removed and cooled to −15 °C. This produced colorless, analytically pure crystals of 2-methylene-1,3-propanediylbis[triphenylstannane] (4): 900 mg (1.2 mmol, 30%); mp 121–122 °C; IR (KBr) 1610, 720, 690 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 2.32 (s, 4 H), 4.59 (s, 2 H), 7.3 (m, 30 H); mass spectrum (CI), *m/e* 679, 405, 351, 274. Anal. Calcd for C₄₀H₃₆Sn₂: C, 63.71; H, 4.81; Sn, 31.48. Found: C, 63.69; H, 5.05; Sn, 31.64.

2-Methylene-1,3-propanediylbis[trimethylstannane] (5). Under dry Ar at −20 °C, a stirred solution of hexamethyldistannane (290 mg, 0.89 mmol) in THF (5 mL) was treated dropwise with a solution of methyllithium (0.71 mL, 1.25 M in ether, 0.89 mmol).¹⁶ The cold yellow mixture was stirred for 20 min, treated with 3-chloro-2-(chloromethyl)-1-propene (54 mg, 0.43 mmol), and then kept at 25 °C for 36 g. Volatiles were removed by evaporation under reduced pressure, and the residue was partitioned between water (5 mL) and CH₂Cl₂ (20 mL). The organic phase was dried over anhydrous Na₂CO₃, and solvent was removed by evaporation under reduced pressure. Molecular distillation of the residue provided an analytically pure sample of 2-methylene-1,3-propanediylbis[trimethylstannane] (5): colorless liquid; 135 mg (0.35 mmol, 81%); bp 95 °C (760 torr); IR (liquid film) 1610, 1275, 830, 760 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 0.10 (s, 18 H), 1.67 (s, 4 H), 4.22 (s, 2 H); mass spectrum (CI, isobutane), *m/e* 384, 369, 205, 165. Anal. Calcd for C₁₀H₂₄Sn₂: C, 31.47; H, 6.34; Sn, 62.19. Found: C, 30.81; H, 6.08.

Reaction of 2-Methylene-1,3-propanediylbis[triphenylstannane] (4) with CCl₄. A solution of 2-methylene-1,3-propanediylbis[triphenylstannane] (4; 150 mg, 0.199 mmol) and AIBN (8 mg, 0.05 mmol) in CCl₄ (2.0 ml) was warmed at 70 °C for 60 h. Solvent was then removed by evaporation under reduced pressure, and the residue was dissolved in ether (25 mL) and washed with a solution of KF (10 mL, 0.1 N) in aqueous methanol (1:1). Filtration separated a fine, white precipitate of triphenyltin fluoride (123 mg, 0.333 mmol, 83.7%). The organic phase was dried, and solvent was removed by evaporation under reduced pressure. Preparative thin-layer chromatography (silica, CCl₄) separated the residue into two components.

One was a colorless solid, (4,4,4-trichloro-2-methylenebutyl)triphenylstannane (8): 18.6 mg (0.0356 mmol, 17.9%); R_f (0.88). Two recrystallizations from petroleum ether (bp 35–60 °C) yielded an analytically pure sample: mp 60–61 °C; IR (KBr) 1620, 1420, 1070, 720, 700, 690 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 2.77 (s, 2 H), 3.18 (s, 2 H), 4.96 (s, 1 H), 5.16 (s, 1 H), 7.3–7.7 (m, 15 H); mass spectrum (EI), *m/e* 351, 197, 154, 120. Anal. Calcd for C₂₃H₂₁Cl₃Sn: C, 52.87; H, 4.05. Found: C, 52.87; H, 4.14.

The other component was a colorless liquid, 1,1,1,5,5,5-hexachloro-3-methylenepentane (7): 37.5 mg (0.129 mmol, 64.8%); R_f 0.93. Molecular distillation provided an analytically pure sample: bp 45 °C (24 torr); IR (liquid film) 1650, 1000, 940, 820, 775, 710, 655 cm⁻¹; ¹ H NMR (90 MHz, CDCl₃) δ 3.71 (s, 4 H), 5.73 (s, 2 H); mass spectrum (CI), *m/e* 217, 181, 157, 143, 121. Anal. Calcd for C₆H₆Cl₆: C, 24.78; H, 2.08; Cl, 73.14. Found: C, 24.88; H, 2.08; Cl, 73.21.

