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SYNTHESIS OF METHYLENECYCLOPROPENES

by

Andrew J. Blakeney

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SYNTHESIS OF METHYLENECYCLOPROPENES

INTRODUCTION

A. The Family of C_4H_4 Compounds

Methylenecyclopropene 1 is a member of the family of C_4H_4 hydrocarbons whose ring strain and bonding make them objects of considerable interest with regard to theory and synthesis. Other prominent

1 2 3

members of this family are cyclobutadiene 2 and tetrahedrane 3.

Cyclobutadiene has been detected spectroscopically at low temperatures but not isolated.^{1,2} No such evidence for the existence of tetrahedrane has been reported, although it has been postulated as an intermediate.^{2,3}

Other members of this family of C_4H_4 hydrocarbons include compounds 4-10. The absence of ring strain and the conjugation of the multiple

4 5 6 7 8 9 10

bonds gives vinylacetylene 4 and 1,2,3-butatriene 5 a stability unmatched by the other members of the C_4H_4 family.^{2,4-6} 5, however, is only stable below 0° .^{2,6} Compounds 6-10 have received little attention because the possibility of their detection, much less their characterization, seems remote.²

B. Methylenecyclopropene and Its Derivatives

Methylenecyclopropene 1 is the simplest cross-conjugated non-heterocyclic system. Due to its relationship with heptafulvene 11 and cyclopropenone 12, methylenecyclopropene and its derivatives have become objects of theoretical study.^{7,8} Methylenecyclopropene 1 is predicted to be of very low stability. MO calculations⁹⁻²¹ have been

used to estimate that 1 possesses only minor resonance stabilization ($\approx 1\beta$). The high index of free valency at C_4 causes an overwhelming tendency to polymerize,⁷ a process which also eases strain.²² Dewar²³ has calculated the strain energy of 1 to be 58.1 kcal/mole and the heat of formation to be 79.1 kcal/mole. Figure 1 shows the MO scheme of 1 as well as the bond orders and free valencies.

MO Scheme of Methylene cyclopropene⁸

bond orders: C^1-C^2	0.818	free valencies: $C^{1(2)}$	0.462
$C^{1(2)}-C^3$	0.453	C^3	0.068
C^3-C^4	0.758	C^4	0.974

total π -electron energy: 4.962β

FIGURE 1

Only two attempts to synthesize 1 have been reported in the literature (equations 1, 2). Photolysis and flash vacuum pyrolysis of

syn-1-methylenecyclopropene-2,3-dicarboxylic anhydride 13 (equation 1) yielded vinylacetylene and small amounts of acetylene and methylacetylene.²⁴ The intermediacy of 1 was not established. A dehydrochlorination-isomerization sequence (equation 2) pursued by Shields and Gardner²⁵ produced only polymer.

Overcoming the predicted instability of methylenecyclopropenes has presented a challenging synthetic task. The basic approach to the synthesis of methylenecyclopropenes has been to synthesize derivatives with functional groups that stabilize the dipolar resonance structure of methylenecyclopropene 1a. Thus, synthetic attempts have incorporated C_4 as part of a system delocalizing the negative charge or have incorporated the three-membered ring into a system to delocalize the positive charge.⁸ Four types of resonance stabilized methylenecyclopropenes (14, 15, 16, 17) have been isolated and studied.

The stability of methylenecyclopropenes of type 14 depends on the electron withdrawing abilities of such substituents as COOR, COR, CN, etc. Methylenecyclopropenes 15 have C_4 incorporated into a cyclopentadienyl system such that both ring systems can fulfill the Hückel definition of aromaticity in the dipolar form. Methylenecyclopropenes 16 contain C_4 as a portion of a quinomethane ($X=O$) or quinodimethane ($X=CR_2$) system. Methylenecyclopropenes 17 are cyclopropenium cyanines which combine the three-membered ring with another donor group.

C. Spectroscopic Properties

Infrared spectra of methylenecyclopropenes show two characteristic bands, a high energy vibration between 1830 and 1880 cm^{-1} and a band between 1520 and 1550 cm^{-1} .^{8,22,26-30} The former is probably predominantly a ring vibration, whereas the latter has a strong component of the exocyclic double bond vibration. Neither of these bands is due to isolated vibrational modes but are due to strong coupling of the oscillators. Only determination of the force constants by complete coordinate analyses will allow conclusions from ir spectra as to the degree of polarity in these molecules. This has not yet been performed.^{8,22}

A better measure of the contribution of the dipolar form of methylenecyclopropenes is provided by nmr spectroscopy.²² Comparison of the chemical shift of the vinyl proton of 18 with the model compound 19 showed an upfield shift of .9 ppm in 18 which reflects increased charge density at the terminal methylene.²⁶ Prior to the work in this thesis, few compounds with an H on C_4 had been

synthesized.^{26,31,32} The chemical shifts of methyl groups and the chemical shifts of the α - and β -methylene protons of the propyl group of 20 and the propyl group of 21 indicate 15% of a unit positive charge on each propyl bearing carbon atom in 20, which correspond to a 50% contribution of the dipolar structure.

The ultraviolet spectra of methylcyclopropenes is very complex because the conjugated chromophores of the unsaturated substituents necessary to stabilize the methylenecyclopropenes obscure information in the cross conjugated species.^{8,17} 20 which is closest to 1 shows a single maximum at 246 m μ ²⁸ which reflects the theoretically predicted high energy of the $\pi \rightarrow \pi^*$ transition.¹³ The absorption of 1 can then be estimated to appear in the region of 205-215 nm using the bathochromic effect of geminal dicyano substitution as determined for ethylene compounds.⁸ The absorption is in agreement with a MO prediction that the $\pi \rightarrow \pi^*$ transition for 1 will be near 200 nm.¹³

D. Methods of Synthesis of Methylenecyclopropene

One of the first syntheses of methylenecyclopropenes was a Wittig reaction of diphenylcyclopropenone (equation 3).²⁶ However, this method has not proven to be of general application. The inverse

functionalization was used by Semenov³¹ to prepare unstable methylenecyclopropenes which were characterized by protonation as cyclopropenium salts (equation 4).

Another method uses cyclopropenium cations as a precursor (equations 5, 6).³⁵ Treatment of a cyclopropenium ion with a Li, Na, or Grignard reagent followed by subsequent hydride abstraction and

deprotonation has proved to be of use especially in synthesizing calicene derivatives (equation 6).^{33,36-39}

A general method of synthesizing methylenecyclopropenes of type 14 and 15 is the classical condensation of reactive methylene compounds with cyclopropanones (equation 7).²⁷⁻²⁹ Yields can be improved

greatly by use of alkoxy cyclopropenium cations⁴⁰ prepared by alkylation of cyclopropenones with trialkyloxonium tetrafluoroborates (equation 8).⁴¹

Reaction of 24 (R=Ø) with 1,3-diketones, however, does not produce 4,4-diacylmethylenecyclopropenes. Reaction of 25 with a copper or zinc chelate of a 1,3-diketone (equation 9) gives high yields of 4,4-diacylfulvenes.^{34,42} Table I lists the method of preparation, yield, and references to a number of methylenecyclopropenes of type 14.

TABLE I. Preparation of Some Methylenecyclopropenes of Type 14⁸

Methylenecyclopropene	Yield (%)	Method	Refs.
<u>R = CH₃</u>			
R' = R'' = CN	41	DIPEA	8
R' = CN, R'' = COOCH ₃	34	DIPEA	8
R' = R'' = COCH ₃	22	Cu-chelate	8
R', R'' = dimedone	58	DIPEA	8
R' = CN, R'' = NO ₂	43	NH ₄ -salt of NC-CH ₂ -NO ₂	8
R' = CN, R'' = COC ₆ H ₅	35	DIPEA	8
R' = CN, R'' = p-NO ₂ -C ₆ H ₄	8	DIPEA	8
<u>R = n-C₃H₇</u>			
R' = R'' = CN	18	Acetic anhydride	28
<u>R = -(CH₂)₅-</u>			
R' = R'' = CN	58	DIPEA	8

TABLE I. (Continued)

Methylenecyclopropene	Yield (%)	Method	Refs.
$\text{Ar} = \text{C}_6\text{H}_5$			
$\text{R}' = \text{R}'' = \text{CN}$	85	DIPEA	49
	24	Acetic anhydride + alanine	29
$\text{R}' = \text{CN}, \text{R}'' = \text{COOCH}_3$	82	DIPEA	49
$\text{R}' = \text{CN}, \text{R}'' = \text{COOC}_2\text{H}_5$	70	DIPEA	8
	15	Acetic anhydride + alanine	29
$\text{R}' = \text{CN}, \text{R}'' = \text{COC}_6\text{H}_5$	66	DIPEA	50
$\text{R}' = \text{R}'' = \text{COCH}_3$	80	Cu-chelate	42
$\text{R}' = \text{R}'' = \text{COC}_6\text{H}_5$	80	Cu-chelate	8
$\text{R}' = \text{COC}_6\text{H}_5, \text{R}'' = \text{CO}_2\text{C}_2\text{H}_5$	62	Cu-chelate	42
$\text{R}' = \text{COCH}_3, \text{R}'' = \text{CONHC}_6\text{H}_5$	78	Cu-chelate	42
$\text{R}' = \text{COC}_6\text{H}_5, \text{R}'' = \text{CHO}$	74	Cu-chelate	42
$\text{R}', \text{R}'' = \text{dimedone}$	64	DIPEA	49
$\text{R}', \text{R}'' = \text{meldrum acid}$	53	DIPEA	49

TABLE I. (Continued)

Methylenecyclopropene	Yield (%)	Method	Refs.
$R', R'' = \text{indane dione}$	64	Acetic anhydride	51
$R' = H, R'' = -CPh=C(CN)_2$	24	DIPEA	8
$R' = COOC_2H_5$	95	DIPEA	8
$R'' = -C=C(CN)_2$ $\quad $ CH_3			
$R' = CN, R'' = NO_2$	61	NH_4 -salt of $NC-CH_2-NO_2$	8
$Ar = p-CH_3-C_6H_4$	59	bis-p-tolylcyclopropenone + $(CF_3)_2C=O$	43
$R' = R'' = CF_3$			
$R' = CH_3$			
$R' = R'' = COCH_3$	74	Cu-chelate	52
$R' = COCH_3, R'' = CONHC_6H_5$	96	Cu-chelate	52
$R' = CN, R'' = NO_2$	96	NH_4 -salt of $NC-CH_2-NO_2$	8

TABLE I. (Continued)

Methylenecyclopropene	Yield (%)	Method	Refs.
$R' = R'' = \text{CN}$	19	DIPEA	8
$R', R'' = \text{dimedone}$	65	DIPEA	8
$R = \text{C}(\text{CH}_3)_3$	27	DIPEA	8
$R' = R'' = \text{CN}$			
$R = \text{H}$			
$R' = R'' = \text{COCH}_3$	16	Cu-chelate	8
$R' = \text{COCH}_3, R'' = \text{COC}_6\text{H}_5$	27	Without base	8

Reaction of bis(trifluoromethyl)ketene with bis(*p*-tolyl)cyclopropenone followed by elimination of CO₂ yields 26 (equation 10).

Quinocyclopropenes (type 16) were among the first stable methylenecyclopropenes to be reported. Kende⁴⁴ prepared 28 from the cyclopropenium cation 27 according to equation 11. This principle of

formation has proved to be general for the quinomethylenecyclopropenes.^{40,45,46} The necessary *p*-hydroxy phenyl cyclopropenium cations are readily available by electrophilic substitution of phenolic components by heterosubstituted cyclopropenium cations 24 or 29 (equation 12).^{33,40,45,46}

Cyclopropenium cyanines may be prepared by reaction of 24 with a large number of donor groups, mainly heterocyclic and carbocyclic systems. Enamines, ketene acetals and 2- or 4-alkylsubstituted heterocyclic quaternary salts of pyridine, quinoline and benzothiazol can be

readily "cyclopropenated."^{40,47} Electrophilic attack by 24 on azulene (equation 14) yields 30.

