# New Synthetic Reactions. Synthesis of Cyclobutanes, Cyclobutenes, and Cyclobutanones. Applications in Geminal Alkylation

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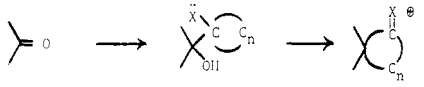
**Abstract:** The chemistry of the adducts of 1-lithiocyclopropyl phenyl sulfide to aldehydes and ketones is reported. Treatment of these compounds with *p*-toluenesulfonic acid under anhydrous conditions or the Burgess reagent yields 1-phenylthiocyclobutenes, which may be hydrolyzed to cyclobutanones, desulfurized to cyclobutanes, or thermalized to dienes. Rearrangement to cyclobutanones can be achieved under four sets of conditions: (1) aqueous fluoboric acid–ether, (2) stannic chloride–methylene chloride, (3) *p*-toluenesulfonic acid in benzene saturated with water, and (4) Meerwein's reagent. Alternatively, the *O*-phenylene phosphite ester of these alcohols, generated by directly quenching the reaction of 1-lithiocyclopropyl phenyl sulfide and the carbonyl compound with *O*-phenylene phosphorochlorodite, rearranges to the cyclobutanone in refluxing aqueous THF in the presence of an acid catalyst. The stereochemistry of this rearrangement is delineated and complements that obtained by the cyclobutanone annelation with diphenylsulfonium cyclopropylide. The approach allows cyclobutanes, cyclobutenes, and cyclobutanones to be generated from both saturated and $\alpha,\beta$-unsaturated carbonyl partners. Application of this approach for geminal alkylation to the total synthesis of the constituent of the sex pheromone of the boll weevil, grandisol, is reported.

The replacement of the two C–O bonds of a carbonyl group by two C–C bonds constitutes a simple geminal alkylation, a synthetically difficult transformation especially with stereochemical control.[1] The use of heteroatom directed ring expansions,[2] as illustrated in eq 1, is a potential solution to the

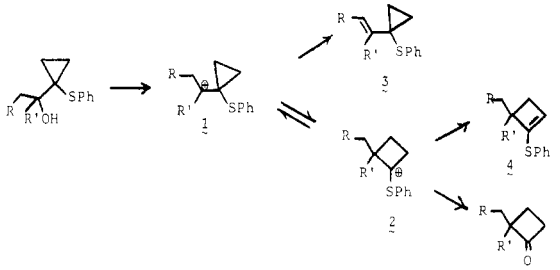


(1)

problem if stereochemical control accompanies this process. Using small rings (i.e., $n = 2$) has the potential of utilizing the strain energy as a driving force for further molecular modification. In previous papers, we have developed this concept utilizing diphenylsulfonium cyclopropylide as the reagent[3] to achieve the overall transformation represented by eq 1 via oxaspiropentane intermediates.[4,5] The limitations of this reagent have been noted. In the accompanying manuscript, we developed a comparable reagent, 1-lithiocyclopropyl phenyl sulfide, and reported its facile addition to carbonyl groups.[6] In this paper, we wish to report that these adducts serve as useful intermediates for the synthesis of cyclobutanes, cyclobutenes, and cyclobutanones. We also wish to report that this stereoselective geminal alkylation procedure permits a synthesis of one constituent of the sex pheromone of the boll weevil.[7]

## Results and Discussion

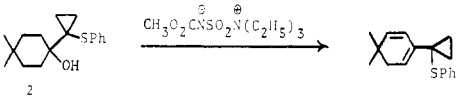
**Direct Preparation of Cyclobutanone Enol Thioethers by Ring Expansion.** Considering the possible pathway for the ring expansion (eq 2), the synthesis of either cyclobutanones or the



(2)

corresponding enolthioethers can be envisioned. In particular, in the absence of nucleophiles, deprotonation of the intermediate **2** should occur. Since the difference in strain energies among cyclobutane, cyclobutene, and cyclopropane is small,[8] depending upon substituents, the deprotonation of the first formed carbonium ion **1** to form **3** could compete with the desired formation of cyclobutene **4.**

Two methods were mainly employed. The first involved treatment of the alcohols with anhydrous *p*-toluenesulfonic acid in refluxing benzene. It was successful as shown in Table I, entries 3, 7, 8, and 10. Two problems limited this method. First, water removal is relatively inefficient. In the case of cyclopropylcarbinol **5** (Table I, entry 2) only cyclobutanone was obtained regardless of the efforts to suppress hydrolysis by incorporating various water traps like molecular sieves, triethyl orthoformate, etc. Second, the products do show some sensitivity to acid-catalyzed decomposition under the reaction conditions. A more general approach appears to be the use of the Burgess reagent,[9] (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester as illustrated in Table I, entries 1, 2, 4, 6, 7, and 9. The major competing process (entries 2 and 6) appears to be simple dehydration without rearrangement (see eq 2). The ratio of the two types of products appear to depend upon the stability of the initial carbonium ion and the strain energy of the olefin. Thus, in the case of primary or secondary cyclopropylcarbinols, smooth rearrangement to the desired cyclobutene thioether occurred. On the other hand, tertiary cyclopropylcarbinols gave mixtures. In the case of a tertiary allylic cyclopropylcarbinol, eq 2, only simple dehydration occurred.[10] It is interesting to note that

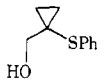
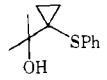
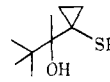
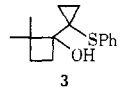
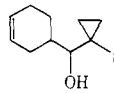
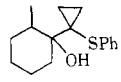
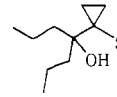
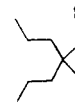
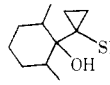
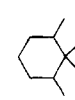
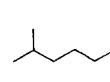
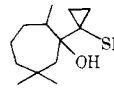
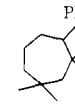


alcohol **3** (Table I, entry 4) showed only the dehydrative rearrangement product. In this case, the competition of deprotonation of the initial carbonium ion compared to rearrangement is eliminated as a result of forming a cyclobutene double bond.

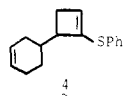
In entries 5 and 7 two regioisomers of the product are possible. The major product in both cases (>90%) is the thermodynamically more stable tetrasubstituted double bond isomer as depicted in Table I. The presence of the alternative isomers **4** and **5** was indicated by a small peak (<5%) at $\delta$ 5.80 and 5.70, respectively.

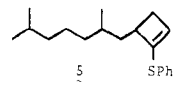
The stereochemistry of these rearrangement products has

Table I. 1-Phenylthiocyclobutene Synthesis

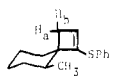
| Entry | Alcohol | Method | Product | % yield |
|---|---|---|---|---|
| 1 |  | $CH_3O_2CN^-SO_2N^+(C_2H_5)_3$ |  **6** | 47 |
| 2 |  **5** | TsOH<br>$SOCl_2$<br>TFAA/TFA<br>$CH_3O_2CN^-SO_2N^+(C_2H_5)_3$[a] |  **7** | 0<br>0<br>11<br>39 |
| 3 |  | TsOH |  **8** | 95 |
| 4 |  **3** | $CH_3O_2CN^-SO_2N^+(C_2H_5)_3$ |  **9** | 92 |
| 5 |  | $SOCl_2$[d] |  **10** | 94 |
| 6 |  | $CH_3O_2CN^-SO_2N^+(C_2H_5)_3$ |  **11** | 37 |
| 7 |  | TsOH<br>$CH_3O_2CN^-SO_2N^+(C_2H_5)_3$[b]<br>$SOCl_2$<br>HF |  **12** | 43<br>22<br>0<br>5 |
| 8 |  | TsOH |  | 95 |
| 9 |  | $CH_3O_2CN^-SO_2N^+(C_2H_5)_3$<br>$SOCl_2$ |  **13** | 93<br>ND[c] |
| 10 |  | TsOH<br>$CH_3O_2CN^-SO_2N^+(C_2H_5)_3$<br>HF |  **14** | 40<br>18<br>0 |

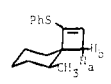
[a] A 40% yield of 1-(2'-propenyl)-1-phenylthiocyclopropane was also obtained. [b] A 24% yield of 1-(4'-hept-3'-enyl)-1-phenylthiocyclopropane was also obtained. [c] Yield not quantitatively determined, but greater than 50%. [d] Performed in refluxing pyridine.

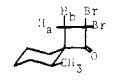

**4**

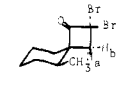

**5**

been examined in the case of **11** and **14.** The NMR spectrum of **11** shows $\delta$ 5.51 (br s, 1 H), 2.28 (d, $J$ = 35 Hz, 1 H), and 0.88 (d, $J$ = 7 Hz, 3 H) for the minor isomer and $\delta$ 5.37 (br s, 1 H), 2.23 (d, $J$ = 13 Hz, 1 H) and 1.00 (d, $J$ = 7 Hz, 3 H) for the major isomer assigned to the vinyl proton, $H_a$, and the methyl group protons, respectively. $H_b$ appears virtually coincident for the two isomers at $\delta$ 1.87. Assuming the conformations depicted for **11***E* and **11***Z* represent the most stable


**11E**

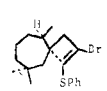

**11Z**

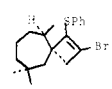

**15E**

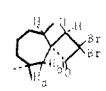

**15Z**

ones, it would be anticipated that the methyl group in **11***E* would be more deshielded by the phenylthio group and $H_a$ would exhibit the greater steric compression and therefore deshielding in **11***Z*. Thus, **11***E* and **11***Z* represent major and minor isomers (ratio 2:1), respectively. A similar trend is seen in the products of halogenative hydrolysis, **15***E* and **15***Z* (vide supra), in which the major product shows absorptions for $H_a$, $H_b$, and the methyl group protons at $\delta$ 3.16 (d, $J$ = 14 Hz, 1 H), 2.84 (d, $J$ = 14 Hz, 1 H), and 1.04 (d, $J$ = 6.5 Hz, 3 H) in the major isomer and at $\delta$ 3.10 (d, $J$ = 14 Hz, 1 H), 2.86 (d, $J$ = 14 Hz, 1 H), and 0.90 (d, $J$ = 65 Hz, 3 H) in the minor isomer.

Higher stereoselectivity was seen in the rearrangement product **14.** Its NMR spectrum showed only one absorption for the vinyl proton ($\delta$ 5.35, br s), the allylic methylene protons (2.28, br s), the protons of each of the two geminal methyl groups ($\delta$ 1.01 and 0.94), and the protons of the secondary methyl group (0.92, d, $J$ = 7 Hz). In dibromocyclobutanone **16** derived from **14,** the NMR shows mainly one isomer [cyclobutyl methylene protons at $\delta$ 3.4, $H_a$ and $H_b$ at 2.12 and 1.80 ($J_{ab}$ = 15 Hz), 1.0f (s, 3 H), 0.87 (d, $J$ = 7 Hz, 3 H), and 0.86 (s, 3 H)] with the hint of a second isomer by the presence of additional signals in the methyl group region. On the basis of analogy to subsequent rearrangements, the stereochemistry is assigned as **14***E* and **16***E*, respectively.


**14E**


**14Z**


**16E**

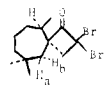
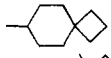
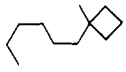

**16Z**

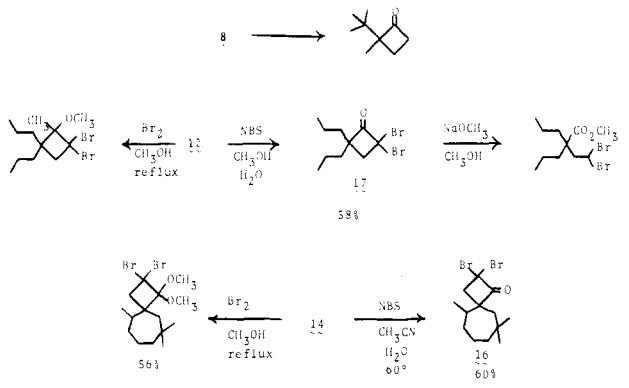
Table II. Cyclobutane Annelation

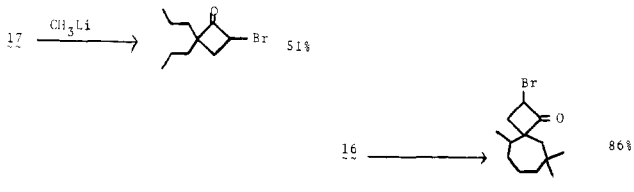
| Enolthioether | Desulfurization agent | Cyclobutane | % yield |
|---|---|---|---|
| 11 | Raney nickel |  | 82 |
| 12 | Raney nickel<br>Nickel boride |  | 94<br>85 |
| 14 | Raney nickel |  | 41[a] |
| 18 | Raney nickel |  | 38[a] |
| 19 | Raney nickel |  | 61 |

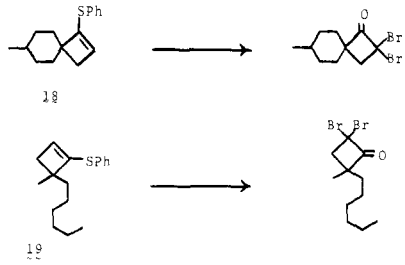
[a] The lower yields in these runs is apparently due to mechanical losses during workup. It subsequently was found that use of isopentane for extractions facilitated the isolation of these volatile hydrocarbons. This modified workup was not employed in these cases.

