Approaches to the Elucidation of the Nature of 1,4-Dehydrobenzene

Thesis by

Gilbert Collier Johnson

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1979

(submitted January 5, 1979)

Acknowledgement

I would like to thank my advisor, Dr. Robert G. Bergman, who provided a fascinating and diverse environment in which to learn, and who tolerated a frequently uneven course of progress as I did learn. The Caltech community as a whole has my gratitude, more people than I can name here, who worked in the shops, offices, and other laboratories. Their skills and efforts made for a much easier time. I would also like to acknowledge the efforts of Dr. Günther Maier in his collaboration with us on a low temperature photolysis.

I would like to specifically thank Drs. R. H. Grubbs, D. A. Evans, P. B. Dervan, and S. H. Pine for their help and discussion through various stages of the work presented here, and would like to pay special tribute to Duncan W. Brown for his insight, friendship, and support through the dark days when nothing seemed to add up.

Finally, I would like to acknowledge the financial support of the National Science Foundation through grants and a graduate fellowship.

Abstract

Two approaches to the generation of 1,4-dehydrobenzene are described. The first, involving an attempted cycloreversion to generate initially the bicyclic form of the title compound, "butalene," gave negative results. The second approach, pyrolysis of various substituted hexene-diynes to generate substituted 1,4-dehydrobenzenes, gave evidence for the intermediacy of the 1,4-dehydrobenzene diradical in the formation of several isomerization products. A novel 1,2 silicon shift is proposed to give rise to other products through the intermediacy of substituted 1,3-dehydrobenzenes.

Contents

I. General Introduction

In the general area of reactive intermediates in organic chemistry, considerable interest has been focused on the fields of diradical and dehydroaromatic compounds, including much work on trimethylene and trimethylene-methane, 1,3-diradicals, and 1,2-dehydrobenzene or benzyne. Considerably less work has been done with the species of interest here, 1,4-dehydrobenzene or parabenzyne, **1**, where in fact the distinction between diradical and dehydrobenzene is less distinct because of the diverse possibilities of structure and reactivity (Figure 1).

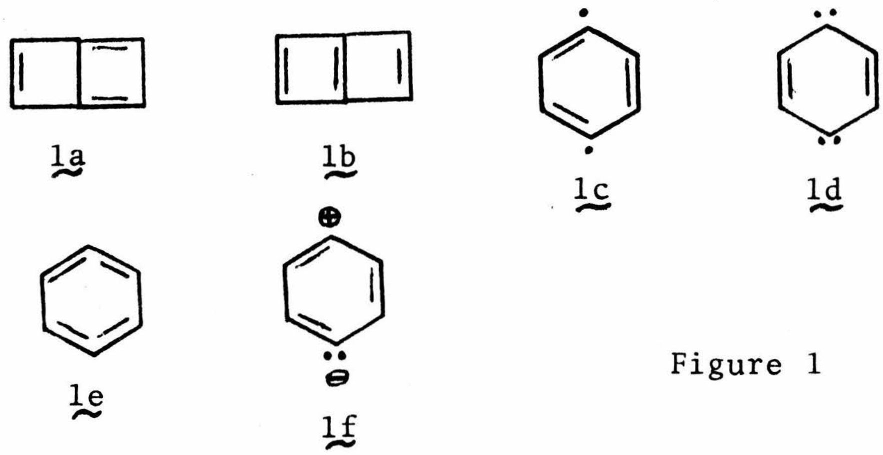


Figure 1

Theoretical calculations(1) have done little to elucidate the geometry, energy surface, or spin multiplicity of 1,4-dehydrobenzene. For instance, structure **1c** could be envisioned either as singlet or triplet, **1d** could even be envisioned as a quintet. The best *ab initio* study published to date, that of Wilhite and Whitten,(1a) suffered somewhat from a restrictive basis set(2) and the consideration of only the benzene geometry.

This study predicts a triplet ground state by 0.15 eV, 3.5 kcal/mole, but that result is far from definitive in light of the fact that distortion of the geometry toward that of 1a, "butalene," could well be expected to stabilize the singlet considerably.

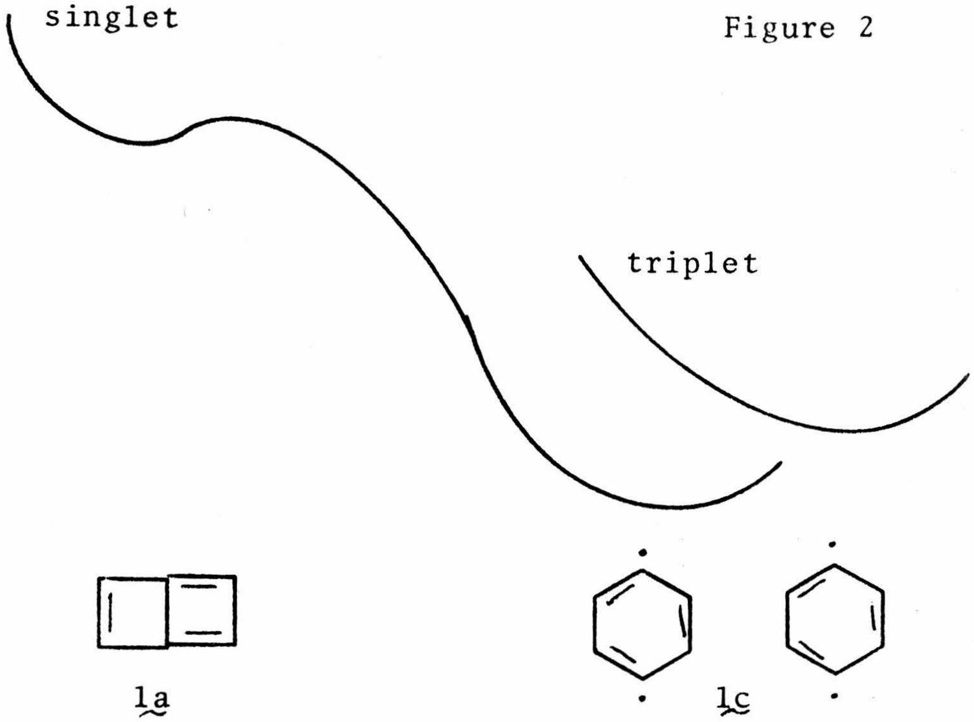


Figure 2

MINDO/3 calculations(1b) (and intuition as well) indicate an energy surface similar to that in Figure 2. Published data on 1 and related species(3) provided some direct information about the species. The work of Chapman et al.,(3e) indicated that 9,10-dehydroanthracene, 2, is not a triplet. That of Bergman and Jones, (3a, b) indicated a radical reactivity for the intermediate formed by pyrolysis of *cis*-3-hexene-1,5-diyne 3. Breslow et al.(3c,d) indicated the possible intermediacy of butalene, structures 1a or 1b, in trapping studies at low temperatures of products of base elimination from 1-chloro Dewar benzene, 4.

The work of Masamune et al.(3f) provided an interesting example of the apparent ambient temperature generation of a 1,4-diradical from strained *cis*-hexene-diynes in which cyclization resulted in the production of two new aromatic rings (Figure 3).

II. Cycloreversion Approach to the Generation of 1,4-Dehydrobenzene

A. Brief Introduction

One possible approach to 1,4-dehydrobenzene is a bond forming elimination reaction from a Dewar benzene (Figure 4).

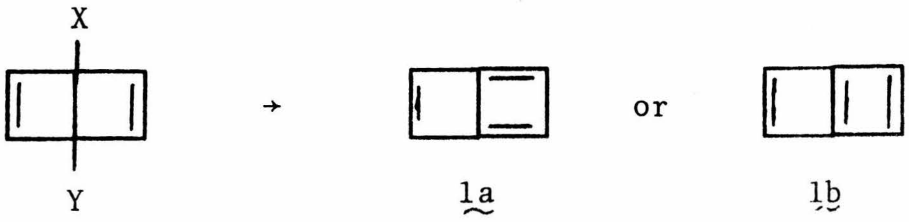
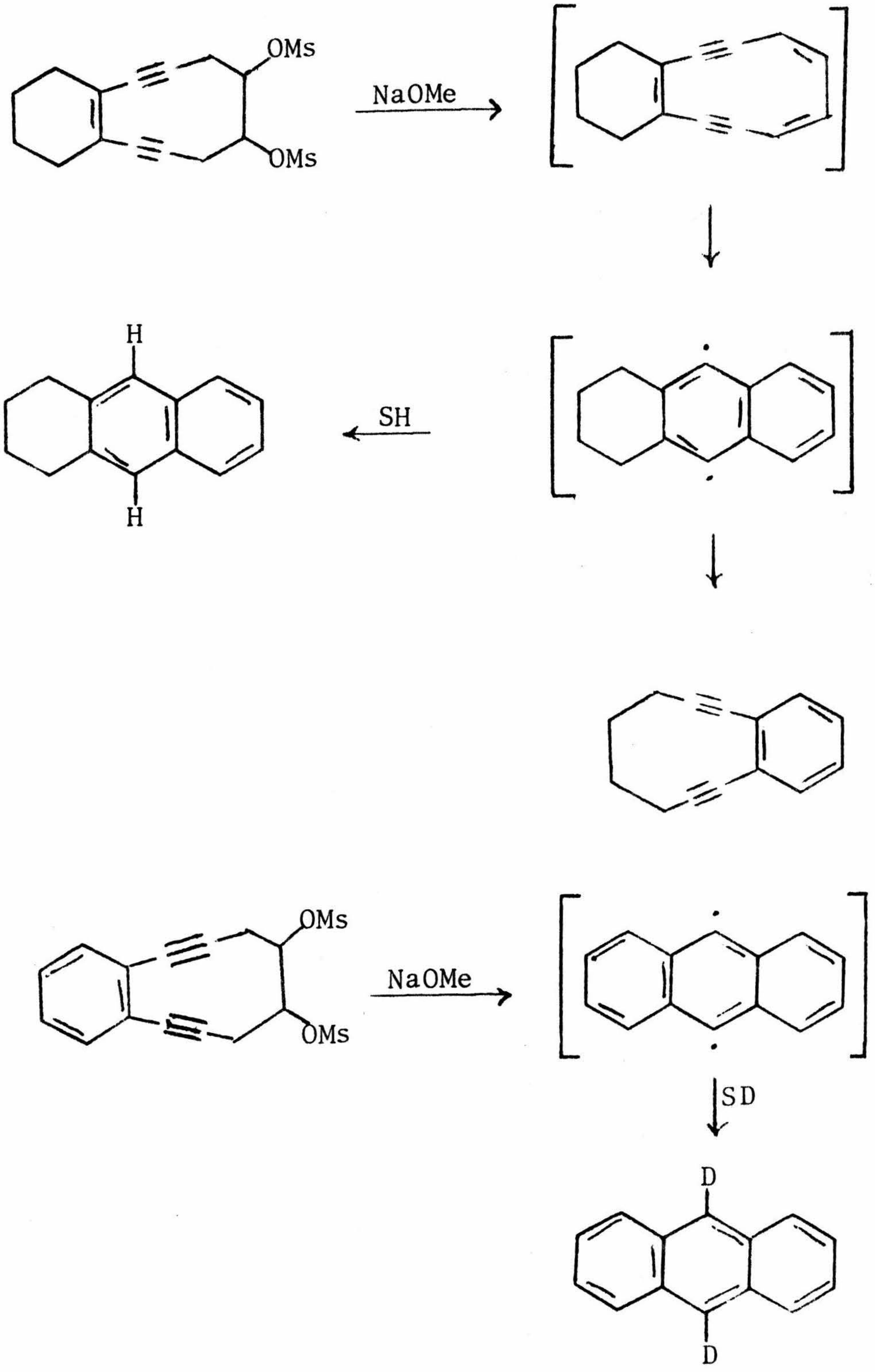


Figure 4

In principal, this is the ideal way to study the para-benzyne species since it should allow exploration of the whole energy surface (singlet, at least) depicted in Figure 2, but it also suffers from the high energy requirement of generating this, the predicted less stable isomer of an already high energy species. The work of Breslow et al.(3c,d) attempted to use this general route, and the ambiguities in the results are perhaps an illustration of the pitfalls inherent in a path that attempts to push a molecule to such extremes.

Figure 3



An alternate route was selected for our attempt to generate the butalene structure, involving a cycloreversion reaction from the Dewar benzene 5.

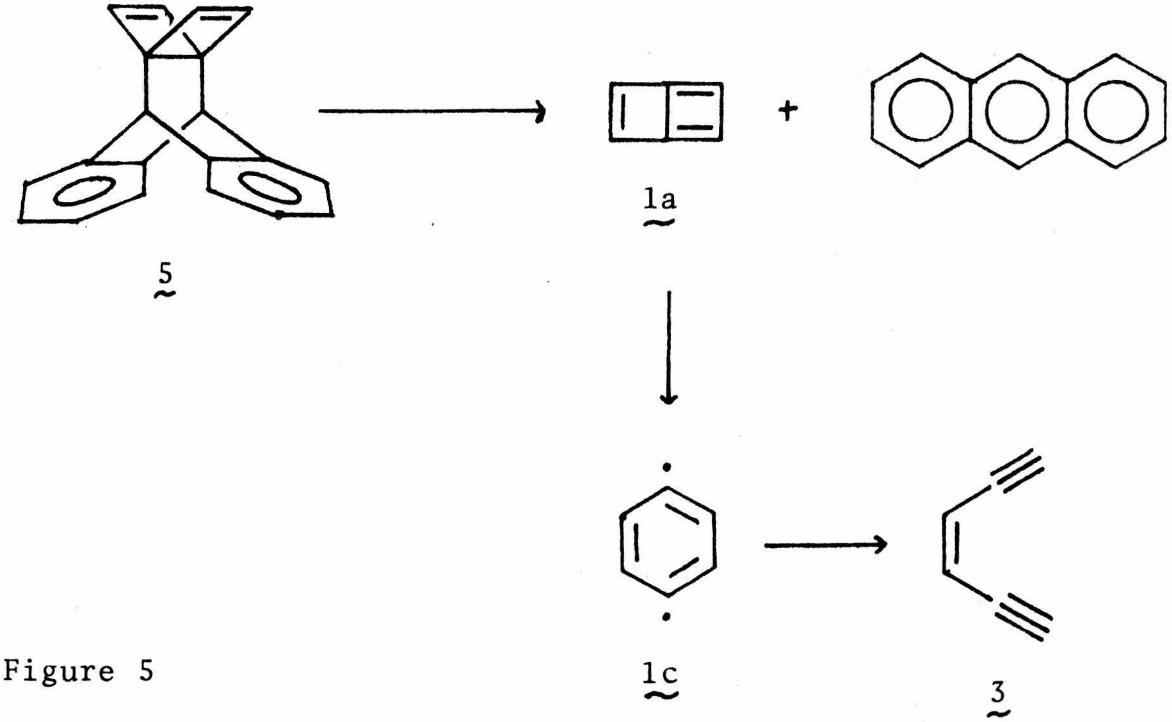


Figure 5

B. Methods and Results

1. Synthesis

Compound 5 could be synthesized by a variation on a known preparation of Dewar benzenes used in these labs.(4) Figure 6 gives the synthesis of 5 from the diene 6. The diene was prepared most conveniently from anthracene and 1,4-dichloro-2-butene by a method supplied by Eaton.(5)

The final step, silver ion promoted rearrangement of the bis-cyclopropene compound 7, was found to proceed best at lower temperatures, where production of the aromatized product trip-

Figure 6

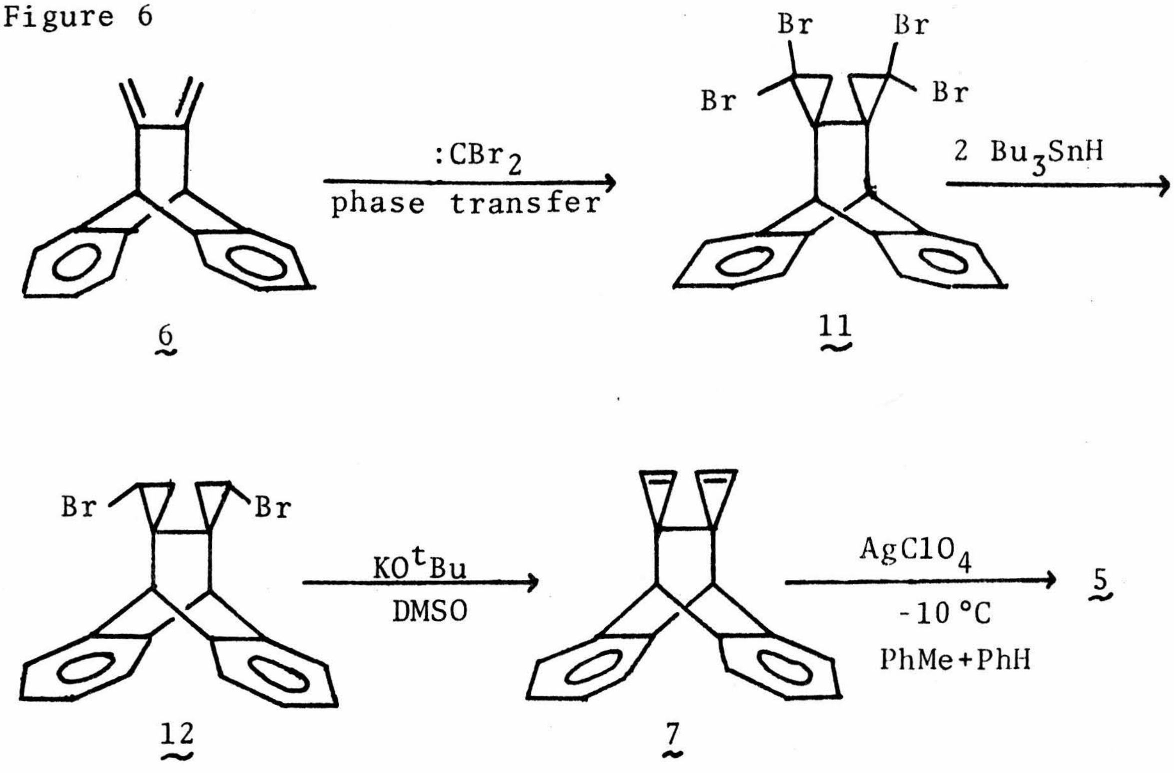
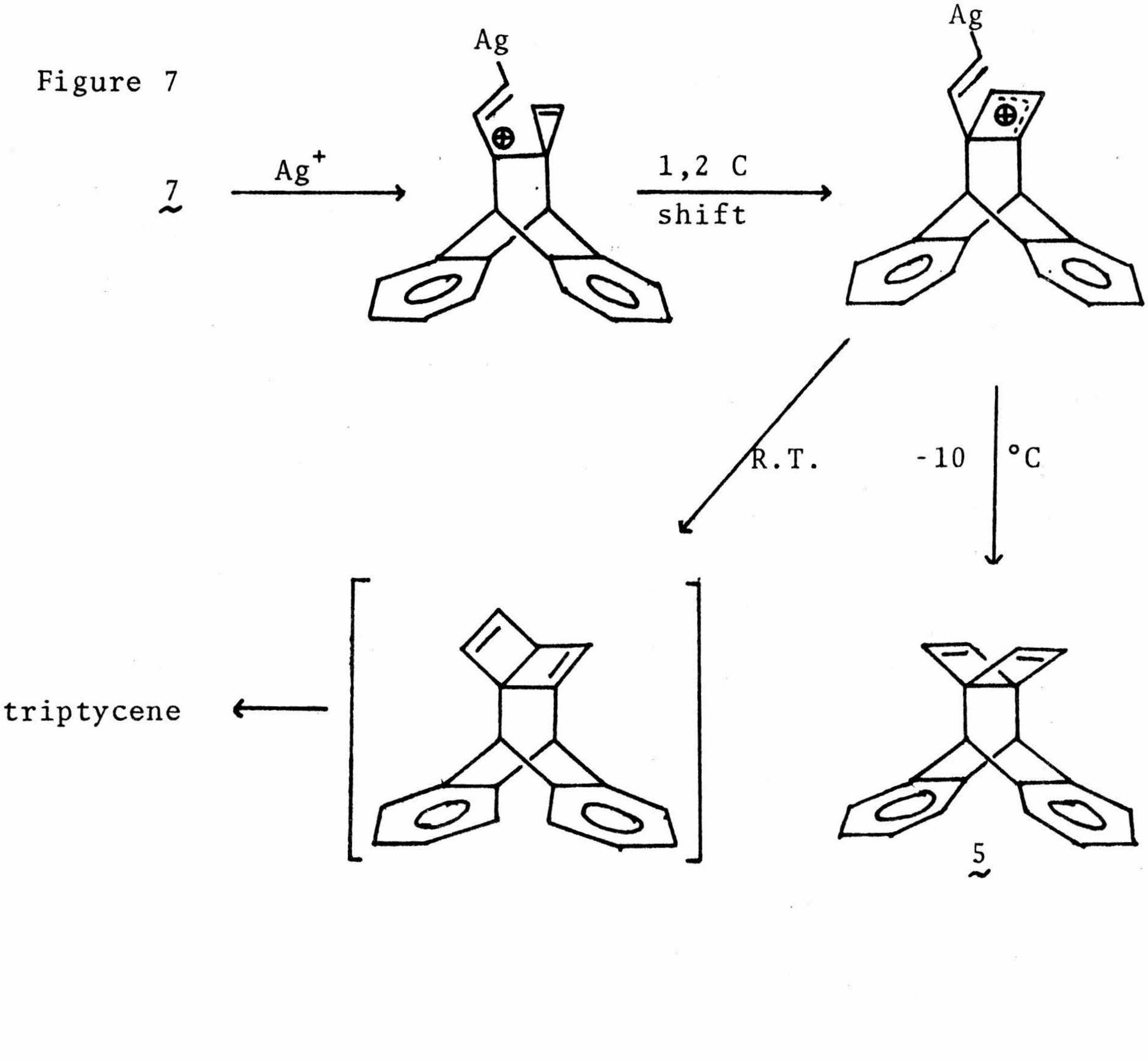


Figure 7



tycene was eliminated, although a side reaction consumed active catalyst and it was not possible to carry the reaction to completion (Figure 7).

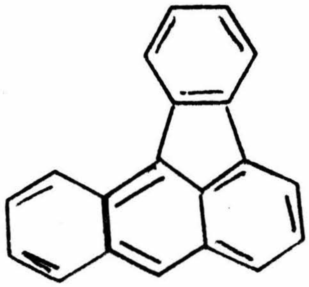
2. Pyrolyses

Compound **5** has been pyrolysed under a variety of conditions, under vacuum, at atmospheric pressure in helium flow, and in the injector port of a gas chromatograph. In brief, at no time was evidence for significant fragmentation to form anthracene and butalene, **1a**, observed. A description of these experiments and discussion of the results follows.

