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GENERATION OF SIMPLE METHYLENECYCLOPROPENES AS REACTIVE INTERMEDIATES

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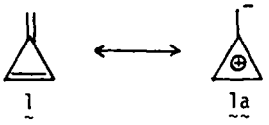
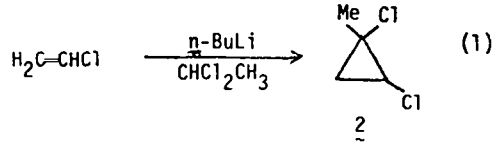
Abstract—The dehydrochlorination of either 1,2 - dichloro - 1 - methylcyclopropane or 1 - bromo - 2 - chloro - 2 - methylcyclopropane with potassium t-butoxide yields 2 - t - butoxy - 1 - methylenecyclopropane. These results are interpreted in terms of methylenecyclopropene as a reactive intermediate which is trapped by addition of nucleophile (t-butoxide) to the cyclopropenyl double bond. The introduction of methanethiol to the reaction medium yields 2 - thiomethyl - 1 - methylenecyclopropene. 2,2 - Dichloro - 1 - methylenecyclopropane reacts with potassium t-butoxide in tetrahydrofuran to yield *trans*- and *cis* - t - butoxybut - 1 - ene - 3 - yne. The addition of thiomethide ion results in the formation of 2,2 - bis(thiomethyl) - 1 - methylenecyclopropane and 2 - t - butoxy - 2 - thiomethyl - 1 - methylenecyclopropane. Other evidence for simple methylenecyclopropenes as reactive intermediates comes from the observation that nucleophiles add nonregiospecifically to the reactive intermediate produced by the dehydrohalogenation of 2 - halo - 1 - alkylidenecyclopropanes. Novel methylenecyclopropane→cyclopropene transformations were found in the reaction of 2 - halomethylenecyclopropanes with thiomethide ion.

As the simplest cross-conjugated cyclic hydrocarbon, methylenecyclopropene (**1**) is a member of the nonbenzenoid aromatic group which defines a class of conjugated, cyclic olefins which may have, in theory, a lower energy content than the opposite acyclic analogues. Although a number of methylenecyclopropenes which are marvels of stability by virtue of stabilization derived from resonance with the aromatic dipole **1a** have been reported,[1,2] simple members of this family have been difficult to synthesize.



1 **1a**

Two attempts[3,4] to prepare the parent were unsuccessful, and prior to our work[5] only the report of Stang[6] describing the addition of unsaturated carbenes to alkynes resulted in the synthesis of simple alkylmethylenecyclopropenes. Tetramethylmethylenecyclopropene prepared via this route was characterized by conversion into a cyclopropenium salt and by cycloaddition with cyclopentadiene. We report here the results of a study which utilizes new precursors to **1** and some of its derivatives and more complete data on the precursor reported previously in preliminary form.[7]

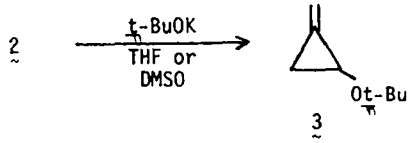


(1)

2

The starting material used initially in this study, compound **2**, was prepared in low yield (~10%) by addition of chloromethylcarbene[8] to vinyl chloride, eqn (1). Careful distillation of the product resulted in the separation of the geometrical isomers of **2**, although stereochemical assignments were not made.

The reaction of **2** (major isomer) with potassium *t*-butoxide in tetrahydrofuran at −30 to −40° for 1 hr gave **3** in 37% yield (eqn 2), whereas the minor isomer gave **3** in 32% yield. In dimethyl sulfoxide **3** was produced in ~33% yield from each of the isomers of **2**.



(2)

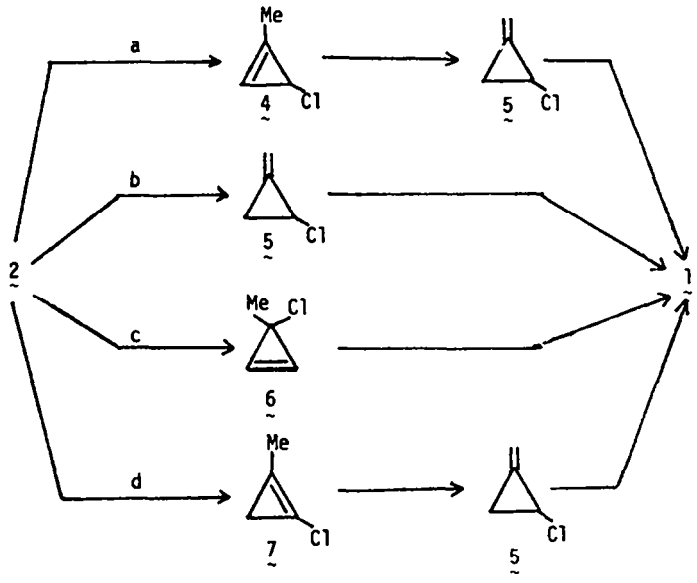
3

The result of eqn (2) is rationalized by assuming a series of elimination-isomerization reactions[3,9] which lead to **1** as a reactive intermediate via intermediates **4**–**7**. Paths which utilize these intermediates are illustrated in Scheme 1.