It is interesting to note that rearrangement occurred upon treatment of these adducts with the Burgess reagent. This reagent has been recommended for dehydration without rearrangement in the case of cyclopropylcarbinols.[8] The presence of the sulfur substituent clearly enhances the propensity for rearrangement sufficiently so that rearrangement competes effectively with or even completely dominates over the process of simple dehydration.

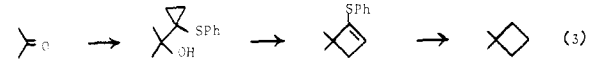
The compounds were characterized by their spectral properties (see Experimental Section) and chemical transformations. As an enol thioether they can be hydrolyzed to their corresponding ketones as was done for **8.** Halogenative hydrolysis produces the $\alpha,\alpha$-dibromocyclobutanone or its ketal directly.[11] These dibromocyclobutanones have already proven to be versatile intermediates for geminal alkylation.[7c,12] Since the direct bisbromination of cyclobutanones is sometimes problematical, this alternative approach is a useful addition. In an attempt to extend this geminal alkylation procedure to organometallic additions to the $\alpha,\alpha$-dibromocyclobutanone, only debromination occurred. While, to our knowledge, such metal–halogen exchange has not been observed for organolithiums with bromo ketones, it has been observed in the case of dibromo esters.[13] This reaction has also been applied to 1-phenylthiocyclobutenes **11** (vide supra), **18,** and **19.**







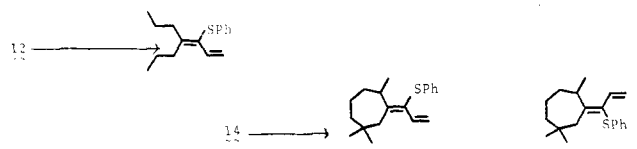
**Cyclobutane and Diene Formation.** The 1-phenylthiocyclobutenes are useful intermediates. For example, desulfurization and hydrogenation of the double bond can provide a synthesis of monoalkyl- or 1,1-dialkylcyclobutanes from aldehydes and ketones, respectively. Indeed, treatment of several of these substrates with either Raney nickel in acetone or ethanol or nickel boride in ethanol[14] leads smoothly to the cyclobutane as summarized in Table II. As eq 3 illustrates, in



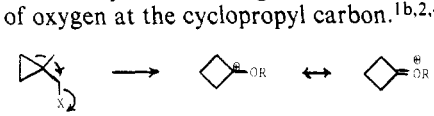
(3)

a three-step sequence the two C–O bonds of a carbonyl group are replaced with two C–C bonds of a cyclobutyl ring (i.e., a cyclobutane annelation).

Alternatively, the cyclobutene can serve as a diene precursor. Conrotatory thermal ring opening proceeds smoothly at ~150 °C. The addition of a trace amount of 2,6-dimethyl-4-*tert*-butylphenol as a stabilizer improves the cleanliness of the reaction. In the case of **14,** the products were approximately an equimolar mixture of the two isomers. Thus, no stereochemical control is evident in these reactions.



**Cyclobutanone Formation.** Rearrangements of cyclopropylcarbinols to the cyclobutane ring has been facilitated by the presence of oxygen at the cyclopropyl carbon.[1b,2,4,5,15] Even so, depending upon the substitution at the carbinyl position, this rearrangement can be made reversible. In the case where S and O compete, oxygen dominates. Thus, no ring enlargement was observed during attempts to rearrange 1-phenylthio-1-dimethoxymethylcyclopropane (eq 4).[16] The subtle effect that substituents can play on these rearrangements is in part a reflection of the close strain energy of a cyclopropane (~27 kcal/mol) and a cyclobutane (~26 kcal/mol).[8] In light of these considerations, replacing oxygen by sulfur to achieve the desired ring expansion to cyclobutanones is not an obvious analogy—especially since oxygen is able to stabilize an adjacent positive charge to a much larger extent than sulfur. These premonitions were somewhat fulfilled by the fact that no single set of reaction conditions applied to all of the cyclopropylcarbinols examined. Experimentation appears to be necessary in each case to obtain optimum results. In every case except one, one of three sets of conditions was highly successful in achieving the desired rearrangement in good isolated yields. Table III summarizes the results.





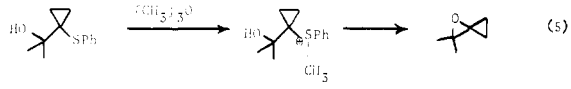
(4)

The initial reaction conditions were devised from the viewpoint of generating a carbonium ion in the absence of a nu-

cleophile and thus employed a protonic acid with a nonnucleophilic anion—treatment of the alcohol with 48% aqueous fluoboric acid in the presence of ether at room temperature (method A). The adducts derived from sterically unhindered saturated and $\alpha,\beta$-unsaturated ketones normally rearrange nicely under these conditions. However, increasing steric hindrance such as in the cases of Table IIIA, entries 2 and 6, and Table IIIB, entries 6 and 7, led to no reaction. Apparently the aqueous conditions preclude protonation of the alcohol of these highly hydrophobic adducts. Ring size also appears to play a role, since the adducts of the cyclobutanones (Table IIIA, entries 1 and 8) fail to react under such mild conditions for generating a carbonium ion. In one case, concentration was crucial and successful reaction required dropwise addition of the alcohol to a cold (0 °C) mixture of fluoboric acid and ether.

A more vigorous and somewhat more general set of conditions employs anhydrous stannic chloride in methylene chloride, normally at room temperature, but sometimes lower (method B). This method is quite successful in most of the cases that failed as well as many that succeeded under method A. Reaction time, determined by TLC monitoring, is important for optimum yields. Use of titanium tetrachloride in lieu of stannic chloride gave more decomposition and was not pursued. In several instances, severe decomposition accompanied rearrangement. This appeared to be particularly true of the adducts derived from saturated aldehydes. In these cases, the use of *p*-toluenesulfonic acid in benzene saturated with water[17] at reflux (method C) was preferred.

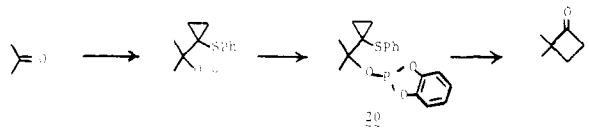
An attempt was made to convert the adducts to oxaspiropentanes by S-alkylation followed by base treatment (eq 5).[18]



(5)

However, treatment of the adducts with trimethyloxonium fluoroborate and workup by addition of sodium hydroxide led only to rearranged cyclobutanone (method D) as in Table IIIA, entry 6, and Table IIIB, entry 2. Apparently, the Meerwein's reagent simply plays the role of an "acid" to effect the rearrangement. This reagent played a similar role in catalyzing the ring expansion of ketones with diazoacetic ester.[19] The generality of this approach for ring expansion has not been explored.

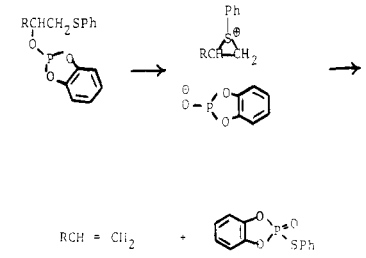
A slightly different approach envisioned converting the alcohol into a slightly better leaving group in order to allow rearrangement under milder conditions. Upon addition of 1-lithiocyclopropyl phenyl sulfide to a carbonyl group, the generated alkoxide was quenched with *o*-phenylene phosphorochlorodite to give the phosphite **20.** Simply warming these



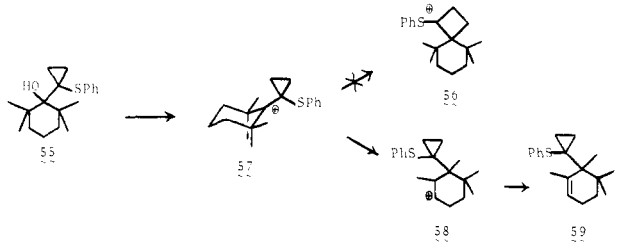
adducts in THF did not lead to rearrangement, but the addition of a catalytic amount of acid to aqueous THF at reflux led to smooth ring expansion and hydrolysis to give the cyclobutanones as summarized in Table IV. The adducts from an aldehyde, a saturated ketone, and an unsatured ketone all have been successfully rearranged.

It is interesting to contrast the above results with those of Kuwajima in the case of simpler $\beta$-hydroxy sulfides which undergo a net reductive elimination upon refluxing in THF.[21] The failure of our adducts to follow a similar path presumably reflects the strain of the thianiumspiropentane intermediate or of the alkylidenecyclopropane.

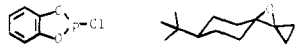
In one case (i.e., **55**), all attempts to effect a rearrangement



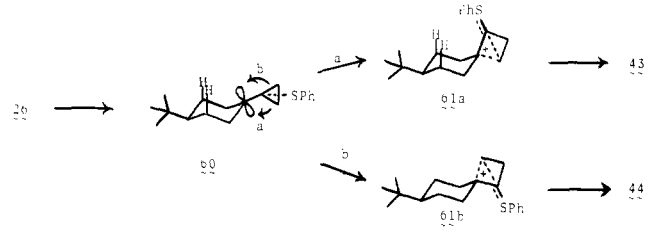
to a cyclobutane system failed. The steric interactions associated with the generation of three contiguous quaternary carbon atoms as in **56** either precludes the ring expansion or makes it more reversible. Furthermore, the initial carbonium ion **57** suffers a severe eclipsing interaction between the cyclopropyl unit and the flanking equatorial methyl groups. Some release of this steric "strain" can be achieved by a 1,2-methyl shift to **58,** which ultimately loses a proton to give the observed product **59.** Thus, in extreme cases, steric factors override the directive effects of sulfur.



