Reactions and Rearrangements of 5,6-Disubstituted Bicyclo[2.1.1]hexenes

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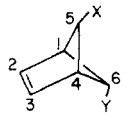
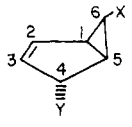
Halogenation of benzvalene (I) with either Br_2 or Cl_2/CCl_4 gives only one adduct, *anti,syn*-5,6-dihalobicyclo[2.1.1]hexene, IIa or IIb. This adduct is thermally unstable and rearranges to *exo,anti*-4,6-dihalobicyclo[3.1.0]hexene, IIIa or IIIb (half-life at 50 °C for IIa = 18 min; for IIb = 77 min). Treatment of IIb with 1 equiv of KCN in aqueous acetonitrile gives *anti,syn*-5-chloro-6-cyanobicyclo[2.1.1]hexene (IIc) and *endo,endo*-3,5-dicyanotricyclo[2.2.0.$0^{2,6}$]hexane (IVa). IIc slowly rearranges to 6-*anti*-chloro-4-*exo*-cyanobicyclo[3.1.0]hexene (IIIc) (calculated half-life at 50 °C = 10^5 min). The mechanism of the rearrangement of IIa–c to IIIa–c in light of kinetic and deuterium-labeling data as well as the mechanism of formation of IIc is discussed. When treated with KOAc in aqueous acetonitrile or AgOAc in benzene, IIb gives *endo,endo*-3,5-diacetoxytricyclo[2.2.0.$0^{2,6}$]hexane (IVb). When IVb is treated with HCl/CCl_4, it rearranges to *anti,syn*-5,6-diacetoxybicyclo[2.1.1]hexene (IId). When heated, both IId and IVb rearrange to *exo,anti*-4,6-diacetoxybicyclo[3.1.0]hexene (IIId). In contrast, IVa is thermally stable and does not rearrange in acid.

Now that benzvalene (I), the highly strained structural isomer of benzene, has become a readily available compound,[1] it is possible to investigate its chemistry as well as the chemistry of compounds derived from it that were previously unknown or obtainable only with great difficulty. Bicyclo[2.1.1]hexenes, compounds that are closely related structurally to the thoroughly investigated bicyclo[2.2.1]heptenes, have not been studied extensively, primarily because of their synthetic inaccessibility.[2] In addition, because of their structural similarity, it has been assumed that they would react in a similar fashion. In most of the previously reported reactions of substituted bicyclo[2.1.1]hexenes, that has been the case.[2] Kinetic and deuterium-labeling experiments herein reported suggest that 5,6-disubstituted bicyclo[2.1.1]hexenes react differently. Unanticipated reaction pathways are followed; unusual and novel rearrangements occur in this highly labile ring system.

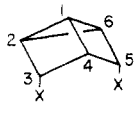
I



II a X=Y=Br
b X=Y=Cl
c X=Cl;Y=CN
d X=Y=OAc
e X=Y=CN
f X=OAc;Y=H



III a X=Y=Br
b X=Y=Cl
c X=Cl;Y=CN
d X=Y=OAc
e X=Y=CN
f X=OAc;Y=H



IV a X=CN
b X=OAc

Results and Discussion

When an ethereal solution of I (0.01 M to 1.5 M) is treated with 1 M Br_2/CCl_4 or 1 M Cl_2/CCl_4 at 0 °C, a large number of products could conceivably be formed. Only IIa and IIb (*anti,syn*-5,6-dihalobicyclo[2.1.1]hexene) are formed in quantitative yield. The reaction is not simply the result of addition across the C-5 to C-6 bicyclobutane bond of I because I-d_2, specifically deuterated at C-5 and C-6, gives IIab-d_2 deuterated at C-2 and C-5.[3] It is likely that the halogen initially adds in an ionic[4] fashion to the double bond of I to give a halonium ion intermediate that then rearranges before reacting with halide as adumbrated in Scheme I.

Compound IIa does not readily undergo nucleophilic displacement reactions; it instead rearranges to *exo,anti*-4,6-dibromobicyclo[3.1.0]hexene (IIIa). IIb, however, when treated with 1 equiv of KCN in aqueous acetonitrile, gives in 40% yield *anti,syn*-5-chloro-6-cyanobicyclo[2.1.1]hexene (IIc).[5] A second product, formed in 32% yield, is *endo,endo*-3,5-dicyanotricyclo[2.2.0.$0^{2,6}$]hexane (IVa),[6] mp 147–148 °C.

When excess KCN is used, IVa is the sole product. When IIc reacts with excess KCN in aqueous acetonitrile, again IVa is formed quantitatively. IVa is a thermally stable compound that does not rearrange in the presence of acids.

Similarly, if compound IIb is allowed to react with excess KOAc in aqueous acetonitrile, *endo,endo*-3,5-diacetoxy-

(1) T. J. Katz, R. J. Roth, N. Acton, and E. J. Carnahan, *Org. Synth.*, **53**, 157 (1973).

(2) See F. Bond, C. Ho, and O. McConnell, *J. Org. Chem.*, **41**, 1416 (1976); F. Bond and C. Ho, *ibid.*, **41**, 1421 (1976), and references cited therein; R. J. Roth, *Synth. Commun.*, **9**, 751 (1979).

(3) R. J. Roth and T. J. Katz, *J. Am. Chem. Soc.*, **94**, 4770 (1972); R. J. Roth, Ph.D. Dissertation, Columbia University, 1972.

