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Ionic Reactions of the Isodicyclopentadienes: Roles and Properties of the Allylic Cations

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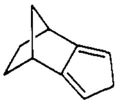
Corresponding to the three isodicyclopentadienes **1**–**3**, four allylic cyclopentenyl cations, **6**–**9**, have been generated in solution and characterized by their NMR spectra. A series of interconversions among derivatives of these allylic systems has been studied mechanistically with the aid of deuterium labeling. Derivatives of the secondary–tertiary cation **6** are the most favored at equilibrium; dienes **2** and **3** are shown to be intermediates in the formation of the most favored allylic structure from the others. In ionic 1,4-addition of methanol to diene **3**, the normal and anti-Markovnikov products are formed competitively, and this process is rationalized on the basis of special torsion at the ring junction. However, the formation of dichloride **14** from diene **1** is shown to involve the labile allylic intermediate **16** and no inverse addition mechanism.

The three isomeric norbornacyclopentadienes (isodicyclopentadienes) **1**, **2**, and **3** have been studied in various Diels–Alder reactions and found to exhibit a range of reactivity.[1-6] The facial selectivity of the diene reactions has aroused special theoretical interest, centered largely around π and σ orbital interactions arising in the norbornane or norbornene ring.[7] Thus, certain monosubstituted ethylenes as dienophiles add only on the endo (α) face of diene **1**, while tetracyanoethylene shows a marked preference, both kinetic and thermodynamic, for adding to the exo (β) face.[4]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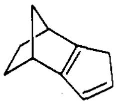
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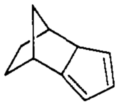
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Another concerted reaction of these diene isomers is the 1,5-sigmatropic rearrangement which interconverts the stable **1** with the unstable **2** and which has been specifically followed by deuterium labeling.[3] This reaction shows a measurable facial selectivity as well as a kinetic isotope effect[3,8] but no evidence of separate ions being involved.

In testing for the pososible involvement of 1,4-dipolar ions in cycloadditions it was found that tetracyanoethylene (TCNE) catalyzes the addition of water or methanol to the double bond of sesquinorbornene[9] and also to the diene system of **3**[4] and that this ionlike addition reaction could also be induced by strong acids. There are thus some systems of great interest where cycloadditions and sigmatropic and ionic rearrangements can compete in ways that may be revealed by the structural changes occurring.

In this paper we characterize the allylic cations and allylic products resulting from ionic addition of water, methanol, and hydrogen chloride to the isodicyclopentadienes.

Ionic Additions to Isodicyclopentadiene Isomer 3. In our previous report[4] it was shown that the addition of water to **3**, catalyzed by strong acid, led to the two allylic alcohols **4**-OH and **5**-OH, the former in the greater amount. In the acid catalysis accompanying the rearrangement of the (2 + 4) to the (2 + 2) TCNE adduct of **3**, only the favored alcohol **4**-OH was formed. This product would be the result of proton addition to C-5 of the diene to yield the secondary–tertiary allylic cation **6**, followed by reaction with water at the one tertiary position in that cation. The other alcohol, **5**-OH, appears to be the result of attack of a proton at C2 in opposition to Markovnikov's rule;

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[1] Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M.; *J. Am. Chem. Soc.* **1981**, *103*, 2022.

[2] Böhm, M. C.; Carr, R. V. C.; Gleiter, R.; Paquette, L. A.; *J. Am. Chem. Soc.* **1980**, *102*, 7218.

[3] Bartlett, P. D.; Wu, C. *J. Am. Chem. Soc.* **1983**, *105*, 100.

[4] Bartlett, P. D.; Wu, C. *J. Org. Chem.* **1984**, *49*, 1880.

[5] Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491.

[6] Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R.; *J. Org. Chem.* **1983**, *48*, 1250.

[7] Houk, K. N. (Chapter 1); Gleiter R., Böhm, M. C., (Chapter 4). In "Stereochemistry and Reactivity of Systems Containing π Electrons"; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983.

[8] Washburn, W. N., private communication. Washburn, W. N.; Hillson, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 4575.

[9] Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *49*, 1875.

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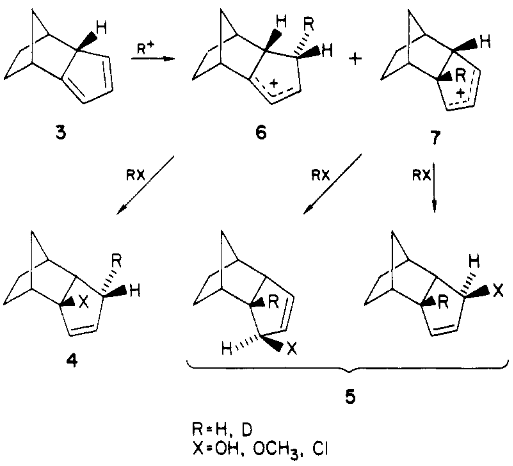
Table I. Electrophilic Addition to 3



RX	catalyst	solvent	total yield, %	ratio of 4/5
H_2O	p-TsOH	CH_3CN	85	7.4
CH_3OH	p-TsOH	CH_3OH	65	6.0
HCl		Et_2O	80	4.0

without isotopic labeling the same structure would result whether the subsequent attack of water occurred at C3 or at C5.

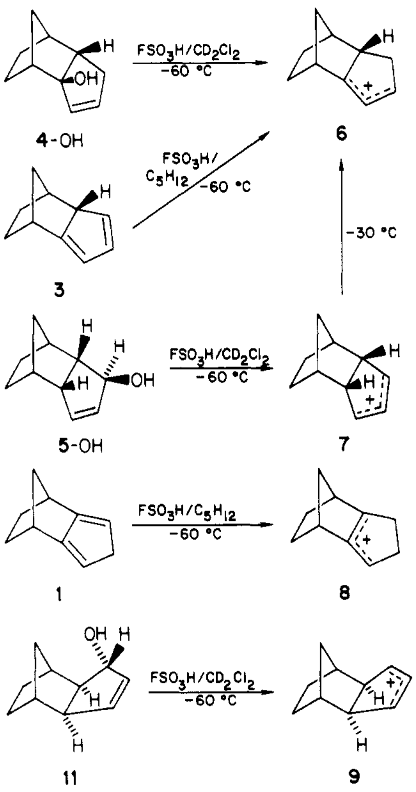
If there were anything concerted about this hydration, the addition of D_2O would yield 5-OD(*d*) deuterated at C-2 from 1,2-addition and at C-6 from 1,4-addition (the hydroxyl-bearing carbon being defined as C-5 in each case), but in this experiment the deuterium was equally distributed between C2 and C6 in the resulting alcohol, indicating intermediacy of the free allylic cation, deuterated 7.

The results of acid-catalyzed methanol addition and hydrochlorination of 3 are similar to those of hydration and are summarized in Table I.

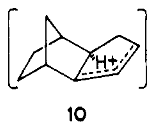
In our previous discussion[4] of the structure of the (2 + 2) adduct of TCNE to diene 3, we deduced the occurrence of an intermediate dipolar ion which looked as if TCNE had attacked the more substituted end of the diene system, and we rationalized the possibility of such an anti-Markovnikov intermediate by noting that ring strain is minimized by sp^3 hybridization of both ring junction carbon atoms. The same consideration can be determining in the present minor formation of 5-OMe and 5-Cl, where initial attack of the proton at carbon atom 2 is the only way to relieve the extra torsional strain at the ring junction, even though the resulting cation is only secondary at both charge-bearing centers.

