Ionic and Free-Radical Bromination of 5,6-Dichloro-2-norbornenes

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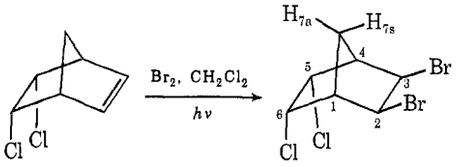
Free-radical bromination of *endo-cis*-5,6-dichloro-2-norbornene (1) with molecular bromine in methylene dichloride at 25° gave exclusively cis-exo dibromide 4, whereas *exo-cis*-5,6-dichloro-2-norbornene (2) afforded a 10:1 mixture of trans (5) and cis (6) dibromides. *trans*-5,6-Dichloro-2-norbornene (3) gave a 1.5:1 mixture of cis (8) and trans (7) dibromides on free-radical bromination. Bromination of 2 and 3 under ionic conditions proceeded stereospecifically trans to afford 5 and 7, respectively. The importance of steric effects and bridging in the free-radical and ionic pathways is discussed.

endo-cis-5,6-Dichloro-2-norbornene (1) brominated sluggishly under ionic conditions, although very facile stereospecific free-radical bromination with molecular bromine in methylene dichloride at 25° was realized.[1] The exo-cis dibromide 4 was the exclusive product.



1 4

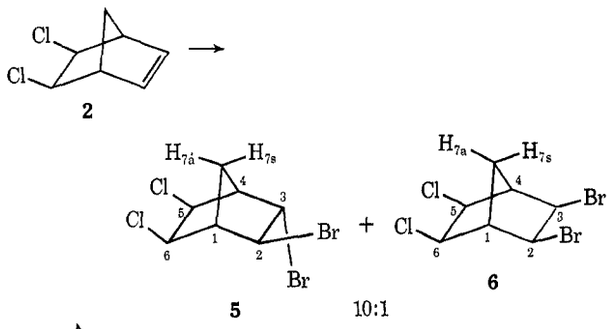
An endo-5,6-chlorine steric effect was suggested to explain these results.[1] The availability of the exo-cis dichloride 2[2,3] and the trans dichloride 3[3] isomers suggests a similar study for further investigation of the directing influence of the chlorine substituents in the free-radical brominations.

Ionic bromination of 2 and 3 was also noted, although no stereochemical results were presented.[1] A comparative study of the ionic and free-radical brominations of 2 and 3 therefore was undertaken to assess the influence of chlorine substitution on the respective product distributions. A further comparison with the ionic product distribution from the bromination of norbornene itself, where extensive 6,1- and 6,2-hydride shifts and Wagner–Meerwein rearrangement predominate,[4,5] was made.

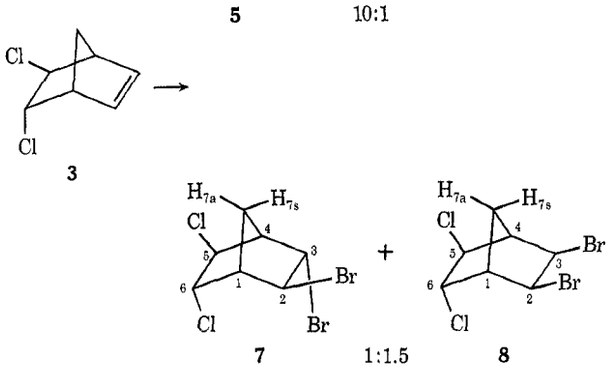
Results

Bromination of olefins 2 and 3 in methylene dichloride solvent at 25° in a nitrogen atmosphere with molecular bromine and illumination with a 275-W sun lamp was instantaneous. Olefin 2 was converted to a mixture of two dibromide products which accounted for >98% of the products. The major product (89–94%) was identified as 5 and the minor product (6–11%) was the cis isomer 6. The trans dichloride 3 afforded a 1.5:1 mixture of cis (8) to trans (7) products under these conditions. The dibromides 7 and 8 accounted for >98% of the products formed.

Olefins 2 and 3 slowly consumed bromine in methylene chloride solvent in the dark and under oxygen at 25° (ionic conditions). Olefin 2 afforded a single product (>99.5%) identified as the trans dibromide 5.



2 5 10:1 6



3 7 1:1.5 8

The trans dibromide 7 was the sole product obtained from the bromination of 3 under ionic conditions.[6]

The dibromides were all stable to the reaction and analytical conditions and the respective product distributions are those of the kinetically controlled addition reactions.

