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^{13}C NMR Studies of Some Tricyclo[3.2.1.$0^{2,4}$]octanes

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The ^{13}C NMR chemical shifts for a series of *exo*- and *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octanes are reported. Comparisons with the parent *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octanes and with bicyclo[2.2.1]heptanes show that most of the chemical shifts are additive. Substituent effect constants are presented for the tricyclo[3.2.1.$0^{2,4}$]octyl system. Pronounced deshielding effects are seen in the *endo* series for C-6 and -7 of the alkene *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene, the epoxide *endo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octan-6,7-*exo*-oxide, and the tetracyclic *endo,exo*-3,3-diphenyltetracyclo[3.3.1.$0^{2,4}0^{6,8}$]nonane. The chemical shifts of C-3 and -8 are diagnostic for *endo vs. exo* substitution.

KEY WORDS ^{13}C NMR Tricyclo[3.2.1.$0^{2,4}$]octanes Substituent effects Geminal diphenyl

INTRODUCTION

Norbornanes and related polycyclic compounds have been used for ^{13}C NMR studies because their rigid structures allow detailed examination of the geometric and distance dependence of ^{13}C shieldings,[1] and data are already available on norbornanes,[1,2] bicyclo-[2.2.2]octanes,[3] and bicyclo[3.2.1]octanes.[1b,4] The shielding effect of cyclopropyl groups has been explored through the use of tricyclo[3.2.1.$0^{2,4}$]octanes.[5]

As part of another study, we have been investigating the effect of geminal diphenyls on the ^{13}C shieldings in a series of derivatives of *endo*- and *exo*-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]octanes, **1nD** and **2xD**, respectively. We report here the ^{13}C NMR spectra for these two series of compounds and a set of substituent effects that work fairly well for these two series and for the previously reported[5] parent compounds.

All the odd-numbered compounds have *endo*-cyclopropyl rings and all the even-numbered compounds have *exo*-cyclopropyl rings. These designations are reinforced by an appended **n** or **x**. The diphenyl-substituted compounds are designated by means of a **D** and the hydrogen series is designated by the use of an **H**. Figure 1 lists the structures of interest and Fig. 2 gives the numbering system used. (The designation of C-9 in the tetracyclics is not correct by the IUPAC Convention, but is convenient because all other compounds are tricyclic.)

The syntheses of tricyclic alkenes **3nD**[6] and **4xD**[7] have already been reported, together with those of derivatives **2xD**,[7] **6xD**,[7] **8xD**[7] and **10xD**.[7] The tetracyclic compound **12xD** was prepared from **4xD** using the Simmons–Smith procedure 5b.

The diphenyl alkane **1nD**, the *exo*-epoxide **5nD**, the *exo*-6 alcohol **7nD** and the tetracyclic compound **11nD** were prepared from the tricyclic **3nD** in standard fashion.[7] The 6-ketone **9nD** was prepared by pyridinium chlorochromate oxidation of alcohol **7nD**.

EXPERIMENTAL

All IR spectra were run on a Beckman Acculab 1 spectrometer. Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Combustion analyses were done by Microtech Laboratories, Skokie, IL. All ^{13}C NMR spectra were obtained at 20 MHz on a 24K Varian FT-80 NMR spectrometer at room temperature using approximately 0.3 M $CDCl_3$ solutions with chemical shifts referred to internal TMS. Normal ^{13}C spectra were recorded with square-wave decoupling, a pulse angle of 37° and an acquisition time of 1.023 s for an 8K data table with a 4000 Hz spectral width. Chromium acetonylacetonate was added to some samples to enhance the quaternary carbon signals. Routine ^{1}H NMR spectra were obtained at 60 MHz on the same solutions with a Varian EM-360 or EM-360A spectrometer. COSY and HETCOR 2D NMR spectra were run on a Varian VXR-300 spectrometer using 1024 data points in each dimension with the standard program supplied by Varian. The 2D NMR spectra were interpreted from contour plots.