The Allylic Cations. By the usual orientation rules one would expect by protonation to form cation 6 from diene 3 and cation 8 from diene 1 or 2. To obtain a characterizable cation from diene 1 or 3 it was necessary to minimize the polymerization which dominated the reaction of 1 with strong acids. The procedure adopted was the slow addition of a dilute solution of 1 or 3 in pentane to a stirred two-phase mixture of pentane and fluorosulfonic acid at −60 °C. After separation of the layers, the acid layer was dissolved in methylene chloride and examined by ^{13}C NMR.

Scheme I



As shown in Scheme I application of this procedure yielded a single initial cation (8) from 1 and a different cation (6) from 3, the same ion 6 being formed from the alcohol 4-OH. Alcohol 5-OH yields cation 7, recognizable by the reduction in the number of its ^{13}C NMR peaks due to its symmetry. The symmetrical cation 9, not seen in any reactions of the dienes, was generated for comparison from 11, the exo isomer of 5-OH. The only other possible cation in this family is the hypothetical 10, having the distorted ring junction of 6 but a configuration at C-6 opposite to the favored one of diene 3. No evidence of the occurrence of 10 was seen in any of these experiments.



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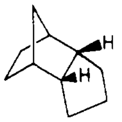
The solution of 7, on warming from −60 °C to −30 °C, underwent a change of its ^{13}C NMR spectrum to that of 6.

The structures of the cations are established by their relation to dienes and alcohols of known structure and the evidence of symmetry (four fewer ^{13}C NMR peaks for 7 and 9 than for 6 and 8). The distribution of the different

Table II. Differences of the ^{13}C Shifts between 7 and 12 (Endo) and between 9 and 13 (Exo)

	δ hydrocarbon − δ cation, ppm	
	endo	exo
methano carbon	−2.7	+4.0
ethano carbon	−7.5	+0.5
bridgehead carbon	−2.8	+8.7
$C_{2,6}$ (ring junction)	−33.2	−29.1

types of carbon in 7 and 9 allows unambiguous assignments to be made; but the variations of chemical shifts show a complex interplay of through-space and through-bond effects of the ionic centers on the environments of the atoms in the norbornane skeleton (Tables II and III). Compared to the saturated 2,3-trimethylenenorbornanes 12 and 13, the ring junction carbons 2 and 6 in the cations 7 and 9 have chemical shifts moved downfield by 33.2 and 29.1 ppm, respectively, while the other five carbons of the norbornane ring are shifted downfield by 2.7–7.5 ppm in the endo and upfield by 0.5–8.7 ppm in the exo isomer. These shifts in the remote carbons are only a few percent of those observed in the atoms bearing the ionic charge.



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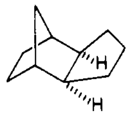

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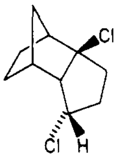
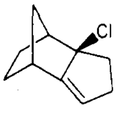
When stirred with excess water in acetonitrile or with excess methanol in the presence of a catalytic amount of *p*-toluenesulfonic acid, diene 1 yielded only brown solid polymers. However, on circulating a dilute solution of 1 in methanol through a column packed with polystyrenesulfonic acid beads over a 48-h period at room temperature, the methyl ether 4-OMe was obtained in 29% yield as the only distillable product. The same product is had by quenching a solution of the cation 6 with methanol.

The most informative reactions proved to be those involving the chlorides. The rearranged product 4-Cl was readily formed on reaction of diene 1 with excess anhydrous hydrogen chloride in ether at −50 °C; but the same reaction conducted in chloroform led to the saturated dichloride 14. The structure of 14, shown by its NMR spectrum, was further refined by preparing a sample of 14 from diene 1 deuterated at the 4α and 4β positions. The 14-d_2 prepared in this way has a parent peak in its GC–mass spectrum heavier by 2 units than the unlabeled molecule. The absence of the δ 37.7 peak in the ^{13}C NMR with no change in the relative intensities of the other peaks indicates that the two deuterium atoms have remained in their original positions. The coupling constant of 9.3 Hz between H-3 and H-2 was thus readily identified and indicates an exo,exo configuration of these two vicinal hydrogens. When DCl was used in excess with undeuterated diene 1, the product 14 showed a parent peak heavier than the unlabeled by 4 mass units. The absence of the corresponding signals in ^{13}C NMR showed that the deuterium in the product was at positions 2, 3, and both faces of 5.

Mechanism of the Cation Rearrangement. Since the monohydrochloride 4-Cl and the dihydrochloride 14 are formed by the same reagents, an obvious possibility would be that 14 results somehow from a further hydrochlorination of 4-Cl. This possibility was ruled out by the observation that isolated 4-Cl, on stirring with excess HCl in chloroform, gave no reaction even on refluxing. It follows that 4-Cl and 14 are both end products, and if the origins of the two are related it must be through the occurrence of a common intermediate. To check this, diene 1 was allowed to react with excess anhydrous HCl in ether at −70 °C for 6 h. The HCl and ether were removed by evacuation to 0.1 torr at −40 °C and the product was redissolved in $CDCl_3$ for ^{1}H and ^{13}C NMR characterization at −50 °C. The major product was the new monochloride 15, derived from cation 8.



14



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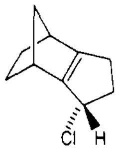


16

The NMR spectra of 15 are very characteristic. The two sp^2 carbon signals are at δ 158.5 (s) and 124.6 nd), indicating that one terminal of the double bond is at the ring junction (C-2). This fact is also reflected in the large difference in the shift values of the two ethano carbons across the norbornyl ring (δ 23.0 and 34.8). This characteristic has generally been observed in the spectra of cycloadducts of diene **2**,[4,5] which, like 15 but for different reasons, have a torque in the bond between C-2 and C-6. The saturated carbon of the ring junction (C-6) bears a chlorine substituent (δ 95.1, singlet in off-resonance spectra). The other two carbons of the cyclopentenyl ring, each bearing two hydrogens, are at 38.3 and 36.7 ppm.

Accompanying the ^{13}C NMR spectrum of 15 was a set of less intense absorptions corresponding to the allylic isomer 16 (see Experimental Section). Direct comparison of peaks of the same multiplicity in the two spectra indicated a ratio of 15/16 between 3.35 at −50 °C and 1.81 at −14 °C. Equilibrium between these two isomers was indicated by the rapid response of the spectral line intensities within 10 min of a temperature change in either direction in the hydrochlorination product of diene 1.