The stereochemistry of the rearrangement suggests reasonable stereocontrol via this approach to spiroannelation, although the approach via diphenylsulfonium cyclopropylide normally has a somewhat higher degree of stereocontrol. More significantly, *the two methods to spiroannelation appear to give complementary stereochemistry.* The adduct **26** from 4-*tert*-butylcyclohexanone gave predominantly the product in which the spiro carbon–carbonyl carbon bond of the cyclo-



butanone is equatorial; whereas, in the related reaction of the oxaspiropentane, the major product has this bond axial. Considering the stereochemistry of **26,** the major cyclobutanone arises from a replacement of the hydroxyl group with retention of configuration. This fact strongly suggests a carbonium ion mechanism. We attribute the stereoselectivity observed to the steric interactions in the transition state for rearrangement. Migration of the cyclopropyl carbon in an equatorial sense (path a in **60**) swings the phenylthio group



over the face of the cyclohexane ring, which leads to steric interactions especially with the $\beta$-axial hydrogens in **61a.** On the other hand, migration of this bond axially (path b in **60**) leads to **61b,** which swings the phenylthio unit away from the cyclohexane ring. The less steric congestion associated with this latter path nicely accounts for the observed stereoselectivity. A preference for axial trapping of the 1-methyl-4-*tert*-butylcyclohexyl cation attributed to torsional effects has been noted.[22] On the other hand, in molecular rearrangements preferential equatorial bond formation attributed to less steric interactions for the migrating group has been found.[23] The role

**Table III.** Cyclobutanone Formation

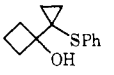
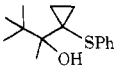
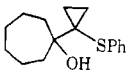
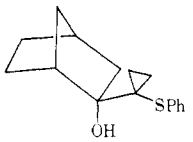
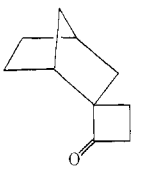
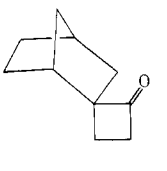
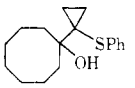
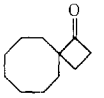
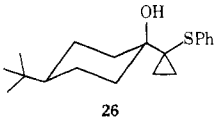
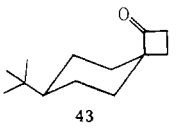
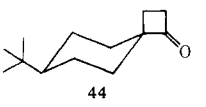
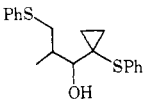
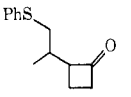
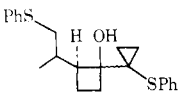
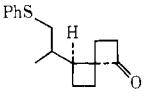
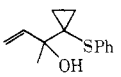
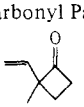
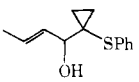
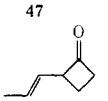
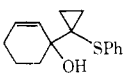
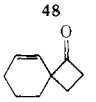
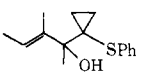
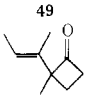
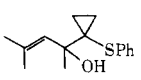
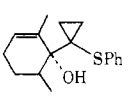
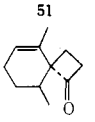
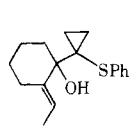
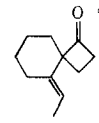
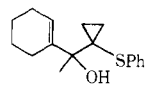
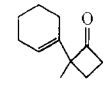
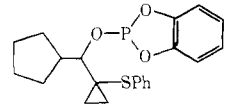
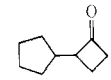
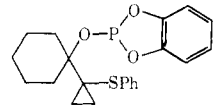
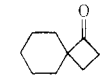
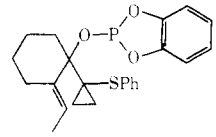
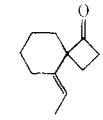
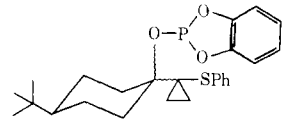
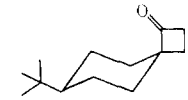
| Entry | Adduct | Method[a] | Product | % yield |
|---|---|---|---|---|
| | A. Rearrangements of Adduct from Saturated Carbonyl Partners | | | |
| 1 |  **21** | B |  **37** | 96 |
| 2 |  **22** | C |  **38** | 91 |
| 3 |  **23** | A |  **39** | 84 |
| 4 |  **24** | A |  **40** 89  **41** 11 | 63 |
| 5 |  **25** | A |  **42** | 100 |
| 6 |  **26** | |  **43**  **44** | |
| | | B | 7 93 | 90 |
| | | D | 45 55 | ND[b] |
| 7 |  **27** | C |  **45** | 90 |
| 8 |  **28** | C |  **46** | 92 |
| | B. Rearrangements of Adducts from Unsaturated Carbonyl Partners | | | |
| 1 |  **29** | A |  **47** | 85 |
| 2 |  **30** | B<br>D |  **48** | 95<br>84 |
| 3 |  **31** | A |  **49** | 91 |
| 4 |  **32** | A |  **50** | 92 |
| 5 |  **33** | A |  **51** | 47 |
| 6 |  **34** | B |  **52** | 88 |

Table III. (*Continued*)

| Entry | Adduct | Method[a] | Product | % yield |
|---|---|---|---|---|
| 7 |  35 | B<br>A |  53 | 94<br>39 |
| 8 |  36 | A |  54 | 83 |

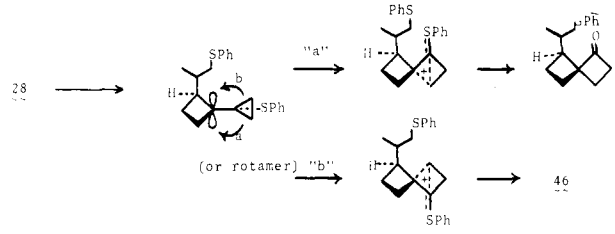
[a] See text for explanation of the various methods. [b] ND = not determined. [c] Cf. P. S. Engel, M. A. Schexnayder, H. Ziffer, and J. I. Seeman, *J. Am. Chem. Soc.*, **96**, 924 (1974).

Table IV. Ring Enlargement via Phosphite

| Entry | Carbonyl partner | Adduct | Product | % yield |
|---|---|---|---|---|
| 1 | Cyclopentanecarboxaldehyde |  |  | 92 |
| 2 | Cyclohexanone |  |  | 90 |
| 3 | 2-Ethylidenecyclohexanone |  |  | 90 |
| 4 | 4-*tert*-Butylcyclohexanone |  |  | 92 |

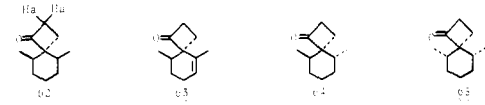
that these conflicting factors play in determining the stereochemistry of these rearrangements remains yet to be established.

Consideration of the steric congestion of the phenylthio group during migration does allow rationalization for the stereochemistry of rearrangement of adducts **28** and **33.** In the conformationally less rigid cyclobutyl system, **28,** the eclipsing




of the propyl substituent and the phenylthio group leads to path b being favored over path a (b:a ~ 85:15). The stereochemical assignments are discussed subsequently.

From **34,** a single cyclobutanone is produced. The previous results suggest that the spiro carbon–carbonyl carbon bond of the annelated cyclobutanone is preferentially produced on the sterically less congested face of the starting ketone. On this basis, cyclobutanone **52** would be expected. Support for this stereochemistry arises from consideration of the $Eu^{3+}$-induced shifts of the saturated methyl protons relative to the methylene group protons $\alpha$ to the carbonyl in **52** ($\Delta\delta$(saturated $CH_3$)/$\Delta\delta(CH_2)$ = 0.55) compared to **62**[24] ($\Delta\delta$(saturated $CH_3$)/$\Delta\delta(CH_2)$ = 1.2). Since this ratio should be sensitive to the stereochemical relationship of the carbonyl group and the



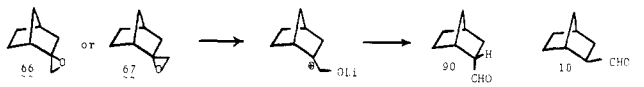
saturated methyl group, **63** would show a similar ratio to that for **62;** whereas, **52** should exhibit a significantly smaller ratio. The latter is indeed found. Confirmatory evidence arises from the fact that hydrogenation of **52** leads to two saturated cyclobutanones, neither of which is identical with **62.** These compounds must have the stereochemistry depicted in **64** and **65.** Since **63** should produce **62** and **64** whereas **52** cannot produce **62,** the stereochemistry depicted in **52** is established.

There is a dependence of the stereochemistry of the product on the method of rearrangement as indicated in the case of **26.** Use of Meerwein's salt for the rearrangement leads to a nearly 1:1 mixture of the two isomers **43** and **44;** whereas, stannic

chloride led to a high preference for **44.** Under the former milder conditions, competition between formation of the conformationally equilibrated cyclopropyl carbonium ion **60**[25] and assisted ionization leading directly to **61a** rationalizes the increased amount of the less stable product.

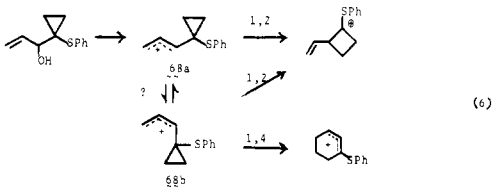
Another variance with the general trends is observed in the case of adduct **24.** Here the product mixture mirrors that seen utilizing diphenylsulfonium cyclopropylide for the cyclobutanone annelation. The observed exo migration is in accord

with the well-known preference for exo additions to C(2) of the norbornyl ring. Furthermore, rearrangement of either **66** or **67** gives the identical mixture of norbornane-2-carboxal-



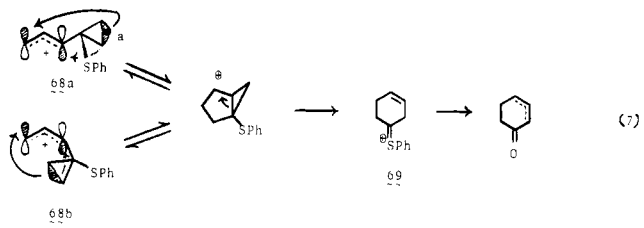
dehydes in which the aldehyde arising from exo-hydride migration predominates.[26] In this case, the stereochemistry of capture of the carbonium ion and of intramolecular rearrangements both predict exo attack. In the two cases (i.e., **24** and **26**) where comparisons can be made between the stereochemistry of our ring expansion and the stereochemistry of external capture of the carbonium ions, the two correlate. Many more examples need to be studied before accepting the validity of such a correlation.

The chemospecificity of this approach to cyclobutanone formation with $\alpha,\beta$-unsaturated carbonyl partners is of high interest. Diphenylsulfonium cyclopropylide undergoes conjugate addition and formation of spiropentanes.[4] On the other hand, the more reactive organolithium reagent reacts only at the carbonyl group.[6] Thus, this approach allows cyclobutanone annelation to be extended to virtually every type of aldehyde or ketone. The regiospecificity of the rearrangement is also of some interest since either 1,2- or 1,4-migration can be envisioned (see eq 6). Orbital symmetry demands that a 1,4-mi-



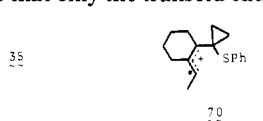
(6)

gration occur either antarafacially or with inversion of configuration at the migrating center.[27] Geometrically, such a 1,4-migration can occur only in the cisoid cation **68b.** While entropy considerations lead one to prefer 1,2-migration, release of strain energy in going to a six-membered ring would favor 1,4-migration. In nondirected cyclopropylallyl cations a $_{\sigma}2_a + {}_{\pi}2_s$ or $_{\sigma}2_s + {}_{\pi}2_a$ addition (eq 7 depicts the latter) of cyclo-

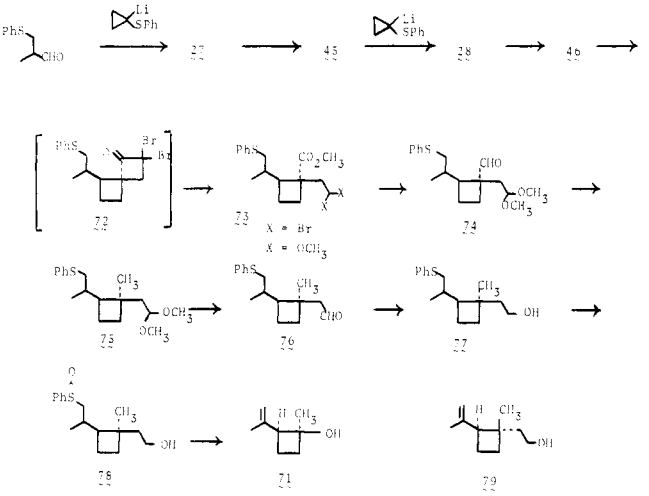


(7)

propyl bond a to the allyl system leads to an initial bicyclo[3.1.0] system which then rearranges to a cyclohexenyl cation.[28] In the present case, the bicyclo[3.1.0] system would be anticipated to ring open to the homoallylic ion **69** and ultimately a cyclohexenone. This process can occur in either the cisoid or the transoid cations, **68a** or **b.** Once again, a thermodynamic driving force in going from a three- to a six-membered ring can be envisioned to assist this process. The failure to observe this latter process, which is common in the all-hydrocarbon system, may be attributed to the effectiveness of the phenylthio group as a directing group. In the initial stages of the concerted cycloaddition pathway, sulfur cannot participate in the stabilization of charge. On the other hand, sulfur participation can occur for either process depicted in eq 6. It could be argued that only the transoid cation **68a** is formed



Scheme I



and thus the 1,4-migration is geometrically precluded. In order to test this point, the geometrically rigid cisoid cation **70** from **34** was generated. Again only cyclobutanone formation is observed. Thus, the rearrangement is a kinetic process in which entropic factors dominate the choice of pathway.