Compound **5** was pyrolysed twice in a vertical flash vacuum pyrolysis oven, sublimed up through the quartz tube to a -78°C Dewar condenser with a -196°C U-trap attached to trap out volatile products, if any. The oven was heated to 500°C and 700°C for the first and second pyrolyses, respectively, and pressure, measured in the attached vacuum system, was 0.05 mm Hg.

At 500°C, the Dewar benzene came through essentially unchanged - NMR showed only starting material, and GC revealed no volatile products. Thin layer chromatography on silica gel was required to show that the recovered Dewar benzene was not, in fact, pure. With pentane as eluent the slightly yellow pyrolysate separated out into three spots. Besides **5**, a trace of anthracene, identified by RF and its blue fluorescence, and a yellow product with an intense green fluorescence were observed. A control sublimation onto a cold finger, as well as the 700°C pyrolysis, both yielded similar small amounts of anthracene, so it is likely that it is being formed by decomposition of the solid 5 in the source flask.

By way of contrast, the 700°C pyrolysis yielded larger amounts of the yellow product, estimated ca. 30% of product by NMR integration, which showed only aromatic absorptions in the NMR. Column chromatography or gas chromatography yielded samples of this product, which was assigned on the basis of its NMR, mass spectrum and comparison with published properties, to be the known 2:3-benzofluoranthene, 8.



8

Reported(6) to be a yellow, somewhat air sensitive solid with a green fluorescence, 8 has the formula $C_{20}H_{12}$, molecular weight 252 (5 has the formula $C_{20}H_{14}$, molecular weight 254). The observed product matched these properties in every respect. The formula was established by precise mass spectroscopy since satisfactory analysis was not obtained, presumably due to the air sensitivity.

Flow pyrolysis was performed in a horizontal oven, 5 being sublimed into a flow of helium and passed through a quartz tube heated to 500°C with a computed 40 second contact time. Solid collected at the outlet of the oven, and except for some visible decomposition of the pyrolysate due to the heat of the oven at the point of deposition, results were qualitatively identical to the flash vacuum pyrolysis - no volatiles collected at -196°C, traces of anthracene and benzofluoranthene 8 detectable only by TLC.

Pyrolyses performed in a gas chromatograph injector were analyzed by two columns, one for detection of involatile anthracene, 5, and triptycene, one for volatile products. As the injector temperature was raised from 260°C to 400°C the high molecular weight column showed production of small amounts of both anthracene and triptycene, but a majority of the material that came through the column came through unchanged. Considerable decomposition of 5 was observed, as evidenced by the deposit of tarry material on the glass injector liner.

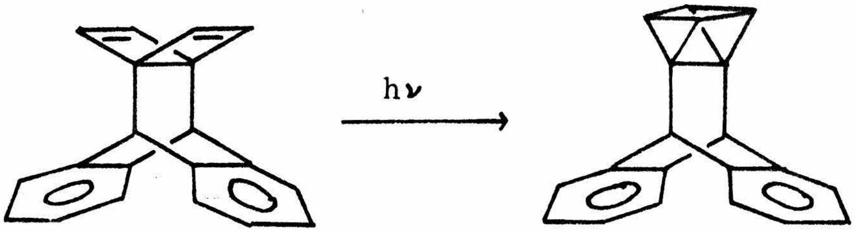
When a column known to separate cis-3-hexene-1,5-diyne, 3, was used to analyze injection port pyrolysate, on one occasion small amounts of material with retention time corresponding to 3 were observed as the pyrolysis temperature was raised from 240°C to 380°C. The amount was very small, and the observation was never reproduced, either on a flame ionization analytical GC or back on the original preparative GC.

Under a similar variety of conditions, pyrolysis of the biscyclopropene 7 yielded triptycene and 5, products expected from the biscyclopropene pyrolysis mechanism elucidated by R. G. Bergman et al.,(7) and traces of anthracene and 8, products of pyrolysis of 5.

3. Photolysis

A sample of **5** was supplied to Prof. G. Maier in Germany, who performed low temperature matrix photolysis on the compound. No fragmentation was observed, but IR bands appeared which he attributed to the closure of the Dewar benzene to give the prismane derivative **9**.(8)

Figure 8



5 **9**

C. Discussion

One thing that is clear from the above pyrolyses and photolysis is that **5** is strongly inhibited against extruding species such as **1a**, **1b**, or **3**. The mechanism of production of **8** has not been investigated, but it is possible to speculate that the first step involves a Cope rearrangement, by analogy to similar attempts to generate cyclobutadiene by reverse Diels-Alder reaction (Figure 9).

A variety of deuterium labelling studies suggest themselves. For instance, starting the synthesis with 9,10-dideutero-anthracene, available from 9,10-dibromoanthracene, would give bridgehead deuterated **5**. Similarly, other simple labellings are suggested by Figure 10.

Figure 9

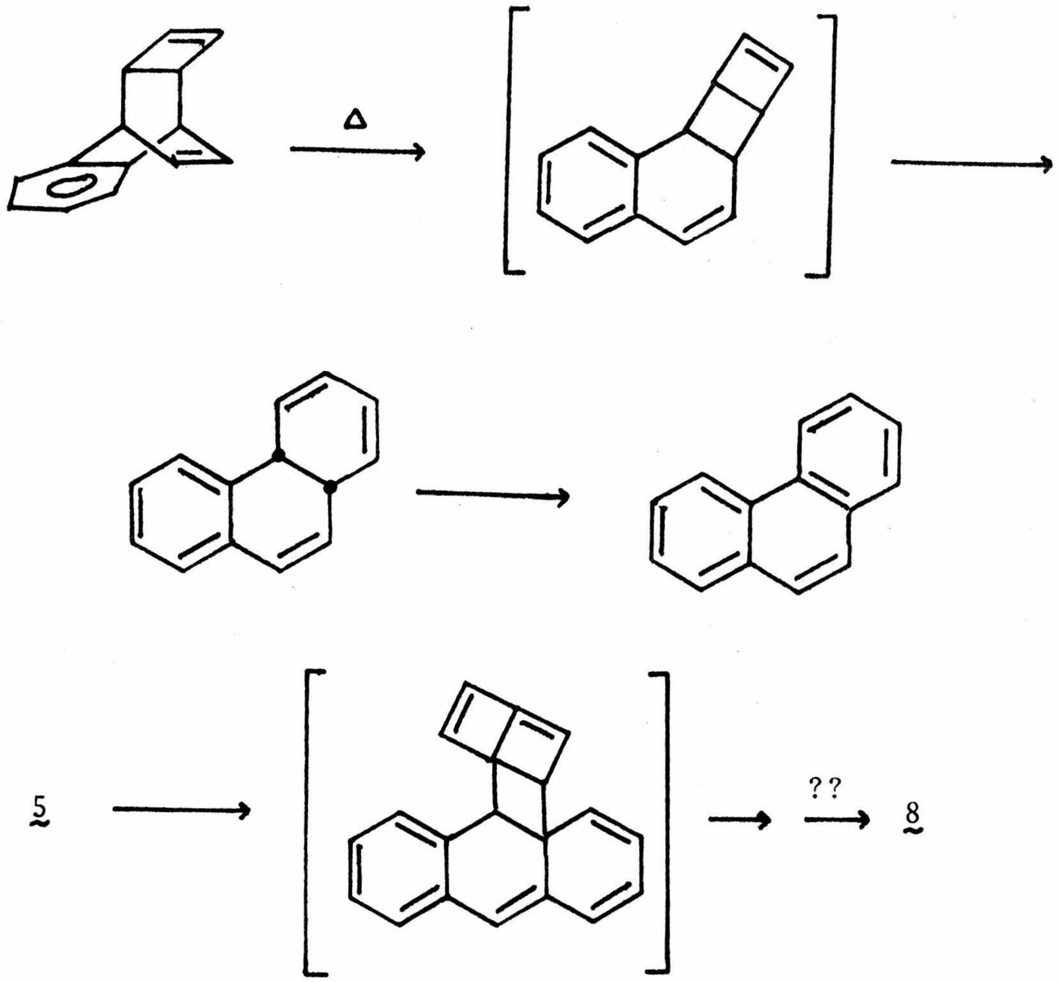
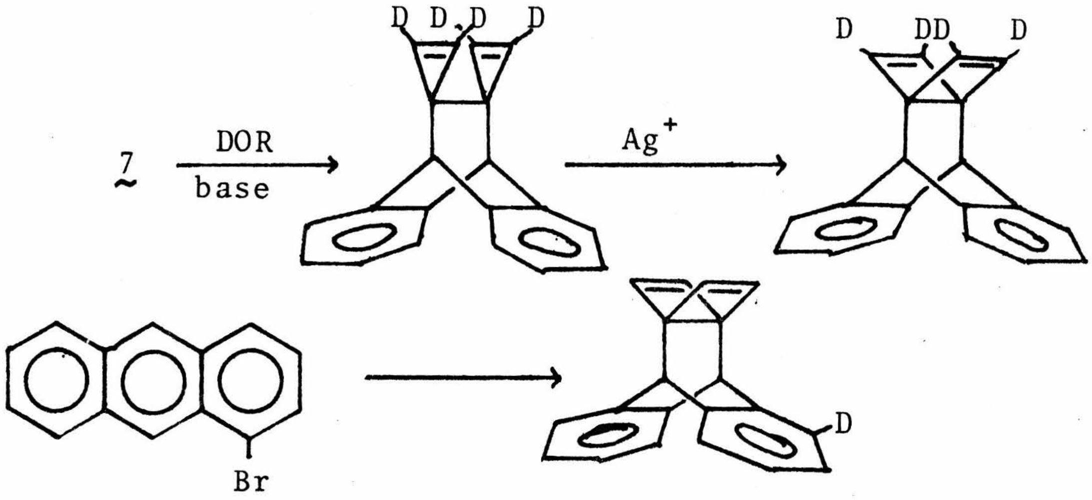
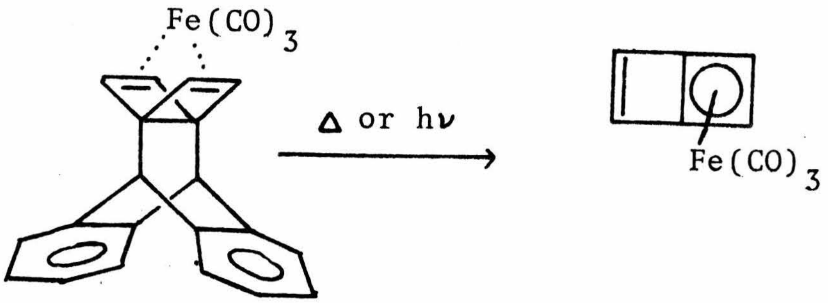


Figure 10



Another intriguing possible use for 5 is complexation to a metal. Aside from the fact that metal complexed Dewar benzenes are virtually unknown,(9) the possibility of stabilizing the structures 1a and 1b by metal complexation exists, as indicated in Figure 11.

Figure 11



Low temperature solution photolyses to isolate the prismane derivative 9 could be attempted (see Figure 8).

D. Experimental

1. General

NMR spectra were recorded on a Varian A-60 spectrometer. Mass spectra and analyses were obtained by the Caltech Analytical Laboratory.

Infrared spectra were recorded on the Beckman IR 4210 in Professor David A. Evans' laboratories. Two gas chromatographs were used, for analytical work on a Perkin-Elmer 3920B with flame ionization detector, and for routine and preparative GC, a Varian 90-P with thermal conductivity detector. In all cases helium was the carrier gas.

Gas chromatography columns used were as follows:

Column 1. 20' 1/4" glass, packed with 10% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 250°C, Perkin-Elmer 3920B.

Column 2. 5' 1/4" glass, packed with 8% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 275°C, Varian 90-P.

Column 3. 10' 1/4" glass, packed with 20% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 210°C, Varian 90-P.

Column 4. 4' 1/4" glass, packed with 8% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 275°C, Varian 90-P.

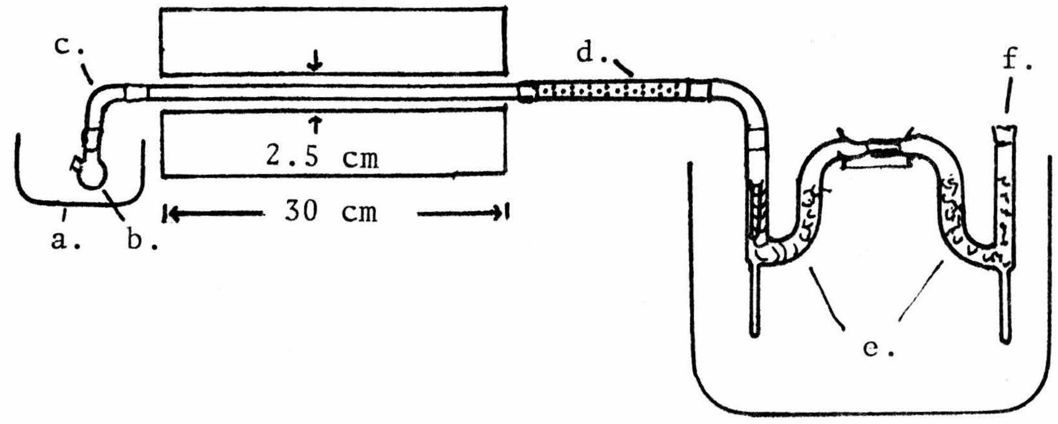
Column 5. 2' 1/4" glass, packed with 8% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 300°C, hand fitted single piece column, Varian 90-P.

Three pyrolysis apparatuses were used, one for flow pyrolysis, and two for flash vacuum pyrolysis - a second design of flash pyrolysis apparatus was necessary to attain temperatures higher than 500°C.

Flow pyrolysis was performed in a horizontal oven, a Hoskins Manufacturing Company Type FD 303A Electric Furance, the pyrolysis tube was 35 cm long, 12 mm quartz tubing with 14/20 outer joints formed on the ends (Figure 12).

Flash pyrolyses up to 500°C could be accomplished with the apparatus of Figure 13. Above 500°C modification was necessary because of difficulties with pyrex to quartz joints at high temperature (Figure 14).

Figure 12



a. heated oil bath

b. source flask with N_2 inlet

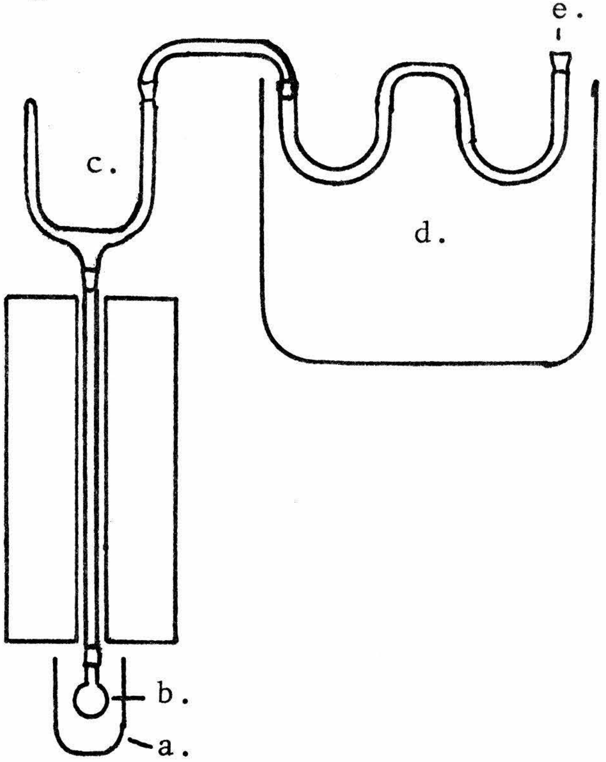
c. insulated elbow

d. Vigreaux column, solids collector

e. glass helices packed traps in LN_2 bath (-196°C)

f. to drying tube and bubble flowmeter

Figure 13



a. oil bath

b. source flask

c. -78°C condenser

d. -196°C traps

e. vacuum system

Figure 14

a. temperature bath

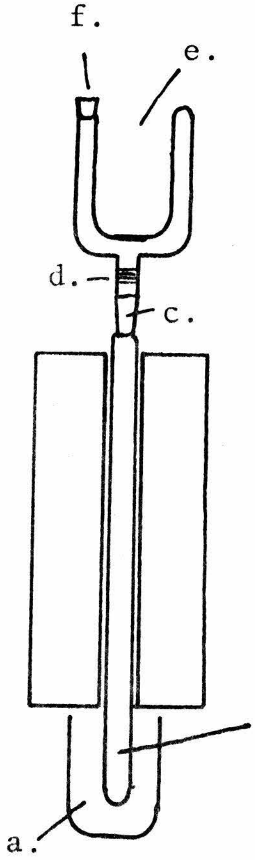
b. 25 mm quartz tube

c. 19/38 quartz joint

d. quartz to glass graded seal

e. -78°C condenser

f. -196°C traps and vacuum system



2. Syntheses

2,3-Bis(chloromethyl)-dibenzo[2.2.2]bicyclooctadiene, 10.(5)

Twenty-five gm anthracene (Aldrich, 98+%) and 62.5 gm 1,4-dichloro-2-butene (Aldrich, 98%, mixture of *cis* and *trans* isomers, 3.5 equivalents) were introduced into a 100 ml thick wall pyrolysis tube, carefully degassed through four freeze-pump-thaw cycles (to 0.01 mm Hg or below), and sealed under vacuum. The tube was placed in a sealed-tube oven, brought to 220°C and left at that temperature for 16 hours. The oven was allowed to cool to ca. 100°C before the tube was removed, frozen in liquid nitrogen, and cracked open. Upon warming, considerable hydrogen chloride escaped. The mixture was then dissolved in 750 ml 95% ethanol, treated with activated charcoal, filtered hot through Celite, and concentrated to 600 ml on a steam bath. Upon cooling to 0°C product crystallized out 29.5 gm after careful drying, 69%, mp 137-140°C (reported(5) 139-141°C).

2,3-Bismethylene-dibenzo[2.2.2]bicyclooctadiene, 6.(5)

Twenty gm **10** was stirred in 250 ml DMSO (Baker, stored over 4A seives) and 25 gm potassium *tert*-butoxide (Alfa, 98%, 3.3 eq) added quickly. After 14 hours the mixture was poured into 500 ml ice water and extracted twice with 200 ml diethyl ether. The combined ether layer was washed sequentially with two 100 ml portions of saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated to yield crude product which was recrystallized from 250-300 ml 95%

ethanol. Yield 14.2 gm, 94%, mp 145-7°C (reported(5) 147-8°C). NMR (δ $CDCl_3$): 4.87 (s, 2H), 5.11 (s, 2H), 5.28 (s, 2H), 7.0-7.5 (m, 8H), in agreement with reported data.(5)

2',2',3",3"-Tetrabromo-2,3-bis(spirocyclopropane)dibenzo-[2.2.2]bicyclooctadiene, 11.

In a three-neck flask equipped with rapid overhead stirring, nitrogen inlet, and dropping funnel, 2.30 gm diene 6 was dissolved in 5 ml bromoform (MCB, distilled and fractionally crystallized at 4°C before use), 5 ml dichloromethane, 0.2 ml ethanol and ca. 36 mg Stark's catalyst(10) (Aliqual 336, methyltricaprylyl ammonium chloride). Twenty-five ml 50% aqueous sodium hydroxide was added over 10 minutes at 0°C with rapid stirring. The ice bath was removed and the reaction stirred 1.5 hours before the ice bath was returned and an additional solution of 5 ml bromoform, 5 ml dichloromethane, 0.2 ml ethanol and ca. 36 mg catalyst was added. After an additional four hours of stirring at room temperature the reaction was poured onto 100 gm ice and 100 ml dichloromethane. The aqueous layer was separated and washed twice with 20 ml dichloromethane. Combined organics were washed twice with 50 ml cold 3% hydrochloric acid, twice with 50 ml saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, and evaporated to leave a black oil. Bromoform and other volatiles were removed by stirring at 0.1 mm Hg for four hours, then 100 ml dichloromethane and 10 gm silica gel were added, dichloromethane removed and the silica gel dried by evacuation to 0.1 mm Hg for two hours - considerable additional bromoform was removed at this point. The product, absorbed on silica gel, was layered onto a "short column" of 10 additional grams of silica gel in petroleum ether. Elution with three to four liters of petroleum ether (which can be recycled) and concentration to ca. 100 ml yielded 5.1 gm, 89%, of the tetrabromide, mp 195-7°C. Recrystallization from chloroform gave an analytical sample. Calculated for $C_{20}H_{14}Br_4$: C 41.85%, H 2.45%; observed: C 42.27%, H 2.54%. NMR (δ $CDCl_3$): 1.53 (d, 2H, J=8.5 Hz), 3.42 (d, 2H, J=8.5 Hz), 4.30 (s, 2H), 7.0-7.7 (m, 8H). IR (KBr cm^{-1}): 1455 (m, sh), 1448 (m, sh), 1409 (m, sh), 1093 (m), 1045 (m, sh), 1010 (s, sh), 1000 (s, sh), 966 (m, sh), 880 (m, sh), 857 (m, sh), 832 (m, sh), 752 (s, sh), 741 (s, sh), 669 (m, sh), 658 (m, sh), 617 (s, sh).

2',3"-Dibromo-2,3-bis(spirocyclopropane)-dibenzo(2.2.2)bicyclooctadiene, **12**.

To a stirred slurry of 1.51 gm of the tetrabromobiscyclopropane **11** in 10 ml dry benzene under nitrogen was added 1.53 gm tri-n-butyltin hydride over 10 minutes. The temperature of the reaction should be kept below 30°C. After an additional 30 minutes, 1 ml chloroform was added at 0°C, solvent was removed on a rotary evaporator, the syrupy suspension filtered, and collected crystals were washed with pentane. One recrystallization from chloroform yielded 0.65 gm, 70%, **11**, mp 201-4°C. A second recrystallization yielded analytically pure material, calculated for $C_{20}H_{16}Br_2$: C 57.72%, H 3.88%;

observed: C 57.88%, H 3.92%. Mp analytical sample 205°C, NMR (δ $CDCl_3$): 0.78 (d of d, J_1=15 Hz, J_2=8 Hz), 0.98 (d of d, J_1=15 Hz, J_2=5 Hz), overlapping, total 4H, 2.43 (d of d, 2H, J_1=8 Hz, J_2=5 Hz), 4.08 (s, 2H), 7.0-7.5 (m, 8H). IR (KBr, cm^{-1}): 1470 (m, sh), 1450 (s), 1425 (m, sh), 1287 (m, sh), 1243 (s), 1026 (m, sh), 1013 (m, sh), 920 (s, sh), 888 (m, sh), 853 (m, sh), 757 (vs, sh), 743 (vs, sh), 677 (s, sh), 630 (s).

2,3-Bis(spirocyclopropene)-dibenzo(2.2.2)bicyclooctadiene, 7.

