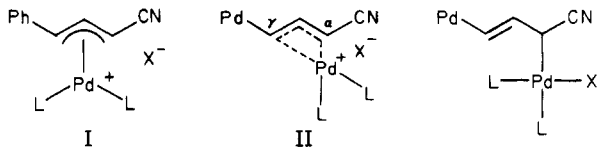
A general correlation between regioselectivity and stereospecificity phenomena is apparent from the results given in Table II, although the change in mode of reactivity for each of the two parallel series occur at slightly different points.

It seems that characterizing nucleophiles with indicator substrate **14** is even more informative than stereochemical characterization, as nucleophiles can be divided into three categories correlating with increasing "hardness": (A) "soft" nucleophiles that attack at the γ position, (B) "intermediate" nucleophiles that attack at the α position, (C) "hard" nucleophiles that fail to substitute at either the γ or α positions but give rise to reduced product **17** instead.

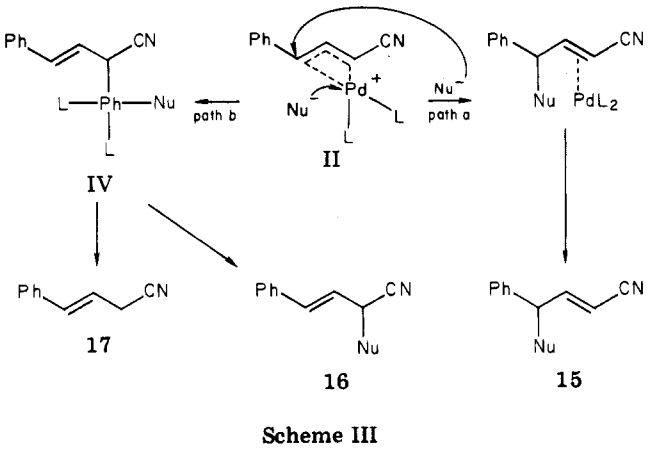
This three-fold behavior may be explained by kinetic arguments. The palladium atom in the η^3 palladium intermediate is probably unsymmetrically positioned with respect to the two ends of the allylic system, lying closer to the α-carbon atom (structure II rather than structure I).[22,23]



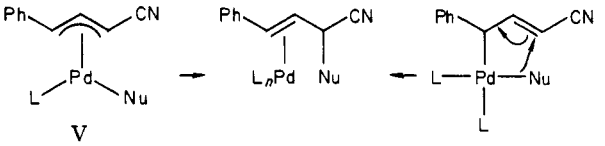
I II III

Consequently, external nucleophilic attack must occur at the γ carbon, which is less strongly bound to the metal (path a in Scheme II).

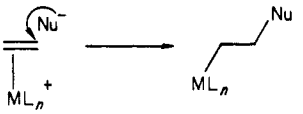
Scheme II



Scheme III



Path a is analogous to the more thoroughly investigated nucleophilic attack on electrophilic η^2 metal complexes (eq 1), which was studied both experimentally[25] and theoretically.[26]



(1)

The direct attack of the nucleophile at the metal (path b) may lead to formation of a (σ-allyl)palladium complex IV, which upon a subsequent reductive elimination will form the α-substituted product **16**. The formation of reduced product **17** in most reactions involving "hard" nucleophiles is more intriguing. One may envision the involvement of some electron-rich intermediate evolving from a one-electron or two-electron transfer from the nucleophile to neutral complex IV, or even a palladium–carbene complex related to IV.[21]

Assuming two alternative structures (V and VI) for intermediate complex IV suggests the possible existence of two other mechanistic pathways along which the reductive elimination may procede (Scheme III). Studies to explore these possibilities are currently in progress.

Acknowledgment. We thank the U.S.–Israel Binational Science Foundation and the Israel Academy of Sciences and Humanities for their generous support.