**Grandisol Synthesis.** In order to demonstrate the utility of this approach to alkylations, a synthesis of one of the constituents of the sex pheromone of the boll weevil, grandisol (**71**), was undertaken[29] (Scheme I). Thus a double-barrelled cyclobutanone annelation converts the readily available 2-methyl-3-phenylthiopropionaldehyde[6] to **46** in an overall yield of 82%. Ring cleavage initiated by bromination was not complicated by the presence of the phenylthio group. Presumably, under our bromination conditions attack at sulfur is reversible. The crude dibromocyclobutanone **72** smoothly fragments to **73** (X = Br) upon treatment with methanolic sodium methoxide. The crude dibromide **73** (X = Br) is directly solvolyzed to the acetal **73** (X = $OCH_3$) to complete the geminal alkylation procedure in an overall yield of 86%. Standard chemistry transforms the carbomethoxy group to a methyl group and the $\beta,\beta$-dimethoxyethyl group to a $\beta$-hydroxyethyl group via intermediates **74–76.** The final stage requires the generation of the isopropenyl group. Attempts to S-alkylate **77** and effect a base-catalyzed elimination of the resultant sulfonium salt led to complex reaction mixtures. On the other hand, oxidation of **77** to the sulfoxide and pyrolysis of the crude sulfoxide led smoothly to the desired product **71.** This approach for introduction of an isopropenyl group is highlighted by the absence of any double bond isomer—a problem that complicates many of the alternative methods.

Because of the presence of an asymmetric center in the isopropyl side chain, assignment of the stereochemistry around the cyclobutyl ring is difficult until the final step. Even so, the NMR spectra of many of the intermediates are remarkably simple. For example, **74** shows only two aldehyde protons at $\delta$ 9.75 and 9.50 in the ratio of 9:1, which presumably corresponds to the isomers around the cyclobutyl ring, since an isomeric ratio at the side-chain carbon of about 3:2 is indicated by a pair of doublets for the secondary methyl group at $\delta$ 0.92 and 0.97. Compound **76** shows essentially one quaternary methyl group at $\delta$ 1.23 (a small peak at $\delta$ 1.14 may correspond to the other isomer) and one pair of doublets (~1:1 ratio) for the secondary methyl group at $\delta$ 0.91 and 0.97. The assignment of the stereochemistry for the major isomer as that depicted in **71** derives from the NMR spectrum of the final product, in which the asymmetric center in the side chain has been removed. Two signals appear for the saturated methyl group at $\delta$ 1.17 and 0.92 for the major (grandisol) and minor (fragranol **79**[30]) isomers, respectively, in about a 5:1 ratio. This route

provides grandisol in ~32% overall yield from α-methacrolein.

## Conclusions

The flexibility for annealing a cyclobutane ring onto a carbonyl group is substantially enhanced by the addition of this two-step procedure—addition of 1-lithiocyclopropyl phenyl sulfide followed by rearrangement of the resultant adduct. As a result, the utility of this type of approach for creation of molecular architecture, i.e., geminal alkylation, secoalkylation, lactone annelation, etc., is improved. In addition, this new approach provides a direct entry into substituted cyclobutenes and cyclobutanes from carbonyl partners.

It appears that the two approaches for cyclobutanone formation developed by us are complementary. (1) *The substituted carbon–carbonyl carbon bond of the cyclobutanone (bond a of* **79a**) *is introduced onto the sterically more hindered face of the starting ketone via the ylide reagent, but on the sterically less crowded face (bond a of* **79b**) *via the cyclopropyl phenyl sulfide.* (2) Conjugate addition with formation of spiropentanes occurs with α,β-unsaturated carbonyl partners for the ylide; however, only reaction at the carbonyl group occurs with the anion. (3) Sterically hindered carbonyl partners react more rapidly with the anion than with the ylide. (4) Economically, the anion reagent is less expensive than the ylide. This last fact will sometimes make 1-lithiocyclopropyl phenyl sulfide the reagent of choice. Nevertheless, it clearly does not supplant the ylide—not only because of the complementary features pointed out above, but also because the milder conditions for formation of the cyclobutanones via the ylide allows application to many sensitive and polyfunctional molecules.

## Experimental Section

**General.** Melting points were taken on a Thomas-Hoover melting point apparatus. All melting and boiling points are uncorrected. Unless otherwise stated, infrared spectra were determined in carbon tetrachloride or chloroform solution on a Beckman IR-8 or Perkin-Elmer 267 spectrophotometer. NMR spectra were determined in carbon tetrachloride solution on a Varian A60A, Varian EM 360, or Jeolco MH-100 spectrometer; chemical shifts are given in δ with $Me_4Si$ as the internal standard. Splitting patterns are designated as s, singlet; d, doublet, t, triplet; q, quartet; br, broad; m, multiplet. Coupling constants are given in hertz. Mass spectra were taken on a AEI MS-902 high-resolution mass spectrometer at an ionizing voltage of 70 eV and an ionizing current of 98 mA. All exact mass determinations were obtained on the MS-902 instrument. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

All experiments were carried out under an atmosphere of dry nitrogen. In experiments requiring dry solvents, ether, tetrahydrofuran, and dimethoxyethane were distilled from sodium-benzophenone. Methylene chloride was distilled from calcium hydride. Apparatus for experiments requiring dry conditions was dried by flaming in a nitrogen stream.

During workup of the reactions, general drying of the solvent was performed over anhydrous magnesium sulfate or anhydrous sodium sulfate as indicated. Thin-layer or preparative thick-layer plates were made of E. Merck AG Darmstadt silica gel PF-254 activated by drying for 2 h at 140 °C. Removal of material from the silica gel was accomplished by successive washings with ether. Column silica gel was obtained from W. R. Grace and Co.

**Preparation of Phenylthiocyclobutenes. Method A (use of *p*-toluenesulfonic acid).** A mixture of 550 mg (1.98 mmol) of 2,6-dimethyl-1-(1′-phenylthiocycloprop-1′-yl)cyclohexan-1-ol and 190 mg of *p*-toluenesulfonic acid monohydrate in 10 mL of dry benzene was refluxed for 90 min with azeotropic removal of water. After cooling to room temperature, the benzene solution was washed with 2 mL of saturated aqueous sodium bicarbonate solution and 2 mL of saturated aqueous sodium chloride. After drying and concentrating in vacuo, chromatography (hexane) indicated a single product, 489 mg (95% yield), of 5,9-dimethyl-1-phenylthiospiro[3.5]non-1-ene: IR ($CCl_4$) 3105, 2999, 2943, 1661, 751 $cm^{-1}$; NMR ($CDCl_3$) δ 7.1–7.6 (m, 5 H), 5.55 (br s, 1 H), 2.0 (br s, 2 H), 1.2–1.8 (m, 8 H), 0.95 (d, $J$ = 6 Hz, 6 H). Anal. Calcd for $C_{17}H_{22}S$: C, H, S.

**Method B (use of Burgess reagent).** A mixture of 1.0 g (4.0 mmol) of 2,2-dimethyl-1-(1′-phenylthiocycloprop-1′-yl)cyclobutan-1-ol (**3**) and 1.19 g (5.0 mmol) of (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester in 10 mL of benzene was refluxed for 2 h. After cooling to room temperature, 2 mL of water was added and the product isolated as above to give 850 mg (92%) of 5,5-dimethyl-1-phenylthiospiro[3.3]hept-1-ene (**9**): IR ($CCl_4$) 3090, 2930, 2885, 1660, 1578, 1478, 688 $cm^{-1}$; NMR ($CDCl_3$) δ 7.2–7.6 (m, 5 H), 5.56 (dd, $J$ = 1.8 and 1.0 Hz, 1 H), 2.56 (dd, $J$ = 12 and 1 Hz, 1 H), 2.1 (dd, $J$ = 12 and 1.8 Hz, 1 H), 1.5–2.4 (m, 4 H), 1.19 (s, 3 H), 1.10 (s, 3 H). Calcd for $C_{15}H_{18}S$: 230.1129. Found: 230.1129.

**Method C (thionyl chloride).** To a solution of 80 mg (0.31 mmol) of cyclohex-3′-en-1′-yl(1″-phenylthiocycloprop-1″-yl)methanol in 10 mL of pyridine was added 53 mg (0.44 mmol) of thionyl chloride. After refluxing for 12 h, the reaction was cooled to room temperature, diluted with 75 mL of ether, and washed with water followed by 20 mL of 3 M aqueous hydrochloric acid. After drying and evaporation in vacuo, PLC (hexane) gave 70 mg (93% yield) of 2-(cyclohex-3′-en-1′-yl)-1-phenylthiocyclobutene: IR ($CCl_4$) 1679, 1579, 1472 $cm^{-1}$; NMR ($CDCl_3$) δ 7.0–7.6 (m, 5 H), 5.67 (br s, 2 H), 2.45 (s, 4 H), 0.8–2.2 (m, 7 H).

The remaining examples are summarized in Table V.

**Spectral Properties of Additional Phenylthiocyclobutenes and Some Vinylcyclopropanes. 6:** IR ($CCl_4$) 3075, 3620, 1710, 1580, 1560, 1478, 689 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 265 sh (3915), 244 (6143); NMR ($CCl_4$) δ 7.0–7.5 (m, 5 H), 5.78 (s, 1 H), 2.58 (m, 2 H), 2.48 (m, 2 H).

**7:** IR ($CCl_4$) 3070, 3055, 1712, 1580, 1565, 1482, 685 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 266 (5573), 235 (7100); NMR ($CCl_4$) δ 7.4–7.6 (m, 2 H), 7.1–7.4 (m, 3 H), 5.62 (s, 1 H), 2.24 (s, 2 H), 1.18 (s, 6 H); MS *m/e* (rel %) 190 (100), 173 (37), 134 (61), 119 (30), 117 (30), 110 (29), 91 (16), 86 (40), 83 (54), 81 (42), 79 (45). Calcd for $C_{12}H_{14}S$: 190.0816. Found: 190.0816.

2-(1′-Phenylthiocycloprop-1′-yl)propene: IR ($CCl_4$) 3080, 3060, 1645, 1585, 1485, 895, 685 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 249 (5630); NMR ($CCl_4$) δ 7.1–7.5 (m, 5 H), 4.84 (br s, 1 H), 4.80 (br s, 1 H), 1.92 (s, 3 H), 1.11 (s, 4 H); MS *m/e* (rel %) 190 (82), 149 (12), 129 (17), 110 (35), 91 (26), 85 (26), 81 (100), 79 (52), 57 (44). Calcd for $C_{12}H_{14}S$: 190.0816. Found, 190.0806.

**8:** IR ($CCl_4$) 3080, 3020, 1560, 1470, 685 $cm^{-1}$; NMR ($CCl_4$) δ 7.1–7.5 (m, 5 H), 5.42 (br s, 1 H), 2.45 (d, $J$ = 13 Hz, 1 H), 1.95 (d, $J$ = 13 Hz, 1 H), 1.3 (s, 3 H), 1.0 (s, 9 H); MS *m/e* (rel %) 232 (100), 217 (27), 134 (28), 109 (13), 107 (80), 91 (22), 81 (21), 77 (18). Calcd for $C_{15}H_{20}S$: 232.1285. Found: 232.1281.

**11:** IR ($CCl_4$) 3060, 3050, 1708, 1585, 1482, 682 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 247 (3741); NMR ($CCl_4$) δ 7.30–7.50 (m, 2 H), 7.0–7.3 (m, 3 H), 5.51 and 5.37 (two s, 1 H), 2.28 and 2.23 (two d, $J$ = 13 Hz, 1 H), 1.87 (d, $J$ = 13 Hz, 1 H), 1.1–2.0 (m, 9 H), 1.0 and 0.88 (two d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 244 (55), 229 (18), 164 (17), 139 (22), 135 (100), 119 (23), 117 (24), 109 (25), 105 (23), 93 (54), 81 (50), 79 (54). Calcd for $C_{16}H_{20}S$: 244.1286. Found: 244.1287.

**12:** IR ($CCl_4$) 3070, 1709, 1565, 1482, 690 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 282 sh (3600), 270 (4100); NMR ($CCl_4$) 7.1–7.5 (m, 5 H), 5.50 (t, $J$ = 1 Hz, 1 H), 2.15 (d, $J$ = 1 Hz, 2 H), 1.1–1.7 (m, 8 H), 0.7–1.1 (m, 6 H); MS *m/e* (rel %) 246 (51), 217 (23), 175 (16), 136 (17), 134 (32), 110 (21), 109 (15), 91 (28), 79 (34), 77 (30), 69 (57), 55 (92), 41 (100). Calcd for $C_{16}H_{22}S$: 246.1442. Found: 246.1447.

