Preparation, Stereochemistry, and Rearrangement of Mercurials in the Norbornenyl–Nortricyclyl System
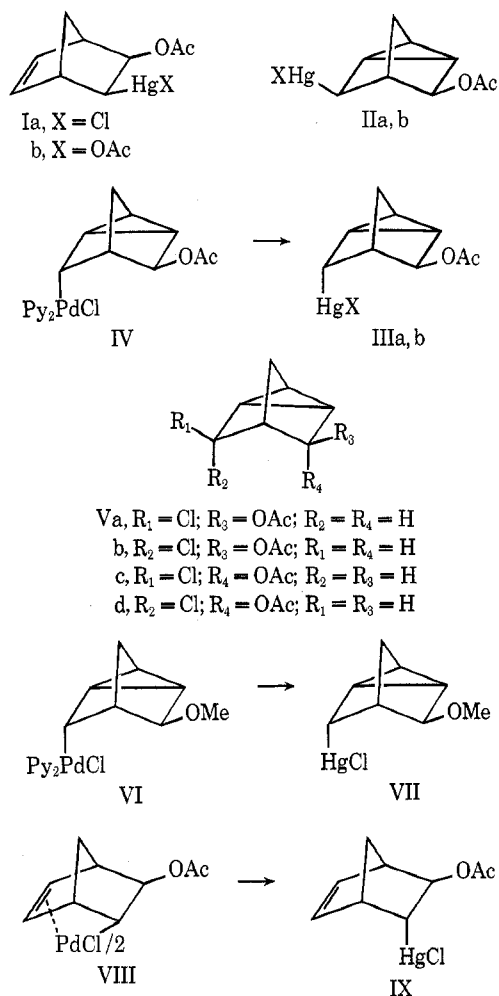
Edwin Vedejs[*1,2] and Mary F. Salomon

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

Received December 3, 1971

Acetoxymercuration of norbornadiene under the conditions of Winstein and Pande affords a 2:1 mixture of *exo,exo*-3-acetoxynortricyclyl-5-mercuric chloride (IIa) and the exo,endo isomer IIIa. An independent synthesis of IIIa is described, starting from the palladium analog IV. The stereochemistry of IIa and IIIa is proved by chlorinolysis to *exo*-3-acetoxy-*exo*-5-chloronortricyclene (Va) and *exo*-3-acetoxy-*endo*-5-chloronortricyclene (Vb), respectively. The rearrangement of *exo,exo*-2-acetoxynorborn-5-enyl-3-mercuric chloride (Ia) into a tricyclic isomer as described by Winstein and Pande is shown to be stereospecific in dimethyl sulfoxide (HgCl₂ catalysis) and to afford IIa. Treatment of the bicyclic palladium complex VIII with mercury affords *exo,endo*-2-acetoxynorborn-5-enyl-3-mercuric chloride (IX). The latter also rearranges to IIa, although seven times more slowly than does Ia.

Winstein and Pande have shown that acetoxymercuration of norbornadiene under kinetic conditions leads to bicyclic mercurial I, which rearranges slowly to a tricyclic isomer II.[3] The rearrangement was also observed when purified Ia was treated with mercuric chloride in dimethyl sulfoxide. The original communication by Winstein and Pande established the exo,cis stereochemistry of I, but no stereochemical assignment has been made for the tricyclic isomer, although the exo,exo stereochemistry appears to have been assumed without proof by some workers. This paper describes stereospecific preparation and structure proof of both possible tricyclic mercurials IIa and IIIa, and presents evidence pertaining to the mechanism of rearrangement of Ia.

Synthesis of *exo,endo*-**3-Acetoxynortricyclyl-5-mercuric Chloride (IIa) and** *exo,endo*-**2-Acetoxynorborn-5-enyl-3-mercuric Chloride (IX).**—We have found that metal exchange occurs between arylmercuric salts and σ-bonded organopalladium complexes, analogously to the exchange reactions between palladium(II) chloride or acetate and phenylmercuric salts reported by Heck.[4] Treatment of the tricyclic palladium complex IV[5] with excess phenylmercuric acetate affords a mixture of products, including biphenyl (54%), *exo,exo*-3,5-diacetoxynortricyclene (20%), and a compound C₉H₁₁HgO₂Cl (57%), assigned the structure IIIa. The absence of olefinic protons in the nmr spectrum strongly suggests a tricyclic carbon skeleton. Reaction of IIIa with chlorine in pyridine at −40° results in the formation of two acetoxy chlorides in a ratio of 96:4. The minor isomer is identical with authentic Va,[6] while the major isomer Vb is also formed upon chlorination of IV. Since the stereochemistry of IV is known,[5,7] and halogen cleavage of carbon–palladium bonds in closely analogous compounds occurs with retention,[8] Vb must be *exo*-3-acetoxy-*endo*-5-chloronortricyclene. The conditions used for chlorination of IIIa are known to cleave carbon–mercury bonds