Acetolysis of 2-Methylene-1,3-propanediylbis[triphenylstannane] (4). A solution of 2-methylene-1,3-propanediylbis[triphenylstannane] (4; 58 mg, 0.077 mmol) in CHCl₃ (1 mL) was treated with 2 drops of glacial acetic acid and kept at 25 °C for 40 h. Volatiles were then removed by evaporation under reduced pressure. The residue was dissolved in CH₂Cl₂ and applied to a column of neutral alumina (activity I, 0.25 in. × 1 in.), which was eluted with CH₂Cl₂ (30 mL). Evaporation of the eluate, followed by sublimation of the residue at 60 °C (0.08 torr), yielded pure (2-methyl-2-propenyl)triphenylstannane (13; 27 mg, 0.067 mmmol, 87%), which was identical by NMR and IR with an authentic sample.¹⁷

Reaction of 2-Methylene-1,3-propanediylbis[trimethylstannane] (5) with CCl₄. A solution of 2-methylene-1,3-propanediylbis[trimethylstannane] (5; 32 mg, 0.084 mmol) and AIBN (4 mg, 0.02 mmol) in CCl₄ (0.25 mL) was warmed at 70 °C for 60 h. Solvent was then removed by evaporation under reduced pressure, and the residue was dissolved in ether (20 mL). Treatment of this solution with water (20 mL) containing 4 drops of CF₃COOH destroyed traces of intermediate 16, which were

otherwise difficult to remove. The organic phase was washed with water and dried, and solvent was removed by evaporation under reduced pressure. Preparative thin-layer chromatography (silica, CCl₄) of the residue provided pure 1,1,1,5,5,5-hexachloro-3-methylenepentane (7): 15 mg (0.052 mmol, 62%).

3-(Trimethylstannyl)-2-[(trimethylstannyl)methyl]-1-propanol (17). Under dry Ar at 25 °C, a solution of 2-methylene-1,3-propanediylbis[trimethylstannane] (5; 68 mg, 0.18 mmol) in THF (1 mL) was treated with a solution of borane in THF (0.10 mL, 1.0 M, 0.10 mmol). After 18 h, aqueous NaOH (0.1 mL, 2.4 N, 0.24 mmol) and aqueous H₂O₂ (0.075 mL, 30%, 0.66 mmol) were added. Then the mixture was warmed at 40 °C for 1 h and partitioned between CH₂Cl₂ (50 mL) and aqueous NaCl (10 mL). The organic phase was dried, and solvent was removed by evaporation under reduced pressure. Molecular distillation of the residue provided an analytically pure sample of 3-(trimethylstannyl)-2-[(trimethylstannyl)methyl]-1-propanol (17): colorless liquid; 48 mg (0.12 mmol, 67%); bp 65 °C (0.8 torr); IR (liquid film) 3300, 2950, 2900, 1040, 760 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 0.08 (s, 18 H), 0.87 (m, 4 H), 2.10 (m, 1 H), 3.4 (m, 2 H); mass spectrum (CI, isobutane), *m/e* 385, 369, 205, 165. Anal. Calcd for C₁₀H₂₆OSn₂: C, 30.05; H, 6.56; Sn, 59.39. Found: C, 30.65; H, 6.49.


Thermal Rearrangement of Allenyl Ketones

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The thermal rearrangement of acetylenic ketones to cyclopentenones has been studied carefully, and all the available evidence points to an alkylidene carbene intermediate as illustrated in eq 1.¹ In view of the similarities
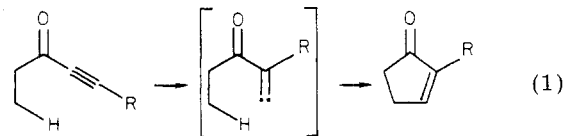
between acetylenes and allenes in many reactions, we felt it would be of interest to examine the behavior of allenyl ketones at high temperatures.