Registry No. (*E*)-**14**, 79311-09-4; **14**·$Pd(Ph_3)_4$ complex, 85235-08-1; (*E*)-**15** (Nu = $CH(CO_2CH_3)_2$), 79311-10-7; (*Z*)-**15** (Nu = $CH(CO_2CH_3)_2$), 79328-42-0; (*E*)-**15** (Nu = morpholino), 85234-92-0; (*Z*)-**15** (Nu = morpholino), 85235-02-5; (*E*)-**15** (Nu = PhO), 85234-93-1; (*Z*)-**15** (Nu = PhO), 85235-03-6; (*E*)-**15** (Nu = CH_3O), 85234-94-2; (*Z*)-**15** (Nu = CH_3O), 85235-04-7; (*E*)-**15** (Nu = $TolSO_2$), 85234-95-3; (*Z*)-**15** (Nu = $TolSO_2$), 85235-05-8; (*E*)-**15** (Nu = 2,4-cyclopentadienyl), 85234-96-4; (*Z*)-**15** (Nu = 2,4-cyclopentadienyl), 85235-06-9; **15** (Nu = 1-methyl-2-cyclohexanonyl), 85234-97-5; **16** (Nu = 1-methyl-2-cyclohexanonyl), 85234-98-6; **16** (Nu = 1-indenyl), 85234-99-7; (*E*)-**16** (Nu = propargyl), 85235-00-3; (*E*)-**16** (Nu = 2-propenyl), 85235-01-4; (*E*)-**17**, 20068-10-4; $Pd(PPh_3)_4$, 14221-01-3; $CH_2(COOCH_3)$·Na, 18424-76-5; Bu_3SnOPh, 3587-18-6; p-$CH_3C_6H_4SO_2Na$, 824-79-3; $Bu_3SnCH{=}C{=}CH_2$, 53915-69-8; $(CH_2{=}CHCH_2)_4Sn$, 7393-43-3; $PhSnBu_3$, 960-16-7; PhHgOAc, 62-38-4; $CH_3{\equiv}CSnBu_3$, 64099-82-7; Bu_3SnOCH_3, 1067-52-3; $NaBH_4$, 16940-66-2; Bu_3SnH, 688-73-3; MeLi, 917-54-4; Me_2CuLi, 15681-48-8; PhLi, 591-51-5; PhZnCl, 28557-00-8; morpholine, 110-91-8; (η^5-2,4-cyclopentadien-1-yl)thallium, 34822-90-7; sodium cyclopentadiene, 4984-82-1; 1-trimethylsilylindene, 18053-75-3; (2-methyl-1-cyclohexen-1-yloxy)tributylstannane, 21750-52-7.

(18) In all experiments, **16** was formed as a single stereoisomer *E*, whereas **15** was obtained as a mixture of *E* and *Z* isomers at about 4:1 ratio, respectively.

(19) Corey, E. J.; Koelliker, U.; Neuffer, J. *J. Am. Chem. Soc.* **1971**, *93*, 1489.

(20) Keinan, E.; Sahai, M., unpublished results.

(21) Keinan, E.; Peretz, M. *J. Org. Chem.*, submitted for publication.

(22) Several crystalline π-allyl palladium complexes related to **14** are currently being analyzed by X-ray difraction in order to verify this hypothesis.

(23) An allylic σ-complex such as III was recently suggested to be the active intermediate in the nucleophilic substitution of dimeric (π-allyl)-palladium chloride complexes in the presence of phosphine ligands: Akermark, B.; Akermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037.

(24) Such arguments were suggested earlier: Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

(25) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

(26) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308.

