Chemical Shifts and Spin–Spin Coupling Interactions in the Nuclear Magnetic Resonance Spectra of *endo-* and *exo-*Norbornene Derivatives

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Proton–proton decoupling has made possible a complete analysis of the nuclear magnetic resonance spectra of three endo–exo pairs of 2-substituted norbornenes. The results show that endo–endo vicinal coupling constants are smaller than exo–exo vicinal coupling constants and that the bridge proton syn to the double bond is not always at higher field than the anti bridge proton. Unequal coupling between the bridgehead and bridge protons and the effect of a substituent on the chemical shift of an eclipsed proton are discussed.

The dependence of proton–proton coupling constants on geminal H–C–H and vicinal H–C–C–H dihedral bond angles has been the subject of extensive theoretical and experimental study. The prediction by Karplus[1] that coupling (J) should vary with the dihedral angle ϕ according to a $\cos^2 \phi$ function has been verified in a number of cases, and coupling constants, have been used to identify configurational and conformational isomers.[2–10] Considerable interest has settled on bicyclic molecules such as the norbornanes and norbornenes because of their rigid structures and the interesting possibilities of strain and substituent effects. Several studies of these molecules have disclosed that factors other than the dihedral angle, such as substituent electronegativity, frequently have a pronounced effect on coupling constants.[6,11–15]

Although a number of norbornene compounds have been studied from this point of view, there have been no investigations in which the chemical shifts and coupling constants have been determined by direct proton–proton decoupling. In addition, there have been few studies which clarify the exact effect of *endo–exo* differences on chemical shifts and coupling constants. In this study both the *endo* and *exo* isomers of three 2-substituted norbornenes were completely analyzed by proton–proton decoupling.

Experimental

The compounds employed for this study were subjected to analytical gas chromatography performed on a Wilkens Hy-Fi Model 600-C gas chromatograph using 5-ft. $\times$ $^1/_8$-in. columns packed with Chromosorb W and on a Wilkens Auto-Prep Model A-90P using a 10-ft. $\times$ 0.25-in. column packed with Chromosorb W. Preparative gas chromatographic separations were performed on the latter instrument using 10-ft. and 20-ft. $\times$ $^3/_8$-in. columns using Chromosorb W as a support.

endo- and *exo-*2-carbomethoxybicyclo[2.2.1]hept-5-ene (II*n* and II*x*) were prepared by the Diels–Alder reaction of methyl acrylate and cyclopentadiene in ether at ambient temperature. The individual isomers were obtained by preparative gas chromatography on a 20-ft. column packed with 30% diethylene glycol adipate at 112° (retention times: *exo*, 26 min.; *endo*, 31 min.). These esters showed identical retention times on two analytical columns (diethylene glycol adipate and silver nitrate in 20M Carbowax) with a sample of an authentic mixture (Aldrich Chemical Co.) which has recently become available. The minor isomer was always eluted first. The physical properties of esters II*n* and II*x* do not permit them to be readily distinguished from one another,[16a] but the *endo* isomer (II*n*) is known to be the predominant isomer,[16a] and is reported to be eluted last on an SE-30 gas chromatographic column.[16b]

*endo-*Bicyclo[2.2.1]hept-5-en-2-ol (I*n*) was prepared by saponification of the corresponding acetate with methanolic potassium hydroxide at ambient temperature. The absence of any of the *exo* isomer was shown by gas chromatography (diethylene glycol adipate and XF-1150 columns). The *endo-*2-acetoxybicyclo[2.2.1]-hept-5-ene [b.p. 99–100° (35 mm.); lit.[17a] 74° (11.5 mm.)] was obtained by very careful fractionation of the *endo* and *exo* isomers through a packed column. The *endo* acetate was shown to be free of the *exo* acetate by gas chromatography on a 5-ft. diethylene glycol adipate column at 106° (retention times: *exo*, 17 min.; *endo*, 19 min.). The mixture of *endo* and *exo* isomers was prepared by the Diels–Alder reaction of cyclopentadiene and vinyl acetate at 185–190°.

