and that the resulting ROOMgX, which is highly soluble in nonpolar solvents, is also presumably nonionic, eq 8 seems to us a more plausible reaction path in this sort of system, although simple electron transfer between radicals and anions may well occur in more highly ionized systems.

Experimental Section

Reagents. Ether solutions of 5-hexenylmagnesium bromide were prepared either from 6-bromo-1-hexene or from the more available 1,2,6-tribromohexane[13] and, as seen in Table I, gave equivalent results. While both lots showed about 5% cyclization during formation, as noted, there was no evidence for further change on storage under $\mathrm{N_2}$. Solutions of *t*-BuOOMgCl were prepared by inverse addition of *t*-BuMgCl to oxygen-saturated ether at −78°. The best yields (89%) were obtained using dilute (0.55 *M*) solutions and slow addition.

Experimental runs were carried out as indicated in Table I. After reaction they were hydrolyzed with aqueous $\mathrm{NH_4Cl}$, reduced with KI and acetic acid when necessary (run C) with quantitative titration of a sample for peroxide, dried, and analyzed by gas–liquid chromatography (glc) using internal standards and prior calibration with authentic samples. Hexene and methylcyclopentane were analyzed on a didecyl phthalate column at 70° using pentane as standard and the alcohols were analyzed on 20% Carbowax 20M at 140° using cyclohexanol as standard.

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[13] R. C. Lamb and R. W. Ayers, *J. Org. Chem.*, 27, 1441 (1962).

The Mechanism of Reduction of Alkylmercuric Halides by Metal Hydrides[1]

George M. Whitesides and Joseph San Filippo, Jr.[2]

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

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Abstract: Reductive demercuration of representative alkylmercuric bromides by metal hydrides has been shown to involve generation of intermediate alkyl radicals by comparison of the product distributions obtained on demercuration with those observed on reduction of the corresponding alkyl chlorides by tri-*n*-butyltin hydride under free-radical conditions. Reductions of neophylmercuric bromide (**1**) and 1,7,7-trimethylbicyclo[2.2.1]heptyl-2-mercuric bromide (**2**) using sodium borodeuteride, diethylaluminum deuteride, deuterio(tri-*n*-butylphosphine)-copper(I), and tri-*n*-butyltin deuteride occur without the rearrangements characteristic of intermediate carbonium ions. Reductions of *exo*- and *endo*-norbornyl-2-mercuric bromides (**3** and **4**) with the same reducing agents yield ~90:10 mixtures of *exo*- and *endo*-norbornane-2-d_1. Reductions of *exo*- and *endo*-2-chloronorbornane with tri-*n*-butyltin deuteride yield an 84:16 mixture of these norbornane-d_1 epimers. The relative yields of 3-acetoxynortricyclene (**13**), *anti*-7-acetoxynorborn-5-ene (**16**), and *exo*-2-acetoxynorborn-5-ene (**17**) obtained on reduction of *cis*-*exo*-2-acetoxynorborn-5-ene-3-mercuric bromide (**5**) and *exo*,*exo*-3-acetoxynortricyclyl-5-mercuric bromide (**6**) with metal deuterides compare closely with those obtained on reduction of *endo*-2-chloro-*exo*-3-acetoxynorborn-5-ene (**8**) and *exo*-3-chloro-*exo*-5-acetoxynortricyclene (**12**) with tri-*n*-butyltin hydride. For comparison, *exo*-2-chloro-*endo*-3-acetoxynorborn-5-ene (**7**), *endo*-2-chloro-*endo*-3-acetoxynorborn-5-ene (**9**), and *exo*-3-chloro-*endo*-5-acetoxynortricyclene (**11**) have also been reduced with tri-*n*-butyltin hydride. The products from reductions of these alkyl chlorides provide evidence that norborn-5-en-3-yl radicals substituted at the 2 and 7 positions interconvert rapidly through appropriate nortricyclyl radicals (*e.g.*, **18** $\rightleftharpoons$ **19** $\rightleftharpoons$ **20** and **21** $\rightleftharpoons$ **22** $\rightleftharpoons$ **23**). Reductive demercuration of the alkylmercuric chlorides is proposed to involve intermediate alkylmercuric hydrides.

The development of promising procedures for the Markovnikov conversion of olefins to alcohols, ethers, and amides based on the generation of alkylmercury compounds by solvomercuration followed by demercuration using sodium borohydride has renewed interest in organomercurials as synthetic intermediates.[3,4] The mechanism of the solvomercuration steps in these procedures is well understood;[5,6] the mechanism of reductive demercuration using metal hydrides is less clear.[7]

The major fraction of the evidence pertinent to the mechanism of reaction of sodium borohydride and alkylmercurials is stereochemical in nature. Reductions of methyl 2-acetoxymercuri-2-deoxy-2,3,4,6-tetra-*O*-acetyl-*β*-D-mannopyranoside and related compounds,[8] *cis*-2-acetoxybicyclo[2.1.1]hexane-3-mercuric acetate,[9] *cis*-*exo*-2-hydroxybicyclo[2.2.1]heptane-3-mercuric chloride,[10] and *trans*-1-hydroxycyclopentyl-2-mercuric acetate[11] are reported to proceed with predominant or exclusive retention of configuration at the carbon atom originally bonded to mercury, while reductions of *eryth-*

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[2] National Institutes of Health Predoctoral Fellow, 1966–1970.

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[4] H. C. Brown and Min-Hon Rei, *ibid.*, **91**, 5646 (1969); H. C. Brown and J. T. Kurek, *ibid.*, **91**, 5647 (1969); W. C. Baird, Jr., and M. Buza, *J. Org. Chem.*, **33**, 4105 (1968); H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, 89, 1522 (1967); H. C. Brown and W. J. Hammar, *ibid.*, 89, 1524 (1967); H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

[5] Reviews: J. Chatt, *Chem. Rev.*, **51**, 7 (1951); N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); W. Kitching, *Organometal. Chem. Rev.*, 3, 61 (1968).

[6] R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969), and references therein.

[7] The reduction of organomercuric halides by other chemical and electrochemical methods has been reviewed: F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968, p 137.

[8] J. H. Leftin and N. N. Lichtin, *Israel J. Chem.*, 3, 107 (1965).

[9] F. T. Bond, *J. Amer. Chem. Soc.*, **90**, 5326 (1968).

[10] F. G. Bordwell and M. L. Douglass, *ibid.*, 88, 993 (1966).

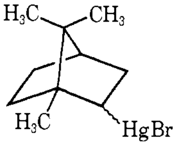
[11] D. J. Pasto and J. A. Gontarz, *ibid.*, **91**, 719 (1969).

ro- and *threo*-2-hydroxybutyl-3-mercuric acetate[11] and of *cis*- and *trans*-4-methylcyclohexylmercuric chloride[12] are reported to take place with loss of stereochemistry. A common mechanism for these reductions involving generation of intermediate free alkyl radicals might be expected to yield products with loss of stereochemistry in each case, while ionic or concerted mechanisms might lead to products with retained stereochemistry. However, each example characterized by retention of stereochemistry on reduction has involved examination of only one of the two possible diastereomers differing in configuration at the carbon atom bonded to mercury. Without a complementary examination of the stereochemical course of the reduction of the second diastereomer, no convincing stereochemical or mechanistic generalization can be drawn from these studies.

A wide variety of important organometallic reactions unrelated to demercuration involve a step in which a carbon–metal bond is transformed into a carbon–hydrogen bond.[13] An interest in this fundamental class of reactions[14,15] has prompted us to attempt to resolve the stereochemical ambiguities posed by previous[8–12] studies of reductive demercuration by examination of the reactions of representative metal hydrides with 2-phenyl-2-methylpropylmercuric bromide (**1**), 1,7,7-trimethylbicyclo[2.2.1]heptyl-2-mercuric bromide (**2**), *exo*- and *endo*-bicyclo[2.2.1]heptyl-2-mercuric bromide (**3** and **4**), *cis-exo*-2-acetoxybicyclo[2.2.1.]hept-5-ene-3-mercuric bromide (**5**), and *exo,exo*-3-acetoxytricyclo-[2.2.1.$0^{2,6}$]heptyl-5-mercuric bromide (**6**).[16] In this paper we wish to report that the product distributions observed on reduction of these organomercury reagents are independent of the nature of the reducing agent, and to suggest that the structures of these products are consistent with a mechanism of reduction involving intermediate free alkyl radicals.

$C_6H_5C(CH_3)_2CH_2HgBr$

1



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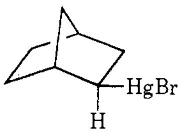

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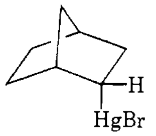

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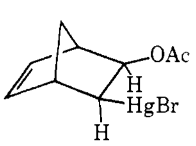

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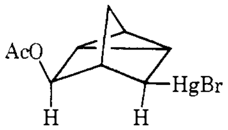

6

Results

Reduction of Neophylmercuric Bromide (1) and 1,7,7-Trimethylbicyclo[2.2.1]heptyl-2-mercuric Bromide (2). One conceivable mechanism for reduction of an alkylmercuric halide by a hydride donor would involve initial formation of an intermediate alkyl carbonium ion by Lewis acid assisted ionization of the carbon–mercury bond in a reaction analogous to those examined by Jensen and Ouellette,[17] followed by conversion of this carbonium ion to hydrocarbon by reaction with metal hydride. As a first step in establishing the mechanism of reduction of alkylmercuric halides by metal hydrides, we have examined the reaction of neophylmercuric bromide (**1**) and 1,7,7-trimethylbicyclo[2.2.1]-heptyl-2-mercuric bromide (**2**) with a selection of metal hydrides. The carbonium ions derived from the organic moieties of these organomercury compounds undergo well-established and characteristic structural rearrangements at rates sufficiently rapid to be at least competitive with reduction, while the corresponding radicals undergo these rearrangements at much slower rates. Studies of the solvolysis of neophyl derivatives have shown that 1,2-aryl migration proceeds concomitantly with ionization,[18] while aryl migration in neophyl radical is relatively slow.[19,20] Similarly, examinations of the solvolysis of norbornanes suggest that ionization of 2-substituted derivatives of 1,7,7-trimethylbicyclo[2.2.1]heptane proceeds directly to the tertiary carbonium ion resulting from Wagner–Meerwein rearrangement without passing through a discrete secondary intermediate.[21,22] Rearrangements of analogous norbornyl radicals are very slow at room temperature.[23] Thus, the *absence* of rearranged products in the reductions of **1** and **2** with metal hydrides should constitute sufficient evidence to exclude carbonium ion intermediates in these reactions.

Table I lists products and yields observed on reduction of **1** and **2** using sodium borodeuteride, diethylaluminum deuteride,[24] deuterio(tri-*n*-butylphosphine)copper(I),[14] and tri-*n*-butyltin deuteride.[25] Glpc analysis of these reaction mixtures did not detect rearrangement products from either **1** or **2** in any instance. Thus, these reactions, and by inference the demercuration reactions of the similar organomercury reagents examined in the following sections, do not proceed by carbonium ion mechanisms.

Reductions of *exo*-Norbornyl-2-mercuric Bromide (3) and *endo*-Norbornyl-2-mercuric Bromide (4). In an effort to detect possible free-radical intermediates in the reduction of alkylmercuric halides by metal hydrides, we compared the composition of the mixtures of *endo*- and *exo*-norbornane-2-d_1 obtained on reduction of *exo*- and *endo*-norbornyl-2-mercuric bromide using each of

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(12) Unpublished work of T. G. Traylor quoted in footnote 27 of ref 10.

(13) For references to representative reactions, *cf.* J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968); R. Cramer, *ibid.*, **1**, 186 (1968); R. F. Heck, *ibid.*, **2**, 10 (1969); L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience, New York, N. Y., 1966, Chapter 4; J. P. Collman in "Transition Metal Chemistry," Vol. 2, R. L. Carlin, Ed., Marcel Dekker, New York, N. Y., 1966.

(14) G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *J. Amer. Chem. Soc.*, **91**, 6542 (1969).

(15) G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Filippo, Jr., *ibid.*, **92**, 1426 (1970).

(16) These names are consistent with the rules of nomenclature of the International Union of Pure and Applied Chemistry. Hereafter, familiar trivial names are sometimes used.

(17) F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, **83**, 4477, 4478 (1961); *ibid.*, **85**, 367 (1963).

(18) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957); W. H. Saunders, Jr., and R. H. Paine, *ibid.*, **83**, 882 (1960).

(19) R. Kh. Freidinger, *Advan. Free Radical Chem.*, **1**, 211 (1965); C. Ruchardt, *Chem. Ber.*, **94**, 2599 (1961.

(20) For example, reduction of neophyl chloride with tri-*n*-butyltin hydride under free-radical conditions (AIBN, *hν*, 25°, neat, or ~10% *n*-hexadecane solution) leads to no detectable isobutylbenzene.

(21) Reviews: J. A. Berson in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3; A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 126 ff.

(22) H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **86**, 5006 (1964).

(23) D. I. Davies and S. J. Cristol, *Advan. Free Radical Chem.*, **1**, 155 (1965).

(24) G. Wilke and H. Muller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

(25) Tri-*n*-butyltin deuteride was prepared by modifications of the method of K. Kuhleim, W. P. Neumann, and H. Mohring, *Angew. Chem., Int. Ed. Engl.*, **7**, 455 (1968).