(3) K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).
(4) R. F. Heck, *J. Amer. Chem. Soc.*, **91**, 6707 (1969), and references cited therein.
(5) E. Vedejs and M. F. Salomon, *ibid.*, **92**, 6965 (1970).
(6) G. M. Whitesides and J. SanFilippo, Jr., *ibid.*, **92**, 6611 (1970).
(7) E. Forsellini, G. Bombieri, B. Crociani, and T. Boschi, *Chem. Commun.*, 1203 (1970).
(8) D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

Ia, X = Cl
b, X = OAc

IIa, b

IV

IIIa, b

Va, R₁ = Cl; R₃ = OAc; R₂ = R₄ = H
b, R₂ = Cl; R₃ = OAc; R₁ = R₄ = H
c, R₁ = Cl; R₄ = OAc; R₂ = R₃ = H
d, R₂ = Cl; R₄ = OAc; R₁ = R₃ = H

VI

VII

VIII

IX

with retention of stereochemistry;[9] so III is assigned the *exo,endo*-3-acetoxynortricyclyl-5-mercuric chloride structure.

Metal exchange is likewise observed upon treatment of the methoxy analog VI with phenylmercuric salts to give biphenyl and *exo,endo*-3-methoxynortricyclyl-5-mercuric chloride (VII). Chlorination of VII as before results in the formation of the known *exo*-3-methoxy-*endo*-5-chloronortricyclene[8] as the major product. Metal exchange also takes place between IV and mercury metal or mercuric chloride, but the products are more difficult to purify.

(9) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe, *ibid.*, **82**, 2466 (1960).

Attempted preparation of the bicyclic mercurial IX by exchange of the bicyclic palladium complex VIII with phenylmercuric salts results in the formation of tricyclic mercurial III. However, exchange with mercury metal affords the desired IX in 30% yield. Analogous exchange between allylpalladium complexes and mercury metal has been reported.[10]

Identification of IX rests on elemental analysis, molecular weight determination, and the characteristic nmr spectrum. In particular, the coupling constant $J_{2,3} = 2.8$ Hz is characteristic of trans 2,3-disubstituted norbornene derivatives. Selective chlorinolysis of the carbon–mercury bond is not possible in this system, and the volatile products (obtained in 99% yield) consist of tricyclic Va (95%) and Vb (5%).

Stereochemistry of Acetoxymercuration of Norbornadiene, *exo,exo*-3-**Acetoxynortricyclyl-5-mercuric Chloride (IIa).**—Acetoxymercuration of norbornadiene (excess diene, 3 days in acetic acid at 25°) affords 3-acetoxynortricyclyl-5-mercuric chlorides in high yield.[3] The crude solid product (collected with 95% ethanol) melts over a wide range and is not homogenous by nmr, with two distinct methine hydrogen signals appearing at δ 4.55 (0.73 H) and 4.81 (0.27 H). The lower intensity signal corresponds exactly in chemical shift to the C₃ methine hydrogen of *exo,endo*-3-acetoxynortricyclyl-5-mercuric chloride (IIIa).

Chlorination of the crude solid in pyridine at −40° results in a 3:1 mixture of Va and Vb as sole products. Similar treatment of the mother liquors (ethanol filtrate) affords relatively more Vb and the corrected Va:Vb ratio is 2:1 (93% overall yield based on starting mercuric acetate). Two minor components are also present in the mother liquor chlorination mixture. One of these is identified as Vc[6] (3% overall yield) while the other minor chlorination product is also tricyclic and must therefore be the endo,endo isomer Vd. This assignment is supported by the chemical shifts of the C₃ and C₅ methine protons of Vd, which are similar to the corresponding chemical shifts of Va owing to the absence of "nearest neighbor" deshielding effects.[8,11]

The major tricyclic product from acetoxymercuration of norbornadiene can be purified by recrystallization from 95% ethanol, mp 150–151°. The nmr spectrum of pure material displays a signal for the C₃ methine proton at δ 4.55 (t, $J = 1.2$ Hz). This substance is assigned the *exo,exo*-3-acetoxynortricyclyl-5-mercuric chloride structure IIa on the basis of chlorination to Va and Vb in a ratio of 93:7.

