The Reduction of Organomercurials. Stereospecific Replacement of Mercury by Deuterium[1]

FREDERICK R. JENSEN, JOHN J. MILLER,[2] STANLEY J. CRISTOL,* AND RONALD S. BECKLEY[3]

Departments of Chemistry, University of California at Berkeley, Berkeley, California 94720, and University of Colorado, Boulder, Colorado 80302

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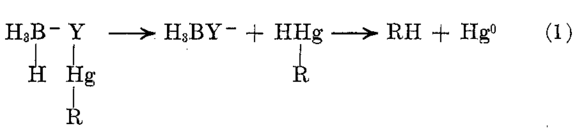
Sodium amalgam reduction of *cis*-8-acetoxymercuri- and *cis*-8-chloromercuridibenzobicyclo[2.2.2]octadien-7-ol acetates (**2** and **3**), *trans*-8-chloromercuridibenzobicyclo[2.2.2]octadien-7-ol (**4**), *cis,exo*-3-methoxy-2-norbornylmercuric chloride (**9**), *exo*-3-methoxy-*endo*-2-norbornylmercuric chloride (**10**), and *cis,endo*-3-methoxy-2-norbornylmercuric chloride (**11**) in alkaline deuterium oxide gives products with stereospecific retention during the replacement of mercury by deuterium. Sodium borodeuteride reduction of *trans*-8-chloromercuridibenzobicyclo[2.2.2]octadien-7-ol acetate (**5**), in addition to those compounds listed above, in aqueous base gives similar products but without stereospecific deuterium incorporation. Borodeuteride reduction of **3** and **4** in alkaline ethanol gives products without complete incorporation of deuterium. The results of these reductions are discussed briefly in mechanistic terms.

The work described in this paper arose from a need to determine rigorously the stereochemistry of oxymercuration products and to prepare specific isomers of β-deuterio alcohols.

During the early stages of this work, only a few papers regarding the specificity of the reduction of organomercurials had appeared. Bordwell and Douglass[4] studied reduction with borohydrides and established the stoichiometry (four mercurials per borohydride), source of hydrogen (only from BH_4^-), and lack of direct displacement character (neopentyl mercurials react readily). They attempted to determine the stereochemistry of the reaction by reducing *cis,exo*-3-hydroxy-2-chloromercurinorbornane with sodium borodeuteride. Only the exo-deuterated alcohol was found. A number of mechanisms were considered, but that shown in eq 1



$$H_3\underset{\underset{H}{|}}{B^-} - \underset{\underset{\underset{\underset{R}{|}}{Hg}}{|}}{Y} \longrightarrow H_3BY^- + H\underset{\underset{R}{|}}{Hg} \longrightarrow RH + Hg^0 \qquad (1)$$

seemed best to them. The final step was considered as an intramolecular extrusion to explain the retention observed. One example reported,[5] however, described at least one case where the reaction occurred with loss of stereochemistry.

Only one paper had considered the stereochemical course of the reduction of an organomercurial by sodium amalgam in deuterium oxide in which the substrate was not a norbornyl moiety. Thus, Wolfe and Campbell[6] studied the reduction of the product from the acetoxymercuration of 3,3,6,6-tetradeuteriocyclohexene. In this sterically unencumbered system, they found complete retention in the deuterated cyclohexanol. The cis isomer was not studied.

Several cases of retention with the sodium amalgam reduction of *exo*-2-mercurinorbornyl moieties had also been reported,[7] but the well-known preference for exo capture of norbornyl intermediates obscures interpretation of these results.

During the period of our investigation much interest has arisen in the oxymercuration–hydrodemercuration reaction.[8-12] This recent interest has prompted us to relay our results, which add the possibility of a stereospecific oxymercuration–deuteriodemercuration procedure for the preparation of stereospecific β-deuterio alcohols and alcohol derivatives to the regiospecificity already indicated,[9] and which also cast more light on the mechanism of the borohydride reduction.

Results

The Dibenzobicyclo[2.2.2]octadiene System.—With the view in mind of developing a general synthesis of 8-deuteriodibenzobicyclo[2.2.2]octadiene-7-ol derivatives, the oxymercuration and subsequent reduction of adducts derived from the readily available dibenzobicyclo[2.2.2]octatriene (**1**) were investigated. The syntheses of *cis*-8-acetoxymercuri- and *cis*-8-chloromercuridibenzobicyclo[2.2.2]octadien-7-ol acetates (**2** and **3**) and *trans*-8-chloromercuridibenzobicyclo[2.2.2]octadien-7-ol and 7-ol acetate (**4** and **5**) are straightforward and are described in the Experimental Section. Identification of the oxymercurial isomers **2–5** (and also the β-deuterio alcohols from their reduction) is facilitated by their simple pmr spectra.[13] Protons on the C-7,8 bridge have a 2.6 ± 0.7 Hz coupling constant with the C-1 and C-4 bridgehead protons. Cis protons at C-7 and C-8 couple with a constant of 8.8 ± 0.8 Hz and corresponding trans protons couple with a constant of 3.5 ± 1.1 Hz. Geminal protons at C-7 or C-8 are coupled with a constant of 13.1 ± 1.1 Hz. Protons cis and vicinal to acetoxy or hydroxy groups are shifted upfield about 0.3–0.4 ppm and protons trans and vicinal are shifted downfield about 0.7 ppm. Although the mercury group shifts the α proton downfield roughly

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[1] Paper LXXV in series Bridged Polycyclic Compounds of University of Colorado group. Paper LXXIV: S. J. Cristol, G. C. Schloemer, D. R. James, and L. A. Paquette, *J. Amer. Chem. Soc.*, in press.

[2] Taken in part from the Ph.D. dissertation of J. J. M., University of California, 1966 (work done on norbornane system); *Diss. Abstr. B*, **28** (1), 112 (1967).

[3] National Science Foundation Trainee, 1968–1970. Taken in part from the Ph.D. dissertation of R. S. B., University of Colorado, 1970. (Work done on dibenzobicyclooctadiene system.)

[4] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, **88**, 993 (1966).

[5] Footnote 27 of ref 4.

[6] S. Wolfe and P. Campbell, *Can. J. Chem.*, **43**, 1184 (1963).

[7] (a) J. K. Stille and S. C. Stinson, *Tetrahedron*, **20**, 1387 (1964); (b) T. G. Traylor and A. W. Baker, *J. Amer. Chem. Soc.*, **85**, 2746 (1963); (c) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

[8] (a) N. S. Zefirov, *Russ. Chem. Rev.*, **34**, 527 (1965); (b) W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

[9] H. C. Brown and P. J. Goeghegan, Jr., *J. Org. Chem.*, **35**, 1844 (1970), and previous papers in this series.

[10] D. J. Pasto and J. A. Gontarz, *J. Amer. Chem. Soc.*, **91**, 719 (1969).

[11] G. A. Gray and W. R. Jackson, *ibid.*, **91**, 6205 (1969).

[12] G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970).

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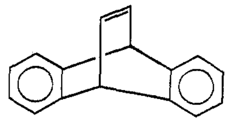

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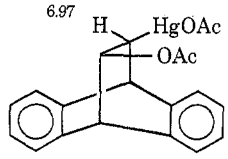

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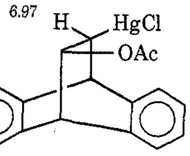

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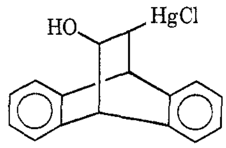

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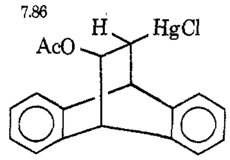

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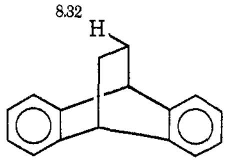
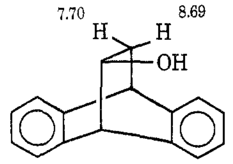
0.6 ppm, similar effects of β-oxy functional groups are observed. The data of importance are shown on the structural formulas. Spectra were run in $CDCl_3$, and the chemical shift values, in τ units, are given.





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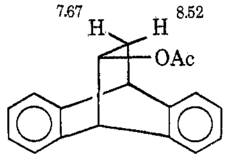

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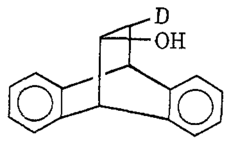
Compound **4** was not sufficiently soluble in $CDCl_3$ and its spectrum was therefore run in DMSO-d_6. The coupling constants of **4** (see Experimental Section) and its conversion to **5** attest to its assigned structure.

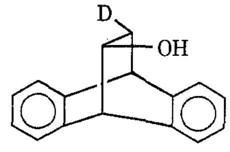
Reduction of mercurials **2**–**5** by either sodium borohydride or sodium amalgam gave good yields of either dibenzobicyclo[2.2.2]octadien-7-ol (**6**)[14] or its acetate (**7**).[14] The pmr spectra of **6** and **7** show good separation of the geminal C-8 protons. Thus, if a deuterium is placed at the C-8 position by either sodium borodeuteride or sodium amalgam reduction in deuterium oxide of the mercurials **2**–**5**, stereochemical analysis of the resulting **6**-*d* or **7**-*d* can be made by integrating the pmr signal of these regions.

