Anal. Calcd for $C_{13}H_{15}N_5O_4$: C, 51.14; H, 5.00; N, 22.61. Found [sample dried to constant weight at 100° (0.1 mm) over P_2O_5]: C, 50.80; H, 5.09; N, 22.78.

A portion of the material was dissolved in acetone and treated with Jones reagent[19] until an orange color persisted for 2 min. Tlc of this material in systems A, B, and C showed it to be identical with **3** in R_f and fluorescence color, and the ultraviolet absorption characteristics at acid, neutral, and alkaline pH values were likewise indistinguishable from those of **3**.

Registry No.—**3**, 33066-26-1; **5**, 33189-80-9.

Acknowledgment.—The authors are pleased to thank Dr. M. J. Mitchell, University of Pennsylvania, for determination of the mass spectrum.

[19] A. Bowers, T. G. Halsell, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

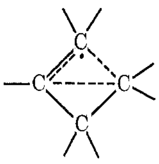
Stereochemistry of the Reduction of Homobenzyl Halides[1]

Bruce B. Jarvis,* Joseph B. Yount, III,[2]
and Tong-Hua Yang[2]

*Department of Chemistry, University of Maryland,
College Park, Maryland 20742*

Received August 31, 1971

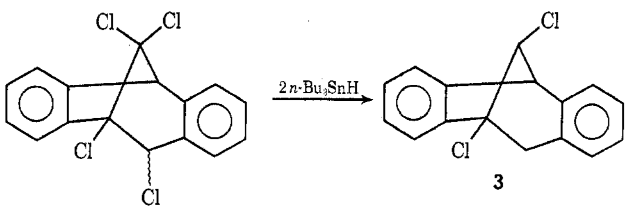
The existence of homoallylic participation in carbonium ion chemistry is well established.[3] The search for analogous participation in free-radical reactions has proven fruitless.[4] The chemical reactivities[5] and physical properties[6] of these radicals are also consistent only with that of equilibrating radicals rather than a single delocalized species such as **1**.



1

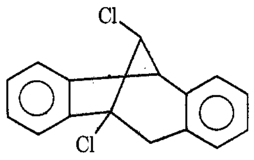
Results and Discussion

Our interest in this problem arose from the observation that treatment of the tetrachlorides **2**[7] with 2 equiv of tributyltin hydride gave only the dichloride **3** with no observable amount of the epimer **4** formed.



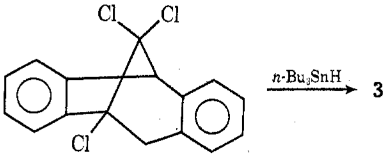
2a, *exo*-Cl
b, *endo*-Cl

3

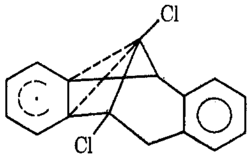


4

Subsequently it was shown that under these conditions the trichloride **5** reacts with tributyltin hydride to give only **3**; no **4** is formed.[1] The structural assignment for **3** is based on elemental analysis and the proton magnetic resonance (pmr) spectrum of **3**: a pair of doublets (1 H each) at τ 5.97 and 5.33 (J_{18} = 2.5 Hz), a pair of doublets (1 H each) at τ 6.95 and 6.33 ($J_{\text{gem-4}}$ = 17 Hz), and aromatic protons (8 H) at τ 2.5–3.0. The value of the coupling constant J_{18} is consistent only with structure **3**.[8] Since it is the ring anti to the C-4 position that has the highest capability for delocalization of a charge or unpaired electron at C-8,[9] the nonclassical radical intermediate (if one were to exist) should be represented by **6**. The dichloride **4** should be the product formed[10] from such an intermediate.



5



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Just what effect the C-5 and C-8 chlorine atoms in **5** have on the stereochemical course of this reaction was not clear. It would be preferable to deal with a radical intermediate that lacked any complicating substituents. For this purpose, the two alkyl bromides **7** and **8** were prepared as shown in Scheme I.

The starting dibromides **9**[13] and **10**[14] have been reported previously. The conversion of **10** to the acetate **11** is analogous to the acetolysis of the corresponding trans dichloride.[15] Treatment of the bromides **7**

[1] For a preliminary communication of a portion of this work, see B. B. Jarvis and J. B. Yount, III, *Chem. Commun.*, 1405 (1969).

[2] Taken in part from the M.S. Theses of J. B. Y., 1970, and T-H. Y., 1970.

