Reduction of 1,1-Dichloro-2-methyl-2-phenylbutane with Triphenyltin Hydride. A 25-ml round-bottomed flask was charged with 2.80 g (13 mmol) of the dichloride and 5.0 g (14.6 mmol) of triphenyltin hydride under nitrogen. The mixture, which immediately became turbid, was stirred (magnetic stirrer) and heated at 78° under nitrogen for 12 hr. The resulting clear mixture was distilled to give 2.24 g (95%) of 1-chloro-2-methyl-2-phenylbutane, bp 62–62.5° (0.4 mm), n^{25}D 1.5213. Glc analysis (10% DC-200 fluid at 120°) showed that a single component was present. *Anal.* Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.56; H, 8.11; Cl, 19.48. Nmr: δ 0.70 (t, J = 7.8 Hz, 3 H), 1.40 (s, 3 H), 1.95 (q, J = 7.8 Hz, 2 H), 3.58 (s, 2 H), and 7.18 ppm (s, 5 H).

A similar reduction of the optically active insertion product, (+)-1,1-dichloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +1.88° (9.22 mmol), was carried out with 10.6 mmol of triphenyltin hydride to give 1.22 g (73%) of (+)-1-chloro-2-methyl-2-phenylbutane, n^{25}D 1.5213, d_4^{25} 1.0295, $[\alpha]^{25}$D +8.55° (neat), pure by glc, with an identical nmr spectrum. *Anal.* Calcd for $C_{11}H_{15}Cl$: C, 72.31; H, 8.28; Cl, 19.41. Found: C, 72.18; H, 8.23; Cl, 19.29.

In another such reaction, starting with (+)-1,1-dichloro-2-methyl-2-phenylbutane with $[\alpha]^{25}$D +1.95°, an 85% yield of (+)-1-chloro-2-methyl-2-phenylbutane with $[\alpha]^{25}$D +8.28° (neat) was obtained, n^{25}D 1.5212.

Preparation of Methyl 3-Methyl-3-phenylpentanoate from 1-Chloro-2-methyl-2-phenylbutane. A 50-ml three-necked flask equipped with a pressure-equalizing dropping funnel topped with a nitrogen inlet tube was flame-dried under nitrogen and charged with 0.25 g (36 mg-atoms) of Li in the form of a dispersion in oil. The oil was washed out with hexane and THF, and the lithium then was covered with 3 ml of dry THF and cooled to −10°. Five drops of 1-chloro-2-methyl-2-phenylbutane was added and then 3 drops of iodomethane. The mixture turned brown; it was stirred for 30 min and then cooled to −78°. The rest of the 1-chloro-2-methyl-2-phenylbutane (1.00 g, 5.5 mmol) was added dropwise with stirring over a 10-min period. The reaction mixture was stirred at −78° for 6 hr and then was poured onto a slurry of crushed Dry Ice in dry diethyl ether. The resulting mixture was allowed to warm slowly to room temperature and acidified with 6 *N* HCl. The ethereal layer was separated and the aqueous layer extracted with ether. The combined ether layers were dried over $MgSO_4$ and the solvent was removed at reduced pressure. A few milliliters of dry ether was added to the residue and treatment with ethereal diazomethane followed. Evaporation of the reaction mixture at reduced pressure was followed by trap-to-trap distillation of the residue at 0.75 mm (pot temperature to 105°). The distillate, n^{25}D 1.5024, 65% yield, was pure by glc (10% UC-W98 at 130°) and was identified as the title compound. *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.74; H, 8.64. Nmr: δ 0.67 (t, J = 7.9 Hz, 3 H), 1.48 (s, 3 H), H), 1.76 (q, J = 7.9 Hz, 2 H), 2.55 (s, 2 H), 3.46 (s, 3 H), and 7.23 (s, 5 H); ir (neat) $\nu_{C=O}$ 1735 cm^{-1}.

This procedure was followed in the reaction of 6.3 mmol of (+)-1-chloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +8.55°, with 0.3 g of lithium (dispersion). After the reaction mixture had been poured onto Dry Ice and acidified, the ether extracts were evaporated and the residue was distilled (trap-to-trap) at 0.4 (pot temperature to 142°) to give a light yellow oil, 0.79 g (62% yield). A 100-mg aliquot of this oil was crystallized from pentane at −78° to give white needles, mp 38.5–42°, $[\alpha]^{25}$D +13.6° (*c* 3.47 in $CHCl_3$). The remaining acid was esterified with diazomethane in ether solution to give 0.60 g (46%) of (+)-methyl 3-methyl-3-phenylpentanoate, bp 76–78.5° (0.5 mm), n^{25}D 1.5022, d^{25}_4 0.9925, $[\alpha]^{25}$D +12.27° (neat). Cram, *et al.*,[12] reported bp 96° (1 mm), n^{25}D 1.5018, and $[\alpha]^{25}$D +12.7° (neat). *Anal.* Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.88; H, 8.81.

In another such reaction sequence starting with (+)-1-chloro-2-methyl-2-phenylbutane, $[\alpha]^{25}$D +8.28°, this ester was obtained in 50% yield, n^{25}D 1.5020, $[\alpha]^{25}$D +12.16° (neat).

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Homotropilidene–Palladium Dichloride Complexes

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Abstract: Homotropilidenes (barbaralone, dihydrobullvalene, bicyclo[5.1.0]octa-2,5-diene, bullvalene, and benzobullvalene) react with bis(benzonitrile)palladium dichloride to form complexes. The dihydrobullvalene complex is shown to have a bicyclic structure derived from addition of palladium dichloride across a vinylcyclopropane unit on the basis of the nmr spectrum and borohydride reduction to bicyclo[3.3.2]deca-2,7-diene. The other homotropilidene complexes have similar structures, although barbaralone and bicyclo[5.1.0]octa-2,5-diene also appear to form π-olefin complexes having the cyclopropane intact underc ertain conditions. In the presence of hydroxylic solvents or upon treatment with silver acetate, the palladium dichloride complexes are converted into derivatives having oxygen substituents in place of chloride. The acetoxy complex obtained from the barbaralone–palladium dichloride adduct is characterized by borohydride reduction to 4-acetoxybicyclo[3.3.1]nona-2,7-dien-9-one and the isomeric 2,6-dien-9-one. The bullvalene–palladium dichloride adduct rearranges to a complex of bicyclo[4.2.2]deca-2,4,7,9-tetraene at 0°. A similar rearrangement occurs with the benzobullvalene complex in refluxing chloroform. A mechanism based on cyclopropyl carbinyl intermediates is proposed.

Interest in homotropilidene–metal complexes has centered on the possibility of metal-moderated Cope rearrangements and metal-induced skeletal rearrangements. Irreversible rearrangements have been observed in the presence of iron (bullvalene, semibullvalene, dibenzosemibullvalene),[3] palladium (bullval-

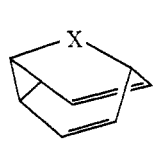
(1) A. P. Sloan Fellow, 1971–1973.

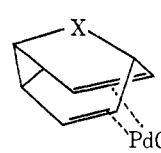
(2) We acknowledge support from the Research Corporation and from the donors of the Petroleum Research Fund, administered by the American Chemical Society.

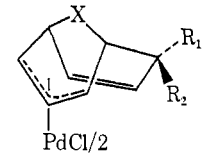
(3) (a) G. N. Schrauzer, P. Glockner, K. I. G. Reid, and I C. Paul, *J. Amer. Chem. Soc.*, **92**, 4479 (1970); (b) G. N. Schrauzer, P. Glockner, and R. Merenyi, *Angew. Chem., Int. Ed. Engl.*, **3**, 509 (1964); (c) R. Aumann, *ibid.*, 10, 189, 190 (1971); (d) R. M. Moriarty, C.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, **93**, 6709 (1971); (e) R. M. Moriarty, K.-N. Chen, C.-L. Yeh, J. L. Flippen, and J. Karle, *ibid.*, **94**, 8944 (1972); (f) R. Aumann, *Angew. Chem.*, **84**, 583 (1972).

ene),[4] mercury (bullvalene),[5] and chromium (bullvalene),[6] while a degenerate Cope rearrangement has been reported only in the case of semibullvalene–tungsten pentacarbonyl.[7,8] Although little evidence is available regarding the mechanism of the irreversible rearrangements, metal-induced cleavage of a divinylcyclopropane C–C bond has precedent[3e] and is generally invoked to rationalize the products. However, it is difficult to isolate complexes derived from cyclopropane cleavage without further reaction. Thus, the bullvalene–palladium dichloride adduct rearranges rapidly even at 0° to a complex of bicyclo[4.2.2]deca-2,4,7,9-tetraene.[4] In order to clarify the structure of the unstable palladium complex and its role in the rearrangement, we have examined the chemical behavior of several homotropilidene–palladium dichloride adducts.

