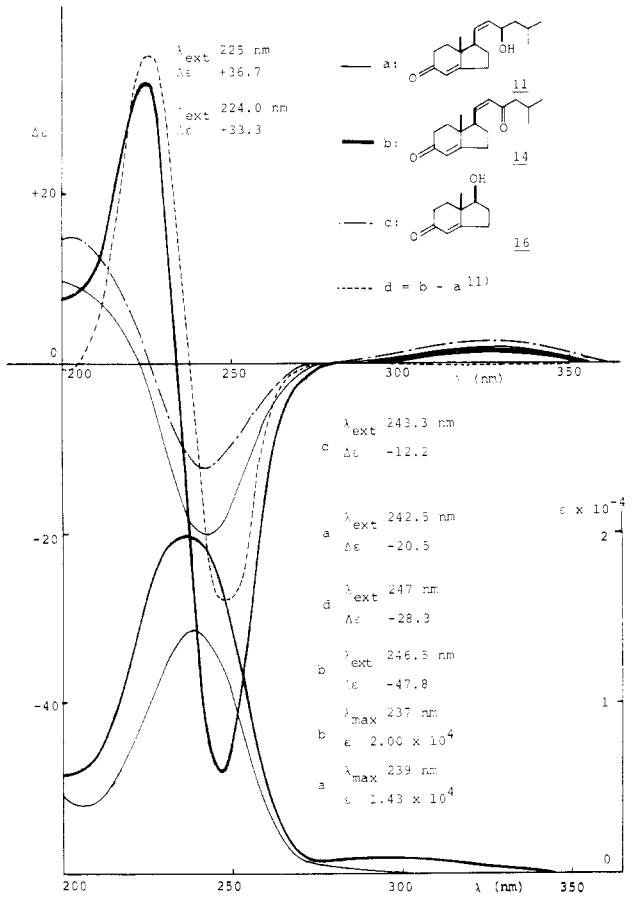

Figure 3.

II, F_a 143.3 (d, $J_{a,c}$ = 14.4 Hz), F_b 81.65 (d, $J_{b,c}$ = 2.54 Hz)], whereas the PIPA ester **13**, derived from (−)-enone **11**, showed only one set of ^{19}F NMR peaks corresponding to that of diastereomer II (Figure 1).

The relative stereochemistry among C(13), C(17), and C(23) (steroidal numbering) in both (±)-**11** and (±)-**12** was confirmed[4] previously by the stereoselective conversions of (±)-**11** and (±)-**12** to (±)-de-AB-isocholesta-8(14),22-dien-9-one and its (±)-C(20) isomer, respectively. We determined here the relative and absolute configuration of (−)-**11** and (−)-**14**, derived from (−)-**11** by Swern oxidation (81% yield), by CD and NMR spectra as follows. The CD spectra of (−)-**11**, (−)-**14**, and the (+)-enone **16** are shown in Figure 3. The simple comparison of CD spectrum of (−)-**11** (curve a) with that of (+)-**16** (curve c, the absolute configuration of **16** is known[9]) led to an *R* configuration at C(13) of (−)-**11**. The NMR spectal studies of (−)-**11** [^1H NOE (17%) between C(13)-methyl and H_b, the coupling constant (J = 10.3 Hz) between H_a and H_b] indicated the cis stereochemistry between the C(13)-methyl and vinyl chain at C(17) and the trans stereochemistry between H_a and H_b. Moreover, the inspection of molecular model of **14** and the observation of lower chemical shift (3.4–4.0 ppm) of H_a in **14** indicated that the side chain of (−)-**14** (Figure 2) was revealed to be *s*-cis configuration. Based on the above consideration, we have applied the exiton chirality method[10] to the conjugated enones for determining the relative and absolute configuration of side chain of (−)-**14**. The exiton theory predicted that (−)-**14** derived from the major product (−)-**11** should have a negative exiton chirality, i.e., left-hand screwness between the two enone chromophores located in C ring and side chain, while the dienone **15**, the enantiomer of (−)-**14** derived from the minor product **12**, should have a positive exiton chirality (Figure 2). The exiton-split CD curve of the enone–enone interaction (Figure 3, curve d[11]) exhibited the strong negative first Cotton effect in the region of the $\pi-\pi^*$ transition around 247 nm, the sign of which was in accordance with the negative exiton chirality between the enone and enone chromophores. These results indicated that the initial 1,4-addition of the (*R*)-vinyl iodide **8** to the cyclopentenone **9** led predominantly to the C(17*R*) configuration as shown in **11** and **14**. Moreover the present (+)-PIPA chloride and the exiton chirality methods should be applicable to determination of the optical purity and the absolute configuration, respectively, in complex molecules.