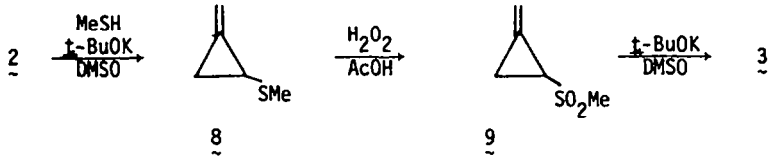
Intermediate **5** appears in paths a, b and d and is expected to undergo dehydrochlorination readily to give **1**. One might escape postulating **5** by assuming that cyclopropenes **4**, **6** and **7** experience addition of the nucleophile prior to elimination of the second molecule of HCl. However, the observation that alkylcyclopropenes undergo double-bond isomerization, when possible, to give alkylidenecyclopropanes rather than add t-butoxide, a weak nucleophile, would seem to undermine this assumption.[9] The isomerization path is not available to intermediate **6** (path c).

Evidence for the discrete existence of methylenecyclopropene as a reactive intermediate is also found in the reaction sequence of Scheme 2. Thus, the reaction of **2** with potassium t-butoxide and methanethiol in dimethyl sulfoxide yields, in addition to **3** (12%), the sulfide **8** in 34% yield. Oxidation of **8** with 30% hydrogen peroxide in glacial acetic acid gave the sulfone **9** in 72% yield. When **9** was treated with potassium t-butoxide in dimethyl sulfoxide, **3** was produced in 11% yield.[10]

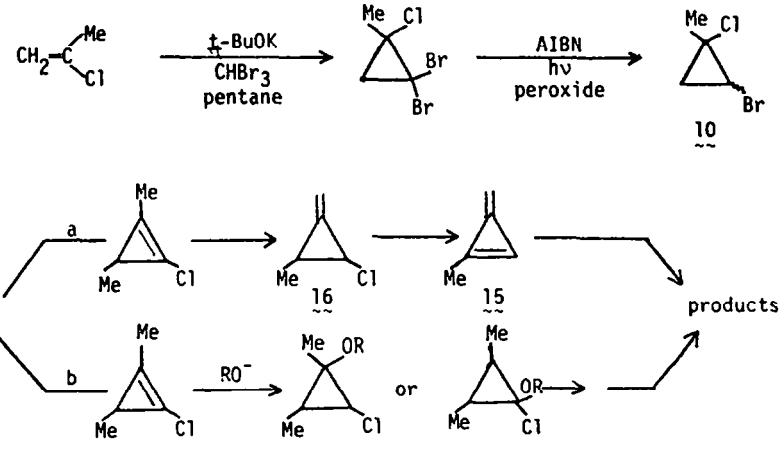
Precursor **10** was also synthesized (Scheme 3) and treated with potassium t-butoxide in tetrahydrofuran at −30° to −40° for 1 hr to yield **3** in 35% yield (eqn 3). In strict analogy to Scheme 1, compounds **11**, **12** and **13**, in addition to **6** which is common to both schemes, are possible intermediates.



Scheme 1.

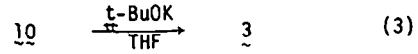


Scheme 2.



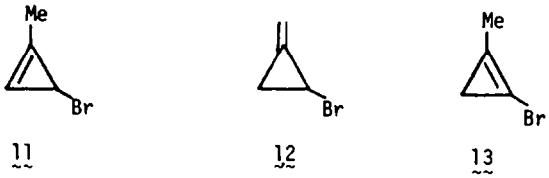
Scheme 3.

Nevertheless, other processes can also be put forward which adequately account for the observations of eqn (2) and (3). For example, an $S_{N}2$ displacement on starting material or on one of the intermediates of Scheme 1, although unprecedented, merits attention. In this regard it is appropriate to note that Shields and Gardner[3] investigated the addition of nucleophiles to reactive intermediates produced in the dehydrochlorination of 14 with either potassium isopropoxide or sodium methoxide-potassium t-butoxide and isolated the adducts illustrated in eqn (4).



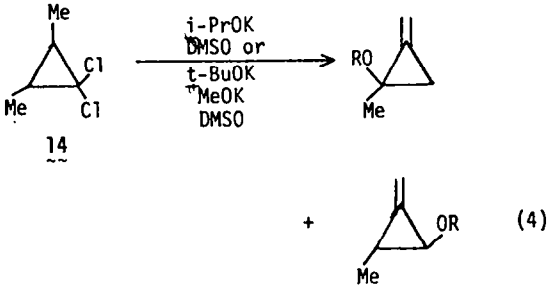
(3)

These products were postulated to arise from addition of nucleophile to methylenecyclopropene **15** (path a,



11 12 13

Scheme 3). The isolation of both regioisomers clearly invalidates an S_N2 displacement on **14** or intermediates such as **16** as the only pathway leading to nucleophilic addition adducts; however, path b of Scheme 3 provides a route to the observed products without the intervention of **15** as a reactive intermediate.