Preparation of Starting Materials. Bullvalene[9] (**1**), dihydrobullvalene[9] (**2**), and barbaralone[10] (**3**) were prepared by known methods. The benzylidene derivative **4** of barbaralone was synthesized by Wittig reaction and was identified on the basis of the characteristic homotropilidene nmr spectrum. Benzobullvalene **5** was obtained by photolysis of 7,8-benzobicyclo[4.2.2]-deca-2,4,7,9-tetraene.[11] As expected,[12] the nmr spectrum of **5** indicates no participation by the aromatic ring in the degenerate Cope rearrangement. Homotropilidene (bicyclo[5.1.0]octa-2,5-diene) (**6**) has been synthesized previously by photolysis of 1,3,6-cyclooctatriene or by carbene addition to cycloheptatriene,[13] but both methods required difficult separations. A convenient synthesis was found using the Wittig reaction of *cis*-cyclopropane-1,2-dicarboxaldehyde[14] with the ylide derived from trimethylene-1,3-bis(triphenylphosphonium) dibromide. The yield of homotropilidene is low (10%), but only a single hydrocarbon product **6** is formed which can be purified easily provided that the Wittig reaction is quenched after 2 min. Longer reaction times result in isomerization of **6** into bicyclo[5.1.0]octa-2,4-diene, the conjugated double bond isomer.

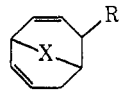


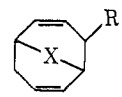




1, X = CH=CH
2, X = CH_2CH_2
3, X = C=O
4, X = C=CHC_6H_5
5, X = C_6H_4
6, X = H,H

7 **13**, X = CH=CH; R_2 = Cl; R_1 = H
8 **14**, X = CH_2CH_2; R_2 = Cl; R_1 = H
9 **15**, X = CO; R_2 = Cl; R_1 = H
10 **15a**, X = CO; R_2 = H; R_1 = OAc
11 **15b**, X = CO; R_2 = H; R_1 = OCH_3
12 **16**, X = C=CHC_6H_5; R_2 = Cl; R_1 = H
17, X = C_6H_4; R_2 = Cl; R_1 = H
18, X = H,H; R_2 = Cl; R_1 = H
18a, X = H,H; R_2 = R_1 = H





21, X = CH_2CH_2; R = H
23, X = CO; R = H
27, X = CO; R = OAc
22, X = CO; R = H
28, X = CO; R = OAc

All of the homotropilidenes studied react rapidly with bis(benzonitrile)palladium dichloride in benzene or methylene chloride, resulting in immediate precipitation of palladium dichloride complexes. The barbaralone complex **9** is relatively stable and can be stored indefinitely, but **8**, **10**, **11**, and **12** slowly decompose at room temperature while **7** rearranges at 0°. All of the complexes decompose in the presence of hydroxylic solvents or upon prolonged exposure to light. In general, the palladium chloride adducts are too insoluble to be recrystallized, and with the exception of the homotropilidene and dihydrobullvalene complexes, too insoluble for nmr spectroscopy.

Due to the low solubility and chemical lability of the homotropilidene complexes, the usual methods of characterization were of limited value. Instead, we have relied on the technique of sodium borohydride reduction of carbon–palladium bonds. Previous studies in these laboratories indicated that skeletal rearrangements do not occur during C–Pd cleavage by borohydride.[15] Thus, the structure of the organic ligands can be deduced from the structure of the reduction products.

Homotropilidene–$PdCl_2$. Freshly prepared homotropilidene (**6**) reacts with bis(benzonitrile)palladium dichloride to form a microcrystalline orange complex. Homotropilidene is displaced from the complex by pyridine, indicating that major structural changes do not occur in the initial reaction. However, the nmr spectrum of the slightly soluble complex is not completely consistent with the π-olefin structure **12** having the homotropilidene skeleton intact. Signals are observed at δ 0.8–2.1, 2.4–2.8, 3.4–4.0, and 4.5–6.1 ppm in an approximate ratio of 3.5:1:1:3.7. The high field signals are characteristic of cyclopropyl protons, but the poor integral and overall complexity of the spectrum suggests that other species are present in addition to **12**.

This tentative conclusion is reinforced by the results of borohydride cleavage at −44°. Hydrocarbons are recovered in 56% yield consisting of bicyclo[5.1.0]oct-2-ene, homotropilidene (**6**), 1,5-cyclooctadiene, 1,4-cyclooctadiene, and cyclooctene derived from over-reduction of the cyclooctadienes. The ratio of bicyclic/monocyclic products is *ca.* 2:1, consistent with the presence of a complex **18**, derived from cyclo-

(4) E. Vedejs, *J. Amer. Chem. Soc.*, 90, 4751 (1968).
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(6) R. Aumann, *Angew. Chem. Int. Ed. Engl.*, 9, 800 (1970).
(7) R. M. Moriarty, C.-L. Yeh, E.-L. Yeh, and K. C. Ramey, *J. Amer. Chem. Soc.*, 94, 9229 (1972).
(8) Relatively stable complexes of bullvalene are known which have frozen, nondegenerate structures: A. Allerhand and H. S. Gutowsky, *ibid.*, 87, 4092 (1965); J. S. McKechnie, M. G. Newton, and I. C. Paul, *ibid.*, 89, 4819 (1967); J. McKechnie and I. C. Paul, *Chem. Commun.*, 44 (1968); also ref 6.
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(11) E. Vedejs, *Tetrahedron Lett.*, 2633 (1968); E. Vedejs and R. A. Shepherd, *ibid.*, 1863 (1970).
(12) J. F. M. Oth, R. Merenyi, H. Rottele, and G. Schroder, *Chem. Ber.*, 100, 3538 (1967).
(13) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, 19, 715 (1963); (b) W. R. Roth and B. Peltzer, *Justus Liebigs Ann. Chem.*, 685, 56 (1965); (c) J. Zirner and S. Winstein, *Proc. Chem. Soc., London*, 235 (1964).
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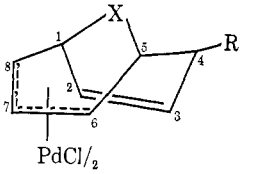
Table I. Nmr Spectra (100 Hz) of Homotropilidene–Palladium Complexes in $CDCl_3$ (δ from TMS)[a,b]

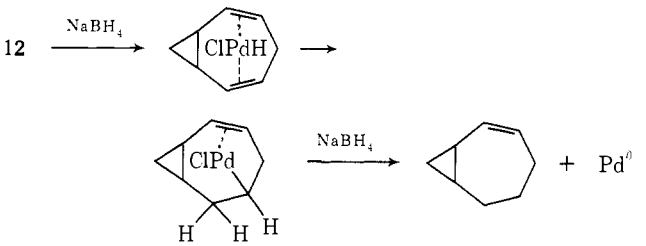


Compd	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9–H_{10}	OAc
14	3.3 (m)	5.6–6.0 (m)	5.6–6.0 (m)	5.29 (d × d)	1.6–2.5 (m)	4.32 (dxd)	5.33 (t)	5.6–6.0 (m)	1.6–2.5 (m)	
	$J_{12} = J_{18} = 8$			$J_{34} = 3.8$		$J_{67} = 8.0$	$J_{67} = J_{78} = 8$			
	$J_{19} = 3$			$J_{45} = 6.7$		$J_{56} = 8.9$				
14a	3.32 (m)	5.1–6.0 (m)	5.1–6.0 (m)	5.18 (s)	2.0 (m)	4.2 (br t)	5.51 (t)	6.16 (t)	1.6–2.2 (m)	2.22 (s)
	$J_{12} = J_{18} = 8$					$J_{67} = J_{56} = 8$	$J_{78} = J_{67} = 8$	$J_{18} = J_{78} = 8$		
15a	3.3 (m)	6.28 (d × d)	5.2–5.9 (m)	5.52 (d)	3.3 (m)	5.2–5.9 (m)	5.2–5.9 (m)	5.2–5.9 (m)		2.18 (s)
	$J_{12} = 3$	$J_{23} = 5$		$J_{34} = 1.8$						
		$J_{12} = 3$								

[a] Chemical shifts at normal MH100 probe temperature; temperature variations cause reversible changes in chemical shifts, especially for H_6 and H_8 in **14**. J values are in hertz. [b] Coupling constants assigned using spin decoupling or $Eu(fod)_3$ techniques.

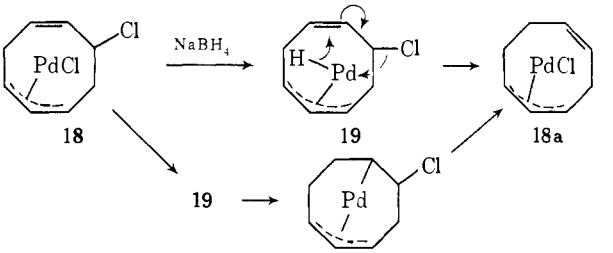
propane ring cleavage, in addition to the π-olefin complex **12**.

