CHEMISTRY LETTERS, pp. 507-510, 1976. Published by the Chemical Society of Japan

UNEQUIVOCAL SIGNAL ASSIGNMENT OF THE ^{13}C NMR SPECTRUM OF 4-HOMOISOTWISTANE AS PROBED BY DEUTERIUM SUBSTITUTIONS

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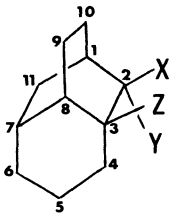
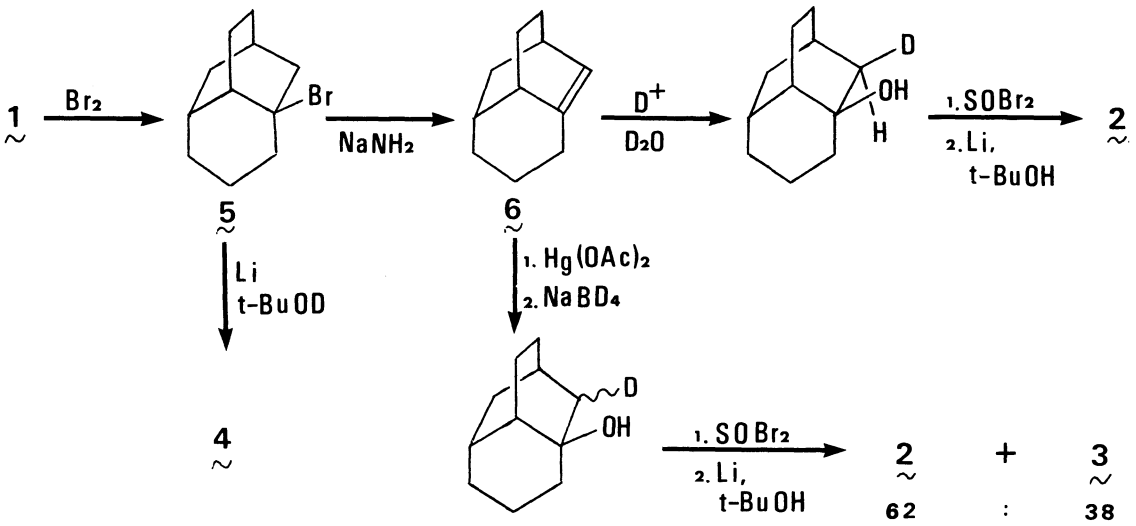
Isotope shifts as well as geminal and vicinal couplings with the deuterium atom were clearly observed in the ^{13}C NMR spectrum of tricyclo[5.3.1.$0^{3,8}$]undecane-2-$\underline{d}_1$ (2 and 3) and -3-$\underline{d}_1$ (4). The phenomena made possible an unambiguous signal assignment in the spectrum of the undeuterated hydrocarbon (1) that had been impracticable so far.

Some tricyclodecylcarbinols and tricycloundecanols have been found[1] to isomerize in the presence of Brønsted acid and hydride source highly selectively to 4-homoisotwistane (tricyclo[5.3.1.$0^{3,8}$]undecane, 1).[2,3] Mechanism of the rearrangement is now under investigation using ^{13}C-labelled carbinol precursors. The ^{13}C atom would be so distributed in the product 1 as rearrangement pathways allow, and the determination of the ^{13}C distribution should be made most conveniently by NMR spectroscopy. The method, however, is invalidated unless we have an unambiguous signal assignment of the ^{13}C NMR spectrum of 1 at hand.[4]

Deuterium substitution has successfully been utilized for otherwise difficult assignments of ^{13}C NMR signals of bi- and polycyclic compounds, where interaction of a deuterium atom with geminal and vicinal ^{13}C nuclei was fully made use of.[5] Some deuterated 4-homoisotwistanes required to the application of the above assignment procedure were easily accessible via 3-bromo-4-homoisotwistane (5)[6] or 4-homoisotwist-2-ene (6).[7] Reduction[6] of 5 with lithium metal in t-butyl alcohol-O-$\underline{d}_1$ gave 4-homoisotwistane-3-$\underline{d}_1$ (4) (88% isotopic purity) in 91% yield. Regio-[7] and stereospecific[8] addition of deuterium oxide to 6 in the presence of sulfuric acid-$\underline{d}_2$ gave 3-hydroxy-4-homoisotwistane-2-exo-$\underline{d}_1$ (3-hydroxy-2) (85% isotopic purity) in 83% yield.[8] The 3-hydroxy-2 thus obtained was treated with thionyl



1 X=Y=Z=H
2 X=D, Y=Z=H
3 Y=D, X=Z=H
4 Z=D, X=Y=H



bromide to give the corresponding bromide (5-2-exo-d_1),[8,9] whereby no change in the configuration of the 2-exo-deuterium was presumed to occur. Lithium-t-butyl alcohol reduction of 5-2-exo-d_1 afforded 2. Regiospecific oxymercuration and subsequent sodium borodeuteride reduction of 6[8] gave a mixture of 3-hydroxy-2 (62%) and 3-hydroxy-4-homoisotwistane-2-endo-d_1 (3-hydroxy-3) (38%)[10] in 86% yield. Thionyl bromide treatment and reduction led to a mixture of 2 and 3 which was not separable even on Golay VPC.