[3] B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

[4] (a) D. I. Davies and S. J. Cristol in "Advances in Free Radical Chemistry," Vol. I, G. H. Williams, Ed., Logas Press, London, 1965; (b) D. I. Davies in "Essays on Free-Radical Chemistry," Special Publication 24 of the Chemical Society, Burlington House, London, 1970, p 201.

[5] (a) G. A. Russell and G. W. Holland, *J. Amer. Chem. Soc.*, **91**, 3968 (1969); (b) S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969).

[6] (a) R. W. Fessenden and R. H. Shuler, *J. Chem. Phys.*, **39**, 2180 (1963); (b) P. Bakuzis, J. K. Kochi, and P. J. Krusic, *J. Amer. Chem. Soc.* **92**, 1434 (1970).

[7] B. B. Jarvis and J. B. Yount, III, *J. Org. Chem.*, **35**, 2088 (1970).

[8] (a) S. J. Cristol, J. R. Mohig, and D. E. Plorde, *ibid.*, **30**, 1956 (1965); (b) A. R. Katrikzky and B. Vallis, *Chem. Ind. (London)*, 2025 (1964).

[9] (a) S. J. Cristol, J. R. Mohig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **85**, 2675 (1963); (b) G. W. Klumpp, G. Ellen, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **88**, 474 (1969).

[10] This assumes that the three-membered ring is opened with inversion. Previous workers who have postulated the existence of bridged radicals (bromine and sulfur atom bridging)[11] have observed products consistent with opening of the ring with inversion. However, serious doubts exist as to whether there is such a phenomenon as free radical bridging involving bromine atoms.[12]

[11] For example, see W. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963).

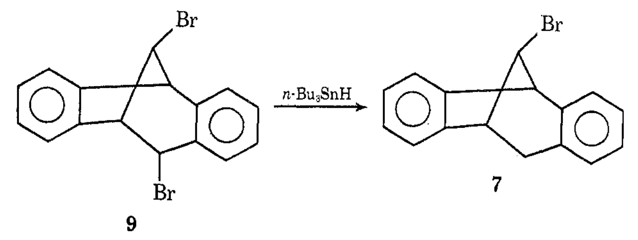
[12] D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *ibid.*, **91**, 7398 (1969).

[13] I. G. Ninulescu, M. Avram, Gh. D. Mateescu, and C. D. Nenitzescu, *Chem. Ind. (London)*, 2023 (1964).

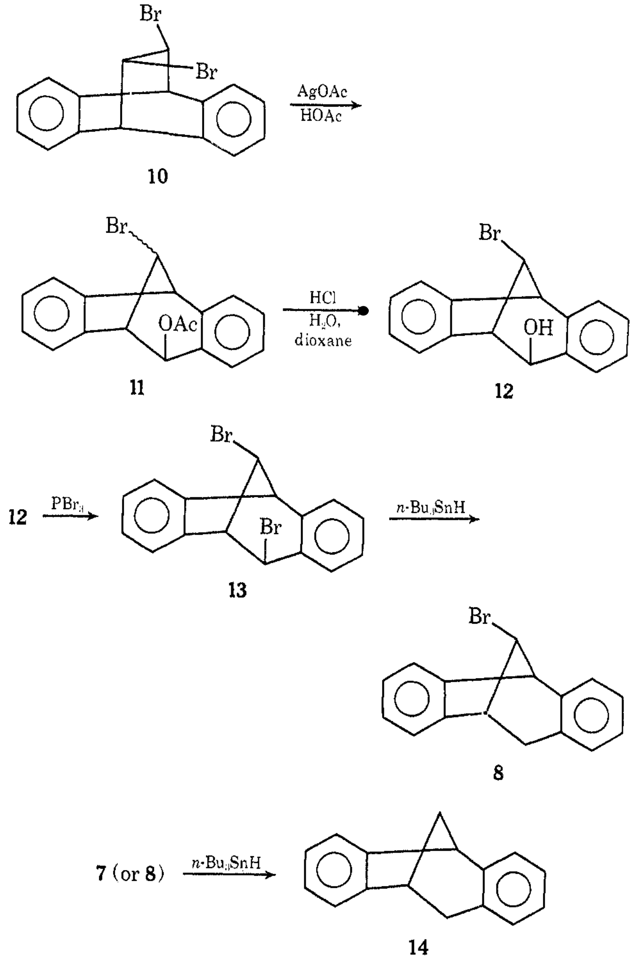
[14] B. B. Jarvis, J. P. Govoni, and P. J. Zell, *J. Amer. Chem. Soc.*, **93**, 913 (1971).