The initial step in reduction of diene–palladium dichloride complexes involves conversion of a Pd–Cl bond into a Pd–H species.[16] Addition of the palladium hydride derived from **12** to one of the double bonds followed by borohydride cleavage of the resulting C–Pd bond would rationalize the formation of bicyclo[5.1.0]oct-2-ene. Recovery of homotropilidene probably is due to displacement of the ligand by norbornene which is present in the reduction medium to minimize overreduction.[15]



Formation of cyclooctadienes can be explained by reduction of **18** to afford an allylpalladium hydride structure **19**. Transfer of hydride from palladium to carbon and chlorine from carbon to palladium in a six-center transition state would result in formation of the allyl complex **18a**. Alternately, the same effect would be achieved by stepwise addition of the palladium hydride to the transannular double bond to place chlorine and palladium substituents at adjacent carbons. Dechloropalladation would afford **18a** which could then be reduced by borohydride at either allylic carbon to form 1,4- or 1,5-cyclooctadiene.

The nmr spectrum of **12** + **18** gradually changes at temperatures above 50°, and signal intensity is enhanced in the olefinic region at the expense of the cyclopropyl region. Borohydride reduction of the heterogenous mixture obtained after prolonged heating affords 1,4- and 1,5-cyclooctadienes and cyclooctene



to the exclusion of bicyclic products. This result suggests slow conversion of **12** into **18**, but the allyl complex **18** could not be isolated in pure form to prove this point.

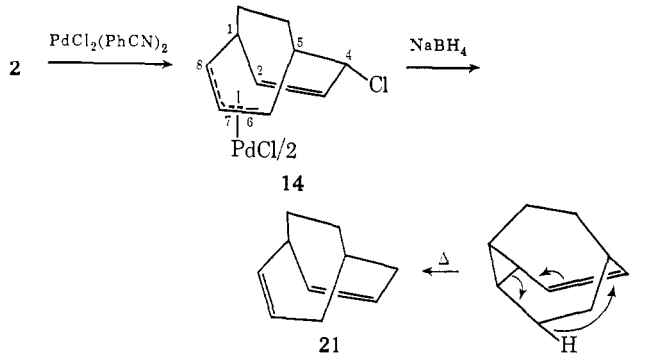
Dihydrobullvalene–$PdCl_2$. The complex **14** was prepared from dihydrobullvalene and bis(benzonitrile)-palladium dichloride. In contrast to the other homotropilidene–palladium dichloride complexes, **14** is sufficiently soluble for molecular weight determination and is clearly dimeric in chloroform. Coordinating solvents such as pyridine or dimethyl sulfoxide displace dihydrobullvalene from the complex provided that anhydrous conditions are maintained. Traces of moisture are sufficient to decompose the complex and even the ethanol stabilizer present in ordinary chloroform attacks the substance to form an uncharacterized ethoxy complex. Borohydride reduction affords a single hydrocarbon product (66%) having four olefinic hydrogens, but no cyclopropyl hydrogens in the nmr spectrum. The hydrocarbon is identified as bicyclo[3.3.2]deca-2,7-diene (**21**) by comparison with a sample prepared from tetrahydrobullvalene[9] by a thermal 1,5-H shift.[17]

On the basis of evidence from borohydride reduction as well as the nmr spectrum (Table I), the dihydrobullvalene–palladium dichloride adduct must have the bicyclic structure **14**. There is no evidence of a rapid equilibrium between **14** and the tricyclic π-olefin complex **8** on the nmr time scale, but displacement of di-

(16) E. Vedejs, M. F. Salomon, and P. D. Weeks, *J. Organometal. Chem.*, 40, 221 (1972).

(17) The analogous thermal rearrangement of dihydrobullvalene has been reported: J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Amer. Chem. Soc.*, **89**, 612 (1967).

hydrobullvane by coordinating agents could be interpreted as evidence that the barrier between **14** and **8** is not large. However, it is also possible to rationalize conversion of **14** to dihydrobullvalene by ligand-induced 1,3-dechloropalladation. The chemical evidence is insufficient to distinguish these alternatives and indicates only that cyclopropane cleavage is readily reversible under certain conditions.

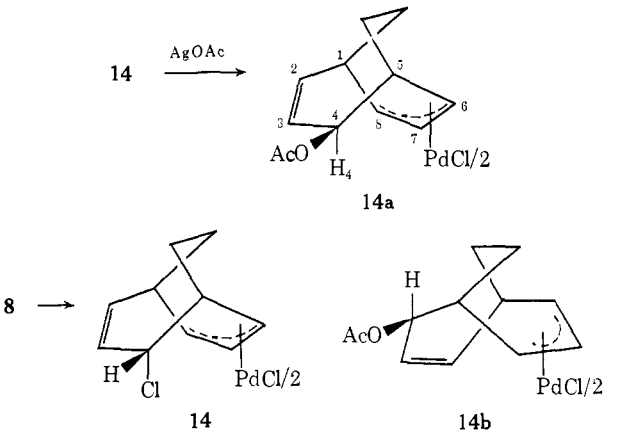


Treatment of **14** with silver acetate results in an acetoxy complex **14a** which could not be crystallized or purified completely. However, the nmr spectrum is sufficiently resolved to permit unequivocal assignment of the doubly allylic H_1 signal at δ 3.32 (m, $J_{1,2} = J_{1,8} = 8$ Hz), a methine proton next to palladium at δ 4.2 (t, $J = 8$ Hz), H_7 at δ 5.51 (t, $J = 8$ Hz), and the proton H_4 next to acetate at δ 5.18 (br s, width at half-height <4 Hz). The acetate methyl group is found at δ 2.22 as a sharp singlet, and H_8 is tentatively assigned at δ 6.16 (triplet, $J = 8$ Hz) from the coupling constants observed for the H_7 signal.

Nearly identical coupling is observed between H_5–H_6, H_6–H_7, H_7–H_8, and H_8–H_1 (*ca.* 8 Hz) in the nmr spectra of both **14** and **14a** indicating a coplanar arrangement of the allylpalladium and bridgehead protons. However, the H_4 methine signal next to acetate in **14a** is an unresolved singlet with coupling constants no larger than 1.5 Hz while in **14** the corresponding proton next to chlorine is a doublet of doublets, $J_{4,5} = 6.7$ Hz and $J_{3,4} = 3.8$ Hz.

The differences in H_4 coupling can be explained if **14** and **14a** have the same conformation of the flexible C_9–C_{10} and C_6–C_7–C_8 bridges and differ in stereochemistry at C_4. Either the *exo*- or the *endo*-acetoxy structures **14a** or **14b** can adopt a conformation having minimal H_4 coupling according to the Karplus relationship. However, on mechanistic grounds the exo acetate is more likely since the silver acetate reaction involves a cationic intermediate which is shielded on the endo face by palladium, possibly involving d orbital participation. Also, exo stereochemistry is observed in the analogous reaction of the barbaralone–palladium dichloride complex with silver acetate (see below). If acetate is exo, as in **14a**, then **14** must have an endo chloride as expected from transfer of chlorine from palladium to carbon in the precursor π-olefin complex **8**. The alternate possibility of exo chloride is ruled out because there would be no steric reason for the *exo*-acetoxy and *exo*-chloro complexes to differ in conformation as required by the differing H_4 coupling constants.

Barbaralone–$PdCl_2$. As the most readily available homotropilidene, barbaralone (**3**) was used most extensively to study the chemistry of homotropilidene–palladium dichloride complexes. The barbaralone complex is nearly insoluble in inert solvents and nmr spectra or molecular weight data could not be obtained. As usual, the organic ligand is displaced by DMSO or pyridine, and the complex is attacked by methanol at room temperature to form a methoxy complex presumed to be **15b**. The tricyclic π-olefin structure **9** is assigned to the barbaralone complex on the basis of infrared carbonyl absorptions at 5.86 and 5.93 μ (KBr). The cyclopropyl ketone carbonyl absorption of barbaralone is broad and occurs in the same frequency range while several bicyclic model compounds (**15a**, **22**, **23**) have carbonyl frequencies at 5.78 ± 0.02 μ.