Ehud Keinan,* Zeev Roth

Department of Organic Chemistry
The Weizmann Institute of Science, Rehovot, Israel

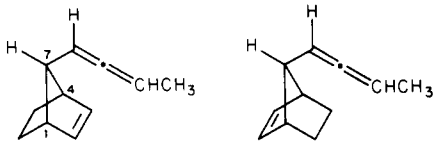
Received October 25, 1982

Thermal Rearrangement of *syn*-7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene: Evidence of Concertedness

Summary: *syn*-7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene (**1**) has been found to thermally rearrange to 1-ethylidene-3a,4,5,7a-tetrahydroindene (**4**) under conditions for which the corresponding anti epimer (**2**) is completely stable. These results are interpreted as supporting a

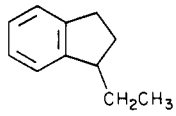
concerted pathway for the 1 → 4 rearrangement.

Sir: Recently we reported[1] on the synthesis and thermal rearrangement of a mixture of *syn*- and *anti*-7-(1,2-butadienyl)bicyclo[2.2.1]hept-2-ene [1 (30%) and 2 (70%)].

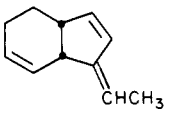


1

2

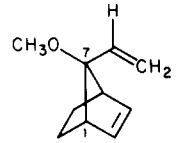


3

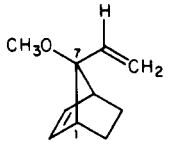


4

Gas-phase pyrolysis of the mixture in a Carius tube at 275 °C for 24 h gave 1-ethylindan (3) as the single isolable product in 28% yield, or about the percentage of 1 in the 1/2 epimeric mixture. We suggested a possible mechanism involving an initial concerted $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$ rearrangement of 1 to the Cope product 4, which through a series of not less than five allowed 1,5-hydrogen shifts may give 1-ethylindan. Our results were contrasted[1] with those obtained with corresponding vinyl systems.[2] For example,[2b] both **5a** and its anti epimer **5b** give the formal Cope product 1-methoxy-3a,6,7,7a-tetrahydroindene under the same conditions. Furthermore, 2-methoxybicyclo[3.2.2]nona-2,6-diene, a formal 1,3-sigmatropic-shift product, was formed, and these results were interpreted in terms of a diradical process initiated by cleavage of the 1,7-bond in 5.



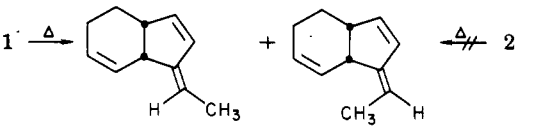
5a



5b

We now report on the successful separation of epimers 1 and 2 and the isolation of intermediate 4 as a thermal rearrangement product of the syn epimer 1. In the discussion that follows, all preparative VPC was performed on a $^3/_8$ in. × 10 ft column of 23% Carbowax 20M on 80/100 Chromosorb W-NAW[3] and both analytical and semipreparative HPLC on a 7.8 mm × 30 cm C_{18} reverse-phase column[4] with 70:30 methanol/water as the mobile phase. Allenes 1 and 2 cannot be resolved by VPC; however, we have been able to obtain a few milligrams of each pure epimer by HPLC using the technique of peak-shave recycle.[5] The separated epimers were isolated from their methanol/water solutions by diluting with five times the volume with water, extracting with ether, and then extracting the ether extracts with brine. Final purification was by preparative VPC[6] of the dried ether solutions. Recycle HPLC analysis of each separated epimer showed no trace of contamination by the other.[7] Furthermore, the ^{1}H NMR spectra of the separated allenes conformed in every way to the interpretation, given the spectrum of their mixture reported earlier.[1]

Approximately 1-μL samples of each pure epimer were then injected onto the gas chromatograph with the oven set at 225 °C, the injector at 300 °C, and with a flow rate of 10.5 mL/min. Under these conditions, the anti allene 2 was completely stable. Only a single peak with a retention time of 24 min was observed, and it was shown by HPLC analysis to correspond to starting allene 2. On the other hand, the syn allene 1 gave in addition to a very small peak at 24 min (verified as residual 1 by HPLC), a new peak at 34 min. Although 34 min was found to be equivalent to the retention time for an authentic sample of 1-ethylindan under these conditions, HPLC analysis showed that this new VPC peak corresponded to two new products in a 45:55 ratio (assuming an equal detector response) and not to 1-ethylindan. A larger quantity of this new product mixture was obtained by injecting up to 50 μL of the more plentiful 1/2 mixture[1,9] at a time under the above conditions. This product mixture was shown by its mass and ^{1}H NMR spectra to be (*E*)- and (*Z*)-1-ethylidene-3a,4,5,7a-tetrahydroindene (racemic (*E*)-4 and (*Z*)-4).



