reaction mixture after 2.5 hr gave a 49% yield of **4**, a 13% yield of **6**, and a 7% yield of **3**.

When Tipson's procedure was used, in which tosyl chloride crystals were added over a period of 30 min, work-up of the reaction mixture after 2.5 hr gave a 46% yield of **4** and an 8% yield of **6**.

No trace of **7** was found in crude **3**, **4**, or **6** isolated in the above procedures.[9]

***cis*-3-(2-Hydroxyethyl)cyclopentanol Di-*p*-toluenesulfonate Ester (6).**—The reaction of the diol **3** with 2.2 mol of tosyl chloride according to the procedure of Tipson[8] gave crude ditosylate **6** in 87% yield, mp 82–84°. Recrystallization from hexane–ethyl acetate gave white needles: mp 89.1–90.0°; nmr ($CHCl_3$) τ 6.11 (t, 2, J = 6 Hz, CH_2OTs), 5.20 (m, 1, CHOTs), 2.25 (d, 4, J = 8 Hz, aromatic), 2.69 (d, 4, J = 8 Hz, aromatic), 7.59 (s, 6, CH_3), and 7.9–9.0 (complex, 9).

Anal. Calcd for $C_{21}H_{26}O_6S_2$: C, 57.51; H, 5.98; S, 14.62. Found: C, 57.42; H, 5.68; S, 14.39.

3-(2-Tosyloxyethyl)cyclopentanone (5).—A sample of 7.21 g of hydroxy tosylate **4** oxidized according to the procedure of Nelson[3] gave 6.34 g (89%) of a yellowish syrup which would not crystallize. Rapid elution through grade I neutral Woelm alumina with 90:10 benzene–ether gave a clear syrup: ir (neat) 1740 cm^{-1} (C=O); nmr ($CHCl_3$) τ 5.91 (t, 2, J = 6 Hz, CH_2OTs), 2.21 (d, 2, J = 8 Hz, aromatic), 2.65 (d, 2, J = 8 Hz, aromatic), 7.57 (s, 3, CH_3), and 7.5–8.9 (complex, 9).

Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43; S, 11.36. Found: C, 59.81; H, 6.21; S, 11.02.

Registry No.—**3**, 21298-09-9; **4**, 21298-10-2; **5**, 21298-62-4; **6**, 21298-11-3; **3** (diacetate), 21275-29-6.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, Grant 1036-G1, and to North Texas State University for a Faculty Research Grant for support of this work.

Stereoisomeric Geminal Dihalonorbornanes[1]

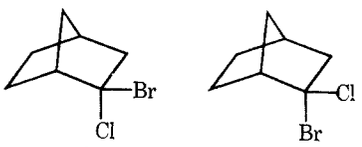
ALBERT J. FRY, WILLIAM B. FARNHAM, BRUCE J. HOLSTEIN, MARYANN MITNICK, AND LEE C. RIGGS

Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457

Received May 15, 1969

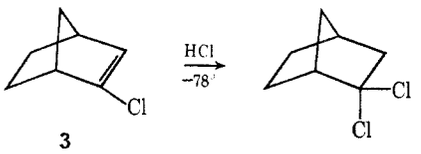
Although geminal halides constitute a rather common class of organic compounds, relatively little is known regarding the mechanisms by which they react. It was only very recently, for example, that hydrolysis of 2,2-dihalopropanes to 2-halopropenes was shown to proceed by the E1, rather than the E2, pathway.[2] Hydrolyses of benzal halides are also thought to proceed *via* initial ionization to α-halo carbonium ions, and some success has been achieved in correlating hydrolysis rates for this class of compound with the relative ability of the halogens to stabilize the carbonium ion to which they are bonded.[3] For example, the faster rate of hydrolysis of benzal chlorobromide relative to benzal dibromide suggests that chlorine is better able to stabilize a carbonium ion than is bromine.[3]

Almost nothing is known of the stereochemical course of reactions involving geminal dihalides, because almost all such compounds now known have both halogens the same, with the resulting symmetry precluding most stereochemical studies. Much information on the reactions and properties of this class of compounds could, however, be obtained by studies involving geminal halides with two *different* halogens bonded to the same carbon, provided that each halogen atom resides in a different, and known, stereochemical environment. For example, investigations involving the stereoisomeric 2-bromo-2-chloronorbornanes (**1** and **2**) could be correlated with an extensive body of literature already available concerning the reactivity of the norbornyl ring system. Isomeric pairs such as **1** and **2** would be a source of considerable information regarding stereochemical features of gas-phase,[4] base-promoted,[5] and solvolytic dehydrohalogenations,[2,6] and of other reactions such as the electrochemical reduction[7] and halogen–metal interchange reaction[8] (metalation) of geminal dihalides. We wish to report the synthesis of **1** and **2** by a route which appears to have some generality for the stereochemically controlled synthesis of isomeric geminal dihalides.



