were applied to the plate, and the imide was found to migrate as expected. It was observed that the imide fluoresced under long-wavelength (366 nm) excitation after chlorination with Cl_2. This observation gave a very sensitive assay for imide (<0.5 nmol of an authentic sample could be detected). In the analysis of the coupled product, a trace of imide was barley detectable on the plate. A comparison of this plate to standards showed that this amount of imide corresponds to <2% of the total peptide.

Acknowledgment. Support of this work by the National Science Foundation and the National Institute of General Medical Sciences is gratefully acknowledged. We also acknowledge with appreciation the gifts of peptides by Dr. W. W. Bromer of Eli Lilly and Co., Indianapolis, Dr. S. I. Sallay, Indiana University–Purdue University, Fort Wayne, and Dr. F. E. DeBons of our laboratory.

Registry No. **4**, 35657-34-2; **9a**, 515-94-6; **9b**, 305-62-4; **14**, 85701-35-5; **15**, 85701-36-6; **20**, 85701-37-7; **21**, 85701-38-8; **22**, 85701-39-9; **23a**, 85701-40-2; **23b**, 85701-41-3; **24**, 55604-95-0; **25**, 85701-42-4; **26**, 85701-43-5; **27a**, 75865-40-6; **27b**, 75851-15-9; **28a**, 85701-44-6; **28b**, 85709-74-6; **29**, 85701-45-7; **30**, 85701-46-8; **31**, 85701-47-9; **32a**, 75851-19-3; **32b**, 85701-48-0; **33**, 24715-24-0; **34**, 85701-49-1; **35**, 75851-26-2; **36**, 75851-25-1; **37**, 75851-24-0; **39**, 85701-50-4; **40**, 85701-51-5; **41**, 85701-52-6; **42**, 75851-27-3; **43**, 77529-79-4; **44**, 85701-53-7; **45**, 85701-54-8; **46**, 85701-55-9; **47**, 66134-74-5; **48**, 85701-56-0; **49**, 85701-57-1; **50**, 85701-58-2; **51**, 13574-13-5; **52**, 7536-59-6; **53**, 85701-59-3; **54**, 85701-60-6; **55**, 85701-61-7; **56**, 85701-62-8; **57**, 3392-07-2; **58**, 85701-63-9; **59**, 85701-64-0; **60**, 85701-65-1; **61**, 4124-76-9; **65a**, 85701-66-2; **65b**, 85701-67-3; **66a**, 85701-68-4; **66b**, 85701-69-5; **67a**, 85701-70-8; **67b**, 85701-71-9; **68a**, 5879-06-1; **68b**, 2746-34-1; **69a**, 85701-72-0; **69b**, 85701-73-1; **70a**, 85701-74-2; **70b**, 85701-75-3; **71a**, 85701-76-4; **71b**, 85701-77-5; **72a**, 85701-78-6; **72b**, 85701-79-7; **73a**, 85701-80-0; **73b**, 85701-81-1; 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide, 1892-57-5; Glu(γ-benzyl ester)·Asp(β-*tert*-butyl ester) copolymer, 65045-19-4; EDC, 85701-82-2; 2,4-diaminobutanoic acid dihydrochloride, 6970-28-1; CDI, 530-62-1; Bz-Gly-Glu-*N*-methylamide, 85701-58-2; pyroGlu-Asp-Phe-amide, 73322-74-4; His-Ser-Gln-Gly-Thr-Phe-Thr-Ser-Asp-Tyr-Ser-Lys, 24870-77-7; Gln-Tyr-Trp-Pro-Phe-Ser-Ala-Ser-Asp-Leu-Trp, 85701-85-5; Trp-Ala-Gly-Gly-Asp-Ala-Ser-Gly-Glu, 62568-57-4; Pro-Leu-Arg-Ala-Ile-Gly-Pro-Pro-Ala-Glu-Pro-Asn-Gly-Leu-Val-Pro-Leu-Gln-Tyr-Trp-Pro-Phe-Ser-Ser-Ala-Asp-Leu-Tyr, 75851-17-1; Ac-Gly-Aspβ-diethylamide, 75851-14-8; Bz-Gly-Asp(β-benzyl ester), 85701-83-3; methylamine hydrochloride, 593-51-1; acetylphenylalanine, 2018-61-3; aspartic acid dibenzyl ester *p*-toluenesulfonate, 2886-33-1; Ac-Phe-Asp, 61884-19-3; valinamide, 13474-14-1; prolinamide, 2812-47-7; Asp β-benzyl ester, 2177-63-1; glycinamide hydrochloride, 1668-10-6; Ac-Gly, 543-24-8; Gluα-Phe-Ala, 85701-84-4; Glu-Val-Phe, 31461-61-7; Glu-Gly-Phe, 42155-93-1; Gluγ-Met, 17663-87-5; *N*-*tert*-butoxycarbonylglutamic acid γ-benzyl ester, 13574-13-5; diethylamine, 109-89-7; glutamic acid γ-benzyl ester, 1676-73-9; *p*-nitrophenyl trifluoroacetate, 658-78-6; Gly-Ile, 19461-38-2; *tert*-butoxycarbonylglycine, 4530-20-5; Gluα-Gly-Ile, 85701-61-7; Val, 72-18-4; Ala-Leu, 3303-34-2; leucinamide hydrochloride, 10466-61-2.