(E)-4 (Z)-4

The high-resolution mass spectrum[10] of this mixture had as its base peak the molecular ion peak at *m/e* 146.109 ($C_{11}H_{14}$; calcd *m/e* 146.110) and in addition exhibited prominent peaks at *m/e* (rel intensity, formula) 131 (93, $C_{10}H_{11}$), 117 (86, C_9H_9), 115 (29, C_9H_7), 105 (35, C_8H_9), and 91 (53, C_7H_7). The mass spectrum reported for 1-ethylindan[1] is similar except that the prominent peak at *m/e* 131 noted above and corresponding to $M^+ \cdot - CH_3$ is absent.

The 60-MHz ^{1}H NMR spectrum[11] (CCl_4) of 4 had resonances at δ 1.7 (br d, 3, CH_3), 1.8 (m, 4, CH_2), 2.6–3.5 (m, 2, CH), 5.0–5.3 (overlapping q, 1, CH_3CH), 5.3–6.5 (m, 4, ring vinyl H's). A 360-MHz ^{1}H NMR spectrum[12] (CCl_4/acetone-d_6) resolved the quartets for the CH_3CH resonances corresponding to (E)-4 and (Z)-4 (δ 5.07 and 5.26) and separated the resonances for the methyl groups belonging to the *E* and *Z* forms as well. A doublet with ^3J = 7 Hz is observed for the downfield methyl at δ 1.73 and a doublet of doublets with ^3J = 7 Hz and ^5J = 2 Hz for the upfield methyl at δ 1.70. Further information was derived through homonuclear decoupling. When the methyl resonances were irradiated, the CH_3CH resonances collapsed to two singlets (of nearly equal area). Furthermore, when the upfield quartet (δ 5.07) was irradiated, the upfield methyl resonance (δ 1.70) collapsed to a singlet.

(1) Duncan, J. A.; Bohle, D. S.; Blanchard, C. A.; Bossé, M. L.; Noland, T. W.; Ford, C. M.; Powell, M. A.; Sutton, M. C.; Eggleston, A. C.; Klevit, R. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 2837–2839.

(2) (a) Berson, J. A.; Jones, M. Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5017–5018, 5019–5020. (b) Berson, J. A.; Walsh, E. J., Jr. *Ibid.* **1968**, *90*, 4732–4733. (c) Berson, J. A.; Miyashi, T.; Jones, G., II. *Ibid.* **1974**, *96*, 3468–3476.

(3) A Varian Model 1520 Chromatograph equipped with a thermal conductivity detector was employed. Helium was used as the carrier gas.

(4) A Waters Associates Model 6000A solvent delivery system, UK6 injector, and 441 absorbance detector (214 nm) were used. The column packing was Waters μBondapak C_{18}.

(5) About 120 μL of a 6% solution of 1/2 in methanol could be processed in a single run.

(6) VPC conditions: Flow rate = 40 mL/min, oven temperature = 160 °C, injector temperature = 150 °C. Retention time for both 1 and 2 was 24 min.

(7) Allenes 1 and 2 were found to have *k'* values[8] of 7.62 and 8.38, respectively, and an α value[8] of 1.10.

(8) Synder, L. R.; Kirkland, J. J. "Introduction to Modern Liquid Chromatography", 2nd ed.; Wiley: New York, 1979; pp 15–82.

(9) Composed of 31.0% syn and 69.0% anti allene as determined by HPLC analysis. Integration values (Hewlett Packard Model 3390A integrator) are corrected for a syn/anti response ratio of 1.26.

