Deuterium Isotope Effects on Carbon-13 Chemical Shifts of Protoadamantane. Evidence for Geometrical Dependence of $^3\Delta$ and $^4\Delta$ Effects

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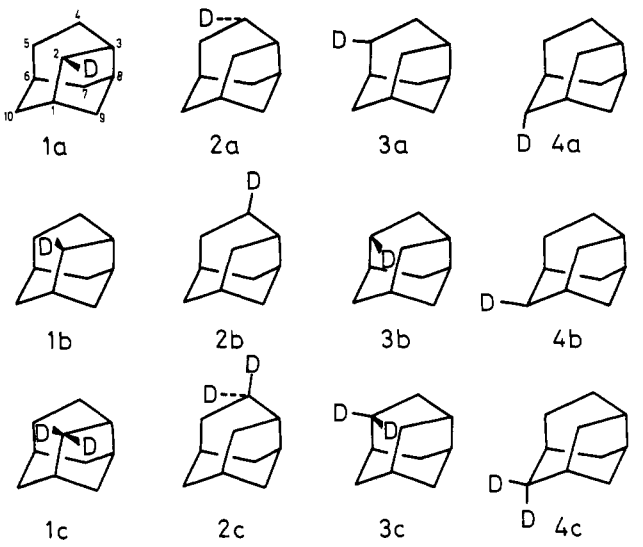
Abstract: The $^1\Delta$, $^2\Delta$, $^3\Delta$, and $^4\Delta$ deuterium isotope effects on carbon-13 chemical shifts were determined for 13 protoadamantane isotopomers: *exo*- and *endo*-protoadamantane-*2*-d_1, -*4*-d_1, -*5*-d_1, and -*10*-d_1, as well as protoadamantane-*2,2*-d_2, -*4,4*-d_2, -*5,5*-d_2, -*10,10*-d_2, and -*6*-d_1. *The results clearly show the additivity of the exo and the respective endo deuterium* $^1\Delta$–$^4\Delta$ *effects as well as the geometrical dependence of the* $^3\Delta$ *and* $^4\Delta$ *effects.* The $^3\Delta$ effect probably originates from an angular-dependent, through-bond, electron-releasing effect of deuterium and a through-space interaction of the C–H(D) dipole and the γ-carbon electrons. The $^4\Delta$ effect appears to operate through a through-space interaction of the C–H(D) dipole and the δ-carbon electrons, steric effect of deuterium, and/or a slight change of the ethano-bridge conformation. The $^1\Delta$ and $^2\Delta$ effects have the expected magnitudes (approximately −400 and −100 ppb, respectively), while the $^3\Delta$ and $^4\Delta$ effects vary from 0 to −55 ppb and from +17 to −14, respectively. The *exo*-protoadamantane enantioisotopomers were prepared by reduction of the corresponding protoadamantanone tosylhydrazones with bis(benzoyloxy)borane followed by decomposition of the reduction product with NaOD in D_2O–THF. The endo enantioisotopomers were obtained by using bis(benzoyloxy)borane-*B*-*d* and NaOH in H_2O–THF.

Deuterium isotope effects[1] on carbon-13 chemical shifts are of great potential use for spectral assignments and structure determinations.[2,3] These effects unambiguously reveal the chemical shifts of the carbons in the neighborhood of the deuterium atom. Combining the information from these shifts with their multiplicities and relative intensities in the partially decoupled and quantitative spectra, respectively, one can easily identify the relevant part of the molecular skeleton. Therefore, if the appropriate isotopomers are available, the structure of the complete molecule can be determined in this way. Nevertheless, this method has not been used extensively chiefly for two reasons: (1) the absence of a simple procedure for selective introduction of deuterium and (2) incomplete understanding of the factors governing direction and magnitude of the $^3\Delta$ and $^4\Delta$ effects.

The intrinsic $^1\Delta$ and $^2\Delta$ deuterium isotope effects on carbon-13 shifts are well-known. In saturated systems, both of these shifts are upfield and the former is considerably larger than the later.[4–7] The $^1\Delta$ and $^2\Delta$ effects are believed to originate from the inductive effect of deuterium.[1,8] At present, data on the $^3\Delta$ and $^4\Delta$ effects in saturated systems are both scarce and controversial.[4–7,9–16]

Chart I



In this work, we have developed a simple method for conversion of sterically hindered ketones into stereospecifically monodeuterated hydrocarbons and prepared *exo*- and *endo*-protoadamantane-*2*-d_1, -*4*-d_1, -*5*-d_1, and -*10*-d_1. Using these eight protoadamantane isotopomers as well as protoadamantane-*2,2*-d_2, -*4,4*-d_2, -*5,5*-d_2, -*10,10*-d_2, and -*6*-d_1 (prepared by the standard procedures), we studied deuterium isotope effects on carbon-13 chemical shifts. The results clearly show the additivity of the exo and the respective endo deuterium $^1\Delta$–$^4\Delta$ effects as well as the geometrical dependence of the $^3\Delta$ and $^4\Delta$ effects.