Supplementary Material Available: A description of the synthetic procedures and the corresponding experimental details (29 pages). Ordering information is given on any current masthead page.

Catalyzed Rearrangements of Ten-Membered-Ring Allenes

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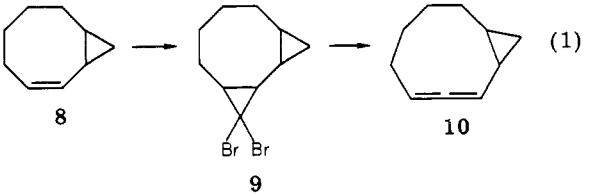
Cyclodeca-1,2,5,8-tetraene (**1**) is shown to rearrange in the presence of various catalysts in acetic acid to *cis,syn*-tricyclo[4.4.0.$0^{2,4}$]deca-5,8-diene (**5**) which is accompanied in some cases by rearranged acetate products, principally *cis,syn*-bicyclo[4.4.0]deca-4,8-dien-2-yl acetate (**3**). Cyclodeca-1,2,5-triene (**6**) rearranges in a similar way, except that acetate product was only observed for Ag(I) catalysts. A related allene, bicyclo[7.1.0]deca-2,3-diene underwent normal oxymercuration without rearrangement.

Earlier work[1] revealed that treatment of allene **1** with mercuric ion in acetic acid did not give the expected oxymercuration[2] product **2** (Scheme I) but instead gave only the rearranged products **3**–**5** (43:3:54 ratio). Similar treatment of allene **6** gave only the tricyclic compound **7**; no acetates corresponding to **3** or **4** were observed. The present study examined the effect of various other catalysts and also the oxymercuration of an isomeric system **10**.

Results and Discussion

Allene **10** was prepared from bicyclo[6.1.0]non-2-ene[1] (**8**) by the method[3,4] which involves addition of dibromocarbenoid to generate **9** (eq 1) which is then treated with



(1)

methyllithium to produce allene **10** as a 70:30 mixture of diastereomers. The exclusive formation of allene product is an interesting contrast with 9,9-dibromobicyclo[6.1.0]-non-2-ene which reacts with methyllithium to give only tricyclic products resulting from transannular insertion into C–H bonds across the ring.[5]

Treatment of **10** with mercuric acetate in acetic acid, followed by lithium aluminum hydride reduction, gives a

(1) Thies, R. W.; Hong, P.-K.; Buswell, R.; Boop, J. L. *J. Org. Chem.* **1975**, *40*, 585.
(2) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783 and references therein.
(3) Skattebol, L. *Acta Chem. Scand.* **1963** *17*, 1683.
(4) Moore, W. R.; Ward, H. R. *J. Org. Chem.* **1962**, *27*, 4179.
(5) Cardenas, C. G.; Shoulders, B. A.; Gardner, P. D. *J. Org. Chem.* **1967**, *32*, 1220.