The fact that 15 is always accompanied by 16 offers an

Table III. ^{13}C NMR Chemical Shifts of Four Norbornacyclopentenyl Cations. In Parentheses are the Off-Resonance Multiplicity, the $^1J_{CH}$ Coupling Constant (Hz), and Assignment (CD_2Cl_2 as Solvent, −50 °C)

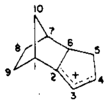
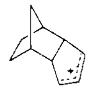
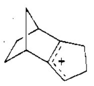
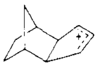
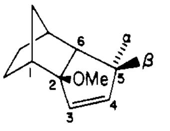
 6	 7	 8	 9
275.4 (s; C_2)	246.3 (d; 173.3; C_3, C_5)	268.7 (s; C_6)	236.0 (d; 173.3; C_3, C_5)
209.1 (d; 174.5; C_4)	151.3 (d; 180.7; C_4)	197.7 (d; 174.5; C_3)	150.5 (d; 181.9; C_4)
137.2 (d; 180.5; C_3)	75.5 (d; 134.3; C_2, C_6)	168.5 (s, C_2)	70.3 (d; 146.5; C_2, C_6)
75.7 (d; 125.7; C_6)	48.7 (d; C_1, C_7)	53.0 (d; C_7)	40.0 (d; 152.6; C_1, C_7)
57.4 (t; C_5)	46.5 (t; C_{10})	49.7 (t; C_5)	28.9 (t; 131.2; C_8, C_9)
46.5 (d; C_1)	31.1 (t; C_8, C_9)	48.0 (t; C_4)	28.2 (t; C_{10})
43.9 (t; C_{10})		41.0 (t; C_{10})	
41.7 (d and t; C_7, C_9)		38.5 (d; C_1)	
21.8 (t; C_8)		26.4 (t; C_9)	
		24.2 (t; C_8)	

Table IV. Reaction of 1 with HCl (or DCl) in Ether To Yield 4-Cl, Isolated as 4-OH

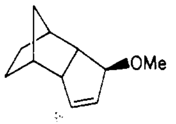
		reactn condn				substrate deuteration		deuterium distribution in product (±0.02)				
no.	reagent	solvent	T1, °C	T2, °C	reagent:substrate	4α	4β	3	4	5α	5β	6
1	HCl	Et_2O	−78	rt[a]	HCl (excess)	0	0	0	0	0	0	0
2	DCl	Et_2O	−78	rt	1.24:1	0	0	0.30	0	0.31	0.31	0.04
3	HCl	Et_2O	−78	rt	1.1:1	1.0	1.0	0.22	1.0	0.23	0.23	0.31
4	HCl	Et_2O	−78	rt	1.1:1	0.74	0.26	0	0.59	0.07	0.07	
5	HCl	Et_2O	−78	rt	HCl (excess)	0.85	0.15	0.05	0.63	0.06	0.08	0.08
6	HCl	CCl_4	80	80	HCl (excess)	0.85	0.15	0.05	0.49	0.05	0	0.02

[a] rt = room temperature.

Table V. Isotopic Labeling in the Formation of 4-OMe and 5-OMe



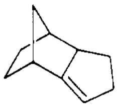
4-OMe



5-OMe

		conditions			deuterium substitution					
					4-OMe			5-OMe		
starting material	reagent	T, °C	t, h	product ratio 4-OMe/5-OMe	5α	5β	6	2	5	6
3	CH_3OD/p-TsOD	0	8	3/1	1.0	0	0	0.5	0	0.5
4-OH	CH_3OD/D_2SO_4	20	3	1/0	0	0	0			
4-OH	CH_3OD/D_2SO_4	65	21	1/0	0	0	1.0			
5-OH	CH_3OD/D_2SO_4	20	3	0/1				0	0	0
5-OH	CH_3OD/D_2SO_4	65	68	3/2	1.0	0	0.95	0.22	0	0.22

explanation of the formation of the dichloride 14 in less ionizing solvents. In chloroform or carbon tetrachloride, HCl addition to the reactive double bond of 16 will be relatively irreversible, 14 being a likely product. Nevertheless, it was desirable to decide between this mechanism and the alternative addition of HCl to 15 in the anti-Markovnikov sense, especially since such abnormal addition remains probable in certain ionic additions to diene 3. For this purpose we prepared the olefins 17 and 18 and noted that both yielded the same chloride 20 on addition of HCl. The absence of the inverse product 19 shows that, despite the behavior of diene 3, anti-Markovnikov addition does not compete with the normal process in addition to the monoolefin 17, and hence presumably not in the case of 15. The facts are well explained by the reactivity of 16.



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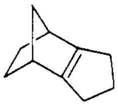

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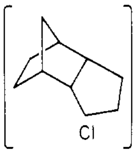

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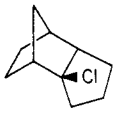

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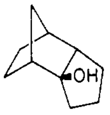

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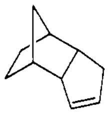

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When the solution of 15 and 16 was warmed to near 0 °C, the ^{13}C spectrum showed a clean exothermic rearrangement to 4-Cl.

Unlike the previously studied[3] thermal interconversions of the dienes 1, 2, and 3, the isomerizations of the cations 6, 7, and 8 are not plausibly formulated as involving concerted intramolecular sigmatropic shifts. The required 1,2-hydrogen shifts would involve localization of the ionic charge with consequent high energy barriers; the alternative 1,4-sigmatropic shifts are symmetry forbidden.[10]

In every respect the cations 6, 7, and 8 appear to be the intermediates in acid-induced reactions of the dienes 1, 2, and 3 and of the alcohols 4-OH and 5-OH and their ethers and chlorides. In each case, the fastest reaction of the cation with any nucleophile is attachment to yield the two allylic isomers in unequal amounts. This happens at −60 °C without rearrangement from one allylic cation to another. The next most rapid reaction to appear as the temperature is raised is reversal of this process, involving reionization and equilibration of the allylic cation with a related diene and proton donor, a process revealed by the isotope exchanges undergone by 4-OH in D_2SO_4 as the temperature is raised from 20 °C to 65 °C (Table V). It is this equilibrium with a diene that opens the way for isomerization from one allylic cation cation to another. Which diene has intervened is revealed by the position of new deuteration in the product, and from the deuterations in Tables IV and V we can reconstruct the deprotonation–reprotonation sequence in these cases. For example, in the rearrangement from 5-OH to 4-OMe (Table V, entry 5) on refluxing in CH_3OD–D_2SO_4, two deuterium atoms are incorporated into the product molecule (at the 5α and 2 positions). The deuterium at 5α arises from the intermediacy of diene 3, and the deuterium at position 2 comes from addition to an intermediate diene 2.

It having been established that the reaction of 4-Cl in basic aqueous solution produced no hydrogen exchange in the framework of 4, we followed the isotopic structures of variously labeled chlorides, preparing solutions of 15 by appropriate combinations of deuterated or undeuterated 1 with HCl or DCl, warming slowly, and examining the ultimate product after its reaction with aqueous sodium carbonate.