Purified IIa or IIIa (or IIb and IIIb) are both stable in acetic acid and do not interconvert, with or without added mercuric acetate. However, addition of freshly distilled norbornadiene causes interconversion of IIb and IIIb at 25°. Loss of stereochemistry does not occur if hydroquinone is added along with the norbornadiene; so the formation of IIIb during acetoxymercuration is probably due to some free radical process initiated by trace impurities in the norbornadiene.[12]

Mercuric Chloride Catalyzed Rearrangement of Ia and IX.—*exo,exo*-2-Acetoxynorborn-5-enyl-3-mercuric chloride (Ia) is available from norbornadiene by acetoxymercuration under kinetic conditions.[3] The reaction is exothermic, and cooling is necessary in order to avoid further rearrangement.[12] Attempted characterization of Ia by chlorinolysis affords only *exo*-3-acetoxy-*exo*-5-chloronortricyclene (Va, 99% yield), as expected from the similar behavior of IX. That formation of Va is not the result of prior isomerization of Ia to IIa is proved by recovery of unrearranged Ia in addition to Va from an experiment with a deficiency of chlorine. In a similar experiment, an equimolar mixture of Ia and IX affords, upon treatment with 0.4 equiv of chlorine, Va (36%), recovered Ia (21%), and recovered IX (43%). This experiment shows that both Ia and IX do not rearrange under the reaction conditions, and that Ia is *ca.* two times more reactive than IX.

As reported by Winstein and Pande,[3] Ia rearranges in dimethyl sulfoxide solution in the presence of mercuric chloride. No rearrangement occurs under similar conditions in the absence of mercuric chloride. The sole product observed by nmr is IIa, a finding which is confirmed by preparative scale experiments. Similarly, the isomer IX (endo mercury) rearranges to IIa, although more slowly than does Ia by a factor of seven at 35.8°. Within the limits of nmr analysis, IX does not rearrange initially to Ia. Both of the tricyclic mercurials IIa and IIIa are stable under the reaction conditions and do not interconvert detectably; so the appearance of IIa is clearly a kinetically controlled process.

Discussion

Our structural assignments depend on the assertion that stereochemistry is retained during metal exchange of the palladium complexes IV and VIII, and also during cleavage of II and III by chlorine. According to Jensen, *et al.*, the chlorine–pyridine reagent cleaves carbon–mercury bonds at −40° with predominant retention.[9] We have found that this reagent converts 3-phenylnortricyclyl-5-mercuric chloride (known to be endo at the phenyl substituent) into *endo,endo*-3-chloro-5-phenylnortricyclene as the major (>90%) product.[13] This result provides strong evidence in favor of a cyclic chlorinolysis mechanism resulting in retention of stereochemistry. No other mechanism is likely to produce the highly hindered endo,endo product in the *endo*-3-phenyl-5-nortricyclyl system. There can be little doubt that chlorinolysis of the analogous (but less demanding) *exo*-3-acetoxy-5-nortricyclyl mercurials II and III likewise occurs with retention, and that metal exchange of IV and related complexes must therefore occur with retention. Similar results are observed in metal exchange between mercuric salts and numerous main groups element–carbon bonds.[14] Retention has also been observed in the only previous example of exchange between mercuric chloride and a transition metal–carbon bond of known stereochemistry.[15] Tentatively, the reaction of IV with phenylmercuric

(10) A. N. Nesmeyanov, A. Z. Rubezhov, L. A. Leites, and S. P. Gubin, *J. Organometal. Chem.*, **12**, 187 (1968).

(11) A. D. Cross and I. T. Harrison, *J. Amer. Chem. Soc.*, **85**, 3223 (1963).

(12) Under typical acetoxymercuration conditions, the rearrangement of Ib is complete after several hours according to nmr analysis. The initial product IIb is converted more slowly into the 2:1 mixture of IIb and IIIb, as judged by the appearance of the appropriate methine signals in the nmr spectrum. Highly purified norbornadiene, obtained by preparative glpc, does not induce interconversion of II and III.