[15] S. J. Cristol, F. P. Parungo, and D. E. Plorde, *ibid.*, **87**, 2870 (1965).

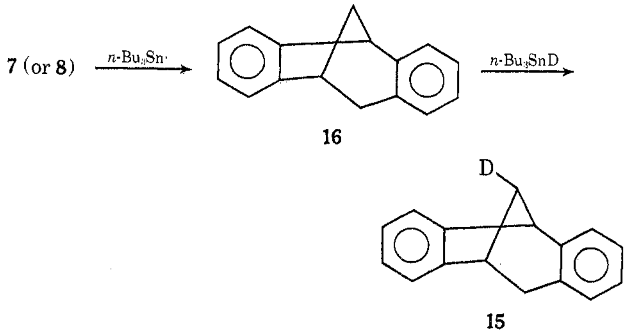
Scheme I



and **8** with tributyltin hydride gave the known[15] hydrocarbon **14**.

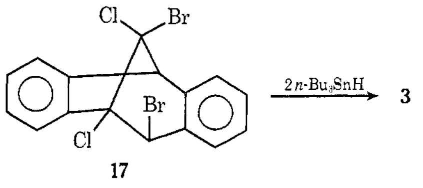


With tributyltin deuteride, **7** and **8** react to give the same deuterated hydrocarbon **15** in which the deuterium atom is in the C-8 anti position. The position of the deuterium atom in **15** is evident from the pmr spectrum. The benzhydryl proton at C-1 appears as a slightly broadened singlet, indicating that it is coupled only to the syn proton at C-8.[8] This result is entirely consistent with that observed in the reduction of **5**; the stereochemistry of the chain transfer to the radical **16** appears to be unaffected by the presence of chlorine atoms at C-5 and C-8.



It is interesting to note that, although **16** reacts with tributyltin hydride (deuteride) in a highly stereoselective manner from the anti side, the difference in reactivity between **7** and **8** is only a factor of two. This figure was obtained by allowing **7** and **8** in separate reaction vessels to react with a stock solution of tributyltin hydride (deuteride) and benzoyl peroxide in benzene. In this manner it was shown that *anti*-**8** reacts *ca.* twice as readily as *syn*-**7** with both tributyltin hydride and tributyltin deuteride. However, the overall reaction rate is much faster with the tributyltin hydride than with the tributyltin deuteride (see Experimental Section). The difference in the selectivity between the abstraction step ($>\mathrm{Sn}\cdot + \mathrm{BrC}< \rightarrow\ >\mathrm{SnBr} + \cdot\mathrm{C}<$) and the chain transfer step ($>\mathrm{SnH} + \cdot\mathrm{C}< \rightarrow\ >\mathrm{Sn}\cdot + \mathrm{HC}<$) depends upon where the transition state lies along the reaction coordinate. The difference in bond energies between the tin–bromine and carbon–bromine bonds is small (*ca.* 3 kcal/mol),[16] whereas there is a large difference (*ca.* 38 kcal/mol)[16] in the bond energies between the strong carbon–hydrogen bond and the much weaker tin–hydrogen bond. The transition state for chain transfer from tributyltin hydride (or deuteride) to the radical **16** must come very early[17] compared with the transition state in the bromine atom abstraction step. However, it is the latter step (halogen atom abstraction) that is the rate-determining step (in part; initiation–termination are also involved),[18] whereas the former step (chain transfer to radical **16**) is the product-determining step. Clearly, differences in rates between reagents reacting from the anti direction *vs.* syn direction in the dibenzobicyclo[3.2.1]octadiene system depend rather strongly upon the position of the transition state along the reaction coordinate.

We also have tested which is a more important factor in the tributyltin hydride reactions in this system: bromine *vs.* chlorine atom abstraction or anti *vs.* syn reactivity. Treatment of tetrahalide **17** with 2 equiv



of tributyltin hydride gives only dichloride **3**. Clearly, in this reaction the increase in reactivity of a bromine atom over the chlorine atom[19] overrides any rate enhancement of an anti halogen atom over a syn halogen atom.