Stang's synthesis of methylenecyclopropenes⁴⁸ involves addition of vinylcarbenes to acetylenes (equation 15). Treatment of a vinyl

triflate with a strong base (KO-t-Bu) generates, via α -elimination, the vinyl carbene which undergoes addition to the multiple bond of the acetylene. However, this synthesis is limited to cases where R and R' are not H and cases where R^2 and R^3 are not aryl. Cases where $\text{R}^2 = \text{R}^3$ should lead to isomeric products, but at this time the only examples synthesized are where $\text{R}' = \text{R} = \text{Me}$, and $\text{R}^2 = \text{R}^3 = \text{Me}$ or Et. Isolation of these compounds has thus far been unsuccessful but they have been

trapped as the Diels-Alder adducts with cyclopentadiene.⁴⁸

E. Reactions of Methylenecyclopropenes

Most methylenecyclopropenes do not undergo clearly defined thermal transformation possibly because of the differences in polarity due to the diverse substituents, particularly those at C₄.⁸ Cyclo-reversion to alkynes and a vinylidene carbene does not occur. Dimerization to give products of type 31 does not occur either.

The photochemical behavior of methylenecyclopropenes is currently under investigation.⁸ Dimerization is the principal photochemical reaction of 4,4-dicyano and 4,4-diacylmethylenecyclopropene. However, on occasions hydrogen abstraction and solvent incorporation are observed.⁸

The success of oxidation of methylenecyclopropenes depends upon the particular methylenecyclopropene selected. Methylenecyclopropenes 32 are very stable to alkaline H₂O₂.⁸ However, calicenes 33 are readily oxidized by atmospheric oxygen to give allenic ketones 35 probably through an intermediate such as 34 (equation 17).⁵³

Oxidation of cyclopropenylidene anthrone with FeCl_3 in hydroxylic solvents⁵⁴ (equation 18) also yields the allenic ketones.

The reactivity of methylenecyclopropenes towards electrophiles and nucleophiles is determined by their electron distribution.⁸ Protonation of the colored methylenecyclopropenes 36 and 38 yields colorless cyclopropenium cations 37 and 39 by attack of the electrophile at C_4 .^{32,55}

Nucleophiles, such as water, alcohol, ammonia, etc., attack the three-membered ring preferentially.⁸ For example, addition of H_2O to

40 yields a ring opened triketone 41.⁸ The separation of the phenyl-bearing carbon indicates that the nucleophile enters at $C_1(2)$ of the methylenecyclopropene systems. Subsequent transformation of the product of attack depends on the nucleophile and the methylenecyclopropene. A graphic example is shown in Scheme I.⁸

Methylenecyclopropenes undergo several types of reactions with systems containing multiple bonds. 1,2-Diphenyl-4-carbethoxy methylenecyclopropene 18 reacts with TCNE 42 to yield 43, formally a (2+2)

cycloaddition (equation 21).³⁴ The reaction of the calicene 44 and TCNE 42 yields 45 which is formally an (8+2) addition product (equation 22).⁵⁶ Other calicenes react to give stable charge-transfer

complexes.⁵⁷ The ring double bond is also capable of cycloaddition reactions (equation 23). Reaction of 46 with diethylamino butadiene followed by elimination of amine gives the diene 47 which yields a

heptafulvene 48 after ring opening (equation 23).⁵⁷

Other heptafulvenes can be synthesized by reaction of methylene-cyclopropenes with 49 by what is believed to be a dipolar (2+2) cyclo-

addition followed by a concerted opening (equation 24)⁵⁸ to give 50.

Reaction of methylenecyclopropenes with electron rich multiple bonds is envisioned as being via dipolar intermediates 51 or 52.⁸

The products are significantly dependent on the substituents at $C_4(R^2)$. 4,4-Dicyanomethylenecyclopropenes react with enamines to produce compounds of the type 53.^{8,59} 4,4-Diacylmethylenecyclo-

propenes and enamines yield compounds of the types 54 and 55.

Schiff bases of the type 56 react with methylenecyclopropene via the tautomeric vinylamine form to give products of "C-C insertion" (equation 28).⁸

1,2-Diphenyl-4,4-diacetyl methylenecyclopropene 40 adds diazoalkanes across the C¹-C² double bond (equation 29) before rearrangement

to give 57.⁶⁰ Other methylenecyclopropenes exhibit similar behavior but the substituents influence the modes of rearrangement.^{60,61} Calicenes, however, react with the exocyclic double bond⁵⁷ (equation 30).

Methylenecyclopropenes have proven valuable in the synthesis of diverse heterocyclic and nonheterocyclic systems. Because the electron withdrawing substituents at C_4 strongly influence the reaction products of methylenecyclopropenes, the methylenecyclopropenes without these groups may exhibit completely different chemistry. Only Stang,⁴⁸ Semenov,³¹ and this thesis report work on such compounds.

RESULTS AND DISCUSSION

The electronic stabilization of methylenecyclopropenes has been summarized in the introduction. The work in this thesis followed alternate concepts, that of steric protection and that of no stabilization or protection at all. Examples are compounds 58-61 which derive their stability from steric shielding by the t-butyl

groups.⁶²⁻⁶⁵ Thus, t-butyl groups seemed to be an appropriate shielding substituent for methylenecyclopropenes. 1,3-Di-t-butylallene 62 was selected as a precursor for the synthesis of sterically protected methylenecyclopropenes.

62 was synthesized by an adaptation of the synthesis by Corey and Borden (equation 31).⁶⁶ Reduction with Na/NH_3 ⁶⁷ (equation 32) provided 63 in 77% yield (b.p. 52-53°, 8mm). 63 exhibited nmr (CCl_4) absorptions at δ .80 (s, 9H), .94 (s, 9H), 1.70-1.87 (m, 2H), and 5.18-5.45 (m, 2H).

Addition of dichlorocarbene by an adaptation of the method of Joshi, Singh, and Pande⁶⁸ gave 64 in 47% yield. 64 exhibited nmr (CCl₄) absorptions at δ 1.05 (s, 9H), 1.14 (s, 9H), and 1.32-1.62 (m, 4H). Dehydrochlorination of 64 could take two paths (equation 33). Along

path a, intermediate 65a could yield 65b or d which would yield 65c or e, respectively, by further dehydrochlorination. Following path b, no further dehydrochlorination or isomerization is possible so the reaction would terminate. When 64 was subjected to dehydrochlorination conditions, a product which exhibited an ir absorption (CHCl_3) at 1829 cm^{-1} characteristic of cyclopropenes⁶⁹ and an nmr spectrum (CCl_4) which had absorptions at δ .95 (s, 9H), 1.18 (s, 9H), and 1.57-2.12 (m, 3H). Only two structure assignments are logically possible, 65a and 66. Cyclopropenes of the type 65a are known to undergo facile double bond migration out of the strained three-membered ring under the conditions of dehydrochlorination.²⁵ Thus, the product (50% yield) was assigned the structure 66. The yield of 66 does not preclude the possibility that some of 64 reacted via path a and then polymerized. However, isolation of 66 indicated that this approach to methylene-cyclopropenes was not satisfactory and subsequently abandoned.

At this point it was noticed that addition of dichlorocarbene to 62 (equation 34) would provide a path to di-t-butylchloromethylene-cyclopropene 67b after subsequent dehydrochlorination if the carbene could be induced to add to the hindered allene in satisfactory yields.

The precursor 67a does not have the disadvantage of two possible dehydrochlorination routes as did 64. Unfortunately, the yield of 67a was minute. Addition of dibromocarbene (equation 35) was more successful. Subsequent efforts raised yields to 41% (b.p. 64-68°, .3mm).

The dibromocarbene adduct exhibited nmr (CCl_4) absorptions at δ 1.14, 1.16 (2s, 18H), 2.25 (d, 1H, $J=3\text{Hz}$) and 6.36 (d, 1H, $J=3\text{Hz}$) and an M^+ at 321.9889 (calcd 321.9931 for $\text{C}_{12}\text{H}_{20}\text{Br}_2$). Two isomers, 68 and 69 were possible. If the bulky carbene approached from the less hindered side of the allene, then 68 would result. However, space-filling molecular models indicate severe steric crowding of the t-butyl groups in 68. The steric crowding of 69 is considerably less although existent. A ^{13}C study was undertaken to determine the stereochemistry, but lack of appropriate models precluded firm conclusions. Coupled and decoupled ^{13}C spectra are included in Appendix I.

After several weeks at room temperature, the dibromocarbene adduct released what appeared to be acid fumes when exposed to air. Examination of the redistilled dibromocarbene adduct indicated that some decomposi-

tion or isomerization had occurred. A doublet pattern at δ 5.75 which was identical to the doublet pattern of the adduct at δ 6.36 showed promise of being an isomerized product. Attempts to induce the isomerization in CCl_4 thermally or thermally with HBr catalysis were of limited success, due to decomposition and incomplete isomerization. Separation of the two isomers by tlc or glpc was not successful. Finally, it was discovered that treatment with 48% HBr in CCl_4 for lengthy periods resulted in almost complete isomerization (> 95%). The isomerized product exhibited an nmr spectrum (CHCl_3) with absorptions at δ 1.07 (s, 9H), 1.27 (s, 9H), 2.10 (d, 1H, $J=3\text{Hz}$), and 5.75 (d, 1H, $J=3\text{Hz}$) and an ir and mass spectrum almost identical with that of the adduct.

The structure of the dibromocarbene adduct was assigned the structure 68 and the isomerized compound was assigned the structure 69 for the reasons stated here. Approach from the least hindered side of 62 favors formation of 68. Acid equilibration should favor the least sterically crowded isomer, which by space-filling molecular models is 69. Thus, the overall assignment of the sequence is shown in equation 36.

Reaction of 68 in THF with KO-t-Bu at -30 - 40° for 1 hour gave a solution of 70 (equation 37). The solution was recooled and filtered

FIGURE 2

FIGURE 3

under N_2 through glass wool in the apparatus shown in Figure 2. Special precautions had to be taken because 70 (as well as 71) proved to be highly reactive with H_2O and unstable in its solution above 0° . After filtration, the cooled (-40°) collection flask was quickly transferred to the apparatus shown in Figure 3. The flask was evacuated and the cooling bath was allowed to warm to -10 - 20° to distill THF and t-BuOH. When a few ml of solution remained, CCl_4 was added via the attached funnel (see Figure 3) and more liquid was allowed to distill. Repetition of this process 6-8 times gave cooled CCl_4 solutions of 70 with which spectral data were obtained. 70 exhibited nmr absorptions at δ 1.05 (t-Bu), 1.30 (t-Bu) and 3.95 (olefinic) and ir absorptions at 1840 cm^{-1} . The mass spectrum shows M^+ at 242.0664 (calcd 242.0669 for $\text{C}_{12}\text{H}_{19}\text{Br}$).

Reaction of 69 under identical conditions yielded 71 (equation 38) which was treated in the same manner as 70. 71 exhibited nmr absorptions at δ 1.03 (t-Bu), 1.24 (t-Bu) and 4.01 (olefinic), an ir absorption at 1840 cm^{-1} and an M^+ at 242.0664 (calcd 242.0669).

Reaction of 70 or 71 with H_2O gave interesting products (equation 38). 70 or 71 was generated and allowed to warm to -10°

whereupon H_2O was added. Workup yielded 72 and 73 in 33% and 45% yields, respectively, for 70 and 44% and 34% yields, respectively, for 71. 72 exhibited nmr (CCl_4) absorptions at δ 1.05 (s, 9H), 1.14 (s, 9H) and 2.21 (s, 2H); ir absorptions (neat) at 1687 and 2218 cm^{-1} , and an M^+ at 180.1510 (calcd 180.1514 for $\text{C}_{12}\text{H}_{20}\text{O}$). 73 exhibited nmr (CCl_4) absorptions at δ 1.07 (s, 9H), 1.30 (s, 9H) and 2.41 (s, 2H) and ir absorptions (neat) at 1637 and 1837 cm^{-1} . 73 did not exhibit an M^+

in its mass spectrum but exhibited an M^+-CO peak at 152.1570 (calcd 152.1565 for $C_{11}H_{20}$), which is characteristic of cyclopropenones.⁷⁰

A mechanism for the formation of these products is shown in Scheme II. Hydration of 70 or 71 could result in intermediates 74, 75, and 76. Intermediate 74 would result from 1,4 addition of H_2O

SCHEME II

and could give 73 directly. Formation of 73 via 75 would require double bond isomerization into the ring. 72 probably results from hydration of the polar exocyclic double bond to give 76, followed by collapse as indicated in the Scheme.