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Table I. Rearrangement of Allene 1 in Acetic Acid[a]

mmol of 1	catalyst	mmol of catalyst	time, h	% yield 1	% yield 3 + 4[b]	% yield 5
0.18	AgOAc	0.14	48		43	17
0.49	$HgSO_4$	0.016	0.5		24[c]	28[c]
0.26	$ZnBF_4$	0.25	72		18	49
0.19	$Rh(Ph_3P)_3Cl$	0.034	144		14	35
0.24	$Rh(Ph_3P)_2(CO)Cl$	0.038	144		6	36
0.15	$Cu(OAc)_2$	0.39	144			87
0.22	CuOAc	0.28	96			92
0.17	TlOAc	0.49	72			89
0.17	$(Ru(CO)_3Cl_2)_2$	0.036	72			79
0.36	$(C_3H_5PdCl)_2$	0.044	24	50[d]		50[d]

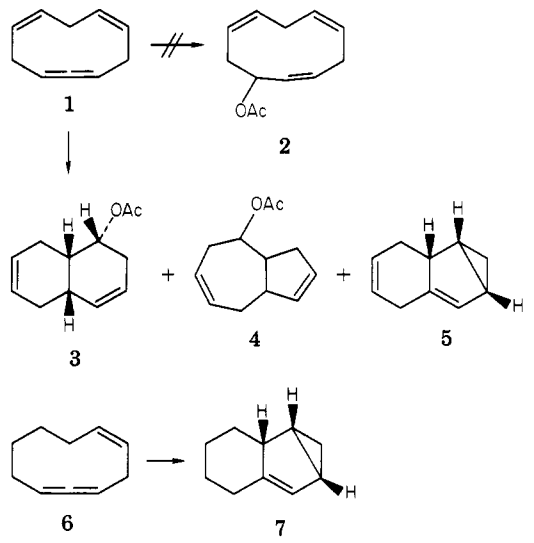
[a] All runs used 1 mL of acetic acid at room temperature. [b] 3 is the dominant acetate product in all cases; e.g., the 3/4 ratio is 43:3 with $HgSO_4$. [c] Isolated yields. [d] These numbers represent only a GLC ratio. In all other cases except $HgSO_4$, the numbers represent yields based on a GLC comparison with an internal standard.

Table II. Rearrangement of Allene 6 in Acetic Acid[a]

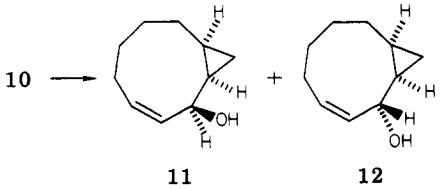
mmol of 6	catalyst	mmol of catalyst	time, h	% yield 6	% yield 15	% yield 7
0.42	AgOAc	0.14	1		13[b]	89
0.68	$HgSO_4$	0.039	0.75	1		70
0.22	$Hg(OAc)_2$	0.030	0.25	4		51
0.29	$ZnBF_4$	0.009	24	29		45
0.48	$Rh(Ph_3P)_3Cl$	0.079	24	5		42
0.52	$Rh(Ph_3P)_2(CO)Cl$	0.066	24	6		43
0.46	CuOAc	0.66	331	40		5
0.34	TlOAc	0.14	7	24[c]		76[c]
0.26	$(Ru(CO)_3Cl_2)_2$	0.06	1	26[c]		74[c]
0.29	$(C_3H_5PdCl)_2$	0.13	24			100
0.077	$(Rh(CO)_2Cl)_2$	0.01	0.25	18		100

[a] All runs used 1 mL of HOAc at room temperature. [b] There are no other acetates formed in >1%. [c] The numbers represent only a GLC ratio. In all other cases the numbers represent yields based on a GLC comparison with internal standard.