Results

The protoadamantane system is an ideal model system for deuterium isotope effect studies on carbon-13 chemical shifts. It

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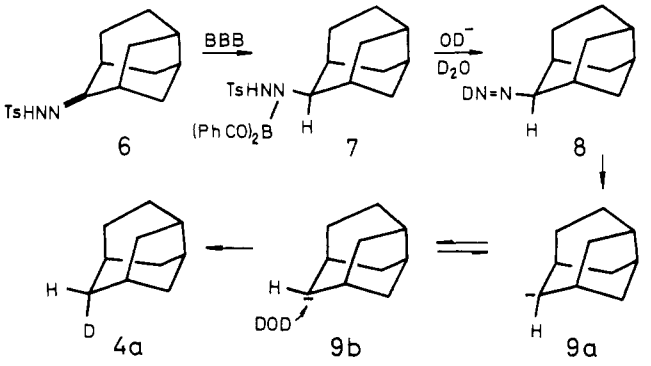
Scheme I



BBB = $(PhCO)_2BH$

is rigid and unsymmetrical, and all of its carbon-13 chemical shifts are well separated. In addition, the four readily available ketones, 2-, 4-, 5-, and 10-protoadamantanone,[17-19] should be good starting materials for preparation of stereospecifically deuterated protoadamantanes. However, the standard methods for stereoselective introduction of deuterium, such as $LiAlD_4$ and $LiB(Et)_3D$ reductions of sulfonates, gave the corresponding protoadamantanols (in addition to the unreacted starting material) rather than the deuterated protoadamantanes.

Recently, Kabalka and co-workers converted tosylhydrazones to the corresponding *regiospecifically* deuterated hydrocarbons by the catecholborane reduction followed by decomposition of the reduction product with $NaOAc{\cdot}3D_2O$.[20a] We tested this method on 10-protoadamantanone tosylhydrazone by using bis(benzoyloxy)borane as the reducing agent[20b] and obtained protoadamantane-*10*-d_1 with a deuterium content as low as 35%. However, when the bis(benzoyloxy)borane reduction product was decomposed with a stronger base, NaOD in D_2O–THF, the deuterium content increased to 85%. A ^2H NMR analysis showed that the deuterium atom was introduced *stereospecifically*, mainly in the exo position (vide infra). Using this modification of the Kabalka's method, we prepared *exo*-protoadamantane-*2*-d_1 (**1a**), -*4*-d_1 (**2a**), -*5*-d_1 (**3a**), and -*10*-d_1 (**4a**) (Chart I) in 70–80% yields starting from the tosylhydrazones of 2-, 4-, 5-, and 10-protoadamantanone, respectively, as illustrated in Scheme I.

The corresponding endo isotopomers, *endo*-protoadamantane-*2*-d_1 (**1b**), -*4*-d_1 (**2b**), -*5*-d_1 (**3b**), and -*10*-d_1 (**4b**), were obtained by reduction of the relevant tosylhydrazones with bis(benzoyloxy)borane-*B*-*d* and decomposition of the reduction products with NaOH in H_2O–THF. The deuterium contents of the endo isotopomers were slightly higher than those of the exo ones (91–93% vs. 85–89% measured by mass spectra). The stereospecificity (the exo/endo ratio) of the deuterium atoms was determined by ^2H NMR and found to be **1a** ≥98/2, **2a** ~71/29, **3a** 82/18, **4a** 82/18, **1b** 5/95, **2b** ~28/72, **3b** 12/88, and **4b** 17/83. The exo and endo deuterium signals of **2** were partially resolved, while those of **1**, **3**, and **4** were completely separated.

The stereopositions of the deuterium atom in **1a–4a** and **1b–4b** were determined by the recently reported Karplus-type relationship of vicinal coupling constants, ^3J(C,D), and the relevant dihedral angles, CC–CD.[21] A comparison of the constants ^3J(C,D) (Table I) with the corresponding dihedral angles CC–CD (estimated from a protoadamantane molecular model) clearly showed that the deuterium atom was situated exo in **1a–4a** and endo in **1b–4b**. These results indicate that the last step in Kabalka's reduction of tosylhydrazones, the decomposition of the diazene intermediate,[20] is an intermolecular rather than an intramolecular process (Scheme I). Bis(benzoyloxy)borane should attack the tosylhydrazone group (e.g., in **6**) from the less hindered, exo side.[22] The base-promoted decomposition of the reduction product **7** will lead, therefore, to the *endo*-diazene derivative **8**. The proton on the nitrogen in the tosylhydrazone (and, presumably, the reduced species) is exchanged by deuterium under the reaction conditions.[20] However, if the deuterated *endo*-diazene derivatives decomposed intramolecularly, the deuterium atom would be situated endo in the products. The results are just opposite. Consequently, the diazene derivatives are probably decomposed (almost exclusively) intermolecularly, by an attack of D_2O from the less hindered, exo side.

In addition to the eight stereospecifically monodeuterated protoadamantanes, **1a–4a** and **1b–4b**, we also prepared protoadamantane-*2,2*-d_2 (**1c**), -*4,4*-d_2 (**2c**), -*5,5*-d_2 (**3c**), and -*10,10*-d_2 (**4c**) as well as -*6*-d_1 (**5**) by using the standard procedures. Isotopomers **1c** and **4c** were obtained from nonenolizable ketones, 2- and 10-protoadamantanone (**1d** and **4d**),[17] respectively, while **2c** and **3c** were prepared from enolizable ketones, 5-[18] and 4-protoadamantanone[19] (**3d** and **2d**), respectively. The former two ketones (**1d** and **4d**) were readily transformed with phosphorus pentachloride to the geminal dichloro derivatives, which were reduced to the corresponding dideuterated protoadamantanes with lithium in *tert*-butyl-*O*-*d* alcohol. Enolizable ketones **2d** and **3d** were first deuterated by an exchange reaction with deuterium oxide and then converted quantitatively into the tosylhydrazones. The tosylhydrazones were reduced to the corresponding dideuterated protoadamantanes by treatment with bis(benzoyloxy)borane followed by decomposition of the reduction product with $NaOAc{\cdot}3H_2O$.[20] Protoadamantane-*6*-d_1 (**5**) was obtained by lithium in *tert*-butyl-*O*-*d* alcohol reduction of 6-bromoprotoadamantane.[23] The deuterium content of **1c–4c** and **5** was higher than 88% (by MS).