4-(1′-Phenylthiocycloprop-1′-yl)hept-3-ene: IR ($CCl_4$) 3085, 3065, 1589, 1485, 690 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm (ε) 253 (12 500); NMR ($CCl_4$) δ 7.0–7.5 (m, 5 H), 5.15 (t, $J$ = 7.5 Hz, 1 H), 1.1–2.5 (m, 6 H), 1.0 (s, 4 H), 0.90 (t, $J$ = 7 Hz, 3 H), 0.82 (t, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 246 (13), 217 (100), 150 (10), 119 (24), 117 (25), 109

**Table V.** Reaction Details for Preparation of Phenylthiocyclobutenes

| Alcohol (wt, mg; mmol) | Method | Rearrangement reagent wt, mg (mmol) | Time, h | Product: wt, mg (% yield) |
|---|---|---|---|---|
| 1-Hydroxymethyl-1-phenylthiocyclopropane (540, 3.0) | B | 894 (3.75) | 12 | **6:** 235 (47) |
| **5** (104, 0.50) | B | 124 (0.52) | 10 | **7:** 37 (39)[a] |
| 2-(1′-Phenylthiocycloprop-1′-yl)-3,3-dimethylbutan-2-ol (250, 1.0) | A | 100 (0.50) | 1 | **8:** 220 (95) |
| **3** | See text | | | |
| 1-(1′-Phenylthiocycloprop-1′-yl)-2-methylcyclohexan-1-ol (262, 1.0) | B | 252 (1.1) | 72[b] | **11:** 89 (37) |
| 4-(1′-Phenylthiocycloprop-1′-yl)-heptan-4-ol (528, 2.0) | B | 500 (2.2) | 72[b] | **12:** 106 (22)[c] |
| (528, 2.0) | B | 500 (2.2) | 3 | **12:** 100 (20)[d] |
| (552, 2.09) | A | 19 (0.1) | 0.5 | **12:** 212 (43) |
| 2,6-Dimethyl-1-(1′-phenylthiocycloprop-1′-yl)cyclohexan-1-ol | See text | | | |
| 3,7-Dimethyl-1-(1′-phenylthiocycloprop-1′-yl)octan-1-ol (78.2, 0.255) | B | 66.9 (0.281) | 0.5 | **13:** 68.4 (93) |
| 3,3,7-Trimethyl-1-(1′-phenylthiocycloprop-1′-yl)cycloheptan-1-ol (608, 2.0) | A | 114 (0.62) | 0.5 | **14:** 229 (40)[e] |

[a] In addition 38 mg (40% yield) of 2-(1′-phenylthiocycloprop-1′-yl)propene was also isolated. [b] Room temperature instead of reflux. [c] In addition 122 mg (26% yield) of 4-(1′-phenylthiocycloprop-1′-yl)hept-3-ene was also isolated. [d] In addition 117 mg (24% yield) of 4-(1′-phenylthiocycloprop-1′-yl)hept-3-ene was also isolated. [e] A 1:1 v/v hexane–carbon tetrachloride mixture was used for the chromatographic isolation.

(13), 93 (20), 91 (32), 56 (20). Calcd for $C_{16}H_{22}S$: 246.1442. Found: 246.1441.

**13:** IR ($CHCl_3$) 3950, 3065, 1708, 1586, 1487, 685 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.0–7.5 (m, 5 H), 2.47 (s, 4 H), 2.05 (m, 2 H), 1.0–1.8 (m, 8 H), 0.91 (d, $J$ = 7 Hz, 3 H), 0.87 (d, $J$ = 7 Hz, 6 H).

**14:** IR ($CCl_4$) 3060, 3040, 1570, 1478, 688 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm ($\epsilon$) 282 (2960); NMR ($CCl_4$) 7.3–7.5 (m, 2 H), 7.1–7.3 (m, 3 H), 5.35 (s, 1 H), 2.28 (s, 2 H), 1.80 (d, $J$ = 16 Hz, 1 H), 2.61 (d, $J$ = 16 Hz, 1 H), 1.1–1.8 (m, 7 H), 0.98 (s, 3 H), 0.94 (s, 3 H), 0.91 (d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 286 (22), 271 (4), 209 (11), 177 (43), 161 (26), 135 (20), 134 (39), 133 (20), 121 (47), 110 (54), 109 (50), 107 (65), 105 (49), 95 (89), 93 (67), 91 (67), 69 (100). Calcd for $C_{19}H_{26}S$: 286.1755. Found: 286.1759.

**Hydrolysis of 4-*tert*-Butyl-4-methyl-1-phenylthiocyclobutene (8).** To a solution of 60 mg (0.26 mmol) of **8** in 10 mL of 1:1 glacial acetic acid was added 70.1 mg (0.26 mmol) of mercuric chloride, 56 mg (0.26 mmol) of mercuric oxide, and 1 g of sodium acetate.[31] After stirring at 60 °C for 1 h, the cooled (25 °C) reaction mixture was diluted with 50 mL of ether and gaseous hydrogen sulfide bubbled through the mixture. A black precipitate formed instantaneously. After 10 min, the solids were removed by filtration and the organic layer washed with saturated aqueous sodium bicarbonate solution. Usual isolation gave 2-methyl-2-*tert*-butylcyclobutanone, identical with an authentic sample (vide infra for spectral data).

**Brominative Hydrolysis of 1-Phenylthiocyclobutenes. Method A (to ketal).** *N*-Bromosuccinimide (414 mg, 2.32 mmol) and 2-phenylthio-3,3-di-*n*-propylcyclobut-1-ene (143 mg, 0.58 mmol) were dissolved in 4 mL of dry methanol (distilled from magnesium methoxide). After refluxing 30 min, the solvent was removed in vacuo to give 550 mg of an oil which was directly subjected to chromatographic isolation (benzene–chloroform 2:1 v/v) to give 128 mg (62%) of 1,1-dibromo-2,2-dimethoxy-3,3-di-*n*-propylcyclobutane: IR ($CCl_4$) 2870, 1188, 1165, 1130, 1068 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.40 (s, 6 H), 2.65 (s, 2 H), 1.0–2.0 (m, 8 H), 0.9–1.0 (m, 6 H); MS *m/e* (rel %) 279 (12), 272 (12), 248 (12), 246 (25), 244 (12), 181 (23), 179 (25), 172 (54), 143 (100). No molecular ion.

In similar fashion **14** (143 mg, 0.50 mmol) and 356 mg (2.0 mmol) of *N*-bromosuccinimide produced 111 mg (56%) of 1,1-dimethoxy-2,2-dibromo-5,9,9-trimethylspiro[3.6]decane.

**Method B (to cyclobutanone).** The phenylthiocyclobutene **14** (114 mg, 0.399 mmol) and 284 mg (1.60 mmol) of NBS were dissolved in 1 mL of freshly distilled acetonitrile and 3 mL of water. After heating at 60 °C for 28 h, the mixture was cooled, poured into water, and extracted with ether. After drying and concentration, chromatographic isolation (3:1 v/v carbon tetrachloride–benzene) yielded 84 mg (60%) of pure 2,2-dibromo-5,9,9-trimethylspiro[3.6]decan-1-one: IR ($CCl_4$) 1798 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.08 (d, $J$ = 14 Hz, 1 H), 2.96 (d, $J$ = 14 Hz, 1 H), 2.08 (d, $J$ = 15 Hz, 1 H), 1.76 (d, $J$ = 15 Hz, 1 H), 1.0–2.0 (m, 7 H), 0.8–1.0 (m, 9 H) (vide supra).

**Preparation of 2,2-Dibromo-4,4-di-*n*-propylcyclobutanone.** From 120 mg (0.49 mmol) of 2-phenylthio-3,3-di-*n*-propylcyclobutene and 349 mg (1.96 mmol) of NBS was obtained 87 mg (58%) of product after chromatographic isolation (hexane–benzene 3:2 v/v): IR ($CCl_4$) 1798 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.98 (s, 2 H), 1.6–1.9 (m, 4 H), 1.1–1.6 (m, 4 H), 0.86 (t, $J$ = 6 Hz, 6 H); MS *m/e* (rel %) 314 (<1), 312 (<1), 310 (<1), 126 (100), 97 (88), 69 (37), 56 (24), 55 (30). Calcd for $C_{10}H_{16}{}^{79}Br_2O$: 309.9569. Found: 309.9565.

**Preparation of 2,2-Dibromo-4-*n*-hexyl-4-methylcyclobutanone.** As above, from 286 mg (1.15 mmol) of cyclobutene **19** and 820 mg (4.6 mmol) of NBS there was obtained 118 mg (32%) of the above dibromocyclobutanone after chromatographic isolation utilizing 3:2 hexane–benzene and 16% yield of a product identified as 1-bromo-2-phenylthio-3-methyl-3-*n*-hexylcyclobut-1-ene.[32] The dibromocyclobutanone was identical by spectroscopic comparison with an authentic sample.[12]

**Preparation of 2,2-Dibromo-7-methylspiro[3.5]nonan-1-one.** As above, from 48.8 mg (0.20 mmol) of cyclobutene **18** and 138 mg (0.80 mmol) of NBS there was obtained 52.8 mg (85%) of dibromocyclobutanone after chromatographic isolation utilizing 3:2 hexane–benzene: IR ($CCl_4$) 1790 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.02 and 2.95 (two s, 2 H), 1.2–2.4 (m, 9 H), 0.96 and 0.92 (two d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 312 (<1), 310 (<1), 308 (<1), 124 (64), 107 (10), 95 (28), 81 (70), 78 (100), 68 (20), 67 (22), 52 (40). Calcd for $C_{10}H_{14}{}^{79}Br_2O$: 307.9412. Found: 307.9413.

**Cleavage of Dibromocyclobutanone 17.** As previously described,[12] 73 mg (0.23 mmol) of **17** was cleaved to 32 mg (40%) of methyl 2-(2′,2′-dibromoethyl)-2-*n*-propylpentanoate after chromatographic isolation (1:1 v/v benzene–carbon tetrachloride): IR ($CCl_4$) 1730 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.59 (t, $J$ = 615 Hz, 1 H), 3.63 (s, 3 H), 2.84 (d, $J$ = 615 Hz, 2 H), 1.4–1.7 (m, 4 H), 1.1–1.4 (m, 4 H), 0.92 (t, $J$ = 6 Hz, 6 H); MS *m/e* (rel %) 304 (24), 302 (51), 300 (26), 365 (41), 263 (41), 158 (62), 129 (100), 123 (39), 97 (48), 82 (33), 81 (60), 69 (57), 67 (38), 55 (82). Calcd for $C_8H_{14}{}^{81}Br^{79}BrO_2$ ($M - C_3H_6$): 301.9342. Found: 301.9340. Calcd for $C_8H_{14}{}^{79}Br_2O_2$ ($M - C_3H_6$): 299.9362. Found: 299.9361.

**Reaction of Dibromocyclobutanones with Methyllithium.** A solution of 84 mg (0.24 mmol) of **16** in 2 mL of dry ether was cooled to −78 °C. Methyllithium (0.170 mL of 1.62 M solution in ether, 0.27 mmol) was added dropwise and the mixture stirred 15 min. Addition of a saturated aqueous ammonium chloride solution quenched the reaction. Separation of layers and extraction of the water layer with additional ether gave after drying ($Na_2SO_4$) a colorless oil. Chromatographic

**Table VI.** Experimental Details for Additional Examples of Cyclobutane Synthesis

| Enol thioether (wt, mg; mmol) | Method (g of nickel derivative) | Solvent | Time, h | Cyclobutane wt, mg (% yield) | Distillation temp[a] °C (min) |
|---|---|---|---|---|---|
| **11** (566, 2.32) | A | Ethanol | 1.0 | 5-Methylspiro[3.5]nonane 272 (82) | 62 (15) |
| **12** | See text | | | | |
| **14** (354, 1.2) | A | Ethanol | 0.5 | 5,9,9-Trimethylspiro[3.6]decane 86 (41) | 81 (0.5) |
| **18** (240, 0.98) | A | Ethanol | 1.0 | 7-Methylspiro[3.5]nonane 51 (38) | 75–80 (15) |
| **19** (450, 1.82) | A | Ethanol | 1.0 | 1-Methyl-1-*n*-hexylcyclobutane 170 (61) | 85–92 (15) |

[a] Flask temperature on microdistillation apparatus.

isolation (1:1 v/v cyclohexane–methylene chloride) gave 54 mg (83%) of 2-bromo-5,9,9-trimethylspiro[3.6]decan-1-one: IR ($CCl_4$) 1790 $cm^{-1}$; NMR $\delta$ 4.85 (dd, $J$ = 7 and 7 Hz (major one)) and 4.56 (dd, $J$ = 9 and 7 Hz (minor one)), total 1 H, 1.1–2.6 (m, 9 H), 0.7–1.0 (9 H).