When 3,4-pentadien-2-one (1a) was pyrolyzed in a flow system at a series of temperatures, the onset of reaction was noted at 433 °C, and complete reaction occurred at 520 °C. A single product was formed in 72% yield,² which was identified as 2-methylfuran (2a) by comparison of its
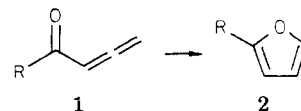
a, R = Me; b, R = Et; c, R = *t*-Bu; d, R = Ph

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(2) Yields are VPC yields, as determined by use of an internal standard.

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spectroscopic properties with literature values.[3-5] Similarly, 2-ethylfuran (2b) was obtained in 72% yield[2] from 4,5-hexadien-3-one (1b). 2-*tert*-Butylfuran (2c) and 2-phenylfuran (2d) were obtained from the corresponding ketones, 1c and 1d, in 78% and 67% yields, respectively.

Two reasonable mechanisms can be envisaged for the rearrangement; both involve a vinylcarbene intermediate and a 1,2 hydrogen shift but differ in the timing of the steps. The first one, illustrated in eq 2, involves initial
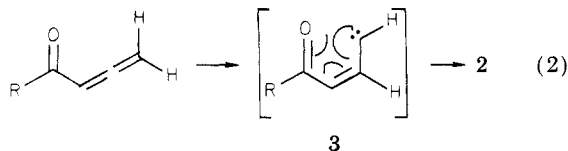

hydrogen migration to give 3 followed by ring closure. Formation of 3 is analogous to the first step of a mechanism which has been proposed for the isomerization of allene to propyne.[6,7] Ring formation giving the carbene 4 is the initial step in the second mechanism (eq 3), and subsequent 1,2 hydrogen migration completes the sequence.
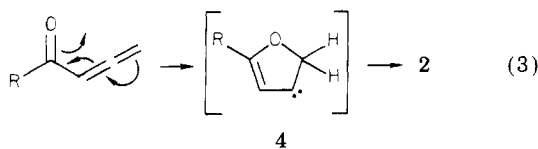
We have no firm basis for choosing between the two mechanisms, although it would seem that if carbene 3 were involved, some products arising by insertion into C–H bonds of the R group might be anticipated. This would be true especially for the *tert*-butyl derivative 1c, in which there are nine suitably located C–H bonds, and for the phenyl derivative 1d. We were unable to detect the C–H insertion products in the pyrolysates. It is possible, of course, that the large aromatic stabilization of furan provides such a strong driving force that the insertion reactions cannot complete.

5-Methyl-3,4-hexadien-2-one (5) and 6-methyl-4,5-heptadien-3-one (6) failed to rearrange at 540 °C and instead
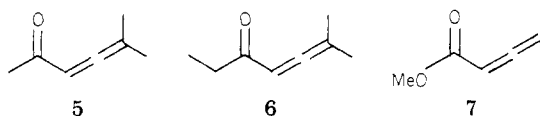
gave only complex mixtures of fragmentation products. Formation of furan derivatives from these ketones would require methyl group migration, and it is known that alkyl groups migrate much less readily than hydrogen in rearrangements involving carbenes.[8]

When methyl 2,3-butadienoate (7) was pyrolyzed at 490 °C, it was recovered unchanged; at 540 °C and above, reaction occurred, but a complex mixture of decomposition products was produced. There was no evidence for the anticipated product, 2-methoxyfuran.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 237 spectrophotometer, and NMR spectra were obtained on a JEOL FX90Q spectrophotometer. VPC analyses were carried out with an F&M 720 gas chromatograph.