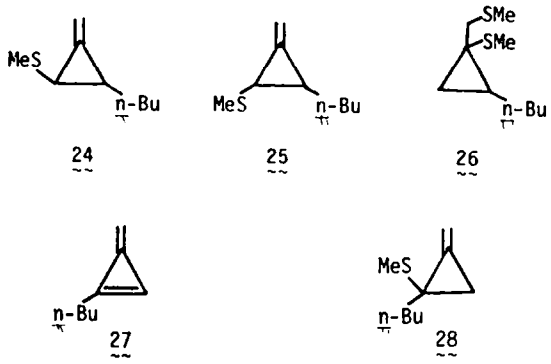


R = isopropyl or methyl

In order to remove some of the ambiguity of Schemes 1 and 3, a mixture of *cis* and *trans* **17** was synthesized[11] from **18** (Scheme 4) and their reactions with strongly alkaline media were investigated. Compound **19**, which is derived from the reduction of **20**, was also isolated by preparative glpc from the reaction products. This compound is, as expected, a single stereoisomer resulting from the addition of the carbene to the less hindered side of the allene.[5]

Treatment of the mixture of monobromides (**17** and **19**) with methanethiol and potassium t-butoxide in dimethyl sulfoxide yielded six major products; however, when **19** was removed from the starting material two of the poorly resolved (gc) peaks were not observed. These products were isolated by preparative glpc and shown to be sulfides **21** and **22**. The conversion of **19** to these products can then be readily explained by invoking methylenecyclopropene **23** which is trapped non-regiospecifically by the nucleophile (Scheme 5).

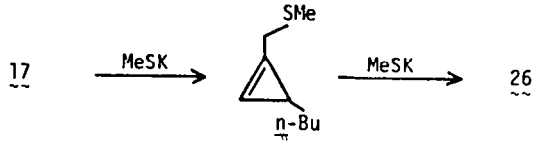
Although the remaining products were difficult to purify, three of them were isolated and structures were assigned tentatively as **24**, **25** and **26**. The fourth product was shown by GC-mass spec to be an isomer of **26**. Although **24** and **25** probably arise from **17** via **27**, the failure to detect the other regioisomer **28** does not invalidate the displacement process.



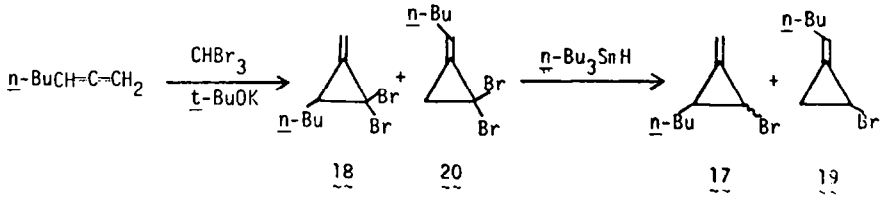
24 25 26

27 28

The disulfide **26** is unexpected. A possible route to this product in illustrated in Scheme 6. This postulate was tested by treating 1 - methylene - 2,2 - dimethyl - 3 - chlorocyclopropane[12] (**29**) with potassium thiomethide in dimethyl sulfoxide. The product expected from the S_N2' reaction, cyclopropene **30**, was isolated in 60% yield, eqn (7). Cyclopropene formation via HCl elimination is, of course, not possible with **29**. To the best of our knowledge, eqn 5 is the first methylenecyclopropane→cyclopropene transformation to be reported.

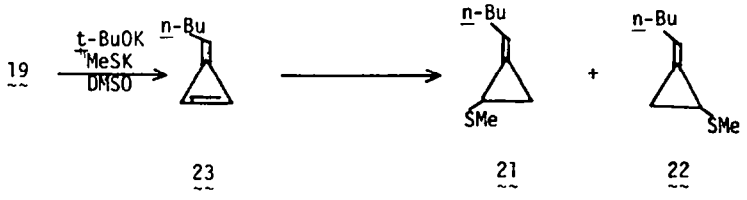


Scheme 6.



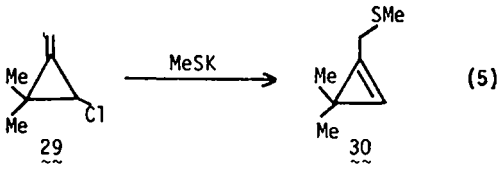
18 20 17 19

Scheme 4.



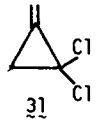
23 21 22

Scheme 5.



29 30 (5)

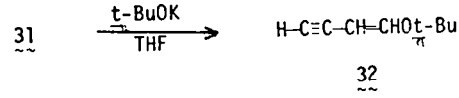
The reaction of 2,2-dichloromethylenecyclopropane (**31**) with potassium t-butoxide and potassium thiomethide was also investigated. The synthesis of **31** from the addition of dichlorocarbene (generated from ethyl trichloroacetate and sodium methoxide) to allene has been reported by Dolbier, Tarrant *et al.*[13] As further purfication of **31** was not required for thier work, they made no attempt to isolate the pure material.



