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Registry No. 1, 17455-13-9; **2**, 14098-24-9; **3**, 14187-32-7; **4**, 33941-15-0; **5**, 16069-36-6; **6** (n = 0), 77877-86-2; **6** (n = 1), 53914-89-9; **6** (n = 2), 86309-73-1; **6** (n = 3), 86309-74-2; **6** (n = 4), 95216-11-8; **6** (n = 5), 95216-12-9; **6** (n = 6), 95216-13-0; **7**, 53914-83-3; **8**, 81336-37-0; **9**, 81336-42-7; **10** (n = 1), 55440-83-0; **10** (n = 2), 55440-84-1; **11**, 55440-80-7; 2,6-pyrido-18-crown-6-$(CN)_2CH_2$, 103201-04-3.

Supplementary Material Available: Tables of atomic positional and thermal parameters and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Excited-State Rearrangements of 1,3- and 1,5-Dienes in a Radio Frequency Plasma

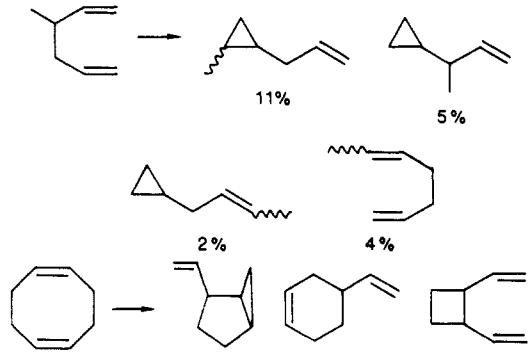
Larry L. Miller* and Yoshikazu Mizobuchi

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received February 11, 1986*

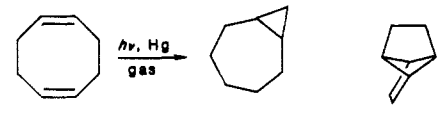
Abstract: 1,3- and 1,5-dienes were reacted by distilling them through an inductively coupled radio frequency plasma. The major liquid products from 1,5-dienes were allylcyclopropanes, and it is proposed that they were formed by a sigmatropic [1,4] vinyl shift. This mechanism accounts for the specific isomers formed from various methylated 1,5-hexadienes. Other isomerizations were observed. The cis and trans isomers of 1,3-hexadiene and 2,4-hexadiene are interconverted under these conditions, and 1,3-cyclooctadiene produced bicyclo[4.2.0]oct-2-ene. Kinetic data are reported.

The gaseous plasma generated by a radio frequency (13.56 MHz) discharge provides an unusual reaction medium and some unusual reactions.[1-3] These reactions are initiated by electron impact events. In the plasma, free electrons are accelerated by the electrical field and collide with neutral molecules. These collisions excite or ionize the molecules, and this naturally leads to chemical reactions. The initial reactions after excitation are often rearrangements or fragmentation and some analogies with photochemistry have been drawn.[1,4-6] In the present study we set out to study rearrangements of hydrocarbon dienes and to compare the reaction products with those from UV photolysis. Previous studies have shown that the plasma products, formed from *cis*-2-butene (*trans*-2-butene and 1-butene), are also obtained by photolysis of *cis*-2-butene at 180 nm in the gas phase.[5] Recently, we have reported the di-π-methane rearrangements of 1,4-pentadiene to vinylcyclopropane and allylbenzene to cyclopropylbenzene.[6]

The present investigation focused on 1,3- and 1,5-dienes. Photochemical isomerizations of 1,3-butadienes to cyclobutenes are well-known for both acyclic[7] and cyclic reactants like 1,3-cyclooctadiene.[8] The rearrangement of 1,5-dienes has received a lot of attention.[9,10] Of particular interest is conversion of 1,5-dienes to allylcyclopropanes in solution, which has been reported by Kropp and Manning.[10] For example, 3-methyl-1,5-hexadiene and 1,5-cyclooctadiene gave the following results.



It was proposed[10] that the higher yield allylcyclopropane products from acyclic 1,5-dienes came from a [1,2] sigmatropic shift mechnism. In the case of 1,5-cyclooctadiene, a [2,3] sigmatropic shift was proposed to explain the allylcyclopropane product.[10] Interestingly, in the gas phase a mercury-sensitized photolysis gave different products from 1,5-cyclooctadiene.[9f,g]



Experimental Section

Analysis. Quantitative analysis was carried out with use of a temperature programmed gas chromatograph (GC) equipped with a flame ionization detector. Isomer yields were computed relative to the peak area for reactant, which was calibrated. A 3 m length, $^1/_8$ in o.d., 20% silicone OV-17 on acid washed and silylated Chromosorb W (80/100 mesh) was used. Gas chromatography–mass spectrometry (a Finnigan 4000 GC-MS interfaced to a VG M82L Multispace Data System) was performed for identification of the molecular weight of the major plasma products.

For the structural analysis of major plasma products, a GC equipped with thermal conductivity detector and preparative columns (3 and 6 m

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lengths, $^3/_{16}$ in i.d., and column packing the same material used for quantitative analysis) was used. The separated components were collected in a dry ice–ethanol cold trap. The trap was like a small size nitrogen bubbler with two small glass stoppers. A solvent ($CDCl_3$) was put in the collection vessel for NMR analysis. The structures of these collected products were determined with ^1H (300 MHz), ^{13}C NMR, and mass spectra. ^{13}C and ^1H NMR chemical shifts are reported in ppm vs. Me_4Si. For the purpose of ^1H NMR assignments, cyclopropyl hydrogens cis to the allyl group are identified as H_α and trans as H_β. Yields are reported on the basis of the total amount of reactant passed through the reactor.

Materials and Apparatus. All 1,5- and 1,3-dienes were purchased and shown to be pure (99.8–97) by GC.

An International Plasma Corp Model PM 105D was used as the radio frequency plasma power supply. A watt meter from Bird Electronic Corp. (Model 43, impedance 50 ohms) was employed for the measurement of forward and minimized reverse power. Tuning was accomplished with a modified Heathkit antenna tuner. The plasma apparatus has been described.[6a] The starting materials went through the plasma zone, and the mixture of products was collected in a liquid nitrogen cold trap. The flow rate was controlled with a Teflon needle valve, and the pressure in the reaction tube was checked by a pressure transducer (MKS Baratron Model 222A). A MKS 254 controller was used for observation of the pressure change. The induction coil was 10 turns of 0.25 in o.d. copper tubing. The average flow rate was calculated from the measured time and the loss of weight of the flask containing the reactant.

Plasmolysis of 1,5-Cyclooctadiene (1). A sample of 17.56 mmol of **1** was passed through the plasma discharge at 20 W. The inverse of average flow rate (r^{-1}) was 4.65 min/mmol, and the range of pressure was from 38 to 30 mTorr. The four products were **2**, benzene, 1,3-cyclohexadiene, and 1,3-butadiene. Relative retention times of **2**, benzene, and 1,3-cyclohexadiene based on the retention time of **1** (25.11 min) were 0.83, 0.56, and 0.54 respectively. The overall yields of **2**, benzene, and 1,3-cyclohexadiene were 18, 5, and 3%, respectively. The conversion of **1** was 66%.