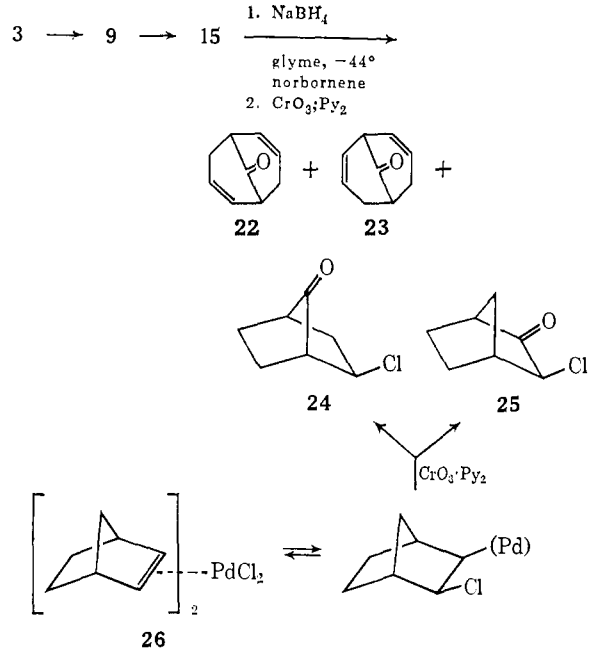


On the other hand, the products of sodium borohydride reduction are more consistent with the bicyclic structure **15**. Two isomeric dienones **22** and **23** are obtained in a combined yield of 14% along with recovered barbaralone (18%) and a mixture of alcohols. Collins oxidation of the crude ether-soluble products increases the yield of **22** and **23** to 30% and of barbaralone to **22**%, but two new ketones **24** and **25** are also formed (19%, 4:1 ratio). The major product **24** is identified as the known *exo*-2-chloronorbornan-7-one[18] and the minor isomer **25** is *exo*-3-chloronorbornan-2-one by comparison with an authentic sample.[19]

The dienones **22** and **23** are readily identified by nmr using the pseudocontact shift reagent $Eu(fod)_3$ since **23** is symmetric with respect to the carbonyl plane (two different bridgehead methines, two equivalent exo methylenes, and two equivalent endo methylenes) while **22** has a C_2 axis of symmetry (equivalent pairs of bridgehead, exo methylene, and endo methylene protons). Since the reduction products are bicyclic, we conclude that the barbaralone–palladium complex exists as the bicyclic isomer **15** in solution while the tricyclic structure **9** is favored in the solid.

The appearance of barbaralone among the borohydride products is consistent with our previous finding that norbornene (which must be present to avoid overreduction[15]) can displace organic ligands in π-olefin palladium complexes such as **12**. A norbornene complex containing palladium of an uncertain oxidation state apparently is then oxidized by Collins reagent to the chloronorbornanones **24** and **25**. Both **24** and **25** are formed in the same ratio by Collins oxidation of authentic norbornene–palladium dichloride complex

(18) R. Cupie, H. W. Tan, and F. M. Hsu, *J. Org. Chem.*, 33, 1542 (1968).
(19) J. B. Miller, *J. Org. Chem.*, 26, 4905 (1961).

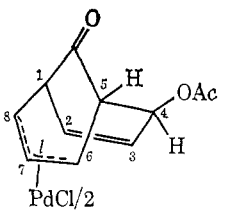


26 although the yield is only 30%. It is unlikely that the ether-insoluble complex **26** is present in the ether extract from borohydride reduction although some soluble source of palladium and chloride ion must be available to generate **26** or an equivalent structure during oxidation. Assuming reversible chloropalladation of norbornene, the formation of **25** is expected from oxidation of the C–Pd bond[16] while **24** would result from similar oxidation and a precedented carbonium ion rearrangement.[20]

Additional evidence bearing on the borohydride reduction was obtained using the acetoxy complex **15a**, available from **9** and silver acetate. In contrast to **9**, **15a** is attacked very slowly by hydroxylic solvents and is not cleaved to barbaralone by coordinating agents. The acetoxy complex is sufficiently soluble for molecular weight determination which agrees with a chlorine-bridged dimeric structure.

The infrared spectrum of **15a** has a strong carbonyl absorption at 5.8 μ and the nmr spectrum contains no cyclopropyl protons, as required for the bicyclic skeleton. Using the pseudocontact shift reagent Eu(fod)$_3$, the C_4 methine proton is rapidly shifted to lowest field (doublet with J = 1.8 Hz), and the two adjacent vinyl protons (H_2 and H_3) are deshielded from the remaining three hydrogens in the olefinic region. An ABXY pattern is observed for H_2 and H_3 with $J_{2,3}$ = 5 Hz, $J_{,12}$ = 3 Hz, and $J_{3,4}$ = 1.8 Hz. From these data and from the appearance of the H_5 signal it is clear that $J_{4,5} \leq 1$ Hz. The absence of appreciable H_4–H_5 coupling can only be reconciled with the *exo*-acetoxy orientation, resulting in a dihedral angle of 70–80° between the C-H_4 and C-H_5 bonds. Exo acetate stereochemistry is consistent with attack by external acetate upon a cationic organopalladium intermediate in the silver acetate reaction, and excludes a mechanism based on internal endo transfer of acetate from palladium to carbon.

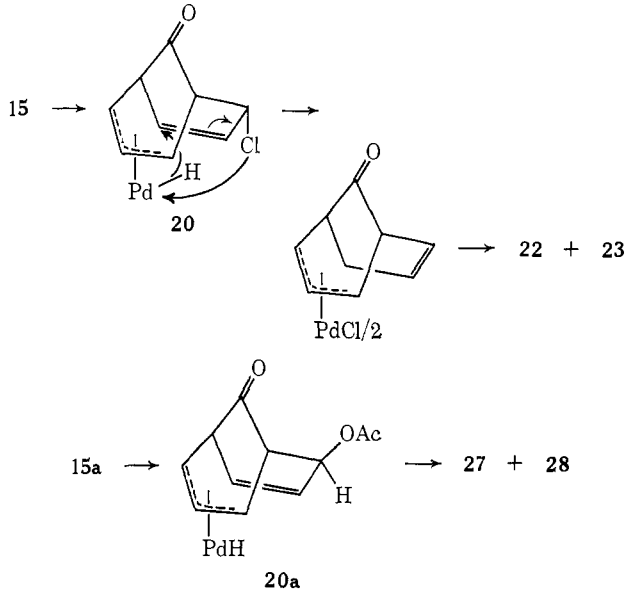
Borohydride cleavage of **15a** followed by Collins oxidation as before produces a mixture of acetoxy ketones (62%). The dienones **22** and **23** are formed in



15a

trace amounts but neither barbaralone nor chloronorbornanones are present as expected from the stability of **15a** toward coordinating agents. The isomeric acetoxy ketones **27** and **28** are difficult to separate and only the major isomer **27** (by a 3 : 1 ratio) is obtained in reasonable quantity and purity. However, the spectral data for both substances are consistent with the expected structures (see Experimental Section).

The contrasting behavior of **15** and **15a** toward borohydride reduction supports the six-center mechanism proposed for reduction of the homotropilidene complex **18**. A cyclic transition state is possible only if the leaving group (Cl, OAc) is on the same side of the molecule as the palladium substituent. By analogy to **14**, the palladium dichloride adduct is assigned endo stereochemistry and reductive displacement of chloride can proceed by the cyclic mechanism. The analogous process is impossible for the *exo*-acetoxy complex **15a** and the initial palladium hydride **20a** collapses to the acetoxy ketones **27** and **28**.



20a

Skeletal Rearrangements. Bullvalene–$PdCl_2$. A palladium chloride adduct of bullvalene is formed at −40° in methylene chloride as an orange solid. Treatment of the isolated complex with DMSO at −40° regenerates bullvalene, but similar treatment at 0° or higher affords only rearranged hydrocarbons. The principal product is bicyclo[4.2.2]deca-2,4,7,9-tetraene (**29**) identified by comparison with an authentic sample.[21] Naphthalene and traces of *cis*-9,10-dihydronaphthalene are also present in variable yield. Attempts to characterize the bullvalene complex by nmr or by borohydride reduction failed due to insolubility of the complex at the low temperatures necessary to avoid rearrangement. In

(20) W. C. Baird, Jr., *J. Org. Chem.*, **31**, 2411 (1966).

(21) M. Jones, Jr., and L. T. Scott, *J. Amer. Chem. Soc.*, **89**, 150 (1967).

the absence of direct evidence, the endo-substituted bicyclic structure **13** is assigned by analogy to the dihydrobullvalene complex **14**.

An ionic rearrangement mechanism offers the most plausible explanation for the formation of **29**. Backside displacement of endo chloride by the bridging double bond followed by a cyclopropylcarbinyl to homoallyl rearrangement would result in the palladium dichloride complex of **29**.