(4) At the suggestion of a referee, a possible radical mechanism was ruled out by the following radical scavenging experiment: An ethereal solution, 0.01 M benzvalene, and 0.015 M isopropyl nitrite, was treated with 1 M Br_2/CCl_4. The only nonvolatile product formed was IIa. Since the same dibromide is formed in the presence as well as the absence of scavenger, the reaction most likely does not proceed by a radical pathway.

(5) This compound, *anti*-5-chloro-*syn*-6-cyanobicyclo[2.1.1]hexene, was previously prepared by allowing benzvalene to react with *N*-chlorosulfonyl isocyanate. T. J. Katz and K. C. Nicolaou, *J. Am. Chem. Soc.*, **96**, 1948 (1974).

(6) The stereochemical assignment in 3,5-dicyanotricyclo[2.2.0.$0^{2,6}$]-hexane (both cyanides down) of the substituents at C-3 and C-5 is based on the ^1H NMR spectrum of IVa. The multiplicities of the peaks in IVa are analagous to those found in the benzvalene–4-phenyltriazolinedione adduct where the stereochemistry is rigidly fixed by the cyclic structure: T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973).

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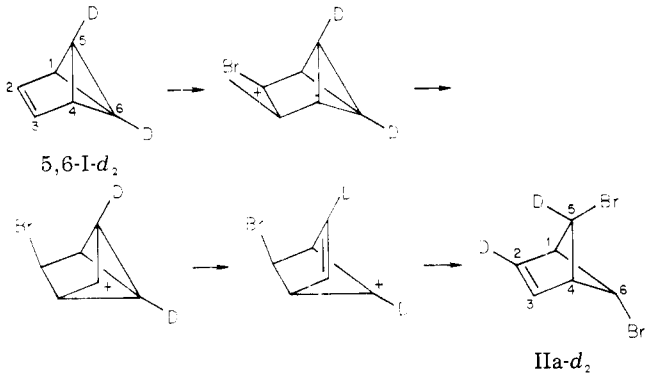
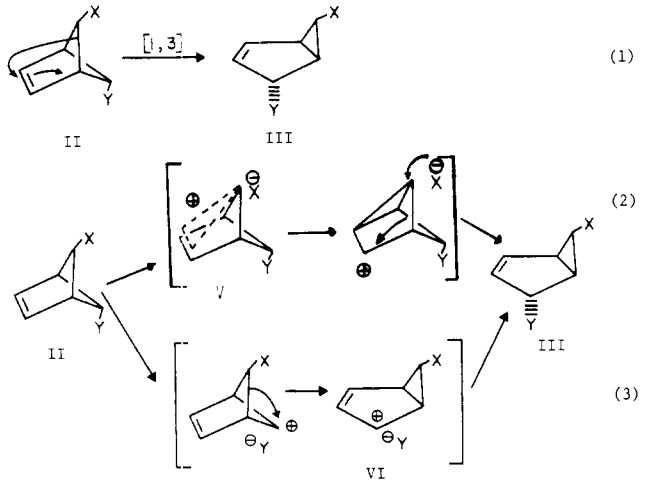
Scheme I



tricyclo[2.2.0.0^{2,6}]hexane (IVb), mp 57–58 °C, is formed in 80% yield. The same product is formed when a benzene solution of IIb is allowed to react with 2 equiv of AgOAc. IVb is thermally more stable than IIa–d but rearranges to IIId at elevated temperatures and rearranges to IId in the presence of acids (HCl/CCl_4).

IIa–d are not thermally stable; on heating in chlorinated hydrocarbon solvents they rearrange to IIIa–d.[7,8] Many rearrangement pathways are feasible in this labile system, including (1) [1,3]sigmatropic shift of the C-1 to C-5 bond with inversion at C-5;[12] (2) ion-pair formation (R^+X^-) to give a nonclassical carbocation intermediate, V, which then collapses to form the thermodynamically more favorable bicyclo[3.1.0]hexene ring system;[12,13] (3) ion-pair formation (R^+Y^-) to give a cyclobutyl carbocation that rearranges to a cyclopropylcarbinyl–allyl bicyclo[3.1.0]hexenylium cation, VI, which ultimately gives the most stable product.[14]



(1)

(2)

(3)

Table I. Kinetic Data for Rearrangement II → III

compd	$k^{50\,°C}$, s^{-1}	$\tau_{1/2}^{50\,°C}$, min	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
IIa	$(6.32 \pm 0.1) \times 10^{-4}$ [a]	1.83×10^{1}	25.0	-1
IIb	$(1.49 \pm 0.1) \times 10^{-4}$ [a]	7.75×10^{1}	26.8	-10
IIc	1.14×10^{-7} [b]	1.01×10^{5}	32.5	-10
IId	7.27×10^{-6} [b]	1.59×10^{3}	26.0	-2
IIf[c]	4.64×10^{-7}	2.49×10^{4}	27.5	-7

[a] Measured directly. [b] Calculated from measurements at higher temperatures. [c] See ref 12.