Substituent effects were calculated with the use of a spreadsheet on a personal computer. For each carbon in each series, the sum of the chemical shift of the unsubstituted polycyclic alkane of the same geometry plus any added substituent effects was subtracted from the observed shift. The standard deviations of the average differences between observed and calculated chemical shifts were computed and then the substituent effect values varied until the differences and deviations were minimized.

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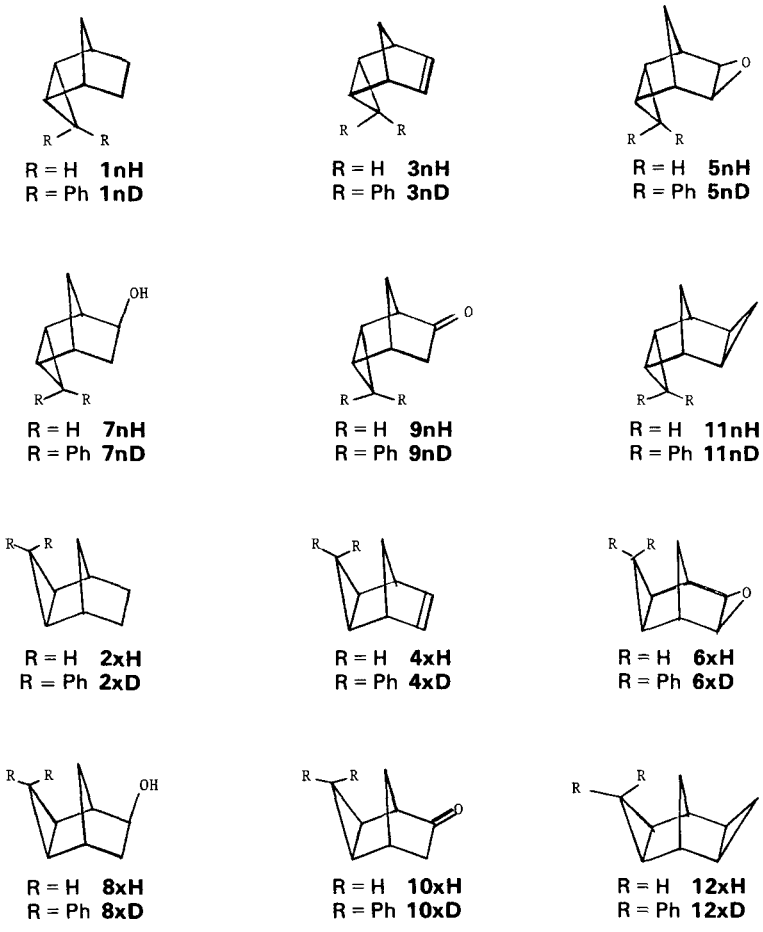

Figure 1. Tricyclo[3.2.1.$0^{2,4}$]octanes used in this study.

Compounds

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octane (1nD).** Diimide reduction of **3nD** using 0.5 mmol each of **3nD** and potassium azodicarboxylate afforded 494 mg (95%) of white crystals of **1nD**; m.p. 126–127 °C; IR ($CHCl_3$), 3060, 3000, 2960, 2920, 2870, 1950, 1600, 1490, 1445, 1315 cm^{-1}; NMR ($CDCl_3$), δ 0.90–1.63 (3H m), 1.93 (2H m), 2.57 (2H t), 6.83–7.73 (10H m). Analysis: calculated for $C_{20}H_{20}$, C 92.26, H 7.74; found, C 92.30, H 7.73%.

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-*exo*-6-ol (7nD).** Hydroboration of **3nD** with borane in THF, followed by oxidation with hydrogen peroxide, yielded 1.059 g (96%) of colorless crystals of the *exo*-alcohol **7nD**; m.p. 143–144 °C; IR ($CHCl_3$), 3600, 3540–3200, 3080, 3000, 2960, 2865, 1950, 1600, 1490, 1450, 1310 cm^{-1}; NMR ($CDCl_3$), δ 0.9 (1H d), 1.33 (1H br s), 1.73 (1H d), 2.00 (4H br s), 2.5–2.87 (2H cm), 3.83 (1H dd), 6.97–7.80 (10H m). Analysis: calculated for $C_{20}H_{20}O$, C 86.92, H 7.29; found, C 87.07, H 7.28%.