2.8 gm potassium *tert*-butoxide (Alfa, 98%) and 50 ml DMSO (Baker, stored over 4A molecular seives) were stirred magnetically and 4.16 gm dibromide **11** added quickly. After one hour, the reaction was poured onto 100 gm ice, and 150 ml water and 250 ml dichloromethane added. The organic layer was separated, washed twice with 250 ml portions of water, dried over anhydrous sodium sulfate, and evaporated to give a crude solid, mp 165°C (dec). Passage through a short column of silica gel with petroleum ether and recrystallization from ethanol-water yielded 1.9 gm, 75%, pure white solid, mp 180-4°C (dec). Satisfactory analysis of this moderately sensitive compound was not obtained, but precise mass measurement established the molecular formula to be $C_{20}H_{14}$, calculated for $^{12}C_{20}{}^{1}H_{14}$ 254.10955, obtained 254.1100. NMR (δ, $CDCl_3$): 3.38 (s, 2H), 6.88 (s, 4H), 7.0-7.5 (m, 8H). IR (KBr, cm^{-1}): 1608 (m), 1450 (m), 1004 (m, sh), 752 (s, sh), 740 (s, sh), 678 (m, sh), 670 (s, sh), 635 (m, sh), 613 (m, sh).

Bis(2,3-etheno)-dibenzo(2.2.2)bicyclooctadiene, 5.

1.0 gm silver perchlorate was dissolved in a mixed solvent consisting of 60 ml toluene and 140 ml benzene, stirred magnetically under nitrogen and cooled to -10°C. 1.07 gm bis-cyclopropene 7 in 20 ml benzene was added over 10 minutes and the solution stirred for 2 hours. The reaction was worked up by washing rapidly with 200 ml 10% aqueous sodium thiosulfate and 200 ml cold water. The organic layers were dried with anhydrous sodium sulfate, solvent removed on a rotary evaporator, and the crude solid run through a short column of silica gel with petroleum ether as eluent. Removal of solvent yielded 850 mg of crude product, shown by NMR to be approximately a 3:1 mixture of product and starting material. Recrystallization from ethanol gave impure recovered starting material, precipitation of the mother liquors with water followed by recrystallization from absolute ethanol yielded 0.55 gm pure 5, 51%. Satisfactory analyses of this compound could not be obtained; precise mass calculated for $^{12}C_{20}{}^{1}H_{14}$ 254.10955, obtained 254.1088. NMR (δ, CCl_4): 4.41 (s, 2H), 6.08 (s, 4H), 6.8-7.2 (m, 8H). IR (KBr, cm^{-1}): 1450 (m), 1270 (m), 1160 (m), 1028 (m, sh), 1015 (m, sh), 970 (m, sh), 797 (s, sh), 782 (s, sh), 768 (s, sh), 740 (m, sh), 726 (s, sh), 628 (m, sh), 615 (m, sh).

3. Pyrolyses

a. Injector Port Pyrolyses

Pyrolysis was performed in the injector port of a Varian 90-P gas chromatograph and monitored by either GC column

3, to separate volatile products, or column 4 to separate starting material and involatile compounds. A sample of 10 µl of a 1% solution of 5 in pentane was injected into the glass lined heated injector. With column 3 at 45°C, 60 ml/min flow rate, the injector temperature was raised from 240°C to 380°C at ca. 30°C intervals. Even at 240°C, a small amount of a volatile product with retention time 3 minutes 50 seconds, corresponding to 3, was observed. This product increased in amount as the temperature was raised to 380°C, the maximum attainable with a cool column oven, but judging qualitatively, very little of 5 was being pyrolysed to form this product. Pyrolyses with column 4 in the oven bore out this qualitative impression - as the injector temperature was raised from 260°C to 300°C, small amounts of triptycene and anthracene were produced, but a large majority of the sample of 5 came through unchanged. Column temperature was 250°C, flow 60 ml/min.

In an attempt to quantify the results of the preliminary pyrolysis in a Varian 90-P, the experiment was repeated in an analytical GC, a Perkin-Elmer 3920B with column 1, flow rate 60 ml/min, temperature programmed to allow detection of volatile products from each injection - 60°C for 16 min, to 250°C at 16°/min, 250°C for 32 min. No volatile products were observed as the injector temperature was varied from 300°C to 400°C. Again, small, variable amounts of anthracene and triptycene were detected. A repeat of the preliminary pyrolyses on the Varian 90-P showed similar negative results.

b. Flow Pyrolysis

In the apparatus illustrated in Figure 12, 150 mg 5 was pyrolysed under the following conditions:

Oil bath, 110°C
Helium flow, 30 ml/min
Oven temperature, 500±5°C
Time required, 1.5 hr

Any volatile products were washed out of the traps with pentane and analyzed by gas chromatography, column 1, flow 50 ml/min, 60°C. No products were observed.

Collected solid was pure by NMR, but TLC (pentane eluent on silica gel without fluorescent indicator) showed, beside starting material, small traces of anthracene (identified by its Rf and characteristic blue fluorescence) and a compound with very low Rf , 0.2, and an intense green fluorescence. This product is discussed below.

c. Flash Pyrolyses

Flash vacuum pyrolyses were carried out in the apparatus pictured in the general experimental section. With the pyrolysis tube out of the oven and the oven ends plugged with quartz wool, the top end covered also with a watch glass, the oven was brought up to the desired temperature. The pyrolysis tube was loaded with ca. 100 mg 5, flushed and stoppered with an inert atmosphere. The plugs were quickly removed from the oven, the tube inserted, traps and vacuum system attached, and the entire system evacuated, as rapidly as possible. After evacuation, the traps were brought to temperature, the oven was stabilized at the desired temperature, and the liquid nitrogen surrounding the sample replaced by the heated oil bath, at 100°C. The sample sublimed quite rapidly and collected on the -78°C trap.

At oven temperature 500°C, the results were qualitatively identical to the 500°C flow pyrolysis. No attempt was made to quantify the small amounts of product. No volatile products were observed. At oven temperature 700°C, the pyrolysate was noticeably yellow, and although no volatile products were observed, TLC showed a large amount of a yellow product, with the same low RF and intense fluorescence as observed previously. NMR showed the presence of low field aromatic absorptions over the range from δ 8.3 to the multiplet of **5** at ca. δ 7.2.

4. Isolation of 2:3-Benzofluoranthene, **8**

When pyrolysate known to contain significant amounts of the then unidentified yellow product were injected onto a GC, a very broad peak with long retention time was observed. Collection yielded small amounts of yellow solid. When neither GC columns 2 nor 4 were found to be suitable at the maximum temperature attainable with a teflon-jointed glass column, column 5 (2' solid glass packed with 8% SE-30 on Chromosorb W) was constructed. With that column, collection of material was much easier, a flow rate of 60 ml/min and a temperature of 280°C giving a retention time of ca. 5 minutes. Collected solid did not yield satisfactory analysis, but precise mass spectroscopy established the sample to be of the formula $C_{20}H_{12}$: calculated for ${}^{12}C_{20}{}^{1}H_{12}$ 252.0939, observed 252.091.

Column chromatography of the pyrolsates on silica gel with pentane eluent yielded larger quantities of purified product for NMR, which showed only low field absorptions, overlapping complex multiplets between δ 7.2 and δ 8.4.

5. Photolysis

A sample of **5** was supplied to Professor Günther Maier in Germany, and was photolysed by Dr. Reisenauer in his group using standard low temperature matrix isolation techniques. Compound **5** in argon matrix at 10 K was photolysed for 18 hours with 254 nm light, giving partial conversion to a new compound, which they assign to be the prismane derivative, **9**, by IR at 10 K. Isolation of the photolysis mixture at room temperature and normal potassium bromide pellet IR shows also partial conversion to a new compound, presumably **9**.

5, IR (Ar, 10 K, cm^{-1}): 1430 (m, sh), 1420 (m, sh), 1277 (m, sh), 1210 (w, br), 1163 (m, sh), 976 (m, sh), 788 (s, sh), 770 (m, sh), 730 (s, sh), 620 (m, sh), 632 (m, sh), 530 (m, sh).

Photolysate, IR (Ar, 10 K, cm^{-1}): In addition to absorptions of **5**, considerably reduced in intensity; 1420 (m, sh, superimposed on absorptions of **5**), 1195 (w, br), 740 (m, sh), 625 (m, sh).

Photolysate, IR (KBr, r.t., cm^{-1}): In addition to absorptions of **5**; 1190 (w), 1182 (w), 780 (s, sh, superimposed), 732 (s, sh, superimposed), 618 (s, sh, superimposed), 475 (w, br).

III. Hexene-diyne Pyrolyses to Generate 1,4-Dehydrobenzenes

A. Introduction and Brief History

Since the original report by Jones and Bergman,(3a) considerable work has been undertaken in these labs to expand and extend the understanding of the nature of the intermediate generated by pyrolysis of *cis*-3-hexene-1,5-diyne, **3**. The original work presented convincing evidence of a symmetrical diradical intermediate. Gas phase pyrolysis of 1,6-dideutero-*cis*-3-hexene-1,5-diyne resulted in equilibration with the 3,4-dideutero isomer with no other scrambled isomers observed. Trapping experiments in methanol yielded benzene and benzyl alcohol but no anisole, indicative of radical as opposed to polar reactivity.

An approximation of the energy surface (Figure 15) was deduced from thermochemical estimates and an approximation of the barrier to rearrangement derived from the half life of **3** at 200°C. Ideally, kinetic measurements would refine the estimates to give a clearer picture of the energy surface. Unfortunately the sensitivity of **3** makes accurate kinetic studies impossible. With this in mind, synthesis of a series of derivatives of **3** was undertaken. One thrust of this effort was to stablize the 3-hexene-1,5-diyne skeleton with bulky substituents.

The first attempt was the synthesis of *cis*-3-*tert*-

Figure 15

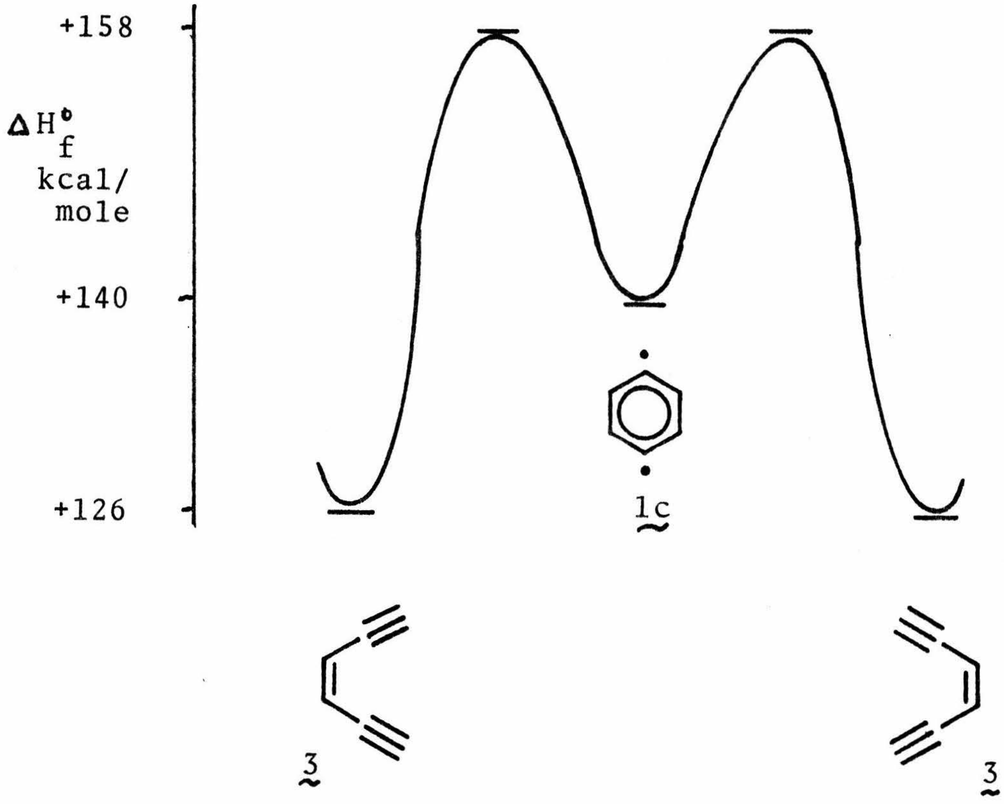
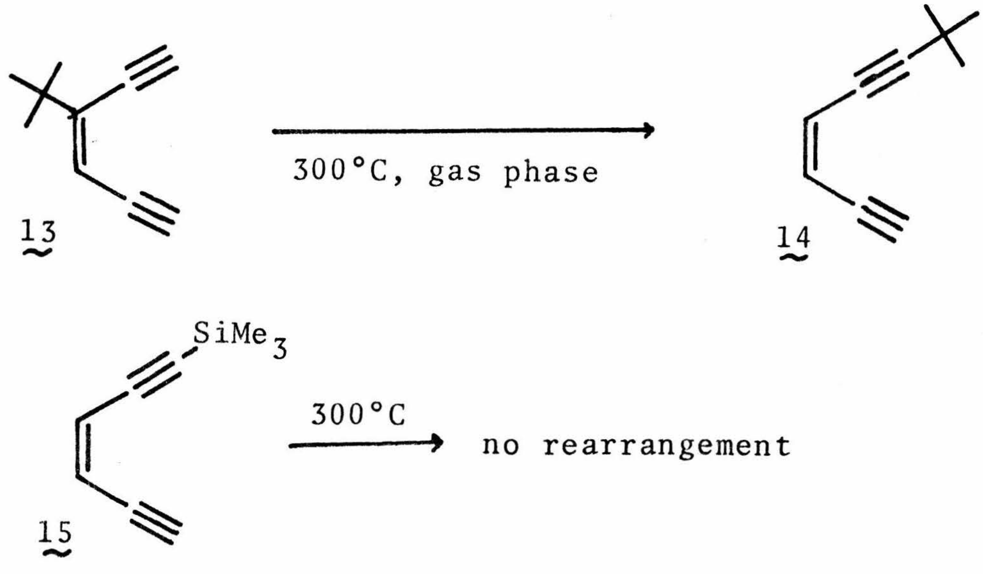


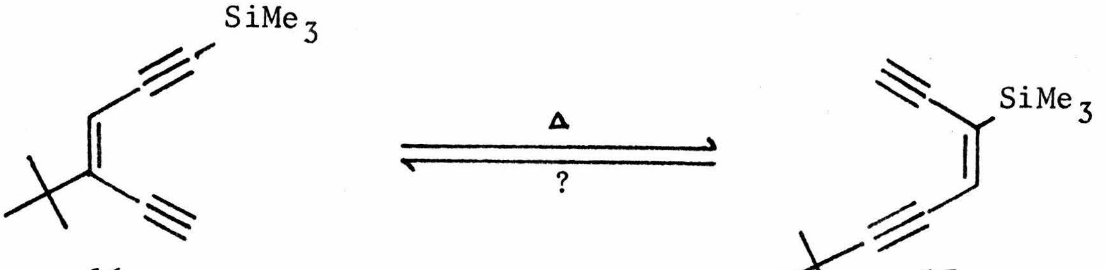
Figure 16



butyl-3-hexene-1,5-diyne,* 13, which yielded, upon atmospheric pressure flow pyrolysis in the gas phase at 300°C, the more stable isomer 14.(12) The tertiary butyl substituent on 13 gave it somewhat improved stability to polymerization over 3, but so far it has not proven suitable for kinetic studies.(12,13)

Also synthesized was the 1-trimethylsilyl derivative 15. Upon pyrolysis of 15 in the gas phase up to 300°C only starting material was recovered. This was consistent with the results of pyrolysis of 13, the more stable isomer being that with the substituent on the triple bond.

As a logical extension of this, compound 16 was prepared and pyrolyzed with the expectation that counteracting substituent effects would allow observation of equilibration. Double substitution was expected to further stablize the compound, making it more suitable for kinetic study.



16 17

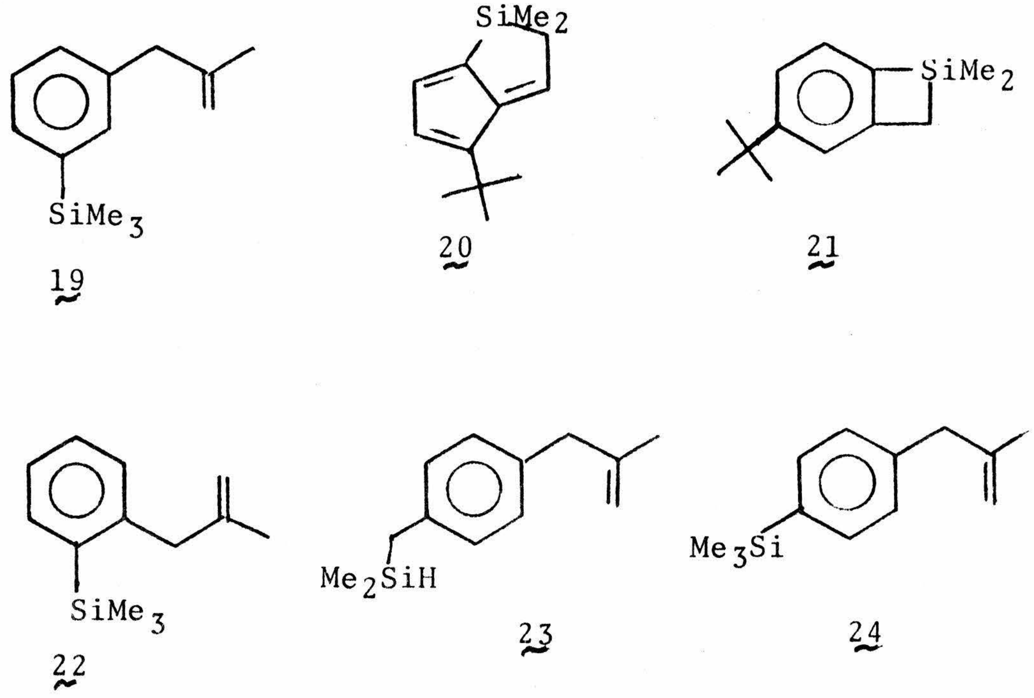
Figure 17

---

*For the purposes of this report, the alkynyl substituents on the double bond have priority over all other substituents in the cis-trans nomenclature convention.

Perhaps surprisingly, 300°C gas phase pyrolysis of 16 resulted only in recovery of starting material. As the temperature was raised, however, conversion to an array of products was observed. At 450°C 16 was largely consumed and four major products (as well as a complex mixture of very minor products) were collected in the pyrolysis traps.(14) The major products were identified to be 19, 20, 21, and 22. Syntheses of authentic samples of 19 and 21 were performed, but structures 20 and 22 were assigned by NMR spectral data. The product assigned as 22 was not obtained pure, not separated from 21 by gas chromatography at that time. As described later, this product has now been purified and on the basis of its proton and carbon spectra has been reassigned as 23. It should be noted that despite the presence of products 19 and 23 in the pyrolysis, no significant amount of 24 is present.

Figure 18



The results of 450°C pyrolysis of **16** suggested that the more simply substituted hexene-diynes **13** and **15** might give rise to similar products at higher temperature. Pyrolysis of **13** at 450°C consumed starting material and yielded no major product, but pyrolysis of **15** yielded 1,1-dimethyl-1-silabenzocyclobutene, analogous to **21**.(14)

The above results made synthesis of **17** a desirable goal pyrolysis was expected to shed light on whether the product array from **16** was indeed arising from a 2-trimethylsilyl-5-*tert*-butyl-1,4-dehydrobenzene intermediate or by some other mechanism.

B. Methods and Results

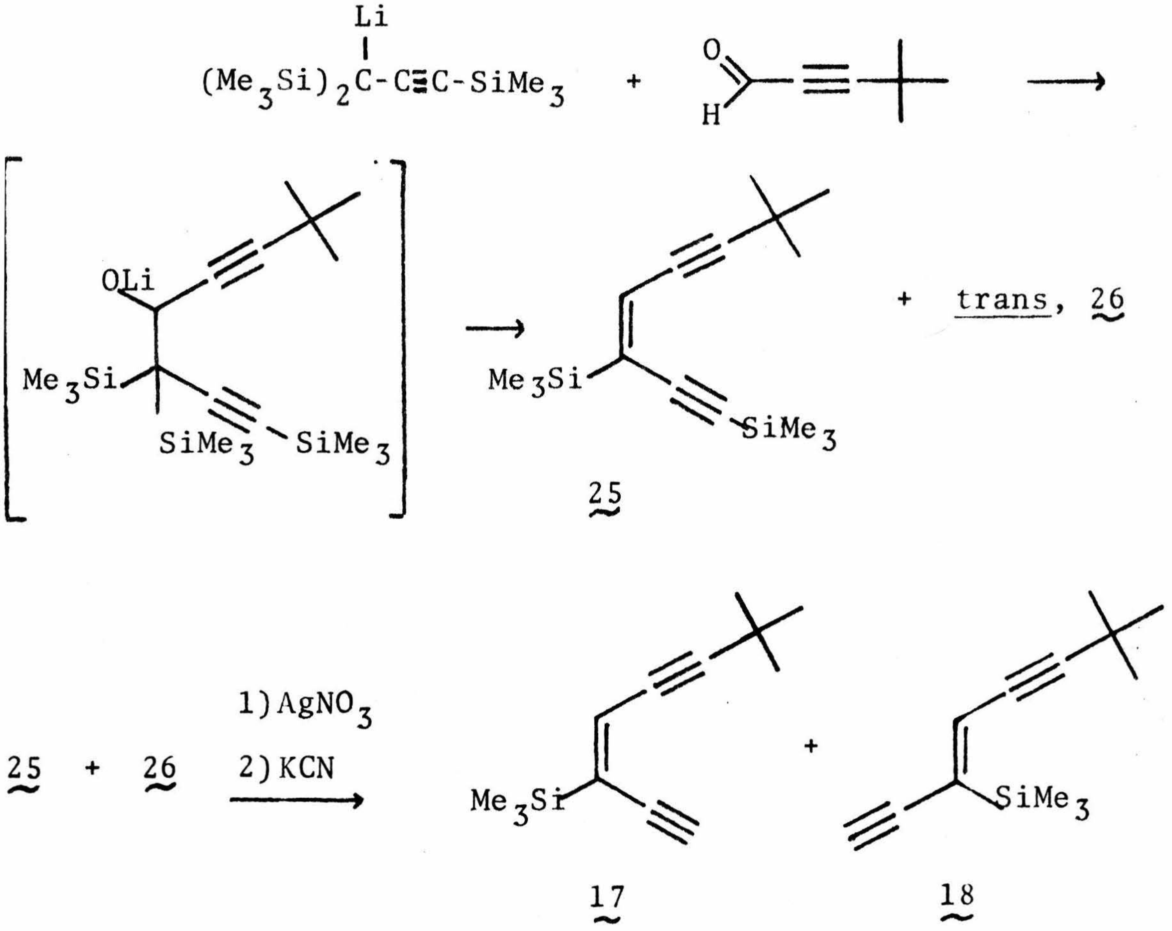
1. Synthesis and Pyrolysis of *cis*-1-*Tert*-butyl-4-trimethylsilyl-3-hexene-1,5-diyne, **17**.