Chromium(II) chloride in aqueous dimethylformamide (DMF) also reacts with the trichloride **5** to give only **3**. Arguments have been presented elsewhere[1,20]

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[16] E. Ebsworth, "Organometallic Compounds of Group IV Elements," Vol. I, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1965, p 46.

[17] G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

[18] K. U. Ingold and D. J. Carlsson, *ibid.*, **90**, 7049 (1968).

[19] H. G. Kuivila, *Accounts Chem. Res.*, **1**, 299 (1968).

[20] B. B. Jarvis and J. P. Govoni, *J. Org. Chem.*, in press.

which suggest that the reactions at the C-8 position in this system are governed by steric control; *i.e.*, reagents have a more open approach from the anti side than from the syn direction. The data presented here support this conclusion.

Experimental Section[21]

Solvolysis of Trans Dibromide 10 in Acetic Acid.—Five grams (13.7 mmol) of **10**[14] was dissolved in 60 ml of acetic acid which contained 2.32 g of silver acetate. The mixture was placed under reflux for 1.5 hr. This was poured into 50 ml of water and extracted with ether. The ether layer was washed with saturated sodium carbonate solution. The ether was dried over magnesium sulfate and the solvent was removed by rotary evaporation. The oil, after treatment with charcoal, was crystallized from carbon tetrachloride–Skellysolve B to give 3.6 g (78%) of product **11**, mp 138–140°.

The pmr spectrum of **11** shows three singlets at τ 4.90 (1 H), 5.73 (1 H), and 7.85 (3 H), a pair of doublets (1 H each) at 4.00 and 6.17 (J_{45} = 2.5 Hz), and a multiplet (8 H) at 2.3–3.0.

Anal. Calcd for $C_{18}H_{15}BrO_2$: C, 62.95; H, 4.37. Found: C, 62.77; H, 4.51.

Acid Hydrolysis of Acetate 11.—One gram (2.91 mmol) of the exo acetate **11** was dissolved in 50 ml of dioxane and treated with 16 ml of 3 *M* hydrochloric acid. The reaction mixture was held at reflux for 2.5 hr, after which it was poured into 200 ml of water. This was extracted with two 50-ml portions of ether, and the ether extracts were washed with saturated sodium carbonate solution. The ether was dried over magnesium sulfate and rotary evaporated. Recrystallization of the residue from Skellysolve B gave 0.65 g (74%) of alcohol **12**, mp 154.5–155.5°.

The pmr spectrum of **12** shows three singlets (1 H each) at τ 4.91, 5.81, and 7.42 (-OH), a pair of doublets (1 H each) at 5.23 and 6.23 (J_{45} = 2.5 Hz), and a multiplet (8 H) at 2.4–3.0.

Anal. Calcd for $C_{16}H_{13}BrO$: C, 63.81; H, 4.02. Found: C, 63.88; H, 4.31.

Reaction of Phosphorus Tribromide with *anti*-8-Bromo-4-*exo*-hydroxydibenzobicyclo[3.2.1]octadiene (12).—To a solution of 1.0 g (3.32 mmol) of **12** dissolved in 20 ml of dry methylene chloride (distilled from phosphorus pentoxide) was added 3 ml of phosphorus tribromide in 2 ml of dry methylene chloride and the mixture was held at reflux for 14 hr. This was treated with saturated sodium carbonate solution until no more carbon dioxide was generated. The resulting solution was extracted with two 100-ml portions of ether, and the ether extracts were combined and dried over magnesium sulfate. After treatment with charcoal, an oily material was obtained which on recrystallization from methylene chloride–Skellysolve B gave 0.93 g (77%) of the dibromide **13**, mp 141.5–143°.

The pmr spectrum of **13** shows two singlets (1 H each) at τ 4.65 and 5.78, a pair of doublets (1 H each) at 4.58 and 5.90 (J_{45} = 2.5 Hz), and a multiplet (8 H) at 2.4–3.0.

Anal. Calcd for $C_{16}H_{12}Br_2$: C, 52.75; H, 3.33. Found: C, 52.50; H, 3.56.

