served preferred formation of the isomer **14a** shows that in this case steric factors must play the most important role.

An alternative way to rationalize the observed regioselectivities is given by a simple qualitative frontier approach. CNDO/2 computations indicate a lowering of LUMO energy and, to a greater extent, of HOMO energy in going from **1** to **2**. CNDO/2 and EH computations suggest that sulfones are less nucleophilic than sulfoxides. In fact, the values of the energies, $-E_{HOMO}$ (eV), of sulfones are in the range 12.1–12.9 (CNDO/2) and 11.2–11.5 (EH) and those of sulfoxides are in the ranges 11.6–12.1 (CNDO/2) and 10.68–10.72 (EH).

Thus, one can reasonably argue that the reactions of **1** are essentially dipole HOMO controlled, while those of **2** involve also the interaction dipole LUMO–dipolarophile HOMO, whose importance increases in going from sulfones to sulfoxides. As a consequence, the observed preferences of **1** to give the R_5 isomer can be well rationalized. In fact, in the interaction nitrilimine HOMO–dipolarophile LUMO, the larger coefficients lead in every case to the R_5 isomers, and this tendency increases according to the sequence Me < Ph < PhCO in correspondence of the lowering of the dipolarophile LUMO energy.

The increase of the propensity to give R_5 isomers in going from sulfoxides to sulfones is attributable to the greater polarization of LUMO's that occurs in the latter case. For the reactions involving **2**, the experimental results could be rationalized taking into account the interaction dipole LUMO–dipolarophile HOMO. Unfortunately, the values of the coefficients in the dipolarophile HOMO's are poorly meaningful, since these frontier orbitals are scarcely localized on the vinylic double bond. Thus, it is impossible to determine the consequences of such an interaction. In conclusion, both approaches help to understand the origin of the observed regioselectivity, showing the important role of both polar and frontier charge-transfer interactions.

Experimental Section

All melting points were determined on a Büchi apparatus and are uncorrected. NMR spectra were recorded on Varian A-60 and EM-390 spectrometers with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard; chemical shifts are given in δ units: s = singlet; d = doublet; m = multiplet; dd = double doublet.

Dipolarophiles. Sulfinyl- and sulfonylalkenes were prepared according to standard procedures.[3a,15]

Dipoles. 1-(α-Chlorobenzal)-2-phenylhydrazine (**1**)[6] and 3,5-dichloromesitylnitrile oxide (**2**)[10] were already known and were prepared according to the reported methods.

Reaction of Compound 1 with Compound 3: General Method. Triethylamine (0.04 mol) was added to a solution of (phenylsulfinyl)alkenes (0.01 mol) and α-chlorobenzaldehyde phenylhydrazone (0.01 mol) in benzene (100 mL), and the mixture was refluxed for 20 h (see Table I). The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with benzene gave the products listed in Table I.

Reaction of Compound 1 with Compound 4: General Method. Triethylamine (0.01 mol) was added to a solution of (phenylsulfonyl)alkenes (0.01 mol) and α-chlorobenzaldehyde phenylhydrazone (0.01 mol) in benzene (50 mL), and the mixture was allowed to stand at room temperature for several hours (see Table I). The benzene solution was washed with water and dried (Na_2SO_4). The solvent was evaporated off, and the residue was chromatographed on silica gel. Elution with toluene gave the products listed in Table I. The reaction of **1** with **4a** gave also as side product 1,2-bis(phenylsulfonyl)ethane.[16]

Reaction of Compound 2 with Compound 3: General Method. 3,5-Dichloromesitylnitrile oxide (0.01 mol) and (phenylsulfinyl)alkenes (0.01 mol) were dissolved in benzene (80 mL) and refluxed, under nitrogen, for variable times (see Table II). After the mixture was cooled, the *N,N'*-bis(3,5-dichloro-2,4,6-trimethylphenyl)urea[13b] was filtered off, the solvent was evaporated, and the residue was chromatographed on silica gel. Elution with benzene gave the product listed in Table II. The reaction of **2** with **3a** gave also as a side product the 1,2-bis(phenylsulfinyl)ethane.