The deuterium isotope effects on carbon-13 chemical shifts of isotopomers **1–5** were determined in 2:1 mixtures of the deuterated and nondeuterated protoadamantanes by using $CDCl_3$ as the solvent. The isotope effects were measured as shifts of the deuterated protoadamantane signals relative to the corresponding signals of nondeuterated protoadamantane. The same solutions were used for the carbon–deuterium coupling constants measurements. The digital resolution was 0.061 Hz or 2.7 ppb, and at least three measurements were performed for each of the isotopomers. The typical line widths were 0.2–0.3 Hz. Both the isotope effects and the coupling constants are collected in Table I.

The carbon-13 chemical shifts corresponding to the carbons α, β, and γ to the deuterium atom were easily assigned by the magnitude of the deuterium-induced shifts, the reduction of the signal intensity by deuterium quadropole relaxation, and the signal broadening due to residual C–D coupling. However, the signals of the δ-carbon atoms were rather sharp singlets, very similar in shape to the corresponding signals of nondeuterated protoadamantane. These signals were assigned by comparison of the respective signal intensities in the spectra of different mixtures of the deuterated and nondeuterated protoadamantanes.

Discussion

The data in Table I clearly show that the sum of the $^n\Delta$ deuterium isotope effects of any pair of the enantioisotopomers is equal (within the experimental error) to the $^n\Delta$ effect of the respective dideuterio isotopomer. In other words, the exo and the corresponding endo $^1\Delta$–$^4\Delta$ effects are essentially additive.[24]

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Table I. Deuterium Isotope Effects on Carbon-13 Chemical Shifts ($^n\Delta$)[a] and the Corresponding Carbon–Deuterium Coupling Constants[b] of Protoadamantane Isotopomers

carbon	isotopomer[c] 1a		1b		1c		2a		2b		2c		3a		3b		3c		4a		4b		4c	
C_1	$^2\Delta$	−90	$^2\Delta$	−90	$^2\Delta$	−180	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^2\Delta$	−89	$^2\Delta$	−104	$^2\Delta$	−193
	0.55	t	~0.3	t	0.43	qn		s		s		s		s		s		s	0.52	t	0.50	t	0.52	qn
C_2	$^1\Delta$	−376	$^1\Delta$	−407	$^1\Delta$	−787	$^3\Delta$	−31	$^3\Delta$	−24	$^3\Delta$	−60	$^4\Delta$	+12	$^4\Delta$	+17	$^4\Delta$	+32	$^3\Delta$	−29	$^3\Delta$	−25	$^3\Delta$	−52
	19.49	t	19.77	t	19.53	qn	1.44	t	0.22	t	1.22	t		s		s		s	1.32	t		br s	1.34	t
C_3	$^2\Delta$	−105	$^2\Delta$	−83	$^2\Delta$	−187	$^2\Delta$	−101	$^2\Delta$	−95	$^2\Delta$	−194	$^3\Delta$	−20	$^3\Delta$	−8	$^3\Delta$	−32	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0
	0.55	t		br s	0.43	qn	0.55	t	0.51	t	0.57	qn	1.11	t		s	1.04	t		s		s		s
C_4	$^3\Delta$	0	$^3\Delta$	−52	$^3\Delta$	−52	$^1\Delta$	−374	$^1\Delta$	−417	$^1\Delta$	−795	$^2\Delta$	−98	$^2\Delta$	−95	$^2\Delta$	−194	$^4\Delta$	+8	$^4\Delta$	−5	$^4\Delta$	0
	0.85	t	0.87	t	0.85	qn	19.18	t	19.58	t	19.27	qn	0.49	t	0.55	t	0.49	qn		s		s		s
C_5	$^4\Delta$	0	$^4\Delta$	+6	$^4\Delta$	+14	$^2\Delta$	−78	$^2\Delta$	−109	$^2\Delta$	−187	$^1\Delta$	−392	$^1\Delta$	−417	$^1\Delta$	−808	$^3\Delta$	−31	$^3\Delta$	−50	$^3\Delta$	−79
		s		s		s	0.55	t	0.44	t	0.49	qn	19.30	t	19.33	t	19.29	qn	1.36	t	0.55	t	0.67	m
C_6	$^4\Delta$	0	$^4\Delta$	−5	$^4\Delta$	−5	$^3\Delta$	0	$^3\Delta$	−23	$^3\Delta$	−18	$^2\Delta$	−90	$^2\Delta$	−107	$^2\Delta$	−193	$^2\Delta$	−91	$^2\Delta$	−104	$^2\Delta$	−200
		s		s		br s		s	0.80	t	0.73	t	0.50	t	0.55	t	0.49	qn	0.47	t	0.49	t	0.49	qn
C_7	$^4\Delta$	0	$^4\Delta$	−14	$^4\Delta$	−15	$^4\Delta$	0	$^4\Delta$	+14	$^4\Delta$	+18	$^3\Delta$	0	$^3\Delta$	−31	$^3\Delta$	−35	$^3\Delta$	0	$^3\Delta$	−34	$^3\Delta$	−32
		s		s		s		s		s		s		s	0.93	t	0.85	t		s	0.99	t	0.98	t
C_8	$^3\Delta$	0	$^3\Delta$	0	$^3\Delta$	0	$^3\Delta$	0	$^3\Delta$	−37	$^3\Delta$	−33	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0
		s	0.54	t	0.55	t		s	1.14	t	0.75	t		s		s		s		s		s		s
C_9	$^3\Delta$	−20	$^3\Delta$	−7	$^3\Delta$	−24	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^5\Delta$	0	$^5\Delta$	0	$^5\Delta$	0	$^3\Delta$	−15	$^3\Delta$	−32	$^3\Delta$	−43
		br s	1.30	t	1.28	t		s		s		s		s		s		s	0.30	t	0.16	t	1.22	t
C_{10}	$^3\Delta$	−15	$^3\Delta$	−27	$^3\Delta$	−42	$^4\Delta$	0	$^4\Delta$	0	$^4\Delta$	0	$^3\Delta$	−12	$^3\Delta$	−55	$^3\Delta$	−63	$^1\Delta$	−421	$^1\Delta$	−453	$^1\Delta$	−875
	1.28	t	0.49	t	0.61	m		s		s		s	1.15	t	0.73	t	0.96	qn	18.90	t	19.41	t	19.20	qn