*exo-*Bicyclo[2.2.1]hept-5-en-2-ol (I*x*) was prepared by hydroboration of bicyclo[2.2.1]hepta-2,5-diene with bis(isoamylborane). The absence of any of the *endo* isomer was shown by gas chromatography (diethylene glycol adipate and XF-1150 columns).

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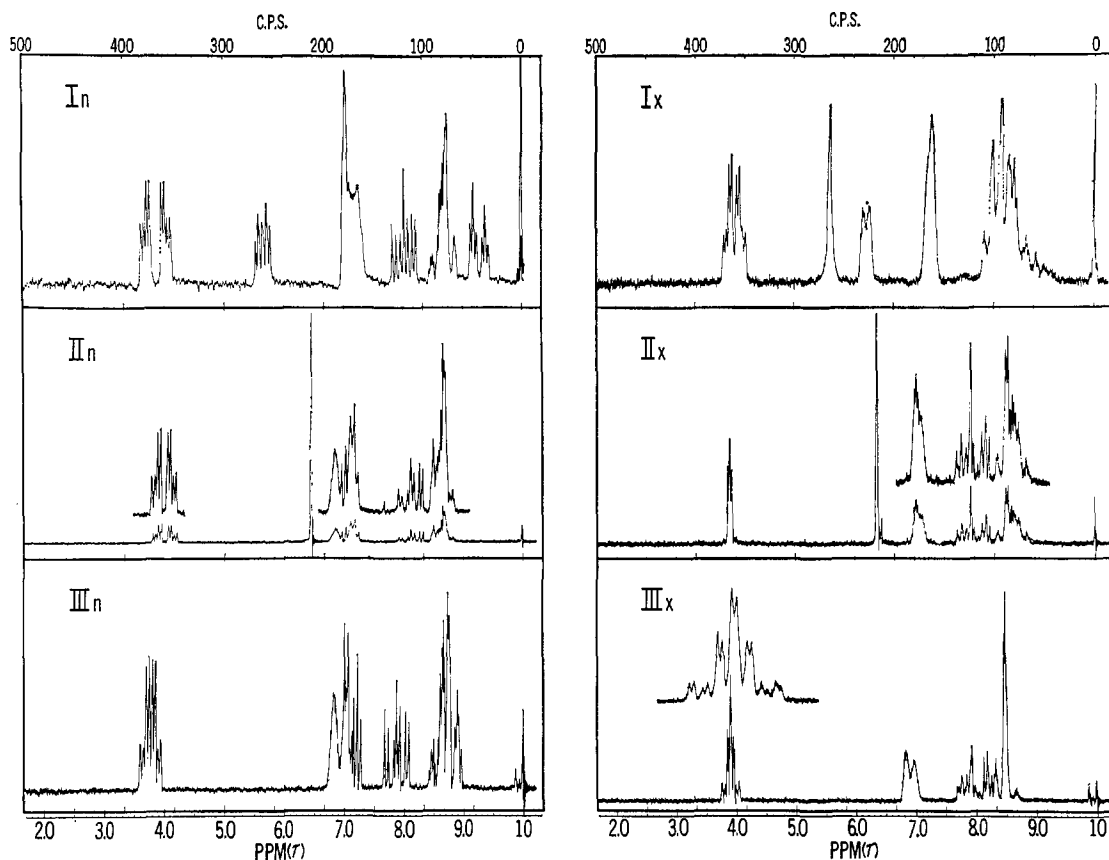
Figure 1. Proton magnetic resonance spectra of *endo-* and *exo-*substituted norbornenes measured at 60 Mc. with TMS as an internal standard.

endo- and *exo-*2-cyanobicyclo[2.2.1]hept-5-ene (III*n* and III*x*) were separated by gas chromatography on a 10-ft. preparative XF-1150 column.[17b]