31

We found that the separation of **31** from the by-product, ethyl methyl carbonate, was nearly impossible by either distillation or column chromatography; however, generation of the dichlorocarbene via sodium n-butoxide and ethyl trichloroacetate gives butyl methyl carbonate which can be separated easily from **31** by distillation. This procedure was used to prepare nearly pure **31** in 19% yield.

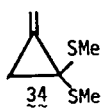
We were surprised to find that **31** and potassium t-butoxide in tetrahydrofuran yielded an 83:14 mixture of *trans* and *cis* - 1 - t - butoxybut - 1 - ene - 3 - yne (**32**) in 42% yield. Another unstable product (< 5%) was also detected, but not characterized.



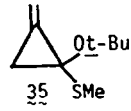
32

The formation of the enynes is puzzling. A possible interpretation involves chloromethylenecyclopropene (**33**) as a reactive intermediate which then experiences the series of events illustrated in Scheme 7. Evidence for **33** arises when methanethiol is added to the reaction medium. Under these conditions **34** and **35** are produced in 99% yield. The ratio of these products is, of course, sensitive to the concentrations of the nucleophiles.

Finally, when **31** was added to methyl mercaptide prepared by the addition of excess methanethiol to potassium t-butoxide in dimethyl sulfoxide, **36** was isolated in 67% yield. This observation provides additional evidence for the proposed $S_{N}2'$ process discussed earlier. (Scheme 8).



34



35

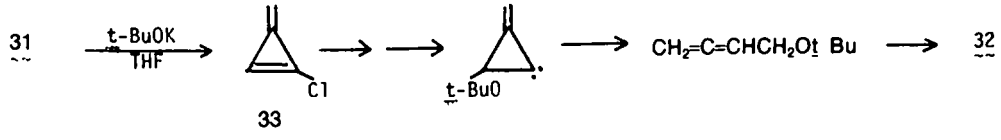
EXPERIMENTAL

PMR spectra were recorded using either a Varian Model EM-390 (90 MHz), XL-100 (100 MHz), A56/60 (60 MHz) or JEOL FX90Q (90 MHz) spectrometer. Chemical shifts (δ) are expressed in ppm downfield from internal TMS. ^{13}C NMR spectra were recorded using the JEOL FX90Q spectrometer. IR spectra were recorded using a Beckman IR spectrometer. High resolution mass spectra were recorded on a double-focusing CEC 21-110 mass spectrometer operated at 70 eV. A Finnigan Model 3300 gas chromatograph-mass spectrometer was used for the GC/MS work. Glpc analyses were carried out on a Model 700 Hewlett Packard gas chromatograph using a thermal conductivity detector with helium as carrier gas. M.ps and B.ps are uncorrected.

Tetrahydrofuran was distilled from sodium-benzophenone ketyl immediately before use. Dimethyl sulfoxide was distilled from calcium hydride under reduced pressure and stored over 4A molecular sieves.

Gaseous reagents were obtained from Matheson Company, Inc. t-BuOK and alkyl lithium reagents were supplied by Ventron Corporation. Tri-n-butyltinhydride was obtained from Chemical Procurement Laboratories, Inc. 1,1-Dichloroethane and bromoform were reagent grade and were distilled prior to use.

Synthesis of 1,2-*dichloro*-1-*methylcyclopropane* (**2**). A soln of 1,1-dichloroethane (108.8 g, 1.1 mol) in anhyd ether (350 ml) was added to a 2-l 3-necked flask fitted with a mechanical stirrer, N_2 purging apparatus, addition funnel and dry ice-acetone condenser. The soln was then cooled to −40° and vinyl chloride (68.7 g, 1.1 mol) was passed into the flask. n-BuLi (1 mol, ~2.2 M) in hexane was then added dropwise to the stirred soln over approximately 3.5 hr. After the addition was complete, the mixture was stirred an additional 1 hr as the soln warmed to room temp. The mixture was added to water (300 ml), extracted with ether and dried over Na_2SO_4. Gas chromatographic analysis showed both isomers (~65:35) of **2** (~10% yield) along with other unidentified products. Distillation through a spinning band column provided the minor isomer in a fraction boiling at 100–105°. Further purification was accomplished by preparative gc (10% Carbowax 20 M on Chromosorb W). NMR δ0.89–1.09 (m, 1 H), 1.72 (s, 3 H) and 3.31–3.51 (m, 1 H). The major isomer was isolated in ~5% yield from the fraction boiling at 115–120°. In



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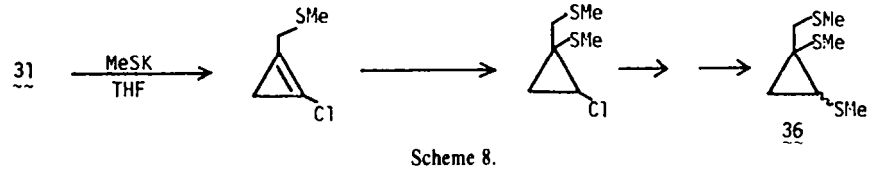
Scheme 7.