3-Cyclopropylcyclopentene (**2**) was obtained from the liquid phase as the major product: mass spectrum, *m/e* (relative intensity) 108.0 (7), 105.0 (2), 93.1 (42), 91.1 (22), 87.9 (1), 85.9 (7), 83.9 (11), 80.2 (100), 79.0 (97), 77.1 (35), 66.9 (98), 65.0 (19), 62.7 (4), 54.4 (6), 53.0 (10), 52.0 (8), 50.9 (13), 50.0 (6), 49.0 (3), 46.8 (4), 41.0 (36), 40.1 (10), 38.9 (46), 36.2 (4), 31.8 (26); ^1H NMR 0.09–0.16 (quartet, 2 H, CH-2′α and O-3′α), 0.36–0.44 (quartet, 2 H, CH-2′β and −3′β), 0.60–0.70 (multiplet, 1 H, CH-1′α), 1.52–1.66 (multiplet, 1 H, CH-4), 2.00–2.14 (multiplet, 1 H, CH-4), 2.14–2.30 (multiplet, 2 H, CH_2-5), 2.30–2.45 (multiplet, 1 H, CH-3), 5.64–5.68 (multiplet, 1 H, CH-2), 5.71–5.75 (multiplet, 1 H, CH-1); ^{13}C NMR and APT 2.97 and 3.30 (number of hydrogens on both carbons was even, 2 H and 2 H, C-2′ and C-3′), 16.17 (odd, 1 H, C-1′), 29.83 (even, 2 H, C-4), 32.18 (even, 2 H, C-5), 50.18 (odd, 1 H, C-3), 130.88 (odd, 1 H, C-1), 134.20 (odd, 1 H, C-2).

Plasmolysis of 1,5-Dimethyl-1,5-cyclooctadiene (3). A sample of 14.47 mmol of **3** was passed throgh the plasma discharge at 50 W. The r^{-1} was 1.92 min/mmol, and the range of pressure was from 90 to 162 mTorr. Two major products were produced from **3** by this reaction. Those were 1,5-dimethyltricyclo[3.3.0.0^{2,6}]octane (**5**) and 1-methyl-3-(1′-methylcyclopropyl)cyclopentene (**4**). Relative retention time of **5** and **4** based on the retention time of **3** (57.10 min) were 0.64 and 0.76, respectively. The overall yields of **5** and **4** were 8% and 8%, respectively. The conversion of **3** was 59%.

1,5-Dimethyltricyclo[3.3.0.0^{2,6}]octane (**5**) was obtained from the liquid phase as one of two major products: mass spectrm, *m/e* (relative intensity) 135.9 (12), 122.3 (9), 120.9 (86), 119.1(2), 109.1 (7), 107.9 (72), 106.5 (74). 103.0 (5), 96.2 (5), 95.0 (55), 94.1 (58), 92.9 (100), 91.0 (92), 89.2 (2), 83.3 (1), 82.2 (30), 80.9 (78), 78.9 (98), 77.0 (45), 74.8 (1), 68.1 (7), 67.0 (12), 65.0 (3), 57.9 (2), 54.8 (27), 52.7 (36), 50.7 (24), 43.1 (8), 42.0 (5), 40.7 (61), 38.7 (68), 31.8 (15); ^1H NMR 0.69 (singlet, 6 H, CH_3-1 and −5), 1.40–1.55 (multiplet, 8 H, CH_2-3, -4, -7, and -8), 2.30–2.34 (triplet, 2 H, CH-2 and -6); ^{13}C NMR and APT 11.15 (odd, 3 H × 2, CH_3 at C-1 and −5), 21.29 (even, 2 H × 2, C-3 and -7), 30.59 (even, 2 H × 2, C-4 and -8), 51.04 (odd, 1 H × 2, C-2 and -6), 52.55 (no H, C-1 and C-5).

1-Methyl-3(1′-methylcyclopropyl)cyclopentene (**4**) was obtained as another major product: mass spectrum, *m/e* (relative intensity) 136.0 (8), 121.0 (10), 109.1 (6), 107.7 (95), 104.9 (5), 103.0 (1), 94.1 (20), 92.9 (99), 90.9 (26), 82.3 (7), 81.0 (100), 79.0 (45), 77.0 (26), 65.0 (6), 62.8 (2), 55.0 (10), 52.8 (23), 50.7 (10), 43.1 (4), 40.7 (35), 38.8 (33), 31.8 (5); ^1H NMR 0.10–0.21 (quartet, 2 H, CH-2′α and −3′α, 0.23–0.34 (quartet, 2 H, CH-2′β and −3′β), 0.93 (singlet, 3 H, CH_3-1′β), 1.62–1.76 (multiplet, 1 H, CH-4), 1.70–1.74 (sexet, 3 H, CH_3-1), 1.92–2.06 (multiplet, 1 H, CH-4), 2.14–2.24 (multiplet, 2 H, CH_2-5), 2.29–2.38 (multiplet, 1 H, CH-3), 5.13–5.17 (heptet, 1 H, CH-2); ^{13}C NMR and APT 11.22 and 11.49 (2 H and 2 H, C-2′ and -3′), 16.80 (odd, 3 H, CH_3 at C-1′), 18.78 (O, C-1′), 21.16 (odd, 3 H, CH_3 at C-1), 28.06 (even, 2 H, C-4), 36.79 (even, 2 H, C-5), 53.42 (odd, 1 H, C-3), 126.74 (odd, 1 H, C-2), 141.27 (no H, C-1).

Plasmolysis of 1,5-hexadiene (6). A 19.35-mmol sample of **6** was passed through the discharge at 20 W. The r^{-1} was 3.80 min/mmol, and the range of pressure was from 20 to 50 mTorr. One major product was produced from **6**. It was 2-propenylcyclopropane[10] (**7**). The relative retention time of **7** based on the retention time of **6** (8.94 min) was 1.35. Overall yield of **7** was 11%. The conversion of **6** was 68%.

2-Propenylcyclopropane (**7**) was obtained from the liquid phase as the major product: mass spectrum, *m/e* (relative intensity) 82.5 (3), 81.2 (5), 79.1 (3), 77.2 (2), 68.1 (4), 66.9 (61), 65.0 (6), 62.4 (1), 55.2 (8), 53.7 (100), 50.4 (9), 40.9 (67), 38.8 (85); ^1H NMR 0.06–0.09 (multiplet, 2 H, CH-2α and −3α), 0.42–0.50 (multiplet, 2 H, CH-2β and −3β), 0.69–0.85 (multiplet, 1 H, CH-1β), 1.93–1.98 (triplet, 2 H, CH_2-1′), 4.93–5.10 (quartet, 2 H, CH_2-3′), 5.82–5.95 (multiplet, 1 H, CH-2′); ^{13}C NMR and APT 4.22 (even, 4 H, C-2 and -3), 10.09 (odd, 1 H, C-1), 38.51 (even 2 H, C-1′), 114.42 (even, 2 H, C-3′), 138.15 (odd, 1 H, C-2′).

Plasmolysis of 2,5-Dimethyl-1,5-hexadiene (8). A 9.96-mmol sample of **8** was passed through the plasma discharge at 40 W. The r^{-1} was 2.28 min/mmol, and a range of pressure was from 68 to 92 mTorr. One major product was produced from **8**. It was 1-methyl-1-(2′-methyl-2′-propenyl)cyclopropane[10] (**9**). Relative retention time of **9** based on the retention time of **8** (40.23 min) was 0.90. Overall yield of **9** was 8%. The conversion of **8** was 58%.

1-Methyl-1-(2′-methyl-2′-propenyl)cyclopropane (**9**) was obtained from the liquid phase as a major product: mass spectrum, *m/e* (relative intensity) 110.3 (3), 95.1 (100), 94.4 (3), 93.0 (8), 91.0 (5), 81.3 (42), 79.0 (10), 77.0 (10), 68.9 (4), 67.2 (45), 66.4 (2), 65.0 (8), 55.0 (81), 53.5 (30), 50.8 (8), 49.9 (3), 41.9 (3), 41.2 (14), 39.8 (29), 39.2 (15), 37.6 (1), 31.8 (2); ^1H NMR 0.25–0.28 (doublet, 4 H, CH_2-2 and -3), 0.93 (singlet, 3 H, CH_3 at C-1), 1.71 (singlet, 3 H, CH_3 at C-2′), 1.90 (singlet, 2 H, CH_2-1′), 4.70 (singlet, 2 H, CH_2-2′); ^{13}C NMR and APT 12.93 (even, 4 H, C-2 and -3), 13.85 (no H, C-1), 22.56 (odd, 3 H, CH_3 at C-1), 22.91 (odd, 3 H, CH_3 at C-2′), 47.64 (even, 2 H, C-1′), 111.51 (even, 2 H, C-3′), 145.06 (no H, C-2′).