Additional evidence for the mechanism in Scheme II was found in the reaction of 70 and 71 with D_2O . Examination of Scheme II shows that it predicts that reaction with D_2O should incorporate one deuterium.

Reaction of 70 or 71 with D_2O gave 77 and 78 which were isolated under identical conditions as 72 and 73. The mass spectra for the two

compounds indicated incorporation of only one deuterium as the m/e for 77 was 181 (M^+) and the m/e for 78 was 153 (M^+-CO). In addition, the singlets in the nmr at δ 2.41 for 73 and 2.21 for 72 collapsed to 1:1:1 triplets ($J \approx 2\text{Hz}$).⁷¹

Hydrogenation of 70 to prove that the ring structure was intact proved to be difficult. The apparatus in Figure 2 easily became clogged with decomposition products, salts, and undissolved KO-t-Bu when reactions on a scale larger than .5 g of 68 were used. The transfer from the collection flask to the hydrogenation bottle exposed the solution to moisture. Experiments with cyclohexene in THF with KO-t-Bu indicated that KO-t-Bu poisoned the Rh/alumina catalyst. Thus, excess base dissolved in the THF would escape filtration and poison the catalyst. In addition, 70 decomposed upon warming. Thus, during the hydrogenation, 70 was decomposing. Hydrogenation of a filtered solution of 70, for one hour followed by workup gave a low yield of a gross mixture of products. Preparative tlc (silica gel, CCl_4) of two combined hydrogenation product mixtures followed by extraction of the high rf products

(.52→.74) with CH_2Cl_2 gave a less complex mixture. Preparative glpc (10% SE-30 on Anakrom ABS) of the major product ($\approx 70\%$ of the fraction as determined by peak areas) gave $\approx 8\%$ yield of a compound assigned the

structure 79. 79 exhibited nmr (CCl_4) absorptions at δ .52-1.76 (m, 3H), .92 (s, 9H), 1.08 (s, 9H) and 5.66-5.78 (m, 1H) and an $m/e = 151$ ($\text{M}^+ - \text{CH}_3$). This product is rationalized by hydrogenolysis of the vinyl bromide⁷² followed by hydrogenation of the cyclopropene double bond.

An attempt to prepare an authentic sample of 73 via a reduction of 68 was then undertaken. Na/NH_3 reduction of geminal dihalocyclopropanes is known to give good yields of cyclopropanes.⁷³ 68, however, was not only a geminal dihalocyclopropane, but also a methylenecyclopropane. Na/NH_3 reduction of 68 gave a mixture of a major product, a minor product, and several trace products. Preparative glpc (10% SE-30 on Anakrom ABS) separated the major product but the minor product could not be obtained pure from several trace products. The nmr spectrum of the minor fraction contained absorptions with the proper ratios at identical

places as 79. Simultaneous injections of 79 and the minor product possessed the same retention times on the Anakrom ABS column at several different temperatures as determined by simultaneous injection. GCMS indicated that the major component of the minor fraction had an m/e = 151 as did 79. The major product exhibited nmr absorptions (CCl₄) at δ .83 (s, 18H), 1.82-2.0 (m, 4H),

of KO-t-Bu in DMSO with MeSH present. These conditions are known to induce dehydrohalogenation followed by isomerization or MeS⁻ addition to the double bond if it cannot be isomerized out of the ring.²⁵ The major product of the reaction was isolated by preparative tlc (silica gel, CCl₄) in 75% yield. Its nmr (CCl₄) spectra surprisingly exhibited six singlets at .89 (9H), 1.04 (9H), 1.82 (1H), 2.00 (3H), 2.37 (3H), and 3.29 (1H) which corresponded to neither 81a nor 81b nor 81c. The ir (neat) spectra contained an absorption at 1782 cm⁻¹ which could be a cyclopropene. The mass spectrum gave an M⁺ at 258.1511 (calcd 258.1475 for C₁₄H₂₆S₂) which indicated that the compound was an isomer of 81c. The data fits the predicted data for 83 and equation 44 provides a possible mechanism.

This mechanism requires a dehydrobromination to give 70 and addition of MeS⁻ to a cyclopropene double bond. Dehydrobromination and addition are known to occur under these conditions.²⁵ Thus, 82 is a reasonable

intermediate. However, the transformation 82-83 is unusual and no precedent for this can be found in the literature. One can avoid 70 by assuming the apparent S_N2' reaction occurs first (equation 45).

However, it has been shown that double bond isomerization out of the three-membered ring is usually more facile than addition of MeS^- .²⁵ Thus, 84a would be expected to yield 84c in preference to 84b.

To check the proposed mechanism for conversion of 68 to 83, 86 was synthesized from 85 by the synthesis of Billups and Shields (equation 46).⁷⁴ The mechanism predicts that 87 should be the product of an S_N2' reaction. 87 was isolated in 60% yield. The nmr (CCl_4) spectrum contained absorptions at δ 1.17 (s, 6H), 2.05 (s, 3H),

3.41 (s, 2H) and 6.81 (s, 1H). The mass spectrum exhibited an M^+ at 128.0666 (calcd for $C_7H_{12}S = 128.0659$).

Attention was focused upon synthesis of 1, following the successful characterization of 70 and 71. There are a number of approaches to methylenecyclopropene 1.^{24,25} Ideally, one would like a compound of the type 88 (R=H) where X is some good leaving group. However,

compounds of this type are not readily available, although alkyl substituted compounds 88 are intermediates in dehydrohalogenation reaction of gem-dihalocyclopropanes (89, R, R' = alkyl).²⁵ This approach to methylenecyclopropenes was tried unsuccessfully by Shields and Gardner with 90.²⁵ They concluded that the first intermediate was of type 91 which polymerized. Base catalyzed isomerization of the double bond around the ring and into the methyl group would not be expected because the intermediate cyclopropene anion is "anti-

Huckel" and probably too energetic to be formed under the conditions. Only intermediate 92 could have been useful in preparing 1. Thus, this approach appears unfruitful.

93 ($X = Cl$) has been prepared by addition of dichlorocarbene to allene^{75,76} and appears to be a possible precursor to 1 and also 94. Although methods of reduction of gem-dihalocyclopropanes to monohalocyclopropene are known,^{77,78} a literature search did not reveal any applications of these methods to compounds of type 93. Synthesis of 88 from 93 may prove to be a superior approach to 1 in the future.

Compounds of the type 95 appeared to offer a reasonable approach to 1. Dehydrohalogenation of 95 ($X = Hal$) could give four possible intermediates, 88, 96-98 (Scheme III). As shown, 96 and 98 are expected to undergo double bond isomerization to 88. Shields and Gardner have shown that 1-alkylcyclopropenes undergo double bond isomerization faster than the addition of a good nucleophile.²⁵ Compounds 97 could dehydrochlorinate to 1 or alternatively yield a

SCHEME III

cyclopropenium cation 99^{65} by solvolysis of the leaving group. 99 could deprotonate to yield 1 or undergo some other reaction.

The first attempt at preparing 95 ($X = \text{Br}$) was by bromination of 1-methylcyclopropene, prepared via the synthesis of Magid.⁸⁰ The bromination was attempted similarly to that of cyclopropene.⁸¹ The attempt was unsuccessful and another synthesis of 93 was sought.

Addition of chloromethylcarbene, generated by the method of Olah,⁸² to vinyl chloride gave 100 in approximately 5% yield (equation 47). Isolation of 100 was effected by distillation followed by glpc on carbowax 20M on Chromosorb W. Preliminary results from a study of the

microwave spectrum of 100 suggest that the chlorines bear a syn relationship.⁸³ The nmr spectrum (CCl_4) of 100 exhibited absorptions at δ 1.12-1.43 (m, 2H), 1.60 (s, 3H), and 2.70-2.99 (m, 1H). The mass spectrum showed the highest molecular weight peak at 123.9836 (calcd for $\text{C}_4\text{H}_6\text{Cl}_2$ 123.9846).

Reaction of 100 with KO-t-Bu in THF at -30 - 40° or DMSO at 15° for 1 hour gave 101 in 37% or 33% yields, respectively, after isolation by glpc. Compound 101 was characterized by its nmr spectrum (CCl_4) which

showed a multiplet at δ 1.19-1.40 overlapping a singlet at 1.20 (11H total) with other signals at 3.35-3.62 (m, 1H) and 5.23-5.57 (m, 2H). Elemental composition was provided by mass spectroscopy, calcd for $\text{C}_8\text{H}_{14}\text{O}$, 126.1044, found 126.1042. The formation of 101 is rationalized in terms of 1 as a reactive intermediate. If the reaction follows paths a, b, or d (Scheme III), then 101 must result from reaction with 1 unless an allylicly activated $\text{S}_{\text{N}}2'$ reaction on the cyclopropane ring

occurs. As of this writing there are no known examples of S_N2' reactions on cyclopropanes that retain the ring structure. The pathway in equation 49 may be ruled out for several reasons. The transformation

$\text{88} \rightarrow \text{102}$ is analogous to the transformation $\text{86} \rightarrow \text{87}$ except with KO-t-Bu . However, KO-t-Bu is a poorer nucleophile than MeS^- .⁸⁴ Additionally, in the transformation of $\text{86} \rightarrow \text{87}$, another possible reaction, dehydrochlorination, is blocked by the gem dimethyls. This reaction is not blocked in 88 . The transformation $\text{103} \rightarrow \text{101}$ should require heat above room temperature,⁸⁵ which it did not receive until glpc. To preclude the possibility of $\text{103} \rightarrow \text{101}$ occurring on the gas chromatograph, nmr's of the crude reaction product were taken and compared with isolated samples. In fact, evidence for rearrangement of 103 on either the injector or detector was observed. Lowered temperature on both the injector and detector eliminated the rearrangement. Attempts to isolate the rearranged product were unsuccessful, as it seemed to decompose upon reinjection.

Only reaction of KO-t-Bu with 99 ($\text{X} = \text{Cl}$) or 97 via paths e, f, and g bypass l as an intermediate. Reaction via path e also competes with deprotonation. Path g implies that addition of the poor nucleophile t-BuO^- is faster than dehydrochlorination. These paths can not

be exhaustively eliminated, so further experimentation was necessary.

One equivalent of 100 was reacted with 6 equivalents of KO-*t*-Bu and 2 equivalents MeSH in DMSO. This essentially implies that when 100 was added to the solution, the species present are 4 equivalents of KO-*t*-Bu, 2 equivalents of *t*-BuOH, and 2 equivalents of KSM_e. The products were 101 (12%) and 104 (34%) (equation 51). 104 possessed an

nmr (CCl₄) spectrum that had absorptions at δ .93-1.73 (m, 2H), 2.10 (s, 3H), 2.20-2.58 (m, 1H) and 5.27-5.53 (m, 2H) and a mass spectrum which showed a mass at 100.0342 (calcd for C₅H₈S = 100.0346). The presence of 104 was expected but the continued presence of a significant amount of 101 was unexpected because of the presence of excess SMe, a much better nucleophile. When the ratio of 100 to KSM_e to KO-*t*-Bu was raised from 1:2:4 to 1:4:4, a 51% yield of 104 was

isolated by glpc with no trace of 101.

