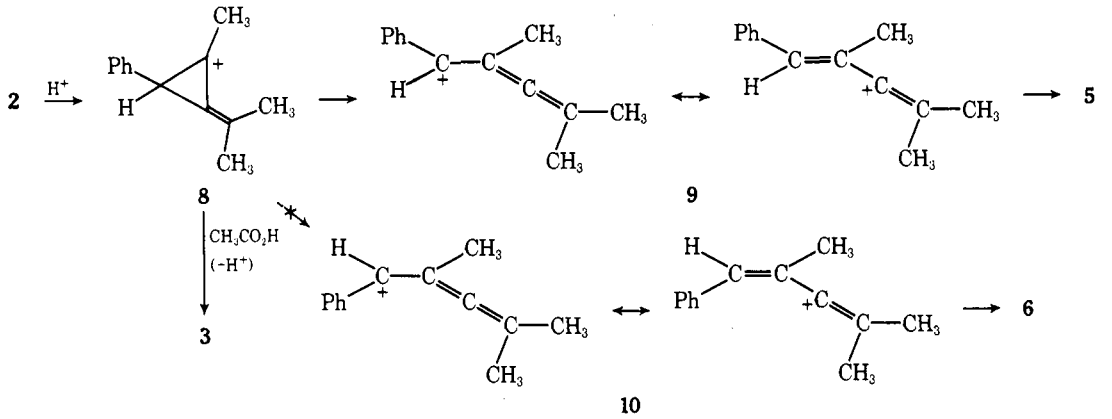
Results and Discussion

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



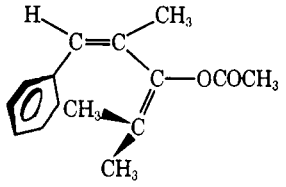
3 **4** **5** **6**

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-



drogens appear as a singlet at δ 7.24 typical of a phenyl group attached to a saturated center. The unsaturated ketone **4** ($\nu_{C=O}$ 1665 cm^{-1}) appears to be a true reaction product and not an artifact of the work-up or separation procedures (by NMR analysis of the acetic acid reaction solution). The NMR spectrum of **4** shows a doublet at δ 1.31 (J = 7.3 Hz) for the isopropyl methyls, a doublet for the vinyl methyl at δ 2.05 (J = 1.3 Hz), a multiplet for the vinyl hydrogen at δ 6.36, and a multiplet for the aromatic hydrogens at ~δ 7.3.

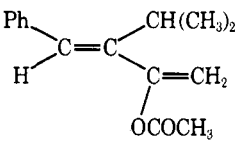
The acetate carbonyl of the major product **5** absorbs at 1755 cm^{-1}, typical of vinyl acetates. The isopropylidene methyls appear as singlets at δ 1.67 and 1.87, while the acetate methyl appears at δ 2.15 and the remaining vinyl methyl as a doublet at δ 1.94 (J = 1.7 Hz). The vinyl hydrogen appears as a quartet at δ 6.58 with the aromatic hydrogens appearing as a broad singlet at δ 7.29. The stereochemistry of **5** is assigned on the basis of mechanistic reasoning, and by NMR spectral comparisons with **6** which is formed from **5** by thermal isomerization in the presence of iodine. Heating a deuteriochloroform solution of **5** in the presence of a trace of iodine resulted in the isomerization of **5** to **6** which possesses an NMR spectrum substantially different from that of **5**. The isopropylidene methyls of **6** are appreciably shielded in **6** (δ 1.06 and 1.17) relative to those in **5** (δ 1.67 and 1.87). In addition, the vinyl hydrogen of **6** is substantially deshielded (δ 7.56) relative to that in **5** (δ 6.58), and the β-styryl methyl group has shifted from δ 1.94 to 2.08. Inspection of molecular models of **5** and **6** indicate that the various groups experience substantially different long-range shielding effects by the phenyl and carbonyl groups in the two structures. It appears that an important conformation of **6** is that in which the isopropylidene group resides in a highly diamagnetic shielding region above the face of the aromatic ring.[5] There is no conformation of **5**



which places the isopropylidene group in such a shielding region.

From a mechanistic point of view, protonation of the methylene double bond of **2** produces the cyclopropyl cation **8**, which undergoes ring opening in a disrotatory manner. Rotation of the phenyl in an outward manner away from the isopropylidene group produces **9**, while inward rotation toward the isopropylidene group produces **10**. As the outward rotation is sterically more feasible, the formation of **9** dominates, ultimately producing **5**.[6] (It should be noted that **9** reacts to produce only **5**; no evidence was found for the formation of an allenyl acetate.) Whether **8** is a distinct intermediate capable of giving rise to **3** and **9**, or a transition state capable only of going to **9**, cannot be defined. The cyclopropyl acetate **3** could also be formed by a different mechanism, for example, via an AdE3 process.[7] The fact that ring opening of **8** involves cleavage of a vinyl C–C bond should be manifest in a slower rate of ring opening relative to cyclopropyl cations, the ring opening of which is calculated to have an energy barrier of only a few kilocalories.[8] If this change in structure results in a significant activation barrier for the ring-opening process, **8** could be an intermediate.

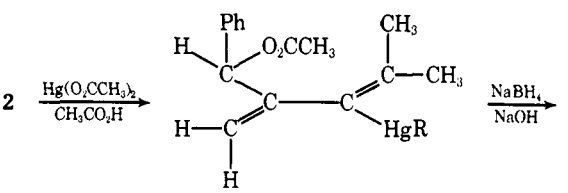
It is important to note that although **2** contains two double bonds, one a methylene and one an isopropylidene type, protonation occurs >98% at the methylene group. The NMR spectrum of the crude reaction product does not contain resonances typical of a terminal methylene in the alternative product **11**. One might have anticipated that pro-



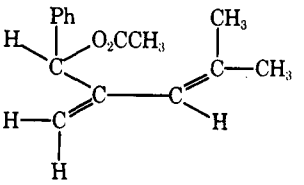
11

tonation on the more highly alkyl substituted double bond would have occurred in keeping with the known effect of alkyl substitution on the reactivity of double bonds toward electrophilic reagents.