Plasmolysis of 2,5-Dimethyl-1,5-hexadiene (8). A 9.96-mmol sample of **8** was passed through the plasma discharge at 40 W. The r^{-1} was 2.28 min/mmol and a range of pressure was from 68 to 92 mTorr. One major product was produced from **8**. It was 1-methyl-1-(2′-methyl-2′-propenyl)cyclopropane[10] (**9**). Relative retention time of **9** based on the retention time of **8** (40.23 min) was 0.90. Overall yield of **9** was 8%. The conversion of **8** was 58%.

1-Methyl-1-(2′-propenyl)cyclopropane (**9**) was obtained from the liquid phase as a major product: mass spectrum, *m/e* (relative intensity) 110.3 (3), 95.1 (100), 94.4 (3), 93.0 (8), 91.0 (5), 81.3 (42), 79.0 (10), 77.0 (10), 68.9 (4), 67.2 (45), 66.4 (2), 65.0 (8), 55.0 (81), 53.5 (30), 50.8 (8), 49.9 (3), 41.9 (3), 41.2 (14), 39.8 (29), 39.2 (15), 37.6 (1), 31.8 (2); ^1H NMR 0.25–0.28 (doublet, 4 H, CH_2-2 and -3), 0.93 (singlet, 3 H, CH_3 at C-1), 1.71 (singlet, 3 H, CH_3 at C-2′), 1.90 (singlet, 2 H, CH_2-1′), 4.70 (singlet, 2 H, CH_2-2′); ^{13}C NMR and APT 12.93 (even, 4 H, C-2 and -3), 13.85 (no H, C-1), 22.56 (odd, 3 H, CH_3 at C-1), 22.91 (odd, 3 H, CH_3 at C-2′), 47.64 (even, 2 H, C-1′), 111.51 (even, 2 H, C-3′), 145.06 (no H, C-2′).

Plasmolysis of 3-Methyl-1,5-hexadiene (10). A 14.13-mmol sample of **10** was passed through the plasma discharge at 40 W. The r^{-1} was 1.28 min/mmol, and the range of pressure was from 100 to 136 mTorr. Three major products were produced from **10**. Those were *cis*-1-methyl-2-(2′-propenyl)cyclopropane[10] (**11**), *trans*-1-methyl-2-(2′-propenyl)cyclopropane[10] (**12**), and *trans*-1,5-heptadiene (**13**). Relative retention times of **11**, **12**, and **13** based on the retention time of **10** (25.59 min) were 1.39, 1.13, and 1.33, respectively. The overall yields of **11**, **12**, and **13** were 7, 6, and 3%. The conversion of **10** was 62%. The yields of **14**, **15**, and **16** if present were less than 1%.

cis-1-Methyl-2-(2′-propenyl)cyclopropane (**11**) was obtained from the liquid phase as one of three major products: mass spectrum, *m/e* (relative intensity) 96.1 (4), 95.1 (4), 82.2 (3), 81.0 (63), 80.2 (3), 79.0 (16), 77.0 (8), 68.9 (3), 67.9 (14), 66.8 (35), 66.0 (4), 64.9 (7), 56.0 (4), 54.9 (100), 53.9 (81), 52.8 (31), 51.9 (1), 50.8 (9), 49.8 (2), 42.9 (1), 41.9 (7), 40.9 (38), 39.9 (4), 38.9 (60); ^1H NMR −0.29 to −0.24 (quartet, 1 H, CH-3α), 0.70–0.83 (multiplet, 3 H, CH-1β, −2β, and −3β), 1.03–1.05 (doublet, J = 5.96 Hz, 3 H, CH_3 at C-1), 2.02–2.06 (triplet, 2 H, CH_2-1′), 4.95–5.14 (quartet, 2 H, CH_2-3′), 5.86–5.98 (multiplet, 1 H, CH-2′); ^{13}C NMR and APT 9.49 (odd, 1 H, C-1), 11.85 (even, 2 H, C-3), 13.30 (odd, 1 H, C-2), 14.74 (odd, 3 H, CH_3 at C-1), 32.66 (even, 2 H, C-1′), 114.04 (even, 2 H, C-3′), 138.94 (odd, 1 H, C-2′).

trans-1-Methyl-2-(2′-propenyl)cyclopropane (**12**) was obtained from the liquid phase as one of three major products: mass spectrm, *m/e* (relative intensity) 95.1 (2), 82.0 (4), 81.0 (66), 80.0 (19), 79.0 (23), 77.0

(9), 68.9 (4), 67.9 (15), 66.8 (46), 65.9 (11), 65.0 (9), 57.9 (2), 55.9 (4), 54.9 (94), 53.9 (100), 52.8 (36), 51.7 (2), 50.9 (9), 49.7 (3), 42.9 (7), 41.9 (10), 40.9 (49), 39.9 (20), 39.1 (71); ^{1}H NMR 0.15–0.26 (multiplet, 2 H, CH-1α and -3α), 0.42–0.49 (multiplet, 2 H, CH-2β and -3β), 1.02–1.05 (doublet, J = 5.54 Hz, 3 H, CH_3 at C-1), 1.94–1.98 (triplet, 2 H, CH_2-1′), 4.93–5.09 (quartet, 2 H, CH_2-3′), 5.83–5.94 (multiplet, 1 H, CH-2′); ^{13}C NMR and APT 12.50 (odd, 1 H, C-1), 12.73 (even, 2 H, C-3), 18.77 (odd, 1 H, C-2), 19.00 (odd, 3 H, CH_3 at C-1), 38.07 (even, 2 H, C-1′), 114.15 (even, 2 H, C-3′), 138.31 (odd, 1 H, C-2′).

trans-1,5-Heptadiene (**13**) was also obtained from the liquid plasma products: mass spectrum, *m/e* (relative intensity) 96.1 (7), 81.0 (37), 79.0 (13), 67.9 (2), 66.9 (21), 54.8 (100), 53.9 (24), 52.8 (19), 43.8 (2), 40.9 (24), 39.8 (4), 38.9 (33), 31.8 (28); ^{1}H NMR 1.61–1.65 (doublet, 3 H, CH_3 at C-6), 2.04–2.10 (singlet, 4 H, CH_2-3 and -4), 4.92–5.06 (triplet, 2 H, CH_2-1), 5.41–5.49 (multiplet, 2 H, CH-5 and -6), 5.74–5.86 (multiplet, 1 H, CH-2); ^{13}C NMR and APT 18.01 (odd, 3 H, CH_3 at C-6), 32.10 (even, 2 H, C-4), 33.89 (even, 2 H, C-3), 114.50 (even, 2 H, C-1), 125.23 (odd, 1 H, C-6), 130.71 (odd, 1 H, C-5), 138.61 (odd, 1 H, C-2). The retention times of isolated and authentic **13** were the same.

Plasmolysis of 1,5-Heptadiene (13). A sample of 17.10 mmol of **13** (91% trans, 9% cis) was passed through the plasma discharge at 40 W. The r^{-1} was 1.38 min/mmol, and the range of pressure was from 70 to 160 mTorr. Four major compounds were produced from **13**. Those were (1′-methyl-2′-propenyl)cyclopropane[10] (**14**), *cis*-2′-butenylcyclopropane[10] (**15**), *trans*-2′-butenylcyclopropane[10] (**16**), and 3-methyl-1,5-hexadiene (**10**). Relative retention times of **14**, **15**, **16**, and **10**, based on the retention time of **13** (23.60 min), were 0.78, 1.31, 1.23, and 0.61, respectively. Overall yields of **14**, **15**, **16**, and **10** were 1, 3, 3, and 1%, respectively. The conversion of **13** was 41%. The recovered **13** was 86% trans and 14% cis.