Scheme I



92:8 ratio of *endo*- and *exo*-bicyclo[7.1.0]dec-3-en-2-ol (**11** and **12**, eq 2). The structural assignments were made from

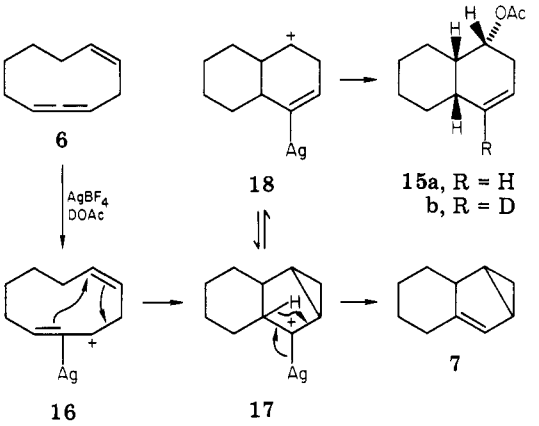


(2)

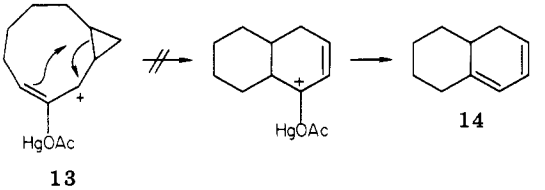
spectral data and by reducing the double bonds in **11** and **12** to produce the known saturated analogues.[6] There was

(6) Thies, R. W.; Billigmeier, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 200.

Scheme II



no evidence of rearranged products which might have arisen from processes like those postulated for compounds **1** and **6**. For example, intermediate **13**, that presumably leads to **11** and **12**, could conceivably rearrange to **14** by the mechanism shown in eq 3 which is quite similar to that



(3)

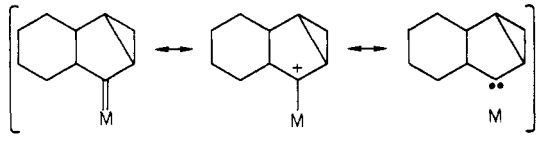
postulated earlier[1] for **1** and **6** (see **6** to **7** in Scheme II). The lack of rearranged products supports the usual observation that oxymercuration does not favor rearrangements.[7] In this case, the cyclopropyl ring apparently

stabilizes the positive center, directing the attack entirely to one side of the allene, but it does not give products which might result from cyclopropylcarbinyl to homoallyl rearrangement.

The situation with systems 1 and 6 is dramatically different; they give only rearranged products with a variety of catalysts as outlined in Tables I and II. For allene 1 both rearranged acetate and tricyclic hydrocarbon products were formed for the first five catalysts; only the tricyclic compound 5 was formed for the lower five catalysts. For allene 6, only tricyclic hydrocarbon 7 is formed in all cases except the Ag(I) catalysts which also generate acetate product. A detailed study of all catalysts was not made, but it was established that the conversion of 6 to 7 is first order in catalyst for $Hg(OAc)_2$ and $(Rh(CO)_2Cl)_2$. The other catalysts were less well-behaved; in most cases some catalyst remained undissolved, and in some cases more catalyst appeared to go into solution as the reaction proceeded. The times listed in Table II provide only a very rough guide of catalytic activities under the conditions used. Initially, we postulated that electrophilic catalysts like Hg(II), Zn(II), and Tl(I) would be more prone to produce acetate products while Rh(I) and Ru(II) might give only tricyclic 5 or 7. This did not prove to be the case; for allene 1 two Rh(I) catalysts gave acetate products, and TlOAc, which usually has chemistry like Ag(I) species,[8] gave only 5.