Table I. Reductions of Neophylmercuric Bromide (1) and 1,7,7-Trimethylbicyclo[2.2.1]heptyl-2-mercuric Bromide (2)[a]

RHgBr	Reducing agent	Solvent	Product yield, %, and isotopic composition	
			t-Butylbenzene[b]	Isobutylbenzene
1	$NaBD_4$	3:1 $THF-H_2O$	100 (85% d_1)	<0.1
1	Et_2AlD	Et_2O	96 (94% d_1)	<0.1
1	$DCuP(n\text{-}Bu)_3$	3:1 $THF-Et_2O$	55 (78% d_1)	<0.1
1	Bu_3SnD	None	90 (93% d_1)	<0.1
			Bornane[c]	Camphane
2	$NaBD_4$	3:1 $THF-H_2O$	100	<0.1
2	Et_2AlD	Et_2O	97	<0.1
2	$DCuP(n\text{-}Bu)_3$	3:1 $THF-Et_2O$	53	<0.1
2	Bu_3SnD	None	100	<0.1

[a] Reductions were carried out at ambient temperature. [b] In each instance the ratio of the yields of *t*-butylbenzene to isobutylbenzene was >99. [c] In each instance the ratio of the yields of bornane to camphane was >99. Camphene was not detected.

Table II. Stereochemistry, Yield, and Isotopic Composition of the Mixture of *endo*- and *exo*-Norbornane-2-d_1 and Norbornane-d_0 Obtained on Reduction of *exo*-Norbornyl-2-mercuric Bromide (3) and *endo*-Norbornyl-2-mercuric Bromide (4)[a]

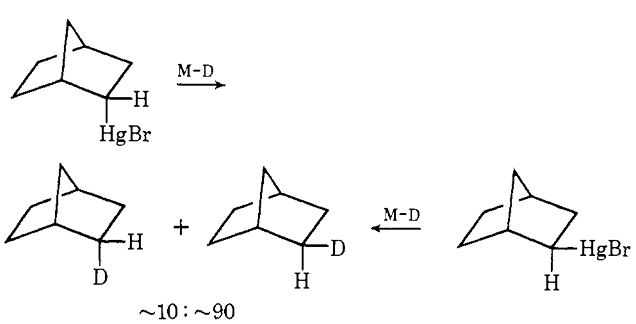
Substrate	Reducing agent	Solvent	Yield, %[b]	*exo*:*endo*[c]	Isotopic composition, % d_1
3	$NaBD_4$	3:1 $THF-H_2O$	96	90:10	84
3	Et_2AlD	Et_2O	99	92:8	96
3	$DCuPBu_3$[d]	3:1 $THF-Et_2O$	63	91:9	84
3	Bu_3SnD	Neat	100	90:10	100
4	$NaBD_4$	3:1 $THF-H_2O$	96	90:10	87
4	Et_2AlD	Et_2O	99	89:11	92
4	$DCuPBu_3$[d]	3:1 $THF-Et_2O$	61	91:9	85
4	Bu_3SnD	Neat	100	90:10	95
endo-2-Chloro-norbornane	Bu_3SnD[e]	Neat	*f*	84:16	94
exo-2-Chloro-norbornane	Bu_3SnD[e]	Neat	*f*	84:16	94

[a] Reductions were carried out at room temperature. [b] Total yield of deuterated and nondeuterated norbornanes, based on starting substrate. [c] The estimated accuracy of these ratios is ±5% (absolute). [d] The $DCuPBu_3$ used contained ~0.25 equiv of pyridine per equivalent of copper.[14] If the reduction was carried out in pyridine, the yield of norbornane was 68%. [e] Carried out using AIBN and light as initiator. [f] Yields were not obtained in these experiments.

the metal deuterides employed in the previous section with that observed on reduction of *endo*- and *exo*-2-chloronorbornane with tri-*n*-butyltin deuteride under free-radical conditions.

Pure *endo*-norbornyl-2-mercuric bromide (**4**) was obtained by preferential destruction of the *exo*-norbornyl-2-mercuric acetate in a mixture of *exo* and *endo* isomers under solvolytic conditions followed by conversion of the *endo*-acetate to **4** on treatment with aqueous potassium bromide solution.[17,26] Pure *exo*-norbornyl-2-mercuric bromide (**3**) was obtained by isolation of *exo*-norbornyl-2-mercuric acetate from a mixture of *exo*- and *endo*-acetates by fractional crystallization, followed by conversion to **3** on treatment with potassium bromide. Reductions of **3** and **4** were accomplished by reaction with the appropriate metal deuteride, and the resulting mixture of *exo*- and *endo*-norbornane-2-d_1 and norbornane-d_0 was isolated by glpc. The ratio of *exo*- to *endo*-norbornane-d_1 in this mixture was determined by ir analysis, using the characteristic bands identified by Nickon and Hammons,[27] and the extent of deuterium incorporation into the mixture was determined by mass spectroscopy. The results of these experiments are summarized in Table II. For comparison, this table also lists the corresponding data for the mixture of norbornane-2-d_1 epimers obtained on reduction of *endo*- and *exo*-2-chloronorbornane using AIBN and light as free-radical initiators.

Three features of the data of Table I are pertinent to the question of the mechanism of reduction of **3** and **4** by metal hydrides. First, reduction of **3** and **4** proceeds with loss of stereochemistry, and the ratio of *exo*- to *endo*-norbornane-2-d_1 obtained in any reduction is independent of the stereochemistry of the starting material. To make certain that this stereochemical result did not simply reflect loss of stereochemistry in the starting organomercury reagents,[28] re-



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(26) S. Winstein, E. Vogelfanger, K. C. Pande, and H. F. Ebel, *J. Amer. Chem. Soc.*, **84**, 4993 (1962).

(27) A. Nickon and J. H. Hammons, *ibid.*, **86**, 3322 (1964). We wish to thank Professor Nickon for supplying us with ir spectra of *exo*- and *endo*-norbornane-2-d_1.

(28) The facile free-radical displacments observed at mercury[29] and other metals[30] provide a low-energy pathway for loss of stereochemistry.

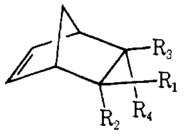
(29) F. R. Jensen, L. H. Gale, and J. E. Rogers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); F. R. Jensen and D. Heyman, *ibid.*, **88**, 3438 (1966); ref 7, Chapter 4.

(30) P. J. Krusic and J. K. Kochi, *ibid.*, **91**, 3942 (1969), and references therein.

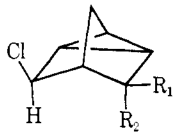
ductions of **3** and **4** with sodium borohydride were carried to ~50% completion. Comparison of the melting point and ir spectra of recovered and starting material established that in these reactions, and presumably in the remaining reactions in Table II, no loss of stereochemistry in the starting material accompanies the reaction. Second, reductions of **3** and **4** with metal hydrides and of *endo*- and *exo*-2-chloronorbornane with tri-*n*-butyltin deuteride lead to approximately the same ratio *exo*- to *endo*-norbornane-2-d_1. Third, the ratio of *exo*- to *endo*-norbornane-2-d_1 in reduction of **3** and **4** is independent of the nature of the metal deuteride used as reducing agent.

Since reduction of alkyl halides with tri-*n*-butyltin hydride using AIBN and photochemical initiation is believed to take place by a radical-chain mechanism,[31] both the similarity in *exo*:*endo* ratios listed in Table II for reductions of the norbornylmercury reagents and of the norbornyl chlorides and the loss of stereochemistry observed during these reactions suggest that alkyl radicals may be intermediates in the organomercury reductions.[32] Moreover, the independence of the *exo*:*endo* ratio observed for reduction of the mercurials to changes in the structures of the reducing agents suggests that these reductions may share a common hydrogen atom donor, *viz.*, that the species involved in hydrogen atom transfer to the presumed intermediate norbornyl radical may be, *e.g.*, a norbornylmercuric hydride, rather than the metal hydrides actually listed in Table II (*vide infra*).

Reductions of *cis-exo*-2-Acetoxynorborn-5-ene-3-mercuric Bromide (5) and *exo,exo*-3-Acetoxynortricyclyl-5-mercuric Bromide (6). The similarity of the product distributions observed on metal hydride reduction of **3** and **4** and on tri-*n*-butyltin hydride reduction of the analogous norbornyl chlorides implicates a free-radical mechanism for the former reactions. However, since this similarity might have been adventitious, it seemed worthwhile to carry out a parallel comparison using an unrelated mechanistic probe. With this goal in mind, we have compared the distribution of substituted norbornenyl and nortricyclyl[23] products obtained on metal hydride reduction of *cis-exo*-2-acetoxynorborn-5-ene-3-mercuric bromide (**5**) and *exo,exo*-3-acetoxynortricyclyl-5-mercuric bromide (**6**) with those obtained on free-radical reduction, using tri-*n*-butyltin hydride, of *exo*-2-chloro-*endo*-3-acetoxy-, *endo*-2-chloro-*exo*-3-acetoxy-, and *endo*-2-chloro-*endo*-3-acetoxynorborn-5-ene (**7**, **8**, and **9**, respectively), and of *exo*-3-chloro-*endo*-5-acetoxy- and *exo*-3-chloro-*exo*-5-acetoxynortricyclene (**11** and **12**). Reductions of **5** and **6** with sodium borohydride had been examined previously by Pasto and Gontarz,[11] and recently reexamined by Grey and Jackson.[33] The results reported by the latter investigators are in excellent agreement with those obtained in our work. Compounds **5** and **6** were synthesized by oxymercuration of norbornadiene, using a procedure based on that developed by Pande and Winstein to prepare the corresponding alkylmercuric chlorides.[34] A mixture of compounds **7–10** was obtained from the Diels-Alder reaction of 2-chlorovinyl acetate with cyclopentadiene, and individual components of the mixture were separated by preparative glpc. Structures could be assigned with confidence to compounds **7–9** on the basis of their nmr spectra (Table III), using correlations between configuration and spectral parameters that have been developed for substituted norbornenes.[35] These correlations also confirm the structure assigned to **5** by analogy with the work of Pande and Winstein.[34] The compound presumed to be **10** was never obtained in sufficient quantity for detailed nmr investigation. It is believed to be a 2-chloro-3-acetoxynorborn-5-ene from the similarity of its ir and mass spectrum to those of **7–9**, and is assigned the *cis-exo* configuration by default, since the three other possible configurations are assigned to **7–9**.



7, $R_1 = Cl; R_4 = OAc; R_2 = R_3 = H$
8, $R_2 = Cl; R_3 = OAc; R_1 = R_4 = H$
9, $R_2 = Cl; R_4 = OAc; R_1 = R_3 = H$
10, $R_1 = Cl; R_3 = OAc; R_2 = R_4 = H$



11, $R_1 = H; R_2 = OAc$
12, $R_1 = OAc; R_2 = H$

In brief, assignments of configuration for **7–9** are based on interpretation of the data in Table III in light of four generalizations derived from prior studies of the nmr spectra of substituted norbornenes: first, all other factors being equal, a C*H*OAc proton is normally less shielded than an analogous C*H*Cl proton; second, in the absence of major perturbations from adjacent substituents, *endo* protons at the 2 and 3 positions of the norborn-5-ene ring system are more shielded than *exo* protons; third, *endo-cis* and *exo-cis* configurations in 2,3-disubstituted norbornenes are easily distinguishable from *trans* configurations on the basis of the magnitude of the vicinal coupling constant, with representative ranges for coupling constants in these configurations being $J_{2x,3x} \cong$ 4–10 Hz, $J_{2n,3n} \cong$ 4–7 Hz, and $J_{3x,3n} \cong$ 2–4 Hz; and fourth, coupling between a bridgehead proton and its vicinal *exo* proton is significant ($J_{1,2x} \sim$ 2.5–4.5 Hz) while the corresponding coupling to the vicinal *endo* proton is small, and coupling between an *endo* proton at the 2 or 3 position and the *anti*-7 proton is significant ($J_{2n,7} \sim$ 2–4 Hz). Thus, the substituents in **5** and **9** are identified as either *endo-cis* or *exo-cis* and those of **7** and **8** as *trans*, by the magnitudes of $J_{2,3}$ in each compound. The *endo-cis* assignment for **9** is based on the moderate values observed for $J_{1,2}$ and $J_{3,4}$, while the *exo-cis* configuration of **5** is confirmed both by the low values of the corresponding vicinal couplings and by the moderate magnitude of $J_{3n,7}$. The *exo*-chloro-*endo*-

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[31] (a) H. G. Kuivila, *Accounts Chem. Res.*, **2**, 299 (1969); (b) *Advan. Organometal. Chem.*, **1**, 47 (1964); (c) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

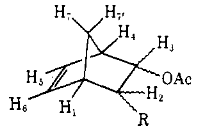
[32] The predominantly *exo* deuteration in these reactions is in agreement with the expectation that 2-norbornyl radical should abstract hydrogen from a suitable donor more readily from the *exo* side; *cf.* D. I. Davies and S. J. Cristol, *Advan. Free Radical Chem.*, **1**, 155 (1965); P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3**, 249 (1970).

[33] G. A. Grey and W. R. Jackson, *J. Amer. Chem. Soc.*, **91**, 6205 (1969).

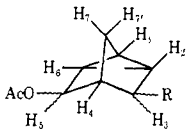
[34] K. C. Pande and S. Winstein, *Tetrahedron Lett.*, 3393 (1964).

[35] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964); P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965); J. C. Davies, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963); B. Franzus, *et al.*, *ibid.*, **90**, 3721 (1968); A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968); C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968); N. Kamezawa, K. Sakashita, and K. Hayamizu, *Org. Mag. Resonance*, **1**, 405 (1969).