(13) E. Vedejs and M. F. Salomon, *Chem. Commun.*, 1582 (1971).

(14) F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, Chapter 5.

(15) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971).

salts is regarded as a four-center process, resulting in IIIa and a phenylpalladium derivative which decomposes to biphenyl and inorganic side products.[4,16] Nothing is known regarding the mechanism of exchange between VIII and mercury metal, although analogous exchange of allylpalladium chloride dimer with mercury metal has been rationalized *via* the intermediate $C_3H_7Pd–HgCl$ which presumably eliminates palladium metal.[10]

The catalyzed rearrangement of Ia and IX to IIa can be explained by formation of a mercuric chloride-olefin complex X or XI, followed by transannular displacement of $ClHg^+$. The final step involves electrophilic substitution at the C-3 mercury bond with inversion in the case of X and retention in the case of XI. A similar mechanism has been proposed by Matteson and coworkers for the mercuric chloride induced conversion of *exo*- and *endo*-5-norbornene-2-boronic acid into nortricyclylmercuric chloride.[17]
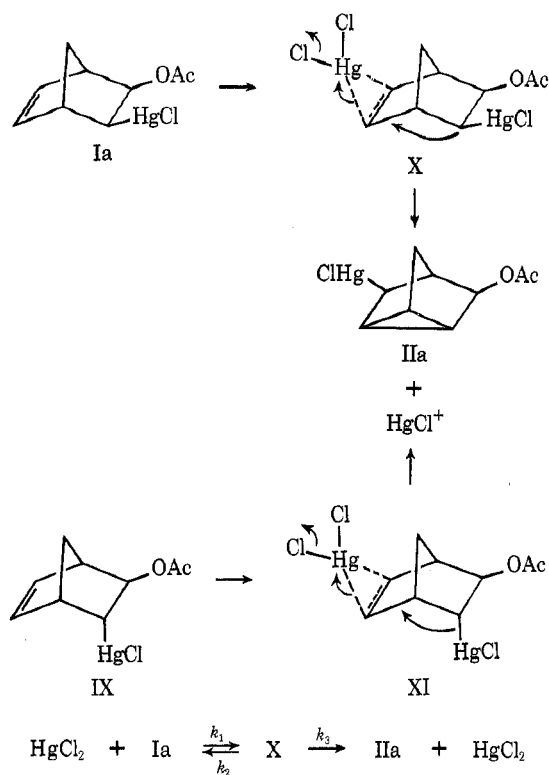
Both Ia and IX rearrange at 35.8° according to first-order kinetics by nmr analysis (80–90% conversion) with apparent first-order rate constants proportional to the concentration of mercuric chloride. Assuming a low concentration of an intermediate such as X or XI, the steady-state approximation leads to a first-order rate expression (eq 1) which is compatible

$$\frac{-d[\text{Ia}]}{dt} = k_{\text{ap}}[\text{Ia}] \qquad k_{\text{ap}} \sim [\text{HgCl}_2]k_1\left(1 - \frac{k_2}{k_2 + k_3}\right) \qquad (1)$$

with the experimental data. Under identical conditions (35.8°), Ia rearranges faster than IX by a factor of seven, a fact which corresponds qualitatively to the greater reactivity of *exo*-5-norbornene-2-boronic acid compared to the endo isomer in the analogous reaction with mercuric chloride. However, the exo/endo rate ratio for the isomeric boronic acids varies from 270 at 45° to 420 at 25°[17] and indicates a greater preference for electrophilic substitution with inversion at the carbon–boron bond.

Stereospecific rearrangement of both Ia and IX to the same product IIa could conceivably be a consequence of initial conversion of one bicyclic isomer into the other. This definitely does not occur in the direction Ia → IX, since the latter would accumulate owing to its slower rate of conversion into IIa, and would have been detected. The alternate possibility IX → Ia cannot be excluded rigorously, since accumulation of less than 5% of Ia could not have been detected. However, ionic or radical mechanisms for the hypothetical conversion IX to Ia are unlikely, since nonstereospecific rearrangement to IIa and IIIa would accompany any such process.[6,13,18] More remote possibilities involve back-side displacement at the endo mercury bond by some mercury species. A concerted displacement lacks any precedent and is ruled out, while a two-step deacetoxymercuration–exo,cis acetoxymercuration sequence is unlikely since deacetoxymercuration generally requires acid catalysis.