Table II. ^{1}H NMR for Rearrangement IIa-d_2 → IIIa-d_2

IIa-d_2			IIIa-d_2		
position	δ	integral	position	δ	integral
$H_{2,3}$	6.67	1.24	$H_{2,3}$	5.94	1.61
H_6	5.86	0.92	H_4	4.89	0.84
H_5	4.63	0.06	$H_{1,5}$	2.67	1.55
$H_{1,4}$	3.15	1.90	H_6	2.23	0.12

Kinetic data for the rearrangement of several bicyclo[2.1.1]hexenes are given in Table I. Presumably for steric reasons and the relative weakness of the carbon–bromine bond, the dibromide IIa is the least stable compound listed. (The diiodide is explosively unstable.) Mechanistically, the most important entries are IIb and IIc. If the dichloride rearrangement follows pathway 1 or 2, the rates of rearrangement of IIb and IIc would be comparable. The rates differ by a factor of 10^3. Clearly, when IIb rearranges to IIIb, the C-6 to chlorine bond is ruptured in the rate-determining step, not the C-5 to chlorine bond. The anti chlorine at C-5 is not exceedingly labile in disubstituted bicyclo[2.1.1]hexenes. IIc and IId have very different substituents at C-5 and C-6, yet they rearrange at similar rates. Since different amounts of energy are needed to break a carbon–oxygen bond, a carbon–chlorine bond, and a carbon–carbon bond, it is unlikely that the rearrangement of IIc or IId involves cleavage of any of these bonds. Monoacetate IIf (which has no C-6 substituent) rearranges at a comparable rate, suggesting that IIc, IId, and IIf rearrange by a [1,3]sigmatropic shift of the C-5 bridge.

When IIa-d_2, deuterated at C-2 and C-5, rearranges to IIIa-d_2, the deuterium distribution is as shown in Table II. The deuterium label at C-5 in IIa is unchanged (within experimental error) while the label in the olefinic position of IIa has been scrambled among C-2, C-3, C-4, C-1, and C-5 in IIIa. This result is consistent with formation of a bicyclo[3.1.0]hexenylium carbocation intermediate (VI) with the cyclopropane ring circumambulating the periphery of the five-membered ring before reacting with the available anion.

Since the bicyclo[2.1.1]hexene system is structurally similar to bicyclo[2.2.1]heptene, it is not unreasonable to assume that it should react in an analogous fashion. It has been shown that *anti*-7-chlorobicyclo[2.2.1]heptene reacts with cyanide ion to give mainly *anti*-7-cyanobicyclo[2.2.1]heptene plus a small amount of *endo*-3-cyanotricyclo[2.2.1.0^{2,7}]heptane (eq 4).[15] The *anti*-5-methoxy acetate of bicyclo[2.1.1]hexene on acetolysis gives *anti*-5-acetoxybicyclo[2.1.1]hexene (eq 5).[12] Surprisingly, treatment of IIb with 1 equiv of KCN gives IIc and not the compound expected by analogy with the above examples

(7) The structure of compound IIIa was proved by reduction in steps to bicyclo[3.1.0]hexene, spectroscopically identical with an authentic sample as prepared by G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

(8) The 4-*exo*,6-*anti* stereochemistry of IIIa is primarily based on its ^{1}H NMR spectrum. For H_4, $W_{1/2}$ = 4.5 Hz. $|J_{4,5}|$ should be 6 Hz if the protons are cis[9] and 2 Hz if trans.[10] H_6 is over the ring and trans to H_1 and H_5 because $J_{1,6} = J_{5,6}$ = 2.0 Hz.[11] Similar reasoning is used in the stereochemical assignments of IIIb-d.

(9) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Am. Chem. Soc.*, **90**, 6096 (1968); E. Ciganek, *ibid.*, **88**, 2882 (1966); E. C. Friedrich, *J. Org. Chem.*, **34**, 528 (1969).

(10) P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965); P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, **32**, 24 (1967).

(11) W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32**, 2976 (1967); A. A. Bothner-By, *Adv. Magn. Reson.*, **1**, 195 (1965).

(12) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Am. Chem. Soc.*, **91**, 4322 (1969).

(13) H. Hogeveen, P. W. Kwant, E. P. Schudde, and P. A. Wade, *J. Am. Chem. Soc.*, **96**, 7518 (1974); S. Winstein and C. Ordonneau, *ibid.*, **82**, 2084 (1960).

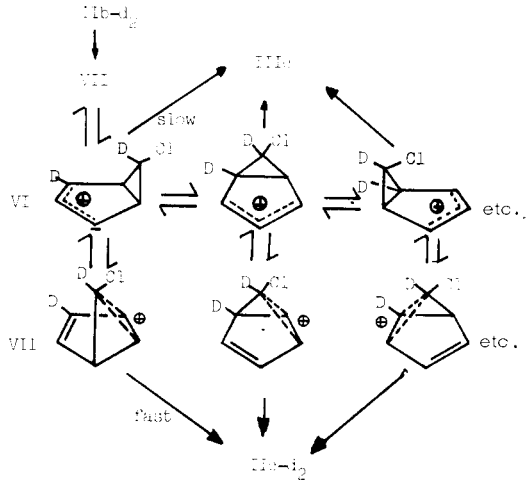
(14) G. A. Olah, G. Liang, and S. P. Jindal, *J. Org. Chem.*, **40**, 3259 (1975); J. A. Berson and N. M. Hasty, Jr., *J. Am. Chem. Soc.*, **93**, 1549 (1971). For a cyclobutyl carbocation rearrangement in a related system see C. W. Jefford, J. Mareda, J. Perlberger, and U. Burger, *ibid*, **101**, 1370 (1979).

(15) H. Tanida and V. Hata, *J. Org. Chem.*, **30**, 977 (1965).