When undeuterated diene 1 reacts with DCl in ether at −70 °C and the product is slowly warmed to room temperature, the resulting 4-Cl has its one deuterium equally distributed among the 3 (0.30 D), 5α (0.31 D), and 5β (0.31 D) positions; the 6-position is only slightly deuterated (0.04 D). Since the formation of 4-Cl from 1 is irreversible, the only way in which this isotopic distribution can be attained

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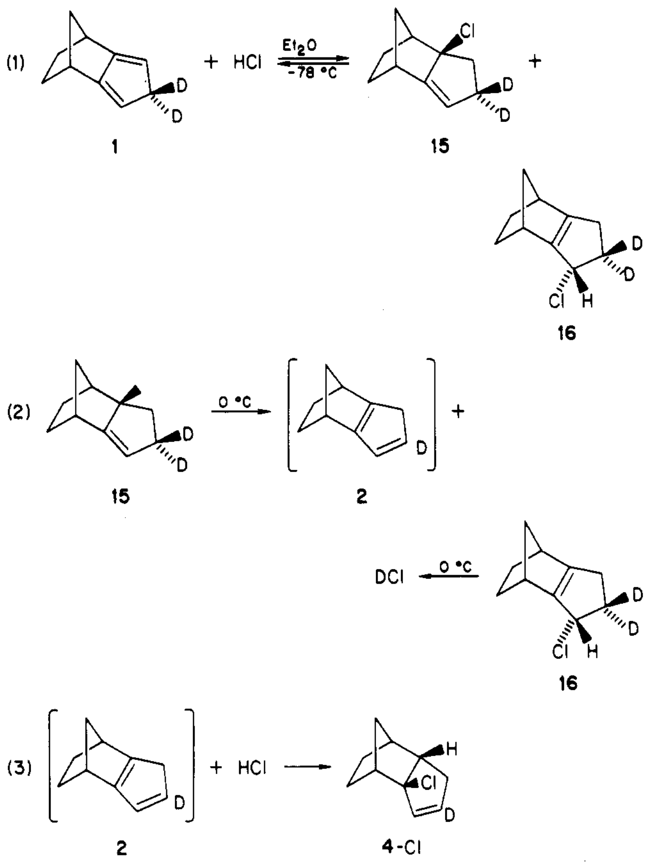
[10] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; p 114.

Scheme II



is by rapid reversal of the initial equilibrium

$$1 + DCl \rightleftharpoons 8\text{-}d + Cl^-$$

in the deuteriochlorination of the diene to yield 15, which involves no attachment of hydrogen at positions 4 or 6. What then are the steps in the irreversible conversion of 15 to 4-Cl?

It is possible[3] to prepare diene 1 deuterated only at position 4 by making the lithium dienide and quenching with deuterated acid. This process puts about 85% of the deuterium at 4α and 15% at 4β. When this process was repeated 5 times, the resulting diene had all its original proton NMR signals except those at 4α and 4β, being specifically deuterated at these two positions. As shown in Table IV, this specimen (entry 3) on reaction with HCl in ether at −78 °C and warming to room temperature, retained one of its deuteriums, while the other deuterium was distributed among the other four locations in the ring of 4-OH. Comparison with the behavior of monodeuterated 1 (entries 4–6) shows that the retained deuterium in the dideuterated sample was the one at position 4α. Thus a stereoselective removal of H from position 4β is involved in the conversion of 15 into 4-Cl and 4-OH.

Scheme II represents a mechanism for this process which could operate within the limitations here established. The basic postulate of Scheme II is that the 1,2-addition of HCl to diene 1 (eq 1), yielding 15 and 16 by way of cation 8, is reversible in ether. This reversible addition assures that all later products from DCl are isotopically equilibrated at C-3 and C-5, while the equivalent exchange at 5α and 5β indicates that the conversion between 1 and 8 is not stereospecific at C-3 and C-5. However, the elimination of DCl in eq 2 to yield diene 2 is at least sufficiently stereoselective so that the irreversible step of eq 3 results in retention of the original D-4α in the product.

As indicated earlier, interconversions of cations 7 and 6 are possible through diene 3, which yields them both by protonation. However, 3 cannot perform this function in transformations of cation 8. Here, it appears that diene 2 is well suited to be an intermediate in the conversion of derivatives of either 7 or 8 into those of 6. However, deuterium labeling has established 3 as the intermediate in the conversion of 5-OH into 4-OH (see above). In our previous experience, 2 has been seen as a highly reactive diene in thermal equilibrium with 1 at 170 °C, or as a product of photolysis of a related diketone.[5] The involvement of 2 in ionic reactions of 4-OH was demonstrated by stirring 4-OH with TCNE in acetonitrile and in the presence of a catalytic amount of p-toluenesulfonic acid for a week at low temperature. Diene 2 was trapped in the form of its Diels–Alder adduct with TCNE.[4] Carried out at slightly higher temperature, acid + 4-OH proves to be a good source of diene 2 under mild conditions.

The pattern of isotope exchanges summarized in Tables IV and V could be predicted from Scheme II, with the exception of the deuteration at position 6. According to the scheme, the hydrogen arriving at position 6 in a fast, irreversible step should reflect the isotopic composition of the free acid at the time reaction 3 takes place. Actually, the isotopic composition of H-6 seems to be heavily weighted toward that of H-4β in the starting material. There is a way in which this could happen within the framework of Scheme II. Diene 2 has repeatedly appeared as an extraordinarily reactive species; it seems possible that this reactivity might reach proportions permitting a "cage effect" or preferential reactivity toward a solvated proton which had just been generated near the position of reactivity in the hydrocarbon structure. Immediately after reaction 2, the solvated proton is very near C-6 where it must become attached in reaction 3. Whereas a concerted sequence is unlikely for reasons mentioned above, a substantial cage effect would produce the observed result of slanting the isotopic composition of H-6 in the product of Scheme II toward that of H-4β in the starting material.

Experimental Section

Isodicyclopentadienes 1, 1-d_1, 3, and 3-d_1 were prepared as described earlier.[3] To prepare the 4α,4β-dideuterated 1-d_2, the deprotonation–deuteration procedure[3,11] used for preparing 1-d_1 was repeated 5 times; the overall deuteration is 2.10 D per molecule.

The acid-catalyzed hydration of 3 and the identification of the two reaction products, *endo*-tricyclo[5.2.1.0^{2,6}]dec-3-en-2-ol (4-OH) and *endo*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-ol (5-OH) were described in an earlier paper.[4]

The LIS reagent used was tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$, from Aldrich. Shifts of peaks were followed on stepwise addition of LIS reagent to the test CDCl$_3$ solution up to a mole ratio of 0.2:1 of reagent:substrate; the ΔEu values are $\Delta\delta$ values extrapolated to 1:1 molar ratio. *endo*-Tricyclo[5.2.1.0^{2,6}]dec-4-en-3-ol, (5-OH),[12] *endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene,[12] *endo*-tricyclo[5.2.1.0^{2,6}]decane[13] (12); *exo*-tricyclo[5.2.1.0^{2,6}]dec-4-en-3-ol[14] (10); *exo*-tricyclo-[5.2.1.0^{2,6}]dec-3-ene,[14] and *exo*-tricyclo[5.2.1.0^{2,6}]decane[15] (13) were

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(16) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley-Interscience: New York, 1980; p 48. (b) Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield Beach, FL, 1982; p 25. (c) Reference 4, note 7. (d) The unsubstituted ethano bridge carbon atoms of the norbornyl structure are easily recognized in ^{13}C NMR; they usually appear at the highest field and their bell-shaped triplets are different from other triplets in the off-resonance spectra.

all prepared from *endo*-dicyclopentadiene (Aldrich) as described; their ^{13}C NMR data are assignments based upon off-resonance multiplicities, relative intensities, and qualitative rules for assigning norbornane derivatives.[16] For the spectral data, see supplementary material section.