Oxidation of 104⁸⁶ (equation 52) with 30% hydrogen peroxide in glacial acetic acid gave 105 in 72% yield. 105 proved to be water

soluble so a special procedure for isolation had to be developed. Treatment of the reaction mixture with water and neutralization with solid NaOH followed by overnight extraction with ether in a continuous liquid-liquid extractor proved to be the most successful procedure. Removal of the ether in vacuo followed by preparative tlc (silica gel, CH₂Cl₂, rf .01-.21) gave pure 105. Detection of 105 on the silica plate by ultraviolet light was unsuccessful. The rf range was determined by development of an analytical plate in an iodine chamber and extrapolated to the larger plate. The possibility remains that yield can be raised by an enlargement of the rf range.

105 exhibited nmr (CHCl₃-d) absorptions at δ 1.60-2.27 (m, 2H), 2.95-3.28 (m, 1H), 2.98 (s, 3H), and 5.65-5.87 (m, 2H), ir absorptions at 1298-1320 and 1135-1152 cm⁻¹, which are characteristic of sulfones,⁸⁷ and a mass spectral peak at 132.0250 (calcd for C₅H₈O₂S 132.0244).

More compelling evidence for the intermediary of 1 in these reactions comes from equation 53. The β -eliminations of sulfones to give alkenes is well known.⁸⁸ Treatment of 105 with KO-t-Bu in DMSO

resulted in isolation of 101 by glpc in 11% yield as the only volatile product. 101 therefore must be produced via 1 or by the first reported example of an Sn^2 reaction on a cyclopropane ring that resisted cleavage.

At this point another simple methylenecyclopropene 108 was generated and trapped as in equation 54. 106 was synthesized by dichloro-

carbene addition to syn-2-butene²⁵ and subjected to dehydrochlorination conditions in the presence of SMe^- . Shields and Gardner have done identical work except with OMe^- as the nucleophile and base.²⁵ 109 was isolated as the major product in > 30% yield. 109 exhibited nmr (CCl_4) absorption at δ 1.03-1.38 (m, 2H), 1.40 (s, 3H), 2.03 (s, 3H),

and 5.12-5.40 (m, 2H) with ir absorption at 1430-1440, 1150, and 888 cm^{-1} . In analogy with work on the generation of 1, it was hoped that following oxidation of 109 to 110, 110 could be transformed back to 109 via 108 (equation 55). 109 was oxidized to 110 in 62% yield.

under conditions identical to that of 104 and exhibited nmr absorptions at δ 1.16-2.30 (m, 2H), 1.58 (s, 3H), 2.82 (s, 3H) and 5.38-5.65 (m, 2H). Addition of 110 to a mixture of KSMc and KO-t-Bu in DMSO unfortunately gave no identifiable reaction products. An alternate elimination of 110 to give 111 probably occurred with subsequent polymerization of the unstable dimethylenecyclopropene.⁸⁹

The final attempt at synthesizing methylenecyclopropenes was an attempt to synthesize 1,2-di-t-butyl-4,4-dimethylmethylenecyclopropene 112, by generation of dimethylvinylidene⁹⁰ followed by addition to

di-t-butyl acetylene (equation 56). These attempts were unsuccessful,

possibly due to steric hindrance by the t-butyl groups.⁹¹

OTHER INVESTIGATIONS

Another investigation was concerned with synthesis of benzocyclopropene 113 (Appendix II) and with the synthesis of 114. Interest in

114 was derived from studies of compounds with small rings fused to aromatic rings (113, 115, 116).⁹²⁻⁹⁴ 114 was synthesized as described in Scheme IV.

SCHEME IV

Naphthalene was reduced with Na and NH_3 as described by Birch⁹⁵ to yield 117. Dichlorocarbene addition to 117 by the method of Skell⁹⁶ gave 118 in 70-80% yields. Reduction with Na/NH_3 gave 119 in 74% yield.²⁵ Spectral data for 118 and 119 may be found in the literature.⁹⁷

Dichlorocarbene addition to 119 by an adaptation of the method of Skell⁹⁶ gave 120 (b.p. 95-96°, 1 mm) in 62% yield. 120 exhibited nmr absorptions (CCl_4) at δ .17-.55 (AB quartet, 2H, $J_{ab}=4\text{Hz}$), 1.25-1.75 (m, 6H), 1.93-2.51 (m, 4H), and 5.40-5.55 (m, 2H) and had an $m/e = 228$.

Bromine addition to 120 at -60° in CHCl_3 gave 121 in 85% yield. 121 exhibited nmr ($\text{CHCl}_3\text{-d}$) absorptions at δ .42-.80 (AB quartet, 2H, $J_{ab}=5\text{Hz}$), 1.23-2.98 (m, 2H), and had an $m/e = 386$.

Treatment of 121 with KOH in refluxing EtOH gave 122 (m.p. 97-98°) in 68% yield. 122 has nmr absorptions at δ .67, .82, 2.38, 2.53 (AB quartet, 2H, $J_{ab}=9\text{Hz}$), 1.85-2.07 (m, 2H), 2.82-3.08 (m, 4H), 5.82-6.03 (m, 2H), and 6.48-6.68 (m, 2H) with an $m/e = 226$.

Addition of 122 to a stirred, cooled slurry of KO-*t*-Bu and THF gave an unstable compound which was tentatively assigned the structure 114 based on an nmr of the crude product. The product polymerized upon further concentration. Work on this project was suspended upon publication of an identical synthesis by Vogel.⁹⁸ Comparison of the spectrum of our crude material with Vogel's published spectrum confirmed our conclusion.

EXPERIMENTAL SECTION

General. ^1H nmr spectra were recorded in CCl_4 or CDCl_3 solution on Varian A-56/60A and Perkin-Elmer R12A spectrometers, and results are expressed as parts per million downfield from internal TMS. ^{13}C spectra and the spectrum for 79 were recorded on a Varian XL-100 spectrometer. Infrared spectra were recorded, as neat films or CCl_4 solution, on a Beckmann IR-8 spectrometer. Melting points and boiling points are uncorrected. Glpc analyses were carried out on a Model 700 Hewlett Packard instrument using a thermal conductivity detector and helium as carrier gas. Columns A, B, and C were 6 ft. columns which were packed with 20% SE-30 on Chromosorb P, 10% carbowax on Chromosorb W, and 10% SE-30 on Anakrom ABS, respectively. All reactions unless noted were run under an atmosphere of nitrogen.

Materials. Pivaldehyde and t-butylethylene were obtained from PCR, Inc., and Pfaltz and Bauer, Inc. 90% n-BuLi in a hydrocarbon solvent was obtained from PCR, Inc. Most gases were obtained from Matheson in lecture bottles. Ammonia was purchased in larger cylinders. Potassium-t-butoxide was obtained from the Ventron Corporation. Deuterium oxide was 99.8% from Stohler Isotopes. $\text{Rh}/\text{Al}_2\text{O}_3$ was from K & K Laboratories. Hexadecyltrimethylammonium bromide was obtained from Eastman Organic Chemicals. β -Methylallyl chloride and triflic acid were obtained from the Aldrich Chemical Co. Pentane was technical grade. All of the above was used without further purification. 1,1-Dichloroethane and CHBr_3 were reagent grade and distilled prior to use. Ether and THF were distilled from sodium-benzophenone ketyl immediately before use. DME and Et_3N were distilled from LiAlH_4 immediately before use.

DMF and DMSO were distilled from CaH_2 immediately before use. All other materials were reagent grade and used without further purification.

Preparation of 1,2-Dibromo-3,3-dimethylbutane

1,2-Dibromo-3,3-dimethylbutane was prepared by the method of Collier and Macomber.⁹⁹ Bromine (95.2 g, 0.595 moles) was added dropwise with stirring to cooled ($0-5^\circ$), neat *t*-butylethylene (50 g, 0.595 moles) in a 250 ml 3-necked flask. After the addition was completed, the solution was poured into a separatory funnel containing 100 ml ether and 100 ml of 10% $\text{Na}_2\text{S}_2\text{O}_3$. After shaking and separation of the layers, the water layer was extracted with 100 ml of ether. The combined layers were then washed successively with an equal volume of H_2O and saturated NaCl solution. The solution was dried over Na_2SO_4 , the ether removed, and the product distilled to yield 113.3 g (78%) of 1,2-dibromo-3,3-dimethylbutane (b.p. $81-83^\circ$, 12 mm).

Preparation of *t*-Butylacetylene

t-Butylacetylene was prepared by the method of Collier and Macomber.⁹⁹ 1,2-Dibromo-3,3-dimethylbutane (113.25 g, 0.506 mole) was added dropwise to a cooled (15°) slurry of 200 ml freshly distilled DMSO and KO-*t*-Bu (134.4 g, 1.2 moles) in a 500 ml 3-necked flask equipped with mechanical stirrer, reflux condenser, and pressure equalizing funnel. The reaction was stirred 0.5 hours after the addition was completed. The reaction vessel was then transferred to a distillation apparatus and the *t*-butylacetylene co-distilled with *t*-butanol. Redistillation yielded 35.28 g (85% yield) of *t*-butylacetylene (b.p. $36-38^\circ$).

Preparation of 1,3-Di-t-butylpropargyl Alcohol

1,3-Di-t-butylpropargyl alcohol was prepared by an adaptation of the method of Corey and Borden.⁶⁶ 90% n-BuLi in hydrocarbon solvent (14 g of solution, 0.21 moles) was added dropwise to a cooled (0-5°) solution of t-butylacetylene (17 g, 0.207 moles) in 50 ml dry THF in a 250 ml 3-necked flask equipped with reflux condenser, mechanical stirrer, and pressure equalizing addition funnel. The reaction was stirred 0.25 hours after the addition was completed. Pivaldehyde (17.8 g, 0.207 moles) was then added dropwise with cooling and the mixture stirred for an additional 0.5 hour. 25 ml H₂O was then added dropwise with continued cooling. After stirring for an additional 0.5 hour, the solution was then poured onto ice water and extracted with ether. The aqueous layer was then back extracted twice with ether. The ether layers were combined, washed exhaustively with saturated NaCl and dried over Na₂SO₄. Distillation yielded 26.68 g (76.6%) of 1,3-di-t-butylpropargyl alcohol, a white solid (b.p. 72-74°, $\approx$ 10 mm).

Preparation of 1,3-Di-t-butyllene 62

Compound 62 was prepared by the method of Corey and Borden.⁶⁶ AlCl₃ (6.512 g, 0.049 moles) was placed in a 1 liter 3-necked flask equipped with reflux condenser, addition funnel, and mechanical stirrer. 400 ml dry THF was added dropwise with cooling (0-5°) to dissolve the AlCl₃. LiAlH₄ (11.248 g, 0.296 moles) was then added in portions to the cooled solution followed by the rapid dropwise addition of a solution of 1,3-di-t-butylpropargyl alcohol in 100 ml THF. The slurry was refluxed for 24 hours and then cooled to 0°. 11.2 ml H₂O, 11.2 ml 15% NaOH solution, and 33.6 ml H₂O were consecutively added dropwise to the

solution (caution: frothing). The reaction was then stirred until the precipitation of white solids. The reaction mixture was then filtered, poured into H₂O and extracted with ether. The H₂O layer was back extracted with ether. The combined ether layers were washed twice with equal volumes of saturated NaCl solution and dried over Na₂SO₄. Removal of solvent by rotary evaporation followed by distillation gave 17 g (74%) 62 (b.p. 72-75°, 54 mm).

Preparation of cis-2,2,6,6-Tetramethylhept-4-ene 63⁶⁷

1,3-Di-t-butylallene (5 g, 0.033 moles) in 16 ml ether was added dropwise to a solution of Na (3.0 g, 0.132 moles) in 80 ml of ammonia in a 250 ml 3-necked flask. After stirring several hours the solution was treated with enough solid NH₄Cl to discharge the blue color. After evaporation of the ammonia, the slurry was treated with H₂O. The layers were then separated and the water layer was extracted with ether. The combined ether layers were washed with saturated NaCl solution and dried over Na₂SO₄. Distillation gave 3.9 g (77%) 63 (b.p. 52-53°, 8 mm). Spectral data: nmr (CCl₄) δ 1.70-1.87 (m, 2H), 0.80 (s, 9H), 0.94 (s, 9H), and 5.18-5.45 (m, 2H).