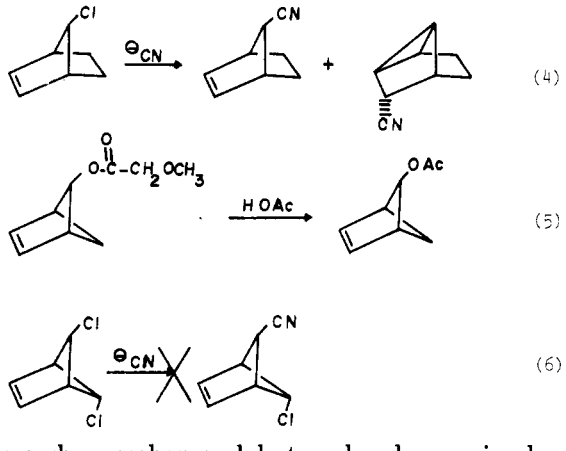
Table III. ^{1}H NMR for IIb-d_2 → IIc-d_2

	IIb-d_2		IIc-d_2		calculated integrals for IIc-d_2	
position	δ	integral	δ	integral	eq 7	eq 8
$H_{2,3}$	6.73	1.29	6.93	1.61	1.29	1.60
H_6	5.73	0.85	4.48	0.82	0.85	0.80
$H_{1,4}$	2.89	1.86	3.07	1.57	1.86	1.60

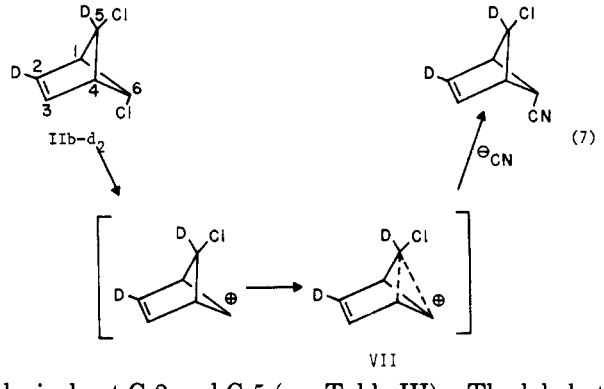
Scheme II



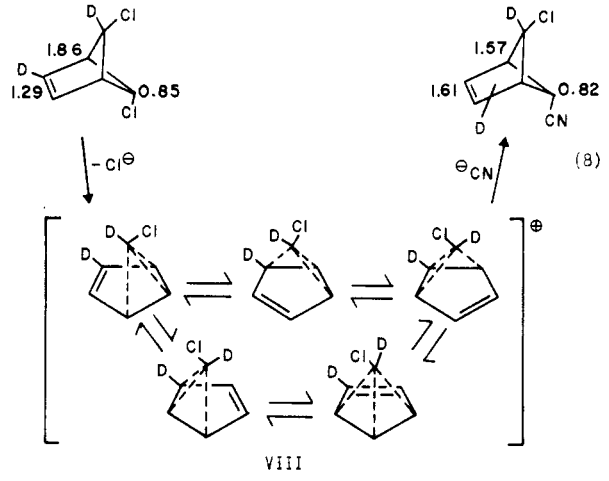
(eq 6). It would appear that under nucleophilic as well as thermal conditions the anti-5 chlorine is not as labile as the syn-6 chlorine.



If a carbon–carbon cyclobutane bond were simply assisting in the displacement of the syn-6 chlorine of IIb-d_2, the deuterium distribution in IIc-d_2 would be unchanged (eq 7). The deuterium labels, however, are no longer



exclusively at C-2 and C-5 (see Table III). The label at C-5 has not changed, but the label at C-2 has been scrambled among positions C-1,4, C-2,3, and C-6. This suggests that a rearranging carbocation has been formed as an intermediate that is then trapped by cyanide ion. If the bicyclo[3.1.0]hexenylium cation (VI) were formed, the product would most likely be the thermodynamically favored 6-*anti*-chloro-4-*exo*-cyanobicyclo[3.1.0]hexene (IIIc).[16] Instead, the 5-*anti*-chloro-6-*syn*-cyanobicyclo-[2.1.1]hexene (IIc) is formed. This implies that there is a distinct energy barrier between cation VI and the cation formed during the IIb → IIc reaction (eq 8). A cation that



could account for the deuterium label distribution in IIc-d_2, allow the one-carbon bridge to circumambulate the cyclopentane ring stereospecifically, and be energetically distinct from the bicyclo[3.1.0]hexenylium cation is VIII.

Conclusions. The bicyclo[2.1.1]hexene skeleton is very labile. There are many alternative low-energy reaction pathways available to it that lead to bicyclo[3.1.0]hexenes, tricyclo[2.2.0.0^{2,6}]hexanes, and differently substituted bicyclo[2.1.1]hexenes. When there is direct competition between π-bond-assisted displacement of a leaving group at C-5 and cyclobutane σ-bond-assisted displacement at C-6, the observed product in the cyanide displacement reaction and the comparative rates of thermal rearrangement both suggest that σ-bond participation is more important. As revealed by the deuterium labeling experiments, seemingly straightforward reactions are, in reality, the result of complex cation rearrangements.