(1′-Methyl-2′-propenyl)cyclopropane (**14**) was obtained from the plasma products in the liquid phase as one of four major products: mass spectrum, *m/e* (relative intensity) 95.0 (3), 80.9 (69), 79.0 (23), 78.3 (9), 77.0 (10), 69.0 (3), 68.0 (87), 67.0 (100), 66.1 (3), 65.0 (12), 62.9 (3), 55.9 (2), 55.0 (84), 54.0 (40), 53.0 (52), 52.0 (6), 50.8 (13), 49.9 (1), 44.7 (1), 43.8 (3), 42.8 (3), 41.9 (2), 41.2 (59), 39.8 (23), 38.8 (63), 38.0 (7), 36.8 (2), 31.8 (50); ^{1}H NMR 0.08–0.14 (doublet, 2 H, CH-2α and -3_α, 0.40–0.47 (doublet, 2 H, CH-2β and -3β), 0.56–0.67 (multiplet, 1 H, CH-1β), 1.07–1.09 (doublet, 3 H, CH_3 at C-1′), 1.39–1.50 (sextet, 1 H, CH-1′), 4.91–5.04 (quartet, 2 H, CH_2-3′), 5.80–5.91 (heptet, 1 H, CH-2′); ^{13}C NMR and APT 3.61 and 3.66 (both even, 2 H and 2 H, C-2 and -3), 17.13 (odd, 1 H, C-1), 19.54 (odd, 3 H,CH_3 at C-1′), 42.33 (odd, 1 H, C-1′), 112.21 (even, 2 H, C-3′), 143.73 (odd, 1 H, C-2′).

cis-2-Butenylcyclopropane (**15**) was also obtained from the plasma products in the liquid phase: mass spectrum, *m/e* (relative intensity) 96.1 (2), 95.0 (12), 80.9 (41), 79.1 (9), 77.3 (5), 68.2 (28), 67.0 (30), 65.4 (3), 62.0 (1), 56.1 (9), 54.7 (100), 52.9 (21), 51.3 (4), 50.2 (10), 49.3 (3), 41.1 (24), 39.8 (8), 38.8 (40), 37.3 (5), 31.8 (7); ^{1}H NMR 0.05–0.10 (quartet, 2 H, CH-2α and -3α), 0.40–0.44 (quartet, 2 H, CH-2β and -3β), 0.67–0.80 (multiplet, 1 H, CH-1β), 1.59–1.61 (doublet, 3 H, CH_3-4′), 1.96–2.00 (triplet, 2 H, CH_2-1′), 5.46–5.49 (triplet, 2 H, CH-2′ and -3′); ^{13}C NMR and APT 4.11 (even, 4 H, C-2 and -3), 10.89 (odd, 1 H, C-1), 12.93 (odd, 3 H, C-4′), 31.48 (even, 2 H, C-1′), 123.94 (odd, 1 H, C-3′), 129.66 (odd, 1 H, C-2′).

trans-2′-Butenylcyclopropane (**16**) was also obtained in the liquid phase: mass spectrum, *m/e* (relative intensity) 95.7 (10), 90.9 (2), 85.9 (1), 82.1 (3), 81.0 (80), 79.0 (16), 77.0 (6), 68.0 (55), 66.9 (74), 65.3 (7), 63.0 (3), 61.5 (2), 55.0 (100), 54.0 (23), 52.9 (44), 51.4 (8), 49.3 (4), 45.9 (1), 42.5 (6), 40.9 (42), 39.8 (16), 38.8 (68), 36.8 (5), 31.8 (15); ^{1}H NMR 0.02–0.07 (quartet, 2 H, CH-2 and -3$_\alpha$), 0.39–0.44 (quartet, 2 H, CH-2 β and -3β), 0.66–0.79 (multiplet, 1 H, CH-1β), 1.65–1.67 (doublet, 3 H, CH_3-4′), 1.86–1.90 (triplet, 2 H, CH_2-1′), 5.46–5.50 (quartet, 2 H, CH-2′ and -3′); ^{13}C NMR and APT 4.18 (even, 4 H, C-2 and -3), 10.69 (odd, 1 H, C-1), 18.06 (odd, 3 H, C-4′), 37.37 (even, 2 H, C-1′), 124.96 (odd, 1 H, C-3′), 130.54 (odd, 1 H, C-2′).

3-Methyl-1,5-hexadiene (**10**) was also obtained: mass spectrum, *m/e* (relative intensity) 95.1 (1), 81.0 (28), 79.0 (5), 77.0 (3), 67.1 (15), 64.9 (3), 54.9 (100), 53.0 (13), 52.1 (3), 50.8 (3), 50.1 (4), 41.9 (3), 40.8 (16), 39.8 (4), 38.8 (28), 37.9 (1), 31.8 (16); ^{1}H NMR 0.99–1.01 (doublet, 3 H, CH_3 at C-3), 2.00–2.16 (multiplet, 2 H, CH_2-4), 2.16–2.28 (sextet, 1 H, CH-3), 4.92–5.06 (quintet, 4 H, CH_2-1 and -6), 5.70–5.81 (sextet, 2 H, CH-2 and -5). The retention times of the isolated and authentic *10* were the same.

Plasmolysis of 1,3-Cyclooctadiene (18). A 16.69-mmol sample of **18** was passed through the plasma discharge at 20 W. The r^{-1} of **18** was 4.18 min/mmol, and the range of pressure was from 36 to 38 mTorr. Three major compounds were produced from **18**. Those were bicyclo-[4.2.0]oct-7-ene (**19**), an unidentified compound, and benzene. The relative retention times of **19** and benzene based on the retention time of **18** (46.55 min) were 0.87 and 0.47, respectively. The overall yields of **19** and benzene were 13 and 5%, respectively. The conversion of **18** was 75%.

Bicyclo[4.2.0]oct-7-ene (**19**) was obtained from the plasma products in the liquid phase: mass spectrum, *m/e* (relative intensity) 108.0 (10), 107.0 (2), 94.1 (2), 93.0 (40), 92.0 (2), 91.0 (16), 82.1 (1), 81.0 (4), 80.0 (65), 79.0 (100), 78.0 (11), 77.0 (29), 68.0 (2), 66.9 (58), 66.0 (26), 64.9 (17), 62.9 (4), 61.9 (2), 55.0 (2), 53.9 (16), 52.8 (13), 51.8 (10), 50.8 (17), 49.8 (8), 41.9 (3), 40.9 (42), 39.9 (10), 38.9 (66), 37.9 (6), 36.9 (2); ^{1}H NMR 1.33–1.73 (multiplet, 8 H, CH_2-2, -3, -4, and -5), 2.81–2.89 (triplet, 2 H, CH-1 and -6), 6.12 (singlet, 2 H, CH-7 and -8); ^{13}C NMR and APT 18.83 (even, 2 H × 2, C-3 and -4), 24.93 (even, 2 H × 2, C-2 and -5), 41.55 (odd, 1 H × 2, C-1 and -6), 140.55 (odd, 1 H × 2, C-7 and -8).

Plasmolysis of 1,3-Hexadiene (20). A 10.47-mmol sample of **20** was passed through the plasma discharge at 40 W. The r^{-1} of **20** was 1.00 min/mmol, and the range of pressure was from 100 to 210 mTorr. Three major compounds were produced from **20**. Those were *trans,trans*-2,4-hexadiene (**21**), *cis,trans*-2,4-hexadiene (**22**), and *cis,cis*-2,4-hexadiene (**23**). The retention times of **21**, **22**, and **23** based on the retention time of **20** (14.24 min) were 1.29, 1.51, and 1.70, respectively. The yields of these compounds were 4, 7, and 2%, respectively. The conversion of **20** was 43%.

trans,trans-2,4-Hexadiene (**21**) was obtained from the plasma products in the liquid phase as one of three major products: mass spectrum, *m/e* (relative intensity) 81.8 (37), 80.8 (3), 80.1 (7), 78.9 (12), 77.1 (8), 68.1 (2), 66.9 (100), 64.9 (21), 63.0 (3), 55.0 (1), 52.3 (18), 50.4 (4), 41.4 (41), 39.7 (9), 39.2 (49), 38.2 (6), 37.0 (1); ^{1}H NMR 1.71–17.3 (doublet, J = 5.87, 6 H, CH_3-1 and -6), 5.50–5.61 (multiplet, 2 H, CH-2 and -5), 5.96–6.07 (quartet, 2 H, CH-3 and -4).