Structural Assignments.—The respective dibromide structures were established by ^{1}H nmr. Tables I and II contain the chemical shift and coupling constant data. Appropriate double-resonance experiments allowed for the assignment of long-range couplings.[7]

The dibromide 4 gave a simple spectrum with the downfield vicinal protons adjacent to bromine (δ 4.88) split into a sharp doublet (J = 2.0 Hz). Long-range coupling with H_{7a} established the source of this splitting, and the protons adjacent to bromine are therefore cis-endo. The vicinal protons adjacent to chlorine (δ 4.41) appeared as a deceptively simple triplet with $J_{H_1H_5} + J_{H_4H_5} = J_{H_4H_5} + J_{H_1H_5} = 4.7$ Hz. The magnitude of these couplings suggests that protons H_5, H_6 are cis-exo.

(1) B. E. Smart, *J. Org. Chem.*, **38**, 2027 (1973).
(2) D. D. Tanner and G. C. Gidley, *ibid.*, **33**, 38 (1968).
(3) J. D. Roberts, F. L. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954).
(4) D. R. Marshall, J. R. Robinson, *et al.*, *Can. J. Chem.*, **49**, 885 (1971).
(5) H. Kwart and L. A. Kaplan, *J. Amer. Chem. Soc.*, **76**, 4072 (1954).

(6) Competitive experiments indicate that the relative rates of ionic bromination are **2** > **3** > **1** with $k_2/k_3 \cong 3.5$. A discussion of the bromination kinetics and halogen inductive effects is reserved for future publication.

(7) Nmr spectra (100 MHz) of dibromides **5**, **7**, and **8** will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-2366.

TABLE I

CHEMICAL SHIFTS[a] FOR DIBROMODICHLORONOBORNANES IN DEUTERIOCHLOROFORM

	Chemical shift				
Nucleus	4	5	6	7	8
H_1	2.90		2.86	2.74	2.87
		2.71[b]			
H_4	2.90		2.86	2.67	2.76
H_2	4.88	3.74	4.16	4.5[c]	4.70
H_3	4.88	4.39	4.16	4.5[c]	4.14
H_5	4.41	4.72	4.10	4.41	3.71
H_6	4.41	4.13	4.10	4.31	4.2[c]
H_{7s}	2.53	2.06		2.24	2.52
			2.28[b]		
H_{7a}	1.62	2.34		2.16	2.14

[a] All chemical shifts are in parts per million (δ) relative to internal tetramethylsilane. [b] Individual resonances not resolved. [c] Not determined accurately owing to interferences.

TABLE II

COUPLING CONSTANTS FOR DIBROMODICHLORONORBORNANES

	Coupling constant, Hz				
Nuclei	4	5	6	7	8
H_1H_2			c		
H_1H_6	a		b	4.5	4.5
H_2H_3		3.3			6.8
H_3H_4		5	c	3.2	
H_4H_5	a		b		
H_5H_6		6.6		3	3.0
$H_{7s}H_5$		1.9	b	2	2.7
$H_{7s}H_6$		1.9	b		
$H_{7a}H_2$	2.0	2	c	2	1.9
$H_{7a}H_3$	2.0		c		1.9
$H_{7s}H_{7a}$	11.8	11.8		11.8	11.6

[a] $J_{H_1H_6} + J_{H_4H_6} = J_{H_4H_5} + J_{H_1H_5} = 4.7$ Hz. [b] $J_{H_1H_6} + J_{H_4H_6} + J_{H_6H_{7s}} = J_{H_4H_5} + J_{H_1H_5} + J_{H_5H_{7s}} \cong 1.6$ Hz. [c] $J_{H_3H_4} + J_{H_1H_3} + J_{H_3H_{7a}} = J_{H_1H_2} + J_{H_2H_4} + J_{H_2H_{7a}} \cong 1.5$ Hz.