Spectra of carbon tetrachloride solutions were obtained with a Varian A-60 n.m.r. spectrometer using tetramethylsilane (TMS) as an internal standard. Decoupling was performed at 56.4 Mc. on a Varian Dual-Purpose spectrometer using a Varian V-3521 integrator circuit to modulate and detect the signal at 2020 c.p.s. Phasing and amplitude of the modulation were adjusted to suppress the center-band signal, and all measurements were made with the first low-field side band employing a Hewlitt Packard 200J audio oscillator to provide the decoupling signal. All coupling constants are reported in c.p.s., and chemical shifts are given in c.p.s. below the TMS standard measured at 60 Mc. as well as in τ-values. A number of normal and decoupled spectra were checked with the FREQUINT IV program[18] which was rewritten by us for use on a CDC 1604 computer. The vinyl proton patterns for all of these compounds are consistent with the expected[16b] pattern for the pattern for the assigned (*exo* or *endo*) geometry.

Assignment of Spectral Lines

Spectral features were assigned on the basis of chemical shifts, integrated areas, magnitudes of splittings, and decoupled splitting patterns. In nearly every case it was possible to decouple clearly each pair of interacting protons. In those cases where the proximity of two peaks precluded mutual decoupling their inter-

(18) Dr. A. A. Bothner-By, private communication.

action could be deduced after decoupling of each from other protons in the molecule.

The assigned chemical shifts and coupling constants are listed in Tables I and II, respectively. The normal

Table I. Chemical Shifts[a]

H	I*n*	II*n*	III*n*	I*x*	II*x*	III*x*
1	174	188	190	163	173	190
	(7.10)	(7.00)	(6.83)	(7.28)	(7.12)	(6.82)
2*n*	...	...	...	227	128	131
				(6.22)	(7.83)	(7.82)
2*x*	261	174	171	...	...	...
	(5.65)	(7.10)	(6.15)			
3*n*	48	78	72	75	77	90
	(9.20)	(8.70)	(8.80)	(8.75)	(8.72)	(8.50)
3*x*	118	112	126	103	112	115
	(8.03)	(8.13)	(7.90)	(8.28)	(8.13)	(8.08)
4	164	172	178	163	179	181
	(7.27)	(7.13)	(7.03)	(7.28)	(7.02)	(6.98)
5	359	353	369	355	366	362
	(4.02)	(4.12)	(3.85)	(4.08)	(3.90)	(3.97)
6	376	366	378	365	366	368
	(3.73)	(3.90)	(3.70)	(3.92)	(3.90)	(3.80)
7*s*	85	83	84	82	82	86
	(8.55)	(8.62)	(8.60)	(8.63)	(8.63)	(8.57)
7*a*	73	78	72	93	90	93
	(8.78)	(8.70)	(8.80)	(8.45)	(8.50)	(8.45)

[a] C.p.s. downfield from TMS measured at 60 Mc. Values in parentheses are shifts in τ-units (p.p.m.).

spectra are shown in Figure 1. Chemical shifts in Table I represent the positions of band centers or are calculated from band-center positions and coupling
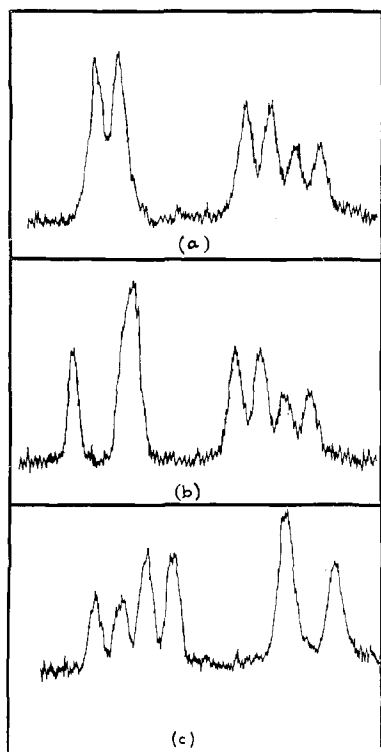
Figure 2. Decoupled spectra of the vinyl resonance of In measured at 56.4 Mc: (a) decoupling frequency at +20 c.p.s. higher field than H$_1$, (b) +188 c.p.s., (c) +179 c.p.s.