Acetoxymercuration of 2. Acetoxymercuration of **2** followed by reductive demercuration with sodium borohydride followed by chromatographic separation produced low, variable yields of acetate **13** along with considerable quantities of bis(acetoxyalkyl)mercury **12b**[9] (see Experimental Section). The structure of **13** is clearly evident from

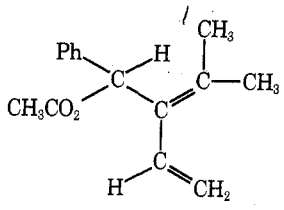


12a, R = O_2CCH_3
b, R = $C_{15}H_{17}O_2$



13

its ir and NMR spectra. Characteristic bands for an alkyl acetate and terminal methylene appear at 1739 and 909 cm^{-1}, respectively. The NMR spectrum displays three vinyl hydrogen resonances at δ 5.02, 5.35, and 5.47 which are broadened by long-range coupling. The resonance pattern is definitely not the expected AMX pattern for a $-CH{=}CH_2$ as would be present in the alternative structure **14**. In addition, the NMR spectrum of **13** contains overlap-

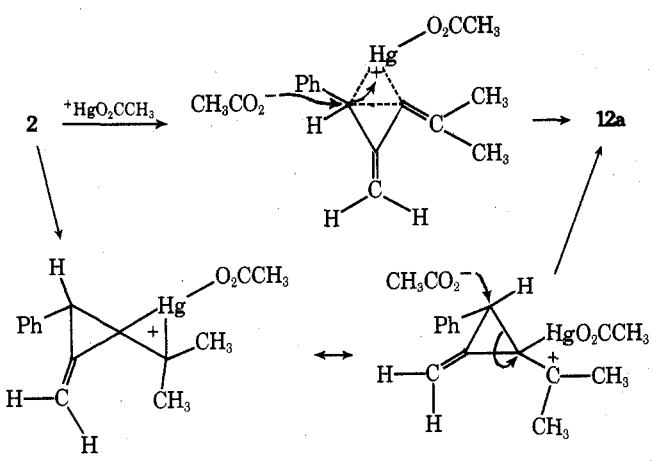


14

ping methyl doublets at δ 1.72 (J = 1.1 Hz), a broadened singlet at δ 6.18 for the benzylic hydrogen, an acetate methyl singlet at δ 2.10, and an aromatic hydrogen singlet at δ 7.27.

The structure of the bis(alkoxyalkyl)mercury compound **12b** is indicated by its mass and NMR spectra. The mass spectrum of **12b** shows a series of parent ion peaks in the *m/e* 655–660 region with relative intensities comparable to the natural abundance ratio of the isotopes of mercury. The NMR spectrum contains two broad vinyl hydrogen resonances at δ 5.08 and 5.30.

Two mechanisms can be written for the formation of **12a**, one involving electrophilic attack on one of the bonds of the three-membered ring, the other involving attack on the isopropylidene double bond. Direct attack on a ring bond has been observed by DePuy and Van Lanen[10] in the solvomercuration of cyclopropanes. Attack on the isopropylidene double bond to produce the intermediate mercurinium ion **15** followed by conjugate attack by acetate ion on the three-membered ring[11] can also produce **12a**. Because of the vinylic nature of the bonds of the three-membered ring in **2** we favor the latter mechanism.



15

The apparent difference in the positions of electrophilic attack on **2** by proton and acetoxymercuri ion can be understood if one considers the mechanism of solvomercuration in greater detail. In prior studies we have shown that formation of the mercurinium ion intermediate occurs in a fast and reversible manner.[12] Attack by acetoxymercuri ion probably is also occurring at the methylene double bond of **2**, but owing to the lesser stabilization afforded the mercurinium ion by the hydrogens in the mercurinium ion formed by attack at the methylene double bond this ion reverts to reactants, while the ion formed by attack on the isopropylidene double bond leads to product formation. Apparently, the acetoxymercuri ion is not a sufficiently strong electrophile to cause sufficient cyclopropyl cation character to be developed which would result in ring opening as do the other electrophiles described in this article.

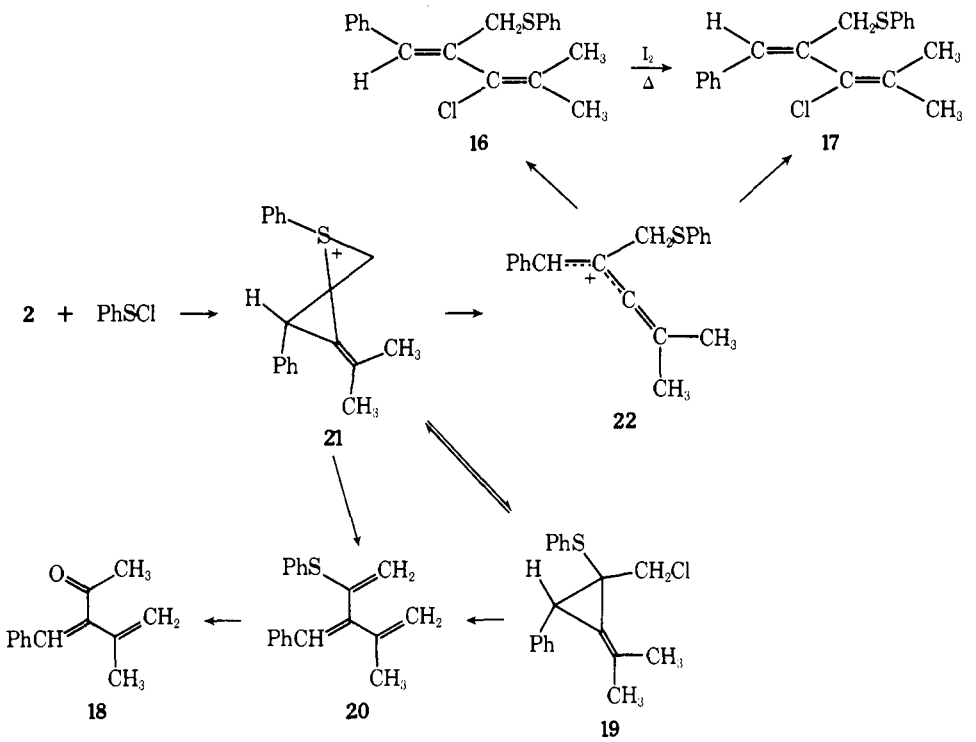
Reaction of 2 with Benzenesulfenyl Chloride. The NMR spectrum of the crude reaction mixture was very complex, indicating the formation of several products. Attempted chromatographic separation on silica gel resulted in the destruction of two of the original products with formation of a ketone whose structure was readily assigned. From the structure of the ketone and the NMR spectrum of the original product mixture structures can be assigned to all of the primary products.