The synthesis of **17** is outlined in Figure 19.

The olefination of the aldehyde followed the method of Peterson et al.,(15) removal of the trimethylsilyl group, that of Corey et al.(16) As indicated, both the desired **17** and *trans* isomer **18** were produced. They could be separated by preparative gas chromatography and pyrolyzed separately.

Pyrolyses of **16**, **17** and **18** at ca. 450°C under conditions similar to those used previously(14) yielded identical product arrays of **19**, **20**, **21** and **23**. The array of isomerized hexene-diynes **16**, **17** and **18** was independent of starting material. The ratio of **16**:**18**:**17** was ca. 100:7:1, consistent with the fact that pyrolysis of **17** at 300°C gave essentially pure **16**.

Figure 19

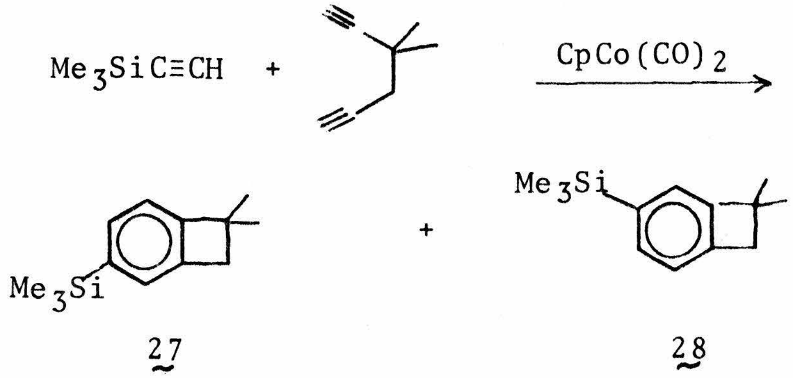


2. Synthesis and pyrolysis of 1,1-Dimethyl-4-trimethylsilylbenzocyclobutene, 27.

One proposed mechanism for formation of 19 involved intermediacy of 27, a compound analogous to 21 (see Discussion). The synthesis of 27 was carried out by an acetylene trimerization as outlined in Figure 20.

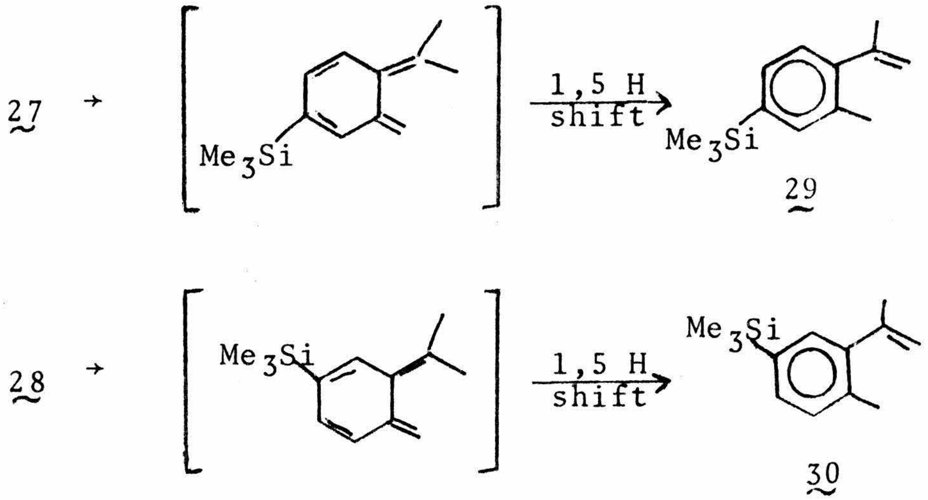
As shown, the trimerization resulted in a mixture of both possible isomers, 27 and 28, which could be separated by gas chromatography and pyrolyzed separately. Pyrolysis under the reaction conditions, or under conditions as severe as

Figure 20



850°C *in vacuo* did not lead to **19**, but only to products **29** and **30**. These are derived from ortho-xylylene intermediates as shown in Figure 21.

Figure 21



Although NMR did not distinguish between **27** and **28** or between **29** and **30**, the synthesis was unambiguous, and it is clear that **27** is not a precursor to **19**.

3. Synthesis and pyrolysis of *cis*-1-trimethylsilyl-6-*tert*-butyl-3-hexene-1,5-diyne, 31.

As a test of the proposed diradical "ring walk" mechanism (see Discussion), 31 was synthesized and pyrolyzed. As noted (Figure 22) coupling resulted in a mixture of the *cis* and *trans* isomers 31 and 32.

Pyrolysis of 31 at 450°C gave mostly *cis*-*trans* isomerization to 32. A somewhat higher temperature of 530°C was required to effect good conversion to three products (Figure 23).

Figure 22

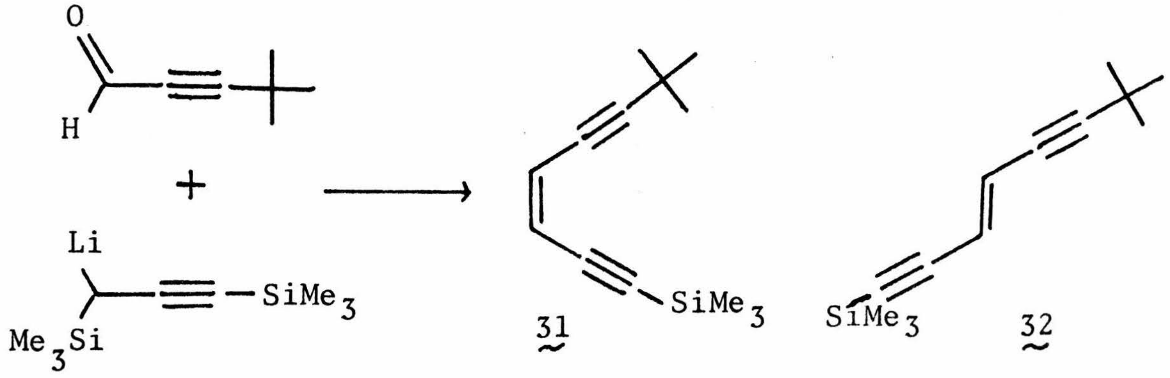
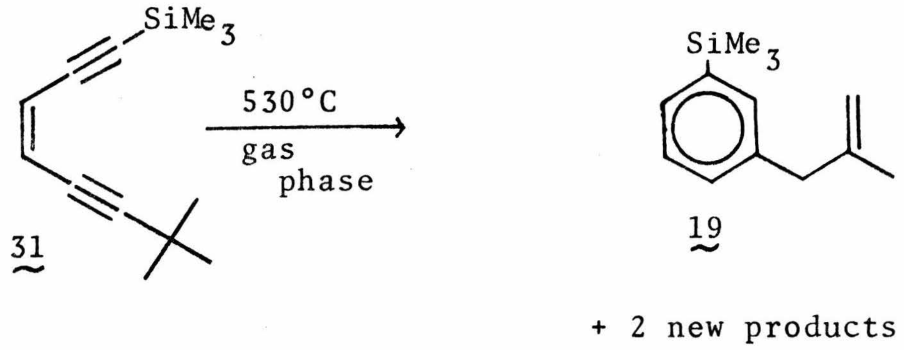


Figure 23

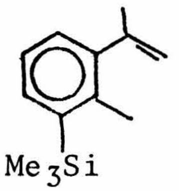


The appearance of 19 and the absence of any *ortho*-methallyltrimethylsilyl-benzene 22 was surprising, but the nature of the new products was even more unexpected. Both showed isopropenyl-toluene NMR signals as in 29 and 30. Figure 24 summarizes the available data.

Figure 24

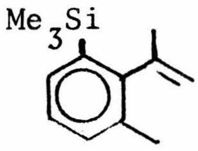
$31 \xrightarrow{530°} 32 + 19 + 29$ *or* 30

+



33

or



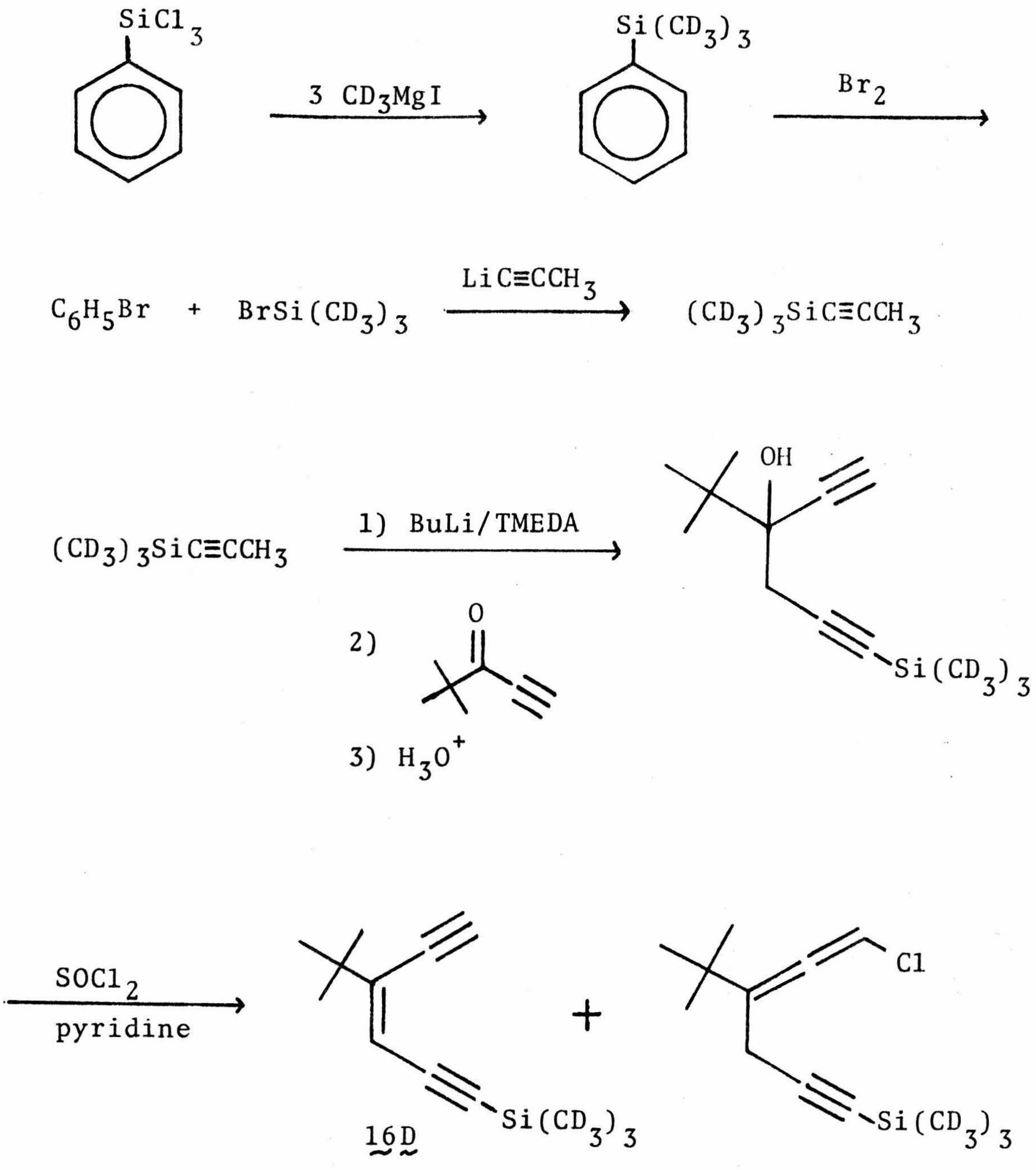
34

As indicated, one of the compounds prepared from 27 and 28 is found in this pyrolysis, as well as a new isomer, 33 and 34 (assigned by NMR and a process of elimination, assuming a 1,2 orientation of the isopropenyl and methyl groups). NMR data are insufficient to distinguish the isomers.

4. Synthesis and pyrolysis of *cis*-1-(trimethylsilyl d-9)-4-*tert*-butyl-3-hexene-1,5-diyne, 16D.

Synthesis of 16D, the silylmethyl d-9 analog of 16, was undertaken to clarify the paths followed by hydrogen atoms in the arrangements. The synthesis followed that of J. Stofko(14) and is outlined in Figure 25.

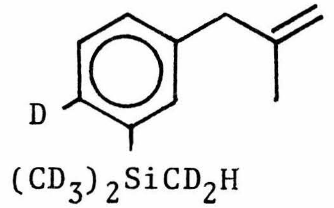
Figure 25



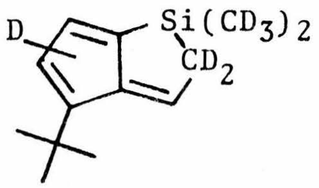
16D

Both 16 and 16D were pyrolyzed in quantities large enough to allow collection of carbon-13 spectral samples. Proton and carbon spectra allow assignments of the products as indicated in Figure 26.

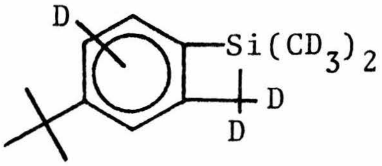
Figure 26



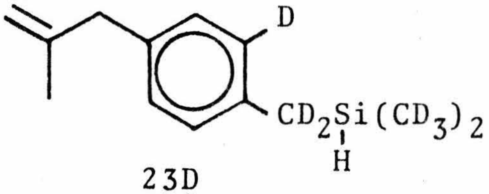
19D



20D



21D



23D

The structure of 19D was assigned by a simple additive chemical shift correlation scheme. The carbon spectra of the following compounds were recorded on the Varian XL-100 spectrometer: benzene, methallylbenzene, 4-deuteromethallylbenzene, trimethylsilylbenzene, and para trimethylsilylmethallylbenzene, 24. In order to exaggerate chemical shift differences between ring carbons, the shift, in Hertz, from the absorption of benzene in deuterochloroform was computed, using the center peak of the deuterochloroform triplet as the internal standard. For example, from the carbon spectrum of benzene in deuterochloroform:

offset, C_6H_6 (Hz)	3464.6
offset, $CDCl_3$ (Hz)	2173.7
shift, C_6H_6 from $CDCl_3$ (Hz)	1290.9

From the spectrum of trimethylsilylbenzene:

offset, C_1*	3766.2
offset, $CDCl_3$	2171.2
shift, C_1 from $CDCl_3$	1595.0
shift, C_6H_6 from $CDCl_3$	1290.9
shift, C_1 from C_6H_6	304.1

Continuing similarly, the following tables are derived:

$Me_3SiC_6H_5$	Shift (Hz from C_6H_6)
C_1	304.1
C_2	125.1
C_3	-13.5
C_4	11.6

$CH_2=C(CH_3)CH_2C_6H_5$**

C_1	286.8
C_2	14.3
C_3	-1.4
C_4	-57.0

Assuming simple additivity of shifts, the spectrum of <u>para</u>-trimethylsilyl-methallyl-benzene can be predicted and this prediction checked against observation:

---

*Assignments taken from references 18a,b.

**Assignments made with the aid of the spectrum of (4-deutero)-methallylbenzene.

$\underline{p}$-(Me_3Si)-C_6H_4-$CH_2C(CH_3)=CH_2$ Predicted shifts

C_1 286.8 + 11.6 = 298.4

C_2 14.3 + - 13.5 = 0.8

C_3 -1.4 + 125.1 = 123.7

C_4 -57.0 + 304.1 = 247.1

For comparison, group quaternary carbons C_1 and C_4:

$\underline{p}$-(Me_3Si)-C_6H_4-$CH_2C(CH_3)=CH_2$

	Predicted shifts	Observed shifts
C_1	298.4	302.9 (quaternary)
C_4	247.1	235.4 (quaternary)
C_2	0.8	0.4 (tertiary)
C_3	123.7	126.6 (tertiary)

This confirmation of the utility of the additivity scheme allows the prediction and comparison of the spectrum of meta-trimethylsilyl-methallylbenzene, 19:

$\underline{m}$-(Me_3Si)-C_6H_4-$CH_2C(CH_3)=CH_2$ Predicted shifts

C_1 286.8 + -13.5 = 273.3

C_2 14.3 + 125.1 = 139.4

C_3 -1.4 + 304.1 = 302.7

C_4 -57.0 + 125.1 = 68.1

C_5 -1.4 + -13.5 = -14.9

C_6 14.3 + 11.6 = 25.9

Again, group quaternary carbons C_1 and C_3 for comparison:

_m_-$(Me_3Si)-C_6H_4-CH_2C(CH_3)=CH_2$

	Predicted shifts	Observed shifts
C_1	273.3	264.4 (quaternary)
C_3	302.7	302.2 (quaternary)
C_2	139.4	140.8 (tertiary)
C_4	68.1	68.9 (tertiary)
C_5	-14.9	-15.9 (tertiary)
C_6	25.9	26.8 (tertiary)

In confirmation of the above assignments of C_1 and C_3, upon pyrolysis of deuterated starting material, **16D**, spectra of **19D** resulted which showed greatly reduced intensity for the absorption assigned as the silicon substituted ring carbon, C_3. This was also observed for silicon substituted carbon in (trimethylsilyl d-9)benzene and 1-(trimethylsilyl d-9)propyne.

The spectrum of **19D** showed that the absorption assigned above as C_4 was so greatly reduced in intensity as to be missing. This was in contradiction to expectations, which called for a symmetrical intermediate and scrambling of the deuterium between C_2 and C_4 (see Discussion, below).

The spectra of **23** and **23D** established the _para_ geometry. Only four types of aromatic carbons were observed in the 45.3 MHz carbon-13 spectra, and the AA'BB' pattern was apparent in the 180 MHz proton spectrum of 23. Also apparent in the 180 MHz spectrum of 23 was the nine line pattern due to the silane proton, split with a coupling constant of ca. 4 Hz by all eight neighboring protons. In the carbon spectrum of 23D deuterium was observed only in the position ortho to the silyl containing group.

Very unfortunately, pure samples of the products assigned as 20, 20D, 21 and 21D were not obtained. Proton NMR of 21D was consistent with the structure in Figure 26, but the carbon spectrum was unsatisfactory and did now allow assignment of the position of the ring deuterium. Proton spectra of 20 and 20D were unsatisfactory and carbon spectra not attempted.

5. Control Pyrolyses

a. Para-methallyl-trimethylsilyl-benzene, 24, absent from the pyrolysis, might have been expected to be a major product. Pyrolysis of 24 had shown it to be stable to the reaction conditions;(14) a repeat of this control and a co-pyrolysis of 24 with 17 demonstrated that 24 was not being consumed in some manner in the pyrolysis.

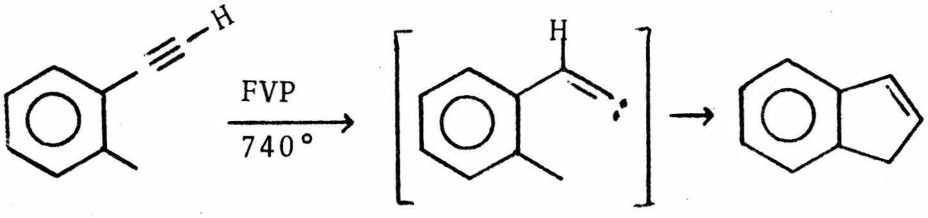
b. Some alkyl and aryl acetylenes have been shown to undergo retro vinylene-acetylene rearrangements,(17) as evidenced by carbon scrambling and carbene derived products (Figure 27).

To test the possibility that silyl groups were undergoing a similar rearrangement and leading to products in the pyrolyses of 16, 17, and 31, two easily available trimethyl-

Figure 27

$$\text{Ad-C}\equiv{}^{14}\text{CH} \xrightarrow[780^\circ]{\text{FVP}} \text{Ad-}{}^{14}\text{C}\equiv\text{C-H} + \text{Ad-C}\equiv{}^{14}\text{CH}$$

Ad = 1-adamantyl ca. 25% ca. 75%



silyl acetylenes were pyrolyzed under the reaction conditions, **35** and **36** (Figure 28). Both compounds were unchanged under the reaction conditions.

Figure 28

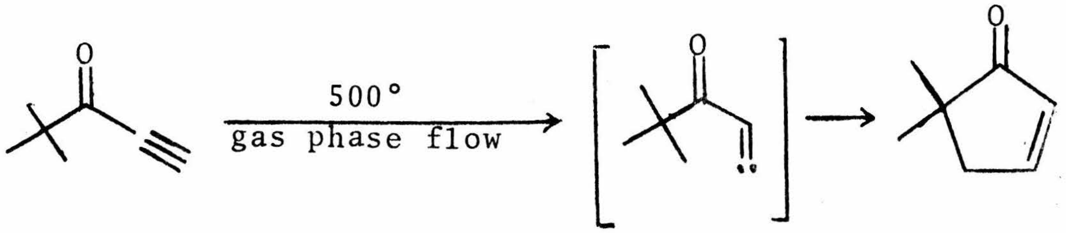
$$\text{Me}_3\text{SiC}\equiv\text{C-(CH}_2)_3\text{CH}_3 \xrightarrow[\text{gas phase flow}]{500^\circ} \text{no reaction}$$

$$\text{Me}_3\text{SiC}\equiv\text{C-CH}_2\text{-SiMe}_3 \xrightarrow[\text{gas phase flow}]{500^\circ} \text{no reaction}$$

c. Pyrolysis of *tert*-butyl ethynyl ketone, **37**, under similar conditions led to partial conversion to the expected product from carbene insertion into a *tert*-butyl methyl group (Figure 29).

d. A repeat pyrolysis of the monosubstituted *tert*-butyl hexene-diyne **13**, with an improved trap system, yielded no major products at all in confirmation of earlier work.(12,14)

Figure 29



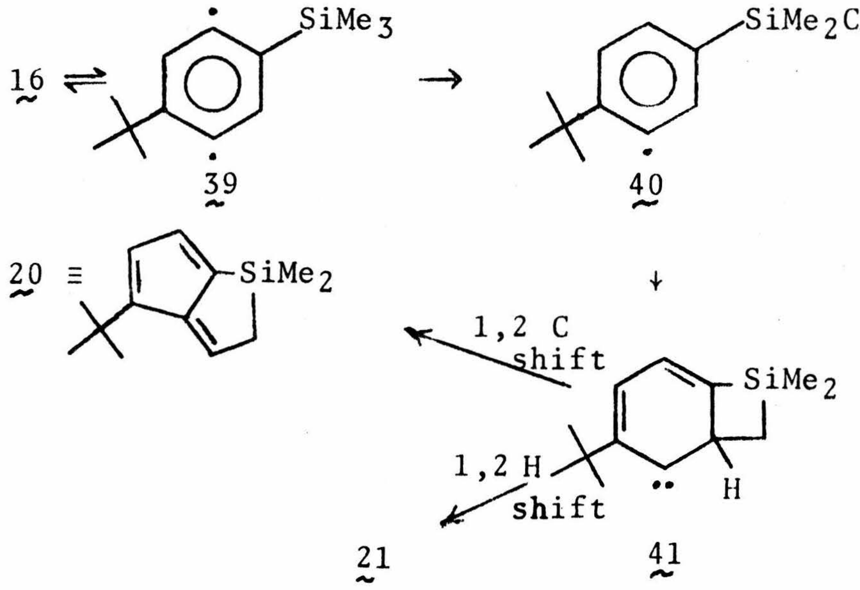
e. Solution pyrolyses of 16 and 17 were undertaken to investigate the possibility of doing trapping studies on the 1,4-dehydrobenzene intermediate. The maximum attainable temperature was ca. 300°C, and a variety of solvents were screened. Briefly, mesitylene gave highest yields of simple trapping, up to 15% yield of para-trimethylsilyl-tert-butylbenzene, 38, and of the saturated hydrocarbons screened (cyclohexane, undecane, and 2,6,10,14-tetramethylpentadecane [pristane]), undecane seemed most promising, giving two products besides the simple trapping product 38. In all cases, 17 was observed to rearrange rapidly to 16 at 300°C, and products were derived from 16. In any event, low yields of products and extensive decomposition make kinetic studies impractical, although large scale pyrolyses to isolate the unknown products from undecane should be possible.