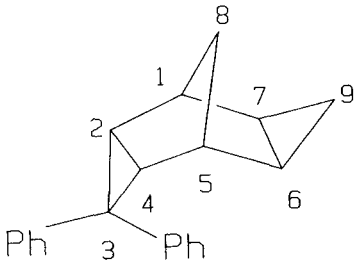

Figure 2. Numbering system used in this study.

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-6-one (9nD).** Pyridinium chlorochromate oxidation of the *endo*-alcohol **7nD** yielded 132.9 mg (97%) of ketone **9nD** as colorless crystals; m.p. 132.5–133.5 °C; IR ($CHCl_3$), 3020–2920, 2880, 1960, 1750, 1600, 1500, 1455, 1420 cm^{-1}; NMR ($CDCl_3$), δ 1.47–1.77 (2H m), 1.87 (2H br s), 2.17–2.57 (2H m), 2.77–3.10 (2H m), 6.80–7.50 (10H m). Analysis: calculated for $C_{20}H_{18}O$, C 87.56, H 6.61; found, C 87.69, H 6.62%.

***endo*-3,3-Diphenyltricyclo[3.2.1.$0^{2,4}$]octan-6,7-*exo*-oxide (5nD).** Oxidation of **3nD** with *m*-chloroperoxybenzoic acid gave 221.9 mg (81%) of the epoxide **5nD** as a white solid; m.p. 134.5–136.5 °C; IR ($CHCl_3$), 3060–2960, 1950, 1600, 1490, 1445, 1370, 1100 cm^{-1}; NMR ($CDCl_3$), δ 1.42 (1H d, J = 9 Hz), 1.82 (1H d, J = 9 Hz), 2.10 (2H t, J = 2 Hz), 2.57 (2H br s), 2.90 (2H m), 6.90–7.76 (10H m). Analysis: calculated for $C_{20}H_{18}O$, C 87.56, H 6.61; found, C 87.88, H 6.59%.

***endo,exo*-3,3-Diphenyltetracyclo[3.3.1.$0^{2,4}0^{6,8}$]nonane (11nD).** The tetracyclic nonane **11nD** was prepared by the Simmons–Smith reaction. Diethylzinc and diiodome-

thane were added to a solution of **3nD** in benzene. Workup of the reaction mixture gave 579.4 mg (71%) of **11nD** as a white solid; m.p. 107–108 °C; IR ($CHCl_3$), 3100–2880, 1950, 1890, 1600, 1485, 1445, 1330 cm^{-1}; NMR ($CDCl_3$), δ −0.28 (1H d of d, J_{gem} = 12.5 Hz, J_{cis} = 7.1 Hz, *anti*-H-9), 0.30 (2H d of d, J_{cis} = 7.1 Hz, J_{trans} = 2.8 Hz, H-6,7), 0.34 (1H m, J_{trans} = 2.8 Hz, *syn*-H-9), 1.28 (1H d, J_{gem} = 9.5 Hz, H-8), 1.41 (1H d, J_{gem} = 9.5 Hz, H-8), 1.93 (2H t, J = 2 Hz, H-2,4), 2.63 (2H bs, H-1,5), 6.96–7.18 (6H m, ArH), 7.27 (2H d of d, J_o = 7.8 Hz, *o*-ArH), 7.58 (2H d of d, J_o = 7.2 Hz, *o*-ArH). Analysis: calculated for $C_{21}H_{20}$, C 92.60, H 7.40; found, C 92.82, H 7.44%.