Early fractions from the column contained pure **16** whose structure was readily assigned from its NMR and mass spectra. The NMR spectrum shows two methyl singlets (δ 1.86 and 1.90), a methylene singlet (δ 4.02), a vinyl hydrogen singlet (δ 6.62), and two five-proton aromatic singlets (δ 7.27 and 7.36). The presence of the $-CH_2SPh$ group, instead of a $-CH_2Cl$ group, is indicated by the mass spectrum, in which the molecular ion undergoes fragmentation by loss of thiophenoxy radical to give a chlorine-containing daughter ion, but does not show a substantial peak for loss of only a chlorine atom. The loss of the group from an allylic position occurs much more readily than from a vinylic position, thus placing the thiophenoxy group at the allylic position.

Later fractions contained a mixture of **16** and its stereoisomer **17**. Compound **17** was formed from **16** by heating with iodine in chloroform solution. Substantial differences exist between the chemical shifts of the isopropylidene methyl groups in **16** and **17**. In **17** these methyls are shielded (δ 1.34 and 1.79) relative to those in **16** (δ 1.86 and 1.90). Compound **17** is a true product of the reaction and is not formed by isomerization during chromatography as indicated by the presence of peaks of **17** in the NMR spectrum of the reaction product mixture.

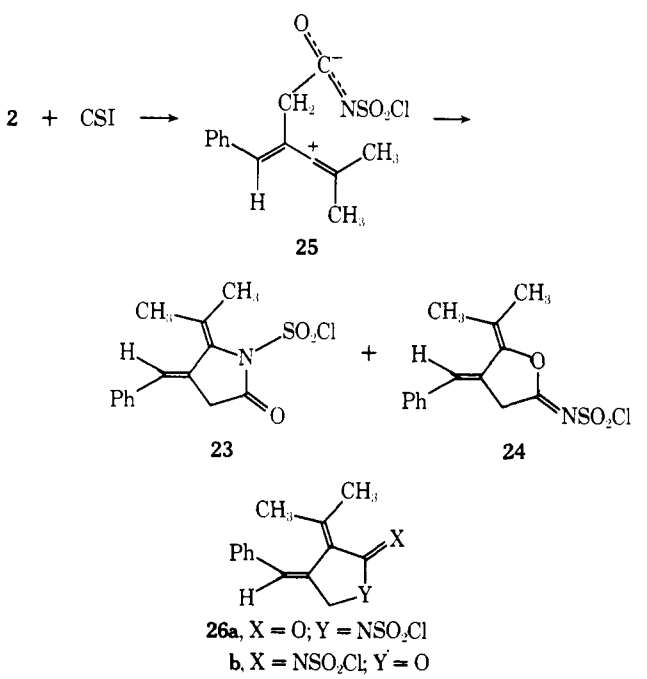
Late fractions from the column contained ketone **18**. The structure of **18** was indicated by its ir ($\nu_{C=O}$ 1663 cm^{-1} and $\nu_{=CH_2}$ 913 cm^{-1}) and NMR spectra [vinyl methyl double doublet (δ 1.96, J = 1.5, 1.0 Hz), ketone methyl singlet (δ 2.39), vinyl methylene multiplets (δ 4.97 and 5.32), and 6 H multiplet (δ 7.30)]. The presence of the benzylidene group was further demonstrated by the formation of benzaldehyde on ozonolysis of **18**. The presence of a methyl ketone was also indicated by the mass spectrum of **18**, in which the only dominant mode of fragmentation of the molecular ion was by loss of methyl radical.

Comparison of the NMR spectrum of **18** with that of the original product mixture clearly showed that **18** was not a primary product, and that it must have been formed by decomposition of one, or more, of the primary reaction products on the silica gel column. Peaks present in the NMR spectrum of the reaction mixture, but not present in the products eluted from the column, include vinyl methyl singlets at δ 1.91 and 1.94, an AB double doublet (δ 3.35 and 3.46, J = 12.0 Hz), terminal methylene hydrogen multiplets (δ 4.88 and 4.98), and a benzylic vinyl hydrogen multiplet (δ 6.09). The presence of an AB system suggests the presence of a $-CH_2X$ group in a structure containing a chiral carbon. The only possible type of structure fulfilling these requirements is one in which the cyclopropane ring is retained. We believe that structure **19** fulfills these requirements, having two vinyl methyls and the diastereotopic methylene hydrogens. The formation of **19** can be visualized as involving chloride ion attack on the intermediate episulfonium ion **21**, instead of **21** undergoing ring opening to **22** which then results in the formation of **16** and **17**. On the surface of the silica gel **19** can give **20** directly, or it can revert to the epi-