According to this mechanism, other homotropilidene–palladium dichloride complexes such as **16** or **17** having a suitably placed nucleophilic sp^2-hybridized carbon should rearrange similarly. The benzobullvalene complex **17** (structure assigned by analogy) was prepared in the usual way. Rearrangement does not occur at room temperature, and benzobullvalene is recovered quantitatively upon treatment of **17** with dimethyl sulfoxide. However, the complex rearranges slowly in refluxing chloroform to afford 7,8-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene after DMSO treatment.[22] Thus, the aromatic double bond is less reactive in displacement of the chloride leaving group but the same rearrangement pathway is still available.

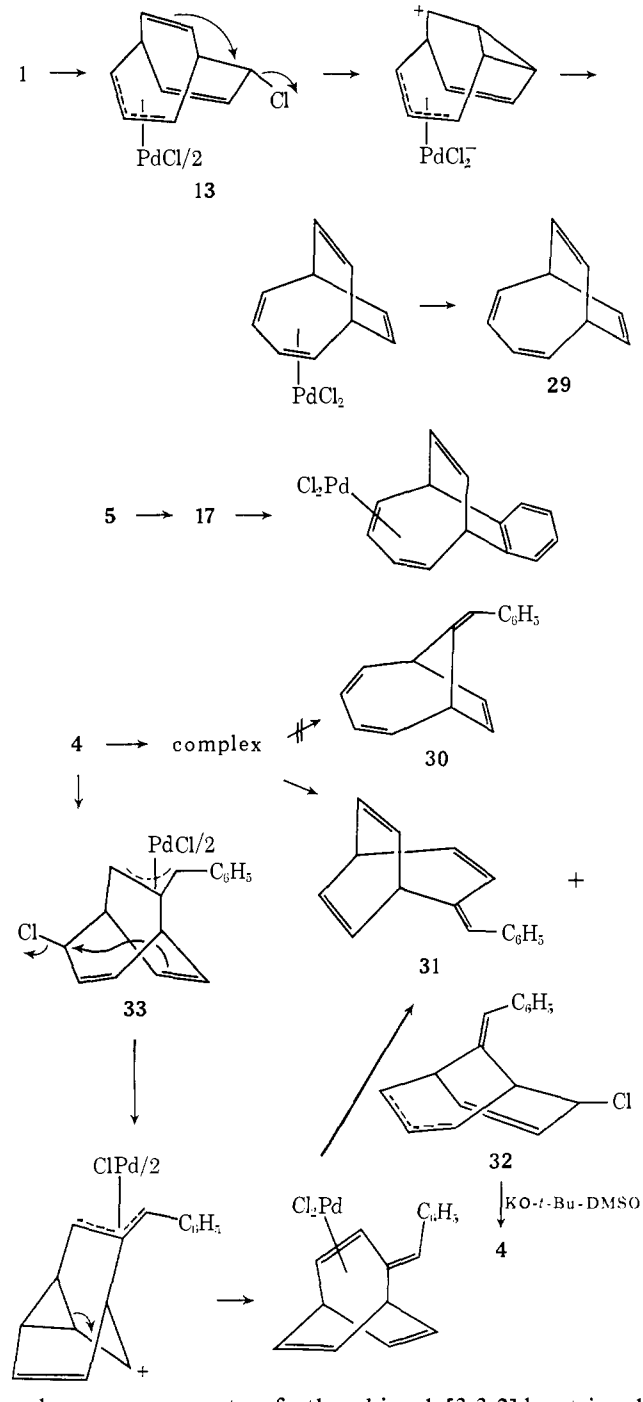
Slow rearrangement is also observed in the case of the palladium dichloride adduct of **4**. The starting hydrocarbon is recovered by DMSO treatment of the complex at 25°, but two new substances (11 : 1 ratio) are formed (19% yield) after several hours at 80° in dimethoxyethane. The minor product is an isomer of **4** but is not identical with an authentic sample of the expected 9-benzylidene derivative **30** of bicyclo[4.2.1]-nonatrienone.[23] Instead, the hydrocarbon proved to be **31**, identified by comparison with a sample prepared from bicyclo[3.2.2]nona-2,6,8-trien-4-one.[24]

The major rearrangement product contains chlorine and corresponds to a hydrogen chloride adduct of **4**, presumably derived from a decomposition pathway involving oxidation of the dimethoxyethane by palladium dichloride. The nmr spectrum of the chloride is consistent with the structure **32**, indicating that trivial addition of hydrogen chloride across a cyclopropane bond had occurred. In support of structure **32**, treatment with potassium *tert*-butoxide in dimethyl sulfoxide regenerates **4** (Scheme I).

The structure of the palladium dichloride complex of **4** has not been established, but the rearranged product **31** is difficult to rationalize on the basis of **16** as the precursor. An alternate mode of cyclopropane cleavage apparently occurs to form **33** as the intermediate. A homoallyl–cyclopropylcarbinyl rearrangement would then account for generation of the bicyclo-[3.2.2] skeleton.

The ionic rearrangements observed for the homotropilidene–palladium dichloride complexes have several precedents. Probably the closest analogy involves the conversion of bullvalene into **29** by mercuric salts,[5] a rearrangement which appears to follow the same mechanistic pathway as the palladium dichloride induced reaction. Addition of electrophiles across the cyclopropane bond of bullvalene has been observed in several instances not involving metal ion catalysis,[25]

Scheme I



and rearrangement of the bicyclo[3.3.2]decatrienyl cation into the cyclopropylcarbinyl derivatives is also precedented. Löffler has reported that treatment of 4-bromobicyclo[3.3.2]deca-2,6,9-triene with silver acetate affords a mixture of products including the tricyclic (40%) and bicyclic (15%) acetates **34** and **35** (Scheme II).[26] Similarly, we have found that acid-catalyzed hydration of bullvalene results in a tricyclic alcohol **36** as the major product. Oxidation of **36** with active MnO_2 followed by catalytic hydrogenation produces a cyclopropyl ketone **38** which is identical with a sample prepared from the diazo ketone **37**.

Ionic rearrangement of the bullvalene–palladium chloride adduct **13** differs from the solvolytic reactions

(22) This experiment was performed by R. P. Steiner (Ph.D. Thesis, University of Wisconsin, 1972).

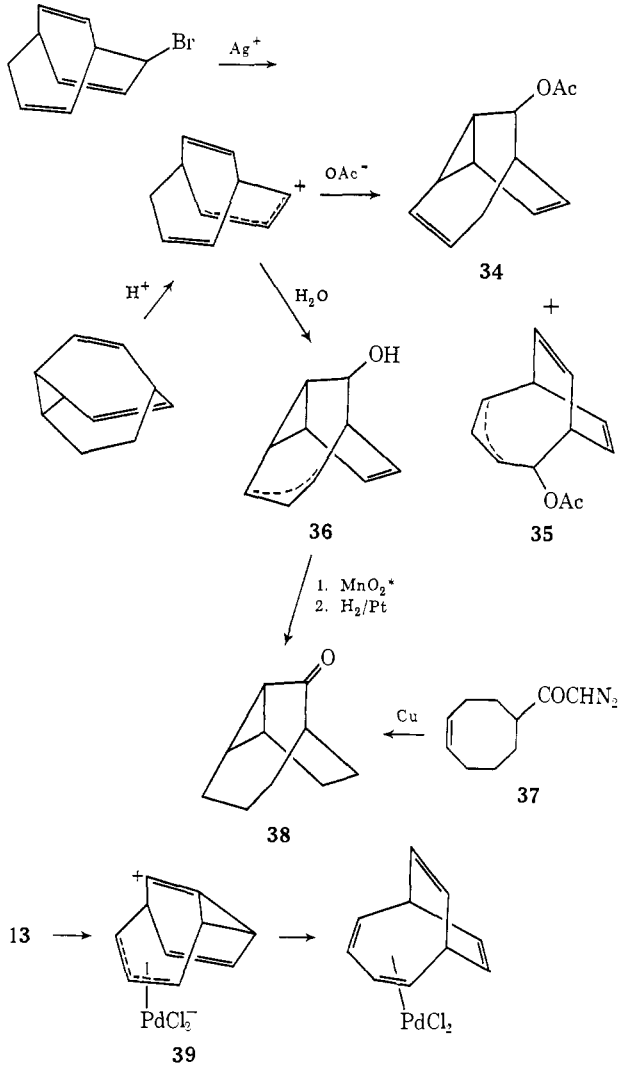
(23) T. A. Antkowiak, D. C. Sanders, C. B. Trimitsis, J. B. Press, and H. Schechter, *J. Amer. Chem. Soc.*, 94, 5366 (1972).

(24) M. J. Goldstein and B. G. Odell, *ibid.*, 89, 6356 (1967).

(25) H. P. Löffler and G. Schröder, *Chem. Ber.*, 103, 2105 (1970), and references therein.

(26) H. P. Löffler, *Tetrahedron Lett.*, 4893 (1971).