Preparation of 1,1-Dichloro-2-t-butyl-3-(2',2'-dimethylpropyl)cyclopropane 64

Compound 64 was prepared by an adaptation of the method of Joshi, Singh, and Pande.⁶⁸ Compound 52 (3.5 g, 0.0227 moles), CHCl₃ (8.1 g, 0.0681 moles), and hexadecyltrimethylammonium bromide (0.082 g, 0.227 millimoles) were stirred vigorously with cooling while NaOH

(6.81 g, 0.170 moles) in 13.6 ml H_2O was added dropwise. The solution was then allowed to warm to room temperature and stirred overnight. The reaction mixture was poured onto ice, acidified with H_2SO_4 , and extracted with ether. The extracts were washed twice with saturated NaCl solution and dried over Na_2SO_4 . Distillation gave 2.5 g (47%) of 64 and 0.4 g (11%) of recovered 63. Spectral data: nmr (CCl_4) δ 1.05 (s, 9H), 1.14 (s, 9H) and 1.32-1.62 (m, 4H).

Reaction of 64 with KO-t-Bu in DMSO/THF

A solution of 64 (1 g, 0.00455 moles) in 1 ml THF was added dropwise to a slurry of KO-t-Bu (2.02 g, 0.0182 moles) in 9 ml THF and 7.5 ml DMSO. The solution was then stirred for 6 hours, poured onto ice water, and extracted twice with pentane. The combined pentane layers were washed four times with H_2O and dried over Na_2SO_4 . Preparative tlc (silica gel, CCl_4) gave 0.45 g (50%) of product which was assigned the structure 66. Spectral data: nmr (CCl_4) δ 0.95 (s, 9H), 1.18 (s, 9H), 1.57-2.12 (m, 3H); ir (CHCl_3) 1829 cm^{-1} .

Preparation of anti-1-neopentylidene-2,2-dibromo-3-t-butylcyclopropane 68

A 250 ml 3-necked flask fitted with a reflux condenser, mechanical stirrer and pressure equalizing addition funnel was charged with pentane (100 ml), 1,3-di-t-butylallene (7 g, 0.0461 moles) and KO-t-Bu (22.4 g, 0.2 moles). CHBr_3 (34 g, 0.136 moles) was then added dropwise to the cooled (0-5°) stirred slurry. After stirring an additional 30 minutes, the solution was poured into 100 ml ice water and the layers separated. Following back extraction of the water layer with 50 ml

pentane, the pentane layers were combined and dried over Na_2SO_4 . Distillation yielded 3.5 g (50% unreacted allene plus 6.1 g (41%) 68 (b.p. 64-68°, 0.3 mm). Spectral data: nmr (CCl_4) δ 1.14, 1.16 (2s, 18H), 2.25 (d, 1H, $J=3\text{Hz}$) and 6.36 (d, 1H, $J=3\text{Hz}$); mass spec 321.9889 (M^+), calcd 321.9931 for $\text{C}_{12}\text{H}_{20}\text{Br}_2$.

Preparation of syn-1-Neopentylidene-2,2-dibromo-3-t-butylcyclopropane 69

1.5 g of 68 in 15 ml CCl_4 was stirred vigorously with 3.6 ml 48% aqueous HBr for 36 hours in a 25 ml flask. The solution was then washed with 15 ml portions of H_2O , 5% NaHCO_3 and saturated NaCl solutions. The combined aqueous layers were then extracted with 20 ml pentane which was then washed with 15 ml of saturated NaCl solution. The pentane and CCl_4 layers were combined and dried over Na_2SO_4 . Distillation (84-86°, 1.4 mm) yielded 1.19 g (79%) of 69. On a smaller scale, 69 could be purified by preparative tlc (silica gel, CH_2Cl_2) in slightly lower yields. Spectral data: nmr (CHCl_3 -d) δ 1.07 (s, 9H), 1.27 (s, 9H), 2.10 (d, 1H, $J=3\text{Hz}$), 5.75 (d, 1H, $J=\text{Hz}$); mass spec 321.9891 (M^+), calcd 321.9931 $\text{C}_{12}\text{H}_{20}\text{Br}_2$.

Preparation of anti-1-bromo-2,4-di-t-butylmethylenecyclopropene 70

Compound 68 (2 g, 0.0062 moles) in 1 ml THF was added dropwise to a slurry of KO-t-Bu (1.04 g, 0.0093 moles) in 30 ml THF at -60-70° in a 50 ml 3-necked flask equipped with magnetic stirrer and pressure equalizing addition funnel. After addition was complete, the temperature was allowed to rise to -30-40° and allowed to stay there for 1 hour. Spectral data: nmr (CCl_4) δ 1.05 (t-Bu), 1.30 (t-Bu) and 3.95

(olefinic); ir (CCl_4) 1840 cm^{-1} ; mass spec 242.0664 (M^+), calcd 242.0669 for $\text{C}_{12}\text{H}_{19}\text{Br}$.

Preparation of syn-1-Bromo-2,4-di-t-butylmethylenecyclopropene 71

Compound 71 was generated from 69 as described earlier for 70. Spectral data: nmr (CCl_4) δ 1.03 (s, t-Bu), 1.24 (s, t-Bu) and 4.01 (s, olefinic); ir (CCl_4) 1840 cm^{-1} ; mass spec 242.0664 (M^+) calcd 242.0669 for $\text{C}_{12}\text{H}_{19}\text{Br}$.

Preparation of Solutions of 70 and 71 for Spectral Studies

A solution of 70 or 71 was prepared as described previously and cooled to -75° . The solution was then transferred by suction to the apparatus as described in Figure 2 and filtered through glass wool into a cooled (-40°) flask. The flask was quickly transferred to the apparatus as described in Figure 3. The flask was then evacuated and the bath was allowed to warm to -10° . After distillation of some liquid from the solution at $2-10^\circ$, some CCl_4 was then added through the non-pressure equalizing funnel. More liquid was allowed to distill off at -10° . This process was repeated 5-6 times before cessation of pumping and restoration to atmospheric pressure by introduction of N_2 . Spectral data were taken immediately. Mass spectral data was void of peaks with molecular weight higher than M^+ when a cooled unfiltered solution was used.

Reaction of 70 with H₂O

Addition of H₂O to a solution of 70 at -10°, followed by extraction into pentane, drying over Na₂SO₄, and removal of solvents in vacuo yielded a crude mixture of mostly 72, 73, and 68. Preparative tlc (silica gel, CH₂Cl₂) yields 73 (0.37 g, 33%), 72 (0.50 g, 45%) and 68 (0.12 g, 6%). Spectral data for 73: nmr (CCl₄) δ 1.07 (s, 9H), 1.30 (s, 9H) and 2.41 (s, 2H); ir (neat) 1637 and 1837 cm⁻¹; mass spectral 152.1570 (M⁺-CO), calcd 152.1565. Spectral data for 72: nmr (CCl₄) δ 1.05 (s, 9H), 1.14 (s, 9H) and 2.21 (s, 2H); ir (neat) 1687 and 2218 cm⁻¹; mass spectral 180.1510 (M⁺), calcd 180.1514.

Reaction of 71 with H₂O

Preparation of 71 from 0.5 g 69 as described previously followed by the workup described for reaction of 70 with H₂O yielded 0.109 g (44%) 73 and 0.084 g (34%) 72.

Reaction of 70 with D₂O

Generation of 70 as described previously, followed by addition of D₂O yielded 77 and 78 which were isolated as described for 72 and 73. Spectral data for 78: nmr δ 1.07 (s, 9H), 1.30 (s, 9H) and 2.35-2.47 (t, 1H, J=2Hz). m/e = 153 (M⁺-CO). Spectral data for 77: nmr δ 1.05 (s, 9H), 1.14 (s, 9H) and 2.16-2.27 (t, 1H, J=2Hz). m/e = 181.

Attempted Reaction of 68 without KO-t-Bu

In the absence of KO-t-Bu, 1.5 g (0.0014 moles) of 68 was subjected to the reaction conditions used for the preparation of 70. Compound 68

was recovered unchanged.

Hydrogenation of 70

A solution of 70 from 0.5 g of 68 was prepared and filtered as described in the preparation of spectral solutions. The solution was rapidly transferred to a pressure bottle and hydrogenated (40 psi) over 0.4 g RH/Al₂O₃ for 1 hour. The solution was filtered, poured into ice water and extracted twice with pentane. The combined pentane layers were washed six times with equal volumes of H₂O and dried over Na₂SO₄. Removal of the pentane in vacuo resulted in a low yield of a complex mixture of mostly unidentifiable compounds. The products from two 0.5 g reactions were combined and subjected to preparative tlc (silica gel, CCl₄). The fraction with the highest rf (0.52-0.74) was extracted with CH₂Cl₂. Removal of the CH₂Cl₂ in vacuo followed by preparative glpc on column C of the major product (≈70% of the fraction as determined by peak areas) gave 0.039 g (≈8%) of 79. Spectral data: nmr (CCl₄) δ 0.52-1.76 (m, 3H), 0.92 (s, 9H), 1.08 (s, 9H) and 5.66-5.78 (m, 1H). m/e = 151 (M⁺-CH₃).

Sodium and Ammonia Reduction of 68

Compound 68 (0.3 g, 0.0009 moles) in 3 ml of ether was added to a solution of Na (0.19 g, 0.00839 moles) in 15 ml of liquid ammonia. The reaction was stirred for 5 hours and then treated with enough NH₄Cl to discharge the blue color. After evaporation of the ammonia, the residue was dissolved in a ether/H₂O mixture. The layers were separated and the water layer extracted with ether. The combined ether layers were then

washed with saturated NaCl solution and dried over Na_2SO_4 . After removal of the ether in vacuo, preparative glpc on column C gave a major product, a minor product, and several trace products. The major product exhibited nmr (CCl_4) absorptions at δ 0.83 (s, 18H), 1.82-2.0 (m, 4H), and 5.25-5.55 (m, 2H); mass spectral $m/e = 168$. The minor product which could not be obtained analytically pure had identical retention times as 79 as determined by simultaneous injections on column C at several temperatures. Comparison of the nmr spectra of 79 and the minor product, indicated the presence of 79 as the major component of the minor fraction. GCMS indicated also that the major component of the minor fraction exhibited a peak at m/e 151 as did 79.

Sodium and Ammonia Reduction of 69

Compound 69 was subjected to the same reaction conditions as described above. Examination of the nmr spectrum and glpc analysis indicated that the product mixture contained only traces of compounds other than the major product of the Na/NH_3 reduction of 68.

Reaction of 68 with KO-t-Bu/DMSO/MeSH

MeSH (0.348 g, 0.008 moles) was passed into a solution of 30 ml of KO-t-Bu (1.104 g, 0.016 moles) in DMSO in a 50 ml 3-necked flask at 15-25°, and stirred for 1.5 hours. 68 (0.646 g, 0.002 moles) was then added dropwise. The resulting solution was stirred for 2.5 hours, poured onto ice water, extracted into pentane, and dried over Na_2SO_4 . Removal of the pentane in vacuo followed by preparative tlc (silica

gel, CCl_4) yielded 0.39 g (75%) of 83. Spectral data: nmr (CCl_4) δ 0.89 (s, 9H), 1.04 (s, 9H) 1.82 (s, 1H), 2.00 (s, 3H), 2.37 (s, 3H) and 3.29 (s, 1H); ir (neat) 1782 cm^{-1} ; mass spectral 258.1511 (M^+), calcd 258.1475 for $\text{C}_{14}\text{H}_{26}\text{S}_2$.