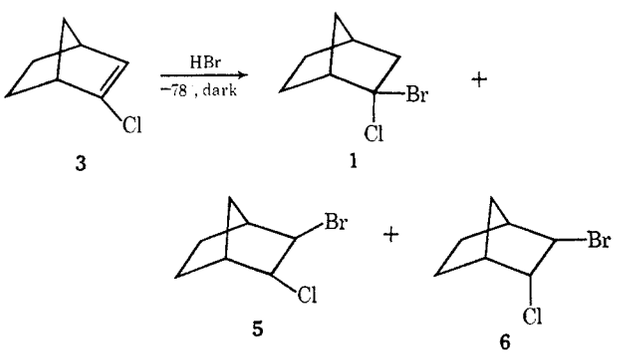
1 **2**

The hydrochlorination of 2-chloronorbornene (**3**) has been shown[9] to proceed rapidly, quantitatively, and regiospecifically[10] to 2,2-dichloronorbornane (**4**).



3 **4**

When **3** is allowed to react in the dark at −78° with liquid hydrogen bromide, there is obtained a mixture of adducts consisting of *exo*-2-bromo-*endo*-2-chloronorbornane (**1**) (95%), *endo*-2-chloro-*exo*-3-bromonorbornane (**5**) (4%), and a third isomer, tentatively assigned as *endo*-2-chloro-*endo*-3-bromonorbornane (**6**) (1%).



3 **1** **5** **6**

(1) Presented in part at the Second Middle Atlantic Regional Meeting of the American Chemical Society, New York, N. Y., Feb 1967.

(2) A. Queen and R. E. Robertson, *J. Amer. Chem. Soc.*, **88**, 1363 (1966).

(3) A. Streitweiser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

(4) A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965).

(5) J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, **88**, 4922 (1966).

(6) A. J. Fry and W. B. Farnham, *J. Org. Chem.*, **34**, 2314 (1969).

(7) (a) A. J. Fry and R. H. Moore, *ibid.*, **33**, 1283 (1968); (b) R. E. Erickson, R. Annino, M. D. Scanlon, and G. Zon, *J. Amer. Chem. Soc.*, **91**, 1767 (1969).

(8) (a) M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965); (b) G. Köbrich, *Angew. Chem.*, **6**, 41 (1967).

(9) A. J. Fry and W. B. Farnham, *Tetrahedron Lett.*, 3345 (1968).

(10) A. Hassner, *J. Org. Chem.*, **33**, 2684 (1968).

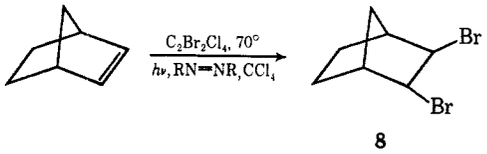
The structure of **5** was based upon comparison of vpc retention time with authentic **5**, and on the low-field (>CHX) nmr region of the crude product mixture, which shows a multiplet at τ 5.52 and a triplet at 6.22; authentic **5** shows a multiplet at τ 5.62 and a triplet at τ 6.32.[11] The third isomer could not be isolated in quantities sufficient for characterization. It is tentatively assigned structure **6**, both because of the evidence (see below) that both minor products are the result of free-radical addition, and by comparison of vpc retention time with authentic **6**.

The structural assignment for **1** is based upon (a) the absence of low-field (>CHX) absorption in its nmr spectrum, which consists of two multiplets, τ 6.75–7.20 and 7.45–8.90, relative areas 2:8; (b) the general resemblance of the nmr spectrum to that of **4** (two multiplets, τ 7.0–7.3 and 8.0–9.0); and (c) the stereochemical preference generally for *exo* attack upon the norbornane ring system,[12] and specifically for *exo,cis* hydrohalogenation in norbornenes.[5,6,13]

Dihalides **5** and **6** are formed in a 70:30 ratio in the free-radical addition of hydrogen bromide to **3**,[14] and are presumably formed in the present case as a result of incursion, to a minor extent, of free-radical addition. This conclusion is supported by the fact that dilution of **3** with carbon tetrachloride before reaction decreases the proportion of **1** in the product from 95 to 85%. The rate expression for ionic addition of hydrogen bromide to olefins is known to be of high kinetic order in HBr,[15] whereas the free-radical addition is lower than second order in HBr;[16] dilution, therefore, will favor the latter pathway.