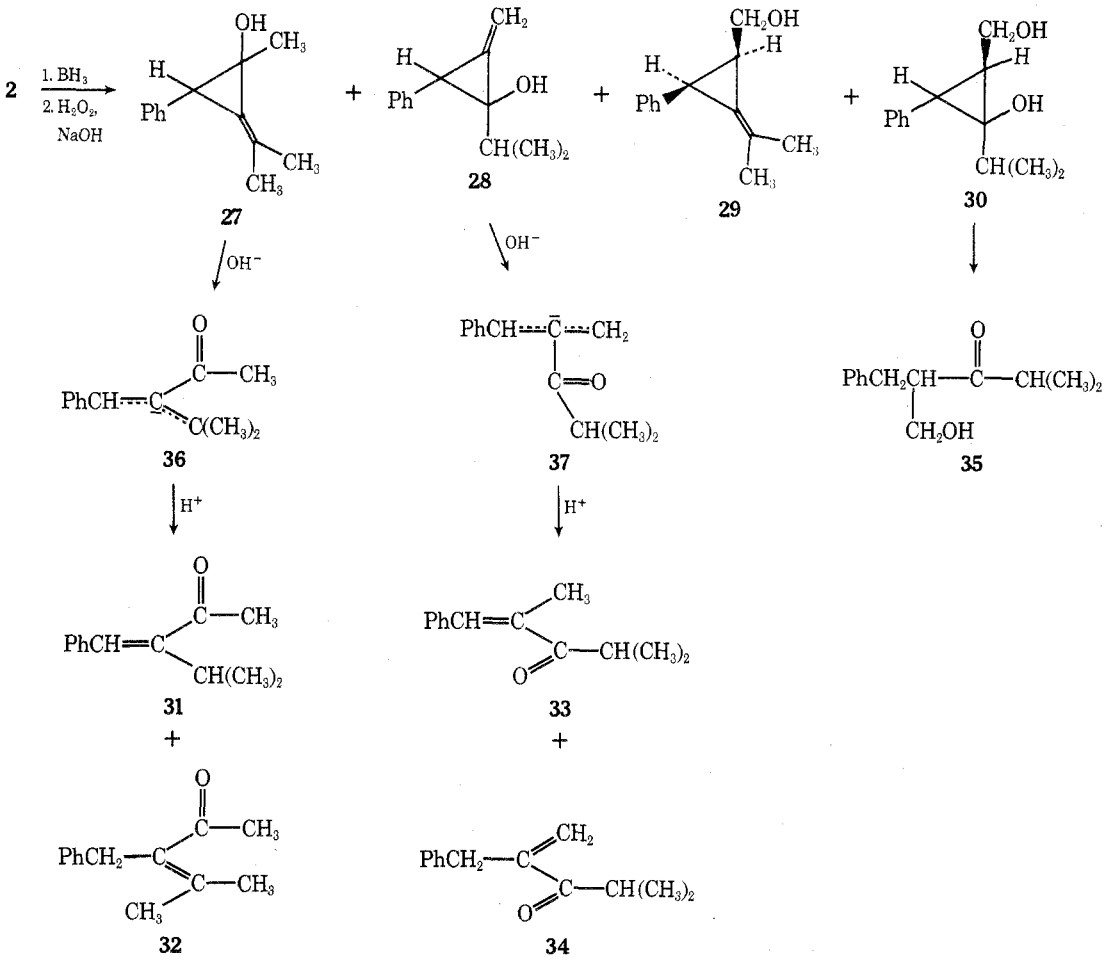


sulfonium ion **21**, which then rearranges to **20** and then hydrolyzes to the ketone **18**. The other product indicated to be present in the original reaction mixture is believed to be **20**, formed in the original reaction as indicated and hydrolyzed during chromatography.

Reaction of 2 with Chlorosulfonyl Isocyanate. The reaction of chlorosulfonyl isocyanate (CSI) with **2** in methylene chloride solution resulted in the clean formation of two products in a 78:22 ratio (by NMR). Attempted separation and purification by chromatography on Florisil (oven dried at 110° for 48 hr) resulted in complete decomposition. Attempted separation by low-temperature crystallization also met with failure. Attempted hydrolysis followed by isolation of the hydrolysis products also was not successful. (The extreme reactivity and sensitivity of the adducts must be due to the presence of the vinyl ester and amide functions. This is in contrast to the stability of the isomeric adducts **26a** and **26b** formed in the reaction of **1** with CSI which can be successfully chromatographed and hydrolyzed.)[13] Although neither product could be isolated in pure form, nor could any derivative thereof, the structures of the two adducts could be easily assigned from the NMR and ir spectra of the mixture. The major product is characterized by a peak in the ir at 1740 cm^{-1} typical for the five membered ring *N*-chlorosulfonyllactam in **23**. The NMR spectrum of **23** shows methyl singlets at δ 2.02 and 2.16, a methylene doublet at δ 3.59 (J = 2.3 Hz), a vinyl hydrogen triplet at δ 6.81 (J = 2.3 Hz), and a multiplet at δ 7.33. The minor adduct **24** ($\nu_{C=N}$ 1595 cm^{-1}) shows methyl singlets at δ 2.06 and 2.22, a methylene doublet at δ 4.20 (J = 2.6 Hz), a triplet at δ 6.50, and a multiplet at δ 7.33. The stereochemistry about the benzylidene group in **23** and **24** is assigned on the basis of mechanistic arguments and the NMR chemical shifts of the isopropylidene methyl groups. The "inside" methyl groups of **26**[13] and similar adducts[13,14] are highly shielded (δ 1.54 and 1.47, respectively, in **26a**) by the "inside" phenyl group. In the isomeric adducts with "outside" phenyl groups, the shielding effect of the phenyl group is absent and both methyls appear in the δ 2.0–2.3 region.[13,14] The absence of a highly shielded methyl group in **23** and **24** is consistent with the indicated stereochemistry. From a mechanistic point of view, in the opening of the three-membered ring during electrophilic attack on the $=CH_2$, the phenyl group moves toward the $-CH_2-$ group instead of toward the more sterically bulky isopropylidene group to produce the dipolar intermediate **25**, which then collapses to **23** and **24**. No evidence was obtained regarding the possible intermediate formation of a β-lactam derivative which would then undergo ring opening to the dipolar intermediate **25**.