The vicinal protons H_2, H_3 and H_5, H_6 adjacent to halogen in **6** appeared as sharp multiplets ($W_{1/2} = 2.2$ Hz) in each case. These narrow resonances suggest that both sets of protons are cis-endo. The downfield resonance (δ 4.16) was assigned to protons H_2, H_3 adjacent to bromine while H_5, H_6 (δ 4.10) were adjacent to chlorine. These assignments were based on the reported downfield shift of protons geminal to bromine relative to chlorine in halogenated norbornanes and norbornenes.[8]

The protons H_5, H_6 vicinal to chlorine in **5** appeared as an AB quartet of doublets at δ 4.13 and 4.72 with $J_{H_5H_6} = 6.6$ Hz. The magnitude of this coupling is consistent with a cis orientation for these protons.[8-13] Long-range $H_{7s}H_{5,6}$ coupling of 2 Hz established the cis-endo orientation of H_5, H_6. The protons H_2 and H_3 adjacent to bromine appeared as a complex downfield multiplet at δ 4.39 and an apparent triplet at δ 3.74. The proton at δ 4.39 was coupled to a bridgehead proton at δ 2.70 by *ca.* 5 Hz, whereas the upfield proton showed no appreciable coupling with H_1 or H_4. The downfield proton H_3 is therefore exo. Proton H_2 (δ 3.74) was coupled to both H_3 and H_{7a} by 3.3 and *ca.* 2 Hz, respectively. The magnitude of $J_{H_2H_3}$ also is consistent with trans coupling in the norbornane system.[8,9,12,13] Proton H_3 showed no appreciable coupling with the bridgehead protons H_{7a}, H_{7s}.

The nmr spectrum of dibromide **8** can be similarly interpreted. Vicinal protons H_2, H_3 geminal to bromine (δ 4.70, 4.14) appeared as an AB quartet of doublets with $J_{H_2H_3} = 6.8$ Hz and $J_{H_{7a}H_{2,3}} = 1.9$ Hz. The endo proton at δ 3.71 adjacent to chlorine was an apparent triplet with $J_{H_5H_6} = 2.7$ Hz and $J_{H_5H_6} = 3.0$ Hz, which suggests trans orientation for H_5 and H_6. Proton H_6 at *ca.* δ 4.2 was coupled to bridgehead proton H_1 (δ 2.87) by 4.5 Hz, which is consistent with exo assignment.

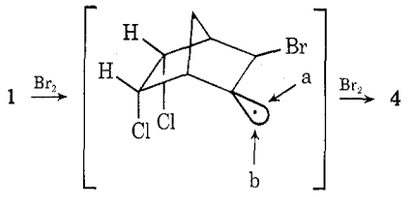
Adduct **7** gave a complex nmr spectrum which was further complicated by the overlap of two proton resonances at *ca.* δ 4.5 at 100 or 220 MHz. Decoupling experiments at 220 MHz established that the upfield proton (δ 4.31) was exo ($J_{H_1H_5} = 4.5$ Hz) and the δ 4.41 multiplet was an endo proton. The δ 4.41 multiplet resulted from a 2-Hz coupling with the methylene bridge proton H_{7s} at δ 2.24 and a trans coupling of ~3 Hz. One proton at δ 4.5 was coupled to the methine bridge proton (δ 2.67) by 3.2 Hz. Irradiation of the δ 4.5 multiplet also revealed a 2-Hz coupling with the methylene proton at δ 2.16. The assignment of the high-field exo proton geminal to chlorine (H_6) was based on the apparent greater shielding from bromine relative to chlorine in dichloronorbornanes[8] (compare also H_{3x} in **5** and H_{6x} in **8**). The endo protons H_2, H_5 adjacent to bromine and chlorine could not be unequivocally assigned. The small chemical shift difference between H_6 (δ 4.31) and the proton at δ 4.41 did not permit effective decoupling experiments. However, irradiation of H_6 did not appreciably alter the δ 4.5 multiplets. Proton H_{7a} was assigned at δ 2.16 based on the similar chemical shift of H_{7a} (δ 2.14) in **8**. The observed 2-Hz coupling of H_{7s} (δ 2.24) with the proton at δ 4.41 further suggests that the latter endo proton (H_5) is adjacent to chlorine.