36

Scheme 8.

another experiment, 6.2 g (5% yield) of the major isomer was isolated from the 100–126° fraction. NMR δ1.12–1.43 (m, 2 H), 1.65 (s, 3 H) and 2.95–3.10 (d of d, 1 H). MS *m/e* 123.9836 (M^+), calc. for $C_4H_6Cl_2$, 123.9846.

Reaction of 1,2 - *dichloro* - 1 - *methylcyclopropane* (**2**) *with potassium t-butoxide in tetrahydrofuran.* The major isomer of **2** (0.5 g, 0.004 mol) was added dropwise at −30 to −40° to a stirred slurry of t-BuOK (3.58 g, 0.032 mol) in THF (20 ml). After stirring for 1 hr, water was added and the soln extracted into pentane. The extracts were washed with water, dried over Na_2SO_4 and concentrated *in vacuo.* Preparative gc (Carbowax 20 M on Chromosorb WAW) yielded 18.6 mg (37% yield) of **3**. NMR δ1.19–1.4 (m, 3 H), 1.2 (s, 9 H), 3.35–3.62 (m, 1 H) and 5.23–5.57 (m, 2 H); MS *m/e* 126.1042 (M^+), calc. for $C_8H_{14}O$, 126.1044. The minor isomer of **2** yielded **3** in 32% yield.

Reaction of 1,2 - *dichloro* - 1 - *methylcyclopropane* (**2**) *with potassium t-butoxide in dimethyl sulfoxide.* The major isomer of **2** (0.30 g, 0.0024 mol) was added dropwise to a stirred soln of t-BuOK (2.15 g, 0.0192 mol) in DMSO (10 ml). The mixture was then stirred 0.5 hr, poured onto ice, and extracted with pentane. The extracts were washed with brine and filtered throught $MgSO_4$. Removal of the solvent *in vacuo* and purification by preparative gc as described above yielded 0.1 g (33% yield)of **3**.

Reaction of 1,2 - *dichloro* - 1 - *methylcyclopropane* (**2**) *with methyl mercaptan and potassium t-butoxide in dimethyl sulfoxide.* Methyl mercaptan (0.38 g, 0.008 mol) was distilled into soln of t-BuOK (2.7 g, 0.024 mol) in DMSO (30 ml) at 15° by means of a tube inserted below the level of the soln. The soln was stirred for 15 min followed by the addition of **2** (0.5 g, 0.004 mol). After stirring for 30 min, the soln was poured onto ice and extracted with pentane. The extracts were washed with brine, dried over Na_2SO_4 and concentrated to 1.5 ml at 1 atm. Purification by preparative gc as described earlier yielded 0.073 g of **3** (14% yield) and 0.136 g of **4** (34% yield). Compound **4** exhibits NMR signals at δ0.93–1.73 (m, 2 H), 2.10 (s, 3 H), 2.20–2.58 (m, 1 H) and 5.27–5.53 (m, 2 H); MS *m/e* 100.0342 (M^+), calc for C_5H_8S, 100.0346.

Synthesis of 1,1 - *dibromo* - 2 - *chloro* - 2 - *methylcyclopropane.* t-BuOK (44 g, 0.392 mol) and petroleum ether (200 ml, 20–40°) were added to a 500 ml 3-necked flask equipped with a dry ice condenser, mechanical stirrer, addition funnel and N_2 purging apparatus. The resulting mixture was cooled to −70° and 2-chloropropene (20 g, 0.261 mol) was added rapidly. $CHBr_3$ (98 g, 0.388 mol) was then added dropwise over a 2 hr period. After the addition was complete, the mixture was allowed to stir at −70° for 1 hr, warmed to room temp. and stirred for 30 min. Water was added and the product extracted into petroleum ether (20–40°). A black tarry substance was removed by filtration. The extracts were then washed with water, dried over Na_2SO_4 and concentrated *in vacuo* to yield 25.5 g of crude product. Distillation through a short Vigreaux provided 13.1 g of product (20% yield), b.p. 35–38/0.6 mm, which was shown to be ~98% pure by glpc (20% SE-30 on Chromosorb P). NMR δ1.93 (s, 3 H) and 1.75–2.05 (m, 2 H).

Synthesis of 1 - *bromo* - 2 - *chloro* - 2 - *methylcyclopropane* (**10**). A 50 ml 3-necked flask equipped with a magnetic stirrer, addition funnel with a rubber septum, reflux condenser and N_2 purging apparatus were flame-dried and cooled. Benzene (20 ml) was then added to the reaction vessel and degassed by passing a stream of N_2 through the benzene for 3 hr. 1,1 - Dibromo - 2 - chloromethylenecyclopropane (6.52 g, 0.0263 mol) and a few milligrams of azobisisobutyronitrile were then added under nitrogen. Tri-*n*-butyltin hydride (7.65 g, 0.026 mol) was added dropwise while maintaining the mixture at 0°. The mixture was then heated to 55° and irradiated with a sunlamp. After 3 h the reaction mixture was distilled using a micro distillation apparatus to afford 3.11 g (70% yield) of **10**, b.p. 100–103. Glpc analyses (20% SE-3- on Chromosorb P) showed two peaks which were separated by preparative glpc for analysis. The major isomer (~65%) exhibits NMR signals at δ1.06 (d of d, 1 H), 1.69 (t, 1 H) and 3.38 (d of d, 1 H). The minor isomer display signals at δ1.16–1.53 (m, 2 H), 1.68 (s, 3 H) and 2.91 (d of d, 1 H).