Experimental Section

General Remarks. Melting points and boiling points are uncorrected. NMR spectra were run in $CDCl_3$, CD_3CN, or CCl_4 with added Me_4Si by using either a P.E.R-24B, Varian A-60A or HR-220 and are reported in δ units. IR spectra were run on a Perkin-Elmer Model 621 or Beckman 4240 instrument and are

(16) A referee has suggested Scheme II to explain both the regiospecific formation of IIc from IIb and concomitant circumambulation: ionization of IIb gives carbocation VII which is in equilibrium with ion VI (which can undergo circumambulation, scrambling the deuterium label). Rapid reaction of VII with cyanide and slow reaction of VI with cyanide would give higher energy IIc rather than lower energy IIIc. This mechanism implies that if carbocation VI can be independently generated, it should react with a nucleophile to give the kinetic product, II, rather than the thermodynamic product, III. When IIIa is treated with KCN/aqueous CH_3CN, a mixture of 6-*anti*-chloro-4-*endo*-cyanobicyclo[3.1.0]-hexene and 6-*anti*-chloro-4-*exo*-cyanobicyclo[3.1.0]hexene (IIIc) (that eventually equilibrates to only IIIc) is formed, probably by a bimolecular reaction pathway. However, when IIb is treated with $AgNO_3/CH_3OH$, the only product formed initially (it ultimately aromatizes) is 6-*anti*-chloro-4-*exo*-methoxybicyclo[3.1.0]hexene. No 6-*anti*-chloro-4-*endo*-methoxybicyclo[3.1.0]hexene is formed (implying an S_N1 rather than a bimolecular pathway) and no 5-*anti*-chloro-6-*syn*-methoxybicyclo-[2.1.1]hexene is formed, suggesting that in this case at least, ion VI does not react slowly with a nucleophile and does not rapidly equilibrate with ion VII. If the same is true in the KCN/aqueous CH_3CN system, Scheme II cannot be correct. In addition, Berson has generated bicyclo[3.1.0]-hexenylium ion under acidic conditions and it does not give any bicyclo[2.1.1]hexene products on reaction with nucleophiles.[14]

reported in cm^{-1}. Mass spectra were obtained on a Finnigan 1015D or P.E.RMU-6D instrument. Microanalysis was done by either Schwarzkopf Microanalytical Laboratory, Woodside, NY, or Galbraith Laboratories, Knoxville, TN. Analytical gas chromatography work was performed on a Varian Model 1200, and preparative work was done with a Varian Model 90 P-3 instrument.

***anti,syn*-5,6-Dihalobicyclo[2.1.1]hexene (IIa and IIb).** An ethereal solution of benzvalene, cooled to 0 °C in an ice–water bath, was treated in a dropwise fashion with a 1 M solution of either bromine or chlorine in carbon tetrachloride. A 10% excess of halogen was added and solvents were then removed at reduced pressure at 25 °C or below. The crude product was used in most of the following experiments. Yields were quantitative (^1H NMR, nitrobenzene as an internal standard). Attempts to purify the product by distillation caused decomposition and/or rearrangement.

IIa: ^1H NMR (60 MHz, CCl_4) δ 6.78 ($H_{2,3}$, t, J = 2.0 Hz, 1.90 H), 5.86 (H_6, t, J = 2.0 Hz, 0.99 H), 4.63 (H_5, s, 1.06 H), 3.15 ($H_{1,4}$, quartet, J = 2.0 Hz, 2.07 H).

IIb: ^1H NMR (60 MHz, $CDCl_3$) δ 6.65 ($H_{2,3}$, t, J = 2.0 Hz, 1.96 H), 5.65 (H_6, t, J = 2.0 Hz, 1.01 H), 4.34 (H_5, s, 1.05 H), 3.01 ($H_{1,4}$, AB quartet, J = 2.0 Hz, 1.98 H).

The structure of the dibromide was proved by reduction in two steps to bicyclo[2.1.1]hexane. A sample of the dibromide (2.62 g, 11.0 mmol) was hydrogenated over PtO_2 (0.11 mmol) in 10 mL of ethyl acetate. After taking up 280 mL of H_2 (11.2 mmol), the reaction mixture was concentrated under reduced pressure. Bulb-to-bulb distillation [bp 45 °C (0.5 mm)] afforded 2.56 g (96%) of *anti,syn*-5,6-dibromobicyclo[2.1.1]hexane: ^1H NMR (60 MHz, CCl_4) δ 4.96 (H_6, m, 0.95 H), 3.87 (H_5, s, 0.95 H), 2.83 ($H_{1,4}$, m, 1.91 H), 1.87 ($H_{2,3}$, AB quartet, J = 8.8 Hz, 4.20 Hz); IR (neat film) 3005 (m), 2980 (m), 2953 (m), 2876 (m), 1463 (w), 1305 (m), 1280 (m), 1260 (s), 1242 (m), 1214 (m), 1111 (m), 870 (m), 840 (m), 831 (s), 777 (s), 678 (m) cm^{-1}. An analytical sample was purified by preparative GLC on a 5 ft × 0.25 in. 20% Carbowax 20M on 60/80 Chromosorb W regular column at 160 °C, followed by reduced pressure distillation. Anal. Calcd for $C_6H_8Br_2$: C, 30.03; H, 3.36; Br, 66.61. Found: C, 30.22; H, 3.24; Br, 66.83.