Reaction of Compound 2 with Compound 4: General Method. A solution of **2** (6 mmol) and **4** (6 mmol) in benzene (60 mL) was refluxed for the time indicated in Table II. The solvent was removed under reduced pressure and the residue was worked up as follows. In the case of **4a**, recrystallization of the crude product from benzene–hexane gave **14a** in 60% yield; the residue from the mother liquor was chromatographed on a silica gel column, with diisopropyl ether as eluant, to afford a further amount of **14a** (13%), followed by **13a** (7%). When starting from **4b**, the product mixture was chromatographed on a silica gel column, with 95:5 benzene–ethyl acetate as an eluant, to give some uncharacterized material, followed by **13b** (54%); further elution gave **14b** (6%). In the case of **4c**, fractional recrystallization of the crude product from benzene–hexane afforded pure **13c**; attempted isolation of **14c** by chromatographic methods was unsuccessful. In the case of **4d**, the crude product was recrystallized from diisopropyl ether–pentane to give a 1:1 mixture of **13d** and **14d**. The residue from the mother liquor was submitted to repeated recrystallizations from diisopropyl ether–ethanol to give **13d**; column chromatography on silica gel of the 1:1 mixture of **13d** and **14d** resulted in a 1:1 mixture of **15d** and **16d**.

Acknowledgment. We thank the C.N.R. (Rome) for financial support.

Registry No. **1**, 15409-32-2; **2**, 13456-86-5; **3a**, 20451-53-0; **3b**, 67652-99-7; **3c**, 40110-66-5; **3d**, 66287-01-2; **4a**, 5535-48-8; **4b**, 28691-72-7; **4c**, 16212-06-9; **4d**, 960-41-8; **7c**, 86729-03-5; **13a**, 86747-53-7; **13b**, 86729-04-6; **13c**, 86729-05-7; **13d**, 86729-06-8; **14a**, 86729-07-9; **14b**, 86729-08-0; **14c**, 86729-09-1; **14d**, 86729-10-4; **15a**, 86729-11-5; **15b**, 86729-12-6; **15d**, 86729-13-7; **16b**, 86729-14-8; **16c**, 86747-54-8; **16d**, 86729-15-9.

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Allylstannanes. Synthesis, Structure, and Reactions of 2-Methylene-1,3-propanediylbis[trimethylstannane] and -[triphenylstannane]

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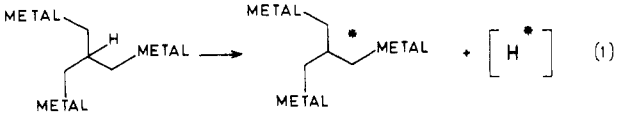
Received January 13, 1983

Compounds in which a carbon–hydrogen bond is adjacent to several carbon–metal bonds promise to be good reducing agents, since transfer of hydrogen may produce a carbocation or a radical highly stabilized by hyperconjugation (eq 1).[1,2] This promise is fulfilled by stannane



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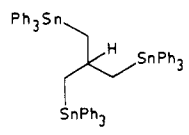
2 and particularly by stannaadamantane 3, which can re-



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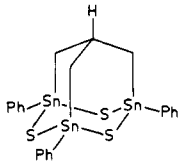

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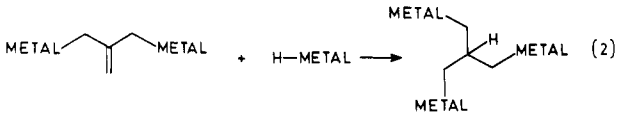
duce alkyl halides to the corresponding hydrocarbons.[3] In principle, tris(metallomethyl)methanes (1) can be synthesized by hydrometalation (eq 2). For example, the



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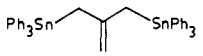

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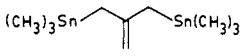
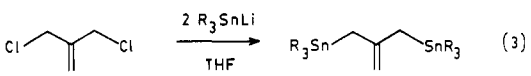


5

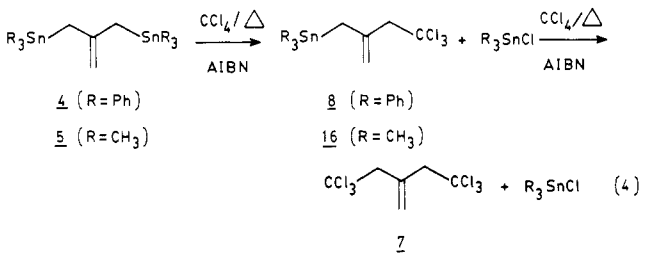
hypothetical addition of triphenyltin hydride to 2-methylene-1,3-propanediylbis[triphenylstannane] (4) would produce stannane 2. Although this approach to the synthesis of compound 2 was in fact unsuccessful, the growing importance of allylstannanes in organic synthesis[4] warrants the following description of the preparation and reactivity of compound 4 and a close relative, 2-methylene-1,3-propanediylbis[trimethylstannane] (5).