Hydroboration of 2. The hydroboration of **2** (3:1 mole ratio of **2**:BH_3) resulted in the formation of a complex mixture of compounds which was partially separated by chromatography on Florisil. Early fractions contained a mixture of the unsaturated ketones **32**, **33**, and **34** in a 35:27:38 ratio (by NMR). The infrared spectrum of the mixture showed characteristic bands for an α,β-unsaturated ketone (1677 cm^{-1}), terminal methylene (923 cm^{-1}), and trisubstituted double bond (870 cm^{-1}). The mass spectrum showed

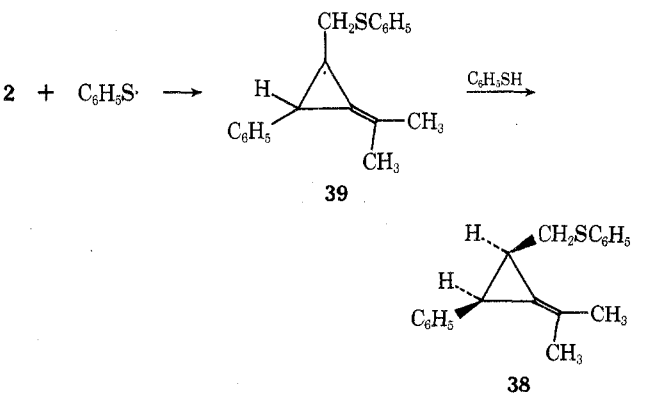


major peaks for loss of methyl and isopropyl radicals from the molecular ions. The NMR spectrum of the mixture was complex, but could be interpreted in terms of specific structures on the basis of relative intensities and peak positions (see Experimental Section for the NMR data). Compound **31** does not appear to have been formed in any substantial amount (i.e., <5%). The unsaturated ketones are formed from the cyclopropanols **27** and **28** which undergo base-catalyzed ring opening[15] to the anions **36** and **37** during the basic oxidation of the intermediate organoboranes.

Intermediate fractions contained the major product **29**. The NMR spectrum of **29** displayed two broadened vinyl methyl singlets at δ 1.88 and 1.92 (long-range coupled to the two cyclopropyl ring hydrogens), a broad multiplet at δ ~2.15, a highly broadened doublet at δ 2.90 with J = 9.2 Hz (the benzylic hydrogen), an AB portion of an ABX system with δ_A 3.52, δ_B 3.19, J_{AB} = 11.6, J_{AX} = 5.6, and J_{BX} = 8.0 Hz, and a singlet at δ 7.13. That structure **29** has the cis stereochemistry is indicated by the large coupling constant (9.2 Hz) between the cyclopropyl hydrogens.[16] This is consistent with the approach of the borane from the least hindered side of the ring opposite the phenyl group as is observed in other hydroboration reactions.[17]

The final fraction isolated possessed both hydroxyl (3430 cm^{-1}) and saturated ketone (1705 cm^{-1}) bands in the infrared spectrum. The structure is assigned as **35** based on its very characteristic NMR spectrum. The diastereotopically related methyls appear as doublets at δ 0.87 and 1.02 with the isopropyl methine hydrogen appearing as a septet at δ 2.47 (J = 6.7 Hz). The diastereotopic benzyl hydrogens appear as two double doublets at δ 2.76 (J = 10.7 and 4.9 Hz) and 2.84 (J = 10.7 and 3.9 Hz). The carbinol methylene hydrogens appear as a tightly coupled AB portion (δ ~3.7) of an ABX system (δ_X ~3.13). Compound **35** is derived from the cyclopropanol **30**, a dihydroboration product, under the basic conditions of the oxidation of the intermediate organoborane.

Addition of Thiophenol to 2. Thiophenol undergoes rapid addition to **2** in the absence of solvent or in benzene solution at room temperature via what we believe to be a radical-chain addition to produce a single product **38**. The



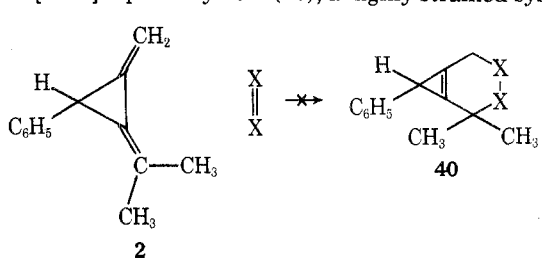
NMR spectrum of the product shows a one-hydrogen doublet (δ 3.11) with J = 6.7 Hz. The chemical shift and the coupling constant indicate a cis relationship between the cyclopropyl hydrogens.[16] No vinyl or saturated methyl resonances (<5%) were present in the NMR spectrum which would be characteristic of an addition product formed by addition to the isopropylidene double bond.