The chlorination of Ia can be explained by initial formation of a chloronium ion, followed by transannular elimination of $HgCl^+$ to form Va. Again, IX

$$\text{HgCl}_2 \;+\; \text{Ia} \;\overset{k_1}{\underset{k_2}{\rightleftharpoons}}\; \text{X} \;\overset{k_3}{\longrightarrow}\; \text{IIa} \;+\; \text{HgCl}_2$$

reacts more slowly than Ia, although by a factor of only two. The formation of a small amount of Vb from IX indicates some contribution from other chlorination mechanisms. In the related bromination of 5-bicyclo[2.2.2]octene-2-mercuric chloride, Matteson and Talbot reported only bicyclic bromide, although the bicyclic boronic acid afforded tricyclic mercurial by the transannular elimination process.[17]

The greater reactivity of Ia compared to IX in both the mercuric chloride catalyzed rearrangement and the reaction with chlorine is unusual, since all previously studied examples of electrophilic substitution of organomercury compounds take place with preferred retention of stereochemistry.[14] However, such reactions are believed to involve four-center transition states or similar cyclic mechanisms which are geometrically impossible for either of the proposed intermediates X or XI. The exo/endo rate difference may be due to unknown stereoelectronic factors which selectively favor the exo isomer Ia by increasing k_3 in eq 1. Alternatively, the ease of attack by the electrophile upon the double bond of Ia compared to IX may influence the relative rates (k_1 in eq 1).

Electrophilic cleavage of carbon–metal bonds most frequently occurs with retention, but predominant inversion of stereochemistry has been observed in halogenolysis of tri-*exo*-2-norbornylborane,[19] *exo*-2-norbornyllithium,[20] 4-*tert*-butylcyclohexyllithium and menthyllithium,[21] a σ-bonded alkyliron complex,[15] *sec*-butyltrineopentyltin,[22] and *sec*-butyl- or *cis*-4-bromocyclohexylcobaloxime.[23] Contradictory stereochemical preferences have also been observed in related 1,3-elimination reactions, implying that orientation of the elec-

(16) K. Graves, *J. Org. Chem.*, **35**, 3273 (1970); P. M. Henry, *ibid.*, **36**, 1886 (1971).

(17) D. S. Matteson and M. L. Talbot, *J. Amer. Chem. Soc.*, **89**, 1119, 1123 (1967); D. S. Matteson and J. O. Waldbillig, *ibid.*, **86**, 3778 (1964).

(18) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(19) H. C. Brown and C. F. Lane, *Chem. Commun.*, 521 (1971).

(20) D. E. Applequist and G. N. Chmurny, *J. Amer. Chem. Soc.*, **89**, 875 (1967).

(21) W. H. Glaze, *J. Org. Chem.*, **34**, 641 (1969).

(22) F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, **93**, 4048 (1971).

(23) F. R. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971).

TABLE I

NMR SPECTRA IN CDCl₃ (δ)

Tricyclic Products

	H₃	H₄	H₅	CH₃	H₁, H₂, H₆, H₇
IIa	4.55 (t, J = 1.2 Hz)	2.37 (br s)	2.59 (br s)	2.03 (s)	1.21–1.76 (4 H, m), 1.97 (1 H, br d, J = 10 Hz)
IIIa	4.81 (t, J = 1.5 Hz)	2.38 (br s)	2.38 (br s)	2.03 (s)	1.17–1.68 (4 H, m), 1.95 (1 H, br d, J = 10 Hz)
Va	4.62 (t, J = 1.2 Hz)	2.27 (br s)	3.99 (t, J = 1.2 Hz)	2.00 (s)	1.58 (3 H, br s), 1.87–2.03 (2 H, m)
Vb	5.30 (t, J = 1.3 Hz)	2.20 (br s)	3.95 (t, J = 1.3 Hz)	2.05 (s)	1.33–1.67 (4 H, m), 1.90 (1 H, br d, J = 9 Hz)
VII	3.69 (t, J = 1.5 Hz)	2.33 (br s)	2.42 (br s)	3.33 (s)	1.1–1.6 (4 H, m), 1.95 (1 H, br d, J = 10 Hz)