Stannanes 4 and 5 were synthesized by the addition of 3-chloro-2-(chloromethyl)-1-propene (6) to solutions of (triphenylstannyl)lithium or (trimethylstannyl)lithium (eq 3). Purification of compound 4 required direct crystallization from hexane, while compound 5 was purified by distillation.



6

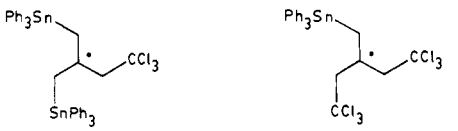
Triphenylstannane 4 resisted radical or electrophilic attack. For example, when mixtures of compound 4 and triphenyltin hydride were heated (AIBN, 75 °C) or irradiated (medium-pressure Hg lamp), the product of addition 2 was not formed.[5] However, a radical reaction with carbon tetrachloride slowly converted triphenylstannane 4 into 1,1,1,5,5,5-hexachloro-3-methylenepentane (7) in 65% yield (eq 4).[6] Triphenyltin chloride, isolated as the



4 (R = Ph)
5 (R = CH3)
8 (R = Ph)
16 (R = CH3)

7

fluoride in 84% yield, is the other final product of this reaction, and (4,4,4-trichloro-2-methylenebutyl)triphenylstannane (8) is formed as an intermediate. Study of the progress of this reaction by NMR showed that substantial amounts of the final product 7 are formed from intermediate 8 before the starting material 4 is completely consumed; that is, the first substitution of triphenylstannyl by trichloromethyl is not dramatically faster than the second. This observation is important because it helps distinguish between stepwise and concerted mechanisms of radical substitution in allylstannanes. Stepwise addition of trichloromethyl to allylstannanes 4 and 8 would produce intermediate radicals 9 and 10, which in principle would



9 10

enjoy different amounts of hyperconjugative stabilization by carbon–tin bonds.[2,7] If the effect of the 2,2,2-trichloroethyl group on the stability of these radicals is negligible[8] and if all of the carbon–tin bonds can achieve an orientation which permits hyperconjugative stabilization, then radical 9 should be more stable than radical 10, and the first substitution should therefore be significantly faster than the second. In contrast, if addition of trichloromethyl and loss of triphenylstannyl are concerted, the first and second substitutions should occur at similar rates. Although this is what we observe, we cannot exclude the stepwise mechanism. The large triphenyltin groups[9] presumably force triphenylstannane 4 to adopt conformations similar to the enantiomeric C_2 structures 11 and 11′,[10] in which both faces of the double bond are sterically shielded.[11] As a result, the first stepwise addition of

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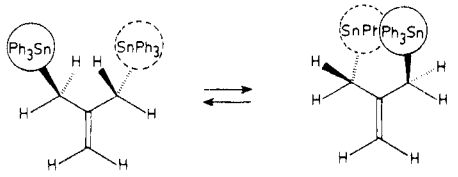
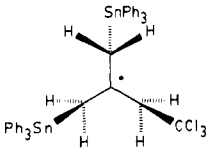


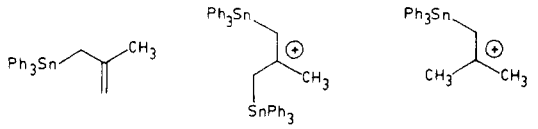
11 11′



12

trichloromethyl might be favored electronically but retarded by the low accessibility of the double bond. Alternatively, interactions of the triphenyltin and trichloromethyl groups may prevent radical **9** from adopting conformations like **12** in which hyperconjugation is maximized.[12]