Acknowledgment. This investigation was supported by the Grant-in Aid for Scientific Research No. 57430030. We thank Professor Nobuo Ishikawa (Tokyo Institute of Technology) for providing (+)-PIPA chloride.

Supplementary Material Available: Experimental procedures and data for compounds used in this study (25 pages). Ordering information is given on any current masthead page.

(9) Micheli, R. A.; Hajos, Z. G.; Cohen, N.; Parrish, D. R.; Portland, L. A.; Sciamanna, W.; Scott, M. A.; Wehrli, P. A. *J. Org. Chem.* **1975**, *40*, 675.

(10) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy Exciton Coupling in Organic Stereochemistry"; University Science Books: CA, 1983.

(11) The CD curve of (−)-**14** contains two Cotton effects, one is due to the enone–enone interaction and the other is due to the helicity of the twisted enone in the C ring, therefore the difference between curve b and curve a shows the real exciton-split CD curve of the enone–enone interaction.

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2-Cyclopentenones from 1-Ethynyl-2-propenyl Acetates

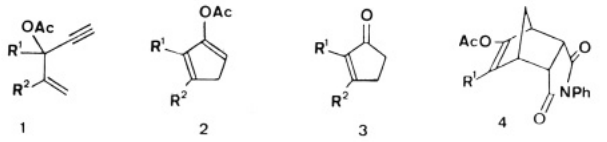
Summary: $PdCl_2(MeCN)_2$ catalyzes the cyclization of 1-ethynyl-2-propenyl acetates **1** to 1,4-cyclopentadienyl acetates **2**, which are cleaved in situ to 2-cyclopentenones **3**.

Sir: The vast literature dealing with the synthesis of 2-cyclopentenones contains a relatively small number of basic strategies.[1] This paper describes a new approach that is, formally, a Pd-catalyzed variant of the Nazarov cyclization[3] and that provides a shortcut to the Ber-

(1) For a recent review, see: Demole, E. P. In "Fragrance Chemistry"; Theimer, E. T., Ed.; Academic Press: New York, 1982; pp 349–396. In addition, see: Ho, T.-L.; Liu, S.-H. *Chem. Ind. (London)* **1982**, 371–372. McCurry, P. M.; Singh, R. K. *J. Org. Chem.* **1974**, *39*, 2317–2319. Reference 2. Also references in each.

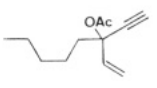
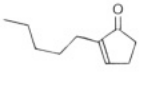
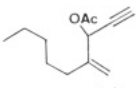
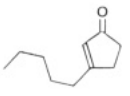
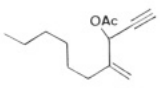
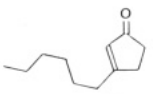
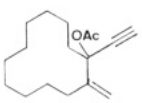
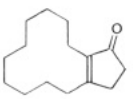
0022-3263/84/1949-0950$01.50/0

trand–Gorè synthesis.[2] Exposure of 1-ethynyl-2-propenyl acetates **1** to 0.025–0.1 equiv of $PdCl_2(MeCN)_2$[4] and 1 equiv



of acetic acid in 0.7–0.8 M acetonitrile solution at 60–80 °C affords 2-cyclopentenones **3** and acetic anhydride. Yields for five substrates are 48–89% on a 0.4–5.2-mmol scale (Table I). The experimental procedure resulted from an optimization with substrate **5** in which the solvent,

Table I. $PdCl_2(MeCN)_2$-Catalyzed Transformation of 1-Ethynyl-2-propenyl Acetates 1 into 2-Cyclopentenones 3

substrate 1	product 3[f]	yield,[g] %
 5[a,b]	 6	50–61
 7[a,b]	 8	48–66
 9[a,b]	 10	65–73
 11[a,b]	 12	63
 13[a,c]	 14	78–89

[a] Reference 6. [b] Acetylation with Ac_2O/4-(dimethylamino)pyridine (DMAP). [c] Reference 2c. [d] Alcohol obtained by Mannich reaction and ethynylation. [e] Reference 2e. [f] Isolation: treatment of the reaction mixture with MeOH/DMAP at room temperature (except for **14**), dilution with Et_2O/pentane, treatment with K_2CO_3, filtration, concentration, Kugelrohr distillation. [g] Limiting values for 2–5 runs using the optimized conditions, corrected for the purities of the Kugelrohr-distilled products (86–98%), on a 0.4–5.2-mmol scale.