Hydrogenolysis of 9.—One gram (2.75 mmol) of **9**,[13] 0.815 g (2.8 mmol) of tri-*n*-butyltin hydride, and 50 mg of benzoyl peroxide were dissolved in 18 ml of dry benzene and held at reflux for 3 hr. The reaction mixture was concentrated and put on a column packed with 50 g of silica gel in Skellysolve B The column was first eluted with Skellysolve B to remove the tributyltin bromide. Eluent of 2% benzene in Skellysolve B gave more tributyltin bromide, followed by small amount of the hydrocarbon **14**. Elution with 5% benzene in Skellysolve B gave desired syn bromide **7**. Several recrystallizations from 95% ethanol gave 0.5 g (64%) of the syn bromide **7**, mp 129.5–130.5°.

The pmr spectrum of **7** shows a doublet (1 H) at τ 6.05, a doublet of doublets (1 H) at 7.33 ($J_{\text{endo-45}}$ = 3.0, $J_{\text{gem-4}}$ = 18.5 Hz), a doublet of doublets that appears a a triplet (1 H) at 5.21 ($J_{18} \cong J_{58}$ = 4.5 Hz), a multiplet (2 H) at 6.34–6.76, and a multiplet (8 H) at 2.6–3.2.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; H, 4.59. Found: C, 67.44; H, 4.66.

Reduction of 8-*anti*-4-*endo*-Dibromobenzobicyclo[3.2.1]octadiene (13) by Tri-*n*-butyltin Hydride.—A mixture of 2.0 g (5.66 mmol) of **13**, 1.7 g (5.7 mmol) of tributyltin hydride, and 100 mg of benzoyl peroxide in 25 ml of dry benzene was allowed to reflux for 3 hr under nitrogen. The solvent was removed, the resulting mixture was put on a column packed with 100 g of silica gel in Skellysolve B, and the column was eluted with 2% benzene in Skellysolve B to elute the tin bromide. On elution with 5% benzene, a trace amount of the completely reduced hydrocarbon **14** was obtained, followed by the expected anti bromide **8**. Five recrystallizations from 95% ethanol gave 1.12 g (71%) of **8**, mp 140–141°.

The pmr spectrum of **8** shows two singlets (1 H each) at τ 5.33 and 5.93, three doublet of doublets (1 H each) at 6.30 ($J_{\text{exo-45}}$ = 5, $J_{\text{endo-45}}$ = 1.8 Hz), 6.63 ($J_{\text{gem-4}}$ = 16.5 Hz), and 7.20, and a multiplet (8 H) at 2.7–3.2.

Anal. Calcd for $C_{16}H_{13}Br$: C, 67.38; H. 4.59. Found: C, 67.28; H, 4.50.

Synthesis of the Tetrahalide 17.—To a solution of 0.63 g (2.28 mmol) of 7,8-dichlorodibenzobicyclo[2.2.2]octatriene[7] in 20 ml of nitromethane was added 2.0 g of bromine, and the vessel was stoppered. The solution was stirred for 3 hr at room temperature after which it was shaken with a mixture of 30 ml of ether and 30 ml of saturated sodium thiosulfate. The ether layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. Crystallization of the oil from ethanol gave 500 mg of **17**, mp 150–151°. A pmr spectrum of the mother liquor showed the presence of a small amount of the endo epimer of **17** (H-4 located at τ 4.03), but no attempt was made to isolate the material.

A pmr spectrum of **17** shows two singlets at τ 4.33 and 5.35 and a multiplet (8 H) at 2.3–2.9.

Anal. Calcd for $C_{16}H_{10}Br_2Cl_2$: C, 44.38; H, 2.30. Found: C, 44.42; H, 2.38.

Tri-*n*-butyltin Hydride Reductions.—Reductions of the halides **2**,[7] **5**,[7] **7**,[7] **8**, and **17** were run in the following manner. Solutions of the halides (0.05 *M*), tri-*n*-butyltin hydride[22] (0.06 or 0.12 *M* if two halogen atoms were to be removed), and benzoyl peroxide (0.001 *M*) in dry benzene under nitrogen were held at reflux for *ca.* 12 hr. The solutions were concentrated and chromatographed over 25 g of silica gel packed in Skellysolve B. The tin compounds were eluted with 2% benzene in Skellysolve B and the desired products were eluted with 5% benzene in Skellysolve B. Products were analyzed by pmr and ir spectroscopy. The reductions all occurred in a highly stereospecific manner to give only one of the possible two epimers in each case. The yields were 70–90%.