For both allenes, Ag(I) catalysts were most effective in generating acetate products relative to tricyclic ones. This was something of a surprise since Ag(I) catalysts are not generally used to add solvent to double bonds as Hg(II) catalysts are. A test with 1,2-cyclononadiene showed no reaction after 18.5 h with AgOAc in acetic acid. A 3-h reaction with $AgBF_4$ and *p*-toluenesulfonic acid in acetic acid also showed no reaction.

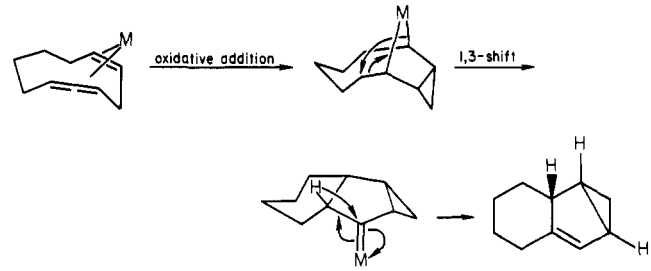
In order to test whether the mechanism proposed earlier[1] for oxymercuration is also consistent with the Ag(I)-catalyzed addition, we reacted allene 6 with $AgBF_4$ in deuterated acetic acid. Such a mechanism predicts (see Scheme II) that the tricyclic product 7 should not incorporate deuterium because the silver ion departs along with an internal hydride shift whereas 15 should have deuterium in the position shown because the silver is lost by an addition–elimination[9] step involving D^+. The mass spectra and NMR spectra substantiated that 7 contained no deuterium and that one deuterium is incorporated in the position shown in **15b**. The reactions of the other catalysts could go by a similar mechanism although it should be noted that other mechanisms are possible.[10] For example, intermediate 17 can be described as the three resonance forms **19a–c** which are like those described earlier for



19a 19b 19c

bicyclobutane rearrangements.[11] For catalysts like Hg(II) the **19a** form is presumably unimportant because the Hg(IV) state is much higher in energy, but for catalysts like Rh(I) this could be an important form. For such catalysts a mechanism can be written (Scheme III) that involves initial complexation to two π bonds followed by oxidative addition and a 1,3-shift of a carbon–metal bond to produce **19a** which can undergo a hydride shift as before. Such a mechanism is also consistent with the deuterium experiment and the stereochemistry of the products. If **19a** equilibrates with the homoallylic form (e.g., 17 → 18 in Scheme II), this could also lead to acetate products.[12] Acetate product 15 does not result from the reaction of 7 with Ag(I) catalyst since a pure sample of 7 when treated under the same conditions gave <1% of 15 after 22 h.

Scheme III



19a

While Scheme III is unlikely for catalysts like Hg(II), it may be that the π complexation is important for all the catalysts and that addition to the allene in Scheme I is also aided by such π complex formation. This provides a possible reason why catalysts like Ag(I) that do not normally react with allenes do so in these systems.[13] Alternatively, it may simply be that formation of 16 is significantly assisted by the homoallylic π bond because it results in a more stable intermediate.

In summary, allene 10 undergoes normal oxymercuration, but allenes 1 and 6 give only rearranged products. Many other catalysts also give the same type of products, but the ratio varies in a way that was not readily correlated. The previous mechanistic scheme is consistent with the data, but an alternative scheme is proposed which is also consistent for catalysts that have higher oxidation states readily available.