Table II. Coupling Constants (c.p.s.)[a]

J	In	IIn	IIIn	Ix	IIx	IIIx
$J_{1,7a} = J_{4,7a}$	1.4	1.3	1.3	1.3	1.4	1.4
$J_{1,7s} = J_{4,7s}$	1.8	1.9	1.9	1.9	1.8	1.8
$J_{2n,7s}$	...	...	...	2.9	3.0	3.0
$J_{3n,7s}$	2.8	3.0	3.1	2.9	3.0	3.0
$J_{5,7a} = J_{6,7a}$	<0.3[b]	0.3[b]	0.4	<0.3	<0.3	0.85
$J_{7a,7s}$	8.4	8.5	8.6	8.5	8.8	?
$J_{1,6}$	2.6	2.8	2.9	2.8	2.8	2.7
$J_{4,5}$	2.9	2.8	2.6	3.0	2.7	3.0
$J_{5,6}$	5.9	5.6	5.6	5.8	?	5.8
$J_{1,5} = J_{4,6}$	...[c]	...[c]	...[c]	...[c]	...[c]	...[c]
$J_{1,2n}$	...	...	...	0	0	0
$J_{1,2x}$	3.5	3.6	3.5	...	...	...
$J_{3n,4}$	0	0	0	0	0	0
$J_{3x,4}$	3.8	3.4	3.6	3.7	3.5	3.4
$J_{1,4}$	0	0	0	0	0	0
$J_{2n,3n}$	...	...	...	5.6	4.4	4.5
$J_{2x,3x}$	8.0	8.8	9.1	...	...	...
$J_{2n,3x}$	...	...	...	3.1	3.8	4.2
$J_{2x,3n}$	3.0	3.4	3.4	...	...	...
$J_{3n,3x}$	12.0	11.8	11.5	12.0	12.3	12.5

[a] All other coupling constants not listed are zero. [b] Coupling was not resolved but was indicated by sharpening of the lines by the decoupling frequency. [c] Not observed in this work but proven by work in ref. 15 to be ~0.5 c.p.s.

constants when possible.[19] Except for the hydroxyl resonance these chemical shifts are relatively insensitive to temperature and concentration changes. In the following discussion the carbon positions and hydrogens will be numbered according to the specialized IUPAC nomenclature for bicyclic terpenes with common names. In addition a letter n is added to the number of a hydrogen to denote an *endo* hydrogen and x is used to denote an *exo* hydrogen. For the 7-hydrogens the letter s specifies the hydrogen *syn* to the double bond and a designates the *anti* hydrogen. The compounds reported are
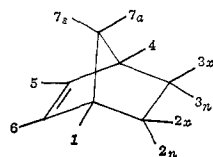
Compound	Substituent	
	2x	2n
In	H	OH
IIn	H	COOCH$_3$
IIIn	H	CN
Ix	OH	H
IIx	COOCH$_3$	H
IIIx	CN	H

An example of the assignment of peaks is afforded by the *endo* alcohol In. The low-field vinyl protons are readily identified as is the peak for the 2x-proton which is shifted downfield by the substituent. The bridgehead protons are identified by their broad patterns re-

(19) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 6.

sulting from several coupling interactions. The bridgehead peak at lower field can be assigned to the 1-proton on the basis of its coupling with the 2x-proton. Decoupling shows no interaction between the higher bridgehead peak and the 2x-peak. The exact assignment of each of the vinyl protons is then possible on the basis of the coupling of one with the 1-bridgehead proton, the other with the 4-bridgehead proton, and their mutual coupling which gives rise to the AB pattern. Decoupling of these interactions is shown in Figure 2. The 3-protons can be assigned through their coupling constants with protons 2 and 4 with one another. The 3x-proton is coupled with both the 2x-proton and the 4-bridgehead proton as well as with the 3n-proton. The 3n-proton shows detectable coupling with the 2x- and 3x-protons but not with the 4-proton. $J_{3n,4}$ is expected to be close to zero because of the unfavorable vicinal dihedral angle.[1]