The cis stereochemistry in **38** must be due to steric effects present in the transition state for abstraction of the

hydrogen atom from thiophenol by the intermediate radical **39**, thiophenol approaching **39** from the least hindered side of the three-membered ring opposite the phenyl group. The structure of the intermediate radical **39**, however, is not indicated by the overall stereochemical outcome of the reaction. A planar radical center would benefit from resonance interaction with the isopropylidene group but suffers from ring bond-angle strain. For a nonplanar radical center it would be the opposite. Should the radical center be nonplanar, inversion between nonplanar forms must be reasonably facile in that as initially formed the nonplanar radical should have the phenyl and phenylthiomethyl functions trans, whereas in the final product the two groups are cis.

General Chemical Properties of 2. The foregoing sections indicate that the diene chromophore of **2** undergoes electrophilic and radical attack only at the exocyclic methylene function to produce both ring-opened and ring-retained products. The greater tendency to form ring-retained products with **2** relative to **1** apparently is due to the more difficult cleavage of a vinyl ring bond in the cation derived from **2** relative to the allylic bond in the cation derived from **1**.[3] The reactivity of **2** and **1** are comparable as indicated by the consumption of approximately equal quantities of **2** and **1** when a mixture is treated with a limited quantity of CSI.

Although **2** contains a conjugated diene chromophore, **2** does not react with dienophiles such as maleic anhydride even under prolonged forcing conditions. Treatment with the very reactive dienophile 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) results in reaction; however, we have not been successful in purifying or characterizing the adduct.[18] In competition experiments **2** and **1** exhibit comparable reactivities with PTAD. The reactivity of **1**, however, is ~320 times less than that of *trans*-1,3-pentadiene,[19] which, in turn, is much less reactive than 1,3-dienes which are permanently constrained in a cisoid conformation (e.g., cyclopentadiene). The lack of reactivity of **2** toward cycloaddition can be attributed to any, or all, of three factors. (1) The diene chromophore of **2** is undoubtedly twisted, which decreases the overlap between the double bonds, which thus lowers the energy of the highest occupied molecular orbital. (2) Because of the geometry of the three-membered ring the termini of the diene chromophore are separated by a greater distance than in the normal cisoid dienes and thus the dieneophile has more difficulty in spanning that distance in the transition state. (3) The product is a $\Delta^{1,6}$-bicyclo[4.1.0]heptene system (**40**), a highly strained system.



2 **40**

Experimental Section

Acetolysis of 2. A solution of 0.7118 g of **2** in 1 ml of acetic acid containing 10 mg of *p*-toluenesulfonic acid was heated in a sealed NMR tube at 115° for 23 hr, at which time NMR analysis indicated complete consumption of **2** with formation of only **3**, **4**, and **5** in a ratio of 3:6:91. The reaction mixture was poured into 10 ml of cold water and was immediately extracted with ether. The extract was washed with 5% sodium bicarbonate until free of acid and dried ($MgSO_4$). The solvent was removed and the residue was chromatographed on a 2 × 36 cm Florisil column.

Elution with 25% dichloromethane–hexane gave ~70 mg of a mixture of **3** and **4**: ir 1736 and 1665 cm^{-1}; NMR of **3** ($CDCl_3$) δ 1.56 (s, 3 H), 1.96 and 2.06 (d's, J = 1.1 Hz, 3 H each), 2.18 (s, 3 H), and 7.24 (s, 5 H); NMR of **4** δ 1.31 (d, J = 7.3 Hz, 6 H), 2.05 (d, J = 1.3, 3 H), 2.27 (m, 1 H), 6.36 (m, 1 H), and 7.3 (m, 5 H).

Further elution with 25% dichloromethane–hexane gave fractions containing **4** and **5** followed by fractions containing pure **5**: ir 1755 cm^{-1}; NMR ($CDCl_3$) δ 1.67 and 1.87 (s's, 3 H each), 1.94 (d, J = 1.7 Hz, 3 H), 2.15 (s, 3 H), 6.58 (m, 1 H), and 7.29 (m, 5 H); mass spectrum $M^{\cdot+}$ 230.1330 (calcd for $C_{15}H_{18}O_2$, 230.1306).

Iodine-Catalyzed Isomerization of 5. A solution of 37 mg of **5** in 0.5 ml of deuteriochloroform containing one small crystal of iodine was sealed in an NMR tube and was heated at 95°. The NMR spectrum was recorded periodically. After heating for 168 hr conversion of **5** to **6** had progressed to ~80% completion: NMR of **6** δ 1.06 and 1.17 (s's, 3 H each), 2.00 (d, J = 1.9 Hz, 3 H), 2.18 (s, 3 H), 7.3 (m, 5 H), and 7.56 (m, 1 H).

Acetoxymercuration–Demercuration of 2. To a stirred solution of 0.0949 g (0.56 mmol) of **2** in 10 ml of acetic acid and 10 ml of tetrahydrofuran was added 0.1842 g (0.58 mmol) of mercuric acetate at 0°. The reaction mixture was stirred at 0° for 75 min and then at 25° for 20 min. A fine, white precipitate formed during the reaction. A solution of 0.0874 g (2.3 mmol) sodium borohydride in 10 ml of 10% sodium hydroxide was slowly added. The reaction mixture was stirred for 45 min and the liquid layer was decanted from the mercury into 20 ml of water. The resulting mixture was extracted twice with ether. The ether extract was washed with water and 5% sodium bicarbonate and dried ($MgSO_4$). Removal of the ether under reduced pressure gave 0.1207 g of material.

Chromatography on silica gel produced two fractions. Elution with 50% dichloromethane–hexane gave 32.5 mg of **13** as a colorless, viscous oil: ir 1739 and 909 cm^{-1}; NMR ($CDCl_3$) δ 1.71 (overlapping d's, J = 1.3 Hz, 6 H), 2.10 (s, 3 H), 5.02, 5.35, 5.47, and 6.20 (bs, 1 H each), and 7.28 (s, 5 H); mass spectrum $M^{\cdot+}$ 230.1316 (calcd for $C_{15}H_{18}O_2$, 230.1306), major peaks at m/e 215 ($M^{\cdot+}$ – $CH_3\cdot$), 188 ($M^{\cdot+}$ – $H_2C{=}C{=}O$), 160, 145, 135, 133, 131, 97.