In a similar reaction, 300 mg (0.97 mmol) of **15** was reacted with 0.68 mL of a 1.6 M solution (1.1 mmol) of methyllithium in ether to give 114 mg (51%) of 2-bromo-4,4-di-*n*-propylcyclobutanone after chromatographic isolation (2:1 v/v benzene–carbon tetrachloride): IR ($CCl_4$) 1786 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 4.82 (dd, $J$ = 9.8 and 7.8 Hz, 1 H), 2.52 (dd, $J$ = 12.2 and 9.8 Hz, 1 H), 2.10 (dd, $J$ = 12.2 and 7.8 Hz, 1 H), 1.1–1.8 (m, 8 H), 0.95 (t, $J$ = 7 Hz, 6 H); MS *m/e* (rel %) 234 (<1), 232 (<1), 126 (96), 97 (100), 69 (62), 55 (42). Calcd for $C_{10}H_{17}BrO$: 232.0463. Found: 232.0460.

**Desulfurization of 1-Phenylthiocyclobutenes. Method A (Raney nickel).** W-2 Raney nickel (2 g) was deactivated by refluxing in 8 mL of acetone (freshly distilled from potassium carbonate) for 2 h. To this suspension was added 350 mg (1.42 mmol) of 2-phenylthio-3,3-di-*n*-propylcyclobut-1-ene in 2 mL of freshly distilled acetone and the resultant mixture refluxed for 14 h. After cooling and filtering, distillation at atmospheric pressure removed the solvent and at reduced pressure (10 mm, pot temp ~80 °C) gave 189 mg (94%) of 1,1-di-*n*-propylcyclobutane. Alternatively, the mixture was diluted with water and extracted with isopentane followed by distillation of the solvent at atmospheric pressure and the product at reduced pressure: IR ($CCl_4$) 2965, 2935, 2875, 1470, 1462 $cm^{-1}$; NMR $\delta$ 0.7–1.5 (m); MS *m/e* (rel %) 140 (2), 121 (29), 119 (96), 117 (100), 84 (24), 69 (27), 57 (93), 55 (65). Calcd for $C_{10}H_{20}$: 140.1585. Found: 140.1585.

**Method B (nickel boride).** To a solution of 0.712 g (3.0 mmol) of nickel chloride hexahydrate in 8 mL of absolute ethanol was added portionwise 0.1135 g (3.0 mmol) of sodium borohydride. After stirring for 30 min, 369 mg (1.5 mmol) of 2-phenylthio-3,3-di-*n*-propylcyclobut-1-ene in 2 mL of absolute ethanol was added and the resultant mixture refluxed for 14 h. The cooled reaction mixture was filtered and then diluted with 50 mL of water. After extraction with three 14-mL portions of hexane, back washing the hexane extracts with water, and drying ($Na_2SO_4$), distillation at atmospheric pressure removed the solvent and at reduced pressure (~10 mm) gave 186 mg (95% yield) of product, identical with the above.

Table VI summarizes the reaction details for the additional examples.

**Spectral Properties of Cyclobutanes.** 5-Methylspiro[3.5]nonane: IR ($CCl_4$) 2960, 2925, 2855, 1465, 1454 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.7–2.0 (m); MS *m/e* (rel %) 138 (17), 111 (84), 110 (57), 96 (52), 95 (71), 81 (69), 69 (88), 68 (64), 67 (58), 55 (86), 41 (100). Calcd for $C_{10}H_{18}$: 138.1409. Found: 138.1408.

5,9,9-Trimethylspiro[5.6]decane: IR ($CCl_4$) 2955, 2925, 2865, 2855, 2845, 1460, 1385, 1375, 1363 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.1–2.1 (m, 15 H), 1.01 (s, 3 H), 0.90 (s, 3 H), 0.84 (d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 180 (2), 137 (10), 109 (37), 95 (27), 82 (100), 69 (33), 67 (36), 55 (43). Calcd for $C_{13}H_{24}$: 180.1878. Found: 180.1877.

7-Methylspiro[3.5]nonane: IR ($CCl_4$) 2940, 2908, 2860, 2835, 1460, 1455, 1448 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 0.8–2.2 (m); MS *m/e* (rel %) 138 (17), 111 (25), 110 (50), 95 (100), 81 (73), 69 (38), 68 (96), 55 (62). Calcd for $C_{10}H_{18}$: 138.1409. Found: 138.1406.

1-Methyl-1-*n*-hexylcyclobutane: IR ($CCl_4$) 2960, 2930, 2875, 2860, 1470, 1385, 1371 $cm^{-1}$; NMR ($CCl_4$) 0.8–1.8 (m); MS *m/e* (rel %) 154 (13), 127 (8), 126 (7), 11 (10), 84 (19), 71 (83), 57 (74), 56 (100), 55 (40). Calcd for $C_{11}H_{22}$: 154.1722. Found: 154.1725.

**Thermal Opening of Phenylthiocyclobutenes.** A solution of 124 mg (0.50 mmol) of 2-phenylthio-3,3-di-*n*-propylcyclobut-1-ene in 1 mL of dry xylene (distilled from sodium hydride) was refluxed for 7 h. After cooling and removal of the solvent in vacuo, the residue was chromatographed (hexane) to give 100 mg (81%) of 3-phenylthio-4-*n*-propylhepta-1,3-diene: IR ($CCl_4$) 1615, 1585, 1482 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm ($\epsilon$) 285 (2630), 243 (20 100); NMR ($CCl_4$) $\delta$ 7.05 (br s, 5 H), 6.67 (dd, $J$ = 16.6 and 10.4 Hz, 1 H), 5.60 (dd, $J$ = 16.6 and 1.8 Hz, 1 H), 5.03 (dd, $J$ = 10.4 and 1.8 Hz), 2.42 (q, $J$ = 8 Hz, 4 H), 1.2–1.8 (m, 4 H), 1.0 (t, $J$ = 6 Hz, 6 H); MS *m/e* (rel %) 246 (100), 217 (42), 203 (19), 175 (22), 169 (17), 147 (15), 134 (21), 123 (13), 121 (16), 110 (18), 109 (13), 107 (45), 106 (39), 95 (44), 91 (72), 79 (51), 55 (43). Calcd for $C_{16}H_{22}S$: 246.1442. Found: 246.1442.

In similar fashion, 78 mg (0.27 mmol) of **14** was converted to 51 mg (66%) of 2-phenylthio-1,1-(1′,5′,5′-trimethylhexamethylene)-buta-1,3-diene as an approximate 1:1 mixture of isomers: IR ($CCl_4$) 1602, 1580, 1478 $cm^{-1}$; UV $\lambda_{max}^{C_2H_5OH}$ nm ($\epsilon$) 281 sh (2500), 248 (17 650); NMR ($CCl_4$) $\delta$ 6.9–7.3 (m, 5 H), 6.78 (dd, $J$ = 16 and 10.4 Hz, 1 H), 5.60 (dm, $J$ = 16 Hz, 1 H), 5.05 (dm, $J$ = 10.4 Hz, 1 H), 3.5 and 3.1 (two m, 1 H), 3.08 and 2.62 (two d, $J$ = 12 Hz, 1 H), 2.16 (d, $J$ = 12 Hz, 1 H), 0.8–2.0 (m, 15 H); MS *m/e* (rel %) 286 (71), 209 (29), 201 (14), 177 (81), 161 (38), 147 (16), 133 (29), 121 (27), 120 (27), 119 (35), 110 (24), 109 (29), 107 (80), 95 (85), 91 (100), 69 (90), 55 (90). Calcd for $C_{19}H_{26}S$: 286.1755. Found: 286.1756.

**Rearrangement to Cyclobutanones. Method A (fluoboric acid).** To a solution of 659 mg (2.36 mmol) of **25** in 20 mL of ether at room temperature was added 1.0 mL of 50% aqueous fluoboric acid solution. (In one case dropwise addition of the solution of the alcohol in ether to the fluoboric acid solution was preferred.) After stirring for 30 min, the reaction was diluted with 150 mL of ether, washed with 20 mL of saturated aqueous sodium bicarbonate solution, dried ($MgSO_4$), and concentrated in vacuo. Chromatographic isolation (10% ether in hexane) gave 392 mg (100%) of cyclobutanone **42:** IR ($CCl_4$) 1775, 1443 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 3.05 (t, $J$ = 9 Hz, 2 H), 1.4–2.1 (m, 16 H); MS *m/e* (rel %) 166 (6), 138 (9), 124 (10), 109 (26), 95 (43), 82 (60), 69 (40), 68 (59), 67 (75), 55 (56). Calcd for $C_{11}H_{18}O$: 166.1358. Found: 166.1355.

**Method B (stannic chloride).** To a solution of 2,4-dimethyl-3-(1′-phenylthiocycloprop-1′-yl)cyclohexen-3-ol, **34** (3.0 g, 10.9 mmol), in 100 mL of methylene chloride at room temperature (frequently 0 °C is preferred) was added anhydrous stannic chloride (2.85 g, 10.9 mmol). After stirring for 2.0 min, water (20 mL) was added followed by ether (200 mL). The organic layer was washed with saturated aqueous sodium bicarbonate solution (20 mL), dried ($MgSO_4$), and the solvents removed in vacuo. The residue was chromatographed on a silica gel column using hexane, and distilled at 75–78 °C (0.2 mm) to give 1.59 g (89%) of cyclobutanone **52:** IR ($CCl_4$) 1786, 1432 $cm^{-1}$; NMR $\delta$ 5.36 (m, 1 H), 2.86 (t, $J$ = 8.5 Hz, 2 H), 1.97 (t, $J$ = 8.5 Hz, 2 H) and 1.65 (br s, 3 H) superimposed on 1.1–2.0 (m, 5 H), 0.97 (d, $J$ = 6.5 Hz, 3 H); MS *m/e* (rel %) 164 (7), 122 (72), 107 (100), 93 (62), 91 (42), 79 (42), 77 (27), 41 (29). Calcd for $C_{11}H_{16}O$: 164.1204. Found: 164.1201.

**Method C (*p*-toluenesulfonic acid).** A mixture of 2-methyl-3-phenylthio-1-(1′-phenylthiocycloprop-1′-yl)propan-1-ol, **27** (6.0 g, 18.2 mmol), and *p*-toluenesulfonic acid (3.5 g, 18.2 mmol) in 85 mL

**Table VII.** Experimental Details for Cyclobutanone Synthesis

| Adduct (wt, mmol) | Method | Rearrangement agent wt, mmol | Solvent, mL | Time, min | Cyclobutanone wt (% yield) | Chromatographic solvent | Ref |
|---|---|---|---|---|---|---|---|
| **21** (1.0 g, 4.81) | B | 170 mg, 0.66[e] | 25 | 20 | **37** 509 mg (96) | A[a] | |
| **22** (250 mg, 1.0) | C | 100 mg, 0.5[f] | 25 | 90 | **38** 127 mg (91) | A[a] | |
| **23** (54 mg, 0.206) | A | 1 mL[g] | 10 | 15 | **39** 26 mg (84) | A[a] | 4 |
| **24** (500 mg, 1.93) | A | 1 mL[g] | 10 | 210 | **40 + 41**[b] 180 mg (63) | Hexane | 4 |
| **25** | See text | | | | | | |
| **26** | | | | | **43 + 44** | | |
| (100 mg, 0.33) | B | 85.4 mg, 0.33[e] | 10 | 10 | 58 mg (90)[c] | A | 4 |
| (322 mg, 1.06) | D | 173 mg, 1.17[h] | 5 | | 169 mg (82)[d] | A | |
| **27** | See text | | | | | | |
| **28** | See text | | | | | | |
| **29** (980 mg, 4.45) | A | 1.0 mL[g] | 10 | 120 | **47** 410 mg (83) | Pentane | |
| **30** (500 mg, 2.27) | A<br>D | 1 mL[g]<br>See text | 5 | 30 | **48** 237 mg (95) | Hexane | |
| **31** (3.70 g, 15) | A | 2 mL[g] | 50 | 45 | **49** 1.85 mg (91) | A | |
| **32** (2.56 g, 26) | A | 3 mL[g] | 50 | 45 | **50** 1.30 g (92) | A | |
| **33** (1.00 g, 4.03) | A | 1 mL[g] | 10 | 15 | **51** 261 mg (47) | A | |
| **34** | See text | | | | | | |
| **35** | | | | | **53** | | |
| (300 mg, 1.09) | A | 1 mL[g] | 10 | 75 | 70.1 mg (39) | A | See text |
| (47.6 mg, 0.174) | B | 45.4 mg, 0.174[e] | 10 | 15 | 26.1 mg (94) | A | See text |
| **36** (100 mg, 0.365) | A | 1 mL[g] | 6 | 180 | **54** 48.6 mg (83) | Hexane | |