Several arguments contribute to our assignment of the 7s- and 7a-bridge protons. The small difference in the local environments of these two protons would be expected to lead to slightly different chemical shifts, a typical AB case with additional small splittings by other protons in the molecule. In the alcohol In, as well as in the other *endo* compounds, the low-field half of this AB pattern is further split into sharply discernible features, while in the upper half additional splitting produces broader peaks. Decoupling shows that the low-field pattern is coupled with the peak assigned as 3n as well as with the bridgehead protons. In a similar manner it is possible to decouple the high-field half of the AB pattern from the bridgehead protons and, in the case of the *endo* nitrile IIIn, it is found that this half of the pattern is weakly coupled also to the vinyl peaks. In the *exo* compounds, however, the situation is reversed. The broad featureless peaks are at lower field (*ca.* 20 c.p.s. lower than in the corresponding *endo* compounds) while the sharper peaks have approximately the same chemical shift as in the *endo* isomers. Now it is the low-field half of the AB pattern in IIIx which is coupled with the vinyl protons, and

in all three compounds decoupling experiments verify a coupling between the high-field half and the 2n- and 3n-protons. Inspection of models indicates clearly that the *endo-exo* replacement of the substituent should have a much greater effect on the nearby 7a-proton relative to the much more distant 7s-proton which remains in a more constant environment near the double bond. Hence the sharp low-field pattern in the *endo* isomers which is coupled to the 3n-proton must be the resonance of the 7s-proton since it is not shifted in the *exo* compounds, while the 7a-proton is represented by the high-field peaks in the *endo* compounds and the lower-field peaks in the *exo* isomers.

Discussion

Coupling Constants. Previous studies[13,14,20,21] have found that vicinal coupling constants in norbornanes are smaller on the *endo* side than for the corresponding *exo* side, i.e., $J_{2x,3x} > J_{2n,3n}$. Other studies[7,13,14,22] have found that *exo-exo* couplings in norbornenes ($J_{2x,3x} \simeq 4.1$–8.0 c.p.s.) are approximately the same as those of the saturated compounds ($J_{2x,3x} \simeq 4$–10 c.p.s.), but no measurements of *endo*-vicinal coupling constants have been reported for the unsaturated compounds. The values in Table II show that for norbornenes *endo-endo* couplings are even smaller ($J_{2n,3n} \simeq 4.4$–5.6 c.p.s.) than those in the norbornanes ($J_{2n,3n} \simeq 6$–7 c.p.s.).

The difference in *endo-* and *exo*-vicinal coupling constants cannot be attributed to differences in dihedral angle. The distortions reported for norbornanes[23,24] are not large enough to account for the change according to the most useful theoretical models.[1] Although changes in electronegativity of substituents have been shown to affect coupling constants, this does not seem to be the cause for this difference because the same difference is observed with the same substituent both *exo* and *endo*, and the *trans* coupling ($J_{2x,3n}$ or $J_{2n,3x}$) remains about the same in *endo-exo* pairs showing different vicinal coupling constants. Changes in carbon atom hybridization appear to be ruled out in the same manner. While the differences in *endo-endo* and *exo-exo* couplings might be attributed to differences in the H–C_2–C_3 angle for *exo* and *endo* protons, Musher's suggestion[13] that long-range contributions from the rest of the molecule to couplings are not yet understood seems more likely at present.

Prior studies of norbornenes[14,15] have reported that the bridge protons 7s and 7a couple unequally with the bridgehead hydrogens 1 and 4. In compounds I–III $J_{1,7s}$ (1.8–1.9 c.p.s.) is always larger than $J_{1,7a}$ (1.3–1.4 c.p.s.). Couplings to the 4-bridgehead proton are not measurably different from those to the 1-proton. The idea that the observed difference is caused by a difference in the dihedral angles between the bridgehead hydrogen and each of the bridge hydrogens (ϕ_1 and
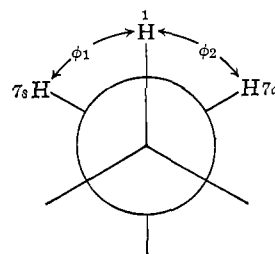

Figure 3. Representation of the dihedral angles ϕ_1 and ϕ_2 between the bridge and bridgehead hydrogens as viewed along the C-1–C-7 bond.