Exo protons geminal to halogen normally appear downfield relative to endo protons in dihalonorbornanes.[8] This was also the case for H_5, H_6 in **8** and H_2, H_3 in **5**. However, for derivative **7** exo proton H_6 was upfield from the endo protons. This suggests appreciable shielding from Br_{3n} and Cl_{6n} on protons H_{5n} and H_{2n}, respectively. This proximity effect has been noted previously.[1] Comparison of derivatives **5** and **6** indicates that Br_{3n} deshields H_{5n} by 0.62 ppm (δ 4.72–4.10) while H_{6n} remains unperturbed (0.03 ppm). Comparison of **7** and **8** reveals a similar deshielding effect (δ 4.41–3.71 = 0.70 ppm). Deshielding by chlorine of *ca.* 0.7 ppm (H_{2n} in **4** and **6** and in **5** and **7**) was also evident. The effects are consistent with the suggested positive magnetic anisotropy of the carbon–halogen bond.[8,14]

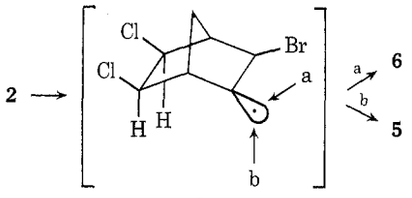
Discussion

Free-radical bromination of olefins **1** and **2** involves initial attack by bromine from the exo side, which is unexceptional for large adducts,[1,12,13] to afford intermediate radicals **1a** and **2a**. The direction of subsequent attack by the propagating bromine molecule on **1a** or **2a** will be determined by the relative steric

(8) P. M. Subramanian, M. T. Emerson, and N. A. Le Bel, *J. Org. Chem.*, **30**, 2624 (1965).
(9) P. Laszlo and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).
(10) F. L. Anet, H. H. Lee, and J. L. Submeier, *ibid.*, **89**, 4431 (1967).
(11) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 5885 (1967).
(12) C. L. Osborne, T. V. Van Auken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968).
(13) A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, **34**, 4108 (1969).
(14) R. F. Zürcher, *J. Chem. Phys.*, **37**, 2421 (1962).



1a



2a

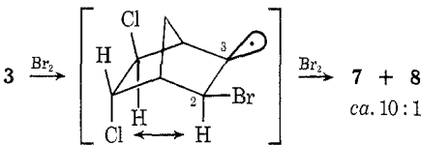
interactions of incoming bromine with the exo bromine substituent and with the endo substituents (Cl or H). For **2a**, nonbonded interaction with the exo bromine substituent is more severe than the endo hydrogen–bromine interaction and attack by path b is preferred. The 5:6 product ratio of 10:1 reflects these factors. However, the endo chlorine substituent provides substantial interference for attack by bromine from the endo direction on intermediate **1a** (path b) and attack from path a is now preferred. The exclusive formation of the exo-cis adduct **4** from olefin **1** is the result. Similar effects have been demonstrated for endo fluorine and endo methyl substituents in the free-radical addition of halogens[1,15] and polyhalomethanes[12,13,15,16] to norbornenes.

The bromination result for olefin **2** also suggests the appropriate stereochemistry for the radical bromination of norbornene itself. The distribution of dibromide products for the free-radical bromination of norbornene is unknown, although it has been suggested that the addition is predominantly *trans*.[1,4,15] Norbornene has an overwhelming preference for ionic bromination, even at −78°, which obviates any meaningful study of the radical pathway. Fortunately, the chlorine substituents in **2** sufficiently deactivate the double bond toward ionic bromination so that the radical process is favored, and the radical product distribution can be obtained with confidence. The 5,6-exo chlorine substituents in **1** are not anticipated to affect the stereochemistry of addition to the double bond, and the 10:1 preference for trans addition of **1** can be applied to the radical bromination of norbornene itself.

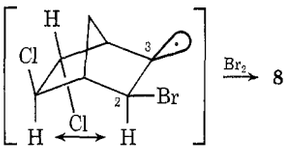
Initial addition of bromine to **3** can afford both intermediate radicals **3a** and **3b**. Subsequent attack by bromine on **3b** occurs from the exo direction, for the endo chlorine completely shields endo attack as in **1a**, with the formation of product **8**. Attack on **3a** by propagating bromine should exhibit stereospecificity similar to that for attack on **2a** with endo attack preferred by a factor of *ca.* 10:1. The observed product distribution of 60% **8** and 40% **7** can be used to calculate the **3b**:**3a** ratio, with the assumption that **3a** leads to 91% **7** and 9% **8**, which gives **3b**:**3a** = 1.4.

The preference for **3b** formation can be explained as follows. Attack at C_2 or C_3 on **3** results in the movement of the olefin hydrogen to an endo position as sp^3

(15) B. E. Smart, *J. Org. Chem.*, **38**, 2039 (1973).
(16) B. E. Smart, *J. Org. Chem.*, **38**, 2035 (1973).