Pd(II) salt,[5] ligand, and ester group were varied.

The alkyl substitution compatible with the cyclization is shown in **1**: R^1 and R^2 can be hydrogen or alkyl but further alkyl groups on the ethynyl and vinyl groups hinder or suppress the reaction.

Trapping experiments with *N*-phenylmaleimide showed that the 1,4-cyclopentadienyl acetates **2**[7] are intermediates in the transformation **1** → **3**. For example, starting with substrates **5** and **7**, the Diels–Alder adducts **4** (R^1 = methyl and pentyl) were obtained. Apart from this and the isolation of an allylic isomer in one case (see below), the enones **3** and acetic anhydride were the only products that could be detected. Rapid cleavage **2** → **3** apparently occurs and the mechanism is unclear. To increase the efficiency of the cleavage, various protic reagents were added in the optimization. Indeed, in the presence of acetic acid with acetonitrile as solvent, the yield of **6** was markedly improved but that of **14** was later found to be practically the same—and the highest in the series—in both the presence and absence of acetic acid. Stoichiometry requires the formal loss of ketene. This could actually occur and work is in progress to clarify this point.

In the case of **13** → **14**, allylic rearrangement[8] to give a primary allylic isomer of **13** was observed as a side reaction. The isomer decomposed under the reaction conditions, presumably by elimination of acetic acid.[9] Propargyl/allenyl rearrangements[10] were not detected.

The cyclization **1** → **2** probably starts with the formation of the chelate **15**.[11] From there, oxidative cyclization combined with 1,2-acetate migration[12] could give the palladiacyclohexadiene **18**,[13] which would reductively

(2) (a) Grimaldi, J.; Bertrand, M. *Tetrahedron Lett.* **1969**, 3269–3272; *Bull. Soc. Chim. Fr.* **1971**, 957–962. (b) Bertrand, M.; Dulcère, J.-P.; Grimaldi, J.; Malacria, M. *C. R. Hebd. Seances Acad. Sci., Ser. C.* **1974**, *279*, 805–806. (c) Roumestant, M. L.; Malacria, M.; Gorè, J.; Grimaldi, J.; Bertrand, M. *Synthesis* **1976**, 755–757. (d) Bertrand, M.; Dulcère, J.-P.; Gil, G. *Tetrahedron Lett.* **1977**, 4403–4406. (e) Bertrand, M.; Dulcère, J.-P.; Gil, G.; Roumestant, M. L. *Ibid.* **1979**, 1845–1846. (f) Bertrand, M. *Parfums Cosmet., Aromes* **1981**, *39*, 29–38. (g) Dulcère, J.-P.; Gorè, J.; Roumestant, M. L. *Bull. Soc. Chim. Fr.* **1974**, 1119–1123. (h) Delbecq, F.; Gorè, J. *Tetrahedron Lett.* **1976**, 3459–3460. (i) Doutheau, A.; Gorè, J.; Malacria, M. *Tetrahedron* **1977**, *33*, 2393–2398. (j) Malacria, M.; Gorè, J. *J. Org. Chem.* **1979**, *44*, 885–886. (k) Baudouy, R.; Delbecq, F.; Gorè, J. *Tetrahedron* **1980**, *36*, 189–195. (l) Balme, G.; Malacria, M.; Gorè, J. *J. Chem. Res. Synop.* **1981**, 244–245. See also: Malacria, M.; Roumestant, M. L. *Tetrahedron* **1977**, *33*, 2813–2817.

(3) Review: Santelli-Rouvier, E. J.; Santelli, M. *Synthesis* **1983**, 429–442.

(4) Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 6, pp 237–238. $PdCl_2$ can be used in place of $PdCl_2(MeCN)_2$, which is presumably formed in situ.

(5) Other catalysts were also examined. $PtCl_2(MeCN)_2$ also catalyzes the reaction but is less active than $PdCl_2(MeCN)_2$.

(6) Mayer, H.; Isler, O. In "Carotenoids"; Isler, O., Ed.; Birkhäuser: Basel, 1971; p 403, and references therein. 3-Methyl-1-penten-4-yn-3-ol and its allylic isomers are available from Fluka AG, Buchs, Switzerland.