Reaction of 2 - *bromo* - 1 - *chloro* - 1 - *methylcyclopropane* (**10**) *with potassium t-butoxide in tetrahydrofuran.* Compound **10** (0.5 g, 0.0029 mol) was added at −30 to −40° to a suspension of t-BuOK (2.65 g, 0.0236 mol) in THF (20 ml). The resulting mixture was then stirred for 1 hr, diluted with water and the product extracted into petroleum ether. The extracts were dried over Na_2SO_4 and the solvent removed *in vacuo.* Purification using preparative glpc as described earlier gave 0.11 g (30% yield) of **3**, identical (NMR and IR) with the sample obtained from **2**.

Reaction of 2 - *bromo* - 1 - *chloro* - 1 - *methylcyclopropane* (**10**) *with potassium t-butoxide and methanethiol in dimethyl sulfoxide.* Compound **10** (1.0 g, 0.0058 mol) was added dropwise to a mixture of *t*-BuOK (5.2 g, 0.0463 mol) and methanethiol (1.12 g, 0.023 mol) in DMSO (50 ml). The product **8** was isolated by preparative glpc in 47% yield and identified by comparison with the sample obtained from **2**.

Synthesis of 2,2 - *dibromo* - 3 - n - *butyl* - 1 - *methylenecyclopropane* (**18**). 1,2-Heptadiene (18.4 g, 0.192 mol) was added rapidly under N_2 to a slurry of t-BuOK (53.9 g, 0.48 mol) in pentane (300 ml) at −78°C. Bromoform (33.5 ml, 0.384 mol) in pentane (70 ml) was then added dropwise while stirring over a 1 hr period. The mixture was allowed to warm to ambient temp. over 1.5 hr and then stirred for 1 hr at ambient temp. The mixture was washed with water (400 ml) and the pentane layer was dried over $MgSO_4$ and concentrated *in vacuo.* Distillation through a 4 in. Vigreaux column yielded 15.5 g of **18** (24.2% yield) and **20** (5.8% yield) b.p. 68–70°/0.2 mm Hg. Analytical samples were isolated by preparative gc (10% OV-17 on Chromosorb WAW). Spectral properties: **18**; ^1H NMR δ0.5–0.9 (m, 3 H), 1.0–1.5 (m, 6 H), 1.9 (m, 1 H), 5.1 (m, 1 H), and 5.5 (m, 1 H); IR (neat) 765, 900, 1040, 1450, 1460, 2880, 2920 and 2960 cm^{-1}; MS *m/e* 265.9309 (M^+), calc for C_8H_{12} $^{79}Br_2$ 265.9305. **20**; ^1H NMR δ0.4–0.8 (m, 3 H), 0.8–1.4 (m, 6 H), 1.6–2.0 (broad s, 2 H) and 6.0–6.3 (m, 1 H); IR (neat) 920, 1015, 1260, 1450, 1460, 1690, 1750 (w), 1850 (w), 2880, 2920, 2960, MS *m/e* 265.9307 (M^+), calc. for C_8H_{12} $^{79}Br_2$ 265.9305.

Reduction of 2,2 - *dibromo* - 3 - n - *butyl* - 1 - *methylenecyclopropane* (**18**) *and* (**20**) *with tri*-n - *butyltinhydride.* The hydride (10.0 g, 0.34 mol) was added dropwise, under N_2, to **18** and **20** (9.21 g, 0.034 mol) at 0°. The mixture was then warmed to 35° and allowed to stand for 24 hr. Distillation provided 4.01 g, b.p. 40–41°/0.2 mm, of *trans*-**17** (7.9% yield), *cis*-**17** (40.4% yield) and **19** (14% yield). Analytical samples were obtained by preparative gc (10% OV-17 on Chromosorb WAW). Spectral properties: *trans*-**17**; ^1H NMR δ0.6–0.9 (m, 3 H), 0.9–1.4 (m, 6 H), 1.4–1.7 (m, 1 H), 2.9 (narrow m, 1 H), 5.35 (t, J = ~2 Hz, 1 H) and 5.6 (d, J = 3 Hz, 1 H); IR (neat) 900, 1180, 1380, 1450, 1460, 2840, 2920 and 2960 cm^{-1}; MS *m/e* 188.0202 (M^+), calc. for C_8H_{13} ^{79}Br 188.0200. *cis*-**17**, ^1H NMR δ0.6–1.0 (m, 3 H), 1.0–1.7 (m, 7 H), 3.3–3.5 (d, J = 8 Hz, 1 H), 5.25 (t, J = ~1 Hz, 1 H) and 5.45 (s, 1 H); IR (neat) 900, 1200, 1370, 1430, 1450, 1460, 2850, 2920, 2960 cm^{-1}; MS *m/e* 188.0202 (M^+), calc. for C_8H_{13} ^{79}Br 188.0200. **19**, ^1H NMR δ0.7–1.0 (m, 3 H), 1.0–1.6 (m, 6 H), 1.8–2.3 (m, 2 H), 3.1–3.4 (m, 1 H) and 5.9–6.2 (m, 1 H); IR (neat) 910 (w), 980, 1030, 1200, 1460, 1470, 1760 (w), 2860, 2880, 2920 and 2960 cm^{-1}; MS *m/e* 188.0202 (M^+) calc. for C_8H_{13} ^{79}Br 188.0200.