Elution with 50–75% dichloromethane–hexane gave 91.0 mg of a white solid identified as a bis(acetoxyalkyl)mercury: mass spectrum $M^{\cdot+}$ series of peaks m/e 655–660 of relative intensities corresponding to the isotopic distribution of mercury (calcd for $C_{30}H_{34}O_4{}^{200}Hg$, 658); NMR ($CDCl_3$) δ 1.6 and 1.9 (bs's), 2.18 (s), 5.09, 5.32, and 6.62 (bs's), and 7.27 (m).

Reaction of 2 with Benzenesulfenyl Chloride. To a stirred solution of 0.1661 g (0.98 mmol) of **2** in 10 ml of dichloromethane containing ~50 mg of calcium carbonate at −70° was added 0.1401 g (0.97 mmol) of benzenesulfenyl chloride in 10 ml of dichloromethane. The reaction mixture was stirred at −60° for 30 min and was then allowed to come to room temperature and stirred for 25 min, producing a yellow solution. The reaction mixture was filtered and the solvent was removed under reduced pressure. The NMR of the reaction product was very complex, showing peaks in the vinyl methyl region at δ 1.34, 1.79, 1.86, 1.88, 1.90, 1.91, and 1.94. Characteristic lower field peaks were at δ 3.35 (d, J = 12.0 Hz), 3.46 (d, J = 12.0 Hz), 4.02 (s), 4.88 (m), 4.98 (m), 6.09 (bs), 6.62 (bs), and 7.3 (m).

Chromatography (78% total recovery based on **2**) on a 1 × 36 cm column of heat-treated silica gel (110° for 48 hr) resulted in immediate blackening of the top of the column upon adding the reaction mixture. Elution with hexane gave 10.5 mg of diphenyl disulfide (mp 55–56°) followed by 45.8 mg of **16** as a pale-yellow, viscous liquid: NMR ($CDCl_3$) δ 1.86 and 1.90 (s, 3 H each), 4.02 (s, 2 H), 6.62 (s, 1 H), 7.27 and 7.36 (s, 5 H each); mass spectrum $M^{\cdot+}$ 314.0880 (calcd for $C_{19}H_{19}ClS$, 314.0896), major peaks at m/e 316 (^{37}Cl containing $M^{\cdot+}$), 314 (^{35}Cl containing $M^{\cdot+}$), 278 ($M^{\cdot+}$ – HCl, low intensity), 207 (^{37}Cl containing $M^{\cdot+}$ – $C_6H_5S\cdot$), 205 (^{35}Cl containing $M^{\cdot+}$ – $C_6H_5S\cdot$).

Further elution with hexane gave 12 mg of a 1:1 mixture of **16** and **17**, the latter identified by NMR spectral comparison with **17** prepared by isomerization of **16** (vide ante).

Elution with 50–100% chloroform–hexane gave 109 mg of **18** as a dark yellow, viscous material: ir (neat) 1663 and 913 cm^{-1}; NMR ($CDCl_3$) δ 1.96 (dd, J = 1.5, 1.0 Hz, 3 H), 2.39 (s, 3 H), 4.97 and 5.32 (m's, 1 H each) and 7.3 (m, 6 H); mass spectrum $M^{\cdot+}$ 186.1042 (calcd for $C_{13}H_{14}O$, 186.1045), major peaks at m/e 186, 171, 143, 128, 115.

Iodine-Catalyzed Isomerization of 16. A solution of 8 mg of **16** in 1 ml of deuteriochloroform containing two small crystals of iodine in a sealed NMR tube was heated in a sand bath at 95–100°. The NMR spectrum was recorded periodically. After about 30 hr an equilibrium mixture of **16** and **17** containing ~77% of the latter was obtained. The NMR spectrum of **17** showed peaks at δ 1.33 and 1.78 (s, 3 H each), 3.91 (s, 2 H), 6.94 (s, 1 H), and 7.27 (m, 5 H).

Reaction of 2 with Chlorosulfonyl Isocyanate. To a stirred

solution of 0.1259 g (0.74 mmol) of **2** in 15 ml of dichloromethane at 0° was added 0.1056 g (0.74 mmol) of chlorosulfonyl isocyanate in 15 ml of dichloromethane. The reaction mixture was stirred at 0° for 15 min and then allowed to come to 25° for an additional 35 min, resulting in a medium-red solution. The solvent was removed under reduced pressure, giving a red, viscous liquid containing **22** and **23** in an 87:13 ratio: ir 1740 and 1595 cm^{-1}; NMR ($CDCl_3$) of **22** δ 2.02 and 2.16 (s, relative intensities 3 H), 3.59 (d, J = 2.3 Hz, 2 H), 6.81 (t, J = 2.3 Hz, 1 H), and 7.33 (m, 5 H); **23** δ 2.06 and 2.22 (s, 3 H each), 4.20 (d, J = 2.6 Hz, 2 H), 6.50 (t, J = 2.6 Hz, 1 H), and 7.33 (m, 5 H).

Attempted chromatographic separation of **22** and **23** on dried Florisil resulted in decomposition of the compounds. Small amounts of several materials were eluted from the column; however, the NMR spectra of all of the fractions contained peaks *not present* in the original reaction mixture. The fractions eluted from the column were not further characterized.

Attempted hydrolysis in pH 5–7 buffer did not yield characterizable products.