Starting Materials. 4-Pentyn-2-one, prepared by oxidation of 4-pentyn-2-ol according to the procedure of Brandsma and Verkruijsse, was stirred with aqueous sodium bicarbonate at 40 °C for 30 min, giving crude 3,4-pentadien-2-one (1a): 60% yield; bp 54–58 °C (60 mm).[9] Purification of this material by preparative VPC (OV-1, 60 °C) gave a product whose IR spectrum corresponded to the recorded spectrum;[10] ^{1}H NMR (CDCl$_3$) δ 2.26 (s, 3 H), 5.25 (d, 2 H, J = 6.3 Hz), 5.78 (t, 1 H, J = 6.3 Hz); ^{13}C NMR δ 217.2, 198.3, 97.3, 79.3, 26.6.

From the reaction of propargylmagnesium bromide with ethyl propionate according to the procedure of Couffignal and Gaudemar,[11] there was obtained in 29% yield a mixture of 4,5-hexadien-3-one (1b) and 5-hexyn-3-one, bp 58–60 °C (40 mm). Treatment of this mixture with aqueous NaHCO$_3$,[9] followed by preparative VPC (OV-1, 90 °C) afforded pure 1b, bp 58–60 °C (40 mm). The IR spectrum of this material agreed with the recorded spectrum:[10] ^{1}H NMR (CDCl$_3$) δ 1.08 (t, 3 H, J = 7.3 Hz), 2.64 (q, 2 H, J = 7.3 Hz), 5.23 (d, 2 H, J = 6.3 Hz), 5.78 (t, 1 H, J = 6.3 Hz); ^{13}C NMR δ 216.4, 201.2, 96.2, 79.2, 32.5, 8.3.

2,2-Dimethyl-4,5-hexadien-3-one (1c), synthesized by the method of Pillot et al., exhibited IR and ^{1}H NMR spectra in agreement with those reported:[12] ^{13}C NMR δ 215.4, 204.0, 90.8, 78.9, 44.3, 26.5.

1-Phenyl-2,3-butadien-1-one [1d; bp 115–125 °C (1 mmHg, Kugelrohr)] was obtained in 75% yield by treating 1-phenyl-3-butyn-1-one[13] with aqueous NaHCO$_3$ at 40 °C for 30 min.[9] This material exhibited IR and ^{1}H NMR properties in agreement with those reported:[14] ^{13}C NMR δ 217.0, 190.9, 137.4, 132.7, 128.6, 128.3, 93.2, 79.2.

5-Methyl-3,4-hexadien-2-one (5), synthesized from 3-methyl-1,2-butadienylmagnesium bromide and ethyl acetate,[11] exhibited IR and ^{1}H NMR spectra which agreed with those reported:[15] ^{13}C NMR δ 211.4, 203.1, 99.8, 96.1, 26.4, 19.4. Similarly, the IR and ^{1}H NMR spectra of 6-methyl-4,5-heptadien-3-one (6), synthesized from 3-methyl-1,2-butadienylmagnesium bromide and ethyl propionate,[11] agreed with the literature report:[15] ^{13}C NMR δ 210.5, 202.7, 99.7, 94.9, 32.2, 19.3, 8.6. The spectroscopic properties of methyl 2,3-butadienoate (7) agreed with those reported.[16]

Thermal Rearrangements. The thermal rearrangements were carried out in a conventional flow system similar to the one previously described.[17] The reaction chamber was constructed of quartz tubing (1.9 cm i.d.) with a heated zone ca. 50 cm long. Liquid samples, customarily in the range 100–150 μL, were delivered by a motor-driven syringe at a rate of 1.7 mL/h. Products were collected in a receiver which was cooled in a dry ice–acetone bath. Helium served as the carrier gas, and flow rates of ca. 100 mL/min were used for all the experiments. Experiments carried out at a series of temperatures showed that detectable rearrangement occurred at ca. 430–450 °C and was complete at ca. 520 °C. Preparative experiments were carried out at 520 °C. The structures of the products were determined by IR and NMR spectroscopy, and yields were determined by VPC by using internal standards as follows: 2a, pentane; 2b, hexane; 2c, benzene; 2d, butylbenzene.

Registry No. 1a, 2200-53-5; 1b, 2200-54-6; 1c, 27552-18-7; 1d, 69626-39-7; 2a, 534-22-5; 2b, 3208-16-0; 2c, 7040-43-9; 2d, 17113-33-6.

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