(7) 1,4-Cyclopentadienyl acetates **2** (or other alkanoates) with R^1 and/or R^2 = alkyl and isomers resulting from [1,5] hydrogen shifts or dimers thereof are unknown, but the three isomers with $R^1 = R^2 = H$ have been reported: Winstein, S.; Shatavski, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183–4184. Mironov, V. A.; Fadeeva, T. M.; Yankovskii, S. A.; Luk'yanov, V. T.; Akhrem, A. A. *Zh. Org. Khim.* **1976**, *12*, 992–997. Muronov, V. A.; Dolgaya, M. E.; Luk'yanov, V. T.; Yankovskii, S. A. *Ibid.* 1436–1442. For a dimer formally derived from 2,4-cyclopentadienyl propionate, see: Breslow, R.; Hoffman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 2110–2111.

(8) Short review: Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer: Berlin, 1980; p 130. In addition, see: (a) Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 5200–5206. (b) Tsuji, J.; Tsuruoka, K.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1701–1702. (c) Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321–324. (d) Grieco, P. A.; Takigawa, T.; Bongers, S. L.; Tanaka H. *J. Am. Chem. Soc.* **1980**, *102*, 7587–7588. (e) Grieco, P. A.; Tuthill, P. A.; Sham, H. L. *J. Org. Chem.* **1981**, *46*, 5005–5007. (f) Golding, B. T.; Pierpoint, C.; Aneja, R. *J. Chem. Soc., Chem. Commun.* **1981**, 1030–1031. For Pd(II)-catalyzed Cope rearrangements, see: Overman, L. E.; Jacobsen, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7225–7231 and references therein.

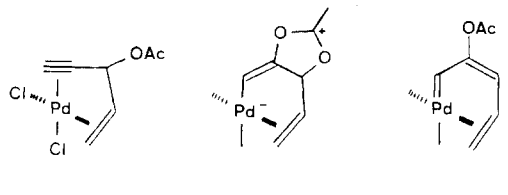
(9) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2541–2542. Exposure of the primary isomers of **5**[6] to $PdCl_2(MeCN)_2$ under the conditions described above brought about elimination exclusively; acetic acid was detected but no attempt was made to identify the dienyne. Rearrangement to the primary isomers, followed by rapid elimination, could be a side reaction in the other cases.

(10) Saucy, G.; Marbet, R.; Lindlar, H.; Isler, O. *Helv. Chim. Acta* **1959**, *42*, 1945–1955. Schlossarczyk, H.; Sieber, W.; Hesse, M.; Hansen, H.-J.; Schmid, H. *Ibid.* **1973**, *56*, 875–944. Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804–1806. Cookson, R. C.; Cramp, M. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1980**, 197–198.

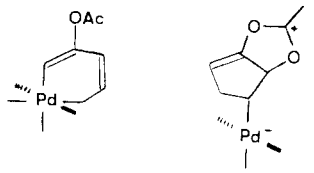
(11) Reference 4, pp 351–384.

(12) Variant of Henry's mechanism for the rearrangment of allylic acetates.[8a]

(13) Or a palladia[2.2.0]bicyclohexene or a vinylpalladiacyclobutene. The intermediacy of the former can be related to the Pd(II)-catalyzed cyclopropanations of olefins with diazo compounds [Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssiè, P. *J. Org. Chem.* **1980**, *45*, 695–702. Majchrzak, M. W.; Kotelko, A.; Lambert, J. B. *Synthesis* **1983**, 469–470. Also references in both.] and to platinacyclobutane chemistry [Hartley, F. R. in ref 4, pp 573–579], cf. **20** → **21**, present work.



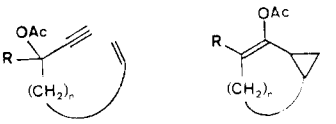
15 16 17



18 19

eliminate **2**. The acetoxonium species **16** could be an intermediate, **15** → **16** → **18**, but could also cyclize to the cyclopentene **19** by migratory insertion, **15** → **16** → **19**; loss of Pd(II) and opening of the acetoxonium ring would liberate **2**. The butadienylcarbene complex **17**[14] is another possible intermediate, **15** → **16** → **17** → **18**, but could again cyclize directly. These speculations involve Pd(II) and Pd(IV) species. Pd(0) and Pd(II) counterparts could be involved instead although this is less likely.

The transformation **1** → **3** was developed after the serendipitous discovery of a related reaction:[15] $PdCl_2(MeCN)_2$ also catalyzes the cyclization of homologues **20** of **1** (n = 2 and 3, R = alkyl) to bicyclic acetates **21**, yields



20 21

for five examples being 10–40%. It was reasoned that chelation of Pd(II) probably channels **20** toward cyclization but is inherently poor for n = 2 and 3 and optimal for n = 0 (i.e., **1**) and for n = 1. The latter case and further variants are under study.