Bicyclic Products

	CH₃	H₁, H₄	H₂	H₃	H₅, H₆	H₇
Ia	2.10 (s)	3.1 and 3.3 (2 br s)	5.0 (d, $J_{2,3}$ = 7 Hz)	2.7 (br d, J = 7 Hz)	5.9–6.4 (m)	1.8 (br s)
IX	2.02 (s)	2.95 and 3.25 (2 br s)	5.04 (m, $J_{2,3}$ = 2.8 Hz)	2.12 (t, J = 2.8 Hz)	6.0–6.4 (m)	1.7 (br q, J_{AB} = 8.5 Hz)
VIII	2.0 (s)	3.07 and 3.35 (2 br s)	5.44 (br, d, J = 2 Hz)	2.85 (dd, J = 2, 4 Hz)	5.9–6.3 (m)	1.81 (br q, J_{AB} = 10 Hz)

tron-rich carbon–metal bond with respect to the electrophilic bond is not critical.[17,24] In the mercuric chloride induced rearrangement of Ia, inversion at C-3 is dictated by molecular geometry. The factors which render Ia more reactive than IX have not been identified, nor is it clear why inversion at the carbon–metal bond is preferred in certain electrophilic substitution reactions as outlined above. Substantial differences exist among the various studied examples with respect to bond lengths, bond angles, skeletal flexibility, degree of aggregation, and nature of the electrophile and leaving group, differences which preclude meaningful comparisons at this time.

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[25] calibrated with known mercurials. Nmr spectra were obtained using Varian HA-100 or A60-A spectrometers.[26] Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Volatile products were analyzed using a Varian Aerograph 90-P3 gas chromatograph. Commercial reagents were used without purification unless specified otherwise.

Di-μ-chlorobis(exo-6-acetoxy-2-norbornene-endo-5σ,2π)dipalladium (VIII).—A suspension of norbornadienepalladium dichloride (7.2 g, 0.027 mol), silver acetate (4.4 g, 0.026 mol), and dry chloroform (400 ml, distilled over P₂O₅) was stirred vigorously for 1 hr under nitrogen. The mixture was filtered and the filtrate was evaporated under the aspirator. The oily product solidified upon standing and was collected with ether, yielding VIII (7.5 g, 97%) as a pale yellow powder. This material was used without further purification. (See Table I for spectral data.)

***trans*-Chloro(exo-5-acetoxy-endo-3-nortricyclyl)dipyridinepalladium (IV).[5]**—Finely ground VIII (16.7 g, 0.029 mol) was

stirred vigorously with anhydrous ether (250 ml) under nitrogen. Dry pyridine (23.3 ml) was added dropwise over 10 min and stirring was continued for 2 hr. The crude IV was filtered (24.1 g, 95%), and stored in a freezer to avoid decomposition. Chlorination of IV in dry CH₂Cl₂ at −78° using a twofold excess of chlorine in CCl₄ followed by the usual work-up and glpc analysis resulted in the formation of Vb (78%) and Va (22%).

***exo,endo*-3-Acetoxynortricyclyl-5-mercuric Chloride (IIIa).**—A mixture of IV (0.24 g, 0.00054 mol), phenylmercuric acetate (0.37 g, 0.0011 mol), and dry acetonitrile (10 ml) was stirred for 20 hr in a flame-dried flask under nitrogen. The solution blackened immediately upon mixing the reactants. Acetonitrile was removed under vacuum and the residue was separated by preparative layer chromatography (plc) on silica gel with 2:1 CHCl₃–hexane, two developments. The following fractions were collected: R_f 0.6–0.7, biphenyl (0.045 g, 54%); R_f 0.2–0.25, *exo,exo*-3,5-diacetoxynortricyclene (0.020 g, 20%); R_f 0.1–0.2, IIb (0.12 g, 57%). Recrystallization of IIb from methanol afforded pure material: mp 136–137°; ir (KBr) 3.26 (w), 5.85 (s), 8.00 (s), 9.6 (s), 12.4 μ (s). *Anal.* Calcd for C₉H₁₁ClHgO₂: C, 27.92; H, 2.86; Cl, 9.15; Hg, 51.80. Found: C, 27.80; H, 2.85; Cl, 9.25; Hg, 51.76. Chlorination of IIb by the usual method (see below) affords Vb (96%) and Va (4%). Vb was collected by glpc as a colorless liquid: ir (neat) 3.25 (w), 5.85 (vs), 8.07 (vs), 12.25 μ (s).