Triphenylstannane **4** was not affected by excess borane or 9-borabicyclo[3.3.1]nonane at 25 °C in THF,[13] but it reacted readily with smaller electrophiles like the proton.[14] For example, although compound **4** was inert toward pyridinium chloride or triethylammonium bromide at 25 °C in chloroform, it was rapidly converted into isobutylene by exposure to mineral acids or silica gel and into (2-methyl-2-propenyl)triphenylstannane (**13**) in 87% yield

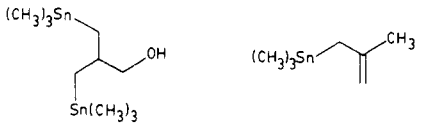


13 14 15

by the action of acetic acid at 25 °C. Study of the acetolysis by NMR established that stannane **13** was formed quantitatively before isobutylene could be detected in the reaction mixture; that is, the first protonolysis is faster than the second by a factor of at least 50. This observation is important because it suggests that protonolyses of allylstannanes occur by a stepwise mechanism. If protonation and loss of tin were concerted, the acetolyses of allylstannanes **4** and **13** would occur at similar rates.[7] In contrast, stepwise protonations of these compounds would produce intermediate cations **14** and **15**. If all of the carbon–tin bonds can achieve an orientation which allows hyperconjugative stabilization of these intermediates, then cation **14** should be more stable than cation **15**,[1] and the first protonolysis should therefore be significantly faster than the second.[14] This is what we observe, possibly because shielding of the double bond in conformations **11** and **11′** does not impose a significant barrier to protonation.

Trimethylstannane **5** proved to be more reactive. In the presence of AIBN, hot carbon tetrachloride converted compound **5** into hexachloride **7** in 62% yield (eq 4).[6] Trimethyltin chloride presumably is the other final product of this reaction, and a compound tentatively identified as (4,4,4-trichloro-2-methylenebutyl)trimethylstannane (**16**) is formed as an intermediate. Substantial amounts of the final product **7** are formed from intermediate **16** before the starting material **5** is completely consumed, so the substitution of trimethylstannyl by trichloromethyl is similar to the substitution of triphenylstannyl; in neither case is the first step dramatically faster than the second. Again, the trimethyltin groups may retard addition of trichloromethyl to the double bond or prevent the product of addition from adopting conformations in which hyperconjugative stabilization is maximized.[15]

Trimethylstannane **5** also reacted readily with electrophiles. For example, hydroboration of compound **5** by borane at 25 °C in THF,[13] followed by oxidation, produced 3-(trimethylstannyl)-2-[(trimethylstannyl)methyl]-1-propanol (**17**) in 67% yield. Protonolysis of trimethylstannane **5**,[14] even by triethylammonium bromide, rapidly produced (2-methyl-2-propenyl)trimethylstannane (**18**). Like triphenylstannane **4**, trimethylstannane **5** was completely consumed before intermediate **18** was converted to isobutylene, so again protonolysis appears to be a stepwise reaction.



17 18

The properties of triphenylstannane **4** and trimethylstannane **5** are therefore similar, but steric[9,15] and electronic[14] factors make compound **5** somewhat more reactive. Qualitative studies confirm that the protonolyses of both allylstannanes are stepwise reactions involving protonation followed by cleavage of the carbon–tin bond. Similar studies are consistent with, but do not require, a concerted pathway for radical substitution. We are continuing to study the structures and reactions of these interesting allylstannanes.

Experimental Section

All infrared (IR) spectra were recorded on a Perkin-Elmer Model 710B spectrometer. A Bruker WH-90 spectrometer was used to obtain ^1H nuclear magnetic resonance (NMR) spectra. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane (δ). Mass spectra were recorded at 70 eV on a VG Micromass 12-12 quadrupole spectrometer by using electron impact (EI) or chemical ionization (CI). Galbraith Laboratories, Knoxville, TN, performed all elemental analyses. Glassware was dried at 120 °C and cooled under dry Ar immediately before use. Tetrahydrofuran was distilled from the sodium ketyl of benzophenone. All other reagents were commercial products of the highest purity obtainable.

