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Articles

Thermal Isomerization of a Vinylcyclobutene to a Cyclohexadiene

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Above 100 °C 5-methylenespiro[3.5]non-1-ene, **1**, undergoes cyclobutene ring opening to (*E*)-triene **2** and apparent 1,3-shift to a hexahydronaphthalene, **3**, in a 3 to 1 ratio. (*E*)-Triene **2** gives **3** in a competitive reaction. The activation energies for all three processes are obtained from a kinetic simulation at three temperatures. It is likely that the (*Z*)-triene **4**, also derived by cyclobutene ring opening, is an intermediate in the **1** to **3** conversion. Speculation on the **2** to **3** conversion focuses on the possible intermediacy of a 3-vinylcyclohexenocyclobutene, **5**. The apparent noninvolvement of a concerted 1,3-shift in the **1** to **3** reaction is discussed.

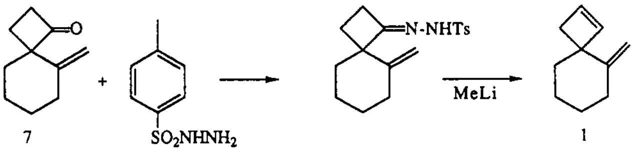
3-Vinylcyclobutenes have been prepared,[1] but their thermal chemistry seems to be dominated by conversion to (*E*)-1,3,5-trienes and not 1,3-shifts to cyclohexadienes. In a study of acyclic conjugated triene isomerizations, Doering suggested that cyclohexadiene formation from (*E*)-1,3,5-hexatriene might proceed by isomerization to the (*Z*)-triene via closure to vinylcyclobutene and then reopening.[2] Other options, including central double bond geometric isomerization via a bisallyl biradical and a direct reaction could not be excluded. Vinylcyclobutenes in the form of bicyclo[3.2.0]hepta-2,6-dienes have been pyrolyzed and found to undergo ring opening to trienes which recyclize to isomerized bicyclo[3.2.0]heptadienes.[3] Because pyrolyses of vinylcyclobutenes have been conducted on highly substituted systems and in systems where the vinyl group is not predisposed geometrically to undergo a direct 1–3 shift, the thermal isomerization of vinylcyclobutene **1** was studied.

Results

Synthesis of 5-Methylenespiro[3.5]non-1-ene (1). The reaction of methylenespironanone (**7**) with *p*-toluenesulfonylhydrazine followed by methyllithium afforded the vinylcyclobutene **1** (Scheme I).

Pyrolysis of 1. Pyrolysis of 5-Methylenespiro[3.5]non-1-ene (**1**) in $CDCl_3$ solvent in sealed NMR tubes from 101 to 137 °C gives hexalin **3** and a triene, **2**, which was subsequently identified as the *E* isomer (vide infra). The triene also rearranges to the hexalin **3**, so simulation of the mole fraction–time data at three temperatures, 101. °C, 115. °C, and 137. °C (Table I), with kinetic Scheme II was attempted. In every case, the Simplex optimization of parameters of a Gear numerical integration[4] led to rate constants which reproduced the experimental mole fractions with an average residual of 0.01 (Table II). What is clear is that reversion of (*E*)-triene **2** to **1** is slow compared to direct conversion of **2** to hexalin.

Scheme I



Scheme II

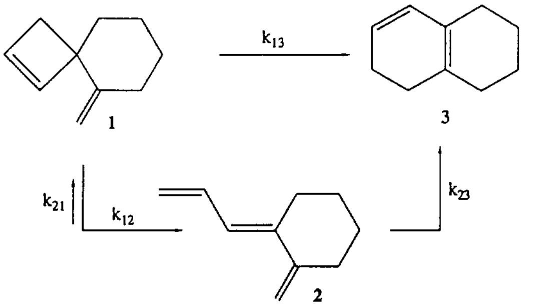


Table I. Pyrolysis Data for Rearrangements of 1 to 2 and 3 at 101, 115, and 137 °C