cis,trans-2,4-Hexadiene (**22**) was also obtained from the plasma products in the liquid phase: mass spectrum, *m/e* (relative intensity) 81.8 (46), 78.8 (1), 76.9 (7), 72.9 (3), 68.9 (3), 66.9 (97), 65.2 (17), 62.9 (3), 56.0 (1), 54.0 (15), 52.9 (2), 51.1 (11), 50.2 (1), 42.9 (1), 41.0 (83), 38.9 (100), 37.3 (2); ^{1}H NMR 1.72–1.79 (quartet, 6 H, CH_3-1 and -6), 5.30–5.43 (sextet, 1 H, CH-5), 5.61–5.74 (sextet, 1 H, CH-2), 5.93–6.01 (triplet, 1 H, CH-4), 6.30–6.41 (triplet, 1 H, CH-3).

cis,cis-2,4-Hexadiene (**23**) was also obtained: mass spectrum, *m/e* (relative intensity) 81.8 (35), 79.0 (13), 76.8 (7), 73.0 (4), 68.1 (5), 66.9 (100), 65.9 (3), 64.9 (19), 55.0 (7), 53.4 (23), 51.9 (2), 50.9 (15), 49.9 (7), 42.0 (5), 41.1 (7), 39.7 (73), 38.2 (11); ^{1}H NMR 1.69–1.83 (sextet, 6 H, CH_3-1 and -6), 5.49–5.60 (quintet, 2 H, CH-2 and -5), 6.24–6.36 (quartet, 2 H, CH-3 and -4).

Plasmolysis of *trans,trans*-2,4-Hexadiene (21). A 11.10-mmol sample of **21** was passed through in the plasma discharge at 40 W. The r^{-1} of **21** was 0.79 min/mmol, and the range of pressure was from 120 to 217 mTorr. Three major compounds were produced from **21**. The retention times of **20**, **22**, and **23** based on the retention time of **21** (19.51 min) were 0.70, 1.12, and 1.24, respectively. The yields were 7, 9, and 3%, respectively. The conversion of **21** was 42%.

1,3-Hexadiene (**20**) was obtained from the plasma products in the liquid phase as one of three major products. **20** was not a single compound but a cis and trans mixture of **20**: mass spectrum, *m/e* (relative intensity) 82.0 (38), 81.0 (8), 79.0 (7), 78.3 (1), 77.0 (4), 69.0 (2), 68.2 (6), 66.9 (100), 65.0 (17), 63.0 (5), 62.1 (2), 61.0 (1), 56.1 (3), 55.2 (9), 53.9 (20), 52.9 (17), 51.9 (8), 50.9 (15), 49.9 (12), 48.9 (2), 42.3 (5), 41.0 (49), 40.0 (12), 38.8 (66), 36.9 (4); ^{1}H NMR 0.90–1.08 (multiplet (nine), 6 H, CH_3-6 of cis and trans), 2.06–2.27 (nine (quintet × 2), 4 H, CH_2-5 of cis and trans), 4.93–5.25 (heptet (quartet × 2), 4 H, CH_2-1 of cis and trans), 5.36–5.52 (sextet, 1 H, CH-4 of cis), 5.68–5.85 (quintet, 1 H, CH-4 of trans), 5.91–6.10 (sextet, 2 H, CH-2 of cis and trans), 6.25–6.40 (sextet, 1 H, CH-3 of trans), 6.57–6.72 (sextet, 1 H, CH-3 of cis); ^{13}C NMR and APT data showed 12 peaks from this mixture.

cis,trans-2,4-Hexadiene (**22**) was also obtained: mass spectrum, *m/e* (relative intensity) 82.1 (40), 81.0 (8), 78.9 (10), 77.0 (5), 74.2 (1), 68.0 (6), 66.9 (100), 64.9 (14), 63.1 (4), 62.0 (2), 56.0 (2), 54.9 (8), 53.9 (20), 52.8 (22), 51.9 (6), 50.8 (13), 49.7 (10), 43.1 (1), 41.9 (8), 40.9 (50), 39.9 (11), 38.8 (60), 36.8 (3); ^{1}H NMR 1.72–1.79 (quartet, 6 H, CH_3-1 and -6), 5.30–5.41 (sextet, 1 H, CH-5), 5.60–5.73 (sextet, 1 H, CH-2), 5.92–6.01 (triplet, 1 H, CH-4), 6.30–6.40 (triplet, 1 H, CH-3).

cis,cis-2,4-Hexadiene (**23**) was also obtained from the plasma products in liquid phase: mass spectrum, *m/e* (relative intensity) 82.1 (41), 81.0 (7), 79.2 (9), 77.0 (5), 74.0 (1), 68.0 (6), 66.9 (100), 65.0 (16), 63.0 (5), 62.1 (2), 60.9 (1), 55.1 (8), 53.9 (20), 52.9 (22), 51.9 (7), 50.8 (16), 49.9 (12), 48.9 (2), 42.1 (8), 40.9 (46), 40.0 (12), 38.8 (67), 36.9 (2), 36.4 (2); ^{1}H NMR 1.66–1.69 (doublet, 6 H, CH_3-1 and -6), 5.42–5.53 (quintet, 2 H, CH-2 and -5), 6.17–6.28 (quartet, 2 H, CH-3 and -4),.

Results

Products. Reactions were performed by distilling the reactant through an inductively coupled radio frequency discharge and

collecting the products in a liquid nitrogen cooled trap. After some minutes, reaction was discontinued and the products were analyzed by gas chromatography. The flow rate and radiofrequency power were selected so that about 50% of the reactant was unchanged. Isolation of pure product components was followed by spectroscopic identification. The products of primary interest, which were the major volatile products, were isomers resulting from rearrangement reactions. In every case there were smaller amounts of unidentified byproducts, and polymer formation was observed on the walls of the reactor. Polymer was especially prevalent with 1,3-dienes.

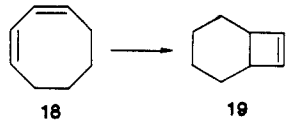
In each reaction of a 1,5-diene, one or more allylcyclopropanes were formed. These compounds were present as the major liquid products in the crude reaction mixture as seen by ^{1}H NMR. Compounds **7**, **9**, **11**, **12**, **14**, **15**, and **16** had been previously reported. In addition to an exact correspondence of ^{1}H NMR data of the isolated compounds with data from the literature, ^{13}C NMR and high-resolution MS results confirmed the structural assignments. No spectroscopic data were available for allylcyclopropanes **2** and **4**. The ^{1}H and ^{13}C NMR results were, however, as expected from the spectra of simpler alkyl- and dialkylcyclopropanes and alkylcyclopentenes. The attached-proton-test (APT) spectrum, which distinguished methylene from methine carbons,[11] confirmed the assignments.

The tricyclic isomer **5** also has not been reported previously, although the analogue **17** has been described.[9f,g] The ^{13}C NMR spectrum of **5** showed peaks at 21 and 51 ppm, which corresponded within 4 ppm to the two peaks previously observed for **17**,[12] and these two peaks were assigned to carbons b and d. The 11-ppm peak was appropriate for a methyl on a cyclobutane a, and the 31-ppm line was assigned to carbon c. Quaternary carbon e was found at 52.5 ppm. The APT spectrum was consistent with these assignments. The ^{1}H NMR of **5** showed a singlet with relative

17

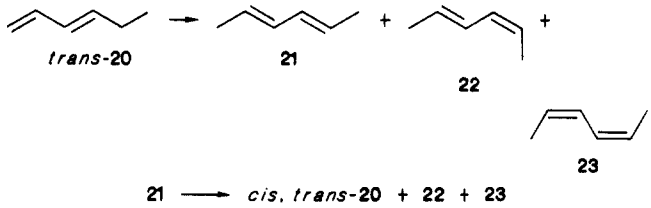
area of six due to the two equivalent methyl groups. There was a multiplet between 1.40 and 1.55 ppm (8 H) assigned to the hydrogens on carbons c and d as well as a triplet (2 H) assigned to the methine hydrogens on carbon b. In comparison to the model **17** (run in CCl_4 not $CDCl_3$)[9c] the triplet was shifted downfield by 0.5 ppm and the multiplet was downfield by about 0.2 ppm.