Hydrochlorination[17] of 2-bromonorbornene (**7**)[18] at −78° in methylene chloride affords *exo*-2-chloro-*endo*-2-bromonorbornane (**2**) in high yield, accompanied by a minor unidentified product (2%) of similar vpc retention time. The structure of **2** is based upon its nmr spectrum (two multiplets, τ 6.9–7.4 and 7.5–8.9, area ratios 2:8), and upon the stereochemical precedents for *exo,cis* hydrohalogenation. The general similarity among the nmr spectra of **4**, **1**, and **2** indicates no significant differences due to carbon–halogen bond anisotropies despite the differing geometries of bromine and chlorine in the dihalides.

Vinyl bromide **7** was prepared by dehydrohalogenation of 2,3-dibromonorbornane (**8**)[18] by the action of potassium *t*-butoxide in dimethyl sulfoxide. The dibromide **8** was in turn prepared in 95% yield by the reaction of norbornene with an equimolar amount of



8

1,2-dibromotetrachloroethane in carbon tetrachloride, presumably *via* a radical-chain process;[19] a 97:3 mixture of the *trans* and *exo,cis* dibromides was obtained. Yields (Table I) in a series of control experiments indicated that the reaction can be initiated either photochemically or by azoisobutyronitrile (AIBN).

TABLE I
PER CENT CONVERSION OF NORBORNENE TO DIBROMONORBORNANES

Conditions[a]	**8**,[b] %
Dark	0
Dark, AIBN[c]	40
$h\nu$[d]	58
$h\nu$,[d] AIBN[c]	94

[a] Solutions were 0.5 *M* in norbornene and 1,2-dibromotetrachloroethane in carbon tetrachloride at 70°; reaction was interrupted after 2 hr. [b] Analysis was by nmr. [c] AIBN = 2,2′-azobisisobutyronitrile, 0.005 *M*. [d] General Electric 275-W sun lamp.

The behavior of **1** and **2** upon treatment with potassium *t*-butoxide in dimethyl sulfoxide is strikingly different. Geminal dihalide **1** is converted cleanly to **3**; dihalide **2** is converted to a mixture of **7** (87%) and **3** (13%). *exo,cis* dehydrohalogenation has previously been demonstrated for norbornyl halides[5] and 2,3-dihalides.[14] The dehydrohalogenation of **2** allows a direct comparison between the better leaving ability of bromine and the stereochemical preference for loss of chlorine; the latter is more important.

Deuterium chloride, generated in the Brown[2] hydrochlorinator from deuteriosulfuric acid and sodium chloride,[20a] may be substituted for hydrogen chloride as addend, as a route to specifically labeled geminal halides. For example, deuteriochlorination of **3** produces an adduct, formulated as 3-*exo*-deuterio-2,2-dichloronorbornane by analogy to the stereochemistry of other hydrochlorinations.[5,6,13,20b]

Experimental Section[21]

***exo*-2-Bromo-*endo*-2-chloronorbornane (1).**—2-Chloronorbornene (**3**) (0.3 g) was placed in a foil-wrapped flask equipped with hydrogen bromide (Matheson) inlet and outlet hoses, and chilled to −78°. Approximately 5 ml of hydrogen bromide was condensed into the flask, and the mixture was allowed to stand for 1 hr at −78°. After warming to room temperature, nmr analysis showed that the olefin had completely reacted. Analysis by vpc (5 ft, 20% SE-30 on Chromosorb W, 120°) showed a major product (95%) and two minor products. The minor products (4 and 1%, respectively) had the same retention times as a mixture of **5** and **6** prepared by free-radical addition of hydrogen bromide (CCl_4, 25°, G.E. sunlamp) to **3**. When 0.1 g of **3** dissolved in 0.1 ml of carbon tetrachloride was hydrobrominated for 20 min at −78° in the dark, the proportions of the minor products increased to 13 and 2%, respectively. Nmr analysis also indicated that these amounted to 15% of the total product, and that **5** was the major of the two. The principal adduct in