Preparation of 2-Chloro-3,3-dimethylenecyclopropane 86

Compound 86 was prepared by Mr. L. P. Lin using the synthesis of Shields and Billups.⁷⁴

Reaction of 86 with KSM_e in DMSO

MeSH (0.41 g, 0.0086 moles) was bubbled into a solution of KO-t-Bu (0.9 g, 0.0086 moles) in 15 ml DMSO. The solution was stirred for 0.5 hours, whereupon 86 was added dropwise with cooling. After stirring an additional 2.5 hours, the solution was poured onto ice water, and extracted twice with pentane. The combined pentane layers were dried over Na_2SO_4 . Removal of pentane in vacuo followed by preparative tlc (silica gel, CCl_4) gave 0.66 g (60%) of 87. Spectral data: nmr (CCl_4) δ 1.17 (s, 6H), 2.05 (s, 3H), 3.41 (s, 2H), and 6.81 (s, 1H); mass spectral 128.0666 (M^+), calcd 128.0659 for $\text{C}_7\text{H}_{12}\text{S}$.

Preparation of 1-Methylcyclopropene⁸⁰ and Its Reaction with Br_2

β -Methylallylchloride (1.38 g, 0.015 moles) in 25 ml ether was added dropwise at 25° over a 15 minute period to a stirred solution of halide-free phenyl lithium (24 ml of 2M solution, 0.045M). After stirring for an additional 45 minutes, 3 ml of EtOH was added dropwise. The solution was warmed gently for 2.5 hours to vaporize the

1-methylcyclopropene which was then condensed in a CCl_4 or CH_2Cl_2 solution in a 3-necked flask cooled to -70° . In one trial, Br_2 was already present in the solution. In others it was added to the solution later. Upon workup, no evidence was found for 1,2-dibromo-1-methylcyclopropane. Instead, the major product appeared to be a dibromo olefin of the general structure

Preparation of 1,2-Dichloro-1-methylcyclopropane 100

Compound 100 was synthesized by W. Chamberlain by the addition of chloromethyl carbene to vinyl chloride as described by Olah.⁸² Thus, vinyl chloride (68.2 g, 1.1 moles) was condensed in a solution of CH_3CHCl_2 (107.8 g, 1.1 moles) and 350 ml anhydrous ether at -40° . $n\text{-BuLi}$ (1 mole, $\approx 2.2\text{M}$) in hexane was added dropwise to the stirred solution over approximately a 3.5 hour period. After the addition was completed, the reaction mixture was stirred an additional hour during which time the reaction mixture was allowed to rise to room temperature. The solution was then treated with H_2O and the layers separated. The H_2O layer was extracted with ether. The combined ether layers were washed with saturated NaCl solution and dried over Na_2SO_4 . Preparative glpc on column B of the fraction boiling at $100\text{--}126^\circ$ gave 6.2 g (5%) of 100. Spectral data: nmr (CCl_4) δ 1.12-1.43 (m, 2H), 1.60 (s, 3H), and 2.70-2.99 (m, 1H); mass spectral 123.9836 (M^+), calcd for $\text{C}_4\text{H}_6\text{Cl}_2$ 123.9846.

Reaction of 100 with KO-t-Bu in THF

Compound 100 (0.5 g, 0.004 moles) was added dropwise to stirred slurry of KO-t-Bu (3.58 g, 0.032 moles) in 20 ml THF maintained at -30-40°. After stirring for 1 hour at -30-40°, H₂O was added and the solution was extracted three times with pentane. The pentane layers were combined and washed 6-8 times with H₂O. After drying with Na₂SO₄, most of the pentane was removed by rotary evaporation. Analysis on columns A and B at various temperatures indicated only one product with a retention time distinct from solvent. Preparative glpc on column B gave 0.186 g (37% of 101). Spectral data: nmr (CCl₄) δ 1.19-1.40 (m, 3H), 1.20 (s, 8H), 3.35-3.62 (m, 1H) and 5.23-5.57 (m, 2H); mass spectral 126.1042 (M⁺), calcd for C₈H₁₄O 126.1044.

Reaction of 100 with KO-t-Bu in THF/Butadiene

Compound 100 was treated with KO-t-Bu in THF as described above. Excess butadiene was condensed in the flask and the reaction was stirred for an additional 0.5 hour. Workup as described above gave 101 as the only product. Addition of 100 to a slurry of KO-t-Bu in THF and excess butadiene gave identical results.

Reaction of 100 with KO-t-Bu in DMSO

Compound 100 (0.3 g, 0.0024 moles) was added dropwise to a mechanically stirred slurry of KO-t-Bu (2.15 g, 0.0192 moles) in 10 ml dry DMSO. 0.5 hours after addition was completed, the slurry was poured onto ice, and extracted thrice with pentane. The combined pentane layers were washed with saturated NaCl and filtered through

MgSO₄ to dry and break up an emulsion. The majority of the pentane was removed by rotary evaporation. Analysis by glpc at various temperatures on columns A and B indicated that 101 was the only product. Preparative glpc on column B gave 0.1 g (33%) of 101.

Reaction of 100 with KO-t-Bu in DMSO/MeSH. Method I

MeSH (0.38 g, 0.008 moles) was condensed in a cold trap and then distilled into a solution of KO-t-Bu (2.7 g, 0.024 moles) in 30 ml dry DMSO at 15° by means of a tube inserted below the level of the solution in the 50 ml 3-necked flask. After stirring for 0.25 hours, 100 (0.5 g, 0.004 moles) was added dropwise. After stirring for another 0.5 hours, the solution was poured onto ice slush and extracted thrice with pentane. The combined pentane layers were then washed with saturated NaCl solution and dried over Na₂SO₄. The solution was then concentrated to ~1.5 ml by distillation at atmospheric pressure. Preparative glpc on column B yielded 0.073 g (11%) of 101 and 0.1363 g (34%) of 104. Spectral data for 104 are: nmr (CCl₄) δ 0.93-1.73 (m, 2H), 2.10 (s, 3H), 2.20-2.58 (m, 1H) and 5.27-5.53 (m, 2H); mass spectral 100.0342 (M⁺), calcd for C₅H₈S 100.0346.

Reaction of 100 with KO-t-Bu in DMSO/MeSH. Method II

MeSH (2.3 g, 0.048 moles) was introduced into a solution of KO-t-Bu (10.86 g, 0.097 moles) in 80 ml of DMSO as described in Method I. 100 (1.5 g, 0.0121 moles) was then added dropwise and the solution stirred for 0.5 hours. Workup and isolation as described in Method I gave 0.72 g (51%) of 104.

Oxidation of 104

30% H_2O_2 (3.1 g solution, 0.0273 moles) in 2 ml AcOH was added dropwise to a solution of 8 ml AcOH and 104 (0.68 g, 0.0068 moles) in a 25 ml flask. The solution was warmed to 65° for 1 hour, cooled to room temperature and then poured onto ice. The acidic solution was then neutralized with solid NaOH, placed into a continuous liquid-liquid extractor, and extracted for 18 hours with ether. The solution was then filtered through MgSO_4 and the ether removed by rotary evaporation. Preparative tlc (silica gel, CH_2Cl_2 , rf 0.01-0.21) gave 0.628 g (70%) of 105 as a viscous oil. Spectral data: nmr (CHCl_3 -d) δ 1.60-2.27 (m, 2H), 2.95-3.28 (m, 1H), 2.98 (s, 3H) and 5.65-5.87 (m, 2H); ir 1298-1320 and 1135-1152 cm^{-1} ; mass spectral 132.0250 (M^+), calcd 132.0244.

Reaction of 100 with KO-t-Bu in DMSO

Compound 100 (0.628 g, 0.0048 moles) in 2 ml DMSO was added dropwise to a cooled (15°) stirred suspension of KO-t-Bu (5.6 g, 0.05 moles) and then stirred for 0.5 hours. The solution was then poured onto ice and extracted three times with pentane. The combined pentane layers were washed twice with saturated NaCl solution and filtered through MgSO_4 . After removal of most of the pentane by rotary evaporation, 0.056 g (9.3%) of 101 was isolated by preparative glpc on column B. Other products were not detected.

Preparation of cis-1,1-Dichloro-2,3-dimethylcyclopropane 106²⁵

Cis-2-butene (28 g, 0.5 moles) was condensed in trap and then poured rapidly into a chilled (-50°) slurry of KO-t-Bu (56 g, 0.5 moles) in 600 ml of pentane in a 1 liter 3-necked flask. CHCl₃ (59.5 g, 0.5 moles) was then added dropwise. The temperature of the solution was allowed to rise to 10° near the end of the addition. After stirring an additional 0.5 hours, the reaction mixture was poured onto ice and the layers separated. The water layer was extracted with pentane. The combined pentane layers were washed with saturated NaCl solution and dried over Na₂SO₄. Distillation provided 38.75 g (53%) of 106 (b.p. 123-126°).

Reaction of 106 with KO-t-Bu in MeSH/DMSO

Compound 106 (4 g, 0.029 moles) was added to KO-t-Bu (32.4 g, 0.29 moles) and MeSH (5.56 g, 0.116 moles) in 150 ml of DMSO in a 250 ml flask. The product was worked up as described previously for 104. Distillation yielded 1 g (30%) of 109 (b.p. 124°). Analytical samples were obtained by preparative glpc on column B. Higher yields could be obtained by glpc of the pot residue which contained 109. Other products of this reaction show an inclination to rearrange thermally during the distillation and also during chromatography. Spectral data: nmr (CCl₄) δ 1.03-1.38 (m, 2H), 1.40 (s, 3H), 2.03 (s, 3H), 5.12-5.40 (m, 2H); ir (neat) 1430-1440, 1150, 888 cm⁻¹.

Oxidation of 109

Compound 109 was oxidized as described previously for the oxidation of 104. Thus, 109 (1 g, 0.0088 moles) yielded 0.8 g (62%) of 110. Spectral data: nmr (CCl_4) δ 1.03-1.38 (m, 2H), 1.40 (s, 3H), 2.03 (s, 3H), and 5.12-5.40 (m, 2H); ir (neat) 1430-1440, 1150, and 888 cm^{-1} .

Reaction of 110 with KO-*t*-Bu in DMSO/MeSH

MeSH (0.33 g, 0.0068 moles) was bubbled into a slurry of KO-*t*-Bu (1.9 g, 0.017 moles) in 35 ml DMSO and allowed to stir for 0.5 hours. Compound 110 (0.25 g, 0.0017 moles) was then added dropwise at 15° . After 0.5 hours the resulting red solution was poured onto ice and extracted twice with pentane. Removal of the pentane *in vacuo* and examination by nmr gave no indication of the presence of 109.

Preparation of *t*-Butylethynyl dimethylcarbinol⁹¹

The desired compound was prepared by the procedure described previously for 1,3-di-*t*-butylpropargyl alcohol. Thus, *t*-butylacetylene (31.9 g, 0.39 moles) and 90% *n*-BuLi (25.2 g solution, 0.36 moles) was reacted to produce the *t*-butyl acetylide. Treatment of the acetylide with acetone (29 g, 0.5 moles) gave 33.03 g (60%) of *t*-butylethynyl dimethylcarbinol (b.p. $84-86^\circ$, 60 mm).

Preparation of *t*-Butylethynyl dimethylcarbonyl Chloride⁹¹

Dry HCl was bubbled through a solution of *t*-butylethynyl dimethylcarbonyl chloride (33 g, 0.236 moles) and CaCl (7 g, 0.0636 moles) in

40 ml of petroleum ether (b.p. 20-40°) for 5 hours. The liquid layer was decanted from the pasty CaCl_2 and shaken with anhydrous K_2CO_3 until neutral. Distillation provided 28 g (75%) of the desired chloride (b.p. 71-73°, 61 mm).

Preparation of Di-t-butylacetylene⁹¹

Over a 3 hour period t-butylethynyl dimethylcarbinyl chloride (27 g, 0.171 moles) in 10 ml ether was added dropwise to a cooled (0°) solution of MeMgBr (prepared from 21.9 g MeBr and 5.69 g Mg) in 37 ml ether. After the addition was complete, the temperature was allowed to warm to 45° over a 3 hour period. After cooling to 0°, 35.1 ml of cold 10% HCl was added slowly. The layers were then separated and the ether solution was washed with dilute Na_2CO_3 solution and dried over anhydrous K_2CO_3 . Distillation provided 10.1 g (43%) di-t-butylacetylene (b.p. 116-118°).