[a] Solvent mixture A is 10% ether in hexane. [b] A ratio of 89:11 for **40/41** was determined by VPC on a 5% Carbowax 20 M on Chromosorb W column. [c] A ratio of 7:93 for **43/44** was determined by VPC on a 5% SE-30 on Chromosorb W column. [d] A ratio of 45:55 for **43/44** was determined as above. [e] Quantity of stannic chloride. [f] Quantity of *p*-toluenesulfonic acid monohydrate. [g] Volume of 50% aqueous fluoboric acid solution. [h] Quantity of trimethyloxonium fluoborate.

of water-saturated benzene was reluxed for 5 h and cooled to room temperature. Water (20 mL) was added followed by chloroform (200 mL). The layers were separated and the organic layer washed with saturated aqueous sodium bicarbonate solution (50 mL), saturated aqueous sodium chloride solution (50 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting oil was distilled at 109–111 °C (0.1 mm) to give 3.5 g (90%) of 2-(1′-phenylthioprop-2′-yl)cyclobutanone, **45:** IR ($CCl_4$) 1783, 1583, 1479, 1438 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.1–7.5 (m, 5 H), 2.6–3.6 (m, 5 H), 1.5–2.4 (m, 3 H), 1.18 and 1.04 (two d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 220 (8), 175 (12), 122 (22), 110 (168), 78 (27). Calcd for $C_{13}H_{16}OS$: 220.0922. Found: 220.0921.

**Method D (Meerwein's reagent).** To a solution of 2.99 g (13.6 mmol) of 1-(1′-phenylthiocycloprop-1′-yl)but-2-en-1-ol, **30,** in 100 mL of methylene chloride at room temperature was added 2.51 g (17.0 mmol) of trimethyloxonium fluoborate. After stirring until all the solid dissolved, 40 mL (20 mmol) of 0.5 M aqueous sodium hydroxide solution was added and stirring continued for 15 h. The reaction mixture was poured into 75 mL of water and extracted with 300 mL of ether. The organic layer was washed with 50 mL of saturated aqueous sodium chloride solution, dried ($Na_2SO_4$), and concentrated by distillation at atmospheric pressure. NMR analysis of the pot residue showed no evidence for oxaspiropentanes and the characteristic cyclobutanone absorption at $\delta$ 2.9. Chromatographic isolation (pentane) gave 1.26 g (84%) of cyclobutanone **48:** IR ($CCl_4$) 1780, 1653, 1435 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.4 (m, 2 H), 3.8 (m, 1 H), 2.96 (m, 2 H), 2.26 (m, 1 H), 1.7 (m, 1 H), 1.68 (d, $J$ = 4 Hz, 3 H); MS *m/e* (rel %) 110 (12), 82 (17), 68 (100), 67 (88), 53 (35), 41 (26). Calcd for $C_7H_{10}O$: 110.0731. Found: 110.0732.

The remaining examples are summarized in Table VII.

**Spectral Properties of Additional Cyclobutanones. 37:** IR ($CCl_4$) 1776, 1425 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.87 (t, $J$ = 9 Hz, 2 H), 2.38 (m, 2 H), 1.7–2.2 (m, 6 H); MS *m/e* (rel %) 110 (15), 82 (38), 68 (38), 67 (72), 54 (100), 53 (29). Calcd for $C_7H_{10}O$: 110.0733. Found: 110.0731.

**38:** IR ($CCl_4$) 1773, 1470, 1458, 1390, 1369, 1362 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 1.76 (m, 2 H), 1.3–2.3 (m, 2 H), 1.22 (s, 3 H), 0.99 (s, 9 H). Calcd for $C_9H_{16}O$: 140.1201. Found: 140.1206.

**47:** IR ($CCl_4$) 1775, 1630, 1440, 910 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.79 (dd, $J$ = 17 and 10 Hz, 1 H), 5.03 (d, $J$ = 17 Hz, 1 H), 4.99 (d, $J$ = 10 Hz, 1 H), 2.97 (t, $J$ = 8.5 Hz, 2 H), 1.5–2.3 (m, 2 H), 1.26 (s, 3 H).

**49:** IR ($CCl_4$) 1776, 1632, 1437 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.86 (dt, $J$ = 11 and 3 Hz, 1 H), 5.64 (d, $J$ = 11 Hz, 1 H), 3.07 (t, $J$ = 8.5 Hz, 2 H), 1.5–2.3 (m, 8 H); MS *m/e* (rel %) 136 (6), 108 (8), 94 (84), 93 (23), 79 (100), 77 (20). Calcd for $C_9H_{12}O$: 136.0885. Found: 136.0888.

**50:** IR ($CCl_4$) 1773, 1439 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.33 (br q, $J$ = 7 Hz, 1 H), 2.91 (t, $J$ = 8 Hz, 2 H), 1.6–2.4 (m, 2 H), 1.61 (s, 3 H), 1.57 (br d, $J$ = 7 Hz, 3 H), 1.25 (s, 3 H); MS *m/e* (rel %) 138 (11), 110 (5), 96 (98), 81 (100), 67 (32), 55 (25). Calcd for $C_9H_{14}O$: 138.1042. Found: 138.1045.

**51:** IR ($CCl_4$) 1779, 1439 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.25 (m, 1 H), 2.95 (t, $J$ = 8.5 Hz, 2 H), 1.7–2.2 (m, 2 H), 1.68 (br s, 6 H), 1.29 (s, 3 H); MS *m/e* (rel %) 138 (2), 123 (2), 110 (3), 96 (30), 95 (39), 81 (75), 67 (68), 55 (40), 39 (104). Calcd for $C_9H_{14}O$: 138.1045. Found: 138.1041.

**54:** IR ($CCl_4$) 1782, 1450, 1440 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.54 (m, 1 H), 2.96 (t, $J$ = 8.5 Hz, 2 H), 1.4–2.3 (m, 10 H), 1.32 (s, 3 H); MS *m/e* (rel %) 164 (15), 136 (5), 122 (95), 107 (90), 94 (24), 93 (58), 80 (100), 78 (28), 67 (20). Calcd for $C_{11}H_{16}O$: 164.1199. Found: 164.1201.

**Hydrogenation of 5,9-Dimethylspiro[3.5]non-5-en-1-one to 64 and 65.** A mixture of 52 mg (0.316 mmol) of **52** and 60 mg of 10% Pd/C in 30 mL of absolute ethanol was hydrogenated at 55 psi for 4 h at room temperature. The catalyst was removed by filtration through Celite and the mother liquid concentrated. Liquid–liquid chromatography on a Corasil II column (2.8 mL/min, hexane) gave two compounds (retention times of 10 and 18 min). **64:** IR ($CCl_4$) 1771, 1455, 1445 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.8 (t, $J$ = 8.5 Hz, 2 H), 0.8–2.2

(m, 16 H). Anal. ($C_{11}H_{18}O$): C, H. **65:** IR ($CCl_4$) 1775, 1445 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.8 (t, $J$ = 8.5 Hz, 2 H), 0.9–2.3 (m, 16 H). Anal. ($C_{11}H_{18}O$): C, H.

**Preparation of Cyclobutanones via Phosphites. Cyclobutanone 53.** 1-Lithiocyclopropyl phenyl sulfide was generated as usual from 2.25 g (15.0 mmol) of cyclopropyl phenyl sulfide and 15.0 mmol of *n*-butyllithium in 50 mL of THF. After stirring at 0 °C for 2 h, 1.5 g (12.1 mmol) of 2-ethylidenecyclohexanone was added, and after an additional 30 min at 0 °C, 2.61 g (15 mmol) of *o*-phenylene phosphorochlorodite was added. Stirring continued for 10 min at 0 °C. Addition of 150 mL of ether and 50 mL of water quenched the reaction. The organic layer was washed with saturated aqueous sodium chloride solution, dried ($MgSO_4$), and concentrated in vacuo. The residue was dissolved into a solution of 20 mL of THF, 5 mL of water, and 5 drops of concentrated hydrochloric acid. After refluxing for 5 h, the cooled mixture was diluted with 100 mL of ether. The organic layer was separated, washed with saturated aqueous sodium bicarbonate solution, dried ($MgSO_4$), and concentrated in vacuo. Chromatography on 250 g of silica gel (hexane) gave 1.78 g (90%) of cyclobutanone **53:** IR ($CCl_4$) 1773, 1655, 1442 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 5.26 (q, $J$ = 7 Hz, 1 H), 2.89 (t, $J$ = 8 Hz, 2 H), 2.0–2.5 (m, 4 H), 1.61 (d, $J$ = 7 Hz, 3 H) superimposed on 1.4–2.0 (m, 6 H); MS *m/e* (rel %) 164 (23), 136 (7), 122 (64), 119 (97), 118 (100), 107 (53), 93 (62), 79 (60), 67 (24). Calcd for $C_{11}H_{16}O$: 164.1201. Found: 164.1201.

**2-Cyclopentylcyclobutanone.** A similar reaction employing 3.0 g (20.0 mmol) of cyclopropyl phenyl sulfide, 15.0 mmol of *n*-butyllithium, 1.47 g (15.0 mmol) of cyclopentanecarboxaldehyde, and 2.62 g (15.0 mmol) of *o*-phenylene phosphorochlorodite gave after rearrangement with 5 drops of concentrated hydrochloric acid for 3 h 870 mg (42%) of 2-cyclopentylcyclobutanone: IR ($CCl_4$) 1775 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 2.7–3.2 (m, 3 H), 0.8–1.6 (m, 11 H). Anal ($C_9H_{14}O$): C, H.

**Spiro[3.5]nonan-1-one.** A similar reaction employing 2.0 g (13.3 mmol) of cyclopropyl phenyl sulfide, 11.0 mmol of *n*-butyllithium, 1.1 g (11.0 mmol) of cyclohexanone, and 1.72 g (11.0 mmol) of *o*-phenylene phosphorochlorodite gave after rearrangement with 5 drops of concentrated hydrochloric acid for 15 h 1.38 g (91%) of spiro[3.5]-nonan-1-one, identical with an authentic sample.

**Cyclobutanone 44.** A similar reaction utilizing 1.20 g (8.0 mmol) of cyclopropyl phenyl sulfide, 8.0 mmol of *n*-butyllithium, 1.0 g (6.5 mmol) of 4-*tert*-butylcyclohexanone, and 1.13 g (6.5 mmol) of *o*-phenylene phosphorochlorodite gave a mixture of an oil and a solid, mp 40–76 °C. A 150-mg aliquot of the solid fraction was rearranged in 15 mL of THF containing 1 mL of water and 3 drops of hydrochloric acid to give 61.1 mg (92%) of cyclobutanone **44,** which was stereohomogeneous by VPC analysis.

**Preparation of 3-(1′Phenylthiocycloprop-1′-yl)-2,3,4,4-tetramethylcyclohexene.** A solution of 410 mg (1.35 mmol) of cyclopropylcarbinol **55** in 10 mL of methylene chloride was treated with 257 mg (1.57 mmol) of titanium tetrachloride. After stirring at room temperature for 45 min, 5 mL of water and 40 mL of ether were added. After separation of layers, the organic layer was washed with saturated aqueous sodium bicarbonate solution, dried ($MgSO_4$), concentrated in vacuo and chromatographed (hexane is eluting solvent) to give 392 mg (75%) of olefin **59:** IR ($CCl_4$) 3067, 2959, 2874, 1582, 1468, 1433, 1374 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.3–7.8 (m, 5 H), 5.5 (br t, $J$ = 6 Hz, 1 H), 1.8–2.2 (m, 2 H), 0.8–1.8 (m, 18 H) ($\delta$ 0.8, 0.9, 1.1, 1.7, singlets superimposed in 18 H multiplet).