(11) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).
(12) P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).
(13) (a) P. von R. Schleyer, *ibid.*, **89**, 3901 (1967); (b) H. C. Brown and K.-T. Liu, *ibid.*, **89**, 3898, 3900 (1967).
(14) N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).
(15) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, p 62.
(16) F. R. Mayo and C. Walling, *Chem. Rev.*, **27**, 351 (1940).
(17) H. C. Brown and M. H. Rei, *J. Org. Chem.*, **31**, 1090 (1966).
(18) H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).
(19) (a) E. H. Huyser and D. N. DeMott, *Chem. Ind.* (London), 1954 (1963); (b) J. W. Wilt and P. J. Chenier, *J. Amer. Chem. Soc.*, **90**, 7366 (1968).
(20) (a) This procedure should prove generally advantageous for the readily monitored *in situ* generation and reaction of deuterium chloride with any substrate. (b) Solvolysis in aqueous ethanol cleanly eliminated deuterium chloride, a result best interpreted by the *exo* configuration for deuterium in the starting material.
(21) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nuclear magnetic resonance spectra were recorded in carbon tetrachloride on a Varian A60-A spectrometer, relative to external tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer Model 137 spectrophotometer. Analytical and preparative vpc separations were made using Varian Aerograph A90-P and 90P-3 gas chromatographs.

the ionic additions, *exo*-2-bromo-*endo*-2-chloronorbornene (1), was separated by preparative vpc.

Anal. Calcd for $C_7H_{10}BrCl$: C, 40.13; H, 4.81. Found: C, 40.27; H, 4.77.

2,3-Dibromonorbornane (8).—To a homogeneous solution of 56.59 g of norbornene and 195.9 g of 1,2-dibromotetrachloroethane in 500 ml of warm carbon tetrachloride was added 1.00 g of azoisobutyronitrile. After 5 min of irradiation with a G.E. sun lamp, vigorous exothermic reaction began, and the light was turned off. After reaction had subsided, the light was turned on, and the solution was refluxed on the steam bath for 8 hr. The nmr spectrum of an aliquot at this time showed no vinylic absorption. After carbon tetrachloride and tetrachloroethylene were removed at the rotary evaporator, 2,3-dibromonorbornane (8) distilled as a colorless oil: yield 145 g (95%); bp 83–85° (3.5 mm) [lit.[14] bp 55° (0.4 mm)]; the nmr spectrum (CCl_4) indicated this to be a mixture of the 2,3-*trans*- and 2,3-*exo,cis*-dibromides, in the ratio of 97:3.[11]

exo-2-**Chloro**-*endo*-2-**bromonorbornane (2).**—A solution of 2.17 g of 2-bromonorbornene (7), prepared from 8,[18] in 20 ml of methylene chloride was hydrochlorinated at −78° for 3 hr by a standard procedure.[17] The product was washed with water and dilute aqueous sodium bicarbonate, and the solvent was removed at the rotary evaporator to afford 2.66 g of a pale yellow oil. Nmr analysis showed this to contain 2.40 g (92%) of 2, contaminated with a small amount of methylene chloride. Distillation afforded 2.08 g (80%) of the chlorobromide 2: bp 42–49° (0.06 mm); mp 34.5–36.0°. Analysis by vpc (2 ft, 10% Zonyl E-7 on Fluoropak 80, 100°) indicated a 98:2 mixture of 2 and a substance of similar retention time. Dihalide 2 was purified by preparative vpc.

Anal. Calcd for $C_7H_{10}BrCl$: C, 40.13; H, 4.81. Found: C, 40.42; H, 4.81.

Dehydrohalogenation of 1.—To a solution of 50 mg of 1 in 0.1 ml of dry dimethyl sulfoxide in an nmr sample tube was added a small amount (*ca.* 8 mg) of potassium *t*-butoxide. The mixture immediately became yellow. Analysis by nmr showed vinyl absorption at τ 4.15 (d, J = 3.2 cps). The vinyl proton in 3 (CCl_4) appears as a doublet at τ 4.33 (J = 3.2 cps); that of 7 is a doublet at τ 3.83 (J = 3.1 cps). Analysis by vpc under conditions (SE-30, 20% on 60–80 mesh Chromosorb W, 5 ft, 130°) where 3 and 7 are cleanly separated indicated the presence of only 3 and a small amount of unreacted 1.

Dehydrohalogenation of 2.—Dehydrohalogenation of 2 by the preceding procedure and analysis by vpc indicated the presence of 3 (13%) and 7 (87%).