Preparation of 2,2-Dimethylsilyl Enol Ether

2,2-Dimethylsilyl enol ether was prepared by the method of Stang.⁹⁰ To a solution of 100 ml dry DMF and Et_3N (60.6 g, 0.6 moles) in a 500 ml 3-necked flask were added Me_3SiCl (32.6 g, 0.3 moles) and isobutyraldehyde (18 g, 0.25 moles). The solution was refluxed with stirring for 12 hours. The mixture was cooled to 0°. After addition of 200 ml pentane, the mixture was RAPIDLY washed with three 300 ml portions of cold saturated NaHCO_3 . The combined aqueous NaHCO_3 washes were extracted with two 125 ml portions of pentane. The combined pentane layers were washed quickly with two 100 ml portions of cold

1.5 N HCl followed by 100 ml of cold saturated NaHCO_3 . Drying over MgSO_4 and distillation gave 17.3 g (48%) of 2,2-dimethylsilyl enol ether (b.p. 114-116°, 650 mm).

Preparation of Triflic Anhydride⁹⁰

A 100 ml 3-necked flask equipped with a pressure equalizing addition funnel and short path distillation apparatus was charged with P_2O_5 (50 g, 0.35 moles). Triflic acid (50 g, 0.33 moles) was added dropwise. The resulting solid was allowed to sit for 1.5 hours. Then the flask was heated to distill 36.8 g (78%) triflic anhydride.

Preparation of 2,2-Dimethyl Triflate⁹⁰

A 500 ml 3-necked flask was equipped with an addition funnel, mechanical stirrer, reflux condenser, and outlet to a 3-way stopcock. The other two avenues of the stopcock led to the N_2 outlet and the pump. The flask was charged with 30 ml (0.06 moles) of 2M $n\text{-BuLi}$ solution in ether. The ether was removed in vacuo and to the residual white solid was added 23 ml DME and a few mg of Ph_3CH as indicator. The resulting red solution was cooled to -60° and to it was added 2,2-dimethylsilyl enol ether (7.2 g, 0.05 moles) in an equal volume of DME over 0.5 hours. After the addition was complete, the reaction mixture was stirred for 1.5 hours and allowed to warm to -30°. Then the light pink solution was cooled to -75° and triflic anhydride (16.2 g, 0.0575 moles) was added dropwise over a period of 0.5 hours. After repacking of the cold bath the solution was allowed to warm to room temperature overnight while stirring. The reaction mixture was diluted with 125 ml pentane and washed with 50 ml of 20% NaHSO_3 . The

aqueous layer was back extracted with two 75 ml portions of pentane. The combined pentane layers were dried over MgSO_4 and the pentane removed in vacuo. Distillation gave 2.57 g (25%) 2,2-dimethyltriflate (b.p. 63-66°, 72 mm).

Attempted Synthesis of 1,2-Di-t-butyl-4,4-dimethylmethylenecyclopropene

This attempted synthesis followed the method of Stang for addition of vinylcarbenes to acetylene.⁴⁸ 2,2-Dimethyltriflate (0.61 g, 0.003 moles) in an equal volume of DME was added dropwise to a slurry of KO-t-Bu (0.37 g, 0.0033 moles), di-t-butylacetylene (0.83 g, 0.012 moles), and 15 ml DME at -50°. The solution was kept at -45-55° for 1 hour. Nmr and ir of the solution gave no indication of the desired product. The solution was warmed to 0° and the spectra repeated with negative results. After warming to room temperature, the reaction was treated with H_2O and extracted with pentane. After several H_2O washings, the pentane was removed in vacuo and the residue examined. No evidence for 1,2-di-t-butyl-4,4-dimethylmethylenecyclopropene was observed. Other experiments with higher concentrations of reactants gave similar results.

Preparation of 1,4:5:8-Tetrahydronaphthalene 117

Compound 117 was synthesized by an adaptation of the method of Birch.⁹⁵ Naphthalene (64 g, 0.5 moles) in 350 ml EtOH and 320 ml ether was added rapidly to ≈1.6 l of well stirred anhydrous ammonia in a 3 liter flask. Na (96 g, 4.17 moles) was then added piecewise. The solution was stirred an additional 2 hours, after which the ammonia was

allowed to evaporate overnight. Water (1.3 l) was then added with cooling and the ether layer separated. The aqueous phase was extracted one additional time with ether. The combined ether layers were then washed twice with saturated NaCl solution and dried over Na_2SO_4 . Distillation (64-68°, 1 mm) yielded 49 g (73%) of solid 117 (m.p. 53-54°, lit. 42°).

Preparation of 9,10-Dichloromethano-1,4,5,8-tetrahydronaphthalene 118

Compound 118 was prepared by reaction of 117 with dichlorocarbene which was generated by the method of Skell and Gardner.⁸² Thus CHCl_3 (65.69 g, 0.552 moles) was added dropwise with cooling to 104 (72.8 g, 0.552 moles) in a stirred slurry of KO-t-Bu (61.8 g, 0.552 moles) and 800 ml pentane. One-half hour after completion of the CHCl_3 addition, the mixture was poured onto an ice slush. After separation of layers, the H_2O layer was extracted with pentane. The combined pentane layers were washed with H_2O and dried over Na_2SO_4 . Distillation (98-102°, 1 mm) provided 56.89 g (48%) of 118. Several repetitions of this process with recovered 117 resulted in a total yield of 70-80%.

Preparation of Tricyclo[4,4,1,0]-undeca-3,8-diene 119⁹⁷

Na (82.8 g, 3.6 moles) was added in small pieces to ≈ 2.2 l of well stirred anhydrous ammonia in a 3 liter 3-necked flask. 118 in 0.2 l of anhydrous ether was added dropwise. The solution was stirred for an additional 5 hours and then treated with enough solid NH_4Cl to discharge the blue color. After evaporation of the ammonia, the residue was cooled and dissolved in a H_2O /ether mixture. The organic layer was

separated and the water layer extracted with ether. The combined extracts were washed with saturated NaCl solution and dried over Na_2SO_4 . Removal of the ether in vacuo followed by distillation of the residue yielded 27.77 g (74%) of 119 (b.p. 55-70°, 2 mm).

Preparation of 120, the Dichlorocarbene Adduct of 119

Reaction of 119 with dichlorocarbene under the conditions described in the preparation of 118 yields 120. Thus, 119 (51.4 g, 0.352 moles) gave 50.13 g (62%) 120 after six reactions (b.p. 95-96°, 1 mm). Spectral data: nmr (CCl_4) δ 0.17-0.55 (AB quartet, 2H, $J_{AB}=4\text{Hz}$), 1.25-1.75 (m, 6H), 1.93-2.51 (m, 4H), and 5.40-5.5 (m, 2H); $m/e = 228$.

Bromination of 120

Br_2 (12.0 g, 0.075 moles) was added dropwise to a mechanically stirred solution of 120 (17.08 g, 0.075 moles) in 125 ml CHCl_3 at -60°. Filtration of the cold precipitated dibromide 121 followed by pentane washings gave 21 g of white crystals. The filtrate was treated consecutively with enough 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution to discharge any red color, and washed twice with saturated NaCl solution. After drying over Na_2SO_4 , the CHCl_3 was removed in vacuo to yield after pentane washing an additional 3.71 g of 121 for an overall yield of 24.71 g (85%) (m.p. 132-134°). Spectral data: nmr (CHCl_3 -d) δ 0.42-0.80 (AB quartet, 2H, $J_{AB}=5\text{Hz}$), 1.23-2.98 (m, 12H), and 4.13-4.58 (m, 2H); $m/3 = 386$.

Preparation of 3,4-Dichloromethano-1,6-methano-2,3,4,5-tetra-
hydro[10]annulene 122

Compound 121 (20.8 g, 0.0536 moles) was treated with KOH (132.16 g, 2.36 moles) in 1 liter anhydrous EtOH and refluxed for 1.5 hours. After cooling, the solution was poured into ice water and extracted twice with CH_2Cl_2 and then with pentane. The CH_2Cl_2 and pentane extracts were combined, washed twice with saturated NaCl solution, and dried over Na_2SO_4 . The solvents were removed in vacuo and the residue triturated with pentane to give a pale yellow solid (m.p. 97-98°). Further recovery from the triturate gave a total of 8.17 g (68%) 122. Spectral data: nmr (CHCl_3 -d) δ 0.67, 0.82, 2.38, 2.53 (AB quartet, 2H, $J_{\text{AB}}=9\text{Hz}$), 1.85-2.07 (m, 2H), 2.82-3.08 (m, 4H), 5.82-6.03 (m, 2H) and 6.48-6.68 (m, 2H); $m/e = 226$.

Reaction of 122 with KO-t-Bu in THF

Addition of 122 (0.15 g, 0.00066 moles) in 3 ml of dry THF to a cooled (0-5°) slurry of KO-t-Bu (1.04 g, 0.0093 moles) and 10 ml of THF for 1 hour followed by treatment with water and extraction into pentane yields an unstable compound. Purification was not accomplished but comparison of the nmr spectrum of the crude product with the published spectrum⁹⁸ indicated the presence of 114.

REFERENCES CITED

1. M. Auron, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam, and C. D. Nenitzescu, Chem. Ber., 97, 382, (1964); E. K. G. Schmidt, Angew. Chem., 85, 820 (1973), Angew. Chem. Int. Ed., 12, 777 (1973); G. Maier, Angew. Chem., 86, 491 (1974), Angew. Chem. Int. Ed., 13, 425 (1974); E. K. G. Schmidt, L. Brener, and R. Petit, J. Amer. Chem. Soc., 92, 3240 (1970); R. H. Grubbs and R. A. Grey, ibid., 95, 5765 (1973).
2. W. J. Hehre and J. A. Pople, ibid., 97, 6941 (1975).
3. J. M. Schulman and T. J. Venanzi, ibid., 96, 4739 (1974); L. B. Rodewald and H. Lee, ibid., 95, 623 (1970); K. Kovacevic and Z. B. Maksic, J. Org. Chem., 39, 539 (1974); R. F. Peterson, Jr., R. T. K. Baker, and R. L. Wolfgang, Tetrahedron Lett., 4729 (1969).
4. M. S. Gordon and W. England, J. Amer. Chem. Soc., 94, 5168 (1972); J. W. Carson, J. D. Young, G. Lege, and F. Ewald, J. Chromatogr. Sci., 10, 737 (1972).
5. M. J. S. Dewar and M. C. Kohn, J. Amer. Chem. Soc., 94, 2699 (1972).
6. P. P. Montijn, L. Brandsma, and J. F. Arens, Rec. Trav. Chim., 86, 129 (1967); J. P. C. M. van Dongen, M. J. A. de Bie, and R. Steur, Tetrahedron Lett., 1371 (1973).
7. A. W. Krebs, Angew. Chem., 77, 10 (1965); Angew. Chem. Int. Ed. Engl., 4, 19 (1965).
8. T. Eicher and J. L. Weber, Fortschr. Chem. Forsch., 57, 1 (1975).
9. D. Wendisch, Methoden der organischen Chemie (edited by Houben, Weyl, and Muller), Georg Thieme Verlag, Bd. IV/3, S.729. Stuttgart, 1971.
10. T. Nakajima, S. Kohda, A. Tajiri and S. Karasawa, Tetrahedron, 23, 2189 (1967).
11. G. Berthier and B. Pullman, Bull. Soc. Chim. Fr., 16, D457 (1949).
12. J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, J. Amer. Chem. Soc., 74, 4579 (1952).
13. A. Julg, J. Chim. Phys., 50, 652 (1953).
14. M. J. S. Dewar and G. J. Gleicher, Tetrahedron, 21, 3423 (1965).
15. E. J. Smutney, M. C. Caserio and J. D. Roberts, J. Amer. Chem. Soc., 82, 1793 (1960).