Reduction of the Monobromides 7 and 8 with Tributyltin Hydride.—The reductions of the syn and anti bromides **7** and **8** were carried out in separate reaction flasks. Two 25-ml three-neck flasks were each equipped with a condenser and a nitrogen inlet. Equal amounts of **7** and **8** (50 mg, 0.17 mmol) were placed in the separate flasks. A stock solution was prepared which consisted of 0.2042 g (0.70 mmol) of tributyltin hydride, 30 mg of dibenzyl (internal standard), and 20 mg of benzoyl peroxide in 20 ml of dry benzene; 10 ml of this solution was injected with a syringe into each flask under nitrogen. The two flasks were immersed into a common oil bath maintained at 50°. At each time interval, a 1-ml aliquot was taken from each flask and quenched with 100 μl of 1,2-dibromoethane. Each fraction was concentrated and injected into a gas chromotograph. The column used was a 5-ft stainless steel column packed with 20% SE-30 on Chromosorb W (column temperature 185°, carrier gas helium, flow rate 130 ml/min). The amounts of the starting bromides and the reduced hydrocarbon were measured by a disc integrator in the recorder.

Preparation of *anti*-8-Deuteriodibenzobicyclo[3.2.1]octadiene (15).—Two hundred milligrams (0.70 mmol) of **7** and 200 mg (0.70 mmol) of **8** were placed in separate sealed tubes. A stock solution was prepared which consisted of 1.024 g (3.5 mmol) of tri-*n*-butyltin deuteride[23] and 150 mg of benzoyl peroxide in 12 ml of dry benzene. Under a nitrogen atmosphere 5 ml of this solution was injected with a syringe into the tube containing **7** and 5 ml into the tube which contained **8**. The two tubes were

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(21) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Proton magnetic resonance spectra were run in carbon tetrachloride solutions (unless otherwise noted) and measured with a Varian A-60D spectrometer with tetramethylsilane (τ 10.00) as the internal standard. *J* values are "observed" ones. Ir spectra were taken on a Perkin-Elmer 337 infrared spectrometer in 0.5-mm matched cells with carbon tetrachloride as the solvent. Microanalyses were performed by Dr. F. K. Kasler, University of Maryland.

(22) H. G. Kuivila and O. F. Beumel, Jr., *J. Amer. Chem. Soc.*, **83**, 1246 (1961).

(23) L. W. Menapace and H. G. Kuivila, *ibid.*, **86**, 3047 (1964).

heated at 100° in a common oil bath overnight. The reactions were found to be complete after 10 hr (incomplete after 2 hr). Each reaction mixture was evaporated down to a small volume and worked up as usual. The product, **15**, from both reactions was shown to be identical by pmr and ir data.

The relative rates of reaction were determined in the same manner as that described for the hydride reduction. Compound **8** reacts *ca.* twice as fast as **7**.

Chromium(II) Chloride Reduction of 5,8,8-Trichlorodibenzobicyclo[3.2.1]octadiene (5).—To a 10-ml flask, flushed with nitrogen gas, was added 0.60 g (1.94 mmol) of **5** and 5 ml of DMF. The flask was capped immediately with a rubber septum. Nitrogen gas was bubbled through the solution of **5** for 30 min. Six milliliters (12 mmol) of Fisher chromium(II) chloride solution (*ca.* 2 *M*) was injected (*via* syringe) into the solution of **5**, and a dark green color immediately appeared. The reaction solution was diluted with 20 ml of water and extracted twice with 40-ml portions of ether. The combined ether layers were washed with 40 ml of water and dried over anhydrous magnesium sulfate, and the ether was removed by rotary evaporation. A pmr spectrum indicated complete conversion of starting material to **3**. The oil was chromatographed over 10 g of alumina and the fractions were crystallized from carbon tetrachloride to give 400 mg (76% yield) of **3**, mp 119–120°.[7]

Registry No.—**3**, 27995-02-4; **7**, 33065-89-3; **8**, 33065-90-6; **11**, 33065-91-7; **12**, 33065-92-8; **13**, 33065-93-9; **17**, 33065-94-0.

Acknowledgment.—Financial support from the donors of the Petroleum Research Fund of the American Chemical Society (Grant No. 1050-G1) and the National Science Foundation (No. GP-9599) is gratefully acknowledged.