Table III. Descriptions of Nmr Spectra for 2-Chloro-3-acetoxynorborn-5-enes and 3-Chloro-5-acetoxynortricyclenes[a]



δ	R₁ = x-HgBr, x-OAc	x-Cl n-OAc	n-Cl x-OAc	n-Cl n-OAc
1 [b]	3.06 m	2.97 br	2.83 br	3.07 br
4	3.26 m	3.13 br	2.98 br, m	3.07 br
2*n*	2.78 d, d	3.42 t		
2*x*			4.02 d, d	4.44 d, d
3*n*	4.98 d		4.47 br, s	
3*x*		5.15 d, d		5.20 d, d
5, 6	6.10	6.16 m	6.25 m	6.22 m
7, 7′ [b]	1.75 br, s	1.94 m	1.77 m	1.53 m
C*H*$_3$CO$_2$	2.08 s	1.94 s	2.00 s	1.97 s
	$J_{1,2n} < 0.5$[e] $J_{2n,3n} = 7.0$ $J_{3n,7} = 2.3$ $J_{3n,4} < 0.5$[e] $J_{3n,7} < 0.5$[e]	$J_{2n,3x} \cong 1.8$ $J_{2n,7} \cong 1.8$ $J_{3x,4} = 3.6$	$J_{1,2x} = 3.4$ $J_{2x,3n} = 1.8$ $J_{3n,7}$[f]	$J_{1,2} = 3.6$ $J_{2x,3x} = 7.6$ $J_{3x,4} = 3.6$



δ	R = x-HgBr x-OAc	x-Cl n-OAc	x-Cl x-OAc
1, 2, 6	1.2–2.00 m	~1.5 m	1.52 s
3*n*	2.66 s	4.34 t	3.84 t
4[d]	2.40 m	2.10 m	2.18 m
5*n*		4.67 t	
5x	4.60 m		4.52 t
7, 7′ [b]	1.2–2.00 m	~1.5 m	~1.9 m
CH$_3$CO$_2$	2.04 s	1.97 s	1.93 s

[a] Spectra of **7–11** were taken at 60 MHz using samples ~1:4 v/v in CCl$_4$; **5** and **6** were taken at 60 MHz using samples 1:4 in CDCl$_3$. Chemical shifts (δ) are in parts per million downfield from internal TMS; coupling constants (J) are in hertz. Coupling constant assignments were confirmed by decoupling. Notation: x = *exo*, n = *endo*, br = broad, s = singlet, t = triplet, d,d = doublet of doublets, m = multiplet. [b] Individual chemical-shift assignments were not made to groups of protons indicated by brackets. [c] Broad singlet, appearing as a partially resolved sextet at expanded sweep widths. [d] Assigned on the assumption that H$_4$ will be shielded by its proximity to the cyclopropane ring; *cf.* D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963); R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (*London*), 786 (1963). [e] No coupling observed; a value of $J \leq 0.5$ Hz would not have been detected. [f] Coupling was detected by double irradiation, but no definite value could be assigned.

acetoxy configuration of **7** was distinguished from the *endo*-chloro-*exo*-acetoxy configuration of **8** by identification of the resonances in each compound due to the C*H*Cl protons, using chemical-shift arguments, and assignment of the stereochemistry of these C–H bonds by examination of the magnitude of $J_{1,2}$.

The compounds assigned the 3-chloro-5-acetoxynortricyclene structures **11** and **12** were prepared by reaction of chlorine with norbornadiene in glacial acetic acid saturated with sodium acetate and isolated by glpc from the resulting mixture of products. The absence of olefinic resonances and presence of C*H*Cl and C*H*OAc resonances in the nmr spectra of these compounds (Table III), and the presence of strong bands in the region 800–830 cm^{-1} in their ir spectra,[36] taken together with their other physical characteristics and their method of preparation[37] leave no doubt that these compounds are in fact 3-chloro-5-acetoxynortricyclenes, although convincing assignments of the configuration of the substituents cannot be made on the basis of the coupling constant or chemical-shift data reported in Table III. It has, however, proved possible to assign configurations to these compounds by examining the relative chemical shifts induced in the C*H*Cl protons of **11** and **12** on addition of tris(dipivaloylmethido)di(pyridinato)europium(III) (Eu(DPM)$_3$Py$_2$), using the elegant technique devised by Hinckley.[38] In this approach to configurational assignment, addition of a solution of Eu(DPM)$_3$Py$_2$ to a solution containing the acetates **11** and **12** results in the establishment of equilibria involving complexes of the form Eu(DPM)$_3$Py–**11** and Eu(DPM)$_3$Py–**12** by replacement of pyridine in the coordination shell of the metal with oxygen atoms of the acetate moieties. The contact shifts observed for the protons of the rapidly exchanging mixture of free and complexed **11** and **12** are assumed to decrease roughly as $1/R^3$, where R is the average distance between the proton under consideration and the europium atom in the coordinated form. Thus, for equal complex formation constants, the C*H*Cl proton of *exo*-2-chloro-*endo*-5-acetoxynortricyclene should show a greater contact shift than that of *exo*-2-chloro-*exo*-5-acetoxynortricyclene, since the mean C*H*Cl–europium distance should be smaller in the former substance.

Examination of the spectra of mixtures of **11**, **12**, and Eu(DPM)$_3$Py$_2$ in carbon tetrachloride demonstrates that the shifts of the C*H*OAc and C*H*Cl protons of **11** and **12** move smoothly downfield on sequential addition of the paramagnetic complex (Figure 1). The shifts in the C*H*OAc protons of **11** and **12** are equal, suggesting that the formation constants for complexes of these compounds with the metal atom are in fact the same. Taken together with this observation, the further observation that the chemical shift of the C*H*Cl proton of **11** increases *ca.* three times as rapidly as that of **12** on increasing the concentration of Eu(DPM)$_3$Py$_2$ is sufficient to assign the *exo*-chloro-*endo*-

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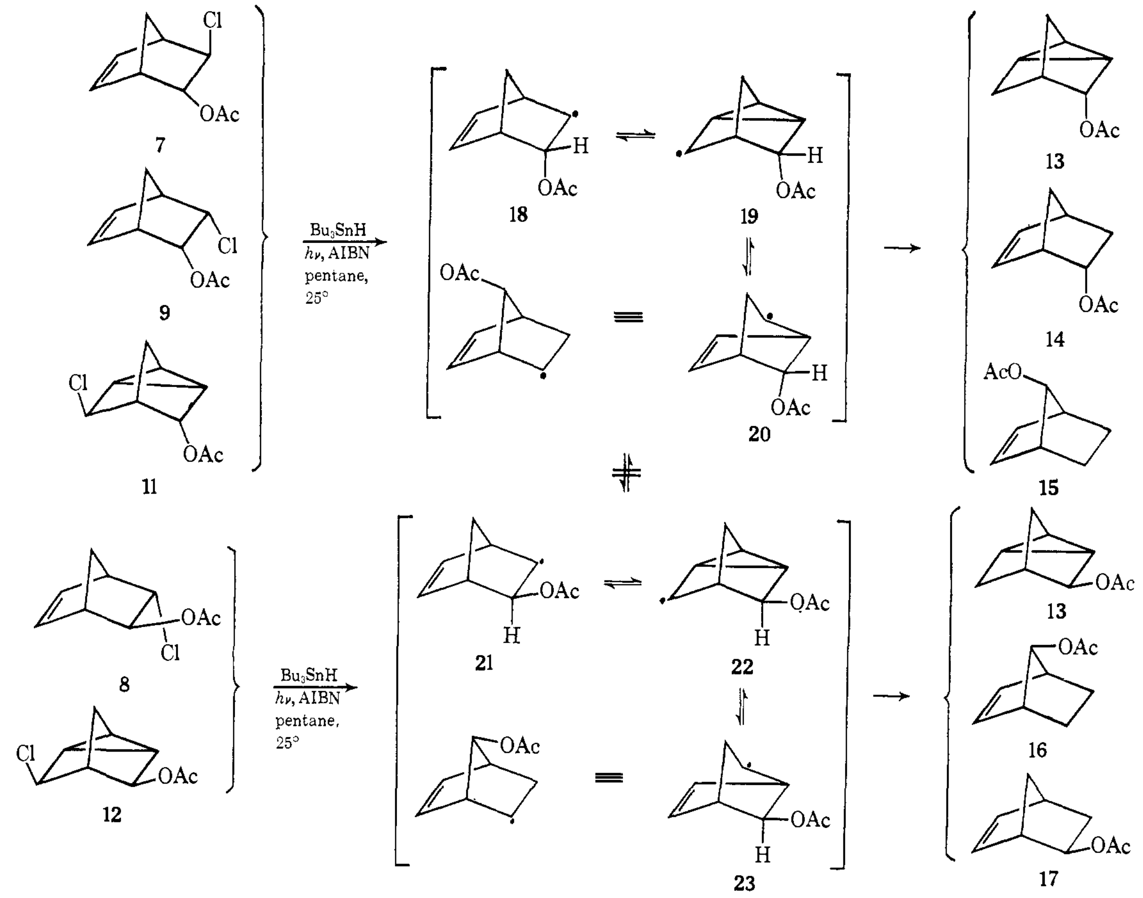
(36) Ir vibrations in this region are characteristic of nortricyclene structures [D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963)].

(37) Addition of bromine to norbornadiene gives, *inter alia*, *exo*-3-bromo-*exo*-5-bromo- and *exo*-3-bromo-*endo*-5-bromonortricyclene: S. Winstein, *ibid.*, **83**, 1516 (1961).

(38) C. C. Hinckley, *J. Org. Chem.*, **35**, 2834 (1970); *J. Amer. Chem. Soc.*, **91**, 5160 (1969). We thank Professor Hinckley for unpublished details concerning both the preparation of Eu(DPM)$_3$Py$_2$ and its application in the problem at hand.

Scheme I. Reductions of Alkyl Halides



acetoxynortricyclene structure to **11**, and the *exo*-chloro-*exo*-acetoxy configuration to **12**. These configurational assignments are convincingly confirmed by the product distributions observed on reduction of **11** and **12** with tri-*n*-butyltin hydride (*vide infra*).

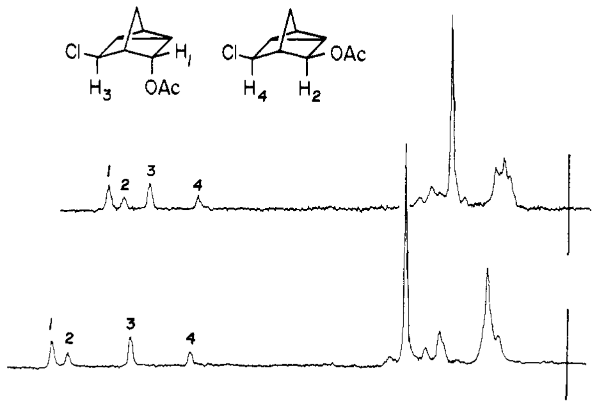


Figure 1. Nmr spectrum (100 MHz, CCl_4) of a mixture of *exo*-3-chloro-*endo*-5-acetoxy- and *exo*-3-chloro-*exo*-5-acetoxynortricyclene (**11** and **12**) (upper); the spectrum of the same mixture diluted to ~3 times its original volume with an ~0.2 *M* solution of $Eu(DPM)_3Py_2$ in CCl_4 (lower). The magnitudes of the observed downfield shifts on addition of the europium salt are: H_1, 0.442; H_2, 0.442; H_3, 0.143; H_4, 0.052 ppm.

Treatment of **7**, **9**, and **11** with tri-*n*-butyltin hydride in pentane under radical conditions produced similar, but not identical, mixtures of 3-acetoxynortricyclene (**13**), *endo*-2-acetoxynorborn-5-ene (**14**), and *syn*-7-acetoxynorborn-5-ene (**15**); reductions of **8** and **12** under similar conditions yielded mixtures of 3-acetoxynortricyclene, *anti*-7-acetoxynorborn-5-ene (**16**), and *exo*-2-acetoxynorborn-5-ene (**17**) (Scheme I and Table IV).[38a] No crossover between these two systems of products was detected. Control experiments established that the starting chlorides did not isomerize under the reaction conditions.

The observation of 3-acetoxynortricyclene and 2-acetoxynorborn-5-ene in these reactions is expected: the 2-norborn-5-enyl and 3-nortricyclyl radicals have been suggested to be discrete, rapidly equilibrating entities in a variety of systems,[23,39] and occurrence of products **13**, **14**, and **17** is easily rationalized on the basis of an unexceptional mechanistic scheme involving equilibrating pairs of radicals **18** ⇌ **19** and **21** ⇌ **22** (Scheme I). The detection of the 7-acetoxynorborn-5-enes **15** and **17** as products of these reductions was not anticipated since the radical rearrangements **19** ⇌ **20** and **22** ⇌ **23** (Scheme I) implied by these products have no direct precedent. However, Davies[40] and others[41] have observed 7-substituted products in

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[38a] Note Added in Proof. Dr. R. Jackson (The Queens University of Belfast) has informed us that independent examinations of systems closely related to those described in Table IV have yielded results in satisfactory agreement with the data reported here.

[39] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966); S. J. Cristol and R. V. Barbour, *J. Amer. Chem. Soc.*, **90**, 2832 (1968); S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 1762 (1969).

[40] J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc. C*, 1498 (1966); C. K. Alden, J. A. Claisse, and D. I. Davies, *ibid.*, 1540 (1966); D. I. Davies and P. J. Rowley, *ibid.*, 2245, 2249 (1967).

[41] E. N. Prilezhaeva, *et al.*, *Zh. Obshch. Khim.*, **35**, 39 (1965); V. F.