Plasma isomers were also formed from 1,3-dienes. 1,3-Cyclooctadiene gave the (2 + 2) addition product **19** identified by comparison with literature data. Two acyclic 1,3-hexadienes



18 **19**

were studied and the products, 1,3-hexadiene isomers, are shown.



trans-**20** **21** **22** **23**

21 ⟶ *cis, trans*-**20** + **22** + **23**

The plasma process simply interconverts all the 1,3-hexadiene isomers. It may be noted that such an isomerization process would only be visible for **18** if the very strained *cis,trans*-1,3-cyclooctadiene had been formed.

Reaction Rates. By using the same apparatus as above, the extent of conversion of reactant and the product yields were studied as a function of applied radio frequency power (P) and flow rate (r). In previous investigations it has been found that increasing the power gives higher conversion.[1] This results because the field strength is higher, the electrons are accelerated more, and these more energetic electrons cause more reactions. Increasing flow rate decreases the conversion. Two interrelated factors, shorter residence time and higher pressure, lead to this result. Several quantitative correlations of conversion with Pr^{-1} have been reported,[1,6,13] and it was of interest to know if this held for 1,5- and 1,3-dienes. Additionally, it was hoped that the yields of allylcyclopropane products could be maximized.

Table I. Conversion of **1** and Yield of **2** as P Is Varied[a]

P (W)	$10^2(1 - A/A_0)$[b]	**2**	yield (mol %)[c] of benzene
10	15.5	3	0.5
20	22.5	6	1
30	32.4	8	2
40	42.9	10	3
50	50.7	10	4
60	61.9	10	6
70	65.9	10	7
80	71.3	9	8
90	78.7	10	10

[a] $r = 0.94 \pm 0.04$ mmol min^{-1}. [b] A: amount of recovered starting material. A_0: total amount of starting material passed through the plasma zone. [c] Yield based on A_0.

Table II. Conversion of **1** and Yield of **2** as r Is Varied[a]

$1/r$ (min mmol^{-1})	$10^2(1 - A/A_0)$	**2**	yield (mol %) of benzene
0.26	1.6	2	0.2
0.34	1.9	2	0.3
0.54	8.8	4	0.5
1.05	18.5	7	1
1.42	27.1	9	2
2.20	37.9	12	3
2.63	45.2	14	3
3.84	57.8	16	4
4.66	65.7	18	5
4.95	70.9	18	6
7.79	84.9	16	7
11.38	92.2	12	7

[a] Power = 20 W.

The data in Tables I and II were obtained with 1,5-cyclooctadiene (**1**).

As shown in Figure 1, there is a linear relationship between log (A/A_0) and Pr^{-1}. Power variation with constant r gave a maximum yield of **2** of only 10%. At low power values, only a small amount of **1** was reacted and with high P values the products **2** became reactive. Benzene as well as polymer formation was favored by high P values. Similar variations were obtained when P was held constant and r was varied. A maximum yield of 18% was obtained by using a flow rate sufficient to convert about 30–35% of the reactant, i.e., **2** was ~60% of the product. Lower flow rates gave higher conversion but other products, while higher flow rates gave a cleaner reaction but low conversion. Following up on these results, it was decided to use a long tube (70.5 cm × 2.45 cm i.d.) and a long induction coil to increase the residence time, while maintaining low P and reasonable r. Thus, it was hoped that conversion and selectivity would be good. Unfortunately, the yields did not improve.

A similar study was performed with 1,5-hexadiene, and similar results were found (Table III and Figure 1). In this case the yield of allylcyclopropane **7** increased as r decreased but leveled off at about 11% (17% of the reacted amount of **6**).

The isomerization of **18** to **19** was also investigated (Table IV). High power again caused high conversion of **18**, but a decreased yield of **19**. A long residence time did not give very high yields because benzene and polymer were formed predominantly.

(11) Patt, S. L.; Shoolery, J. N. *J. Magn. Res.* **1982**, *46*, 535.
(12) Della, E. W.; Cotsans, E.; Hine, D. T.; Pigou, P. E. *Aust. J. Chem.* **1981**, *34*, 913.
(13) Tezuka, M.; Miller, L. L. *J. Am. Chem. Soc.* **1978**, *100*, 4201.

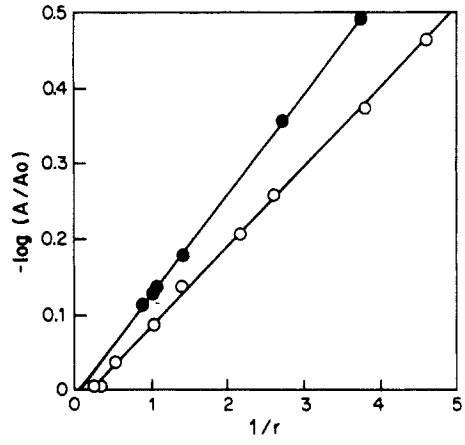
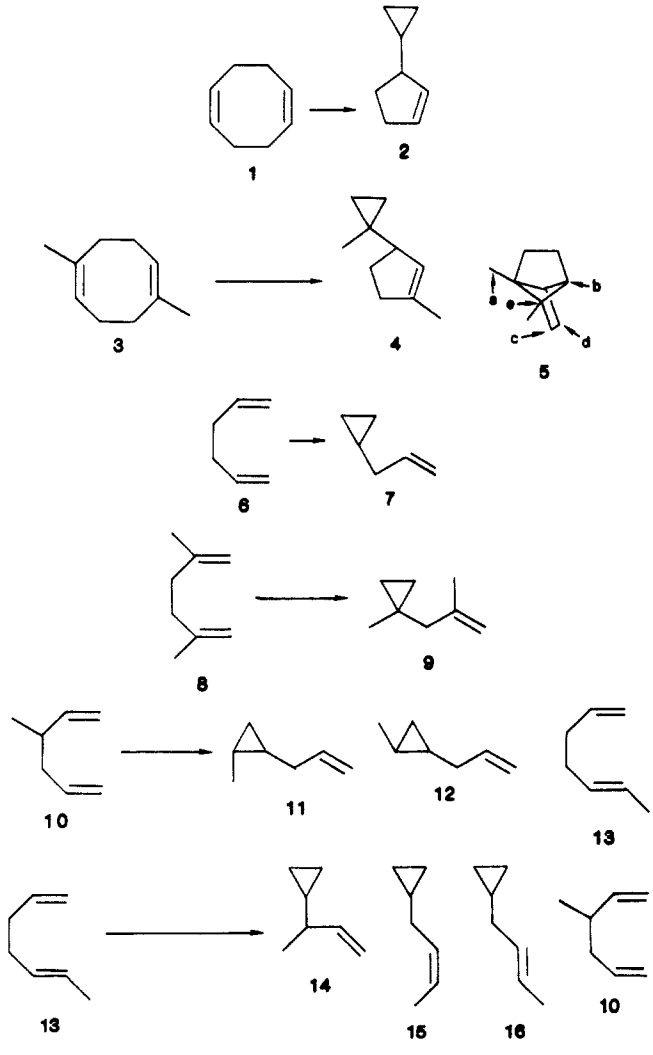


Figure 1. Reaction rate of **1** and **6** as flow rate is changed (power = 20 W): (○) 1,5-cyclooctadiene, $k = 5 \times 10^{-3}$ mmol/min·w, linearity = 0.999; (●) 1.5-hexadiene, $k = 6.8 \times 10^{-3}$ mmol/min·w, linearity = 0.9999.