A sample of the hydrogenated dibromide (540 mg, 2.25 mmol) was added to triphenyltin hydride (2.92 g, 8.32 mmol) and the mixture was stirred under N_2 at room temperature for 1.5 days. Volatile materials were distilled at ambient temperature (15 mm) into a liquid N_2 cooled receiver. A number of C_6 hydrocarbons were formed; benzene, cyclohexene, and bicyclo[2.1.1]hexane were identified by NMR. The fraction of bicyclo[2.1.1]hexane was 27% by preparative GLC (5 ft × $^1/_8$ in. 20% Apiezon L on 100/120 Chromosorb W regular column at 35 °C) and its NMR spectrum was identical with the published one.[17]

IIa-d_2 and IIb-d_2. A solution of 10% Br_2/CCl_4 was added dropwise to an ice-cooled solution of I-d_2 (>95% deuterated at C-5 and C-6) in 3 mL of ether until the bromine color no longer discharged. Solvents were removed under reduced pressure at 0 °C, leaving a pale yellow oil. A 60-MHz ^1H NMR spectrum in CCl_4 of crude IIa-d_2 had the following resonances: δ 6.78 ($H_{2,3}$ m, 1.24 H), 5.86 (H_6, t, 0.92 H), 4.63 (H_5, s, 0.065 H), 3.15 ($H_{1,4}$, t, 1.90 H). IIb-d_2 was prepared in an analogous fashion; ^1H NMR (220 MHz, $CDCl_3$) δ 6.73 ($H_{2,3}$, m, 1.29 H), 5.73 (H_6, t, J = 2.5 Hz, 0.85 H), 2.89 ($H_{1,4}$, t, J = 2.0 Hz, 1.86 H).

5-*anti*-Chloro-6-*syn*-cyanobicyclo[2.1.1]hexene (IIc). IIb (2.10 g, 14.1 mmol) was dissolved in 10 mL of acetonitrile. KCN (0.95 g, 14.6 mmol) dissolved in 1 mL of hot water was added dropwise to the ice–water cooled, stirred solution of IIb. The ice bath was removed and the temperature of the solution slowly rose to room temperature. The reaction was monitored by ^1H NMR. Stirring continued for 5 h. The mixture was diluted with ether, washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. A crude product weighing 1.50 g was obtained that was a 56:44 mixture of IIc and IVa. The two components of the mixture were separated by chromatography on silica gel with petroleum ether and then diethyl ether as eluant. A total of 0.80 g (40%) of IIc was isolated from the initial fractions after bulb-to-bulb distillation [bp 45 °C (0.5 mm)] and 0.64 g (35%) of IVa was isolated from the diethyl ether fraction (mp 147–148 °C).

IIc-d_2. IIb-d_2 (680 mg, 4.5 mmol) dissolved in 10 mL of CH_3CN was treated with KCN (325 mg, 5 mmol) dissolved in 1 mL of H_2O. The mixture was stirred for 3 h at room temperature, concentrated under reduced pressure, and chromatographed on silica gel with petroleum ether to elute IIc-d_2 and then ether to elute IVa-d_2. Petroleum ether was removed under reduced pressure to afford 185 mg (30%) of the crude chloro nitrile IIc-d_2; ^1H NMR (220 MHz,$CDCl_3$) δ 6.93 ($H_{2,3}$, m, 1.61 H), 4.48 (H_6, t, J = 2.5 Hz, 0.82 H), 3.07 ($H_{1,4}$, t, J = 2.0 Hz, 1.57 H).

3,5-Dicyanotricyclo[2.2.0.0^{2,6}]hexane (IVa). IIb (900 mg, 6.04 mmol) was dissolved in 10 mL of CH_3CN. KCN (1.37 g, 20 mmol) dissolved in 1 mL of H_2O was added and the mixture was stirred for 3 h at room temperature. The mixture was diluted with water and worked up as above to afford 640 mg (76%) of IVa (mp 147–148 °C). An analytically pure sample was prepared by sublimation: ^1H NMR of IVa (220 MHz, CD_3CN) δ 3.84 ($H_{3,5}$, d of t, J = 4.2, 1.5 Hz, 1.94 H), 3.30 (H_1, t, J = 3.8 Hz, 1.09 H), 2.92 (H_4, quintet, J = 4.2 Hz, 1.03 H), 2.43 ($H_{2,6}$, distorted t, J = 3.8 Hz, 1.94 H); IR (KBr) 2975 (w), 2240 (m), 1344 (w), 1333 (w), 1314 (w), 1194 (s), 1120 (m), 958 (w), 877 (m), 826 (s), 790 (s), 747 (w), 730 (w) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) parent ion 130 (12), major fragments 129 (52), 104 (33), 103 (100), 102 (26), 90 (90), 76 (94), 63 (22), 51 (37), 49 (32). Anal. Calcd for $C_8H_6N_2$: C, 73.83; H, 4.65; N, 21.52. Found: C, 74.02; H, 4.74; N, 21.52.

IIc (140 mg, 1 mmol) was dissolved in 2.5 mL of acetonitrile. KCN (390 mg, 6 mmol) dissolved in 1 mL of water was added. The mixture was stirred at room temperature for 30 h and then was diluted with dichloromethane. The mixture was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The white crystalline residue of IVa weighed 130 mg (100%) and melted at 145–146 °C. An NMR sample of IVa in Me_2SO-d_6 was heated at 150 °C for 6 h. The sample decomposed slightly, but the spectrum was essentially unchanged. HCl gas was bubbled through an NMR sample of IVa dissolved in CD_3CN. After 3 days at room temperature, some decomposition was evident but the ^1H NMR spectrum showed no rearrangement to IIe or IIIe.