3a

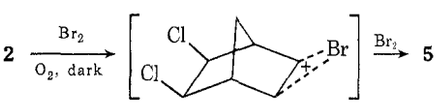


3b

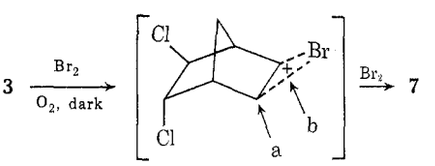
development at the attacked carbon proceeds. The carbon atom which accommodates the odd electron retains its sp^2 configuration and little change in geometry is anticipated. Attack at C_2 (**3a**) therefore generates an endo,endo 1,3-H–Cl interaction, whereas attack at C_3 (**3b**) leads to an endo,endo 1,3-H–H interaction. Hence, attack at C_3 leading to intermediate **3b** is preferred.

The ionic brominations of **2** and **3** proceed slowly at 25° and are stereospecific. No nortricyclyl halide or Wagner–Meerwein rearrangement products are observed, as is the case for norbornene itself.[4,5] The electron-withdrawing chlorine substituents appreciably deactivate the C_1–C_6 bond toward σ participation and also eliminate hydride shifts where positive charge is developed adjacent to the chlorine substituent; hence, rearrangement becomes unfavorable.

The stereospecificity of the ionic brominations suggests bridged intermediates. Without bridging, bromination of **3** is anticipated to exhibit a mixture of cis (**8**) and trans (**7**) adducts as in the radical bromination. Formation of **7** at the exclusion of **8** requires the



9



10

intermediacy of **10** and subsequent preferential attack endo and away from the endo chlorine substituent (path b). Attack *via* path a on **10** incurs severe nonbonded interaction of bromine with the endo chlorine substituent and is excluded. Intermediate **9**, with endo attack by bromine to give exclusively **5**, similarly explains the stereospecific ionic bromination of **2**.

Bridging in ions **9** and **10** provides a mechanism for charge delocalization when the normal σ participation for a norbornyl cation is unfavorable. Furthermore, bridging allows for the partial removal of positive charge to a greater distance from the electron-withdrawing chlorine substituents. These factors further support bridging in 3-bromo-5,6-dichloro-2-norbornyl cations.

In contrast, the lack of stereospecific free-radical addition to **3** argues against bridged bromine radicals. In fact, the preference is for cis addition with **8** as the major adduct. The radical addition results can be adequately explained by steric arguments without invoking bridged species.[17]

Experimental Section

Proton nmr spectra were recorded on a Varian Associates A-60, HA-100, or HR-220 MHz spectrometer. Homonuclear decoupling experiments at 220 MHz were performed by a track sweep method.[18] All compounds were run at 20–30% solutions in $CDCl_3$ at ambient temperature with tetramethylsilane as an internal reference.

All melting and boiling points are uncorrected. The gas chromatography work was performed on a Varian Aerograph Series 200 gas chromatograph fitted with a Brown Potentiometer recorder. The following columns were employed: column A, 5 ft × 0.25 in. 3% SE-30 on 100/120 Aeropak 30; column B, 8 ft × 0.375 in. 25% Triton X305 on Chromosorb W. *endo-cis*-5,6-Dichloro-2-norbornene (**1**) and *exo,cis*-5,6-dichloro-2-norbornene (**2**) were prepared by the procedure of Tanner and Gidley.[2] Two recrystallizations from *n*-hexane afforded pure **1**, mp 75–76° (lit.[3] mp 75–76°). Pure **2** was obtained by preparative vpc (column B, 150°). The procedure of Roberts and Carboni[3] afforded *trans*-5,6-dichloro-2-norbornene, bp 80–82° (20 mm) [lit.[3] bp 76–78° (17 mm)]. All dichloronorbornenes employed were >99.5% pure by vpc (column B).

Brominations. General Procedures.—The brominations under free-radical conditions in CH_2Cl_2 were performed as before.[1,16] Ionic brominations were conducted by treating a solution of the appropriate olefin in CH_2Cl_2 in the dark with bromine (1–1.1 equiv) at 25°. The reaction mixture was continuously purged with a slow stream of oxygen prior to work-up. After complete bromine addition, the reaction mixture was quenched in 5% aqueous sodium thiosulfate, washed with saturated aqueous sodium chloride, and dried over $MgSO_4$. Removal of the solvent on a rotary evaporator afforded the crude dibromide product, which was analyzed by vpc.