C. Discussion

In the pyrolyses of 16 and 17 the observation of products 20 and 21 can be rationalized by an initial hydrogen abstraction from a silyl methyl of the 2-trimethylsilyl-5-

tert-butyl-1,4-dehydrobenzene intermediate 39, followed by closure of the resultant radical onto the ring (Figure 30).

Figure 30

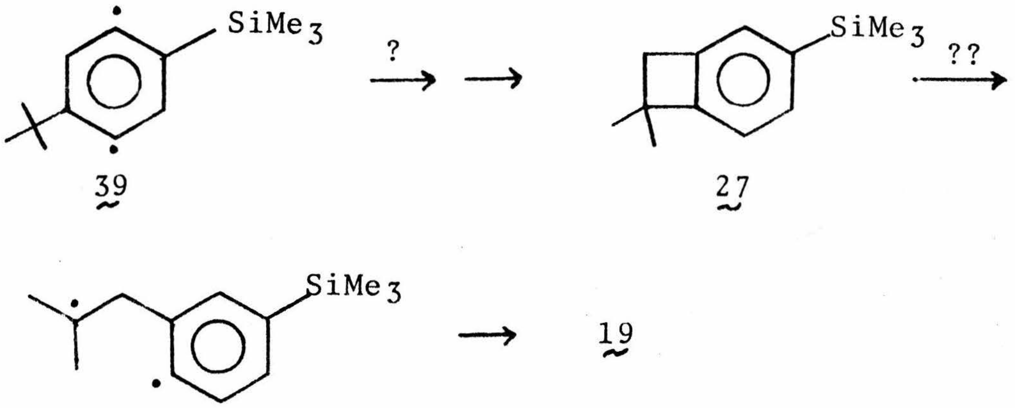


The resonance stablized carbene intermediate 41 would be expected to aromatize to give 21. Less expected but still plausible at 450°C would be the ring expansion to yield a non-aromatic fulvene product such as the product tentatively assigned as 20.

Observation of the 1-sila-benzocyclobutene 21 raised the mechanistic question of whether the product 19, with a rearranged and shifted alkyl substituent and an intact trimethylsilyl group, was derived from a similar process (Figure 31).

The results of pyrolyses of 27 and 28 to give only products derived from ortho-xylylene intermediates eliminated 27 from the reaction path, suggesting that diradical intermedi-

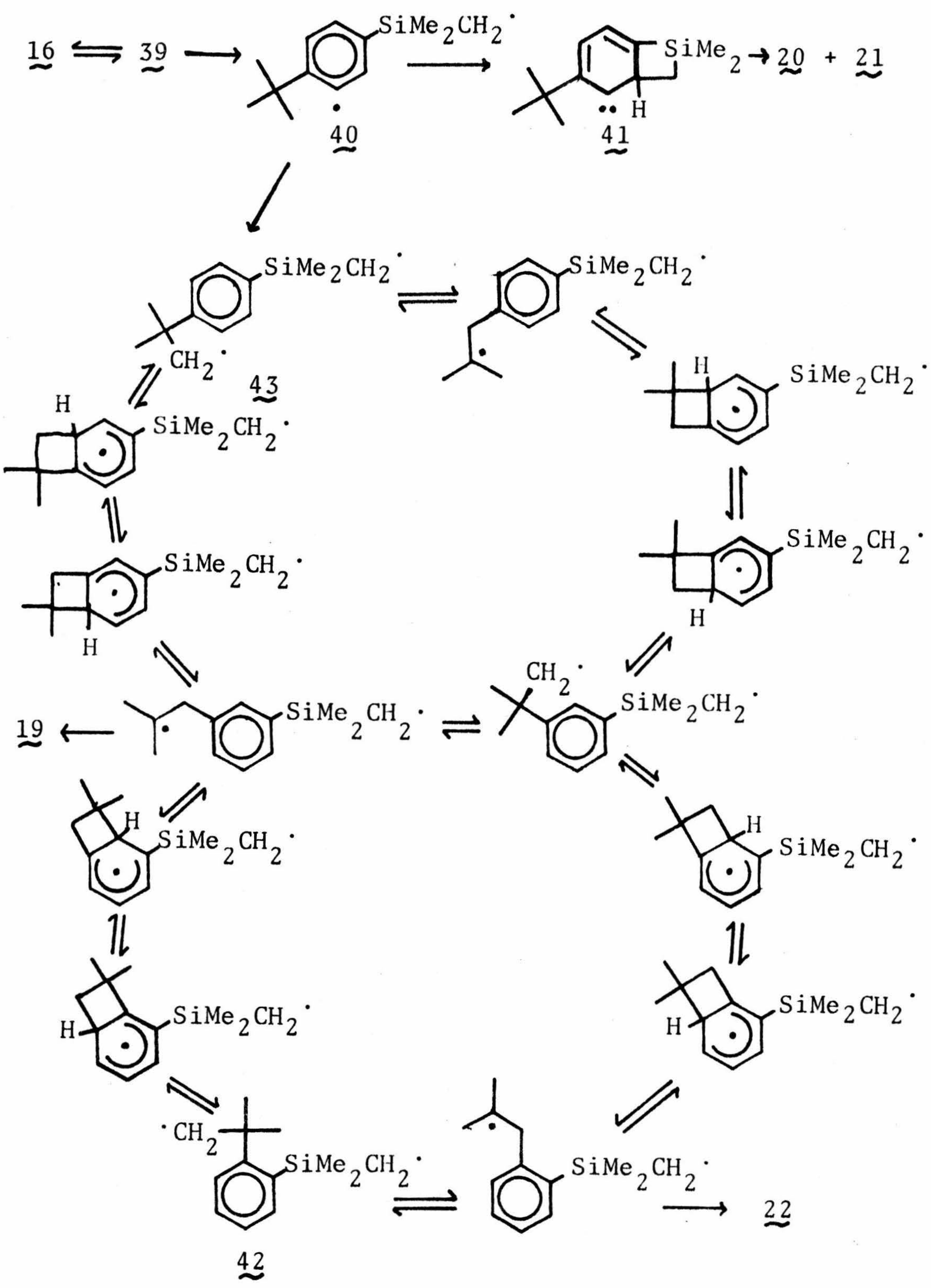
Figure 31



ates must be responsible for production of 19 and 23. At the time, the fourth major product was misassigned to be the *ortho* isomer of 19, 22. A diradical "ring walk" mechanism involving movement of the alkyl substituent was proposed(22) (Figure 32), and as a test of this mechanism the isomeric hexene-diyne 31 was prepared and pyrolyzed. The expectation was that the intermediate diradical 42 would be formed and give rise to 19 and 22. The pyrolysis to yield exclusively 19 and two products with the trimethylsilyl-isopropenyltoluene structure (see Methods and Results) was inconsistent with the proposed ring walk but was also another clear indication that rearrangement around the ring was possible. Solution pyrolyses that might have trapped intermediate diradicals showed that 16 and 17, like their predecessors, were unsuited for solution phase studies.

The difficulty in rationalizing the observation of *meta*

Figure 32

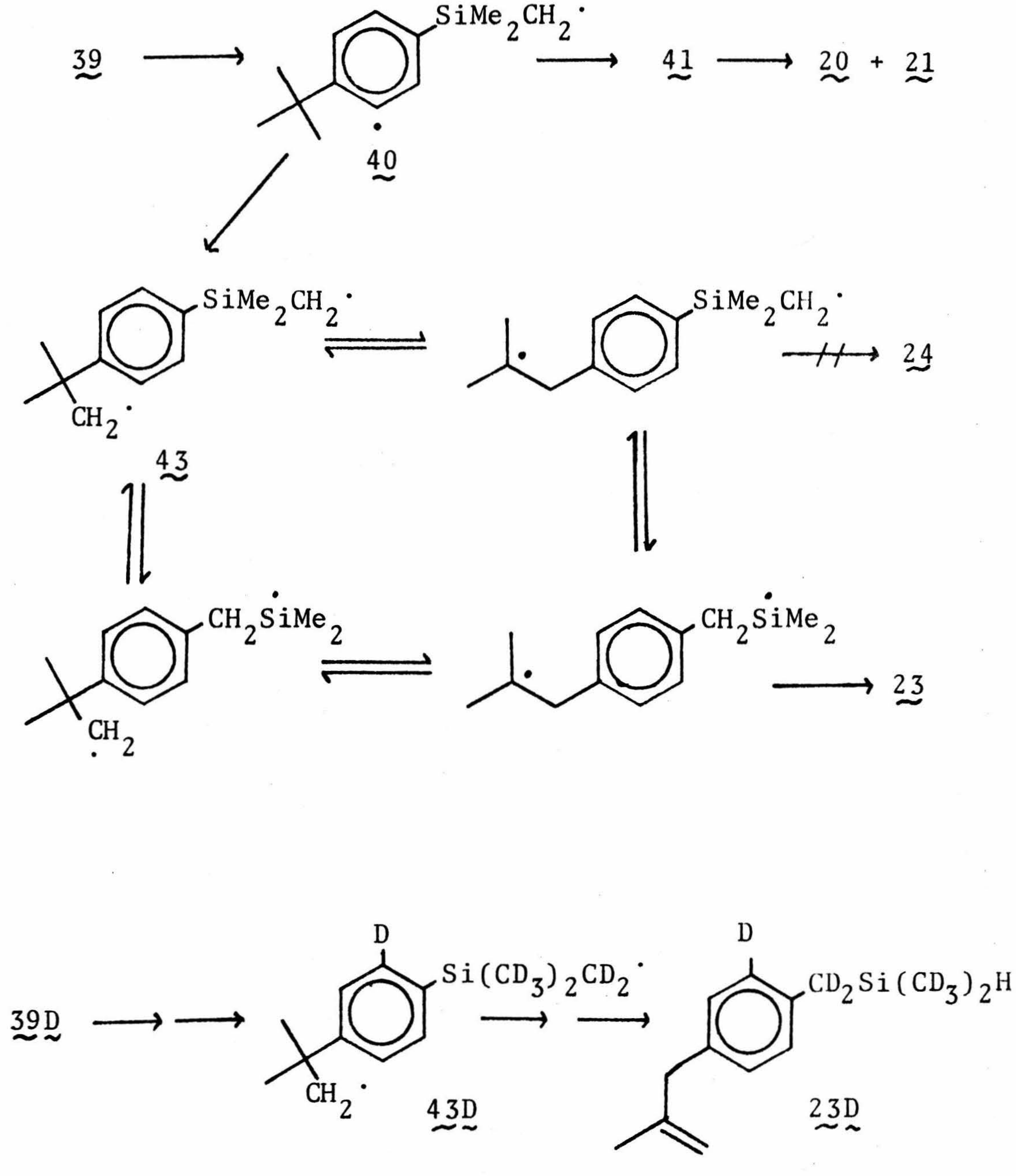

16
39
SiMe2CH2·
40
SiMe2
20 + 21
H
41
SiMe2CH2·
CH2·
43
H
19
SiMe2CH2·
CH2·
42
22

isomer 19 from pyrolyses expected to give rise to intermediates with the substituents in the ortho and para configurations led us to attempt a deuterium labelling study. Synthesis of a trimethylsilyl d-9 analog of either 16 or 17 would undoubtedly yield information about the course of the reaction. At the crudest level it was expected to demonstrate whether or not the trimethylsilyl group in 19D was an intact d-9 group, thereby limiting the number of possible mechanisms.

Synthesis and pyrolysis of 16 and 16D and preparative gas chromatographic separation of all four major products yielded spectral samples which disproved the tentative assignment of the longest retention time product as 22. That product has now been unambiguously reassigned by proton and carbon nuclear magnetic resonance spectra to be 23. The proposed mechanism for formation of 23 is depicted in Figure 33, and is consistent with the structure of the product obtained from deuterated starting material, 23D.

The mechanism pictured indicates that of the two diradicals which might transfer a hydrogen atom across the ring to give rise to methallyl substituted aromatic products, only the one giving rise to 23 does so to any appreciable extent. The silicon centered radical is less stable than the carbon centered radical, and precedent exists for the aryl shift from carbon to silicon at temperatures similar to those employed here.(19) Hydrogen atom transfer to give 23 and not 24 must reflect some special property of the silicon centered radical such as the geometry, or the spatial extent of the silicon

Figure 33


39
SiMe2CH2·
41
20 + 21
40
SiMe2CH2·
CH2·
43
SiMe2CH2·
24
CH2SiMe2
CH2
CH2SiMe2
23
39D
D
Si(CD3)2CD2·
CH2·
43D
D
CD2Si(CD3)2H
23D

p orbital. The silicon-hydrogen bond strength, 90 kcal/mole in trimethylsilane,(20) is lower than the carbon-hydrogen bond strength, 99 kcal/mole in tetramethylsilane.(21)

The observation of specific deuteration of one ring carbon in 19D eliminated the intermediacy of a symmetrical diradical such as 43D. Any "ring walk" mechanism for 43D to yield the meta substituted diradical precursor to 19D would proceed equally in both directions to give 19 partially deuterated at both the 2 and 4 positions on the ring, instead of the specific deuteration at the 4 position which was observed. Obtaining the observed pattern from intermediates such as 40 or 41, which have not become symmetric would give specific deuteration, but it is difficult to write a reasonable mechanism. Several pieces of evidence point to a novel silicon shift to give metabenzyne intermediates instead (Figure 34).

The observation of a small deuterium isotope effect enhancing the amount of 19D relative to the other products is consistent with a partitioning before the abstraction has taken place. Pyrolysis of the 1,6 disubstituted hexene-diyne 31 to yield 19 can also be explained most easily by a silicon shift (Figure 35). The observation of isopropenyltoluene products from 31 is consistent with the proposed change in mechanism, and they can be rationalized by variations on the mechanism pictured.

The alternative tert-butyl group shift (Figure 36) gives from 39 the same intermediate 44 as silicon shift. Pyrolysis of 31 to generate 2-trimethylsilyl-3-tert-butyl-1,4-dehydro-

Figure 34

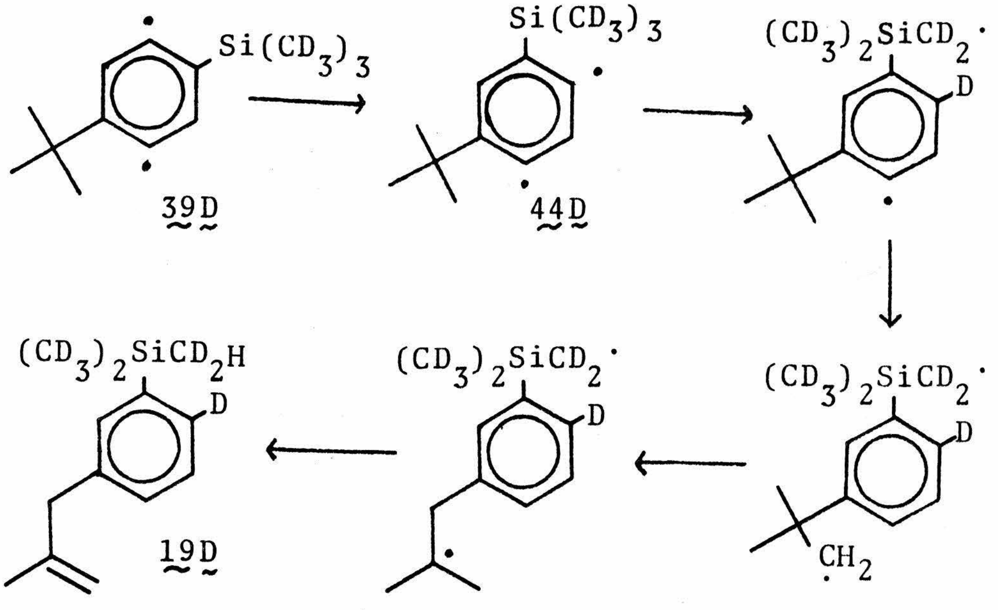


Figure 35

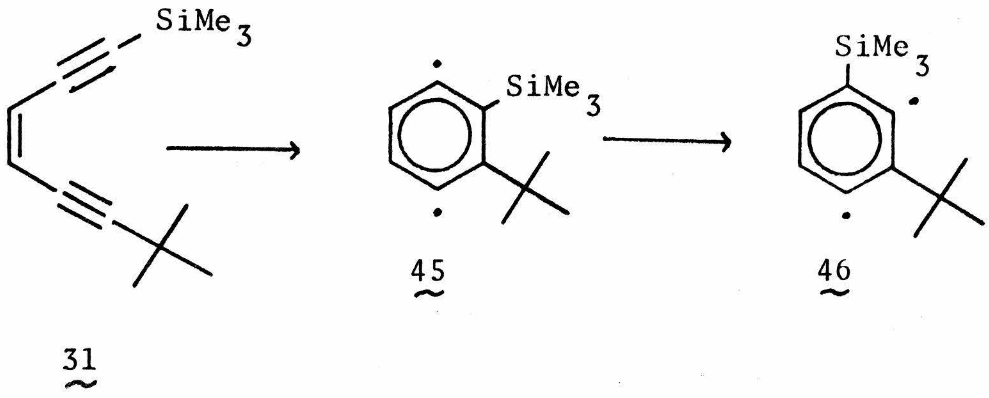


Figure 35 cont. over

Figure 35 cont.

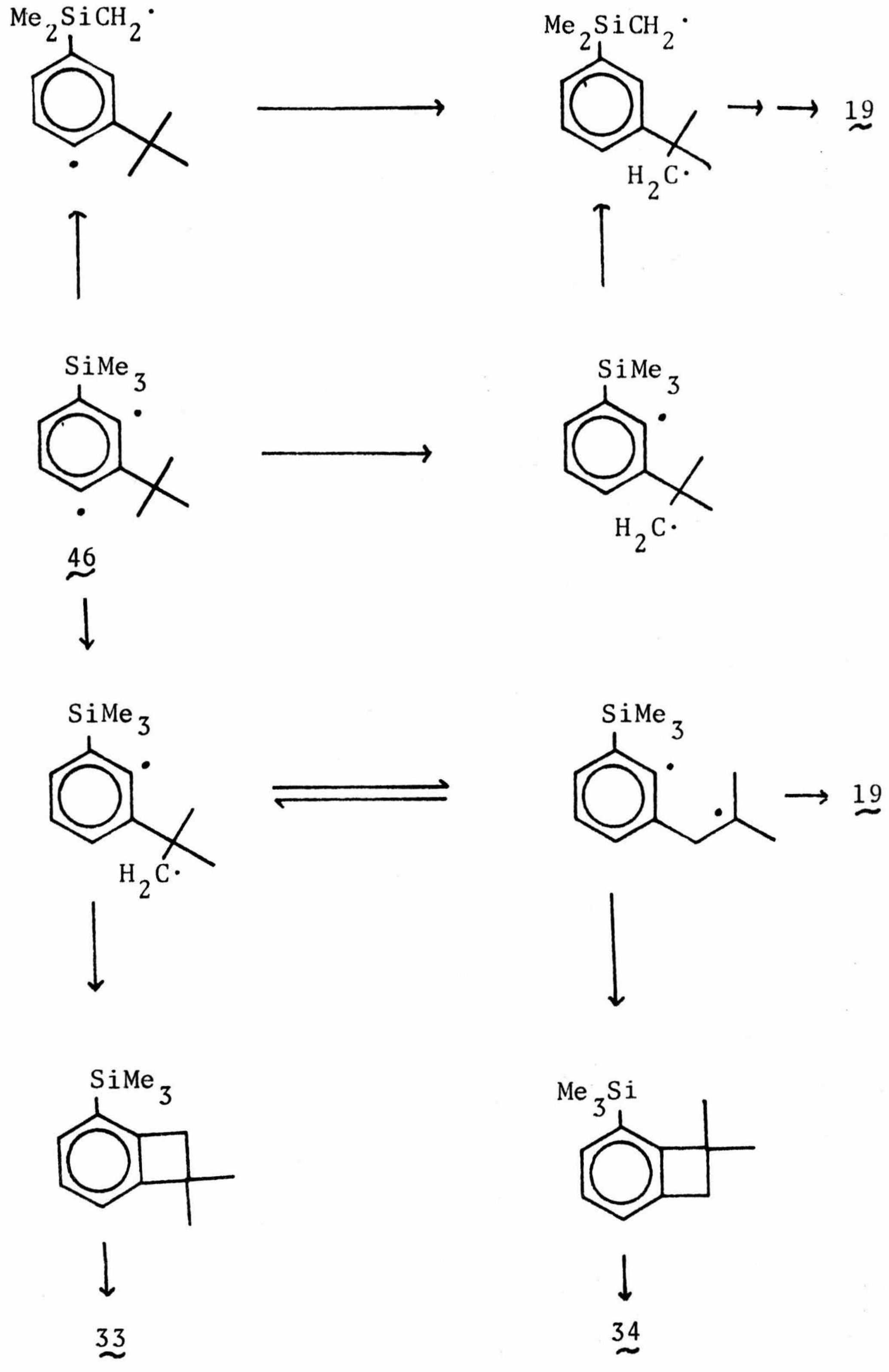
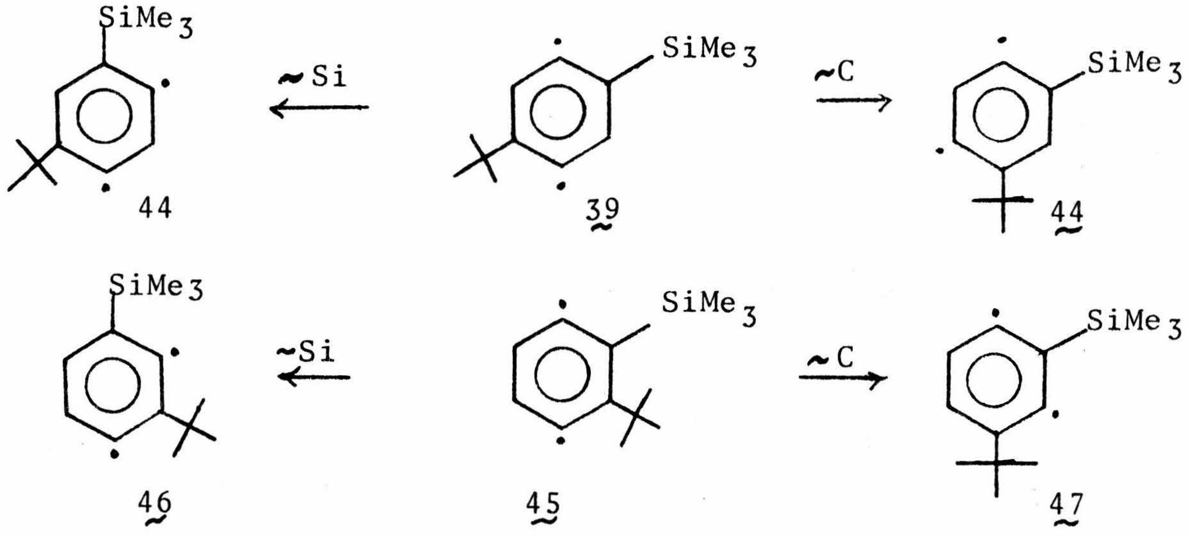