***exo,exo*-3,3-Diphenyltetracyclo[3.3.1.0^{2,4}0^{6,8}]nonane (12xD).** The same procedure as for **11nD** was used on **4xD** to give 718.1 mg (88%) of crystals of **12nD**; m.p. 93–93.5 °C; IR ($CHCl_3$), 3000, 2950, 1950, 1890, 1600, 1490, 1450, 1310 cm^{-1}; NMR ($CDCl_3$, 300 MHz), δ 0.19 (1H d, J_{gem} = 13.1 Hz, H-8 *anti* to diphenylcyclopropane), 0.25 (1H occluded q, *anti*-H-9), 0.31 (1H d, J_{gem} = 13.1 Hz, H-8 *syn* to diphenylcyclopropane), 0.72 (1H m, J_{trans} = 2.8 Hz, *syn*-H-9), 1.03 (2H d of d, J_{trans} = 2.8 Hz, J_{cis} = 4.1 Hz, H-6,7), 1.78 (2H pseudo s, H-2,4), 2.57 (2H s, H-1,5), 7.03–7.57 (10H m, ArH). Analysis: calculated for $C_{21}H_{20}$, C 92.60, H 7.40; found, C 92.60, H 7.48%.

RESULTS AND DISCUSSION

Assignments were made on the basis of relative signal intensities, comparison with the parent compounds,[5] the use of C-13 substituent effects for phenyl substitution[8] and substituent effects for bicyclo-[2.2.1]heptanes,[1a] and by comparison with the assignments on **11nD** and **12xD** where both proton and carbon assignments were confirmed by COSY and HETCOR 2D NMR. Detailed assignments of the 300 MHz proton NMR spectra of **11nD** and **12xD** are provided under Experimental, but the *syn* and *anti* assignments for H-8 in **11nD** should be considered tentative as the COSY results were not conclusive.

Carbon assignments for olefinic, unsubstituted cyclopropyl, oxirane and carbonyl carbons were straightforward. Although protonated and quaternary aromatic carbons were easy to identify and are reported in Table 1, we did not attempt detailed assignments for aromatic carbons.

The signal for C-3, the quaternary cyclopropyl carbon bonded to the two phenyl groups, was absent in the HETCOR spectra and was assigned for the other molecules on the basis of its intensity and its chemical shift as predicted by adding the substituent effect[8] of two phenyls on a branched alkane to the shift of the parent compounds. In the tetracyclic nonanes **11nD** and **12xD**, C-9, the secondary cyclopropyl carbon, was assigned to the most shielded carbon signal. HETCOR allowed the assignment of the H-9 protons. C-2 and -4 and C-1 and -5 were readily assigned from HETCOR spectra and for the other molecules based on intensity and by comparison to parent compounds[5] with the addition of β and γ shifts from the phenyl rings[8] and norbornane substituent shifts.[1a]

With the exception of the carbonyl carbon in **9nD**, the chemical shifts of C-6 and -7 of the *endo*-diphenyl series were all shielded by 2–7 ppm from the corresponding *exo*-diphenyl compounds, but C-8 was significantly more shielded in the *exo* than in the *endo*-diphenyl compounds. This shift of C-8, together with previous assignments, helped us to distinguish between C-6, C-7 and C-8 in the unsymmetrical compounds **7nD** and **8xD** where there was some ambiguity.

Table 1 lists the carbon chemical shifts for the diphenyl tricyclic compounds. Although chemical shift calculations were carried out with norbornane substituent shifts for assignment purposes, it was clear that more accurate substituent constants could be derived for the tricyclo[3.2.1.0^{2,4}]octyl system by first calculating the effect of the 3,3-diphenyl groups on saturated *endo*- and *exo*-alkanes **1nD** and **2xD**, respectively. These results were then combined with ^{13}C substituent shifts for the other functional groups, which were calculated from the parent series.[5] The differences between the observed and calculated shifts were then calculated on a spreadsheet as explained under Experimental. Table 2 lists these new substituent effects for the tricyclo[3.2.1.0^{2,4}]octyl systems. We note that they are similar to Lippmaa's values for norbornanes.[1a] We also note that they are different from the few values reported[1b] for the bicyclo[3.2.1]octanes. Part of the differences between these new substituent values and the norbornyl values can be explained by the effects of *endo*- and *exo*-cyclopropyl groups discussed by Cheng and Stothers[5] for the parent hydrogen compounds. The numbers in parentheses in Table 1 are the differences between the observed and the calculated chemical shifts using this new set of substituent effect values, which were added to the shifts of the parent tricycloalkane of appropriate stereochemistry.