no. of obs	time (s)	mole fractions 1	2	3	temp, °C
1	0	1.0000	0.0000	0.0000	
2	157680	0.6594	0.2394	0.1012	
3	242040	0.5298	0.3226	0.1475	101
4	327840	0.4164	0.4022	0.1813	
5	484860	0.2804	0.4534	0.2661	
6	571680	0.1966	0.4845	0.3188	
1	0	1.0000	0.0000	0.0000	
2	36600	0.6067	0.2823	0.1110	
3	55320	0.4869	0.3734	0.1397	115
4	72600	0.3857	0.4110	0.2034	
5	90660	0.3169	0.4281	0.2550	
6	108240	0.2442	0.4761	0.2797	
7	126900	0.1800	0.5000	0.3200	
1	0	0.1000	0.0000	0.0000	
2	7440	0.4330	0.4208	0.1462	
3	14880	0.1613	0.5376	0.3011	137
4	20880	0.0723	0.5597	0.3679	

The activation parameters for the processes defined by rate constants k_{12}, k_{13}, and k_{23} are determined with good linearity and are not unreasonable; however, those for process k_{21} must be incorrect. This does not call into question the other calculated rate constants since almost

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[1] Courtot, P.; Rumin, R. *J. Chem. Soc., Chem. Commun.* **1974**, 197. *Tetrahedron* **1976**, *32*, 441. Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194. For a nickel-catalyzed 1,3-shift, see: DiFrancesco, D.; Pinhas, A. R. *J. Org. Chem.* **1986**, *51*, 2098.

[2] Doering, W. von E.; Beasley, G. H. *Tetrahedron* **1973**, *29*, 2231.

[3] Miyashi, T., Nitta, M.; Mukai, T. *Tetrahedron Lett.* **1967**, 3433. Baldwin, J. E.; Kaplan, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 668, 1794; **1971**, *93*, 3969.

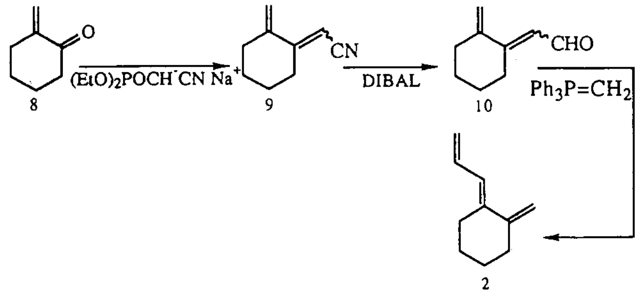
[4] Gilbert, K. E.; Gajewski, J. J. *Comput. Chem.* **1985**, *9*, 191.

0022-3263/92/1957-1970$03.00/0

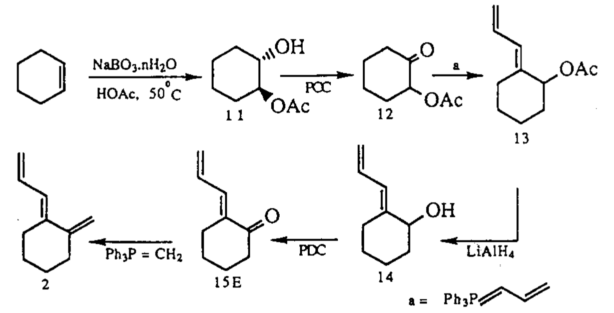
Table II. Rate Constants (s^{-1}) from Simulation of Scheme II

	k_{12}	k_{13}	k_{21}	k_{23}
101 °C	2.02×10^{-6}	6.36×10^{-7}	1.72×10^{-9}	6.71×10^{-7}
115 °C	1.02×10^{-5}	3.07×10^{-6}	1.18×10^{-7}	3.07×10^{-6}
137 °C	1.01×10^{-4}	2.60×10^{-5}	6.69×10^{-6}	1.86×10^{-5}
log A	13.6	11.8	25.8?	9.2
E_{act}	33 000	30 800	58 200?	26 200
r(Arrhenius)	0.9999	0.9999	0.9999	0.9996

Scheme III



Scheme IV



any small value for k_{21} at any temperature will still produce an acceptable fit to the data.