Scheme II



since nucleophiles are not present to trap the cyclopropylcarbinyl cation **39**. There is also additional driving force available for the final cyclopropylcarbinyl to homoallyl conversion. Rearrangement of **39** to the bicyclo[4.2.2]decatetraene skeleton places developing positive charge adjacent to the carbon–palladium bond which may stabilize the cation by d orbital participation.[27] A similar rationale accounts for the mercuric ion induced rearrangement of bullvalene,[5] although metal d orbital participation in the last step would have to be replaced by some other stabilizing effect such as $\sigma-\pi$ conjugation.[28]

Experimental Section

General. Melting points were determined on a hot-stage microscope apparatus and are corrected. Molecular weights were determined with a Mechrolab vapor pressure osmometer.[29] Nmr spectra were obtained using Varian HA-100, T-60, A60-A, XL-100, or JEOLCO MH-100 spectrometers.[30] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or by Spang Microanalytical Laboratory, Ann Arbor, Mich. Volatile products were analyzed using a Varian Aerograph 90-P3 gas chromatograph with 30 psi helium. Mass spectra were done on a MS-9 mass spectrometer. All reactions were done under a nitrogen atmosphere unless otherwise noted. Commercial reagents were used without purification unless specified otherwise. Preparation layer chromatography (plc) was done using Brinkman PF 254 silica gel.

Bicyclo[5.1.0]octa-2,5-diene (Homotropilidene) (6). Trimethylene-1,3-bis(triphenylphosphonium) dibromide (50 g, 69 mmol) was stirred vigorously in dry THF (900 ml) under argon at 0°. *n*-Butyllithium (130 mmol) in hexane was added over 10 min and the red solution was stirred 1 hr at 0° and warmed to 25°. *cis*-Cyclopropane-1,2-dicarboxaldehyde (69 mmol based on the acetal precursor[14]) was added at once with vigorous stirring. After 2 min water (100 ml) and distilled pentane (100 ml) were added. The pentane layer was washed with water, the water layer was extracted with pentane (2 × 50 ml), and the pentane layers were dried ($MgSO_4$) and evaporated at atmospheric pressure under a 12-in. Vigreux column. The residue was distilled (bulb to bulb, 15 mm) and **6** was purified by preparative glpc on 5 ft × 0.25 in. 20% SE-30 on Chromosorb W at 80° to remove residual THF; yield 0.72 g, 10% based on the cyclopropanedicarboxaldehyde precursor. The product was identical by nmr and glpc behavior with an authentic sample.[13]

Using longer reaction times, a second hydrocarbon was formed having a shorter retention time on SE-30. This compound was collected by preparative glpc and was identified as bicyclo[5.1.0]-octa-2,4-diene by nmr and uv (95% ethanol) λ_{max} 259 nm (ϵ 4290) (lit.[13] 258 nm (ϵ 4200)).

Benzobullvalene (5). A solution of 7,8-benzobicyclo[4.2.2]deca-2,4,7,9-tetraene (0.05 g) in ether (50 ml) was photolyzed through a Pyrex test tube using a Hanovia Type 679A39 lamp. The reaction was monitored by thin-layer chromatography and terminated after *ca.* 50% conversion to **5** which was more polar on silica gel than starting material. The mixture was separated by preparative layer chromatography over silica gel with hexane to yield recovered starting material (0.025 g) and **5** (0.02 g) as colorless needles from ether, mp 110–111°, *m/e* 180. Prolonged photolysis (*ca.* 1 hr) resulted in complete conversion of starting material but at least two new products appeared at the expense of **5**. Benzobullvalene nmr (room temperature, $CDCl_3$): δ 7.09 (4 H, br s), 5.80 (2 H, t, J = 4 Hz), 3.52–4.42 (4 H, m), 2.86 (2 H, t, J = 4 Hz); (−70°, $CDCl_3$, δ) 6.9–7.2 (4 H, m), 5.6–6.1 (4 H, m), 3.1 (1 H, br s), 2.83 (1 H, t, J = 4 Hz), 2.27 (2 H, br s).

9-Benzylidinetricyclo[3.3.1.0^{2,8}]nona-3,6-diene (4). Benzyltriphenylphosphonium chloride (6.5 g, 6.0 mmol) in dry THF (50 ml) was cooled to −78° and *n*-butyllithium (5.7 mmol) in hexane was added *via* syringe with rapid stirring. The red solution was stirred at −78° for 1 hr and allowed to warm to room temperature and **3** (0.360 g, 2.5 mmol) in dry THF (10 ml) was added in one portion to the reaction mixture. After the mixture was stirred overnight, water (10 ml) was added and the resulting solution extracted with pentane (4 × 50 ml). The pentane washings were combined, washed with water (3 × 50 ml), dried ($MgSO_4$), and filtered and the solvent, was evaporated *in vacuo*. Preparative layer chromatography (plc) with hexane yielded **4** (0.206 g, 67%) as the major uv active band (R_f 0.3), a white solid which was recrystallized from hexane: mp 76–77°; ir ($CHCl_3$, μ) 6.05, 11.9, 14.4; nmr ($CDCl_3$, δ) 7.2 (5 H, s), 6.4 (1 H, s), 5.7 (2 H, t, J = 7 Hz), 4.7 (2 H, t, J = 7 Hz), 3.6 (3 H, m), 3.0 (1 H, d of t, J = 2, 7 Hz); mass *m/e* 206 (M^+); uv λ_{max}^{MeOH} 265 (log ϵ 4.156). *Anal.* Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.82; H, 7.11.

General Preparation of $PdCl_2$ Complexes. A filtered solution of bis(benzonitrile)palladium dichloride (383 mg, 1 mmol) in dry dichloromethane (20 ml) was added dropwise over 20 min to a stirred solution of the homotropilidene (1 mmol) in dry dichloromethane (20 ml). The reaction was allowed to stir an additional hour after the addition was complete. The solvent was then removed *in vacuo*, and the remaining solid homotropilidene–palladium dichloride complex was washed with pentane until free of benzonitrile. Treatment of the homotropilidene–palladium dichloride complexes with an excess of dimethyl sulfoxide or pyridine resulted in liberation of the uncomplexed homotropilidene after 10 min of stirring at room temperature. Only complexes **8** and **11** were soluble enough for nmr spectra (see Discussion). **8** could be recrystallized from benzene–pentane to give an orange solid which blackened slowly above 120°. Molecular weight ($CHCl_3$) for $C_{20}H_{22}Pd_2Cl_4$, 582 (calcd, 617). The other palladium dichloride

(27) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 7461 (1970); R. S. Bly and R. C. Strickland, *ibid.*, **92**, 7459 (1970); M. Cais, *Organometal. Chem. Rev.*, 1, 435 (1966); M. J. Neugent, R. E. Carter, and J. H. Richards, *J. Amer. Chem. Soc.*, **91**, 6145 (1969).

(28) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970).

(29) We are grateful to Professor P. M. Treichel for making this instrument available.

(30) Provided by a departmental grant from the National Science Foundation.

adducts were microcrystalline and decomposed without melting above 100°.

General Procedure for Sodium Borohydride Reduction. The palladium compound to be reduced (1 mmol) was added to a dimethoxyethane (DME) (40 ml, freshly distilled from the sodium ketyl of benzophenone) containing norbornene (1 ml) and cooled to −60°. Sodium borohydride (0.038 g, 1 mmol) was then added to the rapidly stirred reaction, and the reaction was allowed to stir for 1 hr at −60°. After warming to room temperature, the reaction was stirred for an additional 3 hr and filtered, and pentane or ether was added. The pentane or ether solution was washed with water (3 × 50 ml), dried ($MgSO_4$), filtered, and concentrated by evaporation through a 6-in. Vigreux column. The products were analyzed by glpc after addition of internal standard.

Borohydride Reduction of Homotropilidene–Palladium Dichloride (12 + 18). The complex was prepared in the usual way at −20° and was reduced according to the general method. Pentane-soluble products were analyzed on 20 ft × 1/8 in. SE-30 on Chromosorb W at 60° using toluene as internal standard; in order of increasing retention time, the relative yields were as follows: cyclooctene (9%), 1,4-cyclooctadiene (12%), bicyclo[5.1.0]oct-2-ene (43%), bicyclo[5.1.0]octa-2,5-diene (**6**) (22%), and 1,5-cyclooctadiene (14%); total yield of volatile products, 56%.

The complexes (**12** + **18**) (0.025 g) were heated in dry chloroform (2.5 ml) at 60° for 6 hr. The chloroform was removed *in vacuo* and the dark brown residue was reduced and analyzed as before: cyclooctene (59%), 1,4-cyclooctadiene (23%), and 1,5-cyclooctadiene (18%), combined yield 56%.