(10) Obtained at 70 eV on a CEC-21-110B mass spectrometer.

(11) Obtained on a Varian EM-360L 60-MHz NMR spectrometer.

(12) Obtained on a Nicolet Nt-360 360-MHz NMR spectrometer.

Similarly when the downfield quartet (δ 5.26) was irradiated, the downfield methyl resonance (δ 1.73) collapsed to a singlet.

Although little if any rearrangement of the syn component of the 1/2 allene mixture can be detected at GC oven and injector temperatures at 160 °C or below, substantial rearrangement occurs at higher temperatures. When 50 μL of a 31:69 1/2 mixture was injected (flow rate = 10 mL/min) at column/injector temperatures of 175/175 °C, 200/200 °C, 225/225 °C, and 225/300 °C, the percent of 1 that rearranged was 51.0, 76.8, 79.7, and 86.5%, respectively.[13] For the small 1-μL injection of the pure syn allene at 225/300 °C discussed above, the percent of rearrangement to 4 was determined to be 97.9% by HPLC analysis of collected material.

The diastereomeric trienes 4 obtained from the GC pyrolyses were usually contaminated with about 3–4% of 1-ethylindan.[14] In fact when a triene sample was reinjected on the GC at 225/300 °C, much of it rearranged further to 1-ethylindan as determined by both HPLC and NMR analysis.

Given the fact that anti allene 2 did not rearrange under conditions in which syn allene 1 readily affords a mixture of trienes (*E*)-4 and (*Z*)-4, the 1 → 4 rearrangement is likely a concerted one and the orbital symmetry rules[15] apply. The difference in the thermal stability of 1 and 2 is especially important when compared to the results[2b] with the vinyl systems **5a** and **5b** discussed above. Furthermore, Berson[16] has found that the vinyl hydrocarbon *syn*-7-ethenylnorbornene is stable at 250 °C and at 320 °C it decomposes without rearrangement. Thus the allenyl group likely affords an improved pathway for the Cope rearrangement relative to a vinyl group in the present case. Our current results support our earlier interpretation[1] that the 1 → (*E*)-4 + (*Z*)-4 rearrangement is likely facilitated through the intervention of a $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$[1,17] augmented eight-electron Cope process. Racemic (*E*)-4 would result from the cleavage of the bridgehead C–C bond anti to the methyl group in racemic 1 (i.e., the 1,7-bond in (*S*)-1 or the 4,7-bond in (*R*)-1) whereas racemic (*Z*)-4 would result from cleavage of the C–C bond syn to the methyl group (i.e., the 1,7-bond in (*R*)-1 or the 4,7-bond in (*S*)-1).[18]

Work directed toward the synthesis and rearrangement of a 1-methyl-substituted analogue of 1 is in progress. The observed stereochemistry of such a rearrangement should provide more valuable information concerning the mechanism of these rearrangements.

Acknowledgment. Supported by a M. J. Murdock Charitable Trust Grant of Research Corporation, for which we are most grateful. We also thank Professor C. Klopfenstein of the University of Oregon for securing the 360-MHz ^{1}H NMR spectra for us.

Registry No. 1, 81141-97-1; 2, 81141-98-2; 3, 4830-99-3; (*E*)-4, 85371-48-8; (*Z*)-4, 85371-49-9.

(13) Percentages, corrected for a triene/syn allene response ratio of 0.91, determined by HPLC analysis.

(14) On occasion, considerably more 1-ethylindan relative to triene formed.

(15) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, and Academic Press: New York, 1970.

(16) Berson, J. A., Yale University, personal communication, 1975.

(17) For a discussion of the possible use of an allene moiety as a ($_{\pi}2 + {}_{\pi}2$) component, see: Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37–46, and references therein.