Experimental Section

General Procedures. Spectral measurements utilized Beckman IR8 and Perkin-Elmer 621 and 727B infrared, Varian 360, HA-100, and FT-80 NMR, and Varian-Matt CH7 and CDC110B mass spectrometer instruments. GC analyses were carried out on a Varian 1200 (FID) chromatograph with columns which were approximately 4 ft × 0.125 in. (7% DEGS on 80/100 Chromosorb G). Preparative GC was done on a Varian 920 chromatograph with a 2 ft × 0.25 in. 4.9% OV-101 on 80/100 Chromosorb G column. Elemental analyses were performed by Chemalytics Inc.

10,10-Dibromotricyclo[7.1.0.0^{2,4}]decane (9). A mixture of 2.1 g (18.7 mmol) of potassium *tert*-butoxide, 5 mL of dry pentane, and 1.63 (13.4 mmol) of 8 (prepared earlier[1]) were stirred in an ice–salt bath under nitrogen as 3.35 g (25 mmol) of bromoform

(7) For example, norbornene does not rearrange during oxymercuration: Brown, H. C.; Kawakami, J. H.; Ikegami, S. *J. Am. Chem. Soc.* **1967**, *89*, 1525.

(8) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Interscience: New York, 1972; p 280.

(9) Bach, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 1771.

(10) As outlined earlier,[1] intermediates 17 and 18 could also be reached by addition to the other double bond of the allene followed by transannular participation.

(11) Noyori, R. *Tetrahedron. Lett.* **1973**, 1691. Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 7748. Paquette, L. A.; Brown, A. R.; Chamot, E.; Blount, J. F. *J. Am. Chem Soc.* **1980**, *102*, 643 and references therein.

(12) Intermediates 17 and 18 are formally written as classical ions although nonclassical ions may be involved as described earlier.[1]

(13) *cis*-1,2,6-Cyclodecatriene forms a stable π complex involving one allene π bond and one π bond from a double bond (not necessarily from the same molecule). Devaprabhakara, D.; Nagendappa, G.; Joshi, G. S. *J. Organomet. Chem.* **1971**, *27*, 421.

was added dropwise over 1 h. The reaction was then allowed to come to room temperature and stirred for ca. 20 h. Water (3 mL) was added, and the reaction was taken up in pentane, washed until neutral, and dried over $MgSO_4$. Vacuum distillation gave 2.08 g (53% yield) of **9**: bp 93 °C (1.8mm); IR neat) 3065 (cyclopropyl CH) cm^{-1}; NMR (CCl_4) δ 2.45–0.30 (m, 13 H), 0.18 (q, J = 4 Hz, 1 H). Anal. Calcd for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80. Found: C, 40.89; H, 4.63.

Bicyclo[7.1.0]deca-2,3-diene (10). A solution of 83 mg (0.28 mmol) of **9** in 2 mL of ether was cooled at −78 °C under nitrogen as 2 mL of 2 M methyllithium in ether was dripped in over 1 h. The reaction mixture was kept at −40 °C for 40 min, and then 1.5 mL of water was added at 0 °C. The reaction was taken up in ether, washed until neutral, and dried over $MgSO_4$. Ether was removed at atmospheric pressure, and the allene was bulb-to-bulb distilled to give 30 mg (80%) of **10**: IR 3075 (cyclopropyl CH), 1950 (allene) cm^{-1}; NMR[14] (CCl_4) δ 5.75–5.55 (m, 0.3 H), 5.3–5.1 (m, 0.3 H), 5.1–4.7 (m, 1.4 H), 2.4–0.6 (m, 11 H), 0.45–0.3 (m, 0.3 H), 0.2–0.0 (m, 0.7 H); mass spectrum, m/e (relative intensity) 134 (1), 133 (3), 132 (3), 131 (50.5), 119 (12.5), 117 (5); 105 (18.5), 100 (11), 95 (13), 94 (16), 93 (52.5), 69 (100).