***exo,cis*-5,6-Dichloro-2-norbornene (2).**—A solution of 1.63 g (10.0 mmol) of **2** in 9 ml of CH_2Cl_2 was treated dropwise with a solution of 1.60 g (10.0 mmol) of bromine in 1 ml of CH_2Cl_2. Irradiation was continued 5 min after complete bromine addition. Work-up afforded 3.08 g of semisolid product. Vpc analysis (column A, 165°) indicated a mixture of 89% **5** and 11% **6**. No unreacted starting material (>1%) was evident. The product mixture was treated with petroleum ether (bp 30–60°)–benzene, chilled to 0°, and filtered to afford 405 mg of solid containing 89% **6** and 11% **5** by vpc. Recrystallization from *n*-hexane afforded pure *exo-cis*-2,3-dibromo-*exo-cis*-5,6-dichloronorbornane (**6**), mp 227–228°. The filtrate was concentrated on a rotary evaporator to an oil (~98% **5**) and preparative vpc afforded pure *exo*-2-bromo-*endo*-3-bromo-*exo-cis*-5,6-dichloronorbornane (**5**), mp 57–58°.

Anal. Calcd for $C_7H_8Br_2Cl_2$: C, 26.04; H, 2.50; Br, 49.50; Cl, 21.96. Found (**5**): C, 26.31; H, 2.57; Br, 49.70; Cl, 21.93. (**6**): C, 26.02; H, 2.52.

Three runs of this reaction afforded 89, 91, and 94% **5** and an average **5**:**6** ratio of 10:1 is reported.

When the bromination of **2** was repeated on the same scale under ionic conditions, a 90% yield of **5** was obtained. No **6** (>0.5%) was present by vpc (column A, 150°).

***trans*-5,6-Dichloro-2-norbornene (3).**—Treatment of 16.3 g (0.10 mol) of **3** in 90 ml of CH_2Cl_2 with a solution of 17.0 g (0.106 mmol) of bromine in 10 ml of CH_2Cl_2 under illumination afforded 30.2 g of a mixture of 60% **8** and 40% **7** (column A, 150°) which accounted for 98% of the products. Distillation at 0.5 mm afforded the following fractions: a, 5.9 g (100% **7**), bp 87–90°; b, 3.1 g (68% **7**, 32% **8**), bp 89–90°; c, 9.4 g (47% **7**, 53% **8**), bp 100–107°; d, 8.6 g (100% **8**), bp 109–111°. Each fraction solidified or partially solidified on collection. Recrystallization of fraction a from *n*-hexane gave pure *exo*-2-bromo-*endo*-3-bromo-*exo*-5-chloro-*endo*-6-chloronorbornane (**7**), mp 50–51°. Recrystallization of fraction d from *n*-hexane gave analytically pure *exo-cis*-2,3-dibromo-*exo*-5-chloro-*endo*-6-chloronorbornane (**8**), mp 56–58°.

Anal. Found (**7**): C, 26.29; H, 2.54; Br, 49.47; Cl, 21.90. (**8**) C, 26.26; H, 2.47; Br, 50.28; Cl, 21.61.

Bromination of **3** on the same scale under ionic conditions afforded a 90% yield of **7**. Vpc analysis (column A, 150°) indicated <0.5% **8**.

Control Experiments.—Pure samples of dibromides **5**, **7**, and **8** were not rearranged under the vpc conditions (column A, 150–180°). Solutions of 1 *M* dibromide in methylene chloride were individually irradiated for 30 min in the presence of bromine and were unchanged by nmr and vpc. Dibromide **8** was recovered unchanged after treatment with bromine in CH_2Cl_2 in the dark.

Registry No.—**1**, 2843-35-8; **2**, 14627-78-2; **3**, 2843-39-2; **4**, 39037-42-8; **5**, 39810-57-6; **6**, 39810-58-7; **7**, 39810-59-8; **8**, 39810-60-1; Br_2, 7726-95-6.

Acknowledgments.—The author is indebted to Mr. Lou Walther for performing the double-resonance experiments at 100 MHz and for Mr. Rou Rizzardi for similar experiments at 220 MHz.

(17) A recent publication describes similar electronic and steric effects of nitrile substituents on the stereochemistry of halogen addition to cyanonorbornene derivatives; see S. Kikkawa, *et al.*, *Bull. Chem. Soc. Jap.*, **45**, 2523 (1972).

(18) R. C. Ferguson, to be published.