**Preparation of Cyclobutanone 46.** To a solution of 1.8 g (12.0 mmol) of cyclopropyl phenyl sulfide in 35 mL of tetrahydrofuran at 0 °C was added 8.63 mL (12.0 mmol) of *n*-butyllithium in hexane via syringe. After stirring at 0 °C for 2 h, 2.4 g (11.0 mmol) of 2-(1′-phenylthioprop-2′-yl)cyclobutanone was added via syringe. After stirring at room temperature for 25 min, water (5 mL) and then hexane (100 mL) were added. The layers were separated and the organic layer washed with saturated aqueous sodium chloride solution (10 mL), dried ($MgSO_4$), and the solvents removed in vacuo. The resulting oil was chromatographed on 200 g of silica gel using 15% chloroform in hexane to give 3.61 g (89%) of 1-(1′-phenylthiocycloprop-1′-yl)-2-(1′-phenylthioprop-2′-yl)cyclobutan-1-ol, **28:** IR ($CHCl_3$) 2660, 3550, 3065, 1585, 1477, 1089, 1027 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.0–7.7 (m, 10 H), 3.27 (t, $J$ = 6.5 Hz, 1 H), 1.4–2.8 (m, 6 H), 0.7–1.3 (m, 7 H).

A solution of 7.4 g (20.0 mmol) of *p*-toluenesulfonic acid monohydrate in 100 mL of benzene saturated with water refluxed for 12 h, then cooled to room temperature. Chloroform (100 mL) and then water (20 mL) were added. The organic layer was washed with saturated aqueous sodium bicarbonate solution (25 mL), dried ($MgSO_4$), and concentrated in vacuo. The resulting oil was distilled at 115–119 °C (0.05 mm) to give 4.73 g (92%) of cyclobutanone **46:** IR ($CHCl_3$) 1773, 1584, 1483, 1442 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 7.1–7.5 (m, 5 H), 2.8–3.1 (m, 2 H), 1.1–2.8 (m, 10 H), 0.96 and 0.90 (two d, $J$ = 7 Hz, 3 H); MS *m/e* (rel %) 260 (10), 220 (13), 183 (22), 150 (32), 123 (93), 110 (100), 95 (26), 77 (36). Calcd for $C_{16}H_{20}OS$: 260.1235. Found: 260.1235.

**Preparation of 1-Carbomethoxy-1-(2′,2′-dimethoxyethyl)-2-(1′-phenylthioprop-2′-yl) cyclobutane, 73.** A solution of 3.87 g (14.8 mmol) of cyclobutanone **46** and 9.6 g (30.0 mmol) of pyridinium bromide perbromide in 50 mL of glacial acetic acid was heated to 50 °C for 1 h. The solution was cooled to 25 °C. Hexane (100 mL) was added and the mixture washed with water (100 mL), then saturated aqueous sodium bicarbonate solution (50 mL), and dried ($MgSO_4$). The solvents were removed in vacuo to give 6.2 g (100%) of an oil, a single spot by TLC (IR 1896 $cm^{-1}$).

This oil was dissolved in 100 mL of anhydrous methanol and 2.0 g (37.2 mmol) of solid sodium methoxide was added. This mixture was stirred for 2 min; hexane (300 mL) and then water (100 mL) were added. The hexane layer was separated and dried ($MgSO_4$). The solvent was removed in vacuo to give 6.6 g (98%) of a viscous oil, a single spot by TLC (chloroform): IR 1725, 1580, 1478 $cm^{-1}$; partial NMR $\delta$ 5.7 (d of d, $J$ = 8 and 10 Hz, 1 H), 3.6 (s, 3 H), 1.0 and 0.88 (two d, 3 H).

This oil was dissolved in 100 mL of anhydrous methanol and 5.0 g (29.6 mmol) of silver nitrate was added. This mixture was stirred in the dark at room temperature for 16 h. The mixture was filtered and 100 mL of water added to the filtrate. The filtrate was extracted with hexane (three 100-mL portions). The hexane layer was dried ($MgSO_4$) and the hexane removed in vacuo. The resulting oil was chromatographed on 100 g of silica gel to give 3.1 g (86% for **6**) of **73** (X = $OCH_3$): IR ($CHCl_3$) 1739, 1560, 1475, 1440 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.1–7.5 (m, 5 H), 4.26 (m, 1 H), 3.62 (s, 3 H), 3.18 and 3.22 (two s, 6 H), 2.8–1.2 (m, 10 H), 0.8–1.1 (m, 3 H); MS *m/e* (%) 352 (5), 248 (13), 110 (66), 78 (19). Calcd for $C_{19}H_{28}O_4S$: 352.1708. Found: 352.1708.

**Preparation of 1-(2′,2′-Dimethoxyethyl)-1-hydroxymethyl-2-(1′-phenylthioprop-2′-yl)cyclobutane.** To a mixture of lithium aluminum hydride (291 mg, 30.6 mmol) in 20 mL of tetrahydrofuran was added 2.71 g (7.65 mmol) of **73** (X = $OCH_3$). This mixture was refluxed for 5 h, then cooled to room temperature and diluted with 100 mL of hexane and 5 mL of water. The organic layer was separated, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel using 10% ether in chloroform to give 2.44 g (98%) of the desired alcohol: IR ($CHCl_3$) 3590, 3490, 1575, 1450 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.0–7.4 (m, 5 H), 4.4 (dd, $J$ = 9 and 5 Hz, 1 H), 3.1–3.5 (m, 9 H), 2.1–2.0 (m, 2 H), 1.4–2.1 (m, 7 H), 0.8–1.1 (m, 3 H); MS *m/e* (%) 324 (9), 276 (18), 222 (16), 110 (38), 91 (21), 78 (12). Calcd for $C_{18}H_{28}O_3S$: 324.1759. Found: 324.1759.

**Preparation of 1-Carboxaldehyde-1-(1′,1′-dimethoxyeth-2′-yl)-2-(1′-phenylthioprop-2′-yl)cyclobutane, 74.** To a solution of 1-(2′,2′-dimethoxyethyl)-1-hydroxymethyl-2-(1′-phenylthioprop-2′-yl)cyclobutane (1.77 g, 5.42 mmol) in 10 mL of dimethyl sulfoxide and 15 mL of triethylamine was added a solution of sulfur trioxide–pyridine complex (3.45 g, 21.7 mmol) in 10 mL of dimethyl sulfoxide. This mixture was stirred at room temperature for 20 min. The reaction mixture was poured into water (50 mL) and extracted with ether (three 100-mL portions). The ether layers were combined, washed with water (50 mL), dried ($Na_2SO_4$), and concentrated in vacuo to give a red oil. This oil was chromatographed on 100 g of silica gel with chloroform to give 1.65 g (94%) of aldehyde **74:** IR ($CHCl_3$) 1705, 1580, 1455 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 9.4 (s, 1 H), 7.1–7.4 (m, 5 H), 4.30 (dd, $J$ = 8 and 4 Hz, 1 H), 3.25 and 2.3 (two s, 6 H), 2.96 (dm, $J$ = 13 Hz, 1 H), 1.5–2.6 (m, 9 H), 0.97 and 0.91 (two d, $J$ = 6 Hz, 3 H); MS *m/e* (%) 322 (4), 126 (24), 123 (100), 119 (21), 110 (43), 75 (59). Calcd for $C_{18}H_{26}O_3S$: 322.1603. Found: 322.1603.

**Preparation of 1-(2′,2′-Dimethoxyethyl)-1-methyl-2-(1′-phenylthioprop-2′-yl)cyclobutane, 75.** A mixture of 1.39 g (4.29 mmol) of aldehyde **74,** 772 mg (15.4 mmol) of hydrazine hydrate, and 770 mg (13.7 mmol) of potassium hydroxide in 35 mL of triethylene glycol was heated at an oil bath temperature of 145 °C for 90 min. The reflux condenser was replaced with a distilling head, and the heating continued at an oil bath temperature of 235 °C for 3.5 h. The solution was cooled to 25 °C, poured into water (100 mL), and extracted with ether (three 100-ml portions). The combined ether extracts were dried

($Na_2SO_4$) and concentrated in vacuo. The resulting oil was chromatographed on 75 g of silica gel using chloroform to give 1.13 g (85%) of acetal **75:** IR ($CHCl_3$) 1578, 1475 $cm^{-1}$; NMR ($CHCl_3$) $\delta$ 7.1–7.4 (m, 5 H), 4.36 (m, 1 H), 3.30 (s, 3 H), 3.26 (s, 3 H), 2.98 (br dd, $J$ = 14 and 6 Hz, 1 H), 2.44 (br dd, $J$ = 14 and 7 Hz, 1 H), 1.3–2.0 (m, 8 H), 1.12 (s, 3 H), 0.9–1.0 (m, 3 H). Anal. ($C_{18}H_{28}O_2S$): C, H, S.

**Preparation of 1-Methyl-1-(2′-oxoethyl)-2-(1′-phenylthioprop-2′-yl)cyclobutane, 76.** A solution of 1.0 g (3.25 mmol) of acetal **75** in 10 mL of tetrahydrofuran, 2 mL of water, and 5 drops of concentrated hydrochloric acid was stirred at room temperature for 16 h, after which it was poured into water (50 mL) and extracted with ether (three 10-mL portions). The combined ether extracts were dried ($Na_2SO_4$) and concentrated in vacuo. The resulting oil was chromatographed on 50 g of silica gel using 10% ether in chloroform to give 833 mg (98%) of aldehyde **76:** IR ($CHCl_3$) 2730, 1715, 1579, 1475 $cm^{-1}$; NMR ($CCl_4$) $\delta$ 9.78 and 9.73 (two t, $J$ = 3 Hz, 1 H), 7.1–7.4 (m, 5 H), 2.96 (dd, $J$ = 13 and 2 Hz, 1 H), 2.1–2.7 (m, 3 H), 1.4–2.1 (m, 6 H), 1.2 (s, 3 H), 0.98 and 0.92 (two d, $J$ = 6 Hz, 3 H); MS $m/e$ (%): 262 (7), 220 (15), 176 (18), 110 (47). Calcd for $C_{16}H_{22}OS$: 262.1391. Found: 262.1390.

**Preparation of 1-(1′-hydroxyeth-2′-yl)-1-methyl-2-(1′-phenylthioprop-2′-yl)cyclobutane, 77.** A mixture of 500 mg (1.91 mmol) of aldehyde **76** and 73 mg (1.91 mmol) of lithium aluminum hydride in 15 mL of ether was stirred at room temperature for 1 h. Ether (100 mL) and then water (2 mL) were added. The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo. The resulting oil was chromatographed on a thick-layer silica gel plate using 50% ether in chloroform to give 503 mg (quantitative yield) of alcohol **77:** IR ($CHCl_3$) 3600, 3450, 1578, 1471 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.1–7.4 (m, 5 H), 3.6 (m, 2 H), 2.97 (dm, $J$ = 12 Hz, 1 H), 2.50 (m, 1 H), 1.3–2.0 (m, 7 H), 1.09 (s, 3 H), 0.90 (m, 3 H); MS $m/e$ (%) 264 (12), 246 (16), 178 (13), 154 (27), 110 (56). Calcd for $C_{16}H_{22}OS$: 264.1548. Found: 264.1547.

**Preparation of Grandisol.** To a solution of 250 mg (0.947 mmol) of alcohol **77** in 5 mL of methylene chloride at −78 °C was added a solution of 211 mg (1.04 mmol) of *m*-chloroperbenzoic acid in 5 mL of methylene chloride. This mixture was stirred for 5 min and then poured into 10 mL of 10% aqueous sodium carbonate solution. Methylene chloride (50 mL) was added and the layers separated. The organic layer was dried ($MgSO_4$) and concentrated in vacuo to give 253 mg (95%) of sulfoxide **78** as a yellow oil, which was used without purification: IR ($CHCl_3$) 3420, 3060, 2950, 2860, 1460, 1450, 1050 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.6 (br s, 5 H), 3.6 (m, 2 H), 3.2 (br s, 2 H), 3.0–1.4 (m, 8 H), 1.1 (s, 3 H), 1.0 (m, 3 H).

A mixture of 60 mg (0.214 mmol) of this sulfoxide **78** and 21.4 mg (0.214 mmol) of calcium carbonate in 2 mL of decalin was heated to reflux for 30 min, then cooled to room temperature, and chromatographed on 50 g of silica gel, first with hexane to remove the decaline, followed by ether to give 29 mg (88%) of grandisol. NMR analysis of the grandisol showed it to contain 20% of the isomeric fragranol as shown by the methyl resonances at $\delta$ 1.17 (grandisol) and 0.92 (fragranol). Spectra agreed with the published data. Anal. ($C_{10}H_{18}O$): C, H.

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