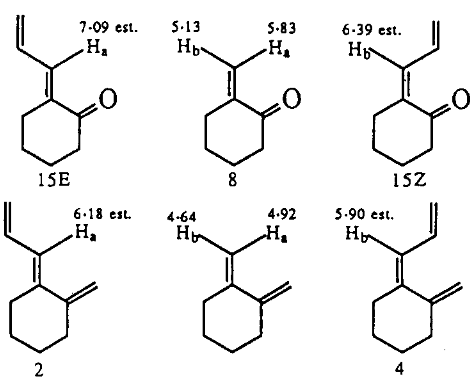
For comparison purposes, triene 2 was pyrolyzed separately at 115 °C and the decomposition was followed by ^1H NMR spectroscopy. The only product identified in this decomposition was hexahydronaphthalene 3. The observed rate constant was close to that obtained from simulated data.

Synthesis of 2. 1-Methylene-2-allylidenecyclohexane (2) was prepared via two routes. In the first, 2-methylenecyclohexanone, 8, was converted to triene 2 according to the sequence of reactions of Scheme III. Horner–Emmons olefination of 8 to afford 9 and its subsequent diisobutylaluminum hydride (DIBAL) reduction product, 10, each gave two isomers (*E* and *Z*) as expected. However, Wittig reaction of 10 with methylenetriphenylphosphorane under the reaction condition gave only one isomer which was assigned structure 2 (see below). It has been observed that conjugated aldehydes 10 are prone to polymerization, and one of the isomers disappears more rapidly than that of the other. Since NOE experiments on 2 were not conclusive (only ~1% NOE was observed), an alternative synthetic route for 2 was sought.

Cyclohexene was converted to triene 2 according to the reaction sequence of Scheme IV. Wittig reaction of 12 with allylic triphenylphosphonium ylide gave only one diastereomer in poor yield (~10%). The stereochemistry of ketone **15E** as shown was determined on the basis of chemical shift values (see below). The *E* isomeric structures in compounds 13, 14, and 2 were assigned on the basis of the structure of ketone **15E**.

Stereochemistry of 15E. The chemical shifts of proton H_a in **15E** and H_b in **15Z**, respectively, can be estimated (Scheme V) from the known chemical shift values of protons H_a and H_b in compound 8 (reasonably assigned by relative proximity to CO) and geminal conjugated vinyl substituent constant value of 1.26 ppm.[5] The observed value (7.02 ppm in $CDCl_3$) is in very close agreement with that calculated for the isomeric structure **15E** and is 0.7 ppm downfield from that expected for H_b in **15Z**. Additional evidence for the stereochemistry follows from the reasonably assigned chemical shift values of vinyl protons of 1,2-dimethylenecyclohexane and the substituent constant value for conjugated vinyl group. The observed shift of H_a (6.12 ppm) in *E* triene 2 is very close to that estimated and is 0.22 ppm downfield from that estimated for *Z* triene 4.[23]

Scheme V



Discussion

Numerous cyclobutene ring opening reactions have been studied since the pioneering work of Criegee.[6] The work of Brauman[7] makes it clear that the reaction benefits from concert by at least 10 kcal/mol. Substitution of a phenyl group on C-3 reduces the activation energy by ca. 6 kcal/mol ($\log k = 12.4 - 26\,000/2.3RT$)[8] while the parent has $\log k = 13.6 - 32\,000/2.3RT$).[9] However, 3-methyl-3-phenylcyclobutene has an activation energy of 30 kcal/mol,[10] which probably reflects the steric difficulty in rotating a methyl or a phenyl inward. The activation energy from the kinetic simulations of the pyrolysis of 1 to 2 is not inconsistent with that for the methyl–phenyl-substituted cyclobutene.

The pathway involved in the process defined by k_{13} most likely includes the (*Z*)-triene 4, which electrocyclizes to hexalin rapidly under the reaction conditions. (*Z*)-Hexatriene itself cyclizes with $\log k = 11.83 - 29\,900/4.6T$;[11] thus at 115 °C it would have a rate constant of 1.2×10^{-5}/s, which is a factor of 2.5 faster than k_{13}. In addition, due to the constraints of the six-carbon ring, triene 4 has one more bond fixed in a cisoid arrangement than hexatriene, thus entropically, its electrocyclization should be much more favorable than that of the acyclic triene.