[a] Values are given in ppb (1 ppb = 0.001 ppm), digital resolution ±2.7 ppb, typical line widths: 0.2–0.3 Hz. Negative sign denotes shielding in the deuterated compound. [b] The constants (in Hz) are printed by underlined characters, digital resolution ±0.061 Hz; s, t, qn, and m denote singlet, triplet, quintet, and multiplet, respectively. [c] The isotope effects ($^n\Delta$) and the corresponding coupling constants ^nJ(C,D) of **5** are C_1 −26 ($^3\Delta$), 1.10 (t); C_2 0 ($^4\Delta$), (s); C_3 0 ($^4\Delta$), (s); C_4 −19 ($^3\Delta$), 0.92 (t); C5 −119 ($^2\Delta$), 0.52 (t); C_6 −484 ($^1\Delta$) 19.93 (t); C_7 −117 ($^2\Delta$), 0.52 (t); C_8 −29 ($^3\Delta$), 0.92 (t); C_9 0 ($^4\Delta$), (s); C_{10} − 117 ($^2\Delta$), 0.52 (t).

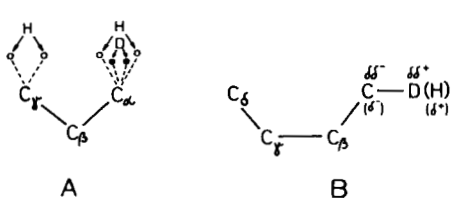

Figure 1. Interaction of the C–H(D) dipole and the γ- and δ-carbon electrons, respectively.

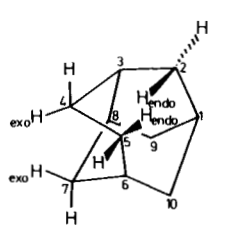

Figure 2. Protoadamantane.

The α-carbon signals of **1a–4a** and **1b–4b** appear as triplets of low intensity, which are shifted upfield by approximately 400 ppb with respect to the corresponding signals of nondeuterated protoadamantane ($^1\Delta$, Table I). Interestingly, the endo $^1\Delta$ effects are slightly larger than the exo ones. The $^2\Delta$ deuterium-induced shifts are also upfield (negative) but 4 times smaller than the $^1\Delta$ shifts. The corresponding carbon–deuterium coupling constants ^1J(C,D) and ^2J(C,D) are nearly independent on the position of the deuterium atom in the molecule: ^1J(C,D) ≈ 19.5 and ^2J(C,D) ≈ 0.5 Hz.[25] Similar values for the $^1\Delta$ and $^2\Delta$ effects as well as for ^1J(C,D) and ^2J(C,D) have been observed in other saturated hydrocarbons having no three- and/or four-membered ring.[5-7] Both $^1\Delta$ and $^2\Delta$ deuterium isotope effects probably originate from a smaller vibrational amplitude of the C–D bond with respect to the C–H bond.[1,8] The bonding electrons are, on the average, closer to the resonating carbon nucleus in the C–D bond and, hence, exert a larger shielding effect.

The $^3\Delta$ effect varies from 0 to −55 ppb (Table I), and the magnitude of this effect as well as the corresponding coupling constant, ^3J(C,D), is clearly stereodependent. The variations of ^3J(C,D) constants are in good agreement with the recently reported Karplus-type angular dependence of these constants.[21] Inspection of a protoadamantane molecular model revealed an apparent dependence of the $^3\Delta$ effect on the dihedral angle between the C_γ–C_β bond and the vicinal C–D bond. This effect is maximal when the dihedral angle is close to 0° and decreases gradually with an increase in this angle to virtually zero between approximately 70° and 140°. A further increase in the angle results again in an increase of the $^3\Delta$ effect, which will reach another maximum at 180°, roughly $^3/_5$ of that at 0°. Recently, Stothers et al. reported a similar stereodependence of the $^3\Delta$ effect within the dihedral angle range between 0° and 90° in *endo*-fenchol-*2-exo*-d_1.[4] The effect at 0° was as large as −80 ppb, while for the dihedral angles ≥90°, the isotope effects were ≤−20 ppb. These values are in good agreement with the magnitudes of the $^3\Delta$ effect observed by Ernst at 24° (−69 ppb) and 96° (∼0 ppb) in a deuterated vitamin B_{12} derivative.[12] Günther[6] and, previously, Kitching[7] found considerably larger $^3\Delta$ shifts for the antiperiplanar (−26 and, approximately, −90 ppb) than for the gauche orientation (−8 and ∼0 ppb) of the C_γ–C_β and the C–D bonds in adamantane-*2*-d_1 and *cis*- and *trans*-4-*tert*-butylcyclohexane-*1*-d_1, respectively. On the other hand, the $^3\Delta$ shifts at ∼0° appear to be larger than those at ∼180°.[12] In addition, Morris and Murray[9] claimed the essential absence of stereoselectivity in the $^3\Delta$ deuterium-induced shifts for atoms C_5 (−70 ppb) and C_7 (−20 ppb) in 4-methylcamphor-*3,3*-d_2, in which the deuterium atoms are in an approximately antiperiplanar relationship with either of these two carbons. However, these $^3\Delta$ shifts were measured relative to Me_4Si, the dihedral angle between the C–D_{endo} and C_7–C_4 bonds was 150° rather than 180° and, in addition, the dihedral angles between the C–D_{exo} and C_7–C_4 bonds and C–D_{endo} and C_4–C_5 bonds were different (90° and 50°, respectively), while the endo deuterium atom was spatially close to the endo C_5 hydrogen atom (vide infra).