Table IV. Relative Yields of Norbornenyl and Nortricyclyl Acetates from Reductions

Substrate no.	Reducing agent	Product, rel yield, % 13	14	15	16	17
7	Bu$_3$SnH[a]	63	22	15	*b*	*b*
9		67	19	14	*b*	*b*
11		55	25	20	*b*	*b*
8		79	*b*	*b*	5	16
12		74	*b*	*b*	5	21
5	NaBD$_4$[c,d]	62 (78)[e]	*b*	*b*	7	31
5	HCuPBu$_3$[f]	65	*b*	*b*	7	28
5	Bu$_3$SnD[d,g]	65 (100)[e]	*b*	*b*	8 (100)[e]	27
5	Bu$_3$SnD[d,h]	70	*b*	*b*	8	22
6	NaBD$_4$[c,d]	61	*b*	*b*	7	32
6	HCuPBu$_3$[f]	66	*b*	*b*	8	26
6	Bu$_3$SnD[d,g]	66	*b*	*b*	7 (100)[e]	27
6	Bu$_3$SnD[d,h]	64	*b*	*b*	8	26

[a] Pentane solution, AIBN, *hν*, 25°. The reproducibility of these numbers is estimated to be ±5% (relative). [b] None observed; limit of detection 0.1%. [c] 3:1 THF–H$_2$O solution, 25°. [d] The product balance in these experiments was >90%, based on **5** or **6**. The same yields (±2%) were obtained when the corresponding metal *hydrides* were used as reducing agents. [e] Numbers in parentheses refer to the per cent deuterium incorporation into the indicated product, measured mass spectroscopically. [f] Et$_2$O solution. The "HCuPBu$_4$" used contained ~0.25 equiv of pyridine per equivalent of copper; see ref 14. The product balance in these experiments was ~25–50%, based on **5** or **6**. [g] No solvent. [h] THF solution.

free-radical additions to polychlorinated norbornadiene, and norborn-2-en-7-yltrimethyltin has been mentioned as a product of addition of trimethyltin hydride to norbornadiene.[42] Thus, involvement of the 7-substituted norbornenyl radicals **20** and **23** in the reductions studied here provides a reasonable and plausible method of rationalizing the product distributions observed in these reactions.[43] Fortunately, inclusion of radicals **20** and **23** and products **15** and **17** in these reactions, although unexpected, is helpful, in that the resulting reaction scheme provides a more detailed "fingerprint" against which to measure the reduction of the organomercury compounds **5** and **6**.

The internal consistency of Scheme I provides the most compelling evidence for the correctness of the structures assigned to the nortricyclenes **11** and **12**. The present assignments lead naturally to the observed products by a reasonable mechanistic scheme; reversal of these assignments would require the postulation of several physically unreasonable steps to reconcile products with starting materials.

The mechanism outlined in Scheme I, together with the quantitative data summarized in Table IV, provides a clear indication of the behavior to be expected for radicals **18–23** under reaction conditions resembling those encountered in the tri-*n*-butyltin hydride reductions of these alkyl halides. For comparison, Table IV also contains the relative yields of products **13–17** observed on reductions of *cis*-*exo*-2-acetoxynorborn-5-ene-3-mercuric bromide (**5**) and *exo*,*exo*-3-acetoxynortricyclyl-5-mercuric bromide (**6**) with sodium borodeuteride, deuterio(tri-*n*-butylphosphine)copper(I), and tri-*n*-butyltin deuteride.[44] The product distributions from both **5** and **6** are very similar, and appear to be independent of the reducing agent. The similarity of these product distributions to those observed on reduction of **8** and **12** provides confirming evidence that free alkyl radicals are intermediates in the reduction of these organomercury compounds by metal hydrides. Thus, **8**, **12**, **5**, and **6** all appear to generate a common set of radicals, **21–23**, on reduction.

The origin of the small but significant differences between the relative yields of product acetates **13**, **16**, and **17** from the alkyl chlorides and the alkylmercuric bromides is not entirely evident. The hydrogen donor in reductions of **8** and **12** is certainly tri-*n*-butyltin hydride. The hydrogen donor to radicals **21–23** in reductions of the mercurials has not been identified with certainty, but might be either an alkylmercuric hydride, mercurous hydride, or some other species (*vide infra*); however, at least in the reductions involving sodium borodeuteride and copper hydride, this hydrogen donor is certainly *not* tri-*n*-butyltin hydride. Thus, the differences in the product distributions observed on reduction of **8** and **12**, and of **5** and **6**, can be rationalized by a scheme in which the rate of interconversion of the intermediate radicals **21** → **23** is comparable to or faster than the rate at which they abstract hydrogen from the hydrogen donor present in the system, and in which the relative reactivities of these radicals differ toward tri-*n*-butyltin hydride and the hydrogen donor present in the alkylmercuric halide reductions.

Reductions of Norbornylmercuric Bromides in the Presence of Di-*t*-butyl Nitroxide. Although the products observed on reduction of the alkylmercury(II) halides examined in this work indicate that alkyl radicals are intermediates in these reactions and that these radicals have lifetimes sufficient to permit rapid rearrangements (*e.g.*, $\mathbf{21} \rightleftharpoons \mathbf{22} \rightleftharpoons \mathbf{23}$), but not slow rearrangements (*e.g.*, neophyl radical → benzyldimethylcarbinyl radical), they do not clearly define the extent to which the generation and subsequent reaction of the intermediate radicals are confined to a solvent cage and the extent to which these radicals become "free" in solution. In an effort to resolve this question, we have examined the reduction of *exo*- and *endo*-norbornyl-2-mercuric bromide (**3** and **4**) with sodium borohydride in the presence of the efficient radical scavenger di-*t*-butyl nitroxide (DTBNO)[45] (40% by volume). Both mercury reagents yielded 10–20% of O-2-norbornyl-N,N-di-*t*-butylhydroxylamine (**24**). The remainder of the norbornyl moieties did *not* appear as norbornane or norbornene; their fate is presently unknown. Although association of DTBNO with **3** and **4** before reduction cannot be rigorously excluded as a step in this reaction,[46] the uv and visible spectra of 1:1

Bystrov, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 381 (1966); *Chem. Abstr.*, **44**, 15761f (1966).

(42) Reference 31a, footnote 32.

(43) Similar conclusions have been reached by Grey and Jackson.[33]

(44) Reductions of these compounds using sodium borohydride in anhydrous THF led to a >95% yield of norbornadiene. Similar eliminations have been observed in other systems.[10]

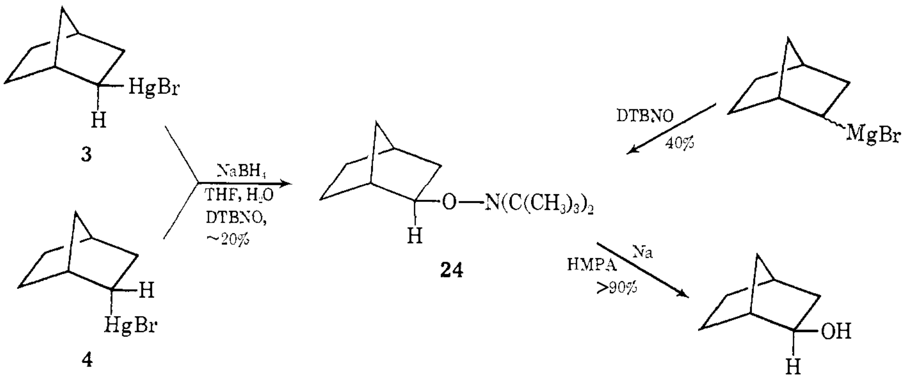
(45) Sterically hindered nitroxyl groups are stable toward hydridic reducing agents; *cf.* A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, p 228; D. J. Kosman and L. H. Piette, *Chem. Commun.*, 962 (1969); A. K. Hoffman, A. M. Feldman, E. Gelblum, and W. G. Hodgson, *J. Amer. Chem. Soc.*, 86, 639 (1964).

(46) DTBNO has been shown to form complexes with AlCl$_3$,[47] BF$_3$,[47] Pd(II),[48] Co(II),[49] Cu(II),[50] and protons.[51]

(47) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 5170 (1969).

(48) W. Beck, K. Schmidtner, and H. J. Keller, *Chem. Ber.*, **100**, 503 (1967).

(49) W. Beck and K. Schmidtner, *ibid.*, **100**, 3363 (1967).



solutions of **4** and DTBNO at concentration of *ca.* 0.1 *M* in THF are the superposition of the spectra of the individual components, and give no obvious indication of association.

The stereochemistry of the coupling product **24** isolated from reduction of both **3** and **4** was assigned as *exo* on the basis of comparison of spectral characteristics with **24** prepared by reaction of DTBNO with norbornylmagnesium bromide.[52,53] The stereochemistry of the substance prepared by the latter route was assigned by reduction to *exo*-norbornan-2-ol using sodium in hexamethylphosphoramide.

The observation of **24** on reduction of either **3** or **4** in the presence of DTBNO is consistent with the hypothesis of intermediate 2-norbornyl free radicals, with the proviso that the coupling of these radicals with DTBNO must take place from the less sterically hindered *exo* side. However, both the relatively low yield observed for **24** and our present inability to account for the remainder of the norbornyl groups present as **3** or **4** at the start of the reaction make detailed discussion of these experiments in terms of radical intermediates difficult.

Discussion

Three lines of evidence establish that reductive demercuration of the alkylmercuric bromides examined here involve intermediate free alkyl radicals, and confirm the basic mechanism for these reductions proposed by Pasto[11] and Grey and Jackson.[33] First, the absence of detectable rearrangement during reduction of neophyl- and bornylmercuric bromide excludes intermediate carbonium ions in these reactions. Second, the relatively high deuterium incorporation into products (78–85%) observed on reduction of neophylmercuric bromide, *endo*- and *exo*-norbornyl-2-mercuric bromide, and *cis*-*exo*-2-acetoxynorborn-5-ene-3-mercuric bromide using sodium borodeuteride in THF–water solution argues strongly against the extensive involvement of carbanionic intermediates under these and presumably also under aprotic reaction conditions. Finally, comparisons of the ratios of *exo*- to *endo*-norbornane-d_1 obtained on reduction of **3** and **4**, and of the ratios of the relative yields of products obtained on reduction of **5** and **6**, with the same ratios derived from reduction of the analogous alkyl chlorides using tri-*n*-butyltin hydride or deuteride under authentic free-radical conditions, establish that the intermediates in the reductive demercuration have the properties expected for free radicals. Moreover, the nature of the products obtained on reduction of **3**, **4**, **5**, and **6** excludes reaction mechanisms requiring concerted carbon–hydrogen bond formation and carbon–mercury bond cleavage, since these mechanisms would not permit the organic moieties sufficient freedom for the loss of stereochemistry or structural rearrangement actually observed.

Although free radicals are thus clearly established as intermediates in the hydride reductions of these organomercuric halides, further details of their generation and ultimate conversion to hydrocarbon remain unclear. The invariance of the product distributions to drastic changes in the nature of the metal hydrides used as the reducing agents suggests that these hydrides are not themselves the species that donate a hydrogen atom to the intermediate alkyl radicals. This supposition is supported by two additional observations. First, the small but real differences in product distributions observed in the reductive demercuration and dechlorination reactions imply that the partitioning of the intermediate alkyl radicals between products *is* in fact responsive to the nature of the hydrogen donor, and that this sensitivity should in consequence be reflected in similar changes in product distributions in the demercuration reaction on changing metal hydride, if the metal hydride were in fact involved in direct reaction with the intermediate radicals. Second, neither borohydride ion nor diethylaluminum hydride is noted for its ability to react with alkyl radicals by hydrogen atom transfer.

In light of these arguments, an alkylmercuric hydride or mercurous hydride generated *in situ* during the reaction would seem the most attractive prospects for the species responsible for hydrogen atom transfer to the intermediate alkyl radical. If the first step in the reaction is assumed to be conversion of the starting alkylmercuric bromide to an alkylmercuric hydride by reaction with metal hydride (eq 1),[54] at least two fundamentally different types of mechanistic schemes can be envisioned for the subsequent conversion of this intermediate to product. In one, homolytic cleavage of the carbon–mercury bond would lead to an alkyl radical and mercury(I) hydride, followed

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(50) L. A. Krinitskaya and S. N. Dobryakov, *Bull. Acad. Sci. USSR*, 3, 558 (1966).

(51) B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **91**, 2169 (1969).

(52) Related reactions of stable aryloxy radicals with Grignard reagents produce similar product mixtures: A. Riecker, E. Müller, and W. Beckert, *Z. Naturforsch. B*, **17**, 718 (1962).

(53) The reaction of DTBNO with norbornylmagnesium bromide was examined in these laboratories by Mr. John Gaasch. We have not prepared O-*endo*-2-norbornyl-N,N-di-*t*-butylhydroxylamine for comparison.

(54) Similar displacements are well known; *cf.* A. P. Ginsberg, *Transition Metal Chem.*, 1, 111 (1965); M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 115 (1965).

$$\mathrm{RHgBr} \xrightarrow{\mathrm{MH}} \mathrm{RHgH} \qquad (1)$$

$$\mathrm{RHgH} \longrightarrow \mathrm{R}\cdot + \mathrm{HgH} \qquad (2)$$

$$\mathrm{R}\cdot + \mathrm{HgH} \longrightarrow \mathrm{RH} + \mathrm{Hg(0)} \qquad (3)$$

$$\mathrm{RHgBr} \longrightarrow \mathrm{R}\cdot \qquad (4)$$

$$\mathrm{R}\cdot + \mathrm{RHgH} \longrightarrow \mathrm{RH} + \mathrm{RHg} \qquad (5)$$

$$\mathrm{RHg} \longrightarrow \mathrm{R}\cdot + \mathrm{Hg(0)} \qquad (6)$$

by rearrangement of the radical and subsequent hydrogen atom transfer from the mercury(I) hydride to the radical, in either a cage or noncage process, to yield products (eq 2–3). A second would involve a radical chain reaction, in which initial generation of an alkyl radical, by some process whose precise nature need not be specified in detail (eq 4), would be followed by hydrogen atom transfer from alkylmercuric hydride to alkyl radical followed by unimolecular decomposition of the resulting alkylmercury(I) intermediate to alkyl radical and mercury(0) (eq 5–6).