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(5) (a) Pascual, von C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164. (b) Silverstein, R. M.; Bassler, G. C.; Merrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; pp 227–228.

(6) For reviews, see: Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 559. Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 47–51.

(7) Brauman, J. I.; Golden, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 1920. Brauman, J. I.; Archie, W. C., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 4262. Stephenson, L. M.; Gemmer, R. V.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8620.

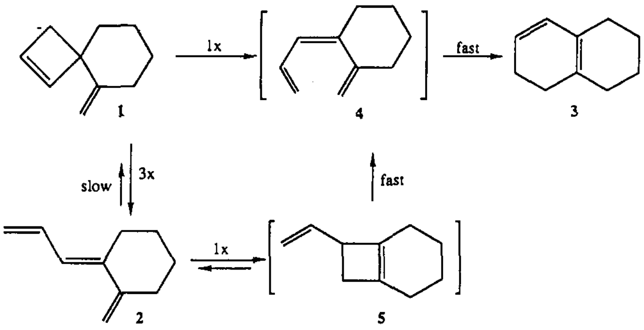
(8) Pomerantz, M.; Hartman, P. H. *Tetrahedron Lett.* **1968**, 991.

(9) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220. Carr, R. W., Jr.; Walters, W. D. *J. Phys. Chem.* **1965**, *69*, 1073.

(10) Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391. The explanation for the electronic effect in eq 3 of this paper, namely, formation of a Huckel 6π electron system, is not obvious considering the preference for conrotation.

(11) Lewis, K. E.; Steiner, H. *J. Chem. Soc.* **1964**, 3080.

Scheme VI. Mechanism with Relative Rate Constants at 115 °C



If all of the "direct" isomerization of 1 to hexalin proceeds via the (*Z*)-triene 4, then the ring-opening preference favors rotation of the 2-methylenecyclohexyl moiety to put the methylene group anti to the butadiene formed, i.e. to make the (*E*)-triene 2. The propensity for inward or outward rotation of hydrocarbon substituents on cyclobutenes generally appears to respond to steric effects (although electronic effects are more important with heteroatom substituents, and there appears to be some electronic preference with aryl substituents to rotate inward which reduces the overall tendency for phenyls to rotate outward),[10] and this ring opening behaves similarly.

The unanswered question associated with the isomerization of 1 is the mechanism for conversion of the (*E*)-triene to the hexalin. The kinetic simulations and independent pyrolysis of the (*E*)-triene makes it clear that reversion to 1 and subsequent ring opening to the (*Z*)-triene is but a minor pathway for the formation of hexalin from 2. Geometric isomerization of the central bond of the (*E*)-triene to (*Z*)-triene via a twisted bisallyl biradical would appear to be too high in energy judging by Doering's results with various trienes which place the activation free energy above 40 kcal/mol which suggest a half-life in excess of 44 years at 137 °C.[2] A direct cyclization appears impossible from molecular models. A possible alternative is cyclization to a different cyclobutene, namely cyclohexenovinylcyclobutene, 5, which does not accumulate but does ring open to the (*Z*)-triene 4, which gives the hexalin (Scheme VI).

MMX molecular mechanics calculations[12] reveal that 5 has a heat of formation about the same as the starting cyclobutene 1. However, the heat of formation calculated for the cyclobutenes is roughly 16 kcal/mol higher than those of the (*E*)- and (*Z*)-trienes, 2 and 4, respectively. This large difference would make impossible triene electrocyclization of 2 to 5 since ring opening of 5 to 2 would be expected to have an activation energy of ca. 25 kcal/mol. The semiempirical MO program MNDO found that 1 is 13.4 kcal/mol less stable than 2, but 5 is only 2.3 kcal/mol less stable than 2. AM1 gives results similar to MMX although there is a 10 kcal/mol discrepancy in the heat of formation of the hexalin 3. Application of Benson group additivities[13] to cyclobutenes 1 and 5 and assuming a strain energy of 30 kcal/mol for each, the heat of formation of each is 35.7 and 37.1 kcal/mol, respectively, both of which are too high relative to the trienes to fit the observations. WINDO, a semiempirical MO program written by Russo and Wilcox,[14] which is usually superior to MNDO for hydrocarbon structure and heats of formation, found that 5 is 4 kcal/mol more stable than 1. Moreover, WINDO found that the cyclobutene 5 is only 6 kcal/mol less stable than the trienes (see Table III).