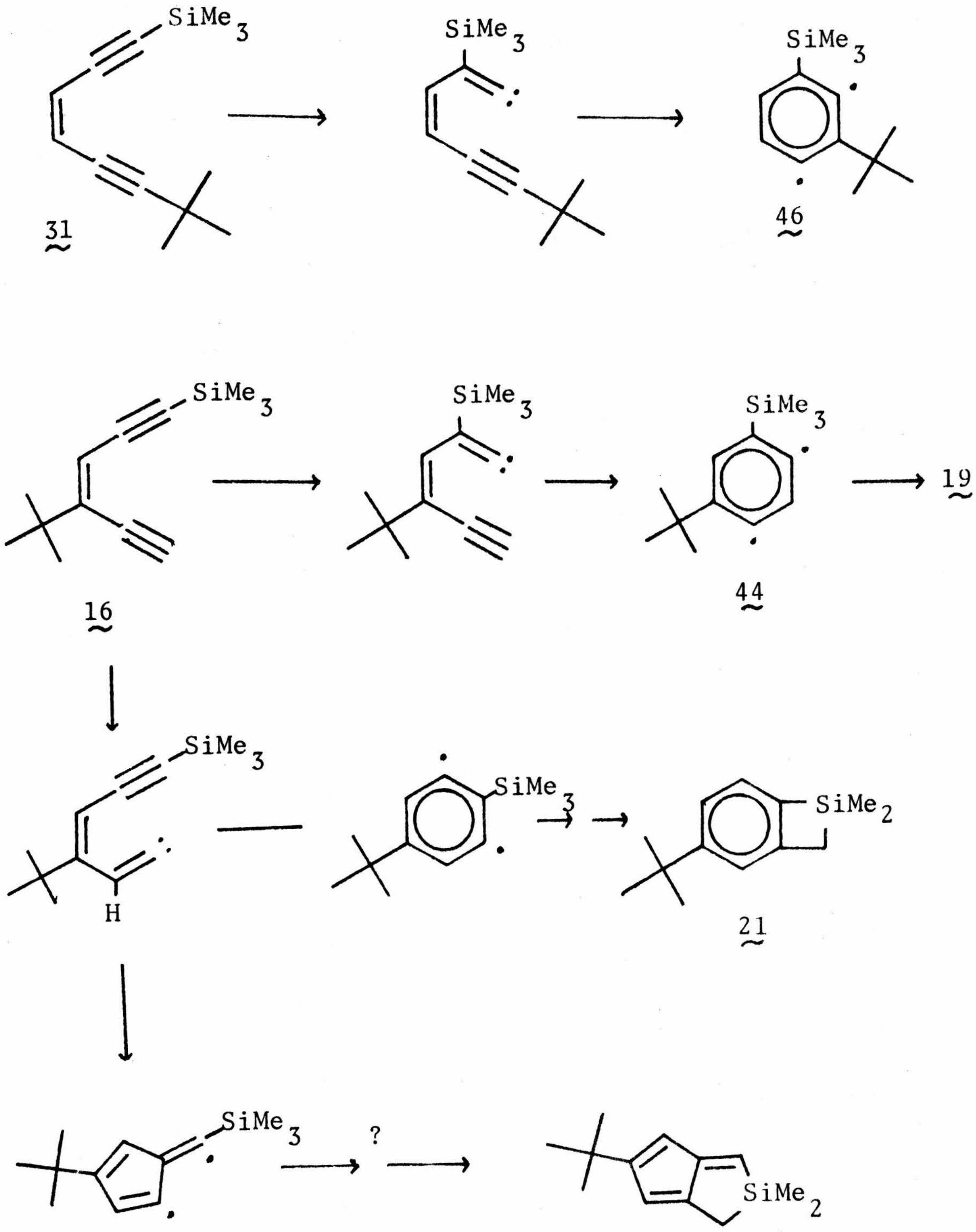
Figure 36



benzene, 45, gives products more consistent with silicon shift. Abstraction from the silyl methyls of 47 is expected to be rapid and would give mainly *tert*-butyl-benzosilacyclobutenes analogous to 21. Pyrolysis of 31 yielded no products with intact *tert*-butyl groups, pointing away from 47.

The observation of the expected carbene derived product, 5,5-dimethyl-2-cyclopentenone, from the pyrolysis of *tert*-butyl ethynyl ketone, 37, raised the possibility that hexene-diynes were activated enough to undergo the retro-carbene re-arrangement. Recent work$^{(13)}$ has also suggested that the re-arrangement of 1-hexyne and 1-trimethylsilyl-1-hexyne occur at temperatures of 550°C and 650°C, respectively. As shown in Figure 37, given the assumption that the rearrangement can occur on either trimethylsilyl substituted or unsubstituted triple bonds in hexene-diynes, this "shift and close" mechanism

Figure 37


SiMe3
31
SiMe3
SiMe3
46
SiMe3
16
SiMe3
SiMe3
44
19
SiMe3
H
SiMe3
SiMe2
21
SiMe3
?
SiMe2

is fully consistent with the observed products 19 and 21, and is in fact indistinguishable from the "close and shift" mechanism involving 1,4-dehydrobenzene intermediates.

Figure 37 shows an alternative assignment for the product now assigned as 20. Derivation of 23 from this mechanism does not seem to be reasonable.

The simplest mechanisms for the formation of the observed product arrays seem to be those involving 1,4-dehydrobenzene intermediates 39 and 45. Observation of rearrangement of 17 to 16 and solution trapping at 300°C to yield 38 strongly implicate 39 as an intermediate at that temperature, implying that closure occurs before shift. A change in mechanism may easily occur upon raising the temperature from 300°C to 450°C, but difficulty in explaining the *para* substituted product 23 from carbene intermediates points away from that mechanism. Other difficulties exist, such as the lack of any products derived from retro-carbene shift on the *trans*-hexene-diynes (Figure 38).

The assumption of a 1,2 trimethylsilyl shift to give 1,3-dehydrobenzenes from 1,4-dehydrobenzenes is not the only possible mechanism that accounts for the observed products and deuterium isotope effect. The alternative mechanism involves a competition between abstraction from silyl and *tert*-butyl methyls (Figure 39).

Results of pyrolysis of 31 are more difficult to rationalize by a similar mechanism (Figure 40).

Figure 38

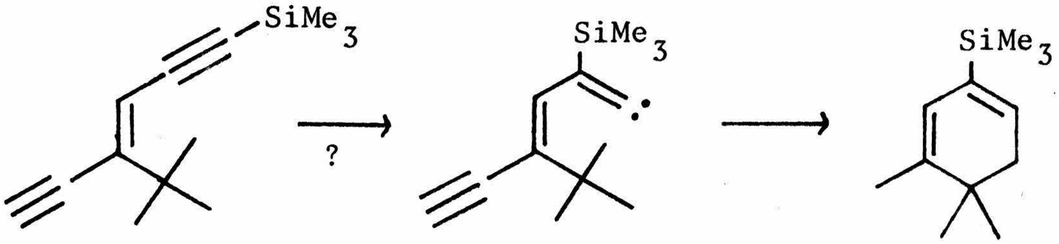


Figure 39

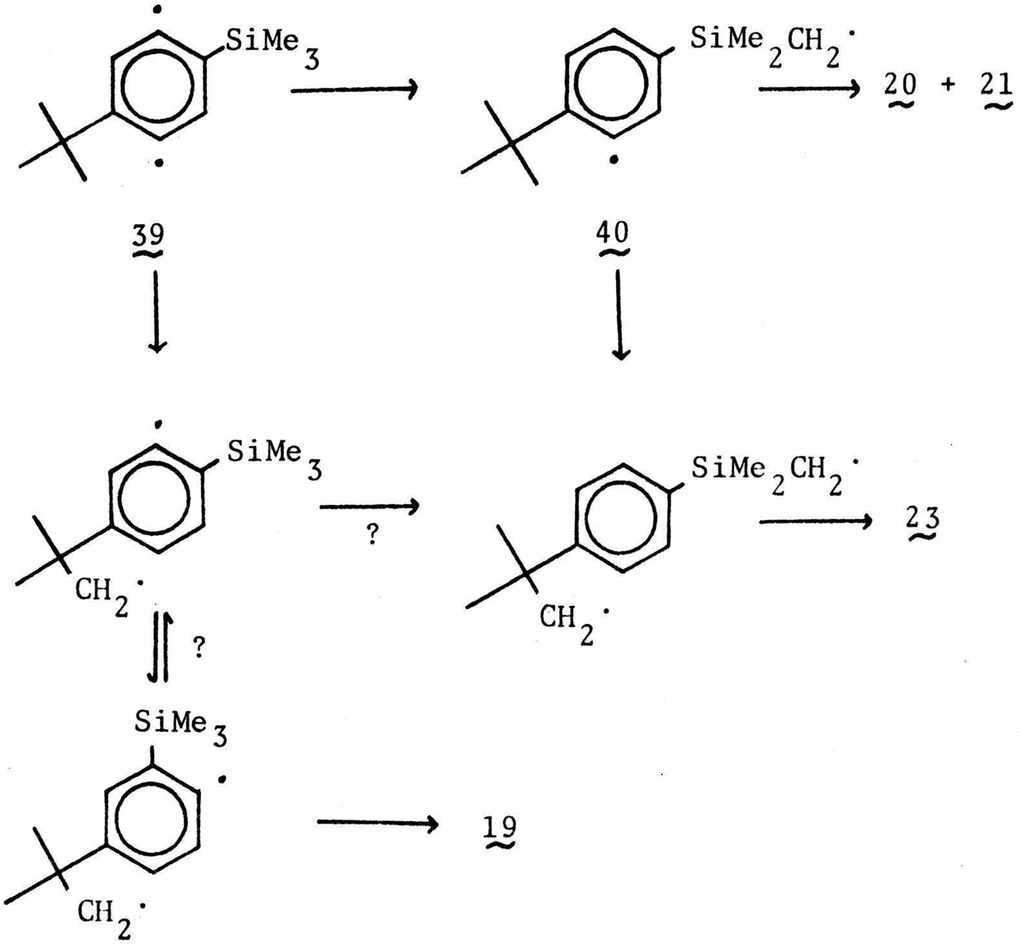
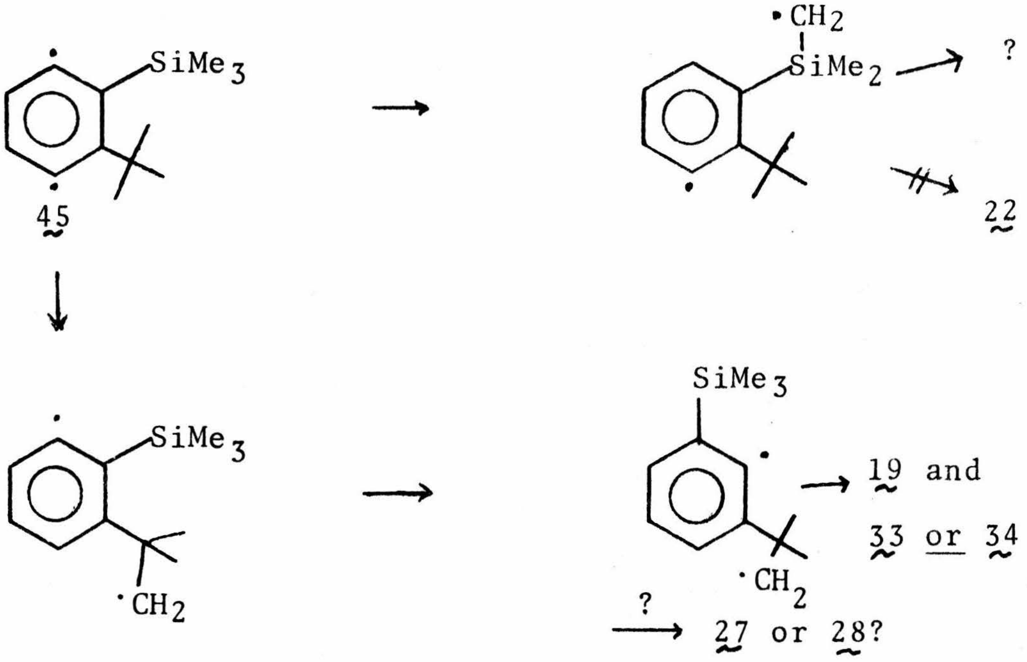


Figure 40

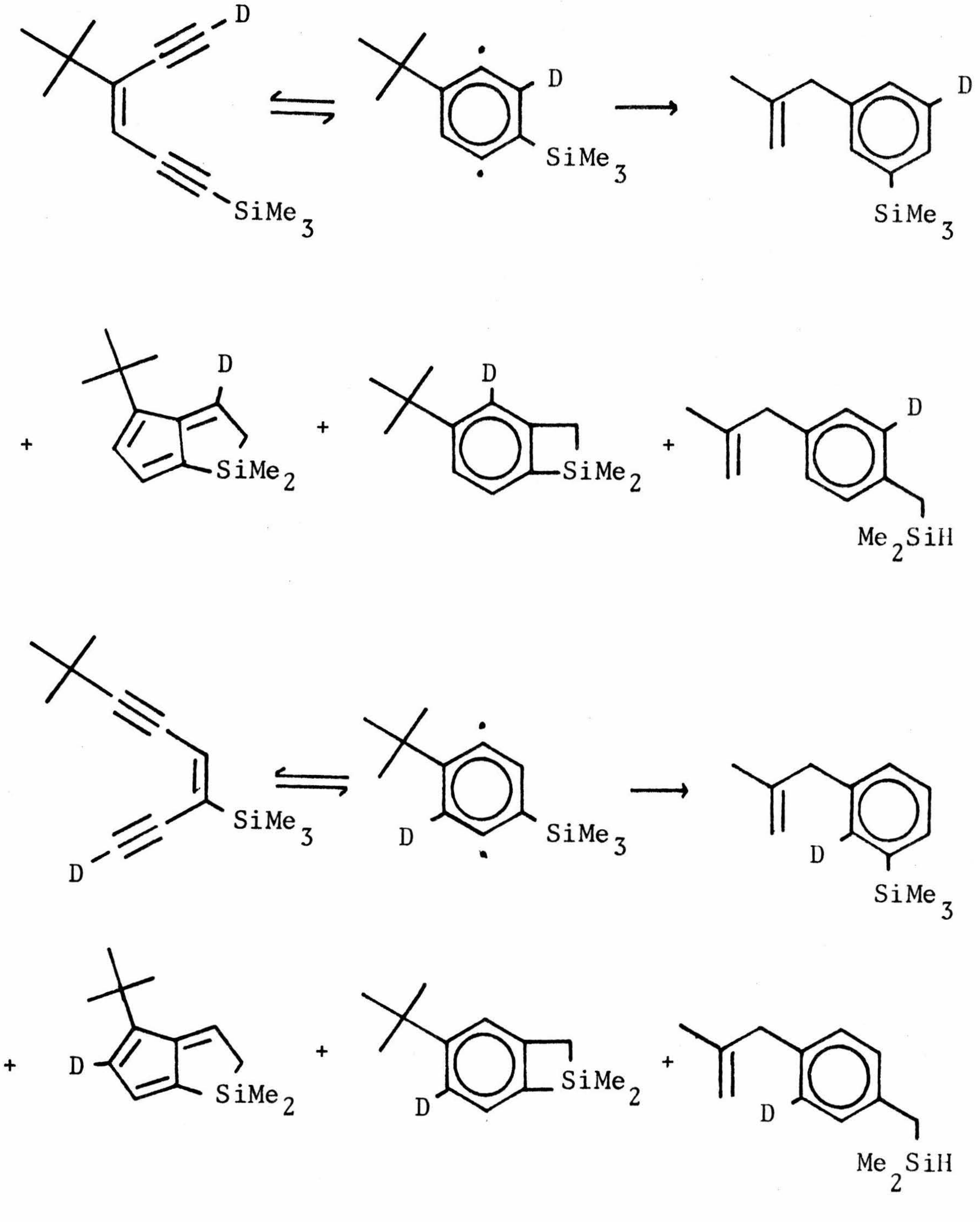


The simplest single assumption remains that in 1,4-dehydrobenzene intermediates, trimethylsilyl groups can undergo 1,2 shifts to give 1,3-dehydrobenzenes. The shift requires temperatures in excess of 400°C and is normally competitive with hydrogen atom abstraction from the silyl methyls. In the case of the sterically crowded intermediate 45, the shift predominates due to strain relief.(23)

Several simple experimental tests of this hypothesis suggest themselves. A single deuterium label specifically placed on the ring should indicate whether or not the trimethylsilyl group does indeed shift, by whatever mechanism. Two such labellings are possible (Figure 41).

If it is possible to collect adequate samples of the

Figure 41


D
SiMe3
D
SiMe3
D
SiMe3
+
D
SiMe2
+
D
SiMe2
+
D
Me2SiH
D
SiMe3
D
SiMe3
D
SiMe3
+
D
SiMe2
+
D
SiMe2
+
D
Me2SiH

product **21** from the pyrolysis of samples of **16** and **17**, a double label would distinguish between two different mechanisms. The retro-carbene mechanism predicts a symmetrical intermediate in the formation of this compound (see Figure 37). The labelling and predictions are outlined in Figure 42.

D. Experimental

1. General

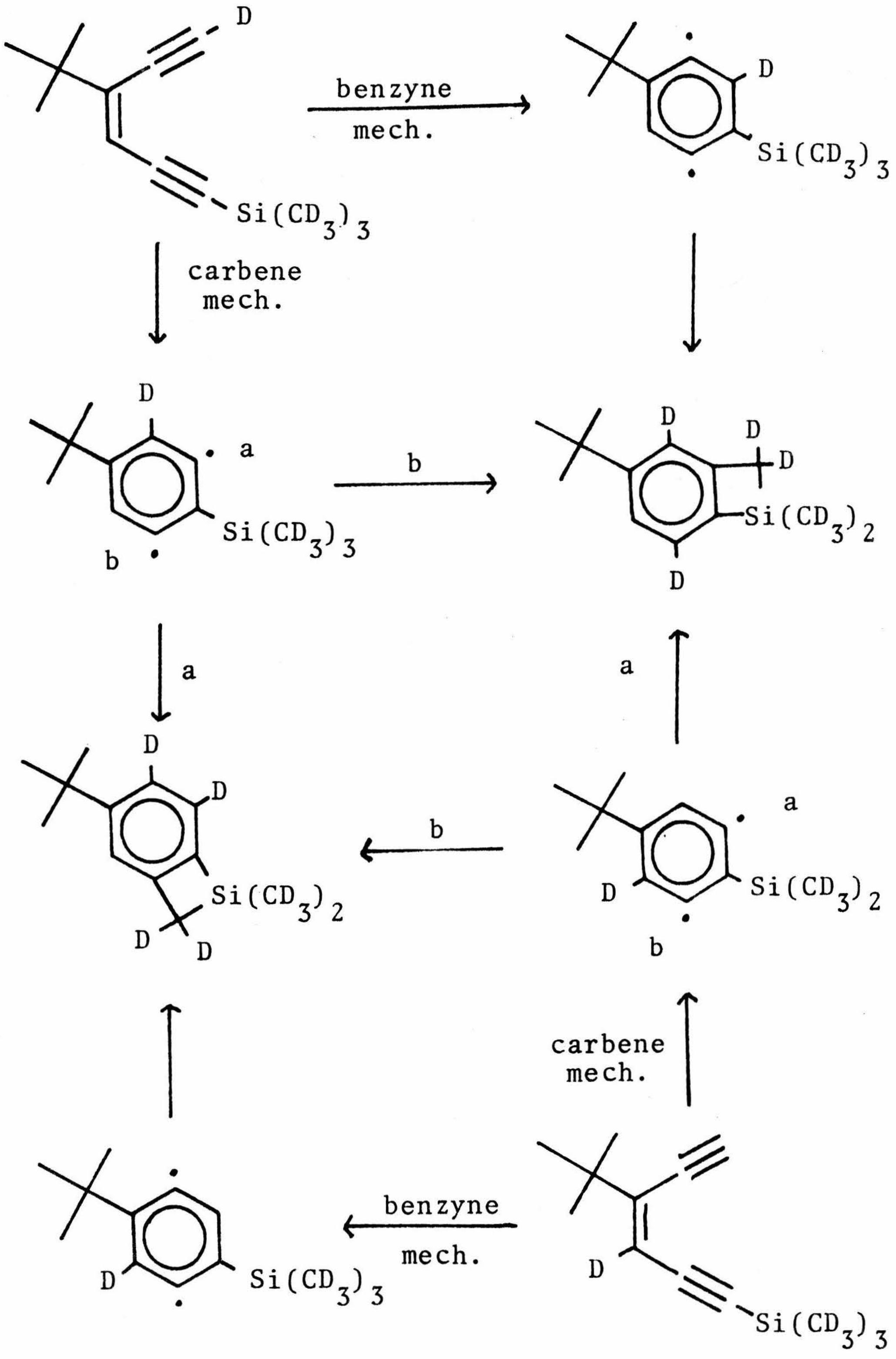
Nuclear magnetic resonance spectra were recorded on a number of machines. Proton spectra were recorded on the Caltech Varian A-60 and EM-390 spectrometers and on the Berkeley 180 MHz Fourier transform instrument. Carbon spectra were recorded on the Caltech Varian XL-100 (operating frequency 25.2 MHz) and the Berkeley instrument (operating frequency 45.3 MHz). In the text the instrument used is indicated by the operating frequency and nucleus. Carbon-13 spectra were recorded in deuterochloroform and the approximate shift from tetramethylsilane computed by assuming that the center peak of the deuterochloroform triplet was at $\delta = 77.000$.