Reductions with sodium amalgam were carried out in 1 *M* NaOD in D_2O solution with a large excess of the reducing agent for relatively long periods of time. Consequently, regardless of the mercurial (**2**–**5**) reduced, because of the hydrolysis of the ester only alcohol **6**-*d* was isolated as the product. Reduction of *cis*-acetoxyalkylmercuric acetate (**2**), *cis*-acetoxyalkylmercuric chloride (**3**), and *trans*-acetoxyalkylmercuric chloride (**5**) with sodium borodeuteride in 1 *M* NaOH in water–tetrahydrofuran (1:1) solution gave mostly acetate **7**-d_1 with short reaction times and mixtures of alcohol **6**-d_1 and acetate **7**-d_1 with longer times. Pmr analysis of the stereochemistry of the incorporated deuterium could be made either on the mixture of **6**-d_1 and **7**-d_1 or on the product **6**-d_1 after transesterification of the acetate part with sodium methoxide in methanol or after reduction with lithium aluminum hydride.

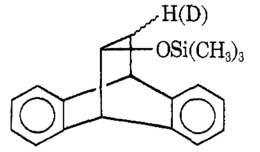
The pmr spectra of the product alcohols **6**-*d* were easily interpreted in terms of a mixture of *cis*-8-deuteriodibenzobicyclo[2.2.2]octadien-7-ol (*c*-**6**) and *trans*-8-deuteriodibenzobicyclo[2.2.2]octadien-7-ol (*t*-**6**). However, it became evident that about 10% of undeuterated **6** was being formed in the aqueous THF system and that a sensitive method of determining the amount of deuterated product was needed. Mass spectral analysis of **6** is unsatisfactory, since a retro Diels–Alder reaction completely removes the bridge and no molecular ion is observed. The trimethylsilyl ether (**8**) gives a peak (M − 15^+) by loss of methyl which is suitable for the determination.[15] Alcohol **6** is easily converted to trimethylsilyl ether **8** with *N*,*N*-bis(trimethylsilyl)acetamide, and the relative amount of **6** in mixture with *c*-**6** plus *t*-**6** may be calculated from the mass spectrometric measurement. Controls with synthetic mixtures of **6**, *c*-**6**, and *t*-**6** showed an accuracy of better than ±2%. Ratios of *c*-**6** to *t*-**6** in the mixtures which contained no more than 13% **6** may be determined to approximately ±5% by pmr.



c-**6**



t-**6**



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Details of the procedures used are given in the Experimental Section. Reductions with sodium borodeuteride were carried out first in aqueous tetrahydrofuran (THF), prompted by the initial communication of Brown and Goeghegan,[16] in view of its technical ease, but it soon became evident that this procedure did not lead to stereospecific replacement of mercury by deuterium. Indeed, as the data in Table I show, reductions of *cis*- and *trans*-β-acetoxy mercurials **3** and **5** lead to almost identical mixtures of *t*-**6** and *c*-**6** with perhaps a small degree of retention predominating (over the 2:1 *t*-**6** to *c*-**6** average result). These data, plus those on the reduction of **2** and **4**, suggest the existence of a long-lived intermediate unable to maintain configuration in the borohydride reductions (*vide infra*), and also make clear the inappropriateness of this procedure for stereospecific labeling with deuterium.

Table I also contains data on the reduction of **2**, **3**, and **4** with sodium amalgam in deuterium oxide containing sodium deuterioxide. These reactions were stereospecific, with complete retention observed.

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[14] K. Alder and H. Rickert, *Justus Liebigs Ann. Chem.*, **543**, 1 (1939).

[15] S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, **34**, 3574 (1969).

[16] H. C. Brown and P. Goeghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

TABLE I

REDUCTION OF DIBENZOCYCLO[2.2.2]OCTYLMERCURIALS IN AQUEOUS SOLVENT SYSTEMS WITH SODIUM BORODEUTERIDE OR WITH SODIUM AMALGAM

Substrate	Reducing agent	Solvent	% D	*t*-6, %	*c*-6, %	Yield, %
2	$NaBD_4$	H_2O–THF (NaOH)	94	75	25	52 as 6-*d*[a]
3	$NaBD_4$	H_2O–THF (NaOH)	91	66	34	88 as 7-*d*[b]
4	$NaBD_4$	H_2O–THF (NaOH)	91	80	20	79 as 6-*d*[b]
5	$NaBD_4$	H_2O–THF (NaOH)	92	70	30	100 as 6-*d*[b]
2	Na/Hg	D_2O (NaOD)	97	0	100	49 as 6-*d*[a]
3[c]	Na/Hg	D_2O (NaOD)	96	14[c]	86[c]	65 as 6-*d*[a]
4	Na/Hg	D_2O (NaOD)	96	100	0	55 as 6-*d*[a]

[a] Yield after recrystallization. [b] Crude yield. [c] The reduction was stereospecific with retention. The sample of **3** was contaminated with approximately 15% of **5**.

Sodium borohydride reductions may be carried out in alcohol solvents, and we decided to see if a solvent change might lead to a change in stereoselectivity of deuterium incorporation. To this end, the sodium borodeuteride reduction was conducted in ethanol solvent containing 1 *M* NaOH. The reduction was noticeably slower in this solvent than in aqueous THF, but was still rapid. To our surprise, analysis showed extensive incorporation of hydrogen in the product (Table II). The deuterated product amounted to only 50 ± 10% of the product (only the alcohols **6** and **6**-*d* were obtained in this solvent regardless of the mercurial substrate, alcohol or acetate). Because of the complication of large amounts of **6** and therefore smaller amounts of *c*-**6** and *t*-**6** in the products of these reductions, the analytical method for *c*-**6** and *t*-**6** is not so reliable as in the reductions in aqueous THF. Thus we do not know whether the variations in these results (Table II) from those in aqueous THF (Table I) are real, or whether the *c*-**6**:*t*-**6** ratio appears different because of the magnitude of the experimental error.

TABLE II

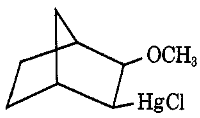
REDUCTION OF DIBENZOBICYCLO[2.2.2]OCTYLMERCURIALS WITH SODIUM BORODEUTERIDE IN ETHANOL

Compd	Time,[a] hr	% D	*t*-6, %	*c*-6, %
3	0	53	84	16
	1	60	69	31
4	0	49[b]	96[b]	4[b]
	1	38[b]	93[b]	7[b]

[a] Time that the sodium borodeuteride was stirred in the solvent system prior to addition of the mercurial. [b] Average of two experiments.

The amount of deuterium incorporation was not changed when the borodeuteride was added to the solution of the mercurial, or when the mercurial was added to a borodeuteride solution which had aged for 1 hr. Furthermore, reduction of dibenzobicyclo[2.2.2]octadien-7-one to 7-deuteriodibenzobicyclo[2.2.2]octadien-7-ol in ethanol and 1 *M* NaOH with sodium borodeuteride gave a product containing 95% deuterium, demonstrating that our results are not due to hydrogen exchange between borodeuteride and solvent. The results are discussed later.

The Norbornyl System.—Most of the stereochemical work was carried out on three norbornyl adducts: *cis,exo*-3-methoxy-2-norbornylmercuric chloride (**9**), *exo*-3-methoxy-*endo*-2-norbornylmercuric chloride (**10**), and *cis,endo*-3-methoxy-2-norbornylmercuric chloride (**11**). The *cis,exo*-mercurial is the principal product of treatment of norbornene with mercuric acetate in methanol (followed by NaCl precipitation), while **10** and **11** result from acid-catalyzed isomerization of **9**.



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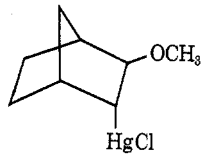

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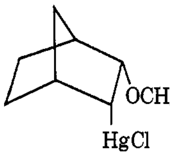

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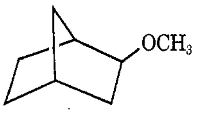
Stereochemical assignments for **9**, **10**, and **11** are based on the results of reduction by borohydride and on pmr analysis. Reductions of **9** and **10** gave only the exo isomer of 2-methoxynorbornane (**12**), and small amounts of norbornene. Reduction of **11** gave only 2-*endo*-methoxynorbornane (**13**) as the organic ether product. The ethers were isolated by glpc and were identified by spectral comparisons with samples of *exo*- and *endo*-2-methoxynorbornane obtained by methylation of the corresponding alcohols.

In the organomercurials, the proton at C-3, α to methoxy, is readily observed in the pmr spectra. The splitting pattern of this proton defines the stereochemistry of the 2-chloromercuri group. The simple doublet (J = 6.5 Hz) observed for H-3 of **9** indicates a single substituent at C-2 with an endo proton. The assigned structure of **10** is based on the simplicity of the H-3 resonance (doublet, J = 2.8 Hz) which indicates endo substitution at C-2. The eight-line pattern of the H-3 resonance of the mercurial **11** (J = 9.5, 3.8, 1.3 Hz) is interpreted as due to the coupling of an exo proton at C-3 with an exo proton at C-2 (J = 9.5 Hz), a proton at C-4 (J = 3.8 Hz), and a long-range coupling with exo H-5 (J = 1.3 Hz).