Reaction of 2 - *bromo* - 3 - n - *butyl* - 1 - *methylenecyclopropanes* (**17**) *and* (**19**) *with potassium* t-*butoxide and methanethiol in dimethyl sulfoxide.* Methanethiol (0.382 g, 0.0079 mol) was distilled under N_2 into a soln of t-BuOK (2.08 g, 0.0185 mol) in DMSO (30 ml). The mixture of **17** and **19** (1.0 g, 0.0053 mol) was then added dropwise, and the resulting mixture stirred at 25° for 2 hr. The product was poured into ice water (40 ml) and extracted into ether. The ether extracts were dried over $MgSO_4$ and concentrated *in vacuo* to yield 0.71 g of crude product. Compounds **21**, **22**, **24–26** (1:3:4:3.8:4.1) were isolated or enriched by preparative gc (10% OV-17 on Chromosorb WAW). A sixth minor product was not isolated. Spectral properties: **24**, ^1H NMR δ0.6–1.0 (distorted t, 3 H), 1.0–1.3 (m, 6 H), 1.6–1.9 (broad m, 1 H), 1.9 (s, 3 H), 2.05–2.2 (broad t, 1 H), 5.2–5.45 (broad t, 2 H); IR (neat) 890, 1220 (w), 1370 (w), 1430, 1460, 2860, 2920, 2960 cm^{-1}; MS *m/e* 156.0972 (M^+) calcd for $C_9H_{16}S$ 156.0973. **25**, (mixed with **24**) ^1H NMR (partial) δ1.1–1.4 (distorted t, 3 H), 2.35 (s, 3 H) and 2.8–2.95 (m, 1 H). **21** and **22**, ^1H NMR δ0.85–1.2 (distorted t, 6 H), 1.25–1.85 (broad m, 12 H), 1.95–2.2 (s, 6 H), 2.25–2.45 (m, 3 H), 2.5–2.8 (m, 3 H), 5.4–5.6 (m, 1 H), 5.7–6.15 (m, 1 H); IR (neat) 890 (w), 1220, 1370 (w), 1430, 1460, 1630, 1660, 2840, 2880, 2920, 2960 cm^{-1}; MS *m/e* 156.0972 (M^+) calcd for $C_9H_{16}S$ 156.0973. **26**, (sample 75% pure) ^1H NMR

δ0.6–1.0 (m, 5 H), 1.2–1.8 (m, 9 H) 2.0 (s, 3 H), 2.1 (s, 3 H); ^{13}C NMR δ13.2, 14.2, 15.0, 16.1, 17.1, 17.6, 22.7, 31.5, 32.3, 33.1; *IR (neat)* 1410, 1430, 1460, 1700, 1770, 2840, 2920, 2960 cm^{-1}; MS *m/e* 204.1011 (M$^+$), calc. for $C_{10}H_{20}S_2$ 204.1006.

Reaction of 2 - *chloro* - 3,3 - *dimethylmethylenecyclopropane* (**29**) *with potassium marcaptide in dimethyl sulfoxide.* Methanethiol (0.41 g, 0.0085 mol) was distilled into a soln of t-BuOK (0.9 g, 0.0080 mol) in DMSO (15 ml). The resulting soln was stirred for 30 min and **29** (1.0 g; 0.0086 mol) in DMSO (10 ml) was added dropwise with cooling. The soln was then stirred for 2.5 hr, poured into ice water, and extracted twice with pentane and the combined extracts dried over Na_2SO_4. Removal of the pentane *in vacuo* followed by preparative tlc (silica gel, CCl_4) gave 0.66 g (60% yield) of **30**. NMR (CCl_4) δ1.17 (s, 6 H), 2.05 (s, 3 H), 3.41 (s, 2 H) and 6.81 (s, 1 H); IR 1746 cm^{-1} (cyclopropane); MS *m/e* 128.0666 (M$^+$), calcd for $C_7H_{12}S$ 128.0659.

Synthesis of 2,2 - *dichloro* - 1 - *methylenecyclopropane* (**31**). n-Pentane (400 ml) and freshly prepared n-BuONa (40 g, 0.42 mol) were added to a 1-l 3-neck round bottom flask equipped with a mechanical stirrer, dry ice condenser, addition funnel and N_2 purging apparatus. The resulting suspension was cooled to −40°. Allene (80 g, 2 mol) was then condensed into the flask. Ethyl trichloroacetate (96 g, 0.50 mol) was added rapidly and the mixture allowed to warm to room temp. with stirring. At −10° refluxing began and at −8° the solution became dark. After warming to room temp (overnight), water (200 ml) was added and the aqueous layer extracted with pentane (200 ml). The organic layer was dried over Na_2SO_4 and distilled at 1 atm through a 1 ft Vigreaux column to afford 12.36 g (24% yield) of **31**, b.p. 95–105°, lit.[12] 90–100°.