The ^1H NMR spectra were obtained on a Varian EM-390 90-MHz spectrometer. The ^{13}C NMR spectra were determined on a JEOL FX-60 (15 MHz) spectrometer. The IR spectra were recorded on a Perkin-Elmer Model 197 spectrophotometer. GC analyses were performed on a Perkin-Elmer Sigma-2000 chromatograph, using SE-30 or Carbowax 1000 packed columns. Preparative GC separations were performed on a Varian 920 Aerograph, using 15-ft Carbowax packed column. HPLC separations were performed on a Waters 204 liquid chromatograph, using a 7.8 mm × 30 cm μ-Porasil column.

High-resolution mass spectral determinations and the isotopic distributions were performed by the Analytical Service Lab at University of Texas (Austin) and by the Midwest Center for Mass Spectrometry, a National Science Facility. Elemental analyses were performed by Schwarzkopf Microanalytical Lab. Melting points are uncorrected.

Acid-Catalyzed Reaction of 3 with Methanol. (a) Formation of 2-Methoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (4-OMe) and 5-Methoxytricyclo[5.2.1.0^{2,6}]dec-3-ene (5-OMe). To a stirred solution of 60 mg (0.6 mmol) of concentrated sulfuric acid in 20 mL (0.5 mol) of dry methanol was added 1.0 g (7.5 mmol) of **3** under nitrogen and with external cooling (ice bath). After 12 h, 1 g of sodium carbonate was added and this mixture was stirred for another 1 h. After filtration and removal of methanol, the residue was distilled at 50 °C (0.5 torr) to give 0.75 g (76%) of product which is a 6.0:1.0 mixture of **4-OMe** and **5-OMe**. The same product ratio was obtained after 10-min and 1-h reaction times while the conversions of **3** to product were 35% and 92%, respectively. The product mixture was then separated by preparative GC to give the pure ethers. For the characterization and spectral data, see supplementary material section.

(b) LIS Experiments on 4-OMe and 5-OMe. The ^1H NMR spectra of **4-OMe** and **5-OMe** were extended by Eu(fod)$_3$. Shifts of peaks were traced by stepwise addition of the LIS reagents. Based on the ΔEu values and the spin-decoupling data of the extended spectrum, assignments of peaks were made.

The δ values, ΔEu values (in parentheses), multiplicities, coupling constants, and the assignments are listed respectively:

(c) Isotopic Labeling. From 150 mg (1.1 mmol) of **3**, 3 mL of methanol-d_1, and 20 mg of sulfuric acid-d_2, after stirring at 0 °C for 24 h, there was obtained 130 mg (70%) of product which is a 3.1:1.0 mixture of **4-OMe-d_1** and **5-OMe-d_1**. The mixture was then separated by preparative GC to obtain pure **4-OMe-d_1** and 5-OMe-d_1.

In 4-OMe-d_1, $H_{5\alpha}$ is missing in the LIS extended proton spectrum; the δ 31.6 peak in ^{13}C NMR becomes a triplet, with $^1J_{CD}$ = 19.5 Hz. In **5-OMe-d_1** the H_2 and H_6 each give an integration of 0.5 H in the LIS extended proton spectrum; in ^{13}C NMR, the δ 52.2 and the 50.4 peaks each become a triplet, $^1J_{CD}$ = 20 Hz.

Similarly, from **3-*d*** and methanol-d_1, there was obtained 4-OMe-d_2 and **5-OMe-d_2**. In the ^{13}C NMR of **4-OMe-d_2**, δ 46.9 (C6) and 31.6 (C5) each became a triplet, with $^1J_{CD}$ being 20.5 and 19.5 Hz, respectively. In **5-OMe-d_2**, the δ 52.1 and 50.4 peaks become tiny triplets.

Alternative Methods To Prepare 4-OMe. (a) From 4-OH. A solution of 0.8 mg of sulfuric acid in 50 μL of methanol was added to a solution of 0.14 g (0.93 mmol) of **4-OH** in 4.0 mL of methanol by syringe. The mixture was stirred at room temperature for 3 h. After evaporation of methanol, the residue was extracted by 10 mL of ether and washed with saturated $NaHCO_3$ solution. Vacuum distillation gave a 0.14-g (85%) yield) of the only product **4-OMe**.

(b) From the Reaction of Methanol and 1. A column (50 × 1 cm) was packed with 20 g of cation-exchange resin (poly(styrenesulfonic acid) type, Amberlyst XN-1010) and washes with methanol to remove free acid. A solution of 2 g (15.2 mmol) of **1** in methanol (100 mL) was circulated through the column at a rate of 2 mL/min for a 12-h period by a metering pump. After the methanol was removed, the residue was distilled to give 0.71 g (28.6% yield) of a single produce, **4-OMe**.

Alternative Methods To Prepare 5-OMe. (a) O-Methylation of 5-OH. To a stirred solution of 4.1 g (27.3 mmol) of **5-OH** in anhydrous ether (30 mL) was added with external cooling (ice bath) 16.5 mL (28.1 mmol) of *n*-butyllithium solution (1.7 M in hexane) under nitrogen. After 1 h, 3 g (23.8 mmol) of dimethyl sulfate was added to this mixture and allowed to react at room temperature for 24 h. This mixture was stirred with 50 mL of 2 N NaOH; the separated ether layer was further washed with 10 mL × 2 of 2 N NaOH and dried over $CaCl_2$ before distillation. There was obtained 3.6 g (80.4% yield) of **5-OMe**, identical with the sample obtained in the addition of methanol to **3**.

(b) From Methanol and 5-OH. A solution of 0.5 g of sulfuric acid in 3.0 mL of methanol was added into a solution of 10.0 g (76 mmol) of **10** in 80 mL of methanol at room temperature, and the mixture was stirred for 8 h. The mixture was filtered through 5 g of anhydrous Na_2CO_3 and the filtrate was distilled to give 8.8 g (80% yield) of **5-OMe**; its identity with the compounds obtained by the other two methods was proved by GC (coinjection), GC–MS, and ^1H and ^{13}C NMR.

Rearrangement from 5-OH to 4-OMe. A solution containing 0.35 g (2.1 mmol) of **5-OH**, 8 mL of methanol-d_1, and 20 g (0.2 mmol) of sulfuric acid-*d* was refluxed under nitrogen for 68 h. After being cooled to room temperature, approximately 1 g of sodium carbonate was added and the mixture was stirred for another 1 h. After filtration, removal of solvent, and distillation at 50 °C (0.5 torr) 0.34 g (89%) of product was obtained which is a 3:2 mixture of **4-OMe-*d*** and **5-OMe-*d***. The two components were separated by preparative GC and the deuterium incorporation was studied by Eu(fod)$_3$-extended ^1H NMR. The ^{13}C NMR data are consistent with the deuterium incorporation pattern.

No deuterium incorporation was detected when **5-OMe** was stirred with methanol-d_1 and sulfuric acid-d_2 at room temperature for 3 h.