General Procedure for Chlorination of Mercurials.—The reagent was prepared by adding 1.2 mmol of a titrated solution of chlorine in carbon tetrachloride to twice the volume of dry pyridine (distilled from CaH). A solution of the mercurial (1 mmol) in dry pyridine (10 ml) was cooled to −44° (Dry Ice-Cl₂CHCHCl₂) and the chlorination reagent was added dropwise over 5 min. After 1 hr at −44°, the mixture was allowed to warm to 25° and pyridine was removed under vacuum below 50°. The residue was extracted with several small portions of pentane, the pentane was evaporated, and the products were analyzed by glpc and nmr, 80–100% yield of volatile products.

***exo,endo*-2-Acetoxynorborn-5-enyl-3-mercuric Chloride (IX).**—The acetoxynorbornenylpalladium complex VIII (300 mg, 0.51 mmol) in dry benzene (10 ml, distilled from CaH₂) was stirred with a large excess of mercury (2 g) for 24 hr. The solution slowly deposited black palladium metal. The mixture was filtered through Celite and the Celite was washed with chloroform (2 × 10 ml). The combined filtrates were evaporated, the residue was purified by plc on silica gel with 2:1 chloroform–hexane (two developments), and the main band was extracted with chloroform to yield IX (106 mg, 30%). Two recrystallizations of IX from methanol afforded pure product: mp 105.5–

(24) S. J. Cristol, A. R. Dahl, and W. Y. Lim, *J. Amer. Chem. Soc.*, **92**, 5670 (1970); B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, **91**, 4320 (1969); A. Nickon and N. H. Werstiuk, *ibid.*, **89**, 3914, 3915, 3917 (1967).

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

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

106°; ir (KBr) 3.27 (m), 3.33 (m), 3.36 (m), 3.39 (m), 3.49 (w), 5.8 (s), 5.86 (s), 6.95 (m), 8.05 (s), 12.95 (m), 13.2 (m), 13.8 (s), 14.05 μ (s). *Anal.* Calcd for $C_9H_{11}ClHgO_2$: C, 27.92; H, 2.86; Cl, 9.15; Hg, 51.80. Found: C, 27.90; H, 2.85; Cl, 9.27; Hg, 51.90.

Chlorination of IX with 1.0 equiv of the chlorine–pyridine reagent afforded Va (95%) and Vb (5%). Treatment of IX with 0.3 equiv of chlorine afforded IX and Va in a ratio of 8:3. No other compounds were present according to nmr analysis (5% of Ia would have been detected).

exo,endo-**3-Methoxynortricyclyl-5-mercuric Chloride (VII).**— A suspension of the methoxy complex VI[5] (0.21 g, 0.0005 mol) and phenylmercuric acetate (0.17 g, 0.0005 mol) in methanol (8 ml) was stirred for 24 hr under nitrogen. After filtration through Celite and evaporation, the product was chromatographed as before to yield biphenyl (23%) and VII (41%): mp 134–137° (recrystallized from methanol); ir (KBr) 3.28 (w), 3.54 (w), 9.1 (s), 12.5 μ (s). *Anal.* Calcd for $C_8H_{11}ClHgO$: C, 26.75; H, 3.09. Found: C, 26.84; H, 3.16. Chlorination of VII followed by glpc analysis on a 4 ft × 0.375 in. 20% FFAP at 90° yielded 96% *exo*-3-methoxy-*endo*-5-chloronortricyclene and 4% of the exo,exo isomer.

Acetoxymercuration of Norbornadiene. *exo,exo*-**3-Acetoxynortricyclyl-5-mercuric Chloride (IIa).**—A stirred suspension of mercuric acetate (25 g, 0.078 mol) in glacial acetic acid (90 ml) was combined with freshly distilled norbornadiene (10 g, 0.11 mol) in acetic acid (10 ml). The mixture was stirred at 25° for 60 hr and 10% aqueous NaCl (100 ml) was then added. The resulting oil was separated, dissolved in hot ethanol (70 ml), and allowed to cool. A white solid precipitated and was collected with ethanol, yielding a mixture of IIa and IIIa (19 g, 64%), mp 114–124°, estimated to contain 73% of IIa and 27% of IIIa by nmr. Evaporation of the mother liquors afforded a brown oil (9.7 g, 32%). Recrystallization from 95% ethanol afforded pure IIa, mp 150–151°.