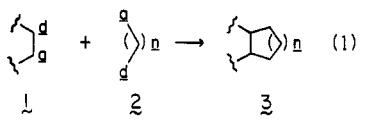
(18) It is perhaps noteworthy that no 1,3-sigmatropic shift of carbon is observed for 1 or 2, given that **5a** and **5b** both give a formal 1,3-shift product (2-methoxybicyclo[3.2.2]nona-2,6-diene),[2b] albeit likely through a diradical mechanism. Apparently an augmented six-electron concerted 1,3-sigmatropic rearrangement ($[{}_{\sigma}2_s + ({}_{\pi}2_s + {}_{\pi}2_s)]$) is not as plausible as the augmented Cope process, especially given the fact that 2, which is precluded from the concerted Cope process but not from the 1,3 process, does not rearrange at all under our established conditions.

James A. Duncan,* Bruce A. Lee, David Teng
Department of Chemistry
Lewis and Clark College
Portland, Oregon 97219
Received February 23, 1983

4-Chloro-2-lithio-1-butene, a Novel Donor–Acceptor Conjunctive Reagent

Summary: Transmetalation of 4-chloro-2-(trimethylstannyl)-1-butene (**10**) provides 4-chloro-2-lithio-1-butene (**11**), which reacts smoothly at −78 °C with aldehydes, ketones, and α,β-unsaturated *N,N',N'*-trimethylhydrazides to produce, after warming of the resultant intermediates in the presence of HMPA, the 3-methylenetetrahydrofuran derivatives **24–29** and the 3-methylenecyclopentanecarboxylic acid derivatives **36–38**, respectively.

Sir: Although conjunctive reagents that are equivalent to synthons possessing both a donor (d)[1] and an acceptor (a)[1] carbon atom (see **2** in eq 1) are known, they are, as yet,



(1)

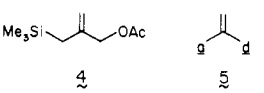
quite rare. This scarcity is particularly true for species in which the d and a centers are separated by one or more carbon atoms (n in **2** ≥ 1) and/or in which these centers are to be deployed "simultaneously" (or sequentially) in a "one-pot" process. Clearly such reagents are (would be) very useful in organic synthesis. For example, the (theoretical) combination of the reagent synthons **2** with substrate synthons **1** containing adjacent a and d sites (e.g., α,β-unsaturated carbonyl compounds) would provide the corresponding cyclic products **3** (eq 1).[2]

We report herein (a) the straightforward, efficient conversion of ethyl (*E*)-3-(trimethylstannyl)-2-butenoate (**6**)[3] into 4-chloro-2-(trimethylstannyl)-1-butene (**10**), (b) transmetalation of the latter substance to provide 4-chloro-2-lithio-1-butene (**11**), and (c) reaction of this novel, functionalized butenyllithium reagent with aldehydes, ketones, and α,β-unsaturated *N,N',N'*-trimethylhydrazides.

Conversion of compound **6**[3] into the corresponding enolate anion, followed by quenching of the latter species

(1) Seebach, D. *Angew, Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(2) For recent, very interesting examples of such a process in which the conjunctive reagent **4** served as the formal equivalent of the a,d synthon **5**, see: Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**,



101, 6429, 6432; **1980**, *102*, 6359. For other pertinent reports, see: Hayakawa, Y.; Yokoyama, K.; Noyori, R. *Ibid.* **1978**, *100*, 1791. Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hirotsu, K. *Ibid.* **1978**, *100*, 5565. Trost, B. M.; Vincent, J. E. *Ibid.* **1980**, *102*, 5681. Danheiser, R. L.; Carini, D. J.; Basak, A. *Ibid.* **1981**, *103*, 1604. Knapp, S.; O'Conner, U.; Mobilio, D. *Tetrahedron Lett.* **1980**, *21*, 4557. Klein, H.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1027. Magnus, P.; Quagllato, D. A. *Organometallics* **1982**, *1*, 1243. Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Ibid.* **1982**, *1*, 1679.

(3) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905.

0022-3263/83/1948-1774$01.50/0