The mercury hydrides postulated in these schemes have no direct analogy in stable mercury reagents. An uncharacterized compound believed to be a mercury hydride has been reported,[55] and the diatomic mercury hydrides HgH and $\mathrm{HgH^+}$ have been detected spectroscopically and their bond energies estimated (8.6 and 53 kcal/mol, respectively).[56] Nonetheless, despite the absence of established precedent, by analogy with other compounds characterized by low metal–hydrogen bond strengths, both RHgH and HgH would be expected to be excellent hydrogen atom donors toward alkyl radicals.

On the basis of presently available evidence there is no way of distinguishing clearly between radical-cage (eq 2–3) and radical-chain (eq 4–6) mechanisms for the conversion of the postulated alkylmercuric hydrides to alkyl radicals and thence to products. If the production of **24** in the reduction of **3** and **4** in the presence of DTBNO does in fact reflect scavenging of intermediate norbornyl radicals, the efficiency of this scavenging is less than that observed for nitroxides in other radical producing reactions.[57] However, it seems possible that the rate of hydrogen transfer from an alkylmercuric hydride to norbornyl radical might compare favorably with the rate of combination of the bulky nitroxyl moiety with this alkyl radical, and that in consequence high efficiency might not be expected. Alternatively, the observation of appreciable scavenging might be rationalized as reflecting some leakage from a predominantly cage reaction.

In conclusion, it is worthwhile to make explicit two general points concerning the reductive demercuration of organomercury reagents by metal hydrides. First, while it is clear from the work reported in this paper that reduction of *alkyl*mercuric halides can be expected to take place through free alkyl radicals, it is not clear that the reductions of other classes of organomercury reagents will follow related mechanisms. In particular, studies of reduction of vinylic mercury compounds by sodium borodeuteride and diethylaluminum deuteride,[58] and of diphenylmercury by lithium aluminum hydride,[59] indicate that these reactions follow mechanisms different in at least certain major details from those involved in reduction of alkylmercuric halides. Second, accepting this limitation on the generality of the reaction, the reduction of alkylmercury reagents with metal hydrides provides a convenient nonphotochemical method of generating free alkyl radicals at low temperatures under mild conditions. As such, the reaction merits further development as a probe for the study of radical reactions.

Experimental Section

General. Melting points were obtained using a Thomas–Hoover capillary melting point apparatus and are corrected. Magnesium sulfate was employed as a drying agent unless otherwise stated. Nmr spectra were determined on Varian T-60 or HA-100 spectrometers. Chemical shifts are reported in parts per million relative to internal tetramethylsilane and coupling constants are in hertz. Infrared spectra were taken in sodium chloride cells on Perkin-Elmer Models 237B or 337 grating spectrophotometers. Mass spectra were obtained on a Hitachi–Perkin-Elmer Model RMU-6D mass spectrometer. Spectra used for deuterium analysis were obtained using a nominal ionizing voltage of approximately 8.3 eV.[60] High-resolution spectra were obtained using a CEC-21-110B mass spectrometer. Analytical glpc analyses were performed on F & M Model 810 instruments equipped with flame ionization detectors and Disc integrators. Response factors were obtained with authentic samples. Preparative and analytical samples were obtained using an F & M Model 720 instrument equipped with thermal conductivity detectors. Static nitrogen atmospheres were employed in all reactions involving organometallic compounds.[61]

Diethyl ether was distilled under nitrogen from lithium aluminum hydride before use. Tetrahydrofuran was used without purification unless noted otherwise. Pentane (Matheson Coleman and Bell spectral quality) was used without purification. AIBN was recrystallized from methanol and stored at −30°. Mercuric bromide was used without purification.

exo-**2-Bromobicyclo[2.2.1]heptane**, prepared by the addition of hydrobromic acid to bicyclo[2.2.1]hept-2-ene,[62] had bp 65° (12 Torr) [lit.[62] bp 82° (29 Torr)]. *exo*-**2-Chlorobicyclo[2.2.1]heptane**, prepared following the procedure of Schmerling,[63] had bp 54° (15 Torr) [lit.[63] bp 52° (11 Torr)]. *endo*-**2-Chlorobicyclo[2.2.1]heptane** was obtained as a gift from Dr. E. Sohl and Professor P. D. Bartlett. **1,7,7-Trimethylbicyclo[2.2.1]heptyl chloride** was purchased from K and K Laboratories. **1,7,7-Trimethylbicyclo[2.2.1]heptane** (bornane), prepared by Wolff–Kishner reduction of camphor,[64] had mp 155–156° (lit.[64] mp 156–157°). **2,2,3-Trimethylbicyclo[2.2.1]heptane** (camphane) was prepared by hydrogenating camphene (Firmenich & Co.) over platinum black in ethyl acetate at 25°. The product was isolated utilizing preparative glpc using a 12-ft, UC-W98 column at 150°. Reinjection of collected samples onto a 24-ft, Hi-Pak SE-30 column at 70° indicated a 70:30 mixture of stereoisomers; these isomers were not characterized individually.

Diethylaluminum deuteride was prepared by reaction of lithium deuteride (Merck Sharp and Dohme, 98% *d*) with diethylaluminum chloride using a modification of the literature procedure.[65] Lithium deuteride (0.98 g, 0.109 mol) was placed in a flame-dried, two-necked flask equipped with a Teflon stirring bar and a reflux con-

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[55] E. Wiberg and W. Henle, *Z. Naturforsch. B*, **6**, 461 (1951). This material, obtained by reaction of lithium aluminum hydride with mercury(II) iodide at −135°, was reported to decompose at temperatures above −125°.

[56] H. L. Roberts, *Advan. Inorg. Chem. Radiochem.*, **11**, 309 (1968).

[57] The efficiency of diphenylnitroxyl as a radical scavenger in the thermal-induced decomposition of AIBN in chlorobenzene (4 *M* in cumene) is reported to be 68%; *cf.* J. R. Thomas and C. A. Tolman, *J. Amer. Chem. Soc.*, **84**, 2930 (1962). See also S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

[58] J. San Filippo, Jr., and G. M. Whitesides, unpublished.

[59] D. H. R. Barton and W. J. Rosenfelder, *J. Chem. Soc*, 2385 (1951); T. G. Traylor, *Chem. Ind. (London)*, 1223 (1959).

[60] K. Biemann "Mass Spectrometry—Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p 223 ff.

[61] D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969, Chapter 7.

[62] J. D. Roberts, E. R. Trumbull, Jr., N. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 72, 3116 (1950).

[63] L. Schmerling, *ibid.*, **68**, 195 (1946).

[64] L. Wolff, *Justus Liebigs Ann. Chem.*, **394**, 86 (1912).

[65] G. Wilke and H. Muller, *ibid.*, **618**, 267 (1958); K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider, *ibid.*, **589**, 91 (1954). The procedure used in our laboratory was devised by Mr. Erwin Stedronsky.

denser. The system was flushed thoroughly with nitrogen, and the open necks were capped with No-Air stoppers. Ether (15–20 ml) was added. Diethylaluminum chloride (Texas Alkyls, 13.8 g, 0.115 mol) was weighed into a stoppered 40-ml centrifuge tube and diluted with ether to a total volume of ~30 ml. Over a period of 30 min, half of this solution was added by cannula to the vigorously stirred suspension of lithium deuteride in ether. The resulting reaction mixture was stirred for 2–3 hr; during this time its temperature was maintained at 55–60° by immersion in an oil bath. The remaining solution of diethylaluminum chloride was added and the reaction mixture again heated at 55–60° for another 2–3 hr. The contents of the reaction vessel were transferred to a stoppered centrifuge tube and the lithium chloride which had precipitated was removed by centrifugation. The supernatant solution was transferred to a bulb-to-bulb distillation apparatus and the solvent removed at room temperature by gradually reducing the pressure to a final value of ~0.01 Torr. The residual liquid was transferred to a stoppered centrifuge tube and the additional lithium chloride which precipitated during concentration was removed by centrifugation. The supernatant liquid was purified by bulb-to-bulb distillation on a high-vacuum line using a bath temperature of 55–60° and a pressure of 10^{-3}–10^{-4} Torr [lit.[66] bp 55–56° (10^{-3}–10^{-4} Torr)]. The isolated yield of diethylaluminum deuteride was 6.7 g (70%) based on lithium deuteride.

The neat diethylaluminum deuteride was diluted with 10–15 ml of olefin-free decane (purified by distillation from a suspension of sodium benzophenone ketyl under nitrogen). An aliquot (1.0 ml) of this solution was withdrawn and hydrolyzed. Subsequent halide[67] and aluminum[68] analyses indicated that the ratio of halide to aluminum in the hydrolyzed aliquot was 0.10.

The isotopic purity of the diethylaluminum deuteride was established by the following procedure. To a flame-dried, one-necked 10-ml flask containing a Teflon stirring bar and fitted with a reflux condenser capped with a No-Air stopper was added 3 ml of 3-hexyne. The flask was cooled to −78° and a 1.0-ml aliquot of the decane solution of diethylaluminum deuteride was injected. The mixture was permitted to warm to room temperature with stirring and then refluxed gently for 1 hr. The solution was cautiously hydrolyzed, first with methanol and then with water at −50°. The reaction products were analyzed without further work-up on an 8-ft, 20% TCEOP on Chromosorb W column at 70° and the resulting *cis*-3-hexene was collected.[69] Mass spectral analysis indicated that the isotopic composition of the 3-hexene was 95% d_1. This value was taken to be the minimum isotopic purity of the diethyl aluminum deuteride.

Diisobutylaluminum Deuteride. The procedure used to synthesize diethylaluminum deuteride was applied with obvious modifications to the preparation of diisobutylaluminum deuteride from 0.990 g (0.123 mmol) of lithium deuteride and 23.4 g (0.128 mmol) of diisobutylaluminum chloride. This procedure yielded 11.5 g (69%) of diisobutylaluminum deuteride, bp 90–96° (10^{-3}–10^{-4} Torr) [lit.[70] bp 112–113° (0.3 Torr)], 96% d_1.

Copper(I) Hydride. In a typical preparation, copper(I) bromide (0.868 g, 6.0 mmol) was placed in a 40-ml centrifuge tube which was capped with a No-Air stopper and gently flamed under a stream of nitrogen. Pyridine (5–10 ml), freshly distilled under nitrogen from calcium hydride, was added and the tube shaken until the copper(I) bromide had dissolved. At −50°, 4.4 ml (6.1 mmol) of a heptane solution of diisobutylaluminum hydride was injected into the centrifuge tube and the resulting dark brown reaction mixture shaken vigorously for several minutes at −50°. The addition of 30 ml of ether to this mixture produced a coarse brown precipitate which was compacted by centrifugation in a centrifuge bucket packed with Dry Ice. The supernatant solution was removed by cannula under a positive pressure of nitrogen, 30 ml of fresh ether was added, and the tube was shaken and again centrifuged. In all, the solid copper(I) hydride was washed four times. The properties of the resulting solid copper(I) hydride have been described elsewhere.[14,71,72]

Copper(I) deuteride was prepared from diisobutylaluminum deuteride (6.1 mmol) and copper(I) bromide (6.0 mmol) using the procedure described for the synthesis of copper(I) hydride. The isotopic purity of copper(I) deuteride produced in this manner is 97.7%.[14]

Hydrido- and Deuterio(tri-*n*-butylphosphine)copper(I). Tri-*n*-butylphosphine (4.0 mmol) was injected into a capped, flushed 40-ml centrifuge tube containing a suspension of copper(I) hydride (deuteride) (~5 mmol) in ~3 ml of ether at −78°. The tube was shaken vigorously for 1 min, then centrifuged for 5–10 min in a centrifuge bucket packed with Dry Ice. The resulting dark brown solution of hydrido(tri-*n*-butylphosphine)copper(I) was decanted from the residual solid copper(I) hydride using a cannula and stored at −78° under nitrogen. This solution was characterized by a ratio of tri-*n*-butylphosphine to copper of 0.95, based on the amount of tri-*n*-butylphosphine initially added, and a ratio of hydride to copper of 0.94.[71]

Tri-*n*-butyltin deuteride was prepared from hexa-*n*-butylditin by a modification of the literature procedure.[25] Naphthalene (1.5 g, 12.0 mmol) was placed in a three-necked, 250-ml flask containing a Teflon stirring bar and equipped with a 60-ml dropping funnel. The system was flushed with prepurified nitrogen. Tetrahydrofuran (125 ml, freshly distilled from LAH under nitrogen) and 2.6 g (110 mg-atom) of sodium were added. The remaining necks were capped with No-Air stoppers and hexabutylditin (32 g, 52 mmol; Alpha Inorganics) was added dropwise over a 1-hr period. The resulting reaction mixture was permitted to stir overnight before cautiously hydrolyzing with deuterium oxide (12 ml, 99.5% *d*). The clear organic supernatant solution was decanted by cannula and the reaction residue extracted with two 20-ml portions of hexane. The combined organic phase was dried ($MgSO_4$) and filtered; the more volatile components were removed under reduced pressure. The residual oil was transferred to a one-necked 50-ml flask equipped with a distilling head which was heated with an infrared lamp. The distillation flask was immersed in an oil bath heated to 50°. The pressure of the system was gradually reduced to, and maintained at, 0.01–0.005 Torr until the distillation of naphthalene ceased. The receiving flask was changed and the pot temperature increased until the remaining liquid began to distil, bp 60–65° (0.01–0.005 Torr) [lit.[73] bp 76–81° (0.7–0.9 Torr)]. The isolated yield of tri-*n*-butyltin deuteride was 20 g (67%). A comparison of the intensities of the Sn–H and Sn–D ir-stretching frequencies (1810 and 1305 cm^{-1}, respectively) in a sample of this material indicated that its isotopic purity was approximately 96–98% Sn–D.