The observed angular dependence of the $^3\Delta$ effect is analogous in many respects to the angular dependence of the vicinal coupling constants. This suggests similar transmission mechanisms for both phenomena. Hence, the $^3\Delta$ effect can be interpreted in terms of an angular-dependent, through-bond electron-releasing effect of deuterium. However, the values of the $^3\Delta$ effect at the dihedral angles close to 0° are considerably larger than those at 180° and, in addition, the $^3\Delta$ shifts for atoms C_9 in **1a** and **4a**, C_2 in **2b** and **4b**, and C_5 in **4b** are somewhat larger than one would expect. Similar, unexpectedly large values of the $^3\Delta$ effect have been reported for two norbornane derivatives[4,9] and a vitamin B_{12} derivative[12] (vide supra). This suggests that another mechanism should also be operating. In all these cases, the deuterium atom is spatially close to the γ carbon in question and/or to a hydrogen atom directly bonded to it. This indicates a through-space interaction of the α-hydrogen (deuterium) atom with the electrons surrounding the γ-carbon nucleus.

A C–H bond is a weak dipole, the hydrogen atom being the positive end. Both the α-carbon atom and the directly bonded hydrogen or deuterium atom should influence through space the electron cloud surrounding the γ-carbon nucleus. However, the substitution of deuterium for the α-hydrogen atom should have a larger effect on the hydrogen influence than on the influence of the α carbon, provided that this hydrogen atom is near to the γ carbon and/or a hydrogen atom directly bonded to it. The distance between the α- and γ-carbon atoms is virtually unaffected by the isotopic substitution, while the bending vibration amplitudes of the C–D bond are smaller than those of the corresponding C–H bond[26] (Figure 1A). Since a dipole-isolated charge interaction is inversely proportional to the cube of the distance between the dipole and this charge and directly proportional to cosine of the relevant angle (provided that all other factors are equal),[27] the α-hydrogen atom will withdraw the electron cloud from the γ-carbon nucleus more than the deuterium atom will. Consequently, substitution of deuterium for the α-hydrogen atom will result, in addition to the through-bond interaction, in a through-space shielding of the γ-carbon nucleus and therefore, in an enlarged upfield shift of the γ-carbon signal. This is in good agreement with Saunders' results on the α-carbon shifts caused by gauche γ substituents.[28] The α-carbon signals are shifted upfield due to *removal* of the γ-hydrogen atom and not due to nonbonded interactions introduced with a substituent which replaced this hydrogen.

The $^4\Delta$ effect is the most intriguing. It falls in the range between −14 and +17 ppb but in most cases is zero. The corresponding coupling constants ^4J(C,D) are virtually negligible. The downfield shifts for atoms C_7 in **2b**, C_2 in **3a**, and C_4 in **4a** (Table I) could be explained by the C–H(D) dipole interaction with the electrons surrounding the δ-carbon nucleus.[29] The C–H(D) dipole is directed with its negative end (carbon) toward the δ-carbon atom and/or a hydrogen atom directly bonded to it (Figure 1B). The C–D bond is slightly shorter than the corresponding C–H bond and, therefore, a slightly weaker dipole.[26] Consequently, the through-space interaction of the dipole with the electron cloud at the δ-carbon nucleus, and, hence, its shielding, will be decreased by substitution of deuterium for the α-hydrogen atom.[30] This is in good agreement with the downfield effects observed for atoms C_4 in norbornane-*1*-d_1 and C_3 in cyclopentane-d_1.[5] In both cases, the geometry of the carbon atom in question with respect to the C–D bond is similar to that shown in Figure 1B.

When the positive end of the C–H(D) dipole (hydrogen) is spatially close to the δ carbon or a hydrogen atom directly bonded to it, one could expect the opposite effect through a mechanism analogous to that illustrated in Figure 1A. However, this effect should work against the steric effect of deuterium.[31,32] An in-

(24) To check the additivity of the effects caused by deuterium atoms bonded to different carbons, we prepared protoadamantane-*exo,exo-4,5*-d_2 and measured its isotope effects. The accuracy of these measurements was lower than that of **1–4** owing to the signal broadening. Nevertheless, the effects of this isotopomer were shown to be equal or very close to the sums of the corresponding effects of protoadamantane-*exo-4*-d_1 (**2a**) and protoadamantane-*exo-5*-d_1 (**3a**).

(25) The only exceptions are ^2J(C,D) for atoms C_1 (∼0.3 Hz) and C_3 (broad singlet) in **1b**. Interestingly, the sole hydrogen bonded to C_3 in **1b** is oriented anti rather than syn to the deuterium atom.

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(29) The $^4\Delta$ effect for atom C_5 in **1a** could not be detected, although the magnitudes of this effect observed for C_5 in **1b** and **1c** indicate that a small downfield effect should exist for this carbon. In addition, both the expected and the observed values of the $^4\Delta$ effect for **1a** and **1b**, respectively, are marginal.

(30) Some of the $^3\Delta$ effects in protoadamantane isotopomers **1–4** are probably little reduced through this mechanism.