Infrared spectra were recorded on the Beckman IR 4210 in Professor D. A. Evans' labs. Mass spectra and analyses were obtained by the Caltech analytical lab unless otherwise noted.

Two gas chromatographs were used, a Varian 90-P for routine and preparative work, and a Perkin-Elmer 3920B with flame ionization detector coupled to a Spectra-Physics Autolab System 1 electronic integrator.

Columns for gas chromatography were as follows:

Figure 42


D
benzyne
mech.
Si(CD3)3
carbene
mech.
a
b
D
Si(CD3)2
Si(CD3)3
a
b
a
b
carbene
mech.
benzyne
mech.

Column 1. 20' 1/4" glass, packed with 8% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 250°C, Varian 90-P.

Column 2. 10' 1/4" glass, packed with 10% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 250°C, Varian 90-P.

Column 3. 20' 5/16" glass, packed with 10% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 250°C, Varian 90-P.

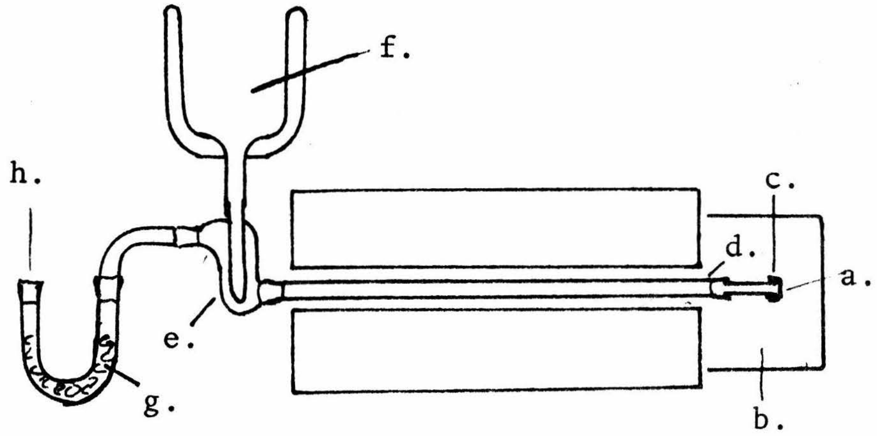
Column 4. 20' 1/4" glass, packed with 10% SE-30 on Chromosorb W-AW-DMCS, 60/80 mesh, conditioned to 250°C, Perkin-Elmer 3920B.

Column 5. 100' open tubular capillary column, packed with SF-96, Perkin-Elmer 3920B.

Pyrolysis apparatus used was similar to that used previously. Flash vacuum pyrolysis apparatus is picture in Figure 14. Flow pyrolyses were performed at atmospheric pressure with nitrogen as the carrier gas in the slightly modified apparatus picture in Figure 43.

Dry diethyl ether was either Mallinkrodt absolute ether from a freshly opened can, or ether from an open can which was stirred over sodium-benzophenone to form the red dianion of benzophenone, vacuum transferred, and transferred to tightly capped bottles in an inert atmosphere (Vacuum/Atmospheres Co. Dri-Lab glove box). MCB tetrahydrofuran was predried over sodium-benzophenone to form the purple dianion of benzophenone. Vacuum transfer and storage in tightly capped bottles under

Figure 43



a. N_2 inlet

b. insulated inlet chamber

c. septum capped inlet with syringe needle N_2 inlet

d. 35 cm quartz tube

e. LN_2 coldfinger

f. vacuum insulated LN_2 source flask

g. glass helices packed U-trap in LN_2

h. to drying tube and flowmeter

inert atmosphere was the same as for ether. Pentane was stirred over portions of conc. H_2SO_4 until the acid layer remained colorless after 12 hours, stirred over two portions of acidic $KMnO_4$, and carefully distilled from P_2O_5.

Butyllithium was purchased from Alfa as ca. 2-2.6 M solutions in hexane. TMEDA (Aldrich 99%) was refluxed over and distilled from calcium hydride. Trimethylsilyl chloride (Aldrich) was stirred over calcium hydride, filtered, and stored at 4°C over fresh calcium hydride.

2. Specific Preparations

4,4-Dimethyl-2-pentynal

4,4-Dimethyl-2-pentynal was prepared from 3,3-dimethyl-1-butyne (Chem. Samp. Co.) by the method of F. Bohlmann et al.(24) Yield from 10 gm, 4.8 gm, 19%.

1-Trimethylsilylpropyne

1-Trimethylsilylpropyne was prepared from propynyllithium (Foote) and trimethylsilyl chloride by the method of Corey et al.(16) Yield from 42 gm propynyllithium, 48.8 gm, 50%, bp 97-99°C (reported(16) 98-100°C).

1,3-*Bis*(trimethylsilyl)propyne

In a 500 ml septum-capped flask, 17.43 gm 1-trimethylsilylpropyne in 250 ml dry diethyl ether under argon at -20°C was treated with 70 ml 2.25 M butyllithium in hexane and 17.43 gm TMEDA. After three hours stirring at -20°C, the mixture was cooled to -78°C and 150 ml dry tetrahydrofuran added by cannula followed by 16.74 gm trimethylsilyl chloride. After one hour at -78°C, the reaction was allowed to warm to ca. 0°C and poured into 500 ml cold 3% hydrochloric acid and washed quickly The ether layer was washed with 500 ml water and dried overnight at 4°C over anhydrous sodium sulfate. Removal of solvent on a rotary evaporator and vacuum distillation yielded 15.80 gm, 55%, bp 67-69°/19 mm Hg. NMR (60 MHz, δ, $CDCl_3$): 0.1 (br. s, 18H), 1.5 (s, 2H).

1,1,3-*Tris*(trimethylsilyl)allene, and 1,3,3-*tris*(trimethylsilyl)propyne

To 250 ml dry diethyl ether, 14.53 gm 1,3-*bis*(trimethylsilyl)propyne, and 8.80 gm TMEDA under argon at -20°C was added 33 ml 2.29 M butyllithium by syringe. After stirring for four hours at -20°C, the solution was cooled to -78°C, 150 ml dry tetrahydrofuran added by cannula and 8.43 gm trimethylsilyl chloride added by syringe. After one hour at -78°C, the reaction was allowed to warm to ca. 0°C, and poured into 500 ml cold 3% hydrochloric acid, washed quickly, and the ether layer washed with 500 ml water. After overnight drying over anhydrous sodium sulfate at 4°C, solvent was removed and vacuum distillation yielded 11.4 gm, 56%, of a fraction boiling 89-90°C/8 mm Hg. NMR showed it to be a three to one mixture of *tris*(trimethylsilyl)allene and *tris*(trimethylsilyl)propyne.(25) NMR (60 MHz, δ, $CDCl_3$): 0.12 (s) and 0.17 (s), total 27H, 1.11 (s, ca. 0.25H), 3.93 (s, ca. 0.75H).

1,3-*Bis*(trimethylsilyl)-6-*tert*-butyl-3-hexene-1,5-diyne (*cis* and *trans*, **25** and **26**)

1.34 gm (5 mmol) of the above mixture of *tris*(trimethylsilyl)allene and *tris*(trimethylsilyl)propyne in 10 ml dry diethyl ether at -20°C under argon with magnetic stirring was treated with 2.2 ml 2.29 M butyllithium and 0.58 gm TMEDA. After five hours stirring at 20°C, 5 ml dry tetrahydrofuran and 0.55 gm 4,4-dimethyl-2-pentynal in 5 ml dry tetrahydrofuran were added sequentially. After an additional 30 min at

-20°C, the cold bath was removed and the solution allowed to warm to above 0°C, then worked up by rapid washing with 10 ml cold saturated aqueous ammonium chloride, 10 ml water, and overnight drying over anhydrous sodium sulfate at 4°C. Removal of solvent under vacuum left a brown oil which was passed through 3 gm silica gel (pentane eluent), yielding after removal of solvent a yellowish oil. Crude yield 1.1 gm impure product, estimated ca. 70%. Preparative gas chromatography (column 2, 160°C, 100 ml/min) yielded spectral samples. MS, both products, m/e 276. Fraction 1, (*cis*, **25**), NMR (60 MHz, δ, CCl_4): 0.08 (s) and 0.12 (s), total 18H, 1.21 (s, 9H), 5.85 (s, 1H), Fraction 2, (*trans*, **26**), NMR (60 MHz, δ, CCl_4): 0.09 (s) and 0.18 (s), total 18H, 1.19 (s, 9H), 6.41 (s, 1H).

cis-1-*Tert*-butyl-4-trimethylsilyl-3-hexene-1,5-diyne, **17**

The mixture of *cis* and *trans*-*bis*(trimethylsilyl)-*tert*-butyl-hexene-diynes **25** and **26** were desilated after the method of Corey et al.(16) A solution of the crude **25** and **26** in 12 ml absolute ethanol was added over 10 minutes to a solution of 2.6 gm silver nitrate in 6 ml water and 18 ml ethanol. After stirring an additional 15 minutes, 4.9 gm potassium cyanide in 10 ml water was added and the reaction stirred for 2 hours, poured into 50 ml water and 50 ml pentane, shaken quickly, the aqueous layer separated and washed once with 25 ml pentane. Combined organics were washed once with 25 ml water and dried over anhydrous sodium sulfate. Removal of solvent yielded 0.65 gm (90%) of a mixture of *cis* and *trans* hexene-diynes **17** and its isomer, **18**. Preparative gas chromatography (column 2, 160°C, 100 ml/min) yielded spectral samples. Fraction 1 (*cis*, **17**), precise mass, calculated for $^{12}C_{13}{}^{1}H_{20}{}^{28}Si$ 204.133, observed 204.130. Satisfactory analysis was not obtained. NMR (60 MHz, δ, CCl_4): 0.18 (s, 9H), 1.28 (s, 9H), 3.41 (s, 1H), 6.00 (s, 1H). Fraction 2, (*trans*, **18**), precise mass, calculated $^{12}C_{13}{}^{1}H_{20}{}^{28}Si$, 204.133, observed 204.132. Satisfactory analysis was not obtained. NMR (60 MHz, δ, CCl_4): 0.27 (s, 9H), 1.28 (s, 9H), 3.18 (s, 1H), 6.52 (s, 1H).

3-Bromo-3-methyl-1-butyne

Distilled 2-methyl-3-butyn-2-ol, 70 gm (Aldrich) was placed in a 500 ml three-necked flask equipped with overhead stirring, argon inlet, ice bath, and dropping funnel charged with 182.4 gm distilled phosphorous tribromide. The phosphorous tribromide was added dropwise over six hours, the reaction stirred one additional hour and allowed to stand for 30 minutes. The organic layer was decanted, and the inorganic layer was washed twice by stirring with 50 ml pentane. Combined organics were degassed and vacuum transferred to give ca. 200 ml clear, yellow liquid. Pentane was removed by distillation through a 6" Vigreaux column, and the remaining liquid distilled under argon from anhydrous potassium carbonate without a distillation column. Yield 120.1 gm (40%), bp 90-97°C.

3,3-Dimethyl-1,5-hexadiyne

After F. Sondheimer et al.(26) and W. D. Huntsman et al.(27)

In a 500 ml three-necked flask fitted with argon inlet, condenser, stopper, addition funnel, and magnetic stirring, 12.2 gm magnesium turnings, ca. 0.2 gm mercuric chloride and 250 ml dry diethyl ether were stirred for 15 minutes. 73.51 gm 3-bromo-3-methyl-1-butyne was then added slowly, at a rate to keep the reaction at gentle reflux. When the addition was complete, heat was applied to maintain reflux and 59.5 gm propargyl bromide (Aldrich, distilled) in 150 ml dry ether was added over 8 hours. The reaction was refluxed an additional 12 hours, then poured into 500 ml cold 4% HCl and washed quickly. The organic layer was washed successively with two 200 ml portions saturated aqueous ammonium chloride, two 200 ml portions of water, and dried over anhydrous sodium sulfate. Ether was distilled off from fresh anhydrous sodium sulfate, and propargyl bromide carefully distilled off through a four-inch glass helices packed column. Product was then distilled over, yield 6 gm (9%), bp 100-102°C.

4-Trimethylsilyl-1,1-dimethylbenzocyclobutene, 27, and 5-trimethylsilyl-1,1-dimethylbenzocyclobutene, 28

A solution of 150 ml octane and ca. 20 μl cyclopentadienyl cobalt dicarbonyl was brought to reflux under argon in a 250 ml flask fitted with a reflux condenser, and a solution of 2.12 gm 3,3-dimethyl-1,5-hexadiyne, 1.96 gm ethynyltrimethylsilane, and ca. 100 μl cyclopentadienyl cobalt dicarbonyl in 50 ml octane was added through the reflux condenser over 50 hours. After four additional hours reflux, the solution was cooled and poured through 5 gm silica gel, washed through with 50 ml pentane. Solvent was removed on a rotary evaporator to a volume of ca. 10 ml and the mixture was chromatographed on 50 gm silica gel, pentane as eluent. NMR spectroscopy showed only the absorptions expected for **27** and **28**. Preparative gas chromatography (column 1, 150°C, 70 ml/min) separated the two isomers for NMR and mass spectroscopy. Fraction 1, NMR (90 MHz, δ, CCl_4): 0.15 (s, 9H), 1.32 (s, 6H), 2.78 (s, 2H), 6.82 (d, 1H, J=7 Hz), 6.90 (s, 1H), 7.11 (d, 1H, J=7 Hz). Fraction 2, NMR (90 MHz, δ, CCl_4): 0.16 (s, 9H), 1.32 (s, 6H), 2.83 (s, 2H), 6.80 (d, 1H, J=7 Hz), 7.02 (s, 1H), 7.13 (d, 1H, J=7 Hz). Precise mass, calculated for $^{12}C_{13}{}^{1}H_{20}{}^{28}Si$ 204.133, obtained (both isomers) 204.130.

cis and trans 1-Trimethylsilyl-6-tert-butyl-3-hexene-1,5-diynes, **31** and **32**

5.44 gm 1,3-Bis(trimethylsilyl)propyne in 100 ml dry diethyl ether, magnetically stirred under argon at -20°C, was treated with 12.3 ml 2.4 M butyllithium and 3.42 gm TMEDA. After stirring for three hours 3.25 gm 4,4-dimethyl-2-pentynal in 50 ml dry tetrahydrofuran was added. After an additional hour at -20°C, the reaction was poured into 100 ml cold 3% aqueous hydrochloric acid and washed rapidly. The organic layer was then washed twice with 100 ml portions of water and dried overnight at 4°C over anhydrous sodium sulfate. Removal of solvent yielded ca. 5 gm very nearly neat oil, estimated yield 75%. Preparative gas chromatography (column 3, 180°C, 80 ml/min) separated the two isomers.

Fraction 1 (cis, 31), MS: M^+, m/e 204, NMR (90 MHz, δ, CCl_4): 0.21 (s, 9H), 1.28 (s, 9H), 5.56 (d, J=10 Hz) and 5.71 (d, J=10 Hz), total 2H. Fraction 2 (trans, 32), MS: M^+, m/e 204. NMR (90 MHz, δ, CCl_4): 0.20 (s, 9H), 1.26 (s, 9H), 5.68 (d, J=18 Hz), 5.89 (d, J=18 Hz), total 2H.

(Trimethylsilyl d-9)benzene(28)

A 25 gm ampoule of d-3 iodomethane (99+ atom % D, Aldrich) was opened and transferred to a 50 ml flask, rinsed in with 20 ml dry diethyl ether. This solution was degassed and vacuum transferred to another 50 ml flask, then transferred to the dropping funnel of a standard apparatus for performing Grignard reactions, a flame-dried 500 ml flask fitted with a reflux condenser and argon inlet, stopper, teflon stopcocked* dropping funnel and magnetic stirring. An additional 80 ml dry diethyl ether was added to the dropping funnel, and this solution was added slowly to 4.20 gm magnesium turnings in 10 ml dry diethyl ether. During the addition a cool (15-20°C) water bath was maintained around the flask. One hour after the addition was complete, 12.2 gm phenyltrichlorosilane was placed in the dropping funnel, rinsed in with ca. 10 ml dry diethyl

---

*Teflon stopcock is important for the addition of phenyltrichlorosilane, see below, which freezes ground glass.

ether. The water bath was maintained at 5-10°C by the addition of ice, approximately 80% of the silane was added dropwise. 100 ml dry diethyl ether was added to the remaining silane and mixed, and the diluted solution was added dropwise over several hours. Thirty minutes after the addition was complete, 10 ml absolute methanol was added dropwise, and the reaction poured into 20 ml cold 3% hydrochloric acid. A semisolid inorganic layer in the reaction flask can be dissolved with a small amount of water. Organics were washed with the hydrochloric acid, 250 ml saturated aqueous sodium bicarbonate, and 250 ml saturated aqueous sodium sulfate. The aqueous layers were washed twice in the same sequence with 50 ml portions of diethyl ether, and combined organics dried overnight at 4°C over anhydrous sodium sulfate. The ether solution was poured through ca. 5 gm silica gel, and solvent removed by distillation through a Vigreaux column. Distillation at reduced pressure yielded 7.51 gm, 81%, (trimethylsilyl d-9)-benzene, bp 85-86°C/49 mm Hg. Mass and NMR spectra showed high deuterium incorporation. IR (neat, cm^{-1}): 2215 (C-D, s, sh), 1110 (s, sh), 995 (s, sh), 710 (s, br). Compare $(CH_3)_3SiC_6H_5$, IR (neat, cm^{-1}): 2950 (C-H, s, sh), 1245 (s), 1108 (s), 840 (s, br), 722 (s).

1-(Trimethylsilyl d-9)propyne(28)

5.01 gm (d-9 trimethylsilyl)benzene was stirred under argon in a septum capped 25 ml flask at 0°C, and 1.57 ml bromine was added by syringe over 30 minutes. After an additional 30 minutes, 0.2 ml cyclohexene was added. The reaction mixture was transferred by double tipped needle into a stirred suspension of 2.2 gm propynyllithium (Alfa, 97%), in 30 ml dry tetrahydrofuran under argon in an ice bath. This reaction was stirred at 0°C for 15 minutes and allowed to warm to room temperature, poured into 50 ml cold 4% hydrochloric acid, washed quickly, and separated. The organic layer was washed with 50 ml saturated aqueous sodium bicarbonate, 50 ml saturated aqueous sodium sulfate, and all aqueous layers washed sequentially with two 20 ml portions of water to remove a majority of the tetrahydrofuran, and dried overnight at 4°C over anhydrous sodium sulfate. Pentane was removed by distillation and the residue distilled under 50 mm Hg dynamic vacuum into a -78°C receiver. Yield (estimated by NMR of the pentane, THF, and product mixture of the -78°C trap) 1.7 gm, 44%. Preparative gas chromatography (column 3, 90°C, 80 ml/min) of the still pot and -196°C trap condensate recovered small amounts of pure material for spectral samples. NMR and mass spectroscopy showed high deuterium incorporation, the infrared spectrum was consistent with the 1-(d-9 trimethylsilyl)-propyne structure. MS, m/e (%): 121 (17), 103 (100). NMR (90 MHz, δ, $CDCl_3$): 1.80 (s, 3H), 0.1 (m, 0.087H, corresponding to 99.0 atom % deuterium incorporation). IR (neat, cm^{-1}): 2920 (m, sh), 2218 (m, sh), 2180 (s, sh), 1440 (w, br), 1025 (m, br), 1000 (m, br), 720 (m, br). Compare $(CH_3)_3SiC\equiv CCH_3$, IR (neat, cm^{-1}): 2960 (s), 2920 (m, sh), 2900 (m, sh), 2180 (s, sh), 1420 (w, br), 1250 (s, sh), 1030 (s), 845 (s, br), 760 (s), 695 (m), 640 (s, sh).

3-*Tert*-butyl-6-(trimethylsilyl d-9)-1,5-hexadiyne-3-ol, **50D**

1-(Trimethylsilyl d-9)propyne, 1.70 gm, in 250 ml dry tetrahydrofuran, stirred under argon at -20°C, was treated with 5.39 ml 2.6 M butyllithium and 1.63 gm (2.12 ml) TMEDA. After 1.5 hour stirring at -20°C, 1.60 gm *tert*-butyl ethynyl ketone was added as rapidly as possible and the solution was allowed to warm to ca. 0°C. The reaction was then poured into 200 ml cold 3% hydrochloric acid, washed, and separated. The organic layer was washed with 200 ml saturated aqueous sodium bicarbonate, 200 ml saturated aqueous sodium chloride, and dried over anhydrous sodium sulfate. Aqueous layers were washed sequentially with two 30 ml portions of pentane and combined organics dried overnight at 4°C over anhydrous sodium sulfate. Solvent was removed on a rotary evaporator and the product chromatographed on 20 gm silica gel using 20% diethyl ether in pentane as eluent. Yield of crude liquid 2.88 gm, ca. 90%, used directly to form the hexene-diyne.

cis-1-(Trimethylsilyl d-9)-4-*tert*-butyl-3-hexene-1,5-diyne, **16D**

2.88 gm **50D** in 13 ml dry diethyl ether was stirred under inert atmosphere at 0°C and treated with a solution of 1.7 gm thionyl chloride and 3 ml pyridine in 6 ml dry diethyl ether, added dropwise over 15 minutes. After an additional 30 minutes at 0°C, the mixture was poured into 50 ml cold 3% hydrochloric acid, washed and separated. The organic layer was washed with 20 ml saturated aqueous sodium bicarbonate, 20 ml saturated aqueous sodium chloride, and dried overnight at 4°C over anhydrous sodium sulfate.

After solvent was removed on a rotary evaporator the product mixture was passed through ca. 1 gm silica gel (10 ml pentane eluent) and recrystallized at low temperature from methanol by the following procedure: The neat oil was dissolved in two volumes absolute methanol and cooled to -78°C in a dry ice/isopropanol cold bath until crystallization was complete. The liquid layer was pipetted off at -78°C under nitrogen flow, and the process was repeated. A final recrystallization from one volume of pentane at -50°C, overnight in an ultra low temperature freezer, yielded large, pure crystals of **16D**. More could be recovered from supernatant liquid by column chromatography on silica gel using pentane as eluent. Separation is poor, but fractions enriched in **16D** come off before the chloroallene impurity. Recrystallization as above, or gas chromatography (column 2, 140°C, 80 ml/min) on impure samples gives pure spectral samples. MS, M^+ m/e 213, NMR (90 MHz, δ, $CDCl_3$): 1.20 (s, 9H), 3.40 (s, 1H), 5.70 (s, 1H). IR (neat, cm^{-1}): 3310 (m, br), 3290 (m, br), 2965 (s), 2220 (m), 2165 (m), 2140 (m), 1480 (m), 1460 (m), 1365 (m), 1250 (m, sh), 1110 (m), 1045 (s), 1000 (s, sh), 840 (m), 760 (s, sh) 725 (s, br). Compare **16**, IR (neat, cm^{-1}): 3310 (m, br), 3290 (m, br), 2965 (s), 2170 (m), 2140 (m), 1475 (m), 1365 (m), 1250 (s, sh), 1110 (m, sh), 1045 (s), 845 (s, br), 760 (s), 645 (m), 630 (m), 610 (m).