Table III. Calculated Heats of Formation of the $C_{10}H_{14}$ Isomers 1–5

method	1	2	3	4	5
MMX[12]	43.2	26.2	7.7	27.2	43.0
MNDO	39.0	25.6	−4.95	25.6	27.9
AM1	47.5	24.2	−4.69	24.0	45.7
Benson[13]	35.7[a]	23.8[b]	4.5[b]	23.8[b]	37.1[a]
WINDO[14]	36.3	26.3	−2.3	27.7	32.3

[a] Assumes 30 kcal/mol strain energy. [b] Assumes no strain energy.

All of the calculations strongly suggest that reversion of the (*E*)-triene to 1 cannot occur under the reaction conditions, and the rate constant k_{21} is relatively small as suggested by the Simplex optimization of the rate data. Some of the calculations allow that (*E*)-triene 2 could cyclize to cyclobutene 5. The transition-state energies for ring opening of 5 to either (*E*)-triene 2 or (*Z*)-triene 4 should be roughly 25 kcal/mol above 5, recalling the 26 kcal/mol activation energy for ring opening of 3-phenylcyclobutene. If cyclobutene 5 were less than 5 kcal/mol less stable than (*E*)-triene 2, then the overall activation energy for conversion of 2 to (*Z*)-triene 4 could proceed via cyclobutene 5.

It is not inappropriate to recognize that conversion of cyclobutene 1 to 5 is possible via a boat-like 3,3-sigmatropic shift (Cope rearrangement), and 5 continues on to the (*Z*)-triene 4. This process cannot be distinguished from ring opening of 1 directly to (*Z*)-triene 4 without other experiments.

What is remarkable about the isomerization reactions of 1 is the lack of evidence for a concerted 1,3-sigmatropic shift to hexalin. At most, 25% of the reaction could proceed this way if no ring opening to the (*Z*)-triene occurs. In this case, the rate of vinylcyclobutane rearrangement makes it clear that the reaction is assisted by the cyclobutene double bond. Alternatively, the rearrangement may be considered to be a cyclobutene ring opening assisted by the exomethylene group. However, the cyclobutene double bond does not migrate so analysis in terms of a pericyclic reaction is not obvious. If the reaction were a cyclobutene-accelerated vinylcyclobutane rearrangement, then inversion at the migrating carbon might be expected, but this requires a disrotatory opening of the cyclobutene. If the reaction were a conrotatory ring opening of the cyclobutene, suprafacial use of the allylic moiety derived from the exomethylene would require retention at the migrating carbon and Mobius overlap around the periphery of the six orbital system. In either event, the reaction appears unable to enjoy concert for factors perhaps not dissimilar to those controlling the Dewar benzene ring opening.[15]

Experimental Section[16]

5-Methylenespiro[3.5]non-1-ene (1). Treatment of spiroketone 7[17] with *p*-toluenesulfonylhydrazine followed by methyllithium according to a literature procedure[18] for similar compounds, afforded a one-pot synthesis of methylenespirononene,

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[12] Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2.

[13] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[14] Russo, S. O., Ph.D. Thesis, Cornell University, 1979.

[15] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[16] For instrumentation used, see: Gajewski, J. J.; Paul, G. C. *J. Org. Chem.* **1991**, *56*, 1986.

[17] Gadwood, R. C.; Lett, R. M. *J. Org. Chem.* **1982**, *47*, 2268.

[18] Dauben, W. G.; Lorber, E. M.; Vietmeyer, N. D.; Shapiro, R. H.; Duncan, J. H.; Tomer, K. *J. Am. Chem. Soc.* **1968**, *90*, 4762.