(31) Touching or overlapping of van der Waals radii of closely spaced hydrogens usually causes a shielding of the carbons attached to these hydrogens.[32] The steric perturbation of the C–H bond involved causes the charge to drift toward carbon.

spection of the protoadamantane molecular model indicates some overlapping of van der Walls radii of the closely spaced endo hydrogens bonded with atoms C_2 and C_5 as well as the exo hydrogens attached to C_4 and C_7[33] (Figure 2). In addition, the exo C_4 hydrogen is spatially close to atom C_7, while the endo C_2 hydrogen is a little closer to C_5 than is the endo C_5 hydrogen to C_2. Owing to the lower vibrational amplitude of deuterium,[1,8] substitution of the endo C_2 and C_5 hydrogens as well as the exo C_4 hydrogen by deuteriums should decrease steric perturbation of the closely spaced hydrogens bonded with C_5, C_2, and C_7, respectively, and result in a deshielding of these carbons. The observed $^4\Delta$ effects arise from both the C–H(D) dipole and steric effect of deuterium, which operate in opposite directions. Consequently, the $^4\Delta$ effect for C_7 in **2a** is zero, while the effects for C_5 in **1b** and C_2 in **3b** are both downfield and the former is smaller than the later. All other $^4\Delta$ effects different from zero are associated with either atom C_4 (in **4b**), C_6, or C_7 (in **1b**). These effects could possibly originate from a through-space interaction of the C–H(D) dipole and the δ-carbon electrons and/or from a slight change of the ethano-bridge conformation caused by substitution of deuterium for the hydrogen atom.

Long-range deuterium isotope effects on carbon-13 chemical shifts have been observed in a few saturated systems.[5,13,34] The effects in flexible systems are equilibrium effects rather than intrinsic ones.[10,34b] In earlier work, Anet and Dekmezian noticed no deuterium-induced shift on a spatially very close δ-carbon atom in a rigid half-cage system.[10] The steric effect of deuterium and the C–H(D) dipole effect probably cancel each other in this case. Recently, however, Ernst and co-workers have reported through-space long-range deuterium isotope effects on carbon-13 chemical shifts in a series of cyclophanes,[11] and Lippmaa et al. described such effects in the less favored *cis*-3-bicyclo[4.4.0]decanone-*2,2,4,4-d*$_4$ conformer.[13] The $^4\Delta$ deuterium isotope effects on carbon-13 chemical shifts, reported in the present work, are the first examples of such effects observed in a rigid saturated system containing no aromatic nuclei.

Combining the information from the $^1\Delta$–$^3\Delta$ deuterium isotope effects observed in **1–4**, with the corresponding carbon-13 chemical shift multiplicities, we were able to unambiguously assign the complete ^{13}C NMR spectrum of protoadamantane (δ 42.13; t, C_9, 40.27; t, C_{10}, 37.49; t, C_2, 35.43; d, C_1, 34.57; d, C_8, 34.22; d, C_3, 32.35; t, C_7, 28.22; d, C_6, 27.83; t, C_5, 23.38; t, C_4). In fact, two isotopomers (e.g., **1b** and **3b**) are sufficient for the assignment. The information from the other isotopomers was used as confirmatory evidence.

In conclusion, the results presented in this work clearly show the additivity of the exo and the corresponding endo deuterium $^1\Delta$–$^4\Delta$ isotope effects as well as the geometrical dependence of the $^3\Delta$ and $^4\Delta$ effects. The $^1\Delta$ and $^2\Delta$ deuterium-induced shifts can easily be recognized by their characteristic magnitudes, coupling constants, and reduction of the signal intensities. This information along with the knowledge of the main factors governing the geometrical dependence of the $^3\Delta$ (and possibly $^4\Delta$) effect should be of great help with spectral assignments and structure elucidations.

Experimental Section

The purity of all compounds was monitored by GC and/or ^{13}C NMR. The deuterium contents were determined by MS by comparing the relative peak intensities of the deuterated and nondeuterated analogues. ^{13}C and ^1H NMR spectra were recorded at 22.50 and 89.55 MHz, respectively, on a JEOL FX-90Q spectrometer equipped with a Texas Instruments 980B computer. ^2H NMR spectra were determined at 15.25 MHz with a JEOL FX-100 spectrometer. IR spectra were taken on a Perkin-Elmer 297 spectrofotometer, and mass spectra were obtained on a Varian CH-7 spectrometer. GC analyses were carried out on a Varian Aerograph 940 or 1800 gas chromatograph. Deuterium oxide (99.7% D) was purchased from Merck and $NaBD_4$ (97% D) from Carl Roth OHG. *tert*-Butyl-*O-d* alcohol was prepared by hydrolysis of *tert*-butyl benzoate with deuterium oxide.[35]

^{13}C and ^2H NMR Measurements. Deuterium isotope effects on carbon-13 chemical shifts were determined in 2 M solutions of 2:1 mixtures of the deuterated and nondeuterated protoadamantanes in $CDCl_3$. The spectra were recorded at 22.50 MHz by using 3000 transients for each spectrum. No exponential filtering was used. The instrument was run with a pulse width of 5 μs, where a 14-μs pulse was equivalent to a 90° flip angle. The isotope shifts were measured relative to the corresponding chemical shifts of nondeuterated protoadamantane by using 16K data points to define the spectral width of 500 Hz. The digital resolution was 0.061 Hz or 2.7 ppb, and at least three measurements were carried out for each of the isotopomers. The agreement of the isotope shifts and the C–D coupling constants determined in different runs was within an error of ±2.7 ppb and ±0.061 Hz, respectively. The typical line widths were 0.2–0.3 Hz. Chemical shifts corresponding to the carbons α, β, and γ to the deuteriums were easily recognized by the characteristic signal broadening, the reduction of the signal intensity, and the magnitude of the deuterium-induced shifts. The δ-carbon signals were rather sharp singlets and were assigned by comparison of the respective signal intensities in the spectra of different mixtures of the deuterated and nondeuterated protoadamantes.