Chlorination of the Acetoxymercuration Products.—The solid mixture II and III from above was chlorinated according to the general method. Analysis of the products on a 10 ft × 0.375 in. 20% DEGS/Chromosorb P at 170° indicated the presence of 75% Va and 25% Vb. Similar treatment of the oily product from the mother liquors from above resulted in quantitative conversion to four products. In order of increasing retention time, these were Vc (11.4%), Va (47.4%), Vb (34%), and Vd (7.2%). The purified material IIa was chlorinated, yielding Va (93%) and Vb (7%).

exo,exo-**2-Acetoxynorborn-5-enyl-3-mercuric Chloride (Ia).**— According to the method of Winstein and Pande,[3] solid mercuric acetate (15.8 g, 50 mmol) was added in small portions to a stirred solution of freshly distilled norbornadiene (10 g, 108 mmol) in acetic acid (50 ml) cooled to 13°. The addition was maintained at a rate such that the reaction temperature did not rise above 15° (total addition time 15 min). After the addition was complete, the reaction mixture was immediately poured with stirring into distilled water (300 ml) containing sodium chloride (6 g, 100 mmol). An oil appeared immediately which solidified after stirring for 5 min. The crude product (15.6 g, 82%) was filtered and washed with methanol (2 × 25 ml) and pentane (2 × 50 ml). Mercurial Ia can be purified by plc or recrystallization without rearrangement. The melting point after two recrystallizations from methanol was 155–156° dec (reported[3] mp 152–153°).

Treatment of Ia with 1 equiv of chlorine in the usual way gave a 99% yield of Va. Treatment of Ia with 0.5 equiv of chlorine afforded a 1:1 mixture of Ia and Va with no detectable IIa or IX by nmr.

A competitive reaction between equal amounts of Ia and IX with 0.4 equiv of chlorine afforded a mixture of Ia, IX, and Va in a relative ratio of 4.7:9.3:8 respectively by nmr of the crude product.

Rearrangement of Compound Ib under Acetoxymercuration Conditions.—The crude acetoxymercuration mixture containing Ib was allowed to stand at room temperature without work-up. Rearrangement of Ib to IIb occurred (disappearance of olefinic nmr signals) and was complete within 6 hr. The characteristic methine signal of IIIb appeared more slowly.

A purified sample of Ib (0.2 g) in acetic acid and freshly distilled norbornadiene (0.02 g) rearranged to IIb within 5 hr at 25°. Rearrangement of IIb to IIIb was detectable after 24 hr and reached a steady state of *ca.* 5:3 of IIb:IIIb after standing for 30 days. Addition of hydroquinone (0.015 g) or use of glpc-purified norbornadiene had no effect on the rearrangement of Ib to IIb but prevented the rearrangement to IIIb.

Mercuric Chloride Catalyzed Rearrangement of Ia and IX in Dimethyl Sulfoxide.—The bicyclic mercurials Ia or IX (0.15 g) were dissolved in 0.50 ml of purified dimethyl sulfoxide (distilled under vacuum from CaH_2, stored over molecular sieves) containing the appropriate concentration of mercuric chloride catalyst. The solutions were transferred into nmr tubes and sealed under nitrogen. The samples were immersed in a water bath at 35.8 ± 0.02° and analyzed periodically by nmr. Progress of the rearrangement was monitored by integration of the olefinic signals of Ia or IX, and also by the disappearance of the methine signals due to C-2 hydrogen of Ia or IX and the appearance of the corresponding signal of IIa. No signals other than those of IIa appeared during any of the rearrangements. Linear plots of log [Ia] or log [IX] *vs.* time were obtained over 2–3 half-lives, but at greater conversion the sensitivity of integration was too low for reproducible measurements. The rate of rearrangement increased with mercuric chloride concentration, and the following apparent first-order rate constants were calculated (Table II).

TABLE II

Starting mercurial	$HgCl_2$ concn in DMSO, M	Rate constant k_{ap}, sec^{-1}
Ia	0.0257	3.0×10^{-5}
Ia	0.0184	2.1×10^{-5}
IX	0.0184	3.1×10^{-6}
Ia	0.0129	1.3×10^{-5}
Ia	0.0055	3.8×10^{-6}

Upon completion of the rearrangement of a typical run using Ia or IX, the DMSO solution was diluted with water and filtered. The solid precipitate was crystallized from methanol to yield IIa (0.14 g), in two crops.

Registry No.—Ia, 1077-98-1; IIa, 32737-75-0; IIIa, 34454-50-7; Va, 31002-62-7; Vb, 34493-26-0; VII, 34493-27-1; VIII, 11096-74-5; IX, 34454-52-9.