Neophylmercuric Bromide (1). An ether solution of neophylmagnesium chloride, prepared from 17 g (0.1 mol) of neophyl chloride and 2.67 g (0.12 g-atom) of magnesium turnings in 50 ml of ether, was added slowly to a suspension of 30 g (0.1 mol) of mercuric bromide in 300 ml of ether. The reaction mixture was cooled in an ice bath during addition. The resulting gray slurry was stirred overnight, then hydrolyzed. The organic layer was separated, dried, and concentrated. Methylene chloride (100 ml) was added to the residual oil and the solution chilled to −30° for 8 hr to produce **1** as lustrous white plates. Recrystallization from methanol (−30°) afforded 10.1 g (24%) of neophylmercuric bromide: mp 45.0–45.5°; ir (CCl_4, CS_2) 2960 (s), 1600 (m), 1518 (s), 1498 (s), 1445 (s), 1385 (s), 1367 (s), 1285 (m), 1198 (s), 1150 (m), 1136 (m), 1028 (s), and 690 cm^{-1} (s); nmr ($CDCl_3$) δ 7.36 (5 H, m, aromatic), 2.40 (2 H, s, $-CH_2-$), 1.44 (6 H, s, $-(CH_3)_2$); $J_{\mathrm{Hg-CH_2}}$ = 187.0 Hz, $J_{\mathrm{Hg-CH_3}}$ = 13.0 Hz.

Anal. Calcd for $C_{10}H_{13}BrHg$: C, 29.02; H, 3.38; Br, 19.32. Found: C, 29.09; H, 3.12; Br, 19.20.

1,7,7-Trimethylbicyclo[2.2.1]heptyl-2-mercuric Bromide (2). An ether solution of bornylmagnesium chloride was prepared by refluxing 17.0 g (0.10 mol) of bornyl chloride with 2.5 g (0.11 g-atom) of magnesium turnings in 150 ml of ethyl ether containing 0.3 ml of methyl iodide for 12 hr. This reagent was added to a suspension of 30 g (0.10 mol) of mercuric bromide in 300 ml of ether at −78°. The resulting gray slurry was stirred overnight at room temperature before being cautiously hydrolyzed, first with methanol, and then with

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(66) K. Ziegler, *et al.*, *Justus Liebigs Ann. Chem.*, **589**, 91 (1954).

(67) The Volhard method was used: A. C. Cumming and J. Kay, "Quantitative Chemical Analysis," Oliver and Boyd, London, 1956, p 194.

(68) A standard analysis employing EDTA and PAN indicator was used: W. T. Elwell and I. R. Scholes, "Analysis of Copper and Its Alloys," Pergamon Press, Elmsford, N. Y., 1967, p 29.

(69) For a discussion of the reaction of alkylaluminum hydrides with alkynes, see H. Reinheckel, J. Haage, and D. Johnke, *Organometal. Chem. Rev.*, **4**, 47 (1969), and references therein.

(70) J. J. Eisch and W. C. Kaska, *J. Amer. Chem. Soc.*, **88**, 2213 (1966).

(71) A detailed description of the analytical methods used in characterizing this substance will be reported in a paper dealing with the chemistry of copper hydride.

(72) J. A. Ditts and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 5769 (1968); **91**, 4088 (1969).

(73) G. J. M. Van Der Kerk, J. G. Noltes, and J. G. H. Suijten, *J. Appl. Chem.*, **7**, 366 (1957).

water. The organic layer was separated and the inorganic residues were extracted with two 100-ml portions of methylene chloride. The combined organic phase was dried, filtered, and concentrated under reduced pressure. The resulting white solid, after recrystallization from 500 ml of boiling methanol, yielded 10 g (29%) of bornylmercuric bromide (containing a mixture of stereoisomers): mp 177–178°; ir ($CHCl_3$) 2950 (vs), 1500 (s), 1383 (m), 1370 (m), 1363 (m), 1310 (m), 1300 (m), 1288 (m), 1268 (m), 1215 (m), 1203 (m), 1190 (m), 1162 (s), 1092 (m), 1068 (m), and 1019 cm^{-1} (w); nmr ($CDCl_3$) δ 0.83 (3 H, s, CH_3), 0.88 (3 H, s, CH_3), 0.95 (3 H, s, CH_3), ~1.0–3.0 (8 H, complex).

Anal. Calcd for $C_{10}H_{17}BrHg$: C, 28.78; H, 4.08. Found: C, 28.78; H, 4.18.

Bicyclo[2.2.1]heptyl-2-mercuric Bromide. A suspension of mercuric bromide (0.30 mol) in 500 ml of dry ether was chilled to −78°. A solution of bicyclo[2.2.1]heptyl-2-magnesium bromide, prepared by reaction of 42 g (0.24 mol) of *exo*-norbornyl bromide with 6.3 g (0.25 g-atom) of magnesium turnings in 200 ml of ether, was added to this suspension over a period of 15 min with vigorous stirring. During the addition, the reaction mixture warmed to ~0°. The mixture was allowed to stir for 2 hr at room temperature, then cautiously quenched with sufficient methanol (~3 l.) at −20° to dissolve the resulting grey solid on warming the solution to reflux temperature. The solution was filtered while hot, then cooled to −50°. Lustrous white crystals of product (a mixture of stereoisomers) formed and were collected by suction filtration. These crystal had mp 148–150° (lit.[26] mp 144–145° for a 53% *endo*, 47% *exo* mixture).

Bicyclo[2.2.1]heptyl-2-mercuric Acetate. Bicyclo[2.2.1]heptyl-2-mercuric bromide (7.50 g, 20.0 mmol; mp 151–153°) was dissolved in 140 ml of benzene and added to a suspension of silver acetate (3.36 g, 2.01 mmol) in 20 ml of benzene. A precipitate of yellow silver bromide formed immediately. The reaction mixture was allowed to stir for 15 min, then filtered and concentrated under reduced pressure. Addition of pentane to the residual oil produced 5.35 g (75%) of lustrous white plates, mp 91–93° (a mixture of stereoisomers) (lit.[26] mp 77–78° for a 53% *endo*, 47% *exo* mixture).

***exo*-Bicyclo[2.2.1]heptyl-2-mercuric Bromide (3).** Recrystallization of 40 g of bicyclo[2.2.1]heptyl-2-mercuric acetate (mp 86–88°) from 2 l. of refluxing pentane yielded 13.1 g of an initial fraction with mp 103–104°. Similar recrystallization of this fraction from a minimum amount of refluxing pentane produced 3 g of a material with mp 110.0–110.5°. An additional recrystallization increased the mp to 110.5–111.0° (1.75 g) [lit.[74] mp for *exo*-bicyclo[2.2.1]-heptyl-2-mercuric acetate 110.0–110.8° (109°)[26]]. A solution of this material (3.0 g, 8.4 mmol) in 20 ml of benzene was shaken for 10 min with 20 ml of a saturated aqueous solution of potassium bromide. The organic layer was separated, dried, and concentrated under reduced pressure. Crystallization of the remaining oil from a minimum quantity of boiling methanol produced 1.7 g (55%) of white needles, mp 169.0–169.5° (lit.[26,75] mp 178–180°).

Anal. Calcd for $C_7H_{11}BrHg$: C, 22.30; H, 2.29. Found: C, 22.34; H, 3.00.

***endo*-Bicyclo[2.2.1]heptyl-2-mercuric Bromide (4).** Bicyclo[2.2.1]heptyl-2-mercuric acetate (5.0 mmol, mp 88–90°) was dissolved in 10 ml of glacial acetic acid containing 1 ml of acetic anhydride. Two drops of 70% perchloric acid were added. An immediate reaction occurred and elemental mercury precipitated. The reaction mixture was stirred for 15 min, then 50 ml of a saturated aqueous solution of potassium bromide was added, and the mixture shaken vigorously for 1 min. The resulting solution was extracted three times with benzene (total volume 200 ml). The extracts were washed with saturated aqueous bicarbonate solution until neutral, dried, and concentrated under reduced pressure to a volume of 10 ml. The addition of 100 ml of pentane to the resulting oil produced 3.8 g of a white granular solid, mp 120.5–121.5° (lit.[26,74] mp 120–121°, pure *endo*).

The infrared spectra of *exo*- and *endo*-bicyclo[2.2.1]mercuric bromide (saturated in CS_2) are similar, but may be distinguished by several characteristic differences. The *endo* isomer has strong, sharp bands at 1305, 1235, 1210, 1104, 950, and 748 cm^{-1} with a very strong band at 1160. The *exo* isomer has strong, sharp absorptions at 1311, 1220, 1170, 1108, and 952 cm^{-1}. Very strong bands are absent in the *exo* isomer. The nmr ($CDCl_3$) spectra of individual *exo* and *endo* isomers exhibited complex, but different, absorptions.

***cis-exo*-Bicyclo[2.2.1]hept-5-ene-2-acetoxy-3-mercuric bromide (5)** was prepared by a procedure similar to that outlined by Pande and Winstein for the preparation of the analogous mercuric chloride.[34] To a stirred suspension of mercuric acetate (0.156 mmol) in glacial acetic acid was added in one portion a solution of bicyloheptadiene (0.22 mol) in 20 ml of acetic acid. After 10 min the resulting mixture was treated with 200 ml of 10% aqueous potassium bromide. Cooling the reaction mixture to −30° resulted in precipitation of a white solid which was collected and dried. This material was dissolved in a minimum amount of ethyl acetate and reprecipitated by addition of pentane at −30°. Recrystallization from warm ethyl acetate yielded 50 g (75%) of **5**: mp 127–128°; ir (CS_2) 3050 (w), 1735 (s), 1215 cm^{-1} (vs).

Anal. Calcd for $C_9H_{11}BrHgO_2$: C, 25.02; H, 2.55; Br 18.51. Found: C, 25.23; H, 2.73; Br, 18.51.

***exo,exo*-Tricyclo[2.2.1.0^{2,6}]hepta-5-acetoxy-3-mercuric bromide (6)** was prepared by a modification of the procedure used to obtain **5**. The same quantities of mercuric acetate, acetic acid, and bicycloheptadiene were used; however, the reaction time was increased from 10 min to 48 hr.[34] Work-up and isolation of the product followed that for **5**. Compound **6**, obtained in 55% yield, had mp 127–128°; ir (CS_2) 3050 (w), 1735 (s), 1230 (vs), 800 cm^{-1} (m, nortricyclene).

Anal. Calcd for $C_9H_{11}BrHgO_2$: C, 25.02; H, 2.55. Found: C, 24.95; H, 2.61.

1,1-Dichloro-2,2-diacetoxyethane. Dichloroacetaldehyde diethyl acetal (100 g, 0.465 mol) was refluxed for 1 hr in 200 g of glacial acetic acid containing 1 g of *p*-toluenesulfonic acid. The resulting mixture was distilled almost to dryness, with the major fraction of distillate boiling at 95–100°. The distillate was treated with 200 g of acetic anhydride containing 1 g of *p*-toluenesulfonic acid and refluxed for 4 hr. The reaction mixture was then distilled slowly through a 30-cm Nester-Faust Teflon spinning band column. The distillate (88 g, bp 75–80°) was primarily ethyl acetate. The remaining liquid was neutralized with solid potassium carbonate, and taken up with ether. The resulting solution was dried and concentrated under reduced pressure, and the residual liquid purified by distillation, bp 67–70° (0.2 Torr), yielding 88 g (85%) of 1,1-dichloro-2,2-diacetoxyethane. Upon standing at room temperature this clear liquid crystallized into large prisms: mp 53–54°; ir (CCl_4) 1780 (vs), 1370 (m), 1220 (vs), 1190 cm^{-1} (s); nmr (CCl_4) δ 6.60 (1 H, d, J = 3.9 Hz, $HC(OAc)_2$), 5.74 (1 H, d, $HCCl_2$), 2.10 (6 H, s, CH_3).

Anal. Calcd for $C_6H_8O_4Cl_2$: C, 33.48; H, 3.72. Found: C, 33.56; H, 3.81.

β-Chlorovinyl acetate was prepared by an adaptation of the method described for the preparation of ethyl β-chlorovinyl ether.[76] Zinc dust (65 g) was added in 10-g portions to a vigorously stirred solution of ammonium chloride (50 g) and ammonium hydroxide (50 ml of a 2 *M* solution) in 250 ml of water in a three-necked flask equipped with overhead stirrer, condenser, and dropping funnel. A solution of cupric sulfate pentahydrate (15 g) in 160 ml of water was added to the resulting suspension over a period of 15 min with vigorous stirring. To the suspension of activated zinc formed by this procedure, 1,1-dichloro-2,2-diacetoxyethane (0.40 mol) was added with vigorous stirring in one portion. The reaction mixture was quickly heated in an oil bath to a bath temperature of 120°. Steam distillation commenced and heating was maintained until no further organic material appeared to distil (15–30 min). The distillate was extracted with ether and the extracts were dried. Distillation through a short Vigreux column afforded 12 g (25%) of a clear liquid having bp 130–140°. Glpc analysis of this liquid using an 8-ft, 20% TCEOP column at 100° indicated that it was composed of two compounds in ~42:58 relative yields. The first peak to elute was *trans*-β-chlorovinyl acetate, having ir (CCl_4) 3090 (H—C=C, m), 1774 (C=O, vs, with overtone at 3520), 1685 (*trans* C=C stretch, w), 1370 (CH_3, s), 1205 (*asym* C—O, vs), 1108 (*sym* C—O, s), 935 cm^{-1} (*trans* out of plane C—H bending, m—s); nmr (CCl_4) AX quartet, δ_A 6.09, δ_X 7.52, J = 11.0 Hz, 1.9 (3 H, s, CH_3CO_2); mass spectrum (70 eV) m/e 120 (12) and 122 (4) (M^+), 43 (100).