Scheme I



However, a linear relationship was observed from $-\log (A/A_0)$ vs. r^{-1} (Figure 2).

Discussion

1,5-Dienes. Previous studies from this laboratory have shown the formation of cyclopropane products in radio frequency plasma chemistry,[6,14] and we were not surprised to find allylcyclopropanes from the 1,5-dienes that were studied. Krop and Manning[10] as well as Srinivasan and co-workers[9] had previously investigated photochemical reactions of these compounds and identified allylcyclopropane products.

(14) Tokuda, M.; Miller, L. L.; Szabo, A.; Suhr, M. *J. Org. Chem.* **1979**, *44*, 4504.

Table III. Conversion of **6** and Yield of **7** as r Is Varied[a]

$1/r$ (min mmol^{-1})	$10^2(1 - A/A_0)$[b]	yield (mol %)[c] of **11**
0.90	23.1	5
1.03	25.9	6
1.09	27.3	6
1.44	34.0	8
2.76	56.2	11
3.80	67.8	11

[a] Power = 20 W. [b] A: amount recovered starting material. A_0: amount passed starting material. [c] Based on A.

Table IV. Conversion of **18** and Yield of **19**

			yield (mol %)	
P(W)	$1/r$ (min mmol^{-1})	$10^2(1 - A/A_0)$	**19**	benzene
20	1.10	19.8	6	2
40	1.14	48.6	10	4
60	1.13	72.1	9	7
80	1.16	80.1	8	10
20	0.76	11.6	4	1
	1.10	19.8	7	2
	1.22	25.4	6	2
	1.67	37.2	8	2
	1.96	45.4	9	2
	2.17	46.0	9	2
	3.29	65.2	12	4
	4.18	74.8	13	5
	9.65	92.9	11	9

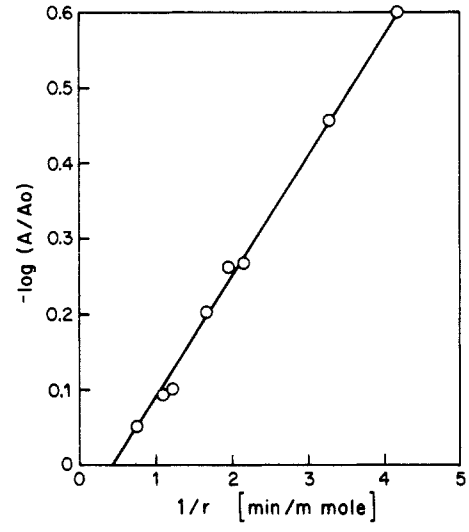
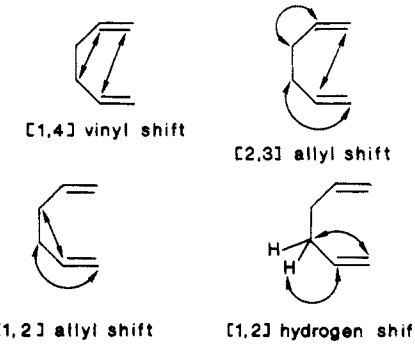
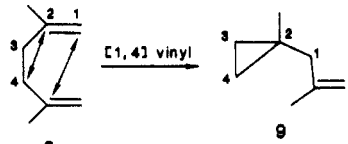


Figure 2. Reaction rate of **18** as flow rate is changed (power = 20 W): $k = 8 \times 10^{-3}$ mmol/min·w, $a = -0.0691$, linearity = 0.998.

Several mechanisms can be envisaged for the simplest reaction, formation of allylcyclopropane (**7**) from 1,5-hexadiene. Of these mechanisms it is easiest to first consider only concerted processes and to use the sigmatropic nomenclature to identify them. The four processes are

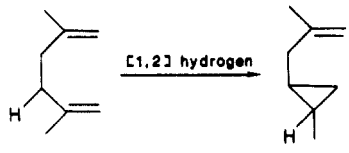


These mechanisms can be distinguished by labeling experiments, and in fact the products from the methyl-substituted compounds suggest that the 1,4 vinyl shift provides the only satisfactory mechanism. This mechanism leads to all the allylcyclopropane products observed and will not lead to other isomers which are not observed. For example, reaction of **8** via the [1,4] vinyl shift is predicted to give only **9**. A [2,3] or [1,2] allyl shift would also



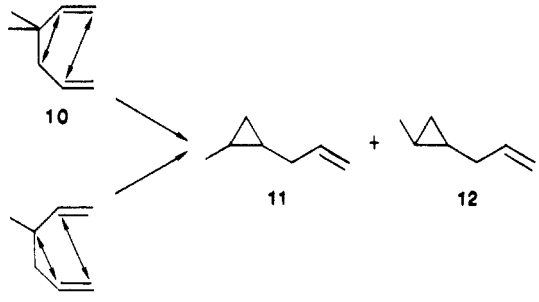
8 **9**

give this product, but [1,2]-hydrogen shift would lead to **24**, which was not observed.



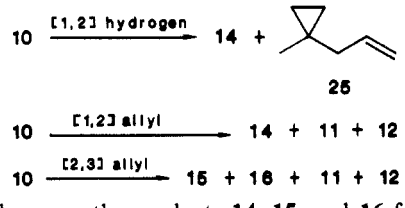
24

Reaction of **10** gives two major products, which are allylcyclopropanes, the cis and trans isomers **11** and **12**. This pair is expected from either of the two possible [1,4]-vinyl shift processes.

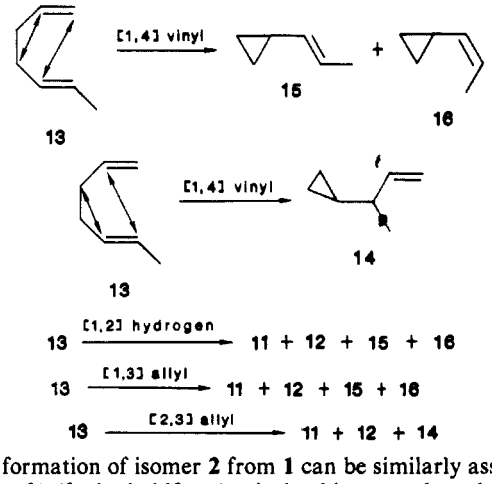


10 **11** **12**

In contrast, the other three possible mechanisms should lead to different sets of allylcyclopropane products, and products **14**, **15**, and **25** are not present in detectable amounts (<1%).



In a similar way, the products **14**, **15**, and **16** from **13** are uniquely associated with the [1,4] vinyl shift, not the other three mechanisms which would produce **11** and **12**. Compound **11** if present was less than 0.1% of the products.

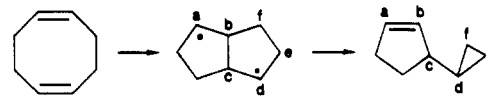


The formation of isomer **2** from **1** can be similarly associated with the [1,4] vinyl shift. Again in this case, the other three mechanisms lead to other isomers. 1,5-Dimethyl-1,5-cyclooctadiene presents the only variance from this set of [1,4] vinyl shifts. In this case the expected product from [1,4] vinyl shift, compound **4**, is formed, but in addition, the tricyclic product **5** is produced.

The mechanism of formation of **5** is particularly intriguing and will bring us to the question of diradical intermediates. It is first noted a photochemical conversion of **1** to **17** is analogous to the **3** to **5** radio frequency process and that these reactions could be concerted (2 + 2) cycloadditions. The isolation of the strained tricyclic product **5** from only the methyl-substituted reactant, but not from **1**, may be related to observations that bulky alkyl substituents favor cyclizations to isolable strained ring systems, when the alkyl groups end up at quaternary, bridgehead carbons, e.g., cyclization to tetra-*tert*-butyltetrahedrane.[15]

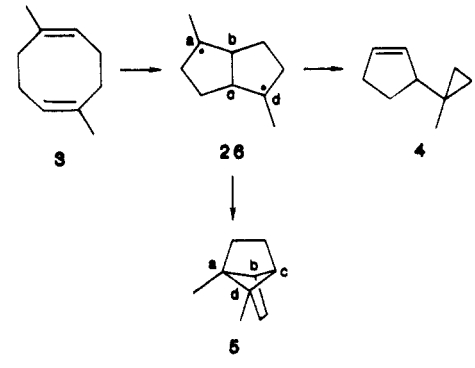
Alternatively, the change in products can be visualized as resulting from a perturbation of a diradical mechanism, which would otherwise lead to net [1,4] vinyl shift. If bond making precedes bond breaking and if the resulting diradical is an energy minimum, the [1,4] vinyl shift mechanism becomes two steps, still leading to the same isomerization products from each reactant.