Reaction of 2,2 - *dichloro* - 1 - *methylenecyclopropane* (**31**) *with potassium t-butoxide in tetrahydrofuran.* Compound **31** (3.0 g, 0.0244 mol) was added to a soln of t-BuOK (27.2 g, 0.242 mol) in THF (120 ml) at 0°. The mixture was then allowed to warm to room temp. over 1.5 hr, poured into water and extracted with ether. The extracts were washed with water, dried over Na_2SO_4 and concentrated *in vacuo* to yield 1.27 g (42% yield) of an 83:14 mixture of *trans* and *cis*-enynes (**32**), respectively. The *trans* isomer displays NMR signals at δ1.33 (s, 9 H), 2.70 (d, J = 3 Hz, 1 H), 4.90 (d of d, J = 12 and 3 Hz, 1 H), 6.95 (d, J = 12 Hz, 1 H); IR (neat) 3300, 3060, 2980, 2100, 1630, 1370, 1240, 1160 cm^{-1}; MS (20 eV) *m/e* 124.0888 (M$^+$), calcd for $C_8H_{12}O$ 124.0809. The *cis* isomer exhibits NMR signals at δ1.33 (s, 9 H), 3.0 (d, J = 3 Hz, 1 H), 4.50 (d of d, J = 8 and 3 Hz, 1 H), 6.65 (d, J = 8 Hz, 1 H); IR (neat) 3300, 3060, 2980, 2100, 1625, 1400, 1370, 1270, 1170 and 1110 cm^{-1}; MS *m/e* (20 eV) 124.0888 (M$^+$), calc. for $C_8H_{12}O$ 124.0890.

Reaction of 2,2 - *dichloro* - 1 - *methylenecyclopropane* (**31**) *with methanethiol and potassium t-butoxide in tetrahydrofuran.* Methanethiol (4.70 g, 0.0977 mol) was added to a soln of t-BuOK (27.2 g, 0.0242 mol) in THF (120 ml) while cooling with an ice/salt bath. 2,2-Dichloro - 1 - methylenecyclopropane (3.0 g, 0.0244 mol) was then added dropwise. The mixture was allowed to warm to room temp over 4 hr, poured into water and extracted with ether. The extracts were washed with water, dried over Na_2SO_4 and concentrated *in vacuo* to yield 3.54 g (91% yield) of a 56:44 mixture of **34** and **35**, respectively. Compound **34** was purified by preparative gas chromatography. NMR δ1.30 (s, 9 H), 1.65 (t, J = 2 Hz, 2 H), 2.25 (s, 3 H), 5.40 (t, J = 2 Hz, 1 H), 5.65 (t, J = 2 Hz, 1 H); IR (neat) 2980, 2930, 1670, 1390, 1360, 1155, 1070 cm^{-1}; MS *m/e* (20 eV) 116.0298 (M$^+$-isobutylene), calc. for C_5H_8OS 116.0296. **35** decomposed during gas chromatography and was purified by preparative tlc (silica gel, CS_2 and CH_2Cl_2, 50:50). NMR δ2.13 (s, 6 H), 2.60 (t, J = 2 Hz, 2 H), 5.60 (t, J = 2 Hz, 2 H); IR (neat) 2980, 2920, 1440, 1210, 920 cm^{-1}; MS *m/e* (20 eV) 146.0220, calc. for $C_6H_{10}S_2$ 146.0224.

Reaction of 2,2 - *dichloro* - 1 - *methylenecyclopropane* (**31**) *with potassium methyl mercaptide in dimethyl sulfoxide.* Methanethiol (0.49 g, 0.0102 mol) was passed into a soln of t-BuOK (0.92 g, 0.0082 mol) in DMSO (30 ml). 2,2 - Dichloromethylenecyclopropane (0.25 g, 0.0021 mol) was then added via a syringe, and the mixture was stirred under N_2 at 25° for 2 hr. The mixture was poured into water (40 ml) and extracted with ether. The ether extracts were dried over Na_2SO_4 and concentrated *in vacuo* to yield 0.34 g of crude product. Purification by preparative gc (10% OV-17 on Chromosorb WAW) yielded 0.27 g (67.5% yield) of **36**. Spectral properties: ^1H NMR δ0.9–1.0 (t, 1 H), 1.2–1.5 (m, 1 H), 2.0 (s, 6 H), 2.2 (s, 3 H), 2.25–2.5 (m, 1 H), 3.5 (s, 2 H); ^{13}C NMR δ14.0, 15.8, 16.3, 22.7, 32.5, 33.5, 38.2; IR (neat) 940, 960, 1040, 1190 (w) 1230, 1260, 1310, 1420, 2840, 2910, 2990 cm^{-1}; MS *m/e* 194.0254 (M$^+$), calc. for $C_7H_{14}{}^{32}S_3$ 194.0258.

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