A solution of 0.14 g (0.93 mmol) of **4-OH**), 5 mL of methanol-d_1, and 10 mg (0.1 mmol) of sulfuric acid-d_2 was refluxed under nitrogen for 21 h. After removal of methanol, the residue was dissolved in 20 mL ether, washed with 10% sodium bicarbonate, and dried over $MgSO_4$. Distillation gave 0.14 g (91%) of product which contains only **4-OMe-*d***. The deuterium substitution was studied by Eu(fod)$_3$-extended ^1H NMR. The ^{13}C NMR data are consistent with ^1H NMR with complete absence of the δ 47.1 peak (C6). No deuterium incorporation was detected when **4-OH** was stirred with methanol-d_1 and sulfuric acid-d_2 at room temperature for 3 h.

Hydrochlorination of 3. A solution of 200 mg (1.9 mmol) of **3** in 10 mL of ether was stirred under nitrogen at −78 °C. Anhydrous HCl, 500 mg (14 mmol) was bubbled into the solution. At 0.5 and 1 h, aliquots had been drawn and neutralized with aqueous sodium bicarbonate before GC analysis. The product ratio of **4-Cl** and **5-Cl** is 4:1. After 1 h, the cold mixture was evacuated to 2 torr to remove excess HCl. The mixture was then further stirred for 8 h while the temperature was raised to 20 °C. Distillation at 80 °C (1 torr) gives 200 mg (63%) of waxy solid which is a mixture of **4-Cl** and **5-Cl** in a 4.6:1 ratio; their identifies were proved by comparing with authentic samples described below. The mixixture was then stirred with 10% sodium carbonate solution for 12 h to complete transformation into the allyl **4-OH** and **5-OH**.

5-Chloro-*endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene (5-Cl). To a solution of 0.55 g (3.7 mmol) of **5-OH** in 10 mL of ether which was stirred at 0 °C was added 0.81 g (6.8 mmol) of thionyl chloride. After 1 h, pyridine (1 mL) was added to the reaction mixture. The mixture was poured into 30 mL of ice water after being stirred for another hour. After ether workup and distillation at 60 °C (1 torr), there was obtained 0.50 g (81%) of **5-Cl**. See supplementary material section.

Reaction of 1 with HCl in Ether. (a) Preparation of 2-Chloro-*endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene (4-Cl). Anhydrous HCl (1.5 g, 41 mmol) was condensed in a cold trap at liquid nitrogen temperature and then vacuum transferred into a reaction flask containing 5.2 g of **1** (39 mmol) in 50 mL of anhydrous ether and cooled in a dry ice bath. The mixture was allowed to stir at −78 °C for 5 h and then warmed up to room temperature. After evaporation of excess HCl and ther on a rotary evaporator, the reaction mixture contains 8.4% of unreacted **1**, 87.0% of **4-Cl**,

Table VI

order of observation	temp, °C	15/16
1	−50	77/23
2	−20	70/30
3	−50	77/23
4	−14	65/35
5	−50	76/24

and 2.5% of the 2:1 HCl adduct as evidenced by GC–MS analysis. Kugelrohr distillation (3–4 times) at 80 °C (1 torr) gave 4.9 g (73% yield) of pure **4**-Cl, waxy solid, bp 72–75 °C (3 torr). See supplementary material section.

(b) Isotopic Labeling Experiment. Results of isotopic labeling by using **1**-d_1, **1**-d_2, and DCl are listed in Table V. The deuterium-labeled allyl chloride was first transformed to the corresponding allyl alcohol and then studied by Eu(fod)$_3$ ^{1}H NMR. Specific and quantitative transformation was achieved by stirring a solution of 1–1.5 mmol of **4**-Cl in 5 mL of ether with 10 mL of 10% aqueous sodium carbonate solution at room temperature for 8 h, followed by ether workup and distillation.

(c) Formation of 6-*exo*-Chlorotricyclo[5.2.1.0^{2,6}]dec-1-ene (15) and 3-Chlorotricyclo[5.2.1.0^{2,6}]dec-2(6)-ene (16). A solution of 200 mg (1.5 mmol) of **1** in 2 mL of ether was stirred under nitrogen in a 10-mm NMR tube and cooled down to −70 °C. Anhydrous HCl (200 mg, 5.5 mmol) was slowly bubbled into the solution. The mixture was allowed to react for 8 h and the temperature was slowly raised to −30 °C. Excess HCl and ether were removed by evacuating the −30 °C reaction mixture to 0.5 torr to give a pink transparent liquid which was then redissolved in CDCl$_3$ to record the ^{13}C NMR spectrum at −30 °C. Two products, **15** and **16**, in a ratio of 3:1, are present in the reaction mixture; the individual ^{13}C NMR spectrum of each compound is easily recognized from the relative intensities (see Table V).

When the temperature of this reaction mixture was raised to about 0 °C, an exothermic reaction occurred with an accompanying color change (pink to green, then to brown); the ^{13}C NMR peaks of **15** and **16** were replaced by those of a single compound, **4**-Cl.

Isotopic labeling using **1**-d_1 gave similar results: in the ^{13}C NMR of **15**, only the 38.0 peak is missing. The relative intensities of other carbons remained the same as in the undeuterated case.

The same results were obtained when the reaction and the NMR observation were both carried out in Et$_2$O-d_{10}. The ^{13}C NMR spectral data at −30 ° are as follows.

15 (Et$_2$O-d_{10}): δ 157.7 (s), 124.6 (d), 96.1 (s), 47.6 (d), 43.4 (t), 37.5 (t), 36.8 (d), 36.2 (t), 34.0 (t), 22.6 (t).

16 (Et$_2$O-d_{10}): δ 159.3 (s), 148.5 (s), 63.7 (d), 51.0 (t), 43.0 (d), 41.4 (d), 40.3 (t), 27.2 (t), 26.8 (t), 25.9 (t).

14 (Et$_2$O-d_{10}): δ 81.4 (s), 60.4 (d), 57.2 (d), 52.3 (d), 42.1 (d), 40.9 (t), 37.2 (t), 36.8 (t), 23.7 (t), 22.8 (t).

It is thus established that there is an equilibrium between **15** and **11** at low temperature, and the free energy difference of **15** and **11** at −50 °C is 0.4 kcal/mol.

(d) Equilibrium between 15 and 16. In order to observe the equilibrium between **15** and **16**, the following experiments were carried out. Diene **1** (200 mg, 1.5 mmol) was dissolved in 1 g of Et$_2$O-d_{10} under argon and cooled to −78 °C. Anhydrous HCl (approximately 5 mmol) was added and the reaction mixture was stirred at −78 °C for 2 h at −40 °C for 1 h before NMR observation. The ^{13}C NMR spectra were taken at the following sequence (Table VI) −50 °C → −20 °C → −50 °C → −1 °C → −50 °C; the sample was allowed to stand for 10 min at each of the temperatures before the spectrum was taken. The ratio of **15** and **16** were estimated from an average of relative intensities of the relevant peaks (having the same multiplicities) in each compound (Table VI).