Preparation of Authentic Bicyclo[5.1.0]oct-2-ene. A solution of acetic acid (0.45 g, 7.5 mmol) in dry pyridine (4 ml) was added slowly to a stirred solution of bicyclo[5.1.0]octa-2,5-diene (0.050 g, 0.47 mmol) and dipotassium azodicarboxylate (0.72 g, 3.7 mmol) in dry pyridine (7 ml) at 60°. After 4 hr stirring, the products were isolated by aqueous pentane work-up and the pentane-soluble products were analyzed by glpc as above. In order of increasing retention time were eluted an unknown (1.5%), bicyclo[5.1.0]oct-2-ene (20%), and starting material (78%). Bicyclo[5.1.0]oct-2-ene was collected by preparative glpc and identified by its nmr spectrum ($CDCl_3$, δ): 0.08 (1 H, m), 0.85 (1 H, m), 1.0–2.6 (8 H, m), 5.4 (1 H, m), 5.72 (1 H, br d, J = 11 Hz).

Reduction of Dihydrobullvalene–Palladium Dichloride (8). **8** was reduced according to the general method. The pentane-soluble products were analyzed at 90° by glpc on 10 ft × 0.25 in. 20% Carbowax on Chromosorb P and found to contain **21** (66%, based on diphenyl ether as an internal standard) as the only volatile product (ret time 27 min): ir (neat, μ) 6.04; nmr ($CDCl_3$, δ) 5.8–6.0 (4 H, m), 2.9–3.0 (2 H, m), 2.15 (4 H, m), 1.8–2.0 (4 H, m); mass m/e 134 (M^+).

Thermal Rearrangement of Tetrahydrobullvalene to 21. Tetrahydrobullvalene[9] (0.050 g, 0.37 mmol) was sublimed from a horizontal glass tube heated to 60° into a 6-in. glass column of packed glass beads heated to 350° under nitrogen flow. The product was collected over 30 min in a Dry Ice–acetone trap. **21** was the sole product according to glpc, ir, and nmr analysis.

Preparation of 14a. A suspension of **8** (0.108 g, 0.35 mmol), silver acetate (0.059 g, 0.35 mmol), and dry dichloromethane (20 ml) was stirred for 45 min. The yellow solution was then filtered through Celite to remove silver halide and the solvent removed *in vacuo*. Plc using 10% acetone in benzene yielded **14a** as a glassy yellow solid (R_f 0.5); ir ($CHCl_3$, μ) 5.80.

Reduction of Barbaralone–Palladium Dichloride (9). **9** was reduced according to the general method. The ether-soluble products were analyzed by glpc on a 10 ft × 0.25 in. 10% Carbowax on Chromosorb P at 160°, and found to contain a 3:1 mixture of **22** and **23** (total yield 14%, based on phenyl ether as an internal standard, retention times 8 and 10 min, respectively) and **3** (17.5%, retention time 20 min). Also isolated by glpc in varying yield was a mixture of alcohols [retention time 25 min; mass m/e 136 (M^+); ir ($CHCl_3$, μ) 2.8, 2.9].

The reaction was repeated and the crude ether-soluble residues were oxidized using Collins reagent (10 mmol) in dry dichloromethane (50 ml). After 15 min of stirring, the reaction mixture was extracted with ether (4 × 50 ml), the ether washes were combined, washed with $CuSO_4$ solution (4 × 50 ml) and water (3 × 50 ml), dried $MgSO_4$, and filtered, and the solvent was evaporated using a 6-in. Vigreux column. Glpc analysis as before showed an increase in the yield of **22** and **23** (30% total, 3:1 ratio) and of **3** (23%). The peaks of retention time 25 min were absent, but two new peaks, 3-chloronorcamphor **25**[19] (retention time 9 min, 4%) and *exo*-2-chloro-7-norbornanone **24**[18] (retention time 13 min, 15%), were detected.

22: waxy solid, mp 38.5–39°; ir ($CHCl_3$, μ) 5.78; nmr ($CDCl_3$, δ) 2.6 (4 H, m), 2.92 (2 H, m), 5.7 (4 H, m); exact mass for $C_9H_{10}O$ 134.07292 (calcd 134.07316).

23: clear oil; ir ($CHCl_3$, μ) 5.78; nmr ($CDCl_3$, δ) 2.4–3.2 (6 H, m), 5.6–6.05 (4 H, m); exact mass for $C_9H_{10}O$, 134.07292 (calcd, 134.07316).

Oxidation of Norbornene–Palladium Dichloride. Norbornene (2 ml) was added to a solution of bis(benzonitrile)palladium dichloride (0.528 g, 1.38 mmol) in glyme (20 ml). The mixture was stirred for 2 hr, and then added in one portion to a dichloromethane (150 ml) solution of Collins reagent (30 mmol). After 30 min, the reaction mixture was filtered, the dichloromethane solution evaporated *in vacuo*, and the residue extracted with ether (3 × 50 ml). The combined ether layers were washed with $CuSO_4$ solution (4 × 50 ml) and water (3 × 50 ml), dried $MgSO_4$, filtered and concentrated using a 6-in Vigreux column. Glpc analysis (see above) showed a 4:1 ratio of **24** and **25** (total yield 30%).

Preparation of 15a. A suspension of **9** (1.02 g, 3.16 mmol), silver acetate (525 g, 3.11 mmol), and dry dichloromethane (20 ml) was stirred for 8 hr. The yellow solution was then filtered through Celite to remove silver halide and the resulting clear yellow solution was concentrated *in vacuo*. The yellow solid **15a** remaining could be recrystallized from dichloromethane–pentane to give an orange powder (0.900 g, 87%): mp 136–141° dec; ir ($CHCl_3$, μ) 5.8; molecular weight for $C_{22}H_{22}O_6PdCl_2$ ($CHCl_3$), 693.8 (calcd, 666.1). *Anal.* Calcd for $C_{22}H_{22}O_6Pd_2Cl_2$: C, 39.67; H, 3.33; Cl, 10.64. Found: C, 39.51; H, 3.38; Cl, 10.88.

Reduction of 15a. **15a** was reduced according to the general method, and the ether-soluble residues were oxidized using Collins reagent, as was done in the reduction of **9** (see above). The ether-soluble products of the oxidation were analyzed by glpc on 5 ft × 40.25 in. 10% FFAP/Chromosorb W at 180°, and found to contain trace amounts of **22** and **23** (*ca.* 1%, retention time 5 min), and 3:1 mixture of **27** and **28** (total yield 62% based on an internal standard, retention times 33 and 35 min, respectively). No trace of **3**, **24**, or **25** was detected. Collection by glpc of **27** and **28** was hindered by tailing, and only **27** could be isolated in a pure state.

27: ir ($CHCl_3$, μ) 5.78; nmr ($CDCl_3$, δ) 2.02 (3 H, s), 2.3–2.9 (2 H, m), 3.0 (2 H, m), 5.5 (1 H, m), 5.68 (2 H, m), 5.75–6.06 (2 H, m); exact mass for $C_{11}H_{12}O_3$, 192.07728 (calcd, 192.07864).

28: ir ($CHCl_3$, μ) 5.78; nmr ($CDCl_3$, δ) 2.0 (3 H, s), 2.6–3.4 (4 H, m), 5.6–6.5 (5 H, m); mass m/e 192 (M^+).

Rearrangement of Bullvalene–Palladium Dichloride Adduct 13. The complex **13** was prepared at −40° using the general method from bullvalene (0.013 g) and bis(benzonitrile)palladium dichloride (0.039 g). The precipitate was stirred at −20° with a mixture of acetone and dimethyl sulfoxide (1 ml, 1:1) for 20 min and allowed to warm to 0°. Water and pentane were added and the pentane layer was dried ($MgSO_4$) and evaporated to yield recovered bullvalene (0.011 g).

Alternately, **13** was stirred with purified methylene chloride (10 ml) at 0° for 5 min. The pale yellow solution was filtered and evaporated *in vacuo* and dimethyl sulfoxide (1 ml) was added. Aqueous pentane work-up as before yielded **29** and naphthalene in a 10:1 ratio according to glpc analysis on 10 ft × 0.25 in. 10% Carbowax on Chromosorb P at 130°. After 2.5 hr reaction time at room temperature prior to DMSO addition, the ratio of **29** to naphthalene was 3:1.

Rearrangement of Benzobullvalene–Palladium Dichloride Complex 17. The complex **17** was prepared from benzobullvalene (**5**) (0.02 g, 0.11 mmol) in the usual way. Dimethyl sulfoxide (2 ml) was added to the complex at 25° and the mixture was stirred 10 min and subjected to aqueous hexane work-up. Benzobullvalene (0.02 g) was recovered.