Anal. Calcd for $C_4H_5O_2Cl$: C, 39.83; H, 4.11 Found: C, 39.53; H, 4.17.

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[74] F. R. Jensen, R. J. Ouellette, G. Knutson, and D. A. Babbe, *Tetrahedron Lett.*, 339 (1963).

[75] In view of the close agreement between the melting point of our mercuric acetate isomers and the values obtained independently by others,[74] we believe that the melting point of 178–180° dec reported by Winstein and coworkers[26] for **3** is incorrect.

[76] D. A. van Dorp, J. F. Arens, and O. Stephenson, *Recl. Trav. Chim. Pays-Bas*, 70, 289 (1951).

The second isomer to elute was *cis*-β-chlorovinyl acetate, having ir (CCl_4) 3092 (H—C=C, m), 1771 (C=O, vs with overtone at 3520), 1647 (*cis* C=C stretch, m), 1410 in-plane C–H bending of *cis* C=C m), 1369 (CH_3, s), 1202 (*asym* C–O, vs), 1072 cm^{-1} (*sym* C–O, s); nmr (CCl_4) δ AX quartet δ_A 5.60, δ_X 7.40, J = 3.5, 1.95 Hz (3 H, s, CH_3CO_2); its mass spectrum was indistinguishable from that of the *trans* isomer.

Anal. Calcd for $C_4H_5O_2Cl$: C, 39.83; H, 4.11. Found: C, 39.72; H, 4.27. Chlorine analyses for both of these compounds were consistently low; however, their physical characteristics leave no doubt concerning their identity.

2-Chloro-3-acetoxybicyclo[2.2.1]hept-5-ene was prepared by the Diels–Alder reaction of β-chlorovinyl acetate and cyclopentadiene. A heavy-walled glass tube was charged with β-chlorovinyl acetate (3 g, 58% *cis*) and 5 ml of freshly cracked cyclopentadiene, sealed, and heated at 120–130° for 12 hr. A preliminary separation of the reaction products was affected by preparative glpc on an 8-ft, 20% SE-30 on Chromosorb W column, and a mixture of the isomers of 2-chloro-3-acetoxybicyclo[2.2.1]hept-5-ene was collected. Further glpc analysis on a 20-ft, 15% DEGS on Chromosorb W column at 180° indicated the presence of the four possible isomers **7–10** in relative yields 40:35:≤2:25, given in order of increasing retention times.

The first isomer to elute on the latter column using a carrier gas flow of 25 cc/min (retention time 65 min) was *exo*-**2-chloro-***endo*-**3-acetoxybicyclo[2.2.1]hept-5-ene (7)**, having ir (CCl_4, CS_2) 3065 (H—C=C, m), 1730 (C=O, vs with overtone at 3460), 1230 (*asym* C—O, vs), 1050 (*sym* C—O, s), with characteristic bands at 1370 (s), 1353 (s), 1330 (s), 1160 (m), 1117 (s), 950 (s), 901 (s), 860 (m), 830 (m), and 710 cm^{-1} (s). Its mass spectrum was characteristic of a 2,3-disubstituted norborn-5-ene, the molecular ion of which undergoes retro-Diels–Alder and other recognized fragmentation and rearrangement reactions:[77] *m/e* 188 (0.5), 186 (1.5), 91 (10, tropylium ion), 79 (15, 1,3-cyclohexenyl ion), 66 (37, cyclopentadienyl ion), 58 (16), 43 (100, acetyl ion).

Anal. Calcd for $C_9H_{11}ClO_2$: mol wt 186.0447. Found: mol wt 186.0455.

The second isomer to elute (retention time 80 min), identified as *endo*-**2-chloro-***exo*-**3-acetoxybicyclo[2.2.1]hept-5-ene (8)**, had an ir spectrum (CCl_4, CS_2) very similar to that of **7**, but lacked the bands at 1160, 950, 860, and 830 cm^{-1} and had new absorptions at 915 (m), 895 (m), and 881 cm^{-1} (m). Its mass spectrum was indistinguishable from that of **8**.

Anal. Calcd for $C_9H_{11}ClO_2$: mol wt 186.0447. Found: mol wt 186.0448.

The fourth isomer to elute (retention time 130 min) was assigned the structure *cis*-*endo*-**2-chloro-3-acetoxybicyclo[2.2.1]hept-5-ene (9)**. Its ir (CCl_4, CS_2) was again very similar to that described for **7**, but lacked the absorptions at 1117, 950, and 901 cm^{-1}, while possessing new bands at 1790 (m, shoulder), 1089 (s), 980 (w), 935 (w), 925 (w), 914 (w), and 903 cm^{-1} (w). Its mass spectrum was very similar to that described for **8**.

Anal. Calcd for $C_9H_{11}ClO_2$: mol wt 186.0447. Found: mol wt 186.0447.

The third isomer to elute (retention time 110 min) was not produced in sufficient quantity to obtain an nmr spectrum. It had ir (CCl_4) very similar to that of **9** but lacked absorption at 1340 and 1089 cm^{-1} while having new bands at 1235 and 1135 cm^{-1}. Its mass spectrum was very similar to those of **7–9**: *m/e* 188 (0.3) and 186 (1.0, M$^+$), 91 (15), 80 (25), 79 (43), 66 (20), 58 (80), 43 (100). On the basis of this spectral evidence the tentative assignment of *cis*-*exo*-**bicyclo[2.2.1]hept-5-ene (10)**, is made to this isomer.

3-Chloro-5-acetoxytricyclo[2.2.1.0^{2,6}]heptane. Norbornadiene (1.0 mol) was dissolved in 250 ml of glacial acetic acid to which sufficient sodium acetate was then added to form a saturated solution. Chlorine was bubbled through this mixture with mechanical stirring while the reaction temperature was maintained at *ca.* 20°. When 1 mol of chlorine had been absorbed, the reaction mixture was neutralized with solid potassium carbonate and the organic layer extracted into ether, dried, and concentrated by distillation at 20 Torr. The residual liquid distilled at 64–65° (0.2 Torr). Glpc analysis on a 20-ft, 15% DEGS column indicated the presence of several major components. The last two peaks to elute (retention times 120 and 130 min, respectively) were collected. The first isomer, to which is assigned the structure *exo*-**2-chloro-***endo*-**5-acetoxytricyclo[2.2.1.0^{2,6}]heptane (11)**, had ir (CCl_4, CS_2) 3065 (cyclopropane C–H, m), 1740 (vs), 1235 (vs), 1050 (s), 830 (nortricyclene[36] (s), together with characteristic absorptions at 1375 (s), 1360 (s), 1315 (s), 1295 (s), 1270 (m), 1170 (m), 1135 (m), 1060 (m), 960 (m), 938 (m), and 922 cm^{-1} (m); mass spectrum, *m/e* 188 (1), 186 (3), 152 (9), 151 (100), 109 (49), 81 (25), 78 (12), 43 (83).

Anal. Calcd for $C_9H_{11}ClO_2$: C, 57.91; H, 5.94; Cl, 19.03. Found: C, 57.74; H, 5.91; Cl, 18.97.

The second isomer eluted was assigned the structure *exo*-**2-chloro-***exo*-**5-acetoxytricyclo[2.2.1.0^{2,6}]heptane (12)**. Its ir (CCl_4, CS_2) was similar to **11**: 3065 (m), 1740 (vs), 1235 (vs), 1050 (s), 820 (nortricyclene band,[36] s), along with characteristic absorptions at 1450 (m), 1372 (m), 1360 (m), 1310 (m), 1290 (s), 1265 (m), 1205 (m), 1130 (m), 1030 (m), 930 (m), 905 (m), and 884 cm^{-1} (m). Its mass spectrum was indistinguishable from that of **11**.

Anal. Calcd for $C_9H_{11}ClO_2$: C, 57.91; H, 5.94; Cl, 19.03. Found: C, 58.01; H, 6.05; Cl, 18.75.

3-Acetoxynortricyclene (13) was synthesized by the literature procedure[78] and isolated by preparative glpc on a 12-ft, 12% TCEOP column: ir (CCl_4) 3065 (m), 1745 (vs), 1230 (vs), and 1042 (s) cm^{-1}; nmr (CCl_4) δ 4.56 (1 H, s, *H*-C-O-Ac), 1.92 (3 H, s, -OC(O)CH_3), 2.05–1.05 (8 H, m, nortricyclene protons); *m/e* 152 (18, M$^+$), 110 (22), 92 (62), 91 (50), 79 (33), 66 (45), 43 (100).

anti-**7-Acetoxynorborn-2-ene (16)** was prepared by refluxing *anti*-7-hydroxynorborn-2-ene[79] (0.8 g) in 2.5 ml of freshly distilled acetic anhydride containing 0.1 ml of dry pyridine for 30 min.[80] *anti*-7-Acetoxynorborn-2-ene was isolated from this reaction mixture by collection from preparative glpc using a 8-ft, 20% SE-30 column at 120° and recollection from a 20-ft, 15% TCEOP column at 120°: ir (CCl_4) 3060 (m), 1740 (vs), 1240 (vs), and 1050 cm^{-1} (s); nmr (CCl_4) δ 6.0 (2 H, m, *HC*=*CH*), 4.25 (1 H, s, *H*COAc), 2.75 (2 H, br m, bridgeheads), 1.90 (3 H, s, CH_3CO_2), 1.90–0.80 (4 H, m, C-2 and C-3 protons); *m/e* 93 (100), 43 (48). *syn*-**7-Acetoxynorborn-2-ene (15)** was obtained as a gift from Drs. W. Bunting and W. C. Baird (Esso Research and Engineering Co). *endo*- and *exo*-**2-acetoxynorborn-2-ene (14 and 17)** were purchased as a mixture (~70% *endo*) from Aldrich Chemicals. The individual isomers were isolated by preparative glpc on a 20-ft, 15% TCEOP column at 120°. The spectral characteristics of the second isomer to elute were in good agreement with those reported for **14**,[81,82] while those for the first isomer coincided with data reported for **17**.[82,83]

Procedures for Reductions. Similar procedures were used to carry out the reductive demercuration reactions for all of the organomercury compounds examined. Representative procedures for each organomercury reagent follow.

Reduction of Neophylmercuric Bromide (1) Using Sodium Borohydride. In a typical experiment 0.0990 g (0.240 mmol) of **1** and 0.0739 g of undecane (an internal glpc standard) were placed in a 12-ml graduated centrifuge tube. The tube was capped with a No-Air stopper and flushed with prepurified nitrogen. THF (4 ml) was added, and 1.0 ml of a 0.25 *M* solution of sodium borohydride in 3:1 THF–H_2O (3 *M* in NaOH) was injected by syringe into the resulting solution. Elemental mercury precipitated immediately. After drying, the reaction mixture was analyzed without further work-up on a 24-ft, 0.125-in. commercial Hi-Pak SE-30 column (Hewlett-Packard) at 90°. The product in these and the following reductions of **1** was identified by comparison of its glpc retention time and mass spectrum with that of an authentic sample of *t*-butylbenzene.

Using Diethylaluminum Hydride. Compound **1** (0.140 g, 0.340 mmol) and 0.121 g of hexadecane (an internal glpc standard) were placed in a 12-ml centrifuge tube; the tube was capped and flushed. Anhydrous ether (3–4 ml) was added, and 0.35 ml (0.85 mmol) of a decane solution of diethylaluminum deuteride was injected by syringe. Elemental mercury precipitated immediately. The reaction mixture was cautiously hydrolyzed and dried. The hydrocarbon fraction of interest was isolated by total collection from preparative glpc using a 12-ft, 20% TCEOP on Chromosorb W

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[77] S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3728 (1967).

[78] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Amer. Chem. Soc.*, **84**, 3918 (1962).

[79] Obtained as a gift from Dr. P. J. Stang and Professor P. v. R. Schleyer (Princeton University, Princeton, N. J.).

[80] This procedure is an adaptation of a similar method used to synthesize the tosylate of *anti*-7-hydroxynorborn-2-ene [S. Winstein and M. Shatovsky, *J. Amer. Chem. Soc.*, 78, 592 (1956)].

[81] P. Laszlo and P. v. R. Schleyer, *ibid.*, **85**, 2709 (1963).

[82] W. L. Dilling, R. D. Kroening, and J. C. Little, *ibid.*, **92**, 928 (1970); E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

[83] J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

column. Detailed analysis was carried out by reinjection of the collected material onto the Hi-Pak column described above.

Using Hydrido(tri-*n*-butylphosphine)copper(I). Compound **1** (0.0717 g, 0.174 mmol), a Teflon-covered stirring bar, and 0.0597 g of undecane (internal glpc standard) were placed in a 40-ml centrifuge tube; the tube was capped and flushed. THF (1–2 ml) was added to bring the components into solution. To this solution was added by syringe 5 ml (2–3 mmol) of a 1:1 Et_2O–THF solution of hydrido(tri-*n*-butylphosphine)copper(I). The reaction mixture was stirred for 1 hr at room temperature. Concentrated hydrochloric acid (0.1 ml) was added and the dark brown reaction mixture shaken vigorously with occasional venting for 5 min. Water (0.5 ml) and five pellets of NaOH were added, and the reaction mixture was again shaken for 5 min, then centrifuged. The resulting clear orange-yellow organic layer was transferred to a clean vessel, dried, and analyzed without further work-up as described previously.