ϕ_2 in Figure 3) was rejected previously on the basis of examination of models.[15] But from Karplus's plot of vicinal coupling constant *vs.* dihedral angle, one finds that the angles corresponding to $J = 1.9$ and 1.4 c.p.s. are 59 and 62°, respectively. Calculations based on the structural data available for norbornanes[23,24] indicate that ($\phi_1 + \phi_2$) should be *ca.* 121°, so that these values for ϕ_1 and ϕ_2 are reasonable. This small change from the undistorted angle might be attributed to a slight flattening of the cyclopentene ring.

Long-range coupling between protons 7s and 3n and between 7s and 2n fall in the range reported for 7s,3n coupling constants.[15,25] This coupling, because of its stereospecificity, is a valuable tool for distinguishing between *syn* and *anti* bridge hydrogens. It can be used in conjunction with the small long-range coupling between the vinyl protons and the bridge proton *anti* to the double bond ($J_{5,7a}$ and $J_{6,7a}$).[14,15] Unfortunately the latter often is not large enough to be detected easily. In the present series only the nitriles IIIn and IIIx showed vinyl bridge coupling clearly. Long-range couplings are a more reliable means of assignment of bridge proton peaks in norbornenes than are chemical shifts, which can be deceptive (see the following section).

In connection with long-range coupling interactions it is important to note that we observed no coupling between the two bridgehead protons. Laszlo and Schleyer[15] also reported no discernible coupling, while King and Butler[26] reported a value of 1.5 c.p.s. for $J_{1,4}$ in norbornene-type compounds. However, the compounds studied by King and Butler differ from those investigated by Laszlo and Schleyer and by us in having an exocyclic double bond on C-7. Our results, then, seem to support the mechanism of Snyder and Franzus[14] for 1,4-coupling in the fragment HCC=CCH.

Chemical Shifts. The chemical shifts of the bridge protons merit particular examination. Recently Snyder and Franzus[14] have shown by studying pairs of 7-substituted norbornenes that the 7-proton *syn* to the double bond appears at higher field than the 7-proton in the epimeric compound. This is not necessarily the case in norbornenes substituted in other positions. On the basis of this study it is apparent that the relative order of the 7s- and 7a-peaks undergoes a shift from the *endo*-substituted compounds to the corresponding *exo* analogs. The sharper 7s-peaks which are

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Table III. Difference in Chemical Shifts[a] of Corresponding Protons in *endo* and *exo* Isomers

| H	(OH) n		x	(CO₂CH₃) n		x	(CN) n		x
1	174	(+)	163	188	(+)	173	190	(0)	190
	(7.10)		(7.28)	(6.86)		(7.12)	(6.84)		(6.84)
2	261	(+)	227	174	(+)	128	171	(+)	131
	(5.65)		(6.22)	(7.10)		(7.86)	(7.15)		(7.82)
3n	48	(−)	75	78	(0)	77	72	(−)	90
	(9.20)		(9.88)	(9.87)		(9.87)	(9.88)		(9.85)
3x	118	(+)	103	112	(0)	112	126	(+)	115
	(8.03)		(8.28)	(8.13)		(8.13)	(7.90)		(8.08)
7a	73	(−)	93	78	(−)	90	72	(−)	93
	(9.88)		(9.85)	(9.87)		(9.84)	(9.88)		(9.85)

[a] Shifts in c.p.s. to lower field from TMS measured at 60 Mc. and in τ-values in parentheses. Positive sign in parentheses indicates the proton of the *exo* isomer appears at higher field.