Geminal diphenyl substitution resulted in the expected downfield shift for C-3 compared with the unsubstituted cases, but the shift was greater than the prediction[8] of 34 ppm derived by doubling the substituent effect for phenyl on a branched alkanes. The average shifts for C-3 compared with the parent compounds were greater for the *endo* (39.9 ± 2.0 ppm) than for the *exo* (37.1 ± 1.1 ppm) compounds. Since we felt that the α shift should be independent of geometry, we used an average value for geminal diphenyls of 37.5 ppm, which minimized the calculated error for the parent alkane of both series. Although C-3 shifts are well calculated in the *exo* series, in the *endo* series only the alkene **3nD** and the ketone **9nD** shifts are close. The interference of the hydrogens from sp^3 carbons with the *endo*-phenyls is substantially greater and hence the substituent shifts are not additive.

The β effect of the phenyls on C-2 and C-4 is different for the two series (12.8 ppm for the *endo* series and 14.7 ppm for the *exo* series), but is in the predicted[9] range of 14 ppm. The γ effect at the bridgeheads is 3.0 ppm for the *endo* series and 0.7 ppm for the *exo* series. The δ effect was expected to be position-dependent. The *endo* series had −1.5 ppm for C-6 and -7 and 2.7 ppm for C-8. The values are also different in the *exo* series with 1.3 ppm for C-6 and -7 and 3.2 ppm for C-8.

In the *endo*-diphenyl series, C-6 and -7 showed deshielding for the alkene **3nD**, the epoxide **5nD** and the