Oxymercuration[14] of Allene 10. A solution of 280 mg (1.96 mmol) of **10**, 640 mg (2.01 mmol) of mercuric acetate, and 5 mL of glacial acetic acid was stirred at room temperature for 30 min. The reaction was taken up in ether, washed with 10% $NaHCO_3$ until neutral, and then dried over $MgSO_4$. The ether solution was then stirred with 100 mg of $LiAlH_4$ for 40 min and quenched with 10% aqueous Rochelles solution. The ether layer was dried ($MgSO_4$) and concentrated to give 110 mg of white solid which GC indicated was a 92:8 mixture[15] of two alcohols (**11** and **12**). The major isomer was obtained in pure form by chromatography on SilicAR with 10:1 pentane–ether as the eluant which gave the endo isomer **11**: mp 85–88 °C; IR (neat) 3620, 3400 (OH), 3100, 3080, 3040 (cyclopropyl CH), 680 (cis C=C) cm^{-1}; NMR (CCl_4) δ 5.6 (dd, J = 8, 10 Hz, 1 H), 5.3 (dt, J = 6, 10 Hz, 1 H), 4.0 (t, J = 8 Hz, 1 H), 2.4–0.6 (m, 12 H), 0.1 (m, 1 H); high-resolution mass spectrum, m/e 152.120 (calcd for $C_{10}H_{16}O$ 152.120).

The mixture of alcohols **11** and **12** was reduced in ether with hydrogen and Adams catalyst which gave two new alcohols which were identified as *endo*- and *exo*-bicyclo[7.1.0]decan-2-ol by comparing GC retention times (coinjection) and mass spectra with known samples.[6]

Structural Assignment of *cis,syn*-Bicyclo[4.4.0]dec-4-en-2-yl Acetate (15). A solution of 47.5 mg (0.35 mmol) of allene **6** and 39.8 mg (0.20 mmol) of $AgBF_4$ in 1.5 mL of glacial acetic acid was stirred in a foil-wrapped flask and monitored by GC. At 36 min there was a 70:30 ratio of **7** to **15** and no starting allene. The reaction workup was as described above except that the products were separated by GC on a DEGS column which gave **7** (assigned previously[1]) and **15**: IR (CCl_4), 3010 (vinyl CH), 1736 cm^{-1} (ester); NMR (CCl_4) δ 5.72–5.48 (m, 1 H), 5.45–5.25 (m, 1 H), 5.05–4.80 (m, 1 H), 2.7–1.1 (m, 15 H; s at 1.98), high-resolution mass spectrum, m/e 194.131 (calcd 194.131).

To establish the position of the double bond relative to the acetate group, enough $Eu(fod)_3$ shift reagent was added to move the chemical shifts downfield to the positions indicated (H_2, δ 11.5; H_3, δ 5.45 and 4.55; H_4, δ 6.23; H_5, δ 5.78) which allowed decoupling experiments that demonstrated that H_2 was coupled to the two H_3 protons which were coupled to H_4. The cis,syn stereochemistry was established by reducing the acetate to the alcohol with $LiAlH_4$ and then reducing the double bond with PtO_2/H_2 as described above which gave the saturated alcohol (mp 85.0–86.8 °C), which showed no melting point depression when mixed with an authentic sample[16] of *cis,syn*-decalin-1-ol (*endo,cis*-bicyclo[4.4.0]decan-2-ol).

General Procedure for Catalytic Rearrangements. A standard solution of comparable weights of allene **1** and naphthalene standard (or allene **6** and tetralin standard) in ether was prepared. A measured portion was transferred to the reaction flask, and the ether was removed under a slow flow of nitrogen. Acetic acid (1 mL) and a weighed portion of catalyst were added (see Tables I and II). The reaction was quenched by adding pentane or ether and washing the organic layer with saturated $NaHCO_3$ and saturated NaCl. The organic layer was dried ($MgSO_4$) and injected onto a GC column, and the product yields were calculated from the peak areas relative to the standard. Another run was made without the standard to ensure that no product peaks were hidden under the standard GC peak.