The crude complex **17** was refluxed in dry chloroform for 1.5 hr and treated with DMSO as before. The hexane-soluble products were analyzed by glpc on 10 ft × 0.25 in. 10% Carbowax on Chromosorb P, and were found to contain 7,8-benzobicyclo[4.2.2]-deca-2,4,7,9-tetraene (50%), benzobullvalene (25%), and phenanthrene (25%), in order of increasing retention time.

Rearrangement of 10. A mixture of **10** (0.725 g, 1.9 mmol) in dry diglyme (40 ml) was heated to 80° for 5 hr. After the mixture was cooled to room temperature, DMSO (1 ml) was added, and the reaction stirred for 30 min. Ether (150 ml) was added, the mixture filtered, and the ether solution was washed with water (3 × 50 ml), dried ($MgSO_4$), filtered, and the solvent removed *in vacuo*. The residue was separated using plc with hexane. The fastest moving uv active zone (R_f 0.5–0.6) was analyzed by glpc at 170° on 5 ft × 0.25

in. SE-30/Chromosorb P and found to contain **4** (0.6%, retention time 9 min), **31** (1.6%, retention time 7 min) and **32** (17.4%), retention time 23 min).

31: white solid, mp 74–76° (from hexane); ir ($CHCl_3$, μ) 6.23, 11.0, 15.5; nmr ($CDCl_3$, δ) 7.4 (5 H, s), 6.6 (1 H, d of t, J = 2, 7 Hz), 6.2–6.0 (4 H, m), 5.5 (1 H, d, J = 11 Hz), 4.4 (1 H, m), 3.4 (1 H, m); mass m/e 206 (M^+); uv λ_{max}^{MeOH} 265 (log ϵ 4.100). *Anal.* Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.77; H, 7.08.

32: ir ($CHCl_3$, μ) 6.24, 11.9, 14.5; nmr ($CDCl_3$, δ) 7.3 (5 H, s), 5.8–6.7 (5 H, m), 4.5 (1 H, m), 3.58 (1 H, m), 2.5–3.3 (3 H, m); mass m/e 244, 242 (ratio 1:3, M^+); uv λ_{max}^{MeOH} 285 (log ϵ 4.198).

Potassium *tert*-Butoxide Treatment of 32. **32** (0.022 g, 0.97 mmol) in ether (1 ml) was added to a rapidly stirred solution of potassium *tert*-butoxide (0.017 g, 0.15 mmol) in dimethyl sulfoxide (1 ml). After the mixture was stirred for 1 hr, water (5 ml) was added and the resulting solution extracted with pentane (4 × 15 ml). The pentene layers were combined, dried ($MgSO_4$), and filtered, and the solvent was evaporated *in vacuo*. Glpc analysis (see above) indicated a 60% conversion to **4**.

9-Benzylidenebicyclo[4.2.1]nona-2,4,7-triene (30). The procedure for the synthesis of **4** (see above) was followed with bicyclo[4.2.1]-nona-2,4,7-trien-9-one[23] (80 mg, 0.6 mmol). Plc with hexane yielded **30** (R_f 0.4, 56 mg, 62%) which could be recrystallized from hexane: mp 76–77°; ir ($CHCl_3$, μ) 6.5, 14.6, 15.2; nmr ($CDCl_3$, δ) 7.2 (5 H, s), 5.8–6.4 (5 H, m), 5.35 (2 H, m), 3.75 (1 H, d, J = 7 Hz), 3.5 (1 H, d, J = 7 Hz); uv λ_{max}^{MeOH} 245 (log ϵ 4.36), 270 (4.059); mass m/e 206 (M^+).

4-Benzylidenebicyclo[3.2.2]nona-2,6,8-triene (31). The procedure for the synthesis of **4** (see above) was followed with bicyclo[3.2.2]-nona-2,6,8-trien-4-one[24] (0.200 g, 1.5 mmol). Plc with hexane yielded **31** (R_f 0.4, 48 mg, 17%).

Hydration of Bullvalene 1. Sulfuric acid (10%, 90 ml) was added to a rapidly stirred solution of **1** (1.292 g, 9.75 mmol) in THF (75 ml). The mixture was heated to 54° and stirred for 34 hr. After cooling to room temperature, the reaction was neutralized with saturated Na_2CO_3 solution and extracted with pentane (4 × 50 ml). The aqueous phase was saturated with NaCl and washed with ether (3 × 50 ml). The combined organic solutions were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Plc with 10% acetone and 10% chloroform in hexane (eight developments) yielded **36** (R_f 0.4, 0.662 g, 46%). **36** was recrystallized from hexane: mp 49.5–50.5°; ir ($CHCl_3$, μ) 2.9, 6.1; nmr ($CDCl_3$, δ) 1.1–2.7 (6 H, m), 4.1–4.7 (2 H, m), 5.5–6.3 (4 H, m). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.08; H, 8.27.

Tricyclo[4.3.1.0^{2,9}]deca-3,7-dien-10-one. To **36** (0.083 g, 0.56 mmol) in ether (10 ml) was added active MnO_2 (0.8 g). After 14 hr of stirring at room temperature, the mixture was filtered and the ether solution concentrated using a 6-in. Vigreux column. Plc with chloroform yielded tricyclo[4.3.1.0^{2,9}]deca-3,7-dien-10-one (R_f 0.5, 0.041 g, 50%): mp 32°; ir ($CHCl_3$, μ), 3.3, 5.93; nmr ($CDCl_3$ δ) 2.15–2.5 (5 H, m), 2.9–3.15 (1 H, m), 5.8–6.1 (4 H, m); uv λ_{max}^{MeOH} 208 (ϵ 3460). *Anal.* Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.17; H, 6.73.

Tricyclo[4.3.1.0^{2,9}]decan-10-one (38) by Catalytic Hydrogenation. Tricyclo[4.3.1.0^{2,9}]deca-3,7-dien-10-one (0.020 g, 0.14 mmol) was dissolved in ethyl acetate (3 ml) containing platinum oxide (20 mg) in an atmospheric hydrogenation flask (10 ml). After 2 equiv of hydrogen gas was taken up (6.1 ml, 15 min), the reaction was filtered and the solvent concentrated *in vacuo*. The residue was separated by plc with chloroform to yield **38** (R_f 0.65, 0.008 g, 38%): ir ($CHCl_3$, μ) 6.0; nmr ($CDCl_3$, δ) 1.3–2.2 (12 H, m), 2.5–2.7 (2 H, m); exact mass for $C_{10}H_{14}O$, 150.10427 (calcd, 150.10439).

Diazo Ketone 37. Cyclooct-4-ene carbonyl chloride[31] (3.9 g, 22.6 mmol) in ether (10 ml) was added to a solution of diazomethane (from 21.5 g of Aldrich Diazald) in ether (100 ml) at 0°. After 2 hr stirring, the solution was warmed to room temperature and the ether and excess diazomethane were blown off using a stream of nitrogen to yield **37** (4.0 g, 97%): ir ($CHCl_3$, μ) 4.75, 6.15; nmr ($CDCl_3$, δ) 5.5–5.8 (2 H, m), 5.2 (1 H, s), 1.2–2.9 (11 H, m).

Tricyclo[4.3.1.0^{2,9}]decan-10-one (38) from 37. **37** (0.692 g, 4.4 mmol) in dry cyclohexane (15 ml) was added over 1 hr to a refluxing, rapidly stirred mixture of anhydrous copper sulfate (0.2 g) and cyclohexane (70 ml). After the addition was complete, the reaction was allowed to stir an additional hour, then cooled to room temperature, and filtered, and the solvent was concentrated *in vacuo*. The residue was separated by plc with 10% acetone in hexane eluent to yield **38** (R_f 0.3, 0.138 g, 24%).

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Oxidation of Organic Compounds with Cerium(IV). XVII.[1] Oxidation of 1,2-Diarylethanes

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Abstract: The oxidation of 1,2-diarylethanes by ceric ammonium nitrate in 70% aqueous acetonitrile containing nitric acid (0.36 *M*) at 80° was found to produce cleavage products only, substituted benzaldehydes, benzyl nitrates, and benzyl alcohols. The relative rates of oxidation of 1,2-diphenylethane, 1-*p*-tolyl-2-phenylethane, 1,2-di-*p*-tolylethane, 1,2-di-*p*-chlorophenylethane, 1,2-di-*m*-chlorophenylethane, and 2,3-diphenyl-2,3-dimethylbutane were found to be 1.00, 30.0, 68.2, 0.292, 0.0415, and 5.39, respectively, by competition studies. A mechanism is proposed which involves the rate-limiting formation of radical cation intermediates which is followed by cleavage of the central carbon–carbon bond of these radical cations to produce a benzyl radical and benzyl cation.

In previous studies of the metal ion oxidations of alkylarenes, mechanisms have been postulated which involve benzyl radicals generated by α-hydrogen atom abstraction[2-5] or radical cation intermediates generated by electron transfer from the π-electron system

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