Reaction of 1 with HCl in CHCl$_3$ or CCl$_4$. (a) Hydrochlorination of 1 in CDCl$_3$; Formation of 2-*exo*,5-*endo*-Dichloro-*endo*-tricyclo[5.2.1.0^{2,6}]decane (14). Compound **15** was prepared from 500 mg (3.8 mmol) of **1** and excess HCl in ether (10 mL) as described in the previous section. After the conversion from **1** to **15** was completed as evidenced by ^{13}C NMR, the excess HCl and ether were removed by evacuation to 0.5 torr at −30 °C. The residue was cooled down to −60 °C, redissolved in 10 mL of CHCl$_3$, and excess HCl bubbled through. Distillation of the reaction mixture at 80 °C (0.5 torr) gave 550 mg (71%) of a colorless solid, **14** mp 62–63 °C. See supplementary material section.

When excess HCl was bubbled into a CDCl$_3$ solution of **4**-Cl at −50 °C and the mixture was stirred for 24 h at room temperature and 1 h at 60 °C, no further hydrochlorination was detected.

(b) Direct Reaction of 1 with HCl in CHCl$_3$ or CCl$_4$. A solution of 200 mg (1.5 mmol) of **1** in 2 mL of CDCl$_3$ was stirred under nitrogen in a 10-mm NMR tube which was cooled in a −50 °C bath. Anhydrous HCl was then slowly bubbled through this solution and the extent of hydrochlorination was periodically checked by ^{13}C NMR at −50 °C. At stages when the amount of added HCl was approximately 0.8, 2.4, and 4.0 mmol, the reaction mixtures had the following compositions, respectively: **1**:**15**:**16** = 6:6:1; **15**:**14** = 4:1; and **14** only. After removal of CDCl$_3$, the reaction mixture was dissolved in 5 mL of petroleum ether and washed with aqueous Na$_2$CO$_3$ solution. Distillation at 80 °C (0.5 torr) gave 220 mg (72%) of **14**. There is an unidentified isomer which has the same molecular weight and the amount is about 4–5% of **14** (GC–MS).

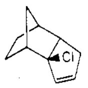
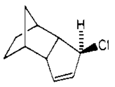
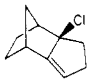
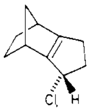
Reaction in CCl$_4$ solution gave similar results.

(c) Isotopic Labeling Experiment. From 1-d_1 and HCl. The product (80% yield) is a mixture of **14**-d_1 (97%) and an isomer (3%, not identified). In the ^{13}C NMR of **14**-d_1, the 37.7 peak splits intto three lines with $^1J_{CD}$ = 20 Hz; the relative intensities of all other carbons are identical with thooe of the nondeuterated **14**, indicating deuterium remaining at its original position.

From 1-d_2 and HCl. From 200 mg (1.5 mmol) of **1**-d_2, 130 mg (42%) of **14**-d_2 was obtained. The two deuterium atoms remain in their original positions as indicated by ^{13}C NMR (the complete disappearance of the C$_4$ peak (δ 37.7)), and the other carbons keep their relative intensities as in the nondeuterated sample. Proton NMR now gives the coupling constant of H$_5$ and H$_6$: J_{H5-H6} = 9.3 Hz, J_{H6-H7} = 4.8 Hz.

14-d_2: ^{13}C NMR (CDCl$_3$) δ 80.9 (s), 61.3 (d), 57.0 (d), 52.9 (d), 42.6 (d), 41.2 (t), 37.0 (t), 24.0 (t), 23.1 (t); ^{1}H NMR (CDCl$_3$) δ 4.50 (d, J = 9.3 Hz, 1 H, H$_2$), 2.84 (dd, J = 9.3, 4.8 Hz, 1 H, H$_6$), 2.57 (br s, 2 H); 2.49 (m, 1 H), 2.15 (m, 1 H), 1.27–1.65 (series of m, 6H).

Table VII. ^{13}C NMR Data of the Four Allylic Chlorides (in Parentheses Are the Off-Resonance Multiplicities and the Tentative Assignments)

 **4**-Cl CDCl$_3$, rt^a	 **5**-Cl CDCl$_3$, rt	 **15** CDCl$_3$, −30 °C	 **16** CDCl$_3$, −30 °C
134.1 (d, C$_3$)	139.4 (d, C$_4$)	157.8 (s, C$_2$)	159.9 (s, C$_2$)
132.9 (d, C$_4$)	132.0 (d, C$_3$)	124.3 (d, C$_3$)	147.2 (s, C$_6$)
90.1 (s, C$_2$)	66.0 (d, C$_5$)	95.6 (s, C$_6$)	65.1 (d, C$_3$)
55.4 (d, C$_6$)	55.1 (d, C$_2$)	47.6 (d, C$_1$)	50.4 (t, C$_5$)
49.8 (d, C$_1$)	52.0 (d, C$_6$)	43.5 (t, C$_5$)	42.2 (d, C$_1$)
41.8 (d, C$_7$)	41.3 (t, C$_{10}$)	38.5 (t, C$_4$)	40.4 (d, C$_7$)
39.6 (t, C$_{10}$)	39.9 (d, C$_1$)	37.5 (d, C$_7$)	39.5 (t, C$_{10}$)
31.5 (t, C$_5$)	39.2 (d, C$_7$)	36.8 (t, C$_{10}$)	28.2 (t, C$_4$)
27.0 (t, C$_8$)	25.0 (t, C$_8$)	34.0 (t, C$_9$)	26.6 (t, C$_9$)
20.2 (t, C$_9$)	22.7 (t, C$_9$)	22.5 (t, C$_8$)	25.3 (t, C$_8$)

^{a} rt = room temperature.

From 1 and DCl. From 0.5 g (3.8 mmol) of **1** and 0.5 g (14 mmol) of DCl, 0.62 g (86%) of deuterated **14**-*d* is obtained. From mass spectrum the extent of deuteration[5] obtained is **14**-d_4:**14**-d_3:**14**-d_2:**14**-d_1:**14**-d_0 = 10.1:28.8:50.6:20.3:3.5. The ^{13}C NMR of this deuterated **14** indicates that the C3, C5, and C6 positions are deuterated ($CDCl_3$): δ 80.9 (s, C2), 61.4 (reduced to $^1/_3$ of original intensity, d, C5), 57.1 (reduced to $^1/_3$ of its original intensity, d, C6), 52.8 (nd, C_1), 42.5 (d, C_7), 41.2 (t, C_{10}), 37.6 (t, C_4), 37.2 (reduced to $^1/_3$ of its original intensity, t, C_3), 24.0 (t, C8), 23.1 (t, C9).

***endo*-Tricyclo[5.2.1.0^{2,6}]decan-2-ol (21).** Compound **4-OH** (0.33 g, 2.2 mmol) was dissolved in 50 mL of EtOAc and hydrogenated in a Parr shaker apparatus at 30 psi using 5% Pd/C as catalyst to give 0.32 g (95%) of **21** as a white solid after removal of EtOac and vacuum sublimation. For the characterization and spectral data, see supplementary material section.