Acknowledgment. The technical assistance of E. Cristoforetti, P. Janin, T. Lander, and P. Mêgard and helpful discussions with E. P. Kündig are gratefully acknowledged.

Registry No. **4** (R′ = CH_3), 88868-51-3; **4** (R′ = $(CH_2)_4CH_3$), 88868-52-4; **5**, 35272-86-7; **6**, 1120-73-6; **7**, 88868-53-5; **8**, 25564-22-1; **9**, 88868-54-6; **10**, 53253-07-9; **11**, 88868-55-7; **12**, 53253-08-0; **13**, 88868-56-8; **14**, 15210-25-0; $PdCl_2(H_3CCN)$, 14592-56-4; *N*-phenylmaleimide, 941-69-5.

(14) Reference 4, pp 292–296. Hartley, F. R. in ref 4, pp 502–510.

(15) The same cyclization, but catalyzed by $ZnCl_2$, had already been reported from these laboratories: Strickler, H.; Davis, J. B.; Ohloff, G. *Helv. Chim. Acta* **1976**, *59*, 1328–1332.

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Additions and Corrections

Vol. 47, 1982

Maria Inês de Almeida, Antonia T. do Amaral, and Luciano do Amaral*. Effects of α Substitution on the Carbonyl Stretching Frequencies of Phenyl Carboxylates.

Page 1569. Table III. The values of h_0, k_{obsd}, and $k_{H_3O^+}$ should be the following: phenyl acetate (3.16, 5.01, 7.41), (2.77×10^{-4}, 3.16×10^{-4}, 3.93×10^{-4}), 2.75×10^{-5}, phenyl allylacetate (5.01, 7.41, 12.59), (1.39×10^{-4}, 1.57×10^{-4}; 1.91×10^{-4}), 6.87×10^{-6}; phenyl allylethylacetate (5.01, 7.41, 12.59), (1.24×10^{-4}, 1.42×10^{-4}, 1.58×10^{-4}), 4.58×10^{-6}; phenyl allylphenylacetate (3.16, 5.01, 7.41), (7.46×10^{-5}, 8.19×10^{-5}, 8.90×10^{-5}), 3.36×10^{-6}; phenyl allylisopropylacetate (3.16, 5.01, 7.41), (5.02×10^{-5}, 5.52×10^{-5}, 6.44×10^{-5}), 3.36×10^{-6}; phenyl allyldimethylacetate (3.16, 5.01, 7.41), (8.67×10^{-5}, 9.02×10^{-5}, 9.54×10^{-5}), 2.05×10^{-7}; phenyl trimethylacetate (13.8, 26.3, 52.5), (1.12×10^{-3}, 1.35×10^{-3}, 1.89×10^{-3}), 3.34×10^{-7}.

Page 1569. Table IV. The values for k_{obsd} for phenyl allylethylacetate, phenyl allylisopropylacetate, and of phenyl allyldimethylacetate are expressed in min^{-1}. The values for k_{OH^-} in the last column have been recalculated and are, respectively, 5.36×10^{-1}, 1.97×10^{-1}, 8.60×10^{-3}, 1.59×10^{-1}, 2.56×10^{-2}, 3.93×10^{-3}, 8.99×10^{-3}, and 1.21×10^{-1}.

Page 1570. Table V. The substituent group parameters were inadvertently scrambled. The correct values are as follows:

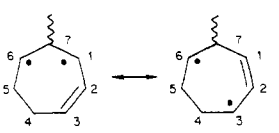
R_1	R_2	R_3	E_s	σ^*	$\nu_{Charton}$
H	H	H	0.00	0.00	0.52[a]
allyl	H	H	−0.60	+0.066	0.74[a]
allyl	Et	H	−0.78	−0.403	0.81
allyl	Ph	H	−0.91	+0.154	0.86
allyl	*i*-Pr	H	−0.91	−0.164	0.86
allyl	Me	Ph	−1.05	+0.371	0.92
allyl	Me	Me	−1.13	−0.258	0.94
allyl	Ph	Ph	−1.48	+0.335	1.07
Me	Me	Me			1.24[a]

In the original printed version of the paper, the mistakes are only in the tables (III, IV, and V). Equation 5 was obtained with correct values. The same is true for the calculations of eq 9–11 and 15.

Vol. 48, 1983

William J. Leigh* and R. Srinivasan. Organic Photochemistry with 6.7-eV Photons. The Divergent Photobehavior of *exo*- and *endo*-7-Methyl-2-norcarene.

Page 3973. Structure **18** is incorrectly drawn. The correct structure is



18