3,5-Diacetoxytricyclo[2.2.0.0^{2,6}]hexane (IVb). IIb (2.70 g, 18.1 mmol) was dissolved in 10 mL of acetonitrile. Potassium acetate (9.00 g, 91.8 mmol) dissolved in 4 mL of water was added to the acetonitrile solution at room temperature with stirring. The mixture was stirred for 19 h, diluted with 20 mL of dichloromethane, washed with water and brine, dried over $MgSO_4$–Norit, filtered, and then concentrated under reduced pressure. The crude brown oily product (2.45 g) was further purified by extraction into petroleum ether. The solution was concentrated under reduced pressure to afford a yellow-orange semisolid which was recrystallized from petroleum ether. A white crystalline product (2.20 g, 62%) was obtained (mp 57–58 °C). The same diacetate could be obtained in 70% yield when a benzene solution (20 mL) of IIb (5.50 g, 36.9 mmol) was stirred with silver acetate (12.5 g, 75.0 mmol) for 10 min. The silver residue was removed by filtration and the filtrate was concentrated under reduced pressure. The organic residue was extracted into petroleum ether, concentrated, and recrystallized as above: ^1H NMR (220 MHz, $CDCl_3$) δ 5.11 ($H_{3,5}$, d of t, J = 4.0, 1.2 Hz, 1.96 H), 3.23 (H_4, m, 1.06 H), 2.53 ($H_{1,2,6}$, m, 2.94 H), 2.00 (OAc, s, 6.04 H); IR (KBr) 2970 (w), 1723 (s), 1386 (m), 1255 (s), 1242 (s), 1110 (w), 1028 (s), 936 (m), 836 (w), 794 (w) cm^{-1}. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.18. Found: C, 61.28; H, 6.30.

4,6-Diacetoxybicyclo[3.1.0]hexene (IIId). The combined products from several kinetic runs were chromatographed on silica gel, first with petroleum ether as eluant and then with diethyl ether. IIId eluted with diethyl ether. Solvents were removed under reduced pressure and the residue was bulb-to-bulb distilled at 65 °C (0.3 mm); ^1H NMR (220 MHz, $CDCl_3$) δ 6.12, 5.65 ($H_{2,3}$ 2 d, J = 5.0 Hz, 0.92 H, 1.02 H), 5.39 (H_4, m, 0.95 H), 3.23 (H_6, m, 0.92 H), 2.23 (H_1 or H_5, m, 1.04 H), 1.95, 1.94 (two acetate singlets superimposed on a multiplet, 7.22 H); IR (thin film) 3065 (w), 3015 (w), 2942 (w), 1753 (s), 1745 (s), 1430 (m), 1367 (s), 1222 (s), 1091 (m), 1008 (m) cm^{-1}.

***anti,syn*-5,6-Diacetoxybicyclo[2.1.1]hexene (IId).** IVa (100 mg, 0.51 mmol) was dissolved in $CDCl_3$ (0.5 mL) with nitrobenzene

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as an internal standard. Hydrogen chloride gas was bubbled through the solution in an NMR tube. The compound rearranged quantitatively to IId: ^{1}H NMR (220 MHz, $CDCl_3$) δ 6.51 ($H_{2,3}$, t, J = 2.0 Hz, 1.91 H), 5.80 (H_6, t, J = 2.6 Hz, 0.99 H), 4.76 (H_5, s, 0.93 H), 3.10 ($H_{1,4}$, q, J = 2.1 Hz, 2.03 H), 2.10 (6-OAc, s), 2.03 (5-OAc, s, 6.14 H); IR (neat film) 3012 (w), 1730 (s), 1428 (w), 1358 (m), 1292 (w), 1235 (s), 1180 (w), 1121 (m), 1068 (m), 1030 (w), 783 (m) cm^{-1}; mass spectrum (chemical ionization), m/e (relative intensity) no parent ion at 196, major fragments at 138 (9), 137 (100), 118 (4), 113 (8), 109 (6), 96 (4), 95 (44), 93 (9), 90 (5), 89 (24), 79 (5), 73 (7), 67 (13), 66 (20), 61 (12).

4,6-Dibromobicyclo[3.1.0]hexene (IIIa). A crude sample of IIa (8 g, 3.14 mmol/g, 25.1 mmol) was warmed on a steam bath for 20 min. Distillation [bp 45 °C (0.5 mm)] yielded 6.20 g (103%) of IIIa which displayed 60-MHz ^{1}H NMR resonances (CCl_4) at δ 6.09, 5.74 ($H_{2,3}$, 5.6 Hz doublets, 1.96 H), 4.89 (H_4, m, 0.89 H), 2.67 ($H_{1,5}$, m, 2.10 H), 2.23 (H_6, 2.0 Hz t, 1.05 H). An analytical sample was prepared by two reduced pressure distillations. Anal. Calcd for $C_6H_6Br_2$: C, 30.28; H, 2.54; Br, 67.17. Found: C, 30.42; H, 2.65; Br, 67.55.

The structure of IIIa was proved by reduction, in 2 steps, to bicyclo[3.1.0]hexene. IIIa (2.4 g, 10 mmol) dissolved in 5 mL of dry ether was added to a stirred mixture of $LiAlH_4$ (750 mg, 20 mmol) in 50 mL of ether in a nitrogen atmosphere. The mixture was stirred at room temperature for 6 h; excess $LiAlH_4$ was then destroyed by addition of H_2O and 15% NaOH. The ethereal solution was filtered and concentrated under reduced pressure. Bulb-to-bulb distillation [bp 50 °C (10 mm)] yielded 1.15 g (72%) of 6-*anti*-bromobicyclo[3.1.0]hexene; ^{1}H NMR (CCl_4) δ 5.88, 5.58 ($H_{2,3}$, 2 d), 2.56 (H_3, m), 2.20 ($H_{1,4}$, m), 2.05 (H_6, m).