4-Bromo-methallylbenzene(14)

In a three liter three-necked flask outfitted with reflux condenser with argon inlet, one liter addition funnel, magnetic stirring, and a stopper, 24.3 gm magnesium turnings, 100 ml dry diethyl ether, and 20 gm 1,4-dibromobenzene were stirred until reaction had begun. A solution of 216 gm 1,4-dibromobenzene in 400 ml dry diethyl ether and 250 and dry benzene was added over ca. three hours at a rate to maintain gentle reflux. After addition was completed, the reaction was refluxed for five hours before 100 gm methallyl chloride in 200 ml dry diethyl ether was added. The reaction was stirred for 16 hours while warm, very gently refluxing, cooled and poured into one liter cold 4% hydrochloric acid, washed and separated. The organic layer was washed with one liter water and dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the oil was distilled at ca. 90°/0.5 mm Hg to separate intractable residue. Every possible combination of reduction, coupling, and nonreaction was present (GC conditions, column 3, 190°, 80 ml/min). Starting material could be precipitated by cooling to -20°C overnight, and distillation at reduced pressure through an efficient glass helices packed column yielded 86.2 gm, 82%, of the desired product, bp 88-90°C/5 mm Hg, identical to an authentic sample.(14) NMR (60 MHz, δ, CCl_4): 1.62 (br. s, 3H), 3.19 (br. s, 2H), 4.76 (br. m, 2H), 6.97 (d, 2H, J=8 Hz), 7.36 (d, 2H, J=8 Hz).

4-Trimethylsilyl-methallylbenzene, 24(14)

In a one liter three-necked flask outfitted with reflux condenser with argon inlet, 500 ml addition funnel, stopper, and magnetic stirring, 3.7 gm magnesium turnings, 2.7 gm bromoethane, and 100 ml ether were stirred until the reaction had begun, and a solution of 21.62 gm 4-bromo-methallylbenzene and 22.8 gm trimethylsilyl chloride in 300 ml dry diethyl ether was added and the reaction brought to gentle reflux with a heat lamp. After 20 hours reflux the reaction was worked up by washing with 300 ml saturated aqueous ammonium chloride and 300 ml water, drying over anhydrous magnesium sulfate, and removal of solvent on a rotary evaporator. Passage through 5 gm silica gel (petroleum ether eluent) and distillation at reduced pressure yielded a fraction boiling 94-96°C/5 mm Hg, 10.4 gm of a mixture ca. 90% pure by gas chromatography (column 3, 190°C, 80 ml/min), estimated ca. 50% yield. Preparative gas chromatography yielded spectral and pyrolysis samples. NMR was identical to that reported.(14) NMR (90 MHz, δ, $CDCl_3$): 0.18 (s, 9H), 1.51 (s, 3H), 3.11 (s, 2H), 4.54 and 4.61 (overlapping br. m's, 2H total), 6.99 (d, 2H, J=7 Hz), 7.26 (d, 2H, J=7 Hz).

4-Deutero-methallylbenzene

In a 50 ml septum-capped flask under argon, a magnetically stirred solution of 5.0 ml 2.6 M butyllithium and 1.0 ml TMEDA in 25 ml dry diethyl ether was treated with 2.0 ml (1.49 gm) 4-bromomethallylbenzene over 15 minutes, with a cool water bath applied as needed to keep the reaction from refluxing. After an additional 30 minutes, 2.0 ml deuterium oxide was added slowly, and the reaction was poured into 50 ml cold 10% hydrochloric acid, washed, and separated. The organic layer was washed with 50 ml saturated aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. Removal of solvent and distillation at reduced pressure yielded a fraction boiling from 80-82°C/30 mm Hg, center cut ca. 0.3 gm, ca. 50% used for nuclear magnetic resonance spectra. NMR (90 MHz, δ, CDCl$_3$): 1.72 (s, 3H), 3.33 (s, 2H), 4.68 and 4.73 (overlapping br m's, 2H total), 7.24 (br. s, 4H).

3. Pyrolyses

a. Pyrolyses of *cis*-1-trimethylsilyl-4-*tert*-butyl-3-hexene-1,5-diyne, **16**, *cis*-1-*tert*-butyl-4-trimethylsilyl-3-hexene-1,5-diyne, **17**, and *trans*-1-*tert*-butyl-4-trimethylsilyl-3-hexene-1,5-diyne, **18**.

The three isomers **16**, **17** and **18** were pyrolyzed in the flow pyrolysis apparatus in Figure 43 under the following conditions:

Pyrolyzed consecutively, flow rate of carrier gas 30 ml/minute, inlet at room temperature, ca. 10 µl (7 mg) over 2 to 3 hours.

Compound	oven: T_{start}	T_{end} (°C)
16	452	456
17	456	452
16	452	452
18	452	450

Samples were analyzed on a flame ionization gas chromatograph (column 4, 145°C) coupled with an electronic integrator, the results from three injections were averaged to insure reproducibility. The results from the above pyrolyses are presented in the table below. The isomerized hexene-diyne 16 and the four major products 19, 20, 21, and 23 comprised ca. 90% of the pyrolysis mixtures, the remainder was a complex array of at least twelve minor products.

Compound Pyrolyzed	Products (%)				
	16	19	20	21	23
16	31.5	19.0	8.7	25.0	13.2
17	23.8	23.3	7.2	27.2	17.4
16	39.1	18.5	7.0	21.9	14.1
18	40.6	17.5	5.9	20.9	12.7

Converting these data to relative yields of the four products 19, 20, 21 and 23 gives the following table:

Compound Pyrolyzed	Products (Relative %)			
	19	**20**	**21**	**23**
16	28.8	13.2	37.9	20.0
17	31.0	9.5	36.2	23.1
16	30.0	11.4	35.6	22.9
18	30.7	10.4	36.7	22.2

An open tube capillary column packed with SF-96 separated the isomeric hexene-diynes and showed that the compounds **16**, **17**, and **18** were present in the reaction mixtures in constant relative amounts. Expressed as percent of unreacted material, the amounts of **16**, **17**, and **18** were 93%, 1%, and 6% respectively.

b. Pyrolysis of 4-*tert*-butyl-1,1-dimethyl-1-silabenzocyclobutene, **27**, and 5-*tert*-butyl-1,1-dimethyl-1-silabenzocyclobutene, **28**.

Although not assigned as to which was the 4 or 5 isomer, the mixture of **27** and **28** was separated by preparative gas chromatography (column 3, 160°C, 80 ml/min) and pyrolyzed under the reaction conditions (oven temperature 530±6°C, carrier flow 30 ml/min, inlet at room temperature) to give the 4-trimethylsilyl-2-methyl-α-methylstyrene, **29**, and 5-trimethylsilyl-2-methyl-α-methylstyrene, **30**, identified by nuclear magnetic resonance spectroscopy.

GC Fraction 1, (corresponds to GC Fraction 1 in the **27**/**28** reaction mixture), MS M^+ m/e 204, NMR (90 MHz, δ, CCl_4): 0.19 (s, 9H), 1.92 (br.s, 3H), 2.16 (s, 3H), 4.68 (br.m, 1H), 5.02 (br.m, 1H), 6.90 (d, 1H, J=7.5 Hz), 6.98 (br.s, 1H), 7.08 (d, 1H, J=7.5 Hz).

GC Fraction 2, (corresponds to GC Fraction 2 in the 27/28 reaction mixture), MS M$^+$ m/e 204, NMR (90 MHz, δ, CCl_4): 0.19 (s, 9H), 1.91 (br.s, 3H), 2.19 (s, 3H), 4.70 (br.m, 1H), 5.01 (br.m, 1H), 6.87 (d, 1H, J=8Hz), 7.08 (br.s, 1H), 7.09 (d, 1H, J=8 Hz).

Flash vacuum pyrolysis of the mixture of 27 and 28 (oven temperature 850°C, 0.01 mm Hg) yielded several minor volatile products, apparently from fragmentation, as well as the mixture of 29 and 30. No evidence for any other isomerization products was observed in the GC.

c. Pyrolysis of *cis*-1-trimethylsilyl-6-*tert*-butyl-3-hexene-1,5-diyne, 31

The *cis* isomer 31 was pyrolyzed in the flow pyrolysis apparatus shown in Figure 43, oven temperature 464±2°C, flow rate 25 ml/min, inlet temperature 70±5°C, ca. 20 μl passed through the tube over 3 hours. No polymeric residue was observed in the inlet flask at the end of the experiment. Flame ionization gas chromatography (column 5, 145°C) showed ca. 15% conversion to a mixture of three products, as well as *cis*-*trans* isomerization of the hexene-diyne to an approximately equal mixture of 31 and 32. The pyrolysis was repeated at an oven temperature of 532±2°C, flow 20 ml/min. GC showed nearly complete conversion to three products. The first two very nearly coeluted on the capillary column, and were collected together when the mixture was separated by preparative gas chromatography for NMR samples (column 4, 160°C, 60 ml/min).

GC Fraction 1, products 1 and 2. Product 1 was identified as one of the isomers **29** or **30** by GC coinjection (column 5, 145°C, 50 psi carrier pressure) and NMR of the mixture. Similarly product 2 was identified to be **19**. The NMR spectra are compared in the table below (90 MHz, δ, CCl_4).

29/**30** GC Fr. 1	P. 1 + P. 2	**19**
0.19, s	0.20, s	0.20, s
-	1.60, br. s	1.59, br.s
1.92, br.s	1.95, br.s	-
2.16, s	2.19, s	-
-	3.19, br.s	3.19, br.s
4.68, br.m	4.64, br.m	4.62, br.m
-	4.73, br.m	4.69, br.m
5.02, br.m	5.05, br.m	-
6.87-7.17, m	6.88-7.23, m	7.0-7.25, m

Integrals of the product mixture NMR spectrum are in good agreement with the above assignment.

GC Fraction 2, product 3. The product was identified by NMR to be an isomer of trimethylsilyl-isopropenyltoluene, but was clearly not either **29** or **30** by gas chromatography. Since the synthesis of the **29**/**30** mixture was unambiguously expected to give two 1,2,4 substituted isomers, product 3 is assigned as one of the 1,2,3 isomers **33** or **34**. NMR (90 MHz, δ, CCl_4): 0.25 (s, 9H), 1.90 (br.s, 3H), 2.23 (s, 3H), 4.65 (br.m, 1H), 5.00 (br.m, 1H), 6.91 (d?, 2H, J=5 Hz), 7.12 (q?, 1H, J=5 Hz).

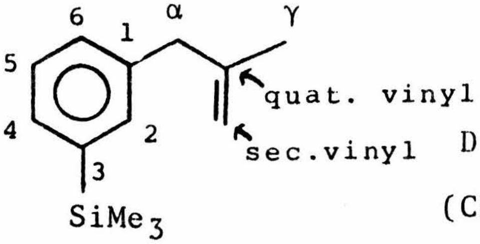
d. Pyrolysis of *cis*-1-(trimethylsilyl d-9)-4-*tert*-butyl-3-hexene-1,5-diyne, **16D**.

Both **16** and **16D** were pyrolyzed in large quantities (ca. 0.5 gm) and the products collected off the preparative gas chromatograph. Pyrolysis conditions: oven temperature 495±5°C, flow rate 30±3 ml/min, inlet temperature 100-120°C. GC conditions: column 3, 145°C, 100 ml/min. Considerable decomposition occurred in the injector port, particularly of the products **20** and **21**.

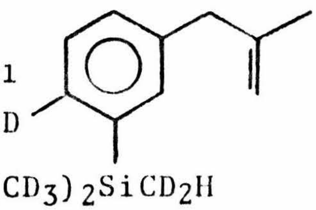
19, ^1H NMR (90 MHz, δ, CCl_4): 0.20 (s, 9H), 1.59 (br.s, 3H), 3.19 (br.s, 2H), 4.62 and 4.69 (overlapping br.m's, 2H total), 7.0-7.25 (m, 4H).

19, ^1H NMR (90 MHz, δ, $CDCl_3$): 0.21 (s, 9H), 1.61 (s, 3H), 3.22 (s, 2H), 4.64 and 4.71 (overlapping br.m's, 2H total), 7.05-7.4 (m, 4H).

19D, ^1H NMR (90 MHz, δ, $CDCl_3$): 0.22 (m, 1H), 1.63 (s, 3H), 3.25 (s, 2H), 4.65 and 4.73 (overlapping br.m's, 2H total), 7.0-7.35 (m, 3H).



19



19D

19, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

Offset, Hz ($CDCl_3$=0.0)	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
1714.8	18	145.214	Quaternary vinyl
1592.8	16	140.362	C3
1555.3	27	138.870	C1
1431.6	64	133.947	C2
1359.8	44	131.093	C4
1317.7	59	129.419	C6
1275.1	49	127.724	C5
877.7	63	111.916	Secondary vinyl
-812.1	72	45.272	α
-1380.8	48	23.895	γ
-1964.8	100	-1.124	Si-CH_3

19 and **19D**, ^{13}C NMR (45.3 MHz, δ TMS, $CDCl_3$)

	19		**19D**	
Assignments	Rel.Int.	Shift,δ	Rel.Int.	Shift,δ
Quat.vinyl	13	145.142	20	ca.145.5
C3	7	140.308	12?	ca.141
C1	10	138.788	26	ca.138
C2	36	133.877	30	133.872
C4	41	131.010	-	-
C6	38	129.331	31	129.307
C5	36	127.638	32	127.487
Sec.vinyl	37	111.851	41	111.841
α	36	44.712	44	44.712
γ	33	22.155	set=33	22.168
$Si-CH_3$	100	-1.069	-	-

Satisfactory spectra of **20** and **20D** were not obtained.

21, ^{1}H NMR (90 MHz, δ, CCl_4): 0.39 (s, 6H), 1.23 (s, 9H), 1.96 (s, 2H), 6.9-7.3 (m, 3H).

21, ^{1}H NMR (90 MHz, δ, $CDCl_3$): 0.49 (s, 6H), 1.32 (s, 9H), 2.15 (s, 2H), 7.2-7.4 (m, 3H).

21D, ^{1}H NMR (90 MHz, δ, $CDCl_3$): 1.30 (s, 9H), 7.2-7.4 (m, 2H).

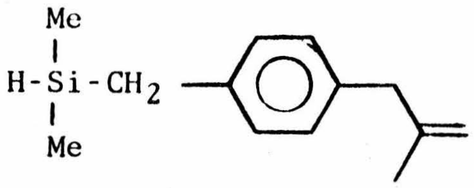
Satisfactory ^{13}C NMR spectra were not obtained.

90 MHz proton spectra of **23** showed a multiplet of at least seven lines centered at ca. 3.9δ, but the Berkeley 180 MHz Fourier transform instrument was required to demonstrate the nine line pattern. The Berkeley instrument also showed more clearly the AA'BB' pattern for the aromatic protons.

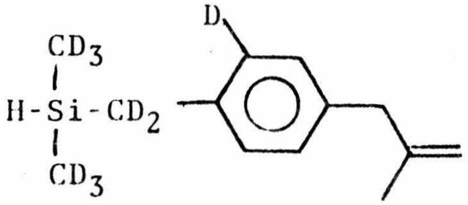
23, ^{1}H NMR (90 MHz, δ, CCl_4): 0.00 (d, 6H, J=4 Hz), 1.55 (s, 3H), 2.00 (d, 2H, J=4 Hz), 3.12 (s, 2H), 3.85 (nonet, 1H, J=4Hz), 4.60 (br.m, 2H), 6.65-7.0 (m, 4H).

23, ^{1}H NMR (90 MHz, δ, $CDCl_3$): 0.10 (d, 6H, J=4 Hz), 1.69 (s, 3H), 2.15 (d, 2H, J=4 Hz), 3.29 (s, 2H), 3.98 (nonet, 1H, J=4 Hz), 4.74 and 4.80 (overlapping br.m's, 2H total), 6.9-7.2 (m, 4H).

23D, ^{1}H NMR (90 MHz, δ, $CDCl_3$): 1.67 (s, 3H), 3.26 (s, 2H), 3.86 (s, 1H), 4.74 and 4.79 (overlapping br.m's, 2H total), 6.9-7.2 (m, 4H).



23



23D

23, ^{13}C NMR (45.3 MHz, δ TMS, $CDCl_3$)

Freq., Hz	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
6589.24	25	145.500	Quat. vinyl
6226.39	27	137.487	C4
6133.43	24	135.435	C1
5833.78	85	128.818	C2+C6
5796.71	100	127.999	C3+C5
5050.46	52	111.521	Sec. vinyl
2001.40	43	44.193	α
1072.74	46	23.687	Si-CH_2-Ar
999.33	46	22.066	γ
-210.83	65	-4.655	Si-CH_3

23D, ^{13}C NMR (45.3 MHz, δ TMS, $CDCl_3$)

Freq., Hz	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
6589.72	85	145.510	Quat. vinyl
-	-	-	C4
6131.84	55	135.400	C1
5833.07	159	128.802	C6
5828.17	167	128.694	C2
5794.59	100	127.953	C5
-	-	-	C3
5049.26	202	111.494	Sec. vinyl
2000.92	195	44.183	α
-	-	-	Si-CH_2-Ar
998.88	174	22.056	γ
-	-	-	Si-CH_3

e. Reference compounds for assignment of carbon-13 spectra.

Benzene, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

Offset, Hz ($CDCl_3$=0.0)	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
1290.9	100	128.348	Ring carbon

Methallylbenzene, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

Offset, Hz ($CDCl_3$=0.0)	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
1712.7	26	145.126	Quat. vinyl
1577.7	17	139.757	C1
1305.2	100	128.917	C2+C6
1289.5	55	128.293	C3+C5
1233.9	72	126.081	C4
877.7	50	111.912	Sec. vinyl
-813.8	37	44.629	α
-1383.6	32	22.038	γ

Methallylbenzene-4-D, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

Offset, Hz ($CDCl_3$=0.0)	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
1712.3	33	145.113	Quat. vinyl
1577.4	27	139.747	C1
1304.9	83	128.908	C2+C6
1286.1	100	128.162	C3+C5
-	-	-	C4
877.7	42	111.914	Sec. vinyl
-813.8	66	44.661	α
-1382.8	32	22.025	γ

Trimethylsilylbenzene, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

Offset, Hz ($CDCl_3$=0.0)	Relative Intensity	Shift, δ ($CDCl_3$=77.000)	Assignments
1595.0	15	140.445	C1
1416.3	100	133.337	C2+C6
1302.5	52	128.810	C4
1277.4	58	127.811	C3+C5
-1966.1	29	-1.206	Si-CH_3

24, ^{13}C NMR (25.2 MHz, δ TMS, $CDCl_3$)

1708.9	12	144.975	Quat. vinyl
1593.8	18	140.397	C4
1526.3	17	137.712	C1
1417.4	94	133.384	C3+C5
1291.3	100	128.364	C2+C6
880.0	44	112.004	Sec. vinyl
-815.0	33	44.582	α
-1381.5	15	22.048	γ
-1964.5	24	-1.142	Si-CH_3

IV. References

1a. Whilhite, D. L. and Whitten, J. L., J. Am. Chem. Soc., 93, 2858 (1971).

b. Dewar, M. J. S. and Li, W-K., J. Am. Chem. Soc., 96, 5569 (1974).

2. Schaefer, H. F. III, "The Electronic Structure of Atoms and Molecules," Addison-Wesley, Reading, Mass., 1972, p. 365.

3a. Jones, R. R. and Bergman, R. G., J. Am. Chem. Soc., 94, 660 (1972).

b. Bergman, R. G., Accts. Chem. Res., 6, 25 (1973).

c. Breslow, R., Napierski, J. and Clarke, T. C., J. Am. Chem. Soc., 97, 6275 (1975).

d. Breslow, R. and Khanna, P. L., Tet. Lett., 3429 (1977).

e. Chapman, O. L., Chang, C.-C. and Kolc, J., J. Am. Chem. Soc., 98, 5703 (1976).

f. Masamune, S. et al., Chem. Commun., 1516 (1971).

4a. Davis, J. H., Shea, K. J. and Bergman, R. G., unpublished results.

b. Bickelhaupt, F. et al, Tet. Lett., 4187 (1975).

5. Eaton, D., private communication.

6a. Stubbs, H. W. D. and Tucker, S. H., J. Chem. Soc., 2939 (1951).

b. Campbell, N. and Marks, A., J. Chem. Soc., 2941 (1951).

7. Davis, J. H., Shea, K. J. and Bergman, R. G., J. Am. Chem. Soc., 99, 1499 (1977).

8. Maier, G., private communication.

9a. Fischer, E. O. et al., Angew. Chem. Int. Ed., 6, 634 (1967).

b. Van Tamelen, E. E., J. Am. Chem. Soc., 89, 3922 (1967).

c. Maitlis, P. M. et al., Chem. Commun., 759 (1967).

10. Starks, C. M., J. Am. Chem. Soc., 93, 195 (1971).

11. Benson, S. W., "Thermochemical Kinetics," John Wiley and Sons, New York, N.Y., 2nd ed., 1976.

12. Shea, K. J. and Bergman, R. G., unpublished results.

13. Lockhart, T. P. and Bergman, R. G., unpublished results.

14. Stofko, J. J. and Bergman, R. G., unpublished results.

15. Peterson, D. J. et al., J. Org. Chem., 33, 780 (1968).

16. Corey, E. J. et al., J. Am. Chem. Soc., 92, 6314 (1970).

17. Brown, R. F. C. et al., Aust. J. Chem., 30, 1757 (1977).

18a. Doddrell, D. et al., Aust. J. Chem., 27, 417 (1974).

b. Schaeffer, C. D. Jr. et al., J. Organometal. Chem., 80, 29 (1974).

19. Wilt, J. W. et al., J. Am. Chem. Soc., 100, 5534 (1978).

20. Walsh, R. and Wells, J. M., J. Chem. Soc. Far. I, 72, 100 (1976).

21. Walsh, R. and Doncaster, A. M., J. Chem. Soc. Far. I, 72, 2908 (1976).

22. Brown, Duncan W., private discussion.

23. Benson, S. W., op. cit., p. 273. The non-nearest neighbor correction for cis-di-tert-butyl alkenes is ca. 10 kcal/mole.

24. Bohlmann, F. et al., Chem. Ber., 86, 63 (1953).

25. West, R. and Jones, P. C., J. Am. Chem. Soc., 91, 6156 (1969).

26. Sondheimer, F. et al., J. Am. Chem. Soc., 85, 52 (1963).

27. Huntsman, W. D. et al., J. Am. Chem. Soc., 89, 342 (1967).

28. McBride, J. J. Jr. and Beachall, H. C., J. Am. Chem. Soc., 74, 5247 (1952).