Thus, **1** could rearrange in a stepwise fashion as follows.



1 **2**

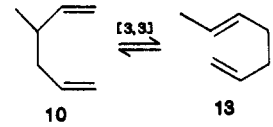
A similar intermediate (**26**) from **3** can give **4**, but can also produce **5**. In this process the methyls can directly perturb the radical centers and cause a change in reaction pathway.



3 **26** **4**

5

We turn our attention now to the origin of the byproducts, **10** and **13**.[16] Since **10** leads to **13** and vice versa, a mechanism unrelated to the allylcyclopropane reaction could be involved. One such mechanism is a [3,3] sigmatropic rearrangement. An alternative, since cleavage products are also found, is that **10** and



10 **13**

13 cleave the allylic bond forming an allyl and a methylallyl radical, which can recombine. If this was the case, cross-coupled products, 1,5-hexadiene and dimethyl-1,5-hexadienes, would be formed in roughly equivalent amounts. The former was in fact present as expected and a fragmentation–recombination mechanism remains a viable explanation.

In general, the major isomers formed from 1,5-dienes can all be explained by intramolecular, concerted, or equivalent diradical processes, and the allylcyclopropane products are well explained by the [1,4] vinyl shift mechanism, which could proceed in a

(15) Meier, G.; Pfriem, S.; Schafer, U.; Matusch, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 520.

(16) The cis isomer of **13**, if present, was in much smaller yield than from **10**. The thermal Cope rearrangment of **10** gave both isomers. Thermally, *trans*-**13** was formed about four times faster than *cis*-**13**.[17]

(17) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

concerted fashion, allowed by orbital symmetry considerations via an excited state rearrangement.

Because the observed kinetics have the same form observed for other radio frequency plasma processes, it seems appropriate to consider these rearrangements as part of the paradigm[1] which invokes electron impact induced electronic excitation and major product formation via neutral species. However, because the yields are low one cannot be sure of mechanistic conclusions based on product structures or yields. Indeed, in this case it is possible that ionic intermediates are involved or that the light generated as a product from some other plasma process gives indirect photolytic conversions.

A comparison with the work of Kropp and Manning[10] is appropriate and reveals some important differences. In both photolysis and plasmolysis, allylcyclopropanes are the major isomers formed from 1,5-dienes. The products from the heptadienes **9** and **10** are, however, not the same. Photolysis gives mixtures in which [1,2] allyl shift not [1,4] vinyl shift products are present in larger amounts. Furthermore, the photoproducts from **1**[9,10] are entirely different from the plasma products. Perhaps there would be a closer correspondence of products if the photolyses were performed in the gas phase at low wavelength (see footnote 16 of ref 10).

1,3-Dienes. The acyclic 1,3-dienes simply undergo allylic isomerization, interconverting the various 1,3-hexadienes. These reactions are reminiscent of the 2-butene to 1-butene radio frequency isomerization.[5] *cis,cis*-1,3-Cycloocadiene (**18**) gives quite different chemistry which is reminiscent of the UV photolysis result. It is recognized, of course, that allylic isomerization of **18** may be occurring undetected and that the 2 + 2 cycloaddition process is distinctly favored by the s-cis conformation of **18.**

Summary. The radio frequency chemistry of alkenes and dienes forms a consistent set. Linear $\log A/A_0$ vs. Pr^{-1} relationships are usually found, and isomerizations, fragmentations, and polymerizations are dominant. Isomerizations are more prevalent in cooler (low Pr^{-1}) plasmas. Simple alkenes and 1,3-dienes isomerize by cis, trans and allylic-type rearrangements; 1,4-dienes give vinylcyclopropanes and 1,5-dienes give allylcyclopropanes. There are correlations in many cases with photochemistry, and it seems possible that photolysis in the gas phase at low wavelength and at the same pressure used for radio frequency chemistry would give an even more thorough correlation.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. 1, 111-78-4; **2**, 45531-46-2; **3**, 3760-14-3; **4**, 103240-53-5; **5**, 103240-54-6; **6**, 592-42-7; **7**, 4663-23-4; **8**, 627-58-7; **9**, 76589-01-0; **10**, 1541-33-9; **11**, 76588-97-1; **12**, 76588-95-9; **13**, 1541-23-7; **14**, 76588-96-0; **15**, 76588-99-3; **16**, 76588-98-2; **18**, 1700-10-3; **19**, 616-10-4; **20**, 592-48-3; **21**, 5194-51-4; **22**, 5194-50-3; **23**, 6108-61-8.

Bimolecular Chemistry of Macromolecules: Synthesis of Bacterial Polysaccharide Conjugates with *Neisseria meningitidis* Membrane Protein

S. Marburg,*† D. Jorn,† R. L. Tolman,† B. Arison,† J. McCauley,† P. J. Kniskern,‡ A. Hagopian,‡ and P. P. Vella‡

Contribution from the Merck Sharp & Dohme Research Laboratories, Rahway, New Jersey 07065, and Merck Sharp & Dohme Research Laboratories, West Point, Pennsylvania 19486. *Received November 20, 1985*

Abstract: Covalently linked macromolecules of biological importance (bacterial-polysaccharide conjugates) are prepared by a general, multistep synthetic method employing a bigeneric spacer that is an oligopeptide spacer molecule whose parts are derived from each of the two modified macromolecules to be covalently linked. The strengths of this synthetic approach are (a) the covalency of the resulting conjugate is readily and absolutely determined and (b) analysis for the bigeneric spacer defines the purification of the conjugate and facilitates the identification of separation procedures that remove contaminating, unconjugated macromolecules. The multistep bigeneric spacer method includes the following steps: (1) covalent modification of one macromolecule to attach basic amine groups that are then bromoacetylated; (2) covalent modification of the second macromolecule with *N*-acetylhomocysteine thiolactone to attach pendant thiol groups; (3) coupling of these macromolecules under mildly basic conditions; (4) determination of the covalency ratio by amino acid analysis of *S*-(carboxymethyl)homocysteine, formed by reaction of bromoacetyl and homocysteinyl moieties, relative to a standard endogenous amino acid; (5) purification of the mixture to maximize the covalency ratio. By this method several conjugates of polydisperse bacterial polysaccharides with an immunogenic *Neisseria meningitidis* membrane protein were prepared and characterized by NMR and chemical analysis.

It has become clear that biological macromolecules have different domains that are independently responsible for such diverse functions as receptor recognition, cell entry, effector control, and effector activity. Moreover, these domains are often physically separable, and appreciation of this fact has generated an increasing body of research devoted to preparing hybrid macromolecules that combine particular properties in a desired way. Thus, the so-called immunotoxins or "magic bullets" seek to destroy cancer cells with high specificity by combining the recognition power of antibodies with highly toxic effector molecules (toxins).[1] A synthetic blood substitute has been prepared by binding an altered hemoglobin molecule to the polysaccharide inulin.[2] Modified hormonal responses have been obtained by coupling insulin to macromolecules

† Rahway, NJ.
‡ West Point, PA.

(1) Uhr, J. S.; Vitetta, E. S. *Monoclonal Antibodies and Cancer*; Boss, B. D., Langman, R., Trobridge, I., Dulbecco, R., Eds.; Academic: Orlando, FL, 1983; pp 85-98.
(2) Iwasaki, K.; Ajisaka, K.; Iwashita, Y. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 513-518.

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