Table 1. ^{13}C NMR shifts[a] of 3,3-diphenyltricyclo[3.2.1.0^{2,4}]octanes

													Aromatic				
				endo series													
Compound	C-1	C-5	C-2	C-4	C-3	C-6	C-7	C-8	C-9	*para*	*para*	Other aromatics				*ipso*	*ipso*
1nD	39.6	39.6	35.9	35.9	57.3	25.3	25.3	56.2		125.6	126.3	127.2	127.5	128.2	131.3	140.5	151.0
	(0.0)[b]	(0.0)	(0.0)	(0.0)	(2.1)	(0.0)	(0.0)	(0.0)									
3nD	44.0	44.0	32.1	32.1	54.9	135.0	135.0	66.2		125.2	125.7	127.7	127.8	128.3	129.9	143.0	149.2
	(−1.3)	(−1.3)	(6.9)	(6.9)	(0.3)	(6.0)	(6.0)	(−0.2)									
5nD	39.7	39.7	34.9	34.9	56.6	53.3	53.3	43.0		126.0	126.5	127.4	127.9	128.4	129.3	145.3	149.1
	(1.2)	(1.2)	(3.0)	(3.0)	(4.9)	(5.4)	(5.4)	(−1.6)									
7nD	37.8	47.5	33.4	33.1	57.0	70.9	38.6	52.3		125.8	126.6	127.4	127.7	128.3	131.1	140.7	150.5
	(−1.4)	(0.8)	(0.3)	(1.7)	(2.5)	(0.0)	(1.1)	(0.5)									
9nD	36.9	53.2	33.8	33.4	56.3	215.3	42.3	54.7		126.2	127.2	127.3	127.5	128.4	131.2	131.4	137.7
	(−0.2)	(−0.5)	(−0.5)	(1.9)	(0.2)	(1.2)	(1.4)	(0.5)									
11nD	38.6	38.6	35.7	35.7	57.0	16.3	16.3	42.2	5.3	125.6	126.8	127.0	127.7	128.2	129.8	144.3	150.4
	(0.5)	(0.5)	(1.6)	(1.6)	(4.5)	(5.5)	(5.5)	(−1.9)									
					exo series												
2xD	36.4	36.4	31.8	31.8	36.4	31.1	31.1	30.0		125.3	125.7	127.7	127.9	128.6	129.1	142.6	148.1
	(0.0)	(0.0)	(0.0)	(0.0)	(−2.1)	(0.0)	(0.0)	(0.0)									
4xD	43.0	43.0	41.6	41.6	57.7	142.1	142.1	37.6		125.7	126.1	127.4	128.2	128.8	129.1	142.9	148.3
	(0.8)	(0.8)	(2.6)	(2.6)	(1.0)	(−0.4)	(−0.4)	(−3.1)									
6xD	37.7	37.7	30.6	30.6	44.7	55.1	55.1	16.5		126.0	126.2	127.7	128.4	128.4	129.1	142.9	147.6
	(0.1)	(0.1)	(−1.2)	(−1.2)	(0.1)	(−1.8)	(−1.8)	(0.1)									
8xD	36.1	44.6	32.4	28.0	40.7	74.5	43.5	27.3		125.8	126.1	127.9	128.3	128.9	129.0	142.5	147.8
	(0.2)	(0.2)	(−0.4)	(−0.5)	(−0.9)	(−1.2)	(−0.8)	(1.0)									
10xD	35.5	49.3	32.7	24.4	43.1	212.4	45.4	29.4		126.3	126.6	127.7	128.5	128.9	129.3	141.8	146.6
	(0.4)	(0.6)	(−1.0)	(−2.1)	(0.2)	(−3.3)	(−0.4)	(1.1)									
12xD	36.5	36.5	35.5	35.5	43.2	18.9	18.9	17.7	6.3	125.6	127.9	128.2	128.5	128.7	128.9	143.6	148.5
	(−0.1)	(−0.1)	(−0.5)	(−0.5)	(−0.6)	(−1.3)	(−1.3)	(0.2)									

[a] In ppm from internal TMS.
[b] Numbers in parentheses are δ(obs.) − δ(calc.).

Table 2. Substituent effects for tricyclo[3.2.1.0^{2,4}]octanes

Substituent	C-1	C-5	C-2	C-4	C-3	C-6	C-7	C-8	C-9
					endo series				
3,3-DiPh	3	3	12.8	12.8	37.5	−1.5	−1.5	2.7	3.4
6,7-C=C	5.7	5.7	−10.7	−10.7	−0.6	103.7	103.7	10.2	
exo-6,7-O	−1.1	−1.1	−4	−4	−3.5	22.6	22.6	−11.6	
exo-6-OH	−0.4	7.1	−2.8	−4.5	−0.7	45.6	12.2	−3.4	
6-C=O	−2.5	14.1	−1.6	−4.4	0.9	188.8	15.6	−1	
exo-6,7-C	−1.5	−1.5	−1.8	−1.8	−2.7	−14.5	−14.5	−12.1	
					exo series				
3,3-DiPh	0.7	0.7	14.7	14.7	37.5	1.3	1.3	3.2	0
6,7-C=C	5.8	5.8	7.2	7.2	18.2	111.4	111.4	10.7	
exo-6,7-O	1.2	1.2	0	0	6.1	25.8	25.8	−13.6	
exo-6-OH	−0.5	8	1	−3.3	3.1	44.6	13.2	−3.7	
6-C=O	−1.3	12.3	1.9	−5.3	4.4	184.6	14.7	−1.7	
exo-6,7-C	0.2	0.2	4.2	4.2	5.3	−10.9	−10.9	−12.5	