6-*anti*-Bromobicyclo[3.1.0]hexene (500 mg, 3.12 mmol) was added to a stirred mixture of Na metal (ca. 230 mg, 10 mmol) in *t*-BuOH (520 mg, 7 mmol) and 5 mL of dry THF at ambient temperature under nitrogen. The mixture was refluxed for 6 h and then cooled to room temperature. The supernatant was decanted from unreacted Na, diluted with 60 mL of isopentane, washed with 150 mL of H_2O, dried over $MgSO_4$, and filtered. The isopentane was removed by spinning-band distillation (Nester/Faust, Annular Teflon spinning-band column) at atmospheric pressure. The pot residue was distilled at room temperature (15 mm) into a liquid N_2 cooled receiver. The distillate was further concentrated by micro spinning-band distillation to 1.6 g. The NMR spectrum of the residue indicated the presence of 11 mol % bicyclo[3.1.0]hexene (by integration of the olefinic and δ -0.25 resonances against THF resonances). A 68% yield was obtained (NMR spectrum identical with authentic material, a sample of which was prepared as described by Wittig).[7]

Rearrangement of IIa-d_2 to IIIa-d_2. An NMR sample of IIa-d_2 in CCl_4 was warmed on a steam bath for 10 min. A 60-MHz ^{1}H NMR was observed as follows: δ 6.09, 5.74 ($H_{2,3}$, 2 d, 1.61 H), 4.89 (H_4, m, 0.84 H), 2.67 ($H_{1,5}$, br s, $W_{1/2}$ = 2.5 Hz, 1.55 H), 2.23 (H_6, m, 0.12 H).

4,6-Dichlorobicyclo[3.1.0]hexene (IIIb). IIIb was prepared in the same fashion as dibromide IIIa, bp 50 °C (3 mm); ^{1}H NMR (60 MHz, CCl_4) δ 6.20, 5.71 ($H_{2,3}$, 2 d, J = 5.0 Hz, 1.01 H, 1.04 H), 4.93 (H_4, m, 0.96 H), 2.45 ($H_{1,5,6}$, m, 2.99 H).

4-Cyano-6-chlorobicyclo[3.1.0]hexene (IIIc). The products from several kinetic runs were combined and chromatographed on silica gel with petroleum ether. The solvent was removed under reduced pressure and the residue was bulb-to-bulb distilled at 50 °C (0.3 mm); ^{1}H NMR (220 MHz, CCl_4) δ 6.11, 5.48 ($H_{2,3}$, 2 d, J = 5.5 Hz, 0.99 H, 0.99 H), 3.54 (H_4, m, 0.94 H), 2.43 (H_6, m, 1.12 H), 2.28 ($H_{1,5}$, m, 1.97 H).

Kinetic Measurements. The rate of conversion of IIa-d into IIIa-d at several temperatures was determined as follows. A ^{1}H NMR tube containing a weighed sample of II, nitrobenzene as internal standard, and 350 μL of solvent was kept in an ice bath until a run was started. Temperature was controlled with a YSI Thermistep Model 63 temperature controller (Yellow Springs Instrument Co., Yellow Springs, OH) to within ±0.1 °C. The sample was withdrawn at intervals and cooled in a dry ice–acetone bath, and the ratio of the integrals of all the resonances of II, III, and nitrobenzene was determined. Duplicate or triplicate runs were made at each temperature and the reaction was followed for at least 3 half-lives. Linear regression analysis of the Arrhenius plots obtained [times vs. ln (mg of II)] gave slopes and half-lives with uncertainties at the 95% confidence level.

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Degenerate Cyclopropylcarbinyl Cation Rearrangement in 2-Bicyclo[*n*.1.0]alkyl Cations[1]

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The ionization of bicyclo[*n*.1.0]alkan-2-ols in superacids (SbF_5, FSO_3H, FSO_3H–SbF_5) to the corresponding carbocations has been investigated by ^{13}C NMR spectroscopy over the temperature range of 0 to -140 °C. The bicyclic system, n = 4, gave a degenerate pair of equilibrating cyclopropylcarbinyl cations, whose interconversion can be frozen out [$\Delta G^{\ddagger}$(-85 °C) = 8.50 ± 0.5 kcal/mol]. This interconversion probably occurs through an unpopulated bicyclo[3.1.1]heptyl cation (cyclobutyl cation). On the other hand, the bicyclo[5.1.0]octyl system gave a mixture of static 2-bicyclo[5.1.0]octyl cation **27** and equilibrating 1-bicyclo[3.3.0]octyl cations **28** at -139 °C. Above -130 °C, ion **27** irreversibly rearranged to ion **28**. The n = 3 and 6 bicyclic systems gave rearranged ions, namely, the 3-cyclohexenyl and 1-cyclopropyl-1-cyclohexyl cations, respectively. The effect of C_1 and C_2 substitution on the cyclopropylcarbinyl cation rearrangement process in the 2-bicyclo[4.1.0]heptyl system has been explored. The ionization of the bicyclo[3.2.0]heptan-6-ol (**9**) and its 6-methyl (**10**) and 6-phenyl (**11**) derivatives was also carried out. Each of **9** and **10** yielded a degenerate equilibrating pair of cyclopropylcarbinyl cations, which were also obtained upon the ionization of the parent bicyclo[4.1.0]heptan-2-ol and its 1-methyl analogue. Alcohol **11**, however, yielded only a static tertiary carbocation.

The ease of interconversion of cyclopropylcarbinyl, cyclobutyl, and homoallyl derivatives in solvolytic studies has been investigated in considerable detail.[2] We have previously studied the nature of cyclopropylcarbinyl cation

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