For the reaction of allene **6** with $Hg(OAc)_2$, solutions of 30 mg of **6** in 2 mL of acetic acid were reacted with catalyst amounts of 2, 4, 6, and 8 mg, and the amount of allene left at 15 min was measured. A plot of log A_0/A vs. [catalyst] gave a linear plot. A similar experiment with 20.6 mg of allene **6** and 4-, 6-, 8-, and 12-mg amounts of $[Rh(CO)_2Cl]_2$ also gave a linear plot.

Reaction of 6 with DOAc and $AgBF_4$. A solution of 48.6 mg (0.06 mmol) of $AgBF_4$ and 1.3 mL of acetic acid-*d* was stirred for 24 h, and the reaction was quenched as described above. A GC separation gave **7**, which displayed the same spectra as those for **7** isolated from reaction with nondeuterated acetic acid, and **15b**, which had a spectrum very similar to **15a** except that the broad doublet-like pattern at δ 5.72–5.48 was replaced by a broad singlet at δ 5.58, and the broad doublet-like pattern at δ 5.45–5.25 was missing (>75%). The mass spectrum of **15b** showed a prominent peak at m/e 135, corresponding to the loss of HOAC (m/e 134 for **15a**).

Stability Control Test for 7. A sample of **7** from the reaction of **6** with $[(C_2H_5)_2Pd\ Cl]_2$ in acetic acid was distilled in a Kugelrohr apparatus. A solution of 8.4 mg (0.064 mmol) of **7**, 7 mg (0.036 mmol) of $AgBF_4$, and 0.3 mL of acetic acid was stirred 23 h. GC showed <1% acetate formation. Then 14 mg of $AgBF_4$ was added, and stirring was continued for 3.5 h, at which time GC again showed <1% acetate.

Reactivity of 1,2-Cyclononadiene. A solution of 40 mg (0.32 mmol) of 1,2-cyclononadiene,[4] 40 mg (0.21 mmol) of $AgBF_4$, and 0.5 mL of acetic acid was stirred 18.5 h; analysis by GC showed no reaction. Addition of 9 mg of *p*-toluenesulfonic acid and stirring for 3 h again showed no reaction.[17]

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Registry No. 1, 38772-62-2; **6**, 85319-55-7; **7**, 85404-36-0; **8**, 2570-07-2; **9**, 85354-12-7; **10** (isomer 1), 71055-04-4; **10** (isomer 2), 71076-10-3; **11**, 85319-56-8; **12**, 85354-13-8; **15a**, 85319-57-9; **15b**, 85319-58-0; AgOAc, 563-63-3; $HgSO_4$, 13766-44-4; $ZnBF_4$, 13826-88-5; $Rh(Ph_3P)_3Cl$, 14694-95-2; $Rh(Ph_3P)_2(CO)Cl$, 13938-94-8; $Cu(OAc)_2$, 142-71-2; CuOAc, 598-54-9; TlOAc, 563-68-8; $(Ru(CO)_3Cl_2)_2$, 22594-69-0; $(C_3H_5PdCl)_2$, 12012-95-2; $Hg(OAc)_2$, 1600-27-7; $(Rh(CO)_2Cl)_2$, 14523-22-9.

(14) The allene is a 30:70 mixture of diastereomers; allene recovered from a partial oxymercuration exhibited a similar spectrum except that the δ 5.75–5.1 and 0.45–0.3 bands were gone.

(15) This ratio is approximate because the alcohols are not completely stable to the GC conditions.

(16) We thank Dr. W. G. Dauben for an authentic sample. Dauben, W. G.; Tweit, R. C.; Mannereskantz, C. *J. Am. Chem. Soc.* **1954**, *76*, 4420.

(17) The stereospecificity of oxymetalation of 1,2-cyclononadiene with mercury, thallium, and lead catalysts has recently been reported: Bach, R. D.; Holubka, J. W.; Willis, C. L. *J. Am. Chem. Soc.* **1982**, *104*, 3980.