1. A sample was purified by bulb-to-bulb distillation at a reduced pressure (0.01 Torr, 25 °C). A pure sample of 1 could be obtained via preparative GC (column temperature <100 °C, 20% OV101 on Chromosorb P column). ^{1}H NMR of 1: δ 6.2 (d, 1 H, J = 2.9 Hz), 6.05 (d, 1 H, J = 2.9 Hz), 4.51–4.46 (m, 2 H), 2.24 (s, 2 H) 2.20–1.96 (m, 2 H), 1.68–1.15 (m, 6 H); ^{13}C NMR δ 153.97, 143.33, 134.61, 104.89, 54.24, 42.95, 38.58, 33.59, 27.82, 24.63; HRMS for $C_{10}H_{14}$ found 134.1087, calcd 134.1096.

1-Methylene-2-allylidenecyclohexane (2). Method A. The reaction of 2-methylenecyclohexanone (8)[19] with the anion derived from NaH and diethyl (cyanomethyl)phosphonate gave a mixture of *Z* and *E* nitriles **9**. The crude nitrile mixture **9** was reduced with diisobutylaluminum hydride followed by acid hydrolysis to give a mixture of aldehydes **10**.[20] Bulb-to-bulb distillation under vacuum (0.01 Torr, 20 °C) led to a 1:1 mixture of *Z* and *E* aldehydes **10** along with some impurities. ^{1}H NMR analysis of this mixture showed 2 doublets (~1:1 ratio) at ~10.0 ppm which correspond to the *E* and *Z* aldehyde protons. One of these aldehydes goes away quickly. The aldehyde mixture was treated with ylide derived from methyltriphenylphosphonium bromide and *n*-butyllithium in diethyl ether for 8 h. Standard workup and solvent removal revealed only one triene. This triene was purified by silica gel flash chromatography and was assigned structure **2**.

Method B. (*E*)-2-Acetoxycyclohexanone (**12**)[21] was treated with the ylide derived from allyltriphenylphosphonium chloride and potassium hexamethyldisilazide (Li-free condition)[21] gave a low yield (~10%) of diene **13**. It was purified by silica gel flash chromatography (8% ethyl acetate in hexanes). The ester **13** was reduced with lithium aluminum hydride in diethyl ether to afford alcohol **14**, which without further purification was oxidized with PDC[22] in methylene chloride (8 h, room temperature) to the ketone **15E**. It was purified by flash chromatography (8% ethyl acetate in hexanes). Wittig reaction of ketone **15E** with the ylide derived from triphenylphosphonium bromide and *n*-butyllithium in diethyl ether gave triene **2** in good yield. Bulb-to-bulb distillation under vacuum (0.01 Torr, room temperature) afforded pure triene **2**.

12: ^{1}H NMR δ 5.20–5.13 (m, 1 H), 2.56–2.25 (m, 4 H), 2.16 (s, 3 H), 2.10–1.60 (m, 4 H).

13: ^{1}H NMR δ 6.60–6.54 (apparent td, 1 H, J = 10, 10.8, and 16.5 Hz), 6.00 (d, 1 H, J = 10.8 Hz), 5.30–5.20 (m, 2 H), 5.11 (d, 1 H, J = 10 Hz), 2.58–2.20 (m, 2 H), 2.09 (s, 3 H), 2.01–1.50 (m, 6 H); HRMS for $C_{11}H_{16}O_2$ found 180.1134, calcd 180.1150.

14: ^{1}H NMR δ 6.69–6.58 (dt, 1 H, J = 10.0 and 16.8 Hz), 6.08 (bd, 1 H, J = 10.8 Hz), 5.23 (bd, 1 H, J = 17 Hz), 5.08 (bd, 1 H, J = 10.0 Hz); HRMS for $C_9H_{14}O$ found 138.1040, calcd 138.1044.

15E: ^{1}H NMR (400 MHz) δ 7.02 (d, 1 H, J = 12 Hz), 6.64–6.54 (ddd, 1 H, J = 10.8, 12 and 18.4 Hz), 5.63 (bd, 1 H, J = 18.4 Hz), 5.52 (bd, 1 H, J = 10.8 Hz), 2.66–2.62 (dt, 2 H), 2.48–2.44 (bt, 2 H, J = 6.4 Hz), 1.90–1.74 (m, 4 H); ^{13}C NMR δ 201.23, 135.73, 135.08, 131.38, 125.89, 40.22, 26.90, 23.43, 23.20; MS 136 (M^+, 3), 119 (6), 105 (100), 91 (45), 79 (30); HRMS for $C_9H_{12}O$ found 136.0888, calcd 136.0882.