16. Yu. Syrkin and M. Dyotkina, Acta Physicochim. URSS, 21, 641 (1946); Chem. Abstr., 41, 1648 (1947).
17. A. Julg and P. Francois, J. Chim. Phys., 59, 339 (1962).
18. O. Chalvet, R. Daudel and J. J. Kaufman, J. Phys. Chem., 68, 490 (1964).
19. S. L. Manatt and J. D. Roberts, J. Org. Chem., 24, 1336 (1959).
20. A. Skancke, Acta. Chem. Scand., 27, 3243 (1973).
21. G. Favini and G. Buoni, Theor. Chim. Acta., 24, 61 (1972).
22. G. L. Closs, "Cyclopropenes," Advances in Alicyclic Chemistry (edited by H. Hart and G. J. Karabatsos), Academic Press, New York, 1966, p. 121-122.
23. N. C. Baird and M. J. S. Dewar, J. Amer. Chem. Soc., 89, 3966 (1967).
24. I. S. Krull, P. F. D'Angelo, D. R. Arnold, E. Hedaya, and P. O. Schissel, Tetrahedron Lett., 771 (1971).
25. T. C. Shields and P. D. Gardner, J. Amer. Chem. Soc., 89, 5425 (1967).
26. M. A. Mattiste, ibid., 86, 942 (1964).
27. E. D. Bergmann and I. Agranat, ibid., 86, 3587 (1964).
28. A. S. Kende and P. T. Izzo, ibid., 86, 3587 (1964).
29. S. Andreades, ibid., 87, 3941 (1965).
30. W. M. Jones and J. M. Denham, ibid., 86, 944 (1964).
31. S. V. Krivun, N. S. Semenov, S. N. Baranov, and V. I. Dulenko, Z. Obsc. Chim., 40, 1904 (1970).
32. T. Eicher, Habilitationsschrift Würzburg, 1967.
33. B. Foschlich and P. Burtle, Tetrahedron Lett., 2661 (1965).
34. S. S. Hecht, ibid., 4385 (1970).
35. W. M. Jones and R. S. Pyron, ibid., 479 (1965).
36. A. S. Kende and P. T. Izzo, J. Amer. Chem. Soc., 87, 4162 (1965).
37. M. Ueno, I. Murata, and Y. Kitahara, Tetrahedron Lett., 2967 (1965).

38. H. Prinzbach, D. Seip, and U. Fischer, Angew. Chem., 77, 258 (1965); Angew. Chem. Int. Ed. Engl., 4, 242 (1965).
39. W. M. Jones and R. S. Pyron, J. Amer. Chem. Soc., 87, 1608 (1965).
40. T. Eicher and A. Löschner, Z. Naturforsch., 21b, 295 (1966).
41. R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, J. Amer. Chem. Soc., 87, 1320 (1965).
42. T. Eicher and A. Löschner, Z. Naturforsch., 21b, 899 (1966).
43. I. Agranat and M. R. Pick, Tetrahedron Lett., 4079 (1973).
44. A. S. Kende, J. Amer. Chem. Soc., 85, 1882 (1963).
45. R. West and D. C. Zecher, ibid., 89, 152 (1967).
46. B. Föhlisch and P. Bürgle, Liebigs Ann. Chem., 701, 67 (1967).
47. T. Eicher and A. Hansen, Tetrahedron Lett., 4321 (1967).
48. P. J. Stang and M. G. Mangum, J. Amer. Chem. Soc., 26, 3854 (1975).
49. T. Eicher, T. Pfister, and N. Krüger, Organic Preparations and Procedures International, 6, 63 (1974).
50. T. Eicher and T. Born, Liebigs Ann. Chem., 762, 127 (1972).
51. I. Agranat, A. Barak, and M. R. Pick, J. Org. Chem., 38, 3064 (1973).
52. T. Eicher and N. Pelz, Chem. Ber., 103, 2647 (1969).
53. H. Prinzbach and U. Fischer, Angew. Chem., 78, 642 (1966); Angew. Chem. Int. Ed. Engl., 5, 602 (1966).
54. I. Murata, K. Takatsuki, and O. Hara, Tetrahedron Lett., 4665 (1970).
55. T. Eicher and K. Eiglmeier, Chem. Ber., 104, 605 (1971).
56. H. Prinzbach, Pure Appl. Chem., 28, 281 (1971) (Calicenes).
57. H. Prinzbach and U. Fischer, Helv. Chim. Acta, 50, 1692 (1967).
58. R. Gompper and G. Seybold, The Jerusalem Symposium on Quantum Chemistry and Biochemistry, Vol. III, p. 215, The Israel Academy of Sciences and Humanities, Jerusalem, 1971.
59. T. Eicher and T. Born, Tetrahedron Lett., 981 (1970).

60. T. Eicher and E. V. Angerer, Chem. Ber., 103, 339 (1970).
61. R. S. Pyron and W. M. Jones, J. Org. Chem., 32, 4048 (1967).
62. F. D. Greene and R. L. Camp, J. Amer. Chem. Soc., 90, 7348 (1968).
63. J. K. Crandall and W. H. Machleder, ibid., 7347 (1968).
64. J. F. Pazos and F. D. Greene, ibid., 89, 1030 (1967).
65. G. Maier and A. Alzerreca, Angew. Chem., 85, 1056 (1973); Angew. Chem. Int. Ed., 12, 1015 (1973).
66. E. J. Corey and W. T. Borden, Tetrahedron Lett., 313 (1969).
67. R. Vaidyanathaswamy, G. C. Joshi, and D. Devaprabhakara, ibid., 2075 (1971); P. D. Gardner and M. Narayana, J. Org. Chem., 26, 3518 (1961).
68. G. C. Joshi, N. Singh, and L. M. Pande, Tetrahedron Lett., 1461 (1972).
69. See reference 22, p. 75.
70. See reference 8, p. 52.
71. A nucleus coupled to a set of n nuclei with spin I will have its resonance split into $2nI+1$ lines. For D, $I=1$ so the pattern becomes $[2(1)(1)+1=3]$ a triplet. For more information see E. D. Becker, High Resolution NMR, Academic Press, New York, 1969.
72. The extreme reactivity of this molecule is illustrated by its hydrogenolysis. Some hydrogenation catalysts are known to cause hydrogenolysis of vinyl halides, but under normal conditions Rh/Al_2O_3 does not. For further information see G. E. Ham and W. P. Coker, J. Org. Chem., 28, 194 (1964).
73. See reference 25. For other reductions see K. Hoffmann, S. F. Orochena, S. M. Sax, and G. A. Jeffrey, J. Amer. Chem. Soc., 81, 992 (1959); W. von E. Doering and A. K. Hoffmann, ibid., 76, 6162 (1954).
74. T. C. Shields and W. E. Billups, Chem. and Ind., 1999 (1967).
75. D. Seyferth, J. M. Burlitich, R. J. Mingsz, J. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, J. Amer. Chem. Soc., 87, 4259 (1965).
76. H. G. Peer and A. Schors, Rec. Trav. Chim., 86, 161 (1967).

77. J. T. Groves and K. W. Ma, J. Amer. Chem. Soc., 96, 6527 (1974); C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, ibid., 87, 3158 (1965); D. Seyferth, H. Yamazaki, and D. Alleston, J. Org. Chem., 28, 703 (1963).
78. C. L. Osborn, T. C. Shields, B. A. Shoulders, C. G. Gardenas, and P. Caubene, Tetrahedron, 27, 5741 (1971); H. Nozaki, T. Aratani, and R. Noyori, ibid., 23, 3645 (1967).
79. For leading references see "Heteroatom-substituted Cyclopropenium Compounds," Fortschr. Chem., 40, 47 (1973).
80. R. M. Magid, T. C. Clarke, and C. D. Duncan, J. Org. Chem., 36, 1320 (1971).
81. K. B. Wiberg and W. J. Bartley, J. Amer. Chem. Soc., 82, 6375 (1960).
82. G. A. Olah, J. M. Bollinger, ibid., 90, 6082 (1968); S. Arora and P. Binger, Synthesis, 801 (1974).
83. Our appreciation to Mr. J. Stevens for this study.
84. Shields and Gardner (reference 25) found that the stronger base and weaker nucleophile was necessary to induce dehydrohalogenation in the presence of MeS^- .
85. T. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, J. Amer. Chem. Soc., 87, 3026 (1965).
86. For other $\text{H}_2\text{O}_2/\text{AcOH}$ oxidations, see L. Fieser and M. Fieser, Reagents for Organic Syntheses, 1, 459 (1967), J. Wiley and Sons, New York.
87. J. L. Bellamy, Advances in IR Group Frequencies, p. 220, The Chaucer Press, Ltd., Suffolk, 1968.
88. J. E. Hoffmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, Chem. and Ind., 1243 (1963).
89. R. Bloch, P. Le Perche, and J. M. Conia, Angew. Chem. Int. Ed., 9, 798 (1970), found I^+ to be unstable. For theoretical calculations see J. J. Miller, Tetrahedron, 25, 1349 (1969) and references therein.
90. P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, J. Amer. Chem. Soc., 96, 4562 (1974).

91. Hydrogenation of di-*t*-butylacetylene with Raney nickel took twice the usual time to add two hydrogen atoms. Addition of Br₂ in CS₂ occurred slowly, but incompletely and with evolution of some HBr. For further information see: G. F. Hennion and T. F. Banigan, J. Amer. Chem. Soc., 68, 1202 (1946).
92. W. E. Billups, A. J. Blakeney, and W. Y. Chow, J. C. S. Chem. Comm., 1461 (1971).
93. R. P. Thummel, ibid., 899 (1974) and references therein.
94. W. E. Billups and W. Y. Chow, J. Amer. Chem. Soc., 95, 4099 (1973).
95. A. J. Birch, A. R. Murray, and H. Smith, J. Chem. Soc., 1945 (1951).
96. P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc., 78, 3409 (1956).
97. E. Vogel, W. Klug, and A. Breuer, Org. Syn., 54, 11 (1974);
E. Vogel and H. D. Roth, Angew. Chem., 76, 145 (1964).
98. E. Vogel and J. Sombroek, Tetrahedron Lett., 1627 (1974).
99. W. L. Collier and R. S. Macomber, J. Org. Chem., 38, 1367 (1973).

APPENDIX I

APPENDIX II

In the reaction sequence shown as Scheme 1, the strained species (3), (4), (5), or bond-switch isomers, could be involved as reaction intermediates in the conversion (2) $\rightarrow$ (1). The propensity of these intermediates to rearrange successively to the more stable (1) would account for the success of the reaction.

This work may be found in the literature: W. E. Billups, A. J. Blakeney, and W. Y. Chow, J. C. S. Chem. Commun., 1461 (1971), and W. E. Billups, A. J. Blakeney and W. Y. Chow, Org. Syn., 55, 12 (1976) and is described in more detail in the Ph.D. thesis of Dr. W. Y. Chow, Rice University, 1974.

[†] The major contaminants are dimethyl sulphoxide and t-butyl alcohol. After removal of these by washing with water, the estimated purity of benzocyclopropene is > 90%.

REFERENCES

1. E. Vogel W. G. Grimme, and S. Korte, Tetrahedron Lett. 1965, 3625.
2. R. Anet and F. A. L. Anet, J. Amer. Chem. Soc., 86, 525 (1964); G. L. Closs, Adv. Alicyclic Chem., 1, 64 (1966; G. L. Closs, L. G. Kaplan, and V. I. Bendall, J. Amer. Chem. Soc., 89, 3376 (1967); E. Vogel, S. Korte, W. G. Grimme, and H. Gunther, Angew. Chem. Int. Ed., 7, 289 (1968); H. Durr and L. Schrader, ibid., 8, (1969).
3. The general procedure of Skell and Garner was used. See: P. S. Skell and A. Y. Garner, J. Amer. Chem. Soc., 78, 3409 (1956).

4. T. C. Shields, W. E. Billups, and A. R. Lepley, J. Amer. Chem. Soc., 90, 4749 (1968).
 5. M. P. Cava and N. Narasimhan, J. Org. Chem., 36, 1419 (1971).
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