Using Tri-*n*-butyltin Hydride. Compound **1** (0.11 g, 0.27 mmol) was placed in a 12-ml centrifuge tube and the tube capped and flushed. Tri-*n*-butyltin hydride (1.0 ml) was added to the tube by syringe with shaking. An immediate exothermic reaction occurred and elemental mercury precipitated. Carbon tetrachloride (1.0 ml) was added to destroy the excess tin hydride and the reaction mixture analyzed as described above.

Reduction of Bornylmercuric Bromide (2) Using Sodium Borohydride, Diethylaluminum Hydride, Hydrido(tri-*n*-butylphosphine)-copper(I), and Tri-*n*-butyltin Hydride. The reduction of **2** was performed at room temperature using procedures similar to those employed for reductions of **1** by the same hydrides. Typical experiments employed the following quantities of reagents: **2** (~0.42 mmol), $NaBD_4$ (~0.5 mmol), 3:1 THF–H_2O (3 *M* in NaOH) (1.0 ml); **2** (~0.58 mmol), Et_2AlD (~0.8 mmol), ether (5 ml); **2** (~0.56 mmol), Bu_3PCuD (~4 mmol), 3:1 THF–Et_2O (5.0 ml); **2** (~0.69 mmol), Bu_3SnD (~2 mmol). Glpc analyses and the collection of products from all reductions of **2** were carried out on a 24-ft, 0.125-in. Hi-Pak SE-30 column at 70° with decane as an internal standard. 1,7,7-Trimethylbicyclo[2.2.1]heptane was identified by comparison of its glpc retention time and ir spectrum with those of an authentic sample.

Reductions of *exo*- and *endo*-2-norbornylmercuric bromide (3 and 4) using sodium borohydride, diethylaluminum hydride, hydrido-(tri-*n*-butylphosphine)copper(I), and tri-*n*-butyltin hydride were carried out at room temperature using procedures similar to those used for reduction of **1** using the same hydrides. Typical experiments employed the following quantities of reagents: **3** or **4** (~0.5 mmol), $NaBD_4$ (~0.5 mmol), 3:1 THF–H_2O (3 *M* in NaOH) (0.5 ml); **3** or **4** (~0.48), Et_2AlD (~0.8 mmol), ether (5 ml); **3** or **4** (~0.38 mmol), Bu_3PCuH (~2 mmol), 3:1 THF–Et_2O (5.0 ml); **3** or **4** (~0.35 mmol), Bu_3SnH (~2 mmol). Glpc analyses and collection of products of all reductions of **3** and **4** were carried out on a 8-ft, 20% UC-W98 column at 90° with octane or nonane as an internal glpc standard. Norbornane was identified by comparison of its glpc retention time and mass spectrum with those of an authentic sample. Epimeric compositions of the mixture of *endo*- and *exo*-norbornane-2-d_1 determined by ir analysis of collected samples of norbornane are summarized in Table II.

Infrared analyses of the epimeric composition of *exo*- and *endo*-norbornane-2-d_1 were carried out using the characteristic bands assigned by Nickon and Hammons[27] in the fingerprint region. The results of these analyses were confirmed by comparisons of their spectra of the epimeric mixtures of *exo*- and *endo*-norbornane-2-d_1 obtained from the reductions summarized in Table II with mixtures of known epimeric compositions prepared from authentic samples of these deuterated norbornanes. *exo*-2-Norbornane-d_1 (≥99% *exo*) was prepared using a literature procedure;[84] *endo*-2-norbornane-d_1 (~96 ± 5% *endo*) was prepared by reducing *endo*-2-norbornylmercuric bromide with 2% sodium amalgam in D_2O. The epimeric purity of this material was assayed by comparison of its C–D stretching pattern (CCl_4 solution) with those of solutions of norbornane-2-d_1 prepared by reaction of predominantly *endo*-norbornylmagnesium bromide[85] with D_2O–CH_3OD–DCl (4:5:1) at −50°.[86] In our hands, analyses of mixtures of 2-norbornane-d_1 of known epimeric composition, using the procedure utilized to examine the 2-norbornane-d_1 obtained from reductions, gave values in agreement with the "known" compositions with a maximum deviation of ≤±5%.

Recovery of 3 and 4 from Partial Reductions Using Sodium Borohydride. Solutions of **3** (1.40 g, 3.74 mmol) or of **4** (1.40 g, 3.74 mmol) in THF (2 ml) were placed in 12-ml centrifuge tubes. The tubes were capped and flushed with nitrogen. The addition of 2 ml of a 0.25 *M* solution of sodium borohydride (2.0 mmol) in 3:1 THF–H_2O (3 *M* NaOH) to each vessel produced an immediate precipitate of elemental mercury. The resulting mixtures were dried and filtered. Evaporation to dryness under reduced pressure produced in each instance a white solid whose melting point and ir spectrum (CS_2) were indistinguishable from those of the starting mercurials.

Reductions of *cis*-*exo*-bicyclo[2.2.1]hept-5-ene-2-acetoxy-3-mercuric bromide using sodium borohydride, hydrido(tri-*n*-butylphosphine)copper(I), and tri-*n*-butyltin hydride were carried out at room temperature using procedures similar to those used for reduction of **1** by these hydrides. Typical experiments employed the following quantities of reagents: **5** or **6** (~0.3 mmol), $NaBH_4$ (~0.5 mmol), 3:1 THF–H_2O (3 *M* in NaOH) (1.0 ml); **5** or **6** (~0.3 mmol), $HCuPBu_3$ (~1.0 mmol), 3:1 THF–Et_2O (5.0 ml); **5** or **6** (~0.5 mmol), Bu_3SnH (~0.85 mmol), neat. Glpc analyses and the collections of products were carried out using a 20-ft, 15% DEGS on Chromosorb W column at 110° using pentadecane as an internal glpc standard. Products were identified by comparison of their glpc retention times and ir and mass spectra with those of authentic **13**, **16**, and **17**.

Reduction of *exo*- and *endo*-2-Norbornyl Chloride with Tri-*n*-butyltin Deuteride. *exo*-2-Norbornyl chloride (1.43 g, 1.1 mmol), tri-*n*-butyltin deuteride (0.430 g, 1.5 mmol), and several mg of AIBN were placed in a 4-in., 5-mm glass tube. After flushing the tube briefly with prepurified nitrogen, the tube was sealed and irradiated for 1 hr with a chromatographic hand scanner. The reaction mixture was treated with an equal volume of carbon tetrachloride before analyzing by glpc on an 8-ft, 20% UC-W98 column at 90° and collecting the norbornane-2-d_1. Reduction of *endo*-2-norbornyl chloride was carried out using a similar procedure.

endo-2-Norbornyl chloride was demonstrated not to isomerize under the reduction conditions by carrying out the reduction using an excess of norbornyl chloride. At the conclusion of the reduction, unreacted halide was isolated by glpc; its ir spectrum was indistinguishable from that of starting material.

Tri-*n*-butyltin Hydride Reduction of 7, 8, 9, 11, and 12. Approximately 20-μl samples of **7**, **8**, **9**, **11**, and **12** were trapped directly from glpc into 5-mm glass tubes and diluted with 100-μl portions of pentane. Tri-*n*-butyltin hydride (40–50 μl) was added along with several mg of AIBN. The reaction mixtures were degassed by several freeze–thaw cycles (liquid nitrogen, 1 Torr), sealed, and irradiated with long-wavelength ultraviolet light from a chromatographic hand scanner for 30 min at 25°. The acetate isomers were separated from other products in the reaction mixture on an 8-ft, 20% UC-W98 on Chromosorb W column, then repassed for analysis and collection on a 20-ft, 15% DEGS on Chromosorb W column at 110°.

Each of the starting materials **7**, **8**, **9**, **11**, and **12** was treated individually with tri-*n*-butyltin chloride under conditions similar to those employed in their reduction by tri-*n*-butyltin hydride. Similar experiments were carried out with each of the products **13**, **14**, **15**, **16**, and **17** in the presence of tri-*n*-butyltin hydride and chloride. Glpc analysis and ir spectra of these compounds after reclamation in all instances indicated that no isomerism had occurred.

N,N-Di-*t*-butyl-O-2-norbornylhydroxylamine (24).[87] To 5 ml of an ether solution of 0.3 *M* 2-norbornylmagnesium bromide (~1.5 mmol) was added di-*t*-butyl nitroxide[45] (~0.5 g, 3.5 mmol) at ambient temperature until the reaction mixture became pale red. The solution was treated with 1 ml of 1 *M* sulfuric acid and the ether layer was separated. Glpc analysis (8-ft, 10% squalane on Chromosorb P at 80°) showed two peaks of long retention time, in addition to norbornene and norbornane. The peak of longer retention time (40% based on Grignard reagent) was assigned structure **24** on the basis of spectral data: ir (CCl_4) 2970, 2920 (vs), 2840, 1480 (m), 1470 (m), 1380, 1355 (s), 1185 (s), 980 (s), and 925 (m) cm^{-1}; mass spectrum (70 eV), *m/e* 239 (1, M^+), 195 (14), 95 (100), 89 (63), 74 (43), 72 (21), 67 (23), 57 (54), 56 (16), 41 (60).

Anal. Calcd for $C_{15}H_{29}NO$: mol wt 239.2249. Found: mol wt 239.2265.

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[84] H. C. Brown and K. J. Murray, *J. Org. Chem.*, **26**, 631 (1961); H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 1990 (1970).

[85] F. R. Jensen and K. Nakamaye, *ibid.*, 88, 3437 (1966).

[86] The epimeric composition of the Grignard reagent was assayed in turn by conversion to 2-methylnorbornane with retention of configuration.[14]

[87] This preparation and the following reduction were first carried out in these laboratories by Mr. Jack Gaasch.

The peak with shorter retention time was assigned the binorbornyl structure on the basis of mass spectral data (70 eV); *m/e* 191 (6) (M + 1), 190 (34) (M^+), 95 (100).

Anal. Calcd for $C_{14}H_{22}$: mol wt 190.1722. Found: mol wt 190.1724.

Reduction of N,N-Di-*t*-butyl-O-2-norbornylhydroxylamine. A mixture of binorbornyl and **24** (~10 mg, isolated by glpc from the solution obtained by reaction of 2-norbornylmagnesium bromide with DTBNO) was allowed to stir at room temperature for 12 hr in 1 ml of hexamethylphosphoramide containing ~80 mg of sodium.[88] Ether (10 ml) was added to the reaction mixture and excess sodium was destroyed by addition of methanol. The ether layer was separated, washed with three 3-ml portions of water, dried ($MgSO_4$), and concentrated. Glpc analysis of the residual solution showed that the 2-norbornanol present had epimeric composition 95% *exo* and 5% *endo*.

Reduction of Norbornyl-2-mercuric Bromide in the Presence of Di-*t*-butyl Nitroxyl. In a typical experiment, *endo*-2-norbornylmercuric bromide (**4**) (0.27 g, 0.71 mmol) and 0.123 g of tetradecane as internal glpc standard were placed in a 12-ml centrifuge tube. THF (0.5 ml) and DTBNO (2.0 ml, ~14 mmol) were added; the tube was capped with a serum stopper, and flushed briefly with nitrogen. The addition of 1.0 mmol of a solution of sodium borohydride (1 *M*; 3:1 THF–H_2O (3 *M* NaOH)) to this solution at room temperature produced an immediate reaction accompanied by precipitation of mercury. After drying ($MgSO_4$) and adding a weighed amount of tetradecane (internal glpc standard) the reaction mixture was analyzed on a 12-ft, 20% UC-W98 column at 200°. A 20% yield of **24** was observed. Norbornane and norbornene were not observed (<5%) and the remaining products could not be readily identified. Repetition of this experiment using *exo*-2-norbornylmercuric bromide (**3**) yielded similar results. In both instances the collected coupling product **24** displayed a glpc retention time, ir spectrum, and mass spectrum indistinguishable from those of authentic **24** prepared by the reaction of norbornyl-2-magnesium bromide with DTBNO. At mercurial to DTBNO ratios ≤1, significant (≥15%) yields of norbornane were observed. Under these conditions no norbornene was observed.

Eu(DPM)$_3$–2Py.[35] Dipivaloylmethane (7.55 g, 41.0 mmol) was dissolved in 25 ml of ethanol in a 500-ml flask and 50 ml of a 1:1 (v:v) water–ethanol solution of sodium hydroxide (2.0 g) was added. A solution of europium(III) trichloride hexahydrate (5.0 g, 13.7 mmol, Alfa Inorganics), dissolved in 1:1 (v:v) water–ethanol, was added to this solution in one portion. A white precipitate formed immediately. The reaction mixture was stirred for 2 hr at room temperature before diluting with 50 ml of ice-cold water. After stirring for an additional 15 min, the white solid was collected by suction filtration and air-dried overnight. The solid was dissolved in a minimal amount of warm pyridine. This solution was then concentrated to *ca.* one-half its original volume and stored for 2 days at −30°. The resulting white crystals were collected by suction filtration, rinsed with cold (−30°) pentane, and air-dried overnight. The crystals had mp of 92–95° and were isolated in ~50% yield.[89]

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[88] Review: H. Normant, *Angew. Chem., Int. Ed. Engl.*, **6**, 1046 (1967); H. Normant, *Bull. Chim. Soc. Fr.*, 791 (1968); K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970); H. O. House, R.W. Giese, K. Kronberger, J. P. Kaplan, and J. F. Simeone, *ibid.*, **92**, 2800 (1970).

[89] No effort was made to maximize this yield.