coupled to the 3n-protons in In–IIIn remain at approximately the same position in Ix–IIIx and in the latter case are coupled to both 2n and 3n. In the *exo* compounds, the broader 7a-peaks have moved downfield to *ca.* 95 c.p.s. and in the case of IIIx the coupling of this proton with the vinyl protons is still observed clearly. It would be reasonable to expect that the change from *endo* to *exo* substituent would have a greater effect on the *anti* bridge proton than on the more distant *syn* proton. On the basis of solvent effects Laszlo and Schleyer[15] assigned the low-field signal (*ca.* 85 c.p.s.) to the 7s-proton of *endo*-2-chloronorborn-5-ene, and the high-field signal (*ca.* 75 c.p.s.) to the 7a-proton. This assignment agrees well with the spectra of all of the *endo* compounds in this study, but it is apparent from the couplings that the 7a-proton appears at lower field than the 7s-proton in the *exo* isomers. It was shown by Snyder and Franzus[14] that for 7-substituted norbornenes a long-range coupling between bridge and vinyl protons was found only with bridge protons which are *anti* to the vinyl protons. Based on this assignment $J_{1,7a} < J_{1,7s}$ for both the *endo* and *exo* compounds.

Table III compares the chemical shifts of the 1-, 2-, 3-, and 7a-protons in each of the isomeric *endo–exo* pairs. Positive and negative signs between the columns show the direction of shift from *endo* to *exo* compound. Several interesting effects are found. The consistent shift downfield of the 7a-proton in the *exo* isomers has been noted. The 3n- and 3x-protons are affected also by the substituent. The 3x-proton is at lower field than the 3n-proton regardless of the nature or position of the substituent. In the case of the hydroxyl and nitrile groups the eclipsed 3-proton, whether *endo* or *exo*, is at higher field than the corresponding proton in the isomeric compound. This is consistent with a positive diamagnetic anisotropy. Unlike the shift of the 2-protons there does not seem to be a strong dependence on the electronegativity of the substituent for either of the 3-protons.

The effect of the carbomethoxy group is novel. The 3n- and 3x-protons show virtually no difference in chemical shift in compounds IIn and IIx. The carbomethoxy group frequently is assumed to have a deshielding effect on nearby protons, and this assumption is used as a basis for peak assignments. While this appears to be true for the 7a-proton it is apparent that additional factors must be important for the 3n- and 3x-protons. In this connection it is worthwhile to re-examine the resonance frequencies assigned by

Frazer[27] to the 3n- and 3x-protons of *endo*-2-carbomethoxy-*exo*-2-methylbicyclo[2.2.1]hept-5-ene (IVn). The 3n- and 3x-peaks of IVn appear at 77 and 115 c.p.s. from TMS. Frazer assigned the signal at 77

IVn   IVx
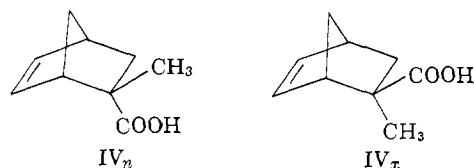
c.p.s. to 3x and that at 115 c.p.s. to 3n. These assignments are contrary to the usual observed order of *endo* protons at higher field than *exo* protons. Laszlo and Schleyer[15] attributed this unusual order to inductive and/or anisotropic effects of the carboxyl group. In the *exo* isomer IVx, the 3x-peak appears at 147 c.p.s. from TMS and that of the 3n-proton at 49.2 c.p.s.[15] In the present study the 3n- and 3x-protons of ester IIn gave signals at 78 and 112 c.p.s., respectively. These frequencies correspond closely to the frequencies observed by Frazer for acid IVn, but the assignments are unequivocally different. It seems possible that the original assignments may have been inverted.