Dehydration of 21. Formation of Tricyclo[5.2.1.0^{2,6}]dec-2(3)-ene (17) and Tricyclo[5.2.1.0^{2,6}]dec-2(6)-ene (18). Compound **21** (0.18 g, 1.2 mmol) was absorbed onto 2 g of neutral alumina (Merck) containing 2% of quinoline. Dehydration of the absorbed alcohol was carried outt at 220–240 °C (40 torr) for 3 h. The distillate which was collected in a cold trap at −78 °C was taken up by pentane and dried over $MgSO_4$. After passing through a short silica gel column (Waters sep-pak), 80 mg (total yield 51%) of product was obtained, which is a mixture of **17** and **18**, in a ratio of 46:54. The mixture was nicely separated by preparative GC, using a 10-ft Carbowax 20 M column at 125 °C to give 25 mg (16%) of **17** and 30 mg (19%) of **18**. For the spectral data, see supplementary material section.

2-Chloro-*endo*-tricyclo[5.2.1.0^{2,6}]decane (20). A 46:54 mixture of **17** and **18** (80 mg, 0.6 mmol) was dissolved in 2 mL of $CDCl_3$ and stirred at −60 °C under N_2. Approximately 0.8 mmol of HCl was slowly bubbled into this mixture. Only one product is formed as evidenced from ^{13}C NMR. The reaction was complete within 1 h at −60 °C. After evaporation of solvent, the mixture was multisublimed at 60 °C (0.5 torr) to give 90 mg (90%) of a white solid. For the characterization and spectral data, see supplementary material section.

Separate reactions in $CDCl_3$ of **17** or **18** with HCl at −50 °C all give the same product, **20**, as indicated by ^{13}C NMR and GC–MS.

Relative Reactivity of 17 and 18 toward HCl Addition. An authentic mixture of **17**, **18**, and tetradecane (internal standard) in chloroform was stirred at −50 °C under nitrogen. The total concentration of **17** and **18** was 0.1 M. A controlled amount of saturated $CHCl_3$ solution of HCl (−50 °C) was added by syringe, and the mixture was stirred at −50 °C for 2 h. The composition of the mixture was analyzed by GC (Carbowax 20 M capillary column). The initial ratio of **17**:**18** was adjusted at 3:1 to 6:1. The extent of reaction was controlled by the amount of HCl added to let only 30–50% of the *more* reactive olefin (**18**) react. The relative rate of **17** and **18** toward HCl addition was calculated by

$$\frac{k_{17}}{k_{18}} = \frac{d \ln [17]}{d \ln [18]} = \frac{\log ([17]_0/[17])}{\log ([18]_0/[18])}$$

For an average of 6 determinations, $k_{17}/k_{18} = (1.5 \pm 0.3) \times 10^{-2}$.

Olefin **22**, another isomer of **17** and **18**, does not react with HCl at −50 °C. As a rough estimation, the relative reactivities toward HCl addition of the three olefins are k_{17}:k_{18}:k_{22} = 1:67:<0.01.

Investigation of the Allylic Cations. (a) Allyl Alcohols as Precursors. A mixture of 1.5 g (15 mmol) of fluorosulfonic acid and 0.5 mL of methylene-d_2 chloride was stirred vigorously in a ^{13}C NMR tube under nitrogen and cooled down to −60 °C. To this mixture was slowly added by a syringe with a long needle a solution of 200 mg (1.3 mmol) allyl alcohol (**4-OH**, **5-OH**, or **11**) and methylene-d_2 chloride (1.0 mL). The red mixture was further stirred for 10 min after the addition. The tube was then inserted into the precooled NMR probe for ^{13}C NMR observation. An additional amount of methylene-d_2 chloride was occasionally needed to avoid the peak splitting which is caused by phase separation.

(b) Dienes as Precursors. The method is a modification of Sorensen's.[17] A mixture of 2 mL (35 mmol) of fluorosulfonic acid and 30 mL of purified pentane was stirred vigorously under nitrogen and cooled to −60 °C.

To this mixture was slowly added a solution of 300 mg (1.3 mmol) of diene (**1** or **3**) in pentane (50 mL) at a rate of 0.3 mL/min by a metering pump. The nozzle of the injection needle was hung directly above the vortex of fluid flow. It was stirred for an additional 0.5 h after the addition was completed. The upper pentane layer was removed by syringe and the residual red solution was evacuated to 0.05 torr for 2 h before 1 mL of methylene-d_2 chloride was added. The reaction mixture was kept below −60 °C during the entire treatment.

Reaction of 4-OMe with TCNE. (a) In the Presence of *p*-TsOH. To a stirred solution of 10 mg (0.05 mmol) of *p*-TsOH in 20 mL of acetonitrile was added in succession 100 mg (0.61 mmol) of **4-OMe** and 160 mg (1.25 mmol) of TCNE. The mixture was stirred at room temperature and under nitrogen for 7 days and became a deep brown solution. After removal of solvent, the black reaction mixture was subjected to flash chromatography (silica gel, 230–400 mesh, pentane/ether eluent) to give 40 mg (25% yield) of the adduct of TCNE to **2**, the properties of which have been fully described.[4]

(b) In the Presence of Water. A solution of 70 mg (0.43 mmol) of **4-OMe** and 65 mg (0.46 mmol) of TCNE in 1.4 mL of acetonitrile-d_3 (distilled over P_2O_5) was stirred under nitrogen in a 10-mm NMR tube at room temperature. No reaction occurred within 4 days as the ^{13}C NMR spectrum remained unchanged. To this mixture was added 20 μL (1.1 mmol) of water and a brown color slowly developed. After 66 h, ^{13}C NMR spectrum of the reaction mixture became a superposition of those of the TCNE–**2** adduct and the unreacted **4-OMe** in a ratio of 1:1 as estimated from the intensities of the related peaks.

Reaction of 1 at 80 °C in CCl_4 solution. Formation of 4-Cl. Through a refluxing solution of 0.50 g (3.8 mmol) of **1** in 10 mL of CCl_4 was bubbled anhydrous HCl slowly for 40 min. After removal of solvent, the residue was distilled 4 times at 70 °C (1 torr) to give 0.45 g (71%) of **4-Cl** as a transparent solid. From GC–MS, the dichloro adduct **14** in the reaction mixture is no more than 5%.

Results of isotopic labeling by using **1**-d_1 and HCl are listed in Table V.

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Registry No. **1**, 6675-72-5; **3**, 89689-33-8; **4-OMe**, 94706-22-6; **4-OH**, 89689-39-4; **4-Cl**, 94706-24-8; **5-OMe**, 94706-23-7; **5-OH**, 58616-86-7; **5-Cl**, 94706-25-9; **6**, 94731-55-2; **7**, 94706-31-7; **8**, 94706-29-3; **9**, 94798-98-8; **11**, 94706-30-6; **14**, 94706-26-0; **15**, 94706-28-2; **16**, 94706-27-1; **17**, 87238-76-4; **18**, 87238-75-3; **20**, 94798-97-7; **21**, 86594-77-6.

Supplementary Material Available: Characterization data on various derivatives of isodicyclopentadiene (^{1}H NMR, ^{13}C NMR, some mass spectral data) and ^{13}C NMR spectra of cations **6**, **7**, **8**, and **9** (13 pages). Ordering information is given on any current masthead page.

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[17] Sorensen, T. S. *J. Am. Chem. Soc.* **1965**, *87*, 5075.