^2H NMR spectra were determined by using the same $CDCl_3$ solutions of the deuterated protoadamantane isotopomers which were used for the deuterium isotope effect studies. The measurements were carried out in a 5-mm NMR tube containing a protoadamantane isotopomer solution held concentrically inside a 10-mm NMR tube with a Teflon spacer. The 10-mm NMR tube contained a 30% aqueous solution of LiCl, which was used for the internal lock. The spectra were 150 Hz wide and the $CDCl_3$ signal was used as the internal standard.

2-, 4-, 5-, and 10-Protoadamantanone Tosylhydrazones (1e–4e). A solution of 2-,[17] 4-,[19] 5-,[18] or 10-protoadamantanone[17] (304 mg, 2 mmol) and tosylhydrazine (390 mg, 2.1 mmol) in methanol (5 mL) was stirred at room temperature for 4 h and then left in a refrigerator overnight. The crystalline product was separated by filtration and dried in a desiccator over $CaCl_2$ to yield 93–97% of the respective tosylhydrazone.

***exo*- and *endo*-2-, 4-, 5-, and 10-Protoadamantane-*d*$_1$ (1a–4a and 1b–4b).** A 1.8 M solution of borane in dry THF (1.7 mL, 3 mmol; prepared from $NaBH_4$ and $BF_3{\cdot}Et_2O$ by the usual procedure) was added to a solution of benzoic acid (740 mg, 6 mmol) in dry THF (8 mL) and stirred at 0 °C. After 15 min tosylhydrazone **1e**, **2e**, **3e**, or **4e** (640 mg, 2 mmol) was added and the mixture was stirred for additional 2 h at the same temperature. Deuterium oxide (2 mL) was added dropwise followed by a 5 M solution of NaOD in D_2O (2 mL, 10 mmol), and the reaction mixture was stirred at reflux for 3 h and then cooled and poured into water (20 mL). The resulting suspension was extracted with pentane (3 × 10 mL). The extracts were combined, washed with a 5% aqueous solution of NaOH (2 × 20 mL) and a saturated solution of NaCl (2 × 10 mL), and dried ($MgSO_4$). The solution was concentrated in vacuo and filtered through a short neutral alumina column (activity I). The solvent was evaporated, and the residue was sublimed in vacuo to yield 70–80% of the respective deuterated protoadamantane.

The endo enantioisotopomers (**1b–4b**) were obtained by the reduction of the tosylhydrazones (**1e–4e**) with bis(benzoyloxy)borane-*B-d* followed by decomposition of the reduction product with NaOH in H_2O–THF. Bis(benzoyloxy)borane-*B-d* was prepared by reaction of benzoic acid with the borane-d_3–THF complex, which was obtained from $NaBD_4$ and $BF_3{\cdot}Et_2O$.

Protoadamantane-*4,4-d*$_2$ (2c) and -*5,5-d*$_2$ (3c) were prepared in 78% and 84% yield, respectively, by the bis(benzoyloxy)borane reduction of the corresponding tosylhydrazones following the procedure described above. However, the reduction product was decomposed with sodium acetate trihydrate[20] (816 mg, 6 mmol) instead of with NaOH in H_2O–THF. The tosylhydrazones were prepared from the respective ketones 5-protoadamantanone-*4,4-d*$_2$ and 4-protoadamantanone-*5,5-d*$_2$, which were obtained by a NaOD-catalyzed exchange reaction of the nondeuterated ketones 5-[18] and 4-protoadamantanone[19] with deuterium oxide in dry dioxane. The purity of **2c** and **3c** was greater than 95% and 98%, respectively (by GC, DEGS, 100 °C), and the deuterium contents of **2c** and **3c** were virtually the same: d_2 88%, d_1 10%, d_0 2% (by MS).

2,2-Dichloroprotoadamantane (1f) and 10,10-Dichloroprotoadamantane (4f). Phosphorus pentachloride (625 mg, 3 mmol) was

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added to a solution of 2-protoadamantanone,[17] **1d** (300 mg, 2 mmol), in carbon tetrachloride (5 mL) and stirred at 0 °C. The reaction mixture was stirred for additional hour at this temperature and overnight at room temperature and then poured onto ice (10 g). The resulting mixture was extracted with pentane (2 × 20 mL). The extracts were combined, washed with saturated $NaHCO_3$ solution (2 × 10 mL), and dried ($MgSO_4$). The solvent was evaporated, and the residue was sublimed in vacuo to give **1f** (348 mg, 87%; 95% pure by ^{13}C NMR): ^{13}C NMR ($CDCl_3$) δ 101.2 (s), 52.4 (d, 2 C), 37.4 (t), 35.0 (t), 33.7 (d), 32.7 (t), 28.0 (t), 27.6 (d), 21.1 (t); ^1H NMR ($CDCl_3$) δ 3.05-2.7 (m, 1 H) 2.7-2.2 (m, 3 H), 2.2-1.15 (m, 10 H); IR (KBr) 2940, 2860, 1460, 920, 895, 880, 805, 760, 740 cm^{-1}; MS, *m/z* 206 (M^+, 3%), 204 (M^+, 5), 171 (34), 170 (29), 169 (100), 168 (54), 133 (60), 91 (51), 79 (44), 77 (26). Anal. ($C_{10}H_{14}Cl_2$) C, H.