Reduction of **9** and **10** with deuterium incorporation led to *cis*-3-deuterio-*exo*-2-methoxynorbornane (*c*-**12**) and *trans*-3-deuterio-*exo*-2-methoxynorbornane (*t*-**12**).



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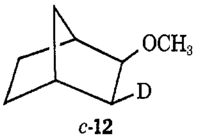
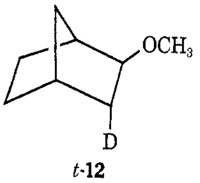
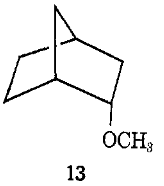


c-**12**



t-**12**



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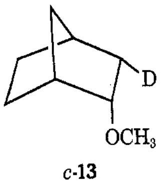

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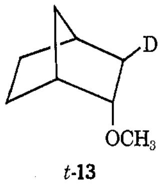

t-**13**

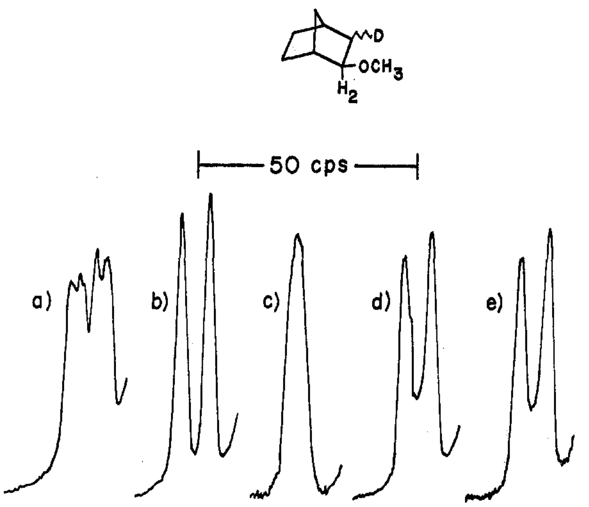

Figure 1.—Resonances of H_2 in the 100-MHz nmr spectra of *exo*-methoxynorbornanes in trifluoroacetic acid: (a) undeuterated compound; (b) Na(Hg)/D_2O reduction product of *cis,-exo*-methoxymercurial; (c) Na(Hg)/D_2O reduction product of *trans*-methoxymercurial; (d) borodeuteride reduction product of *cis,exo*-methoxymercurial; (e) borodeuteride reduction product of *trans*-methoxymercurial. All peaks are centered at τ 6.40 and are on the edge of the absorption of the methoxyl protons (τ 6.54) which is not shown.

By using arguments such as those described for the pmr identification of the stereochemistry of **9** and **10**, one may interpret the shape of the resonance for the proton α to the methoxy group in **12**-*d* as indicative of the exo or endo nature of the proton at C-3 (Figure 1). The actual analysis of the ratio of *c*-**12** to *t*-**12** was made from comparison of the infrared spectra of the product with those of synthetic mixtures. As little as 3% of undeuterated **12** could have been detected easily in the infrared spectrum of a mixture; none was observed.

The deuterated products from the *cis,endo*-methoxymercurial **11** showed more complicated pmr absorptions for the exo proton at C-2 (Figure 2). Sodium amalgam reduction of **11** in deuterium oxide gave a sample of **13**-*d* in which the resonance for the exo proton at C-2, α to the methoxy group, was simplified from that of undeuterated **13** from a doublet of triplets (J = 9.7, 3.6 Hz) with an additional splitting of *ca.* 1 Hz to a doublet of doublets (J = 9.7, 3.6 Hz). Thus one of the 3.6-Hz couplings was lost. This must be due either to a deuterium in the endo position at C-3 or to a deuterium at the C-1 bridgehead. The former is the only logical conclusion, and the product may thus be identified as *endo*-3-deuterio-*endo*-2-methoxynorbornane (*c*-**13**). Sodium borodeuteride reduction of **11** gives a sample of **13**-*d* in which the absorption for the proton at C-2, α to methoxy, is a narrow, complex multiplet ($W_{1/2}$ = 9.3 Hz). This pattern may be confidently assigned to *exo*-3-deuterio-*endo*-2-methoxynorbornane (*t*-**13**).

Since pure samples of *c*-**12** and *t*-**12** were available from the sodium amalgam reductions of **9** and **10**, infrared analysis of the mixtures of these obtained from the borodeuteride reduction of **9** and **10** are accurate to ±3%. This accuracy was not possible for the reduction products of **11**, as a pure sample of *exo*-3-deuterio-*endo*-2-methoxynorbornane (*t*-**13**) was not available. However, the pmr spectral results make it clear that *t*-**13** was the principal product of borodeuteride reduction of **11**. The results of the reductions are summarized in Table III.

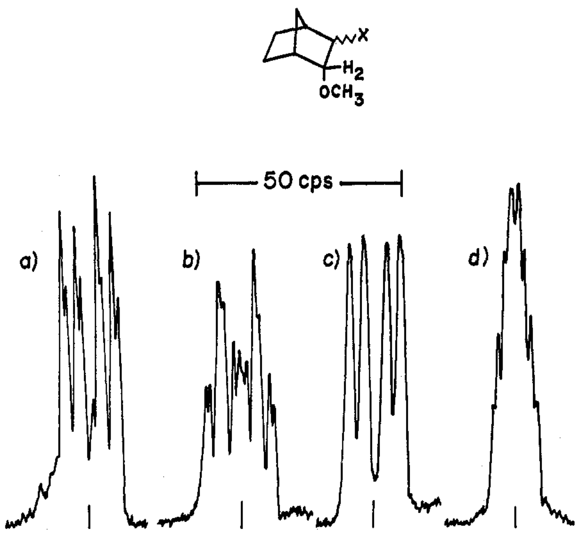

Figure 2.—Resonances of H_2 in the 100-MHz nmr spectra of *endo*-methoxynorbornanes in carbon disulfide: (a) X = *endo*-HgCl, superimposed on Hg^{199} side band of H_3 resonance; (b) X = H; (c) X = D, Na(Hg)/D_2O reduction product of *cis,endo*-methoxymercurial; (d) X = D, borodeuteride reduction product of *cis,endo*-methoxymercurial. Shifts are from internal TMS.

TABLE III

REDUCTION OF NORBORNYLMERCURIALS IN AQUEOUS SYSTEMS WITH SODIUM AMALGAM AND SODIUM BORODEUTERIDE

Substrate	Reducing agent	Solvent	*c*-**12**, %	*t*-**12**, %
9	Na/Hg	D_2O (NaOD)	100	0
10	Na/Hg	D_2O (NaOD)	0	100
9	$NaBD_4$	H_2O (NaOH)	80	20
10	$NaBD_4$	H_2O (NaOH)	84	16
			t-13, %	*c*-13, %
11	Na/Hg	D_2O (NaOD)	0	100
11	$NaBD_4$	H_2O (NaOH)	major	minor

Sodium borodeuteride reduction of **9** and **10** in methanol gave deuterated **12** in the same product ratios (*c*-**12**:*t*-**12**) as in water. The reactions in methanol solution were slower and base was not necessary to suppress olefin formation. No undeuterated **12** could be observed in these products.

The borodeuteride reductions in methanol were carried out in the presence of 2 *M* sodium methoxide to ensure dissolution of the mercurials. When the reductions were quenched prior to completion of the reaction, unreacted mercurial was recovered from the aqueous phase by acidification with hydrochloric acid. After partial conversion, the unreacted mercurial was recovered and found to be unchanged starting material.

Results and Discussion

At the time this work was begun, little information was available regarding either the stereochemistry of reductive demercurations or detailed mechanisms. In the intervening time, a number of papers[10-12] have appeared on borohydride reductions, from which it has become clear that stereospecificity in the replacement of mercury by hydrogen (or deuterium) does not generally obtain. Our results confirm this lack of stereospecificity. The borohydride reaction is technically the easier of the two methods under discussion and would appear to us to be the method of choice for reduction,[9] except when deuterium is to be introduced stereospecifically and/or quantitatively (see below) or when a rearranging radical[10-12] is an intermediate.

While study of the mechanisms of the reductions was not a major impetus for our work, we are in a position to make some statements about them. For the borohydride reduction, the work of Pasto,[10] of Jackson,[11] and of Whitesides[12] clearly implicate alkyl radical intermediates, presumably produced *via* the intermediacy of an alkylmercuric hydride (eq 2), as originally suggested

$$\mathrm{RHgX} + \mathrm{BH_4^-} \longrightarrow \mathrm{RHgH} \tag{2}$$

by Bordwell[4] (eq 1). Pasto[10] has proposed that the alkylmercuric hydride decayed to product *via* a cage process (eq 3). Our attempt to trap the 3-*exo*-meth-

$$\mathrm{RHgH} \longrightarrow [\mathrm{R}\cdot\ \cdot\mathrm{HgH}] \longrightarrow \mathrm{RH} + \mathrm{Hg} \tag{3}$$

oxynorbornyl radical (produced from the RHgD species) with *p*-diisopropylbenzene failed, as did Pasto's attempt[10] to trap the 3-hydroxy-2-butyl radical with undisclosed reagents. Pasto's result suggested the cage process to him.

Whitesides[12] has proposed an alternative mechanism in which the chain propagation steps 4 and 5 are in-

$$\mathrm{R}\cdot + \mathrm{RHgH} \longrightarrow \mathrm{RH} + \mathrm{RHg}\cdot \tag{4}$$

$$\mathrm{RHg}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{Hg} \tag{5}$$

volved.[17] This appears to us to be an attractive alternative, as it accounts for the large amount of undeuterated material produced from **3** and **4** in ethanol (trapping of the free radical by the active α-hydrogen atoms in ethanol); see Table II. The significantly smaller (but still measurable) amount of nonlabeling in aqueous tetrahydrofuran in borodeuteride reductions (Table I) may be related to the speed of the overall reaction—that in ethanol is much slower than that in aqueous THF. It seems reasonable to assume that the rate constant for formation of the alkylmercuric hydride (eq 2) is less in ethanol than that in aqueous THF, while later steps should show little solvent dependence. Therefore, the steady-state concentration of RHgH should be lower in ethanol than in aqueous THF, and, since the rate of eq 4 depends upon RHgH concentration while that of reaction with solvent does not, the lesser deuteration in ethanol may be explained. These speculations are amenable to testing, as are alternative mechanisms, but, in the absence of additional experimental data, further speculation appears unwarranted. Our present preference for the chain process over the cage process may be regarded as tentative in those cases where solvent (or other) capture has not been observed, and it is possible that both processes compete. In any case, use of borodeuteride reduction, even for nonstereospecific deuteration, offers the prospect of incomplete deuteration, when solvents with active hydrogen atoms are present.[18]

When it is necessary to place a deuterium into a molecule stereospecifically, sodium amalgam reduction in D_2O is definitely the method of choice, although somewhat more tedious. In all our cases, which included epimeric examples, as well as in the earlier example, 100% retention of configuration was observed in the replacement of a carbon–mercury bond by a carbon–deuterium bond, and almost complete deuterium incorporation was observed (Table I).

The results of the sodium amalgam reduction are consistent with a mechanism involving two closely linked one-electron transfer steps at the amalgam surface, followed by hydrolysis of the anionic intermediate (eq 6). This is closely analogous to the mechanism

$$\mathrm{RHgCl} \xrightarrow[-\mathrm{NaCl}]{\mathrm{Na}} \mathrm{RHg}\cdot \xrightarrow[-\mathrm{Na}^+]{\mathrm{Na}} \mathrm{RHg}^- \xrightarrow[-\mathrm{OH}^-]{\mathrm{H_2O}} \mathrm{RH} + \mathrm{Hg} \tag{6}$$

proposed[19] for electrolytic reduction of alkylmercuric salts with the last step expanded into two distinct steps. The hydrolysis step can be envisioned as direct electrophilic substitution on carbon, and, by analogy with known electrophilic substitution of organomercurials,[20] retention of configuration is rationalized.

It would clearly be of interest to use sodium amalgam reductions on the dehydronorbornyl–nortricyclyl system to see if the rearrangements observed[10-12] with borohydride reduction can be avoided, as homoallyl and cyclopropylcarbinyl anions seem less prone to rearrangements than the corresponding radicals.[21]

Experimental Section

Preparation of *cis*-8-Acetoxymercuridibenzobicyclo[2.2.2]-octadien-7-ol Acetate (2) and *cis*-8-Chloromercuridibenzobicyclo-[2.2.2]octadien-7-ol Acetate (3).[22]—In a 500-ml, round-bottom flask was placed 4.08 g (20 mmol) of dibenzobicyclo[2.2.2]octatriene (1)[23] and 6.88 g (20 mmol) of mercuric acetate in 200 ml of glacial acetic acid. The solution was stirred at room temperature. After 2 days, a 50-ml aliquot was removed and evaporated on a Rotovac with reduced pressure and a hot water bath. Carbon tetrachloride was twice added to the oil and evaporated to give a white solid. The solid was dissolved in benzene and decolorized with activated charcoal, and the benzene was removed by boiling as heptane was added until crystallization began. Recrystallization from benzene–heptane gave 1.23 g (47%) of **2** as large, clear crystals: mp 200–202°; pmr ($CDCl_3$)[24] τ 2.5–3.0 (m, 8, aromatic H), 4.78 (d of d, 1, J = 3 Hz, 8.5 Hz, H-7), 5.36 (d, 1, J = 3 Hz, H-1), 5.53 (d, 1, J = 2 Hz, H-4), 6.97 (d of d, 1, J = 2, 8.5 Hz, H-8), and 8.07 ppm (s, 6, $OCOCH_3$ and $HgOCOCH_3$); ir (KBr) 1730, 1626, 1222, and 1020 cm^{-1}. Mercury-199 satellites were generally difficult to verify, since usually one of the patterns fell under or close to another peak in the spectrum. The tentative couplings with various protons follow: H-4, 72 Hz; H-1, 30 Hz; H-8, 208 Hz; and H-7, 104 Hz.

Anal. Calcd for $C_{20}H_{18}HgO_4$: C, 45.94; H, 3.47. Found: C, 45.80; H, 3.39.

After 3 days the remaining 150 ml of the acetic acid solution was evaporated on a Rotovac at reduced pressure and elevated temperatures to give a clear oil. Sodium chloride (1.76 g, 30 mmol) was added in a small amount of water. Methanol was added to cause a homogeneous solution, and then more water was added (final volume 400 ml) to precipitate the product. Filtration and recrystallization from acetone–water gave 5.82 g (78%) of **3** as small white crystals. Analogous preparations gave crystals, mp 180.5–182.5° and 186–189°. In all cases, the material melted to a milky, viscous liquid which decomposed as the temperature increased: pmr ($CDCl_3$)[24] τ 2.5–3.0 (m, 8, aromatic H),

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[17] Whitesides[12] apparently succeeded in trapping 20% of norbornyl radical with di-*tert*-butyl nitroxide in aqueous tetrahydrofuran.

[18] Whitesides[12] has noted that their reductions proceeded with only 78–85% deuterium incorporation.

[19] R. E. Benesch and R. Benesch, *J. Amer. Chem. Soc.*, **73**, 3391 (1951).

[20] For references see F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.

[21] S. J. Cristol and P. K. Freeman, *J. Amer. Chem. Soc.*, **83**, 4427 (1961); S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966); **90**, 2832 (1968); S. J. Cristol and R. W. Gleason, *J. Org. Chem.*, **34**, 2363 (1969).

[22] V. L. Sokolov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1285 (1968).

[23] S. J. Cristol and N. L. Hause, *J. Amer. Chem. Soc.*, **74**, 2193 (1952).

[24] Pmr intensities are corrected for Hg-199 satellites.

4.74 (d of d, 1, J = 3.2, 8.5 Hz, H-7), 5.35 (d, 1, J = 3.2 Hz, H-1), 5.51 (d, 1, J = 2.4 Hz, H-4), 6.97 (d of d, 1, J = 2.4, 8.5 Hz, H-8), and 8.10 ppm (s, 3, $OCOCH_3$); ir (KBr) 1739, 1727, 1232, and 1015 cm^{-1}. Mercury-199 couplings were again only tentatively assigned (see above): H-4, 75 Hz; H-1, 32 Hz; H-8, 197 Hz; and H-7, 106 Hz.

Anal. Calcd for $C_{18}H_{15}ClHgO_2$: C, 43.29; H, 3.03. Found: C, 43.43; H, 3.06.

In later preparations, it was found convenient to add the solid sodium chloride directly to the acid solution and then add water to precipitate **3**. When **3** was prepared in this manner, there appeared a small, poorly resolved peak at τ 7.90 ppm, which was not removed by our recrystallization procedure. This is attributed to the trans adduct **5** and amounted to 15–19% of the adduct (pmr estimate).

Preparation of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol (4).[23]—*Dibenzobicyclo*[2.2.2]*octatriene* (**1**) (4.08 g, 20 mmol) was dissolved in 50 ml of acetone, and 50 ml of water containing 3 ml of acetic acid was added. To the resulting suspension was added 6.88 g (20 mmol) of mercuric acetate. The mixture was stirred at room temperature for 1 day as the precipitate dissolved. Sodium chloride (2.36 g, 40 mmol) was added and a precipitate formed. After 3 hr of stirring, the suspended precipitate was filtered to give 4.76 g of white powder. (In some analogous preparations, water was added before the precipitate was filtered, and the product contained unreacted **1**. Olefin **1** was then removed from the product by trituration with ether.) Recrystallization from nitromethane gave two crops (1.13 g, 22%) of fine, white crystals. This material was combined with that of another preparation, and the 3-g sample was recrystallized from 250 ml of nitromethane to give two crops (1.7 g) of small, white crystals: mp 255° (the material does not completely liquefy, but either decomposes or sublimes to a fine, white powder at the top of the capillary tube); pmr[24] [DMSO-d_6, shifts are given in hertz (60 MHz pmr) from the pattern for DMSO-d_5] −300 to −270 (m, 8, aromatic H), −137 to −106 (m, 4, H-1, H-4, H-7, and OH), and 32 Hz (4-line, 1, apparent couplings of J = 3.6 and 2 Hz, H-8). When D_2O was added to the pmr sample, one of the protons at −137 to −106 Hz was "washed out." Double irradiation experiments showed that when the pattern around −137 to −106 Hz was irradiated, the four-line pattern at 32 Hz became a singlet.

Anal. Calcd for $C_{16}H_{13}ClHgO$: C, 42.02; H, 2.87. Found: C, 42.10; H, 2.93.

Preparation of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (5).—A solution of 1.0 g (2.2 mmol) of **4** in 12.0 ml of pyridine and 12.0 ml of acetic anhydride was heated at reflux for 1.2 hr and then stirred at room temperature overnight. The solution was poured onto about 200 ml of ice. The precipitate formed was extracted into 200 ml of chloroform. The solution was washed twice with 200-ml portions of water, once with 100 ml of 10% Na_2CO_3 (aqueous), once with 100 ml of water, and finally with 100 ml of saturated NaCl (aqueous). The chloroform layer was dried ($MgSO_4$) and evaporated on a Rotovac. Decolorization with activated charcoal and recrystallization from acetone–water gave 846 mg (77%) of **5** as small, white crystals: mp 244–245° (melted to a milky liquid); pmr[24] ($CDCl_3$) τ 2.5–3.0 (m, 8, aromatic H), 4.67 (t, 1, J = 3.4 Hz, H-7), 5.51 (d, 1, J = 2 Hz, H-4), 5.54 (d, 1, J = 3.4 Hz, H-1), 7.86 (d of d, 1, J = 3.4, 2 Hz, H-8), and 8.13 ppm (s, 3, $OCOCH_3$); ir (KBr) 1718, 1706, 1255, 1242, and 1030 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}ClHgO_2$: C, 43.29; H, 3.03. Found: C, 43.27; H, 2.93.

Preparation of Dibenzobicyclo[2.2.2]octadien-7-yl Trimethylsilyl Ether (8).[15]—A 150-mg sample of alcohol **6** and 0.7 ml of *N*,*N*-bis(trimethylsilyl)acetamide [BSA, Eastman Organic Chemicals, redistilled, bp 69–72° (33 mm)] were combined in a 10 × 0.5 (i.d.) cm Pyrex tube, and the tube was sealed in a flame. The mixture was heated on a water bath for about 10 min until all of the **6** had dissolved (apparently, temperature and time are not critical if solution is obtained). The tube was opened and placed in a 45 × 0.9 (i.d.) cm Pyrex tube with one end closed off and jacketed in a length of steel tubing. The end containing the sample was placed horizontally in a Kugelrohr oven at 95–100°, and a vacuum (*ca.* 0.2 mm) was applied until all of the material had sublimed onto the cooler part of the tube outside of the oven. In this way, 151 mg (75%) of **8** was obtained: mp 96–98° (lit.[15] 93–95°). Pmr data are presented in ref 15.

Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.83; H, 7.59.

The above procedure was scaled down for the analyses of **6** obtained in the reductions by using about 10 mg of **6** and 0.2–0.3 ml of BSA. The mass spectrum of **8** at 70 eV on a direct probe inlet showed a base peak at m/e 178. The only other peaks over 2% of base were found at m/e (rel intensity) 28 (5), 32 (2), 73 (3), 151 (3), 152 (2), 176 (4), 177 (3), 178 (100), 179 (15), and 205 (3). The M$^+$ peak was present at m/e 294, but was too small to measure. The M − 15$^+$ peak was at m/e 279, represented about 1.5% of the base peak, and gave a measurable peak height of 80–150 mm. At least four scans of the M − 15$^+$ region were made in each analysis. The values for the undeuterated material (relative to m/e 279 = 100%) are tabulated below and compared with the calculated values for $C_{18}H_{19}OSi$. The averages are for a series of nine scans of the region m/e 274–281. The value for the m/e 280 peak varied from +2.6 to −1.2 of the average shown, with all but one of these values within 1.2 of the average.

	Rel intensity	
m/e	Obsd	Calcd
274–278	0	
279	100	100
280	25.9	24.9
281	8.7	5.2

Sodium Amalgam Reduction of *cis*-8-Acetoxymercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (2).—A 375-mg (0.72 mmol) sample of **2**, 5 g of freshly prepared 2% sodium amalgam, and 2.0 ml of 2 *M* NaOD in D_2O were stirred rapidly with a magnetic stirrer in a 10-ml round-bottom flask, fitted with a $CaSO_4$ drying tube. After 1 day, an additional 3 g of the amalgam was added. After another day, some chloroform was added to the reaction mixture, and the mixture was filtered through a glass fiber pad. The chloroform layer was separated, washed with saturated NaCl (aqueous), and dried ($MgSO_4$). Evaporation on a Rotovac gave crude **6**-*d*, which was purified by preparative tlc (silica gel G, 20 × 20 × 0.25 cm plate, developed with 9% ether in benzene) and recrystallized (activated charcoal treatment) from ethanol–water to give 78 mg (49%) of **6**-*d* as white crystals: mp 131–139°; pmr ($CDCl_3$ with D_2O) τ 2.5–3.0 (m, 8, aromatic H), 5.6–6.0 (m, 3, H-1, H-4, and H-7), and 7.73 ppm (very broad d, 1, J = 8.5 Hz, H-8 trans). Without D_2O in the pmr sample, the OH absorption showed up at τ 8.78 ppm.

The trimethylsilyl ether **8**-*d* was prepared: mp 96–97°; mass spectrum m/e (rel intensity) 279 (2.5), 280 (78.8), 281 (17.6), 282 (4.9).

The data are consistent with a product **6**-*d* containing 97% deuterium. Essentially all of the product is *c*-**6**.

Sodium Amalgam Reduction of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol (4).—A 229-mg sample of **4**, 7.0 g of freshly prepared 2% sodium amalgam, and 2.0 ml of 1.66 *M* NaOD in D_2O were stirred for 3 days in a 10-ml, round-bottom flask fitted with a magnetic stirrer and $CaSO_4$ drying tube. About 5 ml of carbon tetrachloride was added, and about 1 hr later the mixture was filtered and the residual amalgam and mercury were washed well with chloroform. The combined organic layers were separated and washed with water. The solution was dried ($MgSO_4$) and evaporated on a Rotovac to give 76 mg of a white solid. Decolorization with activated charcoal in methanol and recrystallization from ethanol–water gave 61 mg (55%) of **6**-*d*: mp 138–140°; pmr ($CDCl_3$ with D_2O) τ 2.5–3.0 (m, 8, aromatic H), 5.6–6.0 (m, 3, H-1, H-4, and H-7), and 8.72 ppm (very broad s, 1, H-8 cis). Without the D_2O in the pmr sample, the OH absorption shows up at the same position as H-8 cis.

The trimethylsilyl ether **8**-*d* was prepared: mp 93–96.5°; mass spectrum m/e (rel intensity) 279 (5.9), 280 (134.6), 281 (37.0), 282 (10.7).

The data are consistent with alcohol **6**-*d*, containing 96% deuterium. Essentially all of the product is *t*-**6**.

Sodium Amalgam Reduction of *cis*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (3).—A 250-mg (0.5 mmol) sample of **3** (containing about 15% of **5**), 7 g of freshly prepared 2% sodium amalgam, and 2.0 ml of 1.66 *M* NaOD in D_2O were treated as described above for **4** to give 72 mg (65%) of **6**-*d*, mp

145–146°. Another recrystallization from the same solvent 6ave a sample of **6**-*d*, mp 139–140.5°.[25]

The trimethylsilyl ether **8**-*d* was prepared: mp 96–97°; mass spectrum *m/e* (rel intensity) 279 (4.6), 280 (99.2), 281 (25.2), 282 (7.8).

The data are consistent with **6**-*d* containing 96% deuterium. Integration of pmr intensities showed that the deuterated product was 86% *c*-**6** and 14% *t*-**6**.

Sodium Borodeuteride Reduction of *cis*-8-Acetoxymercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (2).—To a 525-mg (1.0 mmol) sample of mercurial **2**, in 2 ml of 2 *M* NaOH and 2 ml of THF, was added 21 mg (0.5 mmol) of sodium borodeuteride (Alfa Inorganics, Inc.) and the mixture was stirred for 2.5 hr. The product mixture was decanted from 174 mg (87%) of metallic mercury into water and was extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). Evaporation on a Rotovac gave 287 mg of crude product. Pmr analysis of this product showed about 74% of the acetate **7**-*d* and 26% of the alcohol **6**-*d*. The entire product was transesterified with sodium methoxide in methanol to give 201 mg of a yellow oil, which was purified by preparative tlc (20 × 20 × 0.25 cm plate, silica gel G, developed with 9% ether in benzene). The crude yield of alcohol **6**-*d* from the plate was 150 mg (68%). Decolorization with activated charcoal and recrystallization from ethanol–water gave 115 mg (52%) of **6**-*d*, mp 141–142.7°.

The trimethylsilyl ether **8**-*d* was prepared: mp 94.5–96.5°; mass spectrum *m/e* (rel intensity) 279 (8.1), 280 (121.9), 281 (32.8), 282 (9.4).

The data are consistent with 94% deuterium incorporation in **6**. Pmr data integrations show that the deuterated product was 75% *t*-**6** and 25% *c*-**6**.

Sodium Borodeuteride Reduction of *cis*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (3).—A 250-mg (0.5 mmol) sample of mercurial **3** (containing about 15% **5**) and 10 mg (0.25 mmol) of sodium borodeuteride were placed in a 5-ml, round-bottom flask with a magnetic stirrer and 2 ml of THF. After about 30 sec, 2.0 ml of 2 *M* NaOH (aqueous) was added and a rapid reaction occurred. After 15 min, chloroform was added and the mixture was filtered. The chloroform layer was separated and dried ($MgSO_4$). Liquid mercury (91 mg, 91%) was obtained. Evaporation of the chloroform solution gave 121 mg (88%) of acetate **7**-*d*. Purification by preparative tlc (20 × 20 × 0.25 cm plate, silica gel G developed with 5% ether in benzene) gave 76 mg (57%) of **7**-*d* as an oil: pmr ($CDCl_3$) τ 2.5–3.0 (m, 8, aromatic H), 4.9 (five-line m, 1, H-7), 5.47 (d, 1, J = 3 Hz, H-1), 5.75 (d, 1, J = 2.6 Hz, H-4), 7.70 (very broad d, 0.40, H-8 trans), 8.12 (s, 3, $OCOCH_3$), and 8.48 ppm (very broad s, 0.60, H-8 cis). Lithium aluminum hydride reduction and recrystallization of the product from ethanol–water gave 25 mg of alcohol **6**-*d*, mp 147.5–148.5° (remelts at 137.5–139°).

The trimethylsilyl ether **8** was prepared: mp 95–96.5°; mass spectrum *m/e* (rel intensity) 279 (12.4), 280 (124.0), 281 (32.9), 282 (10.1).

The data are consistent with acetate **7**-*d* and alcohol **6**-*d* containing 91% deuterium. The deuterated product comprises 63% *t*-**6** and 37% *c*-**6**.

Sodium Borodeuteride Reduction of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol (4)—A 229-mg (0.5 mmol) sample of mercurial **4** and 10 mg (0.25 mmol) of sodium borodeuteride were placed together with 2 ml of THF in a 5-ml, round-bottom flask fitted with a magnetic stirrer. After about 1 min, 2.0 ml of 2 *M* NaOH (aqueous) was added, and a rapid reaction occurred as the solution became black. After 15 min, chloroform was added and the product was filtered from 78 mg (78%) of metallic mercury. The chloroform layer was separated and dried ($MgSO_4$). Evaporation of the chloroform on a Rotovac and decolorization of the residue with activated charcoal in methanol, followed by evaporation, gave 88 mg (79%) of crystalline alcohol **6**-*d*. Recrystallization from ethanol–water gave alcohol **6**-*d*, mp 138–140°.

The trimethylsilyl ether **8**-*d* was prepared: mp 96–97°; mass spectrum *m/e* (rel intensity) 279 (13.5), 280 (129.6), 281 (34.4), 282 (10.1).

The data are consistent with a sample of 91% deuterated **6**. The deuterated product is 80% *t*-**6** and 20% *c*-**6** (pmr integrations).

Sodium Borodeuteride Reduction of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (5).—A 200-mg (0.39 mmol) sample of the mercurial **5** and 11 mg (0.25 mmol) of sodium borodeuteride were stirred together in a 5-ml, round-bottom flask with 2 ml of THF for about 30 sec. Sodium hydroxide (2 *M* aqueous, 2 ml) was added and a rapid reaction took place. After 15 min, chloroform was added, and the reaction was decanted from 70 mg (90%) of metallic mercury into 25 ml of water. The reaction mixture was extracted three times with 25-ml portions of chloroform, which were washed with 25 ml of water and 25 ml of saturated NaCl (aqueous). The combined chloroform extracts were dried ($MgSO_4$), and the chloroform was evaporated on a Rotovac to give 118 mg (109%) of a yellow oil. The pmr spectrum showed mostly acetate **7**-*d*. The acetate was reduced with lithium aluminum hydride to give 84 mg (100%) of the crude alcohol **6**-*d*. Repeated recrystallization from aqueous ethanol gave **6**-*d*, mp 138–149°.

The trimethylsilyl ether **8**-*d* was prepared: mp 95.8–97°; mass spectrum *m/e* (rel intensity) 279 (11.0), 280 (125.3), 281 (31.7), 282 (8.2).

The data are consistent with acetate **7**-*d* and alcohol **6**-*d*, which are 92% deuterated. The deuterated product consists of 70% *t*-**6** and 30% *c*-**6** (pmr integrations).

Sodium Borodeuteride Reduction of Dibenzobicyclo[2.2.2]-octadien-7-one.—A 25-mg (0.625 mmol) sample of sodium borodeuteride and 34 mg (0.125 mmol) of mercuric chloride were placed in 5 ml of 0.93 *M* NaOH in ethanol and stirred for 1 hr. The mercury salt partially oxidized some of the borodeuteride. Dibenzobicyclo[2.2.2]octadien-7-one (220 mg, 1.0 mmol) was added, and 18 hr later the reaction was worked up to give only alcohol **6**-*d*.

Pmr analysis of the crude sample showed no evidence of undeuterated **6** and could be interpreted entirely in terms of 7-deuteriodibenzobicyclo[2.2.2]octadien-7-ol: pmr ($CDCl_3$) τ 2.5–3.0 (m, 8, aromatic H), 5.70 (s, 1, H-1), 5.80 (t, 1, J = *ca.* 2.7 Hz, H-4), 7.78 (broad d of d, 1, J = 2.5, 13 Hz, H-8 trans), 8.52 (s, 1, OH), and 8.75 ppm (d of d, 1, J = 2.7, 13 Hz, H-8 cis). Recrystallization from ethanol–water gave crystals of **6**-*d*, mp 141–143°. The trimethylsilyl ether **8**-*d* was prepared: mp 95.5–97.5°; mass spectrum *m/e* (rel intensity) 279 (5.0), 280 (95.6), 281 (25.3), 282 (7.1). The product thus contained 95% deuterated **6**.

Sodium Borodeuteride Reduction of *trans*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol (4) in Basic Ethanol. Experiment 1.—Sodium borodeuteride (6 mg, 0.14 mmol) and 100 mg (0.22 mmol) of mercurial **4** were combined and stirred in a 5-ml round-bottom flask. Absolute ethanolic sodium hydroxide (1.0 ml, 1.0 *M*) was added and the reaction slowly blackened. After 1 hr, the clear supernatant solution was decanted from 36 mg (82%) of metallic mercury into 30 ml of water (the mercury was washed with $CHCl_3$) and extracted with three 30-ml portions of chloroform. The chloroform layers were washed once with 30 ml of cold water and once with 30 ml of saturated NaCl (aqueous). The combined chloroform layers were dried $(MgSO)_4$ and evaporated on a Rotovac to give 49 mg (100%) of crude **6**. The crude product was recrystallized from ethanol–water to give 30 mg (61%) of alcohol **6**, mp 138–139°.

The trimethylsilyl ether **8** was prepared: mp 95.8–97.1°; mass spectrum *m/e* (rel intensity) 279 (110.2), 280 (156.2), 281 (46.2), 282 (13.5).

The data are consistent with 54% deuterium incorporation in the product. The deuterated product appeared to contain 98% *t*-**6** and 2% *c*-**6**. A duplicate run gave 44% deuterium incorporation, with 94% *t*-**6** and 6% *c*-**6**.

Experiment 2.—A 6-mg (0.14 mmol) sample of sodium borodeuteride was dissolved in 1.0 ml of 1.0 *M* ethanolic NaOH and stirred at room temperature for 1 hr. A 100-mg (0.22 mmol) sample of mercurial **4** was added, and the reaction slowly darkened. After 1.2 hr, some of the metallic mercury had beaded, but a black sludge was present. Chloroform was added along with some water, and the reaction mixture was filtered through a tared funnel. The yield of mercury was 39 mg (97%). The product in the filtrate was worked up as in experiment 1 above. Evaporation of the solvents on a Rotovac gave 54 mg (110%) of crude **6**. The crude product was decolorized with activated charcoal and recrystallized from ethanol–water to give 31 mg (63%) of **6**, mp 136–138°.

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(25) In a number of instances during this study, **6** was obtained melting in the range 145–148°. These alcohols had solution ir spectra and pmr spectra identical with those of samples which melted in the 138–142° range. Mixture melting points were made in some instances and melted over the whole range. Remelting of the mixture melting point sample, or of the samples of the higher melting **6**, gave melting points in the 138–142° range. Therefore, **6** forms homomorphs.

The trimethylsilyl ether **8** was prepared: mp 96–97°; mass spectrum *m/e* (rel intensity) 279 (134.5), 280 (129.3), 281 (37.7), 282 (10.3).

The data are consistent with a sample of alcohol **6** with 41% deuterium incorporation. Although the pmr data suggest that the deuterated product consists of 100% *t*-**6** and 0% *c*-**6**, the ir spectrum of this alcohol showed the presence of some *c*-**6**. A duplicate run gave 35% deuterium incorporation, with 86% *t*-**6** and 14% *c*-**6**.

Sodium Borodeuteride Reduction of *cis*-8-Chloromercuridibenzobicyclo[2.2.2]octadien-7-ol Acetate (3) in Basic Ethanol.—A 250-mg (0.5 mmol) sample of mercurial **3** was dissolved in 4.0 ml of 0.93 *M* ethanolic NaOH. To the stirred solution was added 10 mg (0.25 mmol) of sodium borodeuteride, and the mixture was stirred for 1 hr at room temperature. The reaction mixture was decanted from 90 mg (90%) of metallic mercury through glass wool into 30 ml of water. Work-up as above gave 112 mg (101%) of crystalline product, identified from its pmr spectrum as mainly alcohol **6**. There was no sign of the acetate **7**. Two recrystallizations from ethanol–water gave a sample of **6**, which contained some **1** (this does not interfere with pmr or mass spectral analysis), mp 143–145°.

The trimethylsilyl ether **8** was prepared: mp 94–96.5°; mass spectrum *m/e* (rel intensity) 279 (84.9), 280 (116.0), 281 (30.4), 282 (7.6).

The data are consistent with the formation of alcohol **6** with 53% deuterium incorporation. The deuterated products consist of 84% *t*-**6** and 16% *c*-**6** (pmr integration).

In a similar experiment, 10 mg (0.25 mmol) of sodium borodeuteride was stirred with 4.0 ml of 0.93 *M* ethanolic NaOH for 1 hr before 250 mg (0.5 mmol) of **3** was added. Work-up gave 114 mg (103%) of crude **6** and 92 mg (92%) of mercury. The crude **6** was recrystallized twice from ethanol–water to give 42 mg of alcohol **6**, again containing some **1**, mp 137–142°.

The trimethylsilyl ether **8** was prepared: mp 95.5–97°; mass spectrum *m/e* (rel intensity) 279 (53.6), 280 (94.1), 281 (25.0), 282 (6.9).

The data are most consistent with alcohol **6** containing 60% deuterated species. The deuterated product consisted of 69% *t*-**6** and 31% *c*-**6** (pmr integration).

***exo*-3-Methoxy-*exo*-2-norbornylmercuric Chloride (9).**—A mixture of 318.7 g (1.0 mol) of mercuric acetate, 96.1 g (1.0 mol) of norbornene, and 30 ml of concentrated sulfuric acid in 1 l. of methanol was stirred for 1 hr, cooled to 5°, and then poured into 2 l. of cold, 1 *M* aqueous sodium chloride. The precipitate was filtered, washed with water, and dried; the crude yield was 351.2 g (97%), mp 119–121.5°. Crystallization from ethanol gave 305 g (84%), mp 123–124.5° (lit.[26] mp 122–123°). The 100-MHz pmr spectrum (pyridine) shows the following peaks: τ 6.75 (d, 1, J = 6.5 Hz, H-3), 6.84 (s, 3, $-OCH_3$), 7.40 (d of d, 1, J = 6.5, 2.4 Hz, H-2), 7.53 (broad m, 2, H-1 and H-4), and complex absorption between 8.3 and 9.4 (6 protons). Hydrogen–mercury coupling constants were measured in deuteriochloroform: $J_{\mathrm{Hg}^{199}-\mathrm{H}_2} = 192$ Hz; $J_{\mathrm{Hg}^{199}-\mathrm{H}_3} = 82$ Hz.

Analysis of the crude product by nmr indicated it to be 96% *cis,exo*-3-methoxy-2-norbornylmercuric chloride and 4% *cis,exo*-3-acetoxy-2-norbornylmercuric chloride. When oxymercuration was carried out in the absence of acid, the product was 38% acetoxy- and 62% methoxymercurial. When the mixture from oxymercuration in the absence of acid was treated for 1 hr with 1 equiv of sulfuric acid prior to work-up, the distribution was 8% acetoxy- and 92% methoxymercurial. The analyses were performed by comparison of the methoxy protons at τ 6.8 with the acetoxy protons at τ 8.0.

The preparations of *exo*-3-methoxy-*endo*-2-norbornylmercuric chloride (**10**) and *cis,endo*-3-methoxy-2-norbornylmercuric chloride (**11**) by acid-catalyzed rearrangement of **9** will be described in a forthcoming publication.

Reduction of *cis,exo*-3-Methoxy-2-norbornylmercuric Chloride (9) with Sodium Borohydride.—A well-stirred slurry of 3.0 g (8.3 mmol) of **9** in 20 ml of 1.2 *M* aqueous sodium hydroxide was cooled in an ice bath and 110 mg (2.9 mmol) of sodium borohydride was added in one portion. The ice bath was removed and the mixture was stirred for 2 hr. The mixture was then extracted three times with *n*-pentane and the aqueous and organic phases were separated from 1.59 g (95%) of mercury. The organic phase was washed twice with water, twice with cold 3 *M* sulfuric acid, and again with water and then dried ($MgSO_4$). Vpc analysis on the pentane solution showed less than 1% norbornene. Solvent was removed through a 15-in. Podbielniak column and the product was distilled to give 0.71 g (68%) of **12**, bp 57° (26 mm). The pmr and ir spectra of the product were identical with those of authentic *exo*-2-methoxynorbornane (**12**).

Reduction of *exo*-3-Methoxy-*endo*-2-norbornylmercuric Chloride (10).—Reduction of 0.5 g (1.4 mmol) of the mercurial with sodium borohydride (0.7 mmol) in 2 *M* aqueous sodium hydroxide as described above for the *cis,exo*-mercurial gave mercury in 94% yield and a 62% yield of pure (ir) *exo*-2-methoxynorbornane (**12**).

Infrared Analyses.—All samples analyzed were purified by preparative gas chromatography. Isomer distributions were determined by matching the spectra of the unknown mixtures with those of known mixtures. The accuracy is estimated at ±3%. The following bands were used for the analyses: *exo*-2-methoxynorbornane, 7.84 (m), 8.23 (m), 9.75 (w), 10.3 (s), 11.1 (m), and 11.9 μ (m); *endo*-2-methoxynorbornane, 8.15 (m), 9.4 (s), 10.1 (m), 10.25 (s), and 12.4 μ (m); *cis,exo*-3-deuterio-2-methoxynorbornane, 9.78 (s), 9.95 (m), 11.2 (s), 12.6 (w), 12.9 (w), and 13.6 μ (m); *endo*-3-deuterio-*exo*-2-methoxynorbornane, 8.28 (m), 9.92 (w), 10.35 (s), 11.0 (s), 11.35 (w), 13.15 (m), and 13.85 μ (m).

Gas chromatographic analyses and isolations were performed on a Wilkens Model A-90-P3 chromatograph with a 5-ft, 20% Carbowax 20M column. Relative thermal conductivities were corrected by analysis of known mixtures.

Reduction of *cis,exo*-3-Methoxy-2-norbornylmercuric Chloride (9) with Sodium Amalgam in Deuterium Oxide.—A mixture of 5.0 g (13.8 mmol) of **9** and 45 g (43 mmol of sodium) of 2% sodium amalgam with 30 ml of 2 *M* NaOD in D_2O was shaken vigorously for 16 hr. The mixture was extracted three times with ether and the organic phase was washed three times with water, dried ($MgSO_4$) and then reduced in volume to about 2 ml on a 15-in. Podbielniak column. Vacuum transfer of the residual solution left no residue. Vpc analysis indicated a mixture of 79 mol % methoxynorbornane and 21% norbornene. Separation of the products by preparative vpc gave 1.14 g (65%) of the ether: pmr (trifluoroacetic acid) τ 6.40 (d, 1, J = 6.7 Hz, H-2), 6.54 (s, 3, $-OCH_3$), 7.7 and 7.9 (H-1 and H-4), and complex absorption at 8.2–9.2. Infrared analysis showed only the exo-3-deuterated ether *c*-**12**.

Sodium Amalgam Reduction of *cis,endo*-3-Methoxy-2-norbornylmercuric Chloride (11).—A mixture (0.91 g) composed of approximately 80% of the cis,endo isomer and 20% of *syn*-7-chloromercuri-*exo*-2-methoxynorbornane, mp 49–54°, was treated with 3.5 equiv of 2% sodium amalgam as described above for the reduction of the *cis,exo*-methoxymercurial. The ethers were separated from about 1% of norbornene by preparative vpc and were obtained in 55% yield. In the pmr spectrum (CS_2), H-2 of the endo isomer appears as a doublet of doublets (J = 9.7, 3.6 Hz) at τ 6.45 and the methoxy protons appear at 6.9. The *endo*-2-methoxynorbornane (*c*-**13**) had deuterium only in the endo 3-position.

Sodium Amalgam Reduction of *exo*-3-Methoxy-*endo*-2-norbornylmercuric Chloride (10).—A 1.8-g (5 mmol) sample of **10** was reduced with 23 g of 2% sodium amalgam (20 g-atoms of sodium) in 20 ml of 2 *M* NaOD in D_2O as described above for **9** to give 0.359 mg (57%) of methoxynorbornane which was free of undeuterated and exo 3-deuterated ether by ir analysis. When a mixture of 97% of this product and 3% of the ether from the cis,exo mercurial was subjected to ir analysis, the latter was detectable. In the pmr spectrum in trifluoroacetic acid, H_2 appears as a broad singlet ($W_{h/2}$ = 5.2 Hz) at τ 6.4. The remaining protons absorb in the positions cited above for *exo*-3-deuterio-*exo*-2-methoxynorbornane. The product is *t*-**12**.

Reduction of *cis,exo*-3-Methoxy-2-norbornylmercuric Chloride (9) with Sodium Borodeuteride.—A 3-g (8.3 mmol) sample of **9** in 20 ml of D_2O containing six sodium hydroxide pellets was treated with 0.12 g (2.8 mmol) of sodium borodeuteride and worked up after 2 hr as described above for the borohydride reduction. There was obtained 1.48 g (88%) of mercury and 0.82 g (78%) of 3-deuterio-*exo*-2-methoxynorbornane, bp 53° (21 mm). Infrared analysis showed this to be a mixture composed of 80% *exo*- (*c*-**12**) and 20% *endo*-3-deuterio-*exo*-2-methoxynorbornane (*t*-**12**). In the pmr spectrum in trifluoroacetic acid, H_2 appears as a broad doublet (J = 6.3 Hz) at τ 6.40. The bridgehead and methylene protons absorb in the same positions

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[26] M. J. Abercrombie, A. Rodgman, K. R. Barucha, and G. F. Wright, *Can. J. Chem.*, **37**, 1328 (1959).

as in the product of sodium amalgam reduction but show distinct differences in the splitting patterns.

Reduction of 8.3 mmol of **9** with 2.39 mmol of sodium borodeuteride in 20 ml of 2 *M* methanolic sodium methoxide was worked up after 2 hr by separating the mixture from a 73% yield of mercury and pouring it into 100 ml of water. The aqueous phase was extracted with three portions of pentane. The pentane solution was worked up as described above to give a 63% yield of the ether, bp 51–52° (21 mm). Infrared analysis indicated 81% of the exo-3- (*c*-**12**) and 19% of the endo-3-deuterated ether (*t*-**12**) and no undeuterated compound. It was determined that 3% of the latter could have been detected. The aqueous phase from the work-up was titrated to pH 2 with hydrochloric acid. The precipitate was extracted with chloroform and the solution was evaporated to dryness to leave 0.648 g (22%) of **9**, mp 120–122.5°, free of trans isomer (**10**) by ir analysis.

Reduction of *cis,exo*-3-Methoxy-2-norbornylmercuric Chloride (9) with Sodium Borodeuteride in the Presence of Diisopropylbenzene.—A solution of 2.0 g (5.54 mmol) of **9** and 2.5 g (15.4 mmol) of *p*-diisopropylbenzene (Shell Chemical Corp.) in 15 ml of 0.7 *M* methanolic sodium methoxide was treated with 0.082 g (1.92 mmol) of sodium borodeuteride and worked up after 3.5 hr as described above. Mercury was obtained in 82% yield. The ether was partially separated from the aromatic hydrocarbon by fractionation on a 15-in. Podbielniak column and further purified by preparative vpc and was obtained in 71% yield. Infrared analysis showed no undeuterated material. Acidification of the aqueous phase gave 0.255 g (13%) of unchanged mercurial.

Reduction of *exo*-3-Methoxy-*endo*-2-norbornylmercuric Chloride (10) with Sodium Borohydride and Borodeuteride.—A 2.02-g (5.6 mmol) sample of **10** in 20 ml of D_2O containing seven sodium hydroxide pellets was reduced with 0.24 g (5.6 mmol) of sodium borodeuteride and worked up after 2.5 hr in the manner described above for reduction of the cis,exo mercurial. Mercury was obtained in 96% yield. The organic products (72% yield) were 84% *exo*-3-deuterio- (*c*-**12**) and 16% *endo*-3-deuterio-*exo*-2-methoxynorbornane (*t*-**12**) by ir analysis.

Reduction of 0.5 g (1.4 mmol) of the mercurial with 0.026 g (0.7 mmol) of sodium borohydride in 5 ml of heavy water containing two sodium hydroxide pellets gave, after 2 hr, a 94% yield of mercury and a 62% yield of *exo*-2-methoxynorbornane (**12**) which was undeuterated (ir analysis).

A mixture of 1.0 g (2.77 mmol) of **10** and 0.0146 g (0.35 mmol) of sodium borodeuteride in 10 ml of 2 *M* methanolic sodium methoxide gave, after 2 hr, 0.116 g (41% based on borodeuteride) of free mercury and 0.738 g of unchanged **10**, mp 89.5–92°, free of **9** (ir analysis). A small amount of the reduction product was isolated by vpc for ir analysis and found to be 82% *exo*-3-deuterio- (*c*-**12**) and 18% *endo*-3-deuterio-*exo*-2-methoxynorbornane (*t*-**12**). No undeuterated ether was detected.

Reduction of *cis,endo*-3-Methoxy-2-norbornylmercuric Chloride (11) with Sodium Borodeuteride.—A 1.0-g (2.77 mmol) sample of pure **11** was reduced with sodium borodeuteride in basic deuterium oxide as described above for the borodeuteride reduction of the cis,exo isomer. Mercury was isolated in 97% yield. Methoxycyclohexane was added to the organic phase as an internal standard and the yield of methoxynorbornane by vpc analysis, assuming equal thermal conductivities, was 109%. The bulk of the product was isolated by preparative vpc. In the pmr spectrum in carbon disulfide, H-2 absorbed at τ 6.45, methoxy protons at 6.84, H-1 and H-4 at 7.68 and 7.92, and the remaining seven hydrogens between 8 and 9.2. H-2 appears as an eight-line multiplet with $W_{h/2} = 9.3$ Hz. Double irradiation of the downfield bridgehead proton (2.594 kHz, offset at 157 Hz, 100–200 mV input) simplified absorption of H-2 to a broad doublet of doublets with $J = 3.0$ and 1.3 Hz.

Registry No.—**2**, 36807-31-5; **3**, 20556-05-2; **4**, 20556-07-4; **5**, 36807-34-8; *c*-**6**, 21438-85-7; *t*-**6**, 36807-36-0; *c*-**7**-*d*, 6372-64-1; *t*-**7**-*d*, 36807-38-2; **8**, 21438-92-6; **8**-*d*, 36794-38-4; **9**, 36807-39-3; **10**, 36807-40-6; **11**, 36807-41-7; **12**, 10395-53-6; *c*-**12**, 36807-43-9; *t*-**12**, 36807-44-0; **13**, 10395-55-8; *c*-**13**, 36807-46-2; *t*-**13**, 36807-47-3; mercury, 7439-97-6; deuterium, 7782-39-0; sodium borodeuteride, 15681-89-7; sodium amalgam, 11, 110, 524.

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Reduction with Trichlorosilane. IV. Ether from Acetal[1]

REN NAKAO, TSUGIO FUKUMOTO, AND JITSUO TSURUGI*

Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka, Japan

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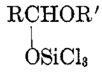
The reduction of acetals derived from formaldehyde, acetaldehyde, acetone, and diethyl ketone to the corresponding ethers with trichlorosilane under γ irradiation has been studied. An acetal reacts at first with chlorosilane to give an α-chloro ether, which is in turn reduced with the silicon hydride under γ irradiation. The present study, especially the reduction of mixed acetal containing a triethylsilyl group, makes clear the reduction sequence of an ester through an acetal type intermediate mentioned in our preceding paper.

Our previous paper reported the reduction of aliphatic esters to dialkyl ethers with trichlorosilane under free-radical conditions.[2] There we considered that the reduction proceeds *via* an acetal type intermediate I. If



$$\underset{\displaystyle\text{OSiCl}_3}{\text{RCHOR}'}$$

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this consideration were true, it might be expected that acetals, in general, are reduced with trichlorosilane to give the corresponding ethers. Furthermore, it might also be expected that the elucidation of the reduction mechanism of acetals may add to understanding the mechanism of the reduction of esters. From these viewpoints, acetals of formaldehyde, acetaldehyde, acetone, and diethyl ketone and some mixed acetals were allowed to react with trichlorosilane in the present paper. Although several papers reported that acetals can be reduced to ethers with lithium aluminum hydride[3] and sodium borohydride,[4] the present method will provide a new synthetic route to ethers in high yields.

Results and Discussion

A degassed mixture of acetal and trichlorosilane was irradiated with γ rays in a sealed tube. The results are summarized in Table I, which indicates comparatively

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(1) Paper III in this series: R. Nakao, T. Fukumoto, and J. Tsurugi, *J. Org. Chem.*, **37**, 76 (1972).

(2) J. Tsurugi, R. Nakao, and T. Fukumoto, *J. Amer. Chem. Soc.*, **91**, 4587 (1969).

(3) E. L. Eliel, V. G. Badding, and M. N. Rerick, *ibid.*, **84**, 2371 (1962), and references cited therein.

(4) J. R. Dias and G. R. Pettit, *J. Org. Chem.*, **36**, 3485 (1971).