tetracyclic **11nD**. This was a surprise because we had expected to see shielding for C-6 and -7 from the γ effect[8] and the anisotropy of the *syn* phenyl ring. However, the phenyl ring signals are symmetrical in the ^{13}C NMR spectrum, so rotation about the *endo*-phenyl—cyclopropyl bond must be rapid on the NMR time scale, and the net effect on C-6 and C-7 is deshielding. Perhaps the deshielding effect is greater because the edge of the ring is closer to C-6 and -7 during rotation; however if that were true, it should hold for all the compounds. Inspection of models suggests that there would be considerable overlap between the π lobes of the *syn* phenyl ring and the π lobes of the alkene carbons. This is supported by the discovery that the products of electrophilic addition on the *endo*-alkene have a new bond formed between the alkene carbon and the *ortho* position on the *syn* phenyl ring.[9] Similar overlap could occur between the strained cyclopropyl and epoxy bonds and the π lobes of the *syn* phenyl ring. The deshielding could occur because of transfer of electron density from the π lobes of the alkene or the strained bonds of the cyclopropyl and epoxy groups via direct overlap to the aromatic π lobes of the ring. A similar deshielding is seen for C-2 and C-4 in the same molecules.

One can simply distinguish between the *endo* and *exo* series by examining the corrected chemical shifts of C-3 and -8 after subtracting any directly bonded substituent shifts. If the corrected chemical shift for C-8 is between 41 and 67 ppm and that for C-3 is between 14 and 21 ppm, the cyclopropyl ring is probably *endo*. If the corrected chemical shift for C-8 is between 13 and 38 ppm and for C-3 is from −2 to 7.2 ppm, the cyclopropyl ring is probably *exo*. In the tetracyclic nonanes **12xD**, **12xH**, **11nD** and **11nH**, one can clearly assign the *endo*- and *exo*-cyclopropyl methylene carbons using this idea. It is interesting that the chemical shift for C-8 in **11nD** and **11nH** fits into the *endo* classification, although there is both an *endo*- and an *exo*-cyclopropyl group in each molecule. The only exceptions that we have discovered to this generalization are the shifts of C-3 for the *exo*-alkenes **4xD** and **4xH** which, at 20 and 19.2 ppm, respectively, are strongly deshielded by the remote double bond. We have been using these substituent constants and this assignment technique quite successfully on new 8-substituted 3,3-diphenyltricyclo[3.2.1.0^{2,4}] octanes.

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REFERENCES

1. (a) E. Lippmaa, T. Pekh, J. Paasivirta, N. A. Belikova and A. Plate, *Org. Magn. Reson.* **2**, 581 (1970); (b) E. Lippmaa, T. Pekh, N. A. Belikova, A. A. Bobyleva, A. N. Kalinichenko, M. D. Ordubadi and A. F. Plate, *Org. Magn. Reson.* **8**, 74 (1976); (c) A. P. Marchand, *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*. Verlag Chemie, Deerfield Beach, FL (1982).
2. (a) R. Bicker, H. Kessler and G. Zimmermann, *Chem. Ber.* **111**, 3200 (1978); (b) G. S. Poindexter and P. J. Kropp, *J. Org. Chem.* **41**, 1215 (1976); (c) J. B. Stothers, C. T. Tan and K. C. Teo, *Can. J. Chem.* **54**, 1211 (1976).
3. (a) J. B. Stothers and C. T. Tan, *Can. J. Chem.* **54**, 917 (1976); (b) P. J. Garrat and R. J. Riguera, *J. Org. Chem.* **41**, 465 (1976); (c) G. E. Maciel and M. C. Dorn, *J. Am. Chem. Soc.* **93**, 1268 (1971).
4. J. B. Stothers and C. T. Tan, *Can. J. Chem.* **55**, 841 (1977).
5. A. K. Cheng and J. B. Stothers, *Org. Magn. Reson.* **9**, 355 (1977).
6. J. W. Wilt and D. R. Sullivan, *J. Org. Chem.* **40**, 1036 (1975).
7. J. W. Wilt and T. P. Malloy, *J. Org. Chem.* **38**, 277 (1973).
8. F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*. Heyden, London (1976).
9. J. Wilt and M. Peeran, in preparation.