2-Methylene-1,3-propanediylbis[triphenylstannane] (4). Under dry Ar at 0 °C, a stirred solution of (triphenylstannyl)lithium[16] (29 mL, 0.27 M in THF, 7.9 mmol) was treated dropwise during 10 min with 3-chloro-2-(chloromethyl)-1-propene (504 mg, 4.03 mmol). During this addition the color of the solution changed from yellow to dark orange. After the mixture had been kept at 25 °C for 20 h, water (0.5 mL) was added, producing a white precipitate. Volatiles were then removed by evaporation under reduced pressure, and the residue was partitioned between water (100 mL) and CH_2Cl_2 (100 mL). The organic phase was dried, and solvent was removed by evaporation under reduced pressure. The residue, a yellow solid, was stirred with hexane (200 mL) for 12 h at 25 °C. After centrifugation, the supernatant solution was

(12) The conformations of a related radical are discussed by: Schlüter, K.; Berndt, A. *Tetrahedron Lett.* **1979**, 929.

(13) For other hydroborations of allylstannanes and allylsilanes, see: Fishwick, M. F.; Wallbridge, M. G. H. *J. Organomet. Chem.* **1977**, *136*, C46. Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571. Fish, R. H.; Broline, B. M. *J. Organomet. Chem.* **1978**, *159*, 255.

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(16) General procedure of: Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.

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, $CDCl_3$) 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 $C_{40}H_{36}Sn_2$: 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 CH_2Cl_2 (20 mL). The organic phase was dried over anhydrous Na_2CO_3, 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, $CDCl_3$) 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 $C_{10}H_{24}Sn_2$: 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 CCl_4. A solution of 2-methylene-1,3-propanediylbis[triphenylstannane] (**4**; 150 mg, 0.199 mmol) and AIBN (8 mg, 0.05 mmol) in CCl_4 (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, CCl_4) 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, $CDCl_3$) 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 $C_{23}H_{21}Cl_3Sn$: 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}; ^1H NMR (90 MHz, $CDCl_3$) δ 3.71 (s, 4 H), 5.73 (s, 2 H); mass spectrum (CI), *m/e* 217, 181, 157, 143, 121. Anal. Calcd for $C_6H_6Cl_6$: 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 $CHCl_3$ (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 CH_2Cl_2 and applied to a column of neutral alumina (activity I, 0.25 in. × 1 in.), which was eluted with CH_2Cl_2 (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 CCl_4. A solution of 2-methylene-1,3-propanediylbis[trimethylstannane] (**5**; 32 mg, 0.084 mmol) and AIBN (4 mg, 0.02 mmol) in CCl_4 (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 CF_3COOH 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, CCl_4) 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 H_2O_2 (0.075 mL, 30%, 0.66 mmol) were added. Then the mixture was warmed at 40 °C for 1 h and partitioned between CH_2Cl_2 (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, $CDCl_3$) 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 $C_{10}H_{26}OSn_2$: C, 30.05; H, 6.56; Sn, 59.39. Found: C, 30.65; H, 6.49.

Acknowledgment. This work was financially supported by Research Corp., the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Education du Québec. We are grateful to Mr. M. Evans, who recorded our mass spectra, and to Dr. L. Blaszczak for helpful discussions.

Registry No. **4**, 86854-53-7; **5**, 86854-54-8; **7**, 86854-56-0; **8**, 86854-55-9; **13**, 2591-44-8; **17**, 86854-57-1; 3-chloro-2-(chloromethyl)-1-propene, 1871-57-4.

(17) Seyferth, D.; Weiner, M. A. *J. Org. Chem.* **1961**, *26*, 4797.

Thermal Rearrangement of Allenyl Ketones

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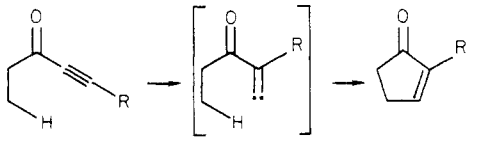
Received October 4, 1982

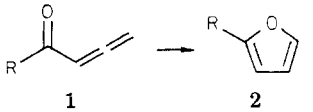
The thermal rearrangement of acetylenic ketones to cyclopentenones has been studied carefully, and all the available evidence points to an alkylidene carbene intermediate as illustrated in eq 1.[1] In view of the similarities



(1)

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



1 2

a, R = Me; b, R = Et; c, R = *t*-Bu; d, R = Ph

(1) Karpf, M.; Huguet, J.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 13 and references cited therein.

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

0022-3263/83/1948-3813$01.50/0