3-*exo*-**Deuterio-2,2-dichloronorbornane.**—Although the addition valve of the analytical unit[17] could be used, we have substituted the valve of the preparative apparatus, connecting the valve to a glass-tipped syringe containing deuteriosulfuric acid *via* a flexible Teflon needle piercing the rubber septum of the valve. Ten grams of sodium chloride (dried at 110°) was added to the lower, 125-ml flask, and 5 ml of deuteriosulfuric acid was placed in the syringe. The 50-ml reaction flask was chilled to −78° and flushed with deuterium chloride using 1 ml of deuteriosulfuric acid, and 3.2 g of 2-chloronorbornene in 1 ml of methylene chloride was injected. Addition began immediately. After uptake of deuteriosulfuric acid had ceased, the system was returned to room temperature and the dichloride was purified by preparative gas chromatography. Mass spectral analysis indicated an isotopic purity of 98.1%.

Registry No.—1, 21690-94-8; 2, 21690-95-9.

Acknowledgment.—Financial support by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged. Mr. Larry Owens and Mr. Bradley Paddock provided helpful technical assistance. Financial support for Mr. Owens was provided by the Office of Economic Opportunity (OEO). Professor James Wilt kindly provided experimental directions and advice concerning free-radical brominations using 1,2-dibromotetrachloroethane. Dr. David A. Evans of the Massachusetts Institute of Technology Mass Spectrometry Laboratory kindly obtained the mass spectra of 4 and its deuterated analog.

Alkyltin Bond Cleavage–Cyclization by 1,4-Dilithio-1,2,3,4-tetraphenylbutadiene[1a]

J. G. ZAVISTOSKI AND J. J. ZUCKERMAN[1b]

Department of Chemistry,
State University of New York at Albany,
Albany, New York 12203

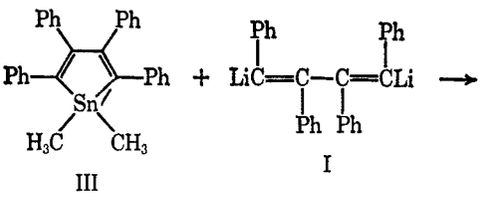
Received May 13, 1969

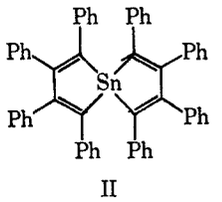
1,4-Dilithio-1,2,3,4-tetraphenylbutadiene (I) has been employed in an apparently general reaction with organometallic and organometalloidal di- and tetrahalides to yield monocyclic and spiro heterocyclopentadienes (metalloles), respectively.[2-4]

We find that the addition of dimethyl- or diethyltin dichloride to ether suspensions of I results in the formation of octaphenyl-1,1′-spirobistannole (II), whereas divinyltin dichloride gives the expected monocyclic products. Divinyltin dichloride undergoes cleavage by I in THF; diphenyltin dichloride resists cleavage in either solvent. The lability series is thus ethyl and methyl >vinyl >phenyl. 1,1-Dimethyl-2,3,4,5-tetraphenylstannole (III) added to the organodilithium reagent also reacts to give the spiro compound, as do trimethyl- and tri-*n*-butyltin chlorides.

When exactly 1 molar equiv of dimethyltin dichloride was added to I, 1,4-bis(trimethylstannyl)-1,2,3,4-tetraphenylbutadiene (IV) and trimethyltin chloride were identified as minor products along with II. No tetramethyltin was found.

Two routes to the spirobistannole are available, alkyltin bond cleavage–cyclization by 1,4-dilithio-1,2,3,4-tetraphenylbutadiene to produce methyllithium (eq 1), or the disproportionation of III, perhaps cata-





+ $2CH_3Li$ (1)

lyzed by the lithium reagent I. We prefer the first route in view of the following observations: (a) the apparent absence of tetramethyltin in the product, (b) isolation of trimethyltin chloride, (c) detection of IV, the likely product of the action of trimethyltin chloride on the dilithio reagent, (d) isolation of the spiro compound in greater than 50% yield, (e) cleavage of tri-

(1) (a) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract No. 024, and at the Octavo Congreso Peruano de Quimica, Cuzco, Peru, Oct 1968; (b) to whom all inquiries should be directed.

(2) F. C. Leavitt, T. A. Manuel, and F. Johnson, *J. Amer. Chem. Soc.*, **81**, 3163 (1959); F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

(3) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).

(4) E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961).