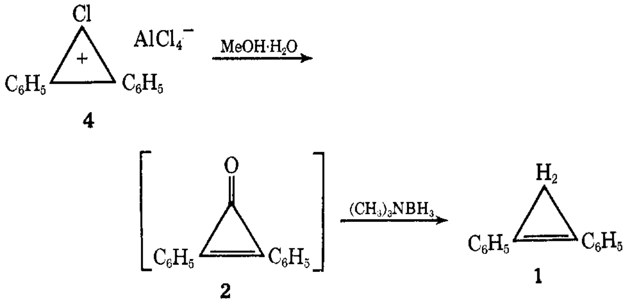
The Reduction of 2,3-Diphenylcyclopropenone and Tropone with Amine–Boranes

W. C. Perkins* and D. H. Wadsworth

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

Received July 22, 1971

As a possible route to 1,2-diphenylcyclopropene (**1**), the reduction of 2,3-diphenylcyclopropenone (**2**) appeared attractive. Breslow and coworkers[1,2] have shown, however, that $LiAlH_4$ or catalytic reduction of **2** gives dibenzyl ketone, presumably through a diphenylcyclopropanone intermediate. Tropone (**3**), a similar ketone, on reduction with $LiAlH_4$ gives some cycloheptatriene, but also 3,4-cycloheptadienol and 3,5-cycloheptadienone.[3]



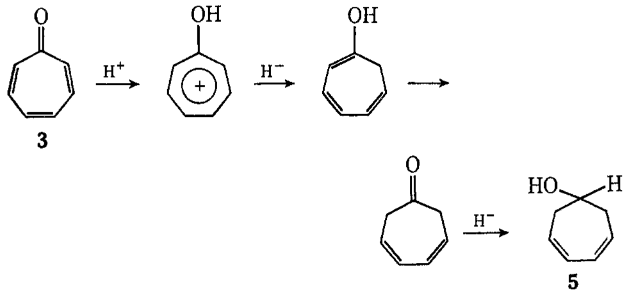
We have found that treatment of 1,2-diphenyl-3-chlorocyclopropenium aluminum chloridate (**4**)[4] in a $MeOH \cdot H_2O$ solution (probable *in situ* formation of **2**) with trimethylamine–borane furnishes **1** in 63% yield. Although isolated **2**, when treated with amine–borane, fails to react, **1** is produced in 90% yield upon subsequent treatment of the reduction medium with anhydrous HCl.

It appears, therefore, that the species being reduced in each case is a Lewis acid complex of ketone **2**. Since **3** also forms a molecular complex with HCl,[5] its reduction in an acidic medium with amine–borane might be expected to produce cycloheptatriene.

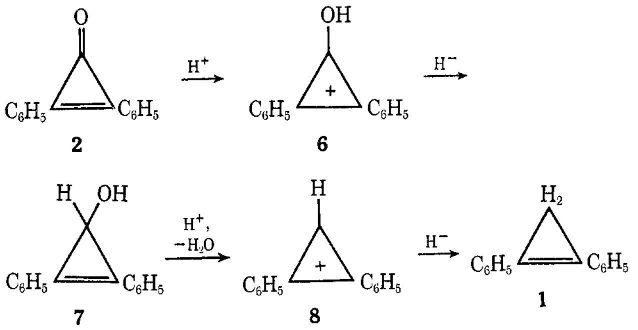
Treatment of **3** with dimethylamine–borane and anhydrous HCl under the reaction conditions, however, gave 3,5-cycloheptadienol (**5**) (the product of a 1,8 conjugate addition)[5,6] as the sole nonvolatile product in 71% yield.

A possible reason for this difference in the observed products from reduction of these vinylogous ketones is summarized in Schemes I and II.

Scheme I



Scheme II



Scheme II illustrates a reduction route which involves dehydration of an intermediate to form a cyclopropenium ion (**8**) that is easily reduced by amine–borane in the acidic medium.[7]

The difference between the reduction of **2** and **3** (Schemes I and II) probably lies in the tendency of the cyclopropenyl intermediate **7** to dehydrate, whereas

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[1] D. N. Kursanov, M. E. Volpin, and Yu. D. Koreshkov, *Zh. Obshch. Khim.*, **30**, 3877 (1960).

[2] R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

[3] A. P. TerBorg and H. Kloosterziel; *Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963).

[4] S. Tobey and R. West, *J. Amer. Chem. Soc.*, **86**, 4215 (1964).

[5] Yu. G. Borod'ko and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **136**, 223 (1961).

[6] O. L. Chapman, D. J. Pasto, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1213 (1962).

[7] W. C. Perkins and D. H. Wadsworth, submitted for publication in *Int. J. Methods Syn. Org. Chem.*