Hydroboration of 2. To 1.3 ml of 0.7 M borane in tetrahydrofuran (0.9 mmol) at 0° was added 0.471 g (2.8 mmol) of **2.** The reaction mixture was stirred for 20 min whereupon the mixture was allowed to come to 25° and was stirred for an additional 15 min. The reaction mixture was cooled to 0° and 10 ml of water was added followed by 2.5 ml of 3 N sodium hydroxide and 2.5 ml of 30% hydrogen peroxide. After stirring for 30 min the mixture was extracted twice with ether. The extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 45 cm Florisil column set in benzene. Elution with benzene gave 99 mg of unreacted **2.**

Further elution with benzene gave 76 mg of a mixture of **32, 33,** and **34** as a yellow liquid: ir 1677, 923, and 870 cm^{-1}; mass spectrum $M^{\cdot+}$ 188.1198 (calcd for $C_{13}H_{16}O$, 188.1201), major peaks m/e 173 ($M^{\cdot+} - CH_3\cdot$) and 145 [$M^{\cdot+} - \cdot CH(CH_3)_2$]. The peaks in the NMR spectrum ($CDCl_3$) could be assigned to the individual components by their relative intensities and positions: **32,** $=C(CH_3)$ singlets at δ 1.97 and 2.06, $-COCH_3$ singlet at 2.37, $C_6H_5CH_2-$ singlet at 3.67, and C_6H_5- at ~7.25; **33,** $-CH(CH_3)_2$ doublet at δ 1.14, $=CCH_3$ broad singlet at 2.03, $-CH(CH_3)_2$ septet at 3.34 (J = 6.7 Hz), $=CH-$ broad singlet at 6.54, and C_6H_5- multiplet at ~7.3; **34,** $-CH(CH_3)_2$ doublet at δ 1.15, $-CH(CH_3)_2$ septet at 2.84 (J = 6.7 Hz), $C_6H_5CH_2-$ broad singlet at 3.57, $=CH_2$ broad singlets at 5.57 and 5.97, and C_6H_5- at ~7.30.

Elution with 10% ether–benzene gave 210 mg of **29** as a viscous, pale yellow liquid: ir ν_{OH} 3670 and 3510 cm^{-1} (nonbonded and bonded O–H); mass spectrum $M^{\cdot+}$ 188.1197 (calcd for $C_{13}H_{16}O$, 188.1201), major peaks m/e 170 ($M^{\cdot+} - H_2O$), 157 ($M^{\cdot+} - \cdot CH_2OH$), 155, 145, 143, 142, 141, 129, *128,* 127, 117, 115; NMR (CCl_4) $=C(CH_3)_2$ broad singlets at δ 1.88 and 1.92, $>CHCH_2OH$ broad multiplet at 2.15 (J = 9.2 Hz), $C_6H_5CH<$ very broad doublet at 2.90 (J = 9.2 Hz), $-CH_AH_BOH$ double doublet at 3.19 (J = 11.6 and 8.0 Hz), $-CH_AH_BOH$ double doublet at 3.52 (J = 11.6 and 5.6 Hz), and C_6H_5- at 7.13.

Elution with 25% ether–benzene gave 57 mg of **35** as a low-melting solid: ir ($CHCl_3$) ν_{OH} 3430 and $\nu_{C=O}$ 1705 cm^{-1}; mass spectrum $M^{\cdot+}$ 206.1310 (calcd for $C_{13}H_{18}O_2$, 206.1307), major peaks m/e 188 ($M^{\cdot+} - H_2O$), 176 ($M^{\cdot+} - CH_2OH$ by a McLafferty-type rearrangement), 175 ($M^{\cdot+} - \cdot CH_2OH$), 145, 133, 117, 105, *91,* and 77; NMR ($CDCl_3$) $-CH(CH_3)(CH_3)$ doublets at δ 0.87 and 1.02 (J = 6.7 Hz), $-CH(CH_3)_2$ septet at 2.47 (J = 6.7 Hz), $-CH_AH_BC_6H_5$ doublets at 2.76 (J = 10.7 and 4.9 Hz) and 2.84 (J = 10.7 and 3.9 Hz), $>CH-$ multiplet at 3.13, $HOCH_AH_BCH<$ multiplet at ~3.7, and C_6H_5- multiplet at 7.3.

Reaction of 2 with Thiophenol. The addition of an equimolar quantity of **2** to thiophenol, either neat or dissolved in benzene (~1 M), open to the laboratory light and atmosphere results in rapid reaction (~30 min) to give a viscous, pale-yellow liquid (after removal of the benzene if carried out in benzene solution). The NMR spectrum of the crude product ($CDCl_3$) showed broad singlets at δ 1.79 and 1.94 (3 H each), a very broad multiplet at 2.39 (1 H), a multiplet at ~2.86 (2 H), a doublet at 3.11 (J = 6.7 Hz, 1 H), and a multiplet at 7.23 (10 H). Chromatography on silica gel (elution with 20% benzene–hexane) gave a single fraction with an NMR spectrum identical with that of the crude product. Mass spectrum $M^{\cdot+}$ 280.1286 (calcd for $C_{19}H_{20}S$, 280.1286), only major fragmentation peak at m/e 171 ($M^{\cdot+} - C_6H_5S\cdot$).

Registry No.—**2,** 30896-86-7; **3,** 57443-49-9; **4,** 57443-50-2; **5,** 57443-51-3; **6,** 57443-52-4; **13,** 57553-35-3; **16,** 57443-53-5; **17,** 57443-54-6; **18,** 57443-55-7; **22,** 57443-56-8; **23,** 57443-57-9; **29,** 57443-58-0; **32,** 14771-80-3; **33,** 57443-59-1; **34,** 57443-60-4; **35,** 57443-62-6; **38,** 57443-61-5; acetic acid, 64-19-7; mercuric acetate, 1600-27-7; e benzenesulfenyl chloride, 931-59-9; diphenyl disulfide, 882-33-7; chlorosulfonyl isocyanate, 1189-71-5; thiophenol, 108-98-5.

References and Notes

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