10,10-Dichloroprotoadamantane (**4f**) was prepared in 84% yield from 10-protoadamantanone[17] (**4d**) following the procedure described above. However, the reaction mixture was stirred at room temperture for 4 h rather than overnight. **4f** (95% pure by ^{13}C NMR): ^{13}C NMR ($CDCl_3$) δ 101.4 (s), 53.8 (d), 46.9 (d), 39.0 (t), 33.8 (t), 32.9 (d), 32.4 (d), 29.2 (t), 23.9 (t), 23.5 (t); ^1H NMR ($CDCl_3$) δ 2.85-1.35 (m, 14 H); IR (KBr) 2940, 2880, 1460, 830, 817, 804, 767, 748 cm^{-1}; MS, *m/z* 206 (M^+, 10%) 204 (M^+, 15) 171 (21), 170 (35), 169 (61), 168 (88), 133 (55), 121 (100), 95 (67), 91 (67) 79 (46) 77 (49). Anal. ($C_{10}H_{14}Cl_2$) C, H.

Protoadamantane-*2,2-d*$_2$ (1c) and -*10,10-d*$_2$ (4c). Lithium (70 mg, 10 mmol) and *tert*-butyl-*O-d*[35] alcohol (2.0 mL, 20 mmol) were added to a solution of geminal dichloride **1f** (348 mg, 1.7 mmol) in THF (7 mL, freshly distilled from $LiAlH_4$). The reaction mixture was refluxed with stirring overnight and then cooled to room temperature and poured into water (20 mL). The resulting suspension was extracted with pentane (2 × 30 mL). The extracts were combined, washed with water (2 × 40 mL), and dried ($MgSO_4$). The solvent was evaporated, and the crude product was sublimed in vacuo to give **1c** (202 mg, 86%; ≥98% pure by GC, DEGS, 100 °C; deuterium content: d_2 84%, d_1 15%, d_0 1%).

Protoadamantane-*10,10-d*$_2$ (**4c**) was obtained in 84% yield from **4f** by the procedure described above (≥97% pure by GC, DEGS, 100 °C; deuterium content: d_2 82%, d_1 16%, d_0 2%).

Protoadamantane-*6-d*$_1$ (5) was prepared in 88% yield by reduction of 6-bromoprotoadamantane[23] with lithium in *tert*-butyl-*O-d*[35] alcohol following the procedure described for preparation of **1c** (≥95% pure by GC, DEGS, 100 °C; deuterium content: d_1 88%, d_0 12%).

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Registry No. 1a, 94596-80-2; **1b**, 94668-58-3; **1c**, 94596-81-3; **1e**, 94596-88-0; **1f**, 94596-91-5; **2a**, 94596-82-4; **2b**, 94668-59-4; **2c**, 94596-83-5; **2e**, 33801-02-4; **3a**, 94596-84-6; **3b**, 94668-60-7; **3c**, 94596-85-7; **3e**, 94596-89-1; **4a**, 94596-86-8; **4b**, 94668-61-8; **4c**, 94596-87-9; **4e**, 94596-90-4; **4f**, 94596-92-6; **5**, 94596-95-9; $(PhCO_2)_2BH$, 94596-93-7; $(PhCO_2)_2BD$, 94596-94-8; D_2, 7782-39-0.

Cyclization of Acetylenic Carbonyl Compounds via Their Silyl Enol Ether Derivatives: A New Intramolecular C-Vinylation Induced by Mercury(II) Salts. Stereochemistry and Functionalization of the Intermediate Vinylmercurial

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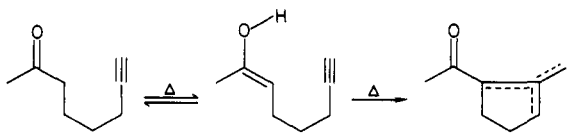
Abstract: By treatment with mercury(II) chloride (1.1 equiv) in the presence of HMDS (0.2 equiv), at room temperature followed by acidification with aqueous HCl-NaI, silyl enol ethers **2**, **5**, and **7** of ε-acetylenic ketones or aldehydes are cyclized in high yield into 2-alkylidene-1-oxocyclopentanes: silyl enol ethers of 4'- and 5'-alkyn-2-ylcycloalkanones **9** and **11** lead to spiro compounds, a methylene-cyclopentane and -cyclohexane unit, respectively, being formed in the reaction. In all products, the exocyclic position of the C=C double bond so formed is fully maintained. The reaction is multistep: a transient α-mercury carbonyl compound is formed, leading, via an intramolecular cis addition, to a vinylmercurial which can be functionalized by electrophilic substitution of the mercury atom with retention of configuration.

The thermal cyclization of unsaturated carbonyl compounds involving at first enolization and then an ene-type reaction, in which the shifted hydrogen is the enol one, is a well-known reaction (for a review, see ref 1). It has been extended to various types of carbonyl compounds, e.g., enones, enals, dienones, ynones, and diynones in particular,[1] but the high temperature necessary causes some compounds (e.g., most of the aldehydes)[2] to decompose or to resinify and an exocyclic double bond, when formed in the process, to migrate.[2,3]



In our continued effort to find conditions under which the reaction temperature of these cyclizations could be lowered, we have shown that mercury(II) salts are efficient catalysts for the cyclization of easily enolizable acetylenic carbonyl compounds;[4] most monoketones react sluggishly, however, suggesting that enolization is rate limiting and the products suffer isomerization of their exocyclic double bond, as in the thermal cyclization.

In this article, we report the *fast regio- and stereospecific room-temperature cyclization* of some representative *acetylenic carbonyl compounds, via their trimethylsilyl enol ethers*, by treatment with mercury(II) chloride, followed by acidification with aqueous HCl-NaI[5] and observations bearing on the *mechanism of this reaction*, and exploit the *completely stereoselective functionalization of the vinylmercurial produced in the reaction.*

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