Similar substituent effects are observed with the 1-bridgehead proton. In this case the signal appears at lower field in the *endo* alcohol In and the *endo* ester IIn. The 4-proton peak appears at higher field than the 1-proton, while in the corresponding *exo* compounds both bridgehead protons have approximately the same chemical shift. The nitriles IIIn and IIIx do not show this. The chemical shifts of the bridgehead protons are different from one another in both compounds, but the position of the nitrile group appears to have no effect. The chemical shift of the 2-proton is interesting in that it is always to higher field when it is *endo*. In cyclopropanes, carboxyl groups have been observed to deshield eclipsed protons,[28,29] although a bromine apparently shields an eclipsed proton. Undoubtedly several factors such as substituent electronegativity and the anisotropies of several of the bonds in the molecule are involved, but, because of the small numbers of compounds examined here and because of a lack of uniformity, it would not be wise to generalize

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the findings regarding the effect of substituent on the chemical shifts of adjacent protons until more compounds have been examined.

Nuclear Magnetic Resonance Study of Acetyl Exchange between Acetic Acid and Acetic Anhydride

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The exchange rate of acetyl groups between acetic acid and acetic anhydride was measured using the nuclear magnetic resonance techniques. The exchange is strongly acid catalyzed. The rate of exchange was measured at $22 \pm 1°$ as a function of AcOH, Ac_2O, and $HClO_4$ concentrations using $CHCl_3$ as a diluent. It was found that the exchange rate is proportional to $HClO_4$ concentration, increases with Ac_2O concentration, and for concentrated solutions of AcOH and dilute Ac_2O is independent of AcOH concentration. The experimental results are discussed in terms of four possible exchange mechanisms. Kinetically it is shown that the perchloric acid predominantly protonates acetic acid molecules. Over a limited concentration range where the exchange rate is independent of AcOH concentration, the results can be explained as a bimolecular reaction between a protonated acetic acid molecule $(AcOH_2^+)$ and a neutral acetic anhydride molecule with a rate constant $k = 560$ sec.$^{-1}$ M^{-1}. Outside this range no simple mechanism seems to fit the experimental results.

Introduction

The occurrence of exchange reactions of the acetyl group between aliphatic acids and anhydrides is well known. Evans, Huston, and Norris[1] have studied the exchange reaction in neutral acetic acid–acetic anhydride system, using the carbon labeling technique. They found that the half-life time of the exchange of acetic anhydride in solvent acetic acid is approximately 10 hr. while that of acetic acid in solvent anhydride is 5 hr.

The exchange reaction between acetic acid and acetic anhydride is strongly acid catalyzed and at appreciable acid concentrations becomes so fast that its investigation by isotope labeling techniques becomes impossible. In the work reported here the nuclear magnetic resonance (n.m.r.) technique, which was previously applied to the study of hydrogen exchange,[2] was used for the investigation of the acetyl group exchange in this system.

The exchange rate was measured as a function of the concentration of perchloric acid, of acetic acid, and of acetic anhydride.

The acetic acid–acetic anhydride system is important as an acetylating agent. The acetylation reaction is catalyzed by perchloric acid. The kinetics of this reaction is discussed by Mackenzie and Winter,[3] and by Burton and Praill.[4] These authors assumed that the exchange of an acetyl group between acetic acid and acetic anhydride, which results in the formation of an Ac^+ ion, is the first step in the acetylation reaction.

Experimental

The main features of the n.m.r. spectrometer have been described previously.[5] The proton frequency was 31.6 Mc.p.s. The sample holders used were cylindrical glass tubes of about 3-mm. d. They were rotated by a small air turbine. The field homogeneity was such that an effective T_2 in water of about 1.2 sec. was observed from the decay of the "wiggles" on fast passage.

Reagents and Preparation of Solutions. B.D.H. acetic acid and chloroform A.R. were used without further purification. The acetic anhydride was Baker and Adamson, ACS grade, and was distilled once. The perchloric acid was 70% A.R., supplied by Mallinckrodt. Its titer was determined by titration against NaOH, using methyl orange as the indicator.

To study the dependence of exchange rate on the concentration of the different species, solutions were prepared in series, the members of each series differing only in the concentration of a single component. The preparation procedure was as follows: for each such series two stock solutions, differing only in the concentration of one of the components, were prepared. By mixing known quantities of the two stock solutions, a series of varying concentration in the desired species was obtained, while the concentration of all the others remained constant. For example, for measuring the dependence of the rate of exchange with respect to

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