2: ^{1}H NMR (500 MHz) δ 6.67–6.59 (ddd, 1 H, J = 10.1, 11.1, and 16.8 Hz), 6.12 (d, 1 H, J = 11.1 Hz), 5.25–5.21 (dd, 1 H, J = 1.8 and 16.8 Hz), 5.10–5.07 (dd, 1 H, J = 1.7 and 10.1 Hz), 4.91 (bs, 1 H), 4.65 (bs, 1 H), 2.40–2.37 (bt, 2 H), 2.28–2.26 (bt, 2 H), 1.67–1.63 (m, 4 H); ^{13}C NMR δ 150.57, 142.67, 132.69, 123.44, 116.82 108.24, 35.36, 28.92, 26.85, 26.07; MS 134 (M^+, 82), 119 (53), 106 (28), 105 (37), 92 (49), 91 (100), 79 (30), 77 (21); HRMS for $C_{10}H_{14}$ found 134.1103, calcd 134.1096.

Kinetic Studies. Samples were prepared by dissolving 1 (7–8 μL) in $CDCl_3$ (0.5 mL) in an NMR tube. The samples were degassed, and the tubes were sealed under vacuum. Tubes were then immersed in constant boiling solvent baths (isobutyl alcohol, *n*-butyl alcohol, and xylene), and the ^{1}H NMR spectra were recorded at different periods of time. Ratios of integrals of olefinic protons of compounds 1–3 were measured and corrected to obtain mole fraction data (Table I).

Acknowledgment. We thank the Department of Energy for support of this work.

Supplementary Material Available: Complete experimental procedures for the preparation of 2 and ^{1}H NMR spectra of 1, 2, 9, 10, 13, 14, and 15E (10 pages). Ordering information is given on any current masthead page.

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[19] Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180.

[20] For synthetic procedures for 9 and 10, see: Dugger, R. W.; Heathcock, C. H. *Synth. Commun.* **1980**, *10*, 509.

[21] Koreeda, M.; Patel, P. D.; Brown, L. *J. Org. Chem.* **1985**, *50*, 5910.

[22] Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

[23] For comparison purposes, the parameters nicely fit the vinyl proton shifts of the *syn-syn-*, *syn-anti-*, and *anti-anti-*1,2-diethylidenecyclobutanes (5.05 ppm vs 4.98 ppm experimental, 5.45 ppm and 5.05 ppm vs 5.47 ppm and 5.0 ppm experimental, and 5.45 ppm vs 5.33 ppm experimental, respectively): Gajewski, J. J.; Shih, C. N. *J. Org. Chem.* **1972**, *37*, 64.

Reactions between Tantalum– or Niobium–Alkyne Complexes and Carbonyl Compounds

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A variety of tantalum–alkyne complexes are generated in situ by treatment of alkynes with low-valent tantalum derived from $TaCl_5$ and zinc. These complexes add regioselectively to carbonyl compounds in a one-to-one fashion to yield (*E*)-allylic alcohols stereoselectively. Iodinolysis of the oxatantalacyclopentene, which is postulated as an intermediate of the reaction, gives a (*Z*)-3-iodo-2-propen-1-ol derivative. In contrast to tantalum–alkyne complexes, niobium–alkyne complexes, prepared with low-valent niobium derived from $NbCl_5$ and zinc, add in situ to aldehydes in a one-to-two fashion to give 1,3-diene derivatives. The dienes are produced through (i) addition of the alkyne complexes with 2 equiv of aldehydes at cis vicinal positions of the alkenes and (ii) deoxygenative elimination of 2,7-dioxanioba-4-cycloheptene complexes.

Since the discovery of transition metal–alkyne complexes, many reports on their structure and reactivities have appeared.[1-12] Recently, they received much attention as useful intermediates in organic synthesis. One of the

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