Chemical shifts (δ_C) of the signals in ^{1}H noise-decoupled ^{13}C FT NMR spectra of 1 through 4 are listed in Table 1, and the spectrum of 4 is reproduced in Fig. 1. The triplet ($J \sim 20$ Hz) for deuterium-substituted carbon atom (C-2 for 2 and 3 and C-3 for 4) were shifted upfield by 0.4 $\sim$ 0.5 ppm from those in 1. The geminal carbon signals (C-1 and C-3 for 2 and 3 and C-2, C-4, and C-8 for 4) were also shifted a little upfield (0.06 $\sim$ 0.12 $\pm$ 0.04 ppm) with significant broadening in the peak width. Dihedral angle dependence of vicinal couplings[5] was observed in the spectrum of 2, the C-11 signal being split into a triplet, whereas the C-10 signal was a little broadened. Similar phenomena were also

Table 1. ^{13}C Chemical Shifts of 4-Homoisotwistane and Its Deuterated Analogs

Compound	δ_C[a]										
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
1	24.61	31.76	30.68	32.19	15.16	32.19	30.68	32.94	26.95	26.17	31.76
2	24.53[b]	31.35[c]	30.62[b]	32.21	15.16	32.21	30.72	32.94	26.97	26.14[b]	31.76[d]
2 + 3	24.49[b]	31.34[e]	30.58[b]	32.19	15.15	32.19	30.68	32.92	26.94	26.13[b]	31.73[f]
4	24.60	31.65[b]	30.16[g]	32.07[b]	15.15[h]	32.20	30.67[h]	32.82[b]	26.91[b]	26.16	31.75

[a] ppm from internal TMS standard, measured with resolution of ± 0.02 ppm for 2.8M solution in $CDCl_3$ at 15.03 MHz on a JEOL JNM FX-60 FT spectrometer. Temperature, 25°; tube, 10 mm; repetition time, 5.0 sec; pulse width, 11 μsec (45°); data points, 4096; no. of pulses, 600; spectral width, 1000 Hz. [b] broadened band. [c] J = 19.5 Hz. [d] triplet, $J = \sim 1.2$ Hz. [e] J = 19.4 Hz. [f] broadened band with shoulder. [g] J = 20.0 Hz. [h] triplet, $J = \sim 1.0$ Hz.

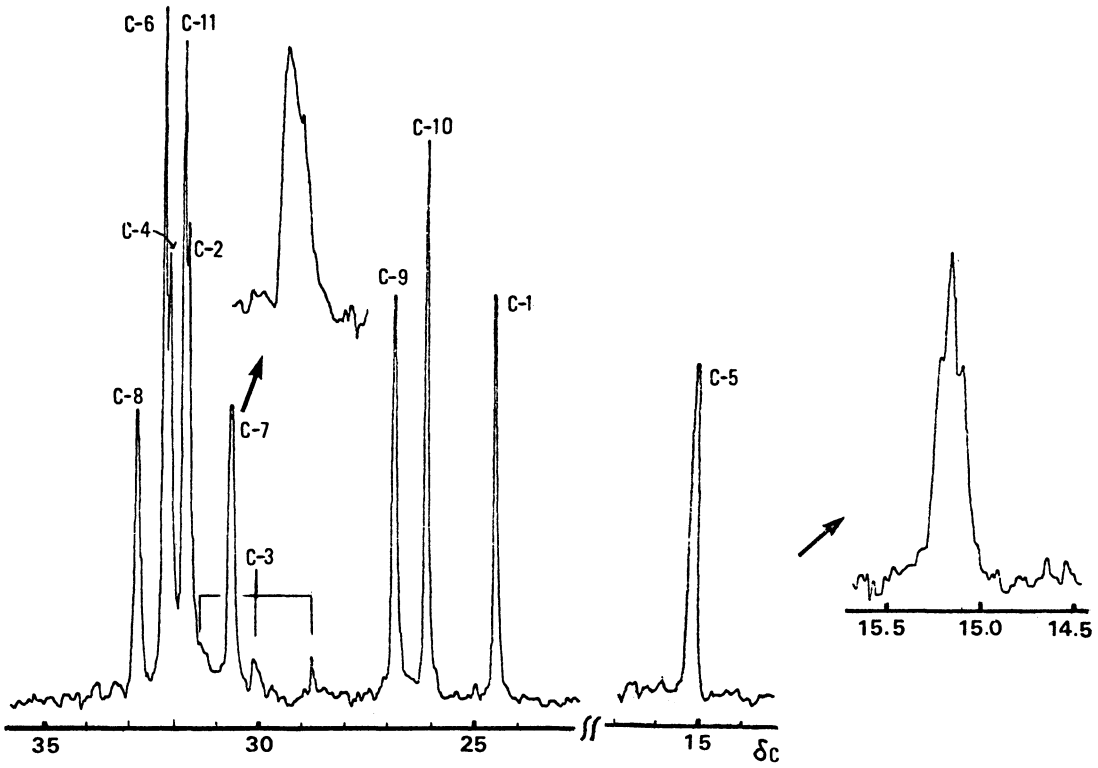


Fig. 1. ^1H Noise-Decoupled ^{13}C NMR Spectrum of 4-Homoisotwistane-3-d_1 (4)

recognized with 4 (Fig. 1).

Isotope effects exhibited in the above deuterated compounds made possible the unequivocal assignment of the ^{13}C NMR signals of undeuterated hydrocarbon 1 as listed in Table 1.

Acknowledgment The authors thank Dr. Siroh Satoh, Director of Application Research Laboratories, Nippon Electric Varian, Ltd., for helpful discussions.

References and Notes

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4) Four out of 8 signals of 1 were assignable[2] to C-1, C-3 (C-7), C-5, and C-8 on the basis of (a) relative intensity of the signals, (b) the spectra with ^{1}H single-frequency off-resonance decoupling, (c) consideration of molecular structure including conformation and symmