1×10^{-6} mol/min which corresponds to approximately 20 bubbles per minute, the rate of hydrogen chloride flow being controlled by a needle valve. After 48 hr the reaction was terminated. Analysis by glpc indicated the presence of the following compounds and their integrated percentages, respectively, in order of their elution: carbon monoxide (2.0%), cyclohexadiene (4.3%), unidentified component (3.5%), 2-chloronorbornene *exo*-oxide (2.3%) 1-chloro-*syn*-7-hydroxynorbornene (3.0%), *exo*-3-chloronorcamphor (49%), *exo*-2-chloro-7-ketonorbornane (29%), *endo*-3-chloronorcamphor (2.3%), and 3,3-dichloro-*exo*-2-norborneol (3.9%).

The second run was made using a semimicro, platinum spinning band column which had been treated with nitric acid, ammonium hydroxide, water, and acetone. After air drying, the rearrangement was carried out as above with 3.6 g (0.025 mol) of 2-chloronorbornene *exo*-oxide. After 96 hr the reaction was terminated. Analysis of the 1.0-g product mixture by glpc indicated the presence of the following compounds and their integrated percentages, respectively, in the order eluted: carbon monoxide (0.6%), cyclohexadiene (1.0%), unidentified component (1.3%), 2-chloronorbornene *exo*-oxide (1.0%), unidentified component (1.3%), 1-chloro-*syn*-7-hydroxynorbornene (2.0%), *exo*-3-chloronorcamphor (52.6%), *exo*-2-chloro-7-ketonorbornane (38%), *endo*-3-chloronorcamphor (2.4%), and 3,3-dichloro-*exo*-2-norborneol (1.0%).

II. Using Anhydrous Hydrogen Bromide. Three rearrangements, the first using a Vigreux column, and the second and third a semimicro spinning band column treated as above, were carried out. The amounts of 2-chloronorbornene *exo*-oxide used were 4.3, 4.0, and 2.5 g. The amounts of distilled product obtained were 1.3, 2.1, and 0.5 g. The reaction times were 96, 105, and 84 hr. The addition of hydrogen bromide was set up in the same manner as in the hydrogen chloride catalyzed rearrangements. The product analyses using glpc were as follows: carbon monoxide (0.8, 1.8, and 0.5%); cyclohexadiene (2.0, 1.6, and 1.2%); unidentified component (2.3, 2.9, and 1.2%); 2-chloronorbornene *exo*-oxide (22.1, 10.3, and 0.9%); unidentified component (0.7, 0.7 and 0.0%); 1-chloro-*syn*-7-hydroxynorbornene (3.5, 3.9, and 1.9%); *exo*-3-chloronorcamphor (33.2, 35.9, and 50.8%); *exo*-2-chloro-7-ketobornane (23.9, 32.6, and 37.7%); *endo*-3-chloronorcamphor (2.9, 3.5, and 2.6%); *exo*-3-bromonorcamphor (0.2, 1.0, and 0.05%); *exo*-2-bromo-7-ketonorbornane (0.1, 1.8, and 0.0%); and 3,3-dichloro-*exo*-2-norborneol (2.3, 2.7, and 2.9%). The amount of *exo*-3-bromonorcamphor for the first and third runs was estimated from large injections and the comparison of the integrated per cent was made with that of 3,3-dichloro-*exo*-2-norborneol. The presence of both bromo ketones is based solely on their glpc retention time comparisons with authentic samples.

Acknowledgment. The authors wish to thank Professor Carl Djerassi for determination of the CD curves. They also acknowledge the support of the National Science Foundation (GP-7818) and the U. S. Army Research Office, Durham (DA-ARO-D-31-124-G584) in this research.

Bridged Polycyclic Compounds. LXIV. The Stereochemistry of Reagent-Promoted 1,3-Eliminations[1]

Stanley J. Cristol, Alan R. Dahl, and Wendel Y. Lim

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received April 14, 1970*

Abstract: The *cis*-1,3-dibromide **1**, which has a relatively rigid W conformation **4**, and the *trans*-1,3-dibromide **2**, which has a sickle conformation **5** (or reversed E and N), were treated with various reducing agents to study the formation of γ-elimination product cyclopropane **3** *vs.* that of simple reduction products. With triphenyltin hydride, simple reduction occurred to give **6**. In aprotic solvents **1** and **2** both gave substantial amounts of cyclopropane **3** with a variety of reducing agents. However, with zinc in ethanol, **2** gave quantitative yields of cyclopropane and **1** gave no **2**, but rather the product (**9**) of simple reduction of one halogen followed by ethanolysis. Heavy treatment of the zinc metal by copper sulfate led to a couple, which reduced **1** to give substantial yields of **3**, competing with formation of **9**. The results are discussed briefly in terms of possible conformational requirements for γ-eliminations.

The formation of three-membered rings by 1,3- or γ-eliminations is an important process in organic chemistry.[2] Most such reactions, involving attack on substrates by electron-donating reagents, appear to be two stage. The first stage involves attack by reagent upon substrate to remove the electrofugal group (E) and to give an anionic or anionoid species. In the second step this species decays, by loss of nucleofuge N, to form the three-membered ring. The required stereochemistry at the atom undergoing internal nucleophilic displacement, *i.e.*, where nucleofuge departs, is relatively easy to study. It has been known for some time that inversion is required for such processes as epoxide formation,[3] aziridine formation,[4] for neighboring group reactions involving anchimeric assistance,[5,6] and has been recently demonstrated in several examples of cyclopropane-ring formation.[7,8]

The question of stereochemistry at the atom undergoing electrofugal loss is, in general, a trivial one for two-stage reactions, as long-lived anions or anionoid species have epimerization or rotational opportunities to avoid stereochemical restrictions in most cases.[9]

---

[1] Paper LXIII: S. J. Cristol, P. R. Whittle, and A. R. Dahl' *J. Org. Chem.*, **35**, 3172 (1970).

[2] For many references, see A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914, 3915, 3917 (1967).

[3] P. D. Bartlett, *ibid.*, **57**, 224 (1935); S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576 (1939).

[4] See, among others, A. Weissberger and H. Bach, *Chem. Ber.*, **64**, 1095 (1931); F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, 74, 944 (1952); O. E. Paris and P. E. Fanta, *ibid.*, 74, 3007 (1952); A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 3640 (1964); **30**, 1748 (1965).

[5] In these cases, in general, activation by electron-donating reagents is not required.

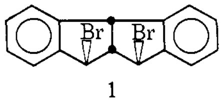
[6] S. Winstein, *Bull. Soc. Chim. Fr.*, **18**, C55 (1955).

[7] H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, **84**, 4831 (1962).

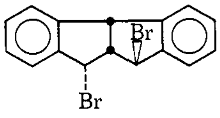
[8] (a) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); (c) *ibid.*, **89**, 401 (1967).

[9] Work described recently[10,11] on the Ramberg–Bäcklund reaction

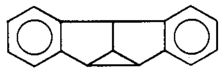
The general questions of conformational requirements in concerted and in stepwise γ-eliminations have been discussed by Nickon and Werstiuk,[2] and they have generated a nomenclature for the various conformational situations possible. The availability[12] of the two dibromides **1** and **2** made it possible for us to look into geometric requirements for a variety of debromination reactions to give the cyclopropane **3** and perhaps to gain some insight into the relative advantages of W (**4**) over *exo*-sickle (**5**) geometry (nomenclature of Nickon and Werstiuk)[2] or *vice versa.* If we may assume[7,8] that nucleofuge must depart with inversion at its carbon site, so long as two-electron reductions are involved, compound **1** is a good model for **4** and **2** for **5**.



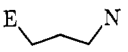
1



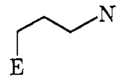
2



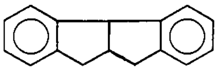
3



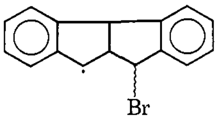
4



5



6



7

As candidate dehalogenating agents, seven reagents were tried. These included triphenyltin hydride, lithium aluminum hydride in tetrahydrofuran, magnesium in ether, sodium in toluene–dimethoxyethane (glyme), zinc in ethanol, zinc–copper couple in ethanol, and triphenylphosphine in benzene. The latter reagent induced some slight reaction, but the dibromides **1** and **2** were largely recovered (with some attendant epimerization) from these experiments, and no further work was conducted with it.

Triphenyltin hydride did not yield cyclopropane **3** from either **1** or **2**, but gave a greater than 90% yield of **6** from either isomer (**3** was inert under these conditions). The mode of reaction of tin hydrides with alkyl halides is well defined,[13] involving a free-radical chain in which (a) $R_3Sn\cdot$ abstracts a halogen atom from the alkyl halide giving a carbon radical, which (b) reacts with R_3SnH to give a carbon–hydrogen bond and an $R_3Sn\cdot$ species. With **1** or **2** this process should yield one (or both) of the epimers of the γ-bromo carbon radical **7**, which now has a choice of hydrogen-atom abstraction from another tin hydride molecule or cyclization[14] *via* an SH2 reaction to give **3**. The observation that **3** was not formed unfortunately precludes our learning anything about the stereochemistry of the SH2 process.

Lithium aluminum hydride has been observed[15,16] to convert 1,3-dihalides to cyclopropanes, 1,2-dihalides to olefins,[17] and to reduce alkyl halides to saturated hydrocarbons.[17] The first two of these processes involve attack on halogen and in many cases the latter may also. It has been suggested[16] that the formation of cyclopropanes involves an organoaluminum intermediate. When the *cis*-dibromide **1** was treated with lithium aluminum hydride in refluxing tetrahydrofuran, 42% cyclopropane **3** and 43% hydrocarbon **6** were isolated. The *trans*-dibromide **2** gave 80% **3** and 16% **6**. Clearly cyclopropane formation has not demonstrated a stereochemical requirement in this reaction. However, it is tempting to assume that the sickle conformation is preferred (required?) for elimination. It can be attained through the intervention of an alkylaluminum intermediate which has the correct geometry when formed (with retention at the *syn*-bromine position) from **2**, but must epimerize when formed from **1**, a reaction which presumably competes with simple reduction leading (ultimately) to **6** *via* **8** or its epimer.

The formation of cyclopropanes from dichlorides with magnesium in ether has been shown to require inversion at the nucleofugal site.[8c] although whether this would be true for **1** and **2** is not certain.[18] In any case, both **1** and **2** are converted in good yield (>80%) to cyclopropane **3**. Again no stereochemical rule is evident. Similarly reduction of **1** and **2** with sodium metal in glyme–toluene gave good yields (83–95%) of **3** without apparent stereochemical requirements.

The reactions described thus far were all conducted in aprotic solvents, and allowed for the formation of long-lived organometallic intermediates, with possibilities for epimerization and consequent loss of stereochemical identity. It was therefore of considerable interest to us to find that **1** and **2** had reasonably different reactions when treated with zinc in the protic solvent ethanol. The *trans* compound **2** was converted quantitatively to the cyclopropane **3** upon treatment with zinc in 95% ethanol, and the product was the same when the zinc was washed with aqueous copper sulfate to prepare various zinc–copper couple compositions before use.

On the other hand, when the *cis*-dibromide **1** was treated with zinc in ethanol, no cyclopropane was formed, and the product which resulted was a mixture of the *syn* and *anti* epimers of the monoethyl ether **9**. This undoubtedly resulted by solvolysis (which is rapid) of the monobromide (**8**) resulting from simple reduction of the dibromide **1**. Mixtures of **1** and **2** gave quantitative yields of mixtures **9** and **3**, according to their compositions. Light coupling of zinc with

---

or on a related debromination, when such opportunities are not available, gives examples where two-stage mechanisms lead to stereochemical consequences.

(10) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

(11) L. A. Paquette and L. S. Wittenbrook, *ibid.*, **90**, 6783 (1968).

(12) S. J. Cristol, W. Y. Lim, and A. R. Dahl, *ibid.*, **92**, 4013 (1970).

(13) (a) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *ibid.*, **84**, 3584 (1962); (b) H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963); (c) L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

(14) See L. Kaplan, *ibid.*, **89**, 1753 (1967), and references therein.

(15) K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963).

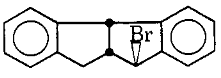
(16) M. S. Newman, J. R. LeBlanc, H. A. Karnes, and G. Axelrad, *J. Amer. Chem. Soc.*, **86**, 868 (1964).

(17) W. G. Brown, *Org. Reactions*, **6**, 469 (1951).

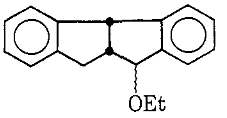
(18) Grignard reagents couple, as do organolithium and organosodium compounds, with alkyl halides which are good carbonium ion sources, and these reactions have been assumed to involve cations.[19] As **1** and **2** would give secondary benzylic cations, such a process appears possible here, at least with **2**, where intramolecular coordination is possible.

(19) See W. G. Young, J. D. Roberts, and H. Wax, *J. Amer. Chem. Soc.*, **67**, 841 (1945); K. W. Wilson, J. D. Roberts, and W. G. Young, *ibid.*, **71**, 2019 (1949); S. J. Cristol, W. C. Overhults, and J. S. Meek, *ibid.*, **73**, 813 (1951); S. J. Cristol and W. C. Overhults, *ibid.*, **73**, 2932 (1951), and references therein.

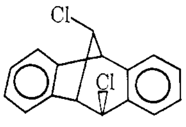
copper did not change the course of the reaction, but treatment with aqueous copper sulfate until the reduction of cupric ion was very slow (approximately 1 g-atom of copper/6 g-atom of zinc) gave a couple which gave about 60% cyclopropane **3** and 40% ethers **9** from **1**. Intermediate copper contents gave less of **3** and more of **9**.



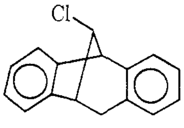
8



9



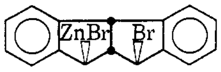
10



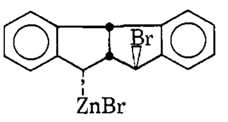
11

The results with zinc can be rationalized in several ways. One may assume a concerted γ-elimination from **2**, with *exo*-sickle conformation **5** required for such a process. However, it is known[8c] that dichloride **10**, which has *exo*-sickle geometry, and which gives cyclopropane **3** on treatment with magnesium in ether, is reduced by zinc in ethanol only at the benzylic carbon–chlorine bond to give **11**, *i.e.*, the cyclopropane is not formed. This experiment suggests that both zinc and magnesium react with **10** to give organometallic intermediates. In an aprotic solvent, the intermediate from **10**, having the appropriate *anti* chlorine substituent, reacts with inversion to give **3**, while, in the protic solvent ethanol, the organozinc compound is attacked by ethanol and protonated faster than it displaces chloride intramolecularly at the sluggish[20] C-8 position of the bicyclo[3.2.1]octadiene ring system.

If we assume that, like **10**, **1** and **2** lead to carbanionoid species with zinc (with retention),[21] it would appear that the product from **1** (presumably **12**) is captured by protonation from ethanol, *i.e.*, to give **8**, before transformation to **3** (*via* the epimerization of **12** to **13**) may occur. On the other hand **2** may lead directly to **13**, which has, compared with the organozinc compound from **10**, the advantages of nucleofugal bromide *vs.* chloride and a benzylic carbon to attack. The data, then, are rationalized by the need for *exo*-sickle conformation **5** for ready γ-elimination.[22]



12



13

Addition to the zinc of substantial amounts of copper seems to us to offer the possibility of diverting the formation of organozinc intermediates to that of organocopper intermediates,[23] which may differ substantially in reactivity toward protonation, epimerization, and cyclopropane formation from the organozinc analogs.

Nickon and Werstiuk[2] studied the reactions of 6-*exo*-*d*-*exo*-2-norbornyl *p*-toluenesulfonate and the 6-*endo*-*d* epimer with potassium *t*-butoxide in *t*-butyl alcohol. Although treatment of their data requires certain assumptions which may be open to question and which possibly make their quantitative data invalid, it is clear that the formation of nortricyclene in their system is attended with loss of *endo* proton favored over loss of *exo* protons. They concluded from this work that conformation **5** is favored over W conformation **4** in γ-eliminations. Our work clearly corroborates their conclusions.

Our results then seem consistent with data on metal-promoted eliminations from the 1,2-dihalides and 1,2-halohydrin derivatives. In such cases, stereospecificity for *anti*-elimination is seen in cases where concerted (or nearly concerted) elimination may be assumed and disappears where organometallic intermediates of relatively long life may be assumed.[24]

It has recently been reported[25] that stereoselective elimination occurs upon treatment of 2,4-dibromopentane isomers with *n*-butyllithium. Thus *meso*-dibromide gives mostly *cis*-1,2-dimethylcyclopropane (9–18% *trans* isomer) and *dl*-dibromide mostly *trans*-dimethylcyclopropane (16–24% *cis* isomer), although the overall yields of these γ-eliminations are very small (2–7%). Their results require that the principal reaction path from each dibromide involves either two retentions or two inversions. These results are clearly not consistent with ours, as it must be assumed that Trost's case involves retention at the site of nucleofugal displacement, if the generally accepted[21] stereochemistry (retention) for metal–halogen interchange is assumed for the first step of the reaction (formation of the bromopentyllithium intermediate). This does not appear to be unreasonable in view of the alternative mechanistic paths[18] for reaction of organolithium compounds with alkyl halides and also fits well with the ideas suggested for the analogous preference for *syn*-β-eliminations over *anti*-β-eliminations with organolithium compounds.[26,27]

Experimental Section

Melting points are uncorrected. Proton magnetic resonance spectra were obtained with a Varian A-60A nmr spectrometer. Infrared spectra were run in carbon tetrachloride, using a Beckmann IR-5 instrument. Compounds **1** and **2** have been reported previously,[12] as have compound **3**[28] and compound **6**.[8c,29] The epimeric ethyl ethers, compounds **9**, were identified by pmr comparison to the analogous monoacetates and monoalcohols,[30] by comparison of the infrared spectra to those of other benzylic ethers,[31] by pmr comparison with the mixture of ethers produced by Williamson synthesis,[30] and by pmr comparison with the analogous methyl ethers.[12]

---

[20] S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **85**, 2675 (1963).

[21] See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, Chapter 13.

[22] The facts discussed in footnote 18 offer an alternative explanation of the results, but require a process which seems unlikely in ethanol.

[23] See E. J. Corey and G. H. Posner, *J. Amer. Chem. Soc.*, **89**, 3911 (1967), and references therein.

[24] (a) S. Winstein, D. Pressman, and W. G. Young, *ibid.*, **61**, 1645 (1939); (b) W. M. Schubert, B. S. Rabinovitch, N. R. Larson, and V. A. Sims, *ibid.*, **74**, 4590 (1952); (c) H. O. House and R. S. Ro, *ibid.*, **80**, 182 (1958); (d) S. J. Cristol and L. E. Rademacher, *ibid.*, **81**, 1600 (1959).

[25] B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, **91**, 4320 (1969).

[26] R. L. Letsinger and E. Bobko, *ibid.*, **75**, 2649 (1953).

[27] S. J. Cristol and R. S. Bly, Jr., *ibid.*, **83**, 4027 (1961).

[28] See ref 12 for references.

[29] W. Baker, J. F. W. McOmie, S. D. Parfitt, and D. A. M. Watkins, *J. Chem. Soc.*, 4026 (1957).

[30] W. Y. Lim, Ph.D. Thesis, University of Colorado, 1967.

[31] M. P. Cava and K. W. Ratts, *J. Org. Chem.*, **27**, 752 (1962).

Treatment of *cis*- (Bis-*anti*-) and *trans*-2,8-Dibromo-3,6-dibenzobicyclo[3.3.0]octadiene (1 and 2) with Sodium in Toluene–Dimethoxyethane (Glyme). A three-necked 100-ml Morton flask was equipped with a nitrogen inlet, a glass-jacketed magnetic stirrer, and a reflux condenser. A dispersion of 100 mg-atoms of sodium metal in 25 ml of dry toluene was prepared by rapid stirring at reflux, followed by cooling with continued stirring. When the temperature had dropped to 40°, 25 ml of dry glyme containing 364 mg (1 mmol) of **1** was added. The reaction mixture was stirred for 1.5 hr and then filtered using dry glyme as a wash. A 100-ml sample of water was added and the mixture extracted with ether. The ether was removed at reduced pressure (aspirator) and the remaining oil crystallized when 95% ethanol was added. Recrystallization from 95% ethanol produced 170 mg (83%) of the cyclopropane **3**. The procedure was repeated using the *trans*-dibromide **2**. The yield of **3** exceeded 90%.

Treatment of 1 and 2 with Magnesium in Ether. A solution of 284 mg (0.78 mmol) of **1** in 50 ml of deoxygenated anhydrous ether was prepared. The surfaces of 500 mg-atoms of magnesium turnings were activated (methyl iodide) and added to the solution. The solution was heated at reflux for 4 hr, cooled, and filtered into 100 ml of 5% hydrochloric acid. The mixture was extracted (ether) and the ethereal fraction dried, neutralized, and decolorized ($MgSO_4$, $NaHCO_3$, charcoal). The ether was removed at reduced pressure (aspirator) and the crude product recrystallized from 95% ethanol to yield 140 mg (87%) of **3**. The experiment was repeated using **2**. The yield was about 80%. A second product insoluble in petroleum ether was also noted but was not identified.

Treatment of 1 and 2 with Triphenylphosphine in Benzene. A solution of 364 mg (1 mmol) of **1** and 530 mg (2 mmol) of triphenylphosphine in 100 ml of benzene was stirred for 48 hr at room temperature. The solvent was removed at reduced pressure (aspirator). Nmr analysis of the residue revealed that no **3** had formed and that all aliphatic peaks were due to **1** with some contamination with **2**.

A solution of 364 mg of **2** and 530 mg of triphenylphosphine in 150 ml of benzene was stirred at 55° for 24 hr. Nmr spectra showed a 50:50 mixture of **1** and **3** had formed with some decomposition (peaks between τ 8 and 9). This experiment was repeated for 80 hr with similar results but more decomposition.

Treatment of 1 and 2 with Triphenyltin Hydride in Benzene. A solution of 364 mg (1 mmol) of **1** and 175 mg (0.50 mmol) of triphenyltin hydride in 150 ml of benzene was stirred for 5 hr at room temperature. Removal of the benzene at reduced pressure (aspirator) and pmr analysis of the residue revealed that the product was 25% 3,6-dibenzobicyclo[3.3.0]octadiene (**6**), and 75% unreacted starting material.

Repeating the experiment with 700 mg (2 mmol) of triphenyltin hydride led to 92% conversion of **1** to **6**.

Identical experiments were performed using **2** as the substrate and the results were identical as indicated by pmr. Under identical conditions **3** was found to be stable.

Treatment of 1 and 2 with Lithium Aluminum Hydride (LAH) in Tetrahydrofuran (THF). Into a stirred solution of 200 mg (0.55 mmol) of **1** in 100 ml of dry THF was added 1 g of LAH, and the solution was stirred for 12 hr. The excess LAH was destroyed with water (*caution*). The solution was filtered and the filtrate extracted with ether. The ethereal solution was dried ($MgSO_4$) and the ether was removed at reduced pressure (aspirator). Pmr spectra showed the residue contained 50% **3** and 50% **6**. Recrystallization from 95% ethanol gave 51 mg (42%) of **3** and 53 mg (43%) of **6**.

Into a solution of 500 mg of **2** in 100 ml of dry THF was added 1 g of LAH. After 12 hr at reflux, the solution was cooled and water was added (*caution*). Work-up as above indicated 81% **3** and 19% **6** by pmr. Recrystallization from 95% ethanol gave 212 mg (80%) of **3** and 43 mg (16%) of **6**.

Treatment of 1 and 2 with Copper-Activated Zinc in Ethanol. Into a stirred solution of 100 mg (0.30 mmol) of **1** in 100 ml of 95% ethanol was added 1 g of copper-activated zinc (one washing with 5 ml of 2% $CuSO_4$). After a 2-hr reflux period, the mixture was filtered while hot and the filtrate poured into 200 ml of cold water. Ether extraction, drying of the ethereal extract ($MgSO_4$), and removal of the ether by distillation yielded 70 mg of crude product. Nmr showed no peaks due to **1**. Thin layer chromatography on silica gel G plates and infrared spectra showed the product to be a mixture of *syn*- and *anti*-2-ethoxy-3,6-dibenzobicyclo[3.3.0]octadiene (**9**), which was known from previous synthesis.[30] Pmr (CCl_4) for the *syn* epimer of pair **9** showed τ 6.40 (1 H, m, C-1 H), 5.05 (1 H, d, C-2 H), 5.62 (1 H, d, C-5 H), 7.0 (2 H, m, C-8 H), 6.48 (2 H, quartet, methylene H of ethoxide), 8.72 (3 H, t, methyl H of ethoxide); $J_{15} = 7$, $J_{12} = 7$, $J_{18\text{-}anti}$ and $J_{18\text{-}syn}$ were indeterminate; pmr (CCl_4) for the *anti* epimer of pair **9** τ 6.8 (1 H, m, C-1 H), 5.38 (1 H, d, C-2 H), 5.32 (1 H, d, C-5 H), 6.9 (2 H, m, C-8 H), 6.42 (2 H, quartet, methylene H of ethoxide), 8.81 (3 H, t, methyl H of ethoxide); $J_{15} = 7$, $J_{12} = 2$, $J_{18\text{-}anti}$ and $J_{18\text{-}syn}$ were indeterminate.

To a stirred suspension of 1 g of **2** in 100 ml of 95% ethanol was added 2 g of copper-activated zinc (one washing with 2% $CuSO_4$). After the same treatment used above, 550 mg of crude product was obtained. Recrystallization from 95% ethanol gave 510 mg (96%) of **3**.

Dehalogenation of 1 and 2 with Zinc and Zinc Treated with 2% Copper Sulfate Solution. To a solution of 1 g of a mixture of 70% **1** and 30% **2** in 150 ml of 95% ethanol was added 2.0 g of zinc dust. The mixture was refluxed for 2 hr. The same work up as above gave an oil containing **3** (30%) and **9** (70%) as determined by nmr.

The experiment was repeated using 2 g of zinc washed once or twice with 10 ml of 2% $CuSO_4$ solution with identical results. However, the zinc–copper sample from three or four washings gave 60% **9** and 40% **3**, and that from five or six washings gave 70% **3** and 30% **9**. More than six washings did not increase the copper content of the metallic reagent as evidenced by the persistence of the blue color of the cupric ion in the wash solution.

Acknowledgment. The authors wish to express their gratitude for financial support from the Institute of General Medical Sciences (Public Health Service Grant GM-12139).