^{13}C–H Coupling Constants in Cyclic Systems; a Probe for Hyperconjugation and Homoconjugation?

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^{13}C–H coupling constants have been determined for bicyclic and tricyclic carbonyl compounds. In comparison to acyclic and monocyclic ketones these systems show an increase in the coupling constant at the bridgehead alpha to the carbonyl group.

Les constantes de couplage ^{13}C–H ont été déterminées dans le cas de composés bicycliques et tricycliques comportant une fonction carbonyle. Par comparaison avec des cétones acycliques ou monocycliques, ces systèmes ont montré une augmentation de la constante de couplage pour la position en tête de pont alpha du groupe carbonyle. [Traduit par le journal]

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Introduction

The correlation between hybridization and coupling constant for directly bonded ^{13}C—H and ^{13}C—^{13}C nuclei has provided an experimental tool for the estimation of s character in a carbon–hydrogen or carbon–carbon bond (1–10). In this area experimental and theoretical studies (11–13) have centered mainly on alicyclic hydrocarbons to avoid substituent effect problems.

Our study of the chemistry of bicyclic diones (14) has necessitated that we obtain hybridizational and conformational information on these systems. To that end a study of ^{13}C–H and ^{13}C–^{13}C coupling constants in bicyclic and tricyclic systems has been undertaken to ascertain whether or not the coupling constants are hybridizational probes in the presence of polar groups.

Results and Discussion

This communication reports the coupling constants for C_1—H, C_3—H, and C_4—H in **1**–**16**. The data are listed in Table 1.

TABLE 1. ^{13}C–H coupling constants*

Substrate	C-1	C-3	C-4
1	142 ± 1	130 ± 2	142 ± 1
2	152 ± 1	134 ± 1	142 ± 2
3	157 ± 1		157 ± 1
4	142 ± 1		142 ± 1
5	153 ± 1	138 ± 1	155 ± 1
6	155 ± 1	130 ± 2	144 ± 2
7	144 ± 2		139 ± 2
8	152 ± 1		142 ± 2
9			150 ± 2
10	159 ± 1		158 ± 1
11	155 ± 1		143 ± 2
12		134 ± 2	143 ± 1
13			159 ± 1
14	152 ± 1		152 ± 1
15	144 ± 1		144 ± 1
16	141 ± 1		133 ± 2

*The ^{13}C shift assignments for a majority of the substrates have been reported previously (15–17).

That the difference between J_{C_1-H} and J_{C_4-H} in ketones **2** and **8**, and the thione **11** as well as J_{C_4-H} in **8** and **9** is not accountable directly in terms of an inductive effect is established by the following facts. The J_{C-H} values (CH_3-) for ethane, acetone, and acetophenone are 126, 127, and 127 Hz, respectively (12). Also, Ellis and Maciel (8) have shown that J_{C-H} alpha to the carbonyl group in 2,2-dimethylcyclopropanone (160), cyclobutanone (134.8), and cyclopentanone (129.5), respectively, is identical to J_{C-H} for the corresponding precursor hydrocarbon (cyclopropane, 161; cyclobutane, 134.6; cyclopentane, 128.5). Interestingly, a correlation, which utilizes the Swain–Lupton F (field effect) values (18) for $-I^+$ and $-I^-$ groups (12), provides information about the influence of inductive effects on J_{C-H}. The plot of J_{C-H} *vs.* the F values (Fig. 1) for a series of substituted methanes CH_3—X, where X is a $-I^+$ or $-I^-$ group, establishes that distinct correlations exist for the two types of substituents. The plot for the latter is located at a constant 15–20 Hz below the $-I^+$ plot. Thus, although the same sensitivity to $-I^+$ and $-I^-$ substituents is indicated, there must be either an attenuation of the inductive effect or there are

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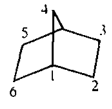

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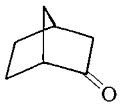

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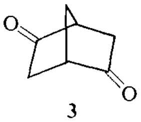

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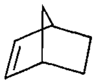

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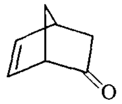

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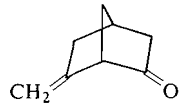

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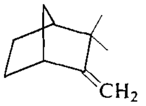

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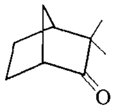

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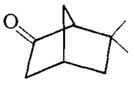

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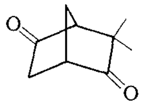

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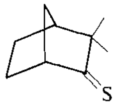

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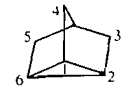

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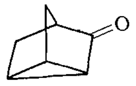

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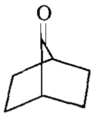

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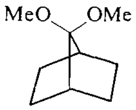

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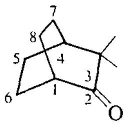

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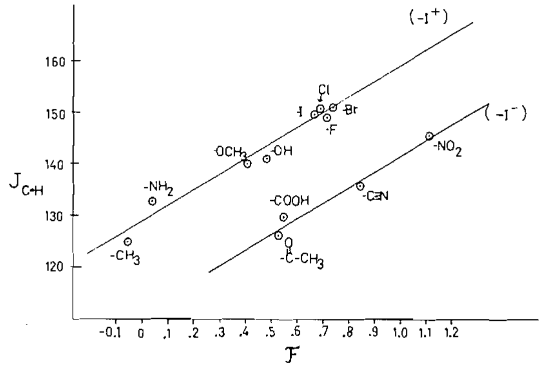

FIG. 1. Plot of J_{C-H} (H—CH$_2$—X) *vs.* the field effect values *F*.

other unknown factors which operate by a constant factor to decrease J_{C-H}. Conceivably, hyperconjugative interaction between C—H bonds and the π system of the $-I^-$ substituent (19) could contribute to the attenuation constant. Nevertheless, the correlations support the contention that $-I^+$ and $-I^-$ substituents interact differently with C—H bonds.

Strain effects also do not account adequately for the increase in J_{C-H} at the bridgehead since J_{C_4-H} and J_{C_3-H} in the [2.2.1]-system are insensitive to the total strain energy.[2] That is, while the strain energy (20) increases through the series **1**, **4**, and **12** (18.4, 22.8, 42.9 kcal/mol, respectively) the change in J_{C_4-H} is minimal. Compare also J_{C_3-H} for **1** and **12**. Furthermore, a comparison of the C–H coupling constants (alpha to the carbonyl) and strain energies (SE) (21) for cyclobutanone, cyclopentanone, and norcamphor with those of the parent hydrocarbons establishes that there is no correlation between ΔJ and Δ(SE).

Several factors may contribute to the unexpected increase in J_{C_1-H} in **2**, **3**, **8**, **9**, **10**, **11**, and **14** and J_{C_4-H} in **13**. Conceivably, hyperconjugative interaction between the appropriate strained σ bond and the carbonyl or thiocarbonyl is important and alters the hybridization at C-1 and C-4. Interestingly, Olah *et al.* (22) have reported a J_{C_1-H} value of 152 ± 5 Hz for the 2-phenylnorbornyl cation. Also, while the effect of a benzoyl group on J_{C-H} in a methyl group is minimal (*vide supra*) there is an increase of 11 Hz

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[2] It is understood that not all the "strain" in each case is located in the bridgehead bonds.

TABLE 2. Coupling constant and strain energy differences

	SE			
Substrate	Ketone	Hydrocarbon	Δ(SE)	ΔJ*
Cyclobutyl	29.03	27.17	1.86	0
Cyclopentyl	6.40	7.53	—1.13	0
Bicyclo[2.2.1]heptyl	18.54	17.90	0.64	10±2†

*Alpha to the carbonyl group.
†At C-1.

TABLE 3. ^{1}H chemical shifts (p.p.m.)

Substrate	H-1	H-4	H-5	H-6	Reference
Norcamphor	2.39	2.54			26
Nortricyclane		1.91			23
Nortricyclanone		1.80			
Norbornene	2.81	2.81	5.93	5.93	27
Norbornenone	2.87	3.14	6.54	6.09	27

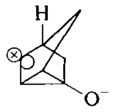
in $J_{\alpha C-H}$ and $J_{\beta C-H}$ in the conjugated system benzoylcyclopropane (173 Hz) over cyclopropane (162 Hz) (23). Possibly, the attenuating hyperconjugation component (*vide supra*) is removed in the [2.2.1]-systems because the bridgehead C—H bond is aligned perpendicular to the π system, thereby unmasking the inductive effect of the carbonyl group. Conceivably, the alignment of the lone pairs on the oxygen or sulfur with respect to the C—H bond is critical in the norbornyl systems and in benzoylcyclopropane.

Nevertheless, the J_{C-H} values for 7-norbornanone (152 ± 1), nortricyclanone (159 ± 1), and the ketal **15** (144 ± 1) account for the reactivity order observed in the KO-*t*-Bu-catalyzed exchange studies carried out by Gassman and Zalar (24). While 25% of C-1,C-4 hydrogen in 7-norbornanone is exchanged for deuterium after 48 h at 200°, exchange is 75% complete at C-4 in nortricyclanone after only 29 h. The dimethyl ketal of nortricyclanone does not exchange at C-4.

Therefore, since J_{C_1-H} for camphenilone (**8**) is 152 ± 1 Hz, it is likely that some of the deuterium incorporated into **8** at C-1 and -6 via homoenolization (25) is actually introduced through exchange at the bridgehead. We are currently studying base-catalyzed exchange in 6,6-dimethylcamphenilone to check this.

We propose therefore that the upfield shift of C_1—H over C_4—H in norcamphor and C_4—H in nortricyclanone (Table 3) over nortricyclane, is in each case primarily a consequence of "sp-like" hybridization rather than shielding by the carbonyl in the former and the cyclopropyl ring in the latter (23). ^{13}C chemical shift data for nortricyclanone and nortricyclane (Table 4) further support this proposal. That is, while C-1 experiences a downfield shift of 12.1 p.p.m. in norcamphor over norbornane the downfield shift of C-4 in nortricyclanone relative to nortricyclane is only 6.8 p.p.m. and is consistent with more "sp-like" hybridization at C-4, as established by J_{C_4-H}.

The data for norbornenone (**5**) are of interest. While the effect of the introduction of a double bond into norcamphor on J_{C_1-H} is minimal, J_{C_3-H} and J_{C_4-H} (155 ± 1) show dramatic increases. Therefore, in a valence bond description, **17** contributes significantly to the ground state of norbornenone and affects J_{C_4-H}. That **17** must be considered is further supported by ^{1}H and ^{13}C chemical shift data listed in Tables 3 and 4 respectively.



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Possibly, cyclic conjugation, resulting from conjugation (through space) between C-6 and the carbonyl group at C-2 and hyperconjugation through three σ bonds (28, 29, 30, 31), operates

TABLE 4. ^{13}C chemical shifts*

Substrate	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Reference
Norbornane	37.3	30.6	30.6	37.3	30.6	30.6	39.2	16
Norcamphor	49.4	216.1	44.6	35.1	27.0	23.6	37.2	This work
Nortricyclane	11.7	11.7	34.1	30.6	34.1	11.7	34.1	9
Nortricyclanone	18.5	16.3	214.1	37.4	31.2	18.5	31.2	This work
Norbornene	42.0	24.8	24.8	42.0	135.8	135.8	48.8	16
Norbornenone	55.8	212.8	36.7	40.0	143.0	130.8	50.8	16

*Downfield from TMS.

in **5**. The cyclic conjugation could alter J_{C-H} by changing the molecular orbital description of the carbon framework and ΔE for the C—H bond. Several σ-coupled systems, namely diazabicyclooctane (29, 32), *exo*- and *endo*-dicyclopentadienones (28), diazaadamantone (28), tricyclo-[4.4.2.0^{1,6}]dodeca-3,8-diene-11,12-dione (33), and *exo*- and *endo*-polycyclic cyclobutanones (34) warrant study to determine whether or not the C–H coupling constants on the σ framework are influenced by this hyperconjugation. The bridgehead coupling constants in diones **3** and **10** are 157–159 Hz. The unexpected increase in J_{C-H} over norcamphor may be due to improved hyperconjugative alignment of the C_1—C_6 and C_4—C_5 bonds as a result of a synchro-twist (35) as indicated by models and/or the interaction of the carbonyl groups via three σ-bond conjugation.

Although the contribution of each of the factors which determines the magnitude of J_{C-H} cannot be described precisely at present, the bridgehead coupling constants for the diones **3** (C-1, C-4; 157 ± 1) and **11** (C-1, C-4; 159 ± 1) and norbornenone (**5**) (C-4; 155 ± 1) establish that enhanced rates of base-catalyzed exchange should be expected at these sites. Studies on 3,3-dimethylnorbornenone and 3,3,6,6-tetramethylnorbornane-2,5-dione are presently underway.

Experimental

The ^{13}C-H spin–spin coupling constants were obtained on a Varian HA-100 spectrometer at 23.5 kG and 25.1 MHz. The operating probe temperature was +55 °C. Field frequency stabilization was achieved by use of an external (1.5 mm capillary) $^{13}CS_2$ lock and chemical shift measurements required for the location of appropriate carbons were made initially relative to internal dioxane and then to tetramethylsilane. A sample volume of 0.2–0.3 ml was used in a 5 mm o.d. sample tube with dioxane or CCl_4 as solvent where necessary. A signal accumulation of 300–500 scans on a Varian Associates C-1024 time averaging computer was required. J_{C-H} was obtained from the doublets and triplets by drawing an envelope for each absorption (broadened by long range coupling) and using the center (at half the peak width at half height) of the Gaussian curves. Each value quoted is the mean of 3–4 determinations. Our value of 142 ± 1 for J_{C_1-H} in norbornane is identical to that obtained from satellite studies (36). Furthermore, our value of J_{C_1-H} for **6** was identical to that obtained on an XL-100 FT system.[3] The comparisons provide a calibration for our values.

The ketones and diones used in this study were prepared in conjunction with base-catalyzed exchange studies (14) and the syntheses will be described in subsequent publications.

Thiocamphenilone (11)

Camphenilone (1.0 g, > 98% purity) was dissolved in absolute ethanol (25 ml), and HCl and H_2S were bubbled through the reaction mixture (37) for 2h. The reaction was monitored by withdrawing and quenching aliquots with solid sodium bicarbonate under pentane and analyzing the pentane solutions by g.l.p.c. on a 10 ft × $\frac{1}{4}$ in. 10% Carbowax on a Chromosorb W column maintained at 150° with He as the carrier gas. When the reaction was 85–95% complete the mixture was quenched by adding it to a slurry of solid $NaHCO_3$ and purified pentane that was cooled in ice. The pentane solution that was obtained after filtration was concentrated by distillation through a 6 in. helix-packed column until two layers separated. The pentane layer was removed, dried, and concentrated further (2–3 ml). The thione (0.30 g), an orange glassy solid, was isolated by preparative g.l.p.c. utilizing the conditions described above.

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[3] We thank Dr. I. C. P. Smith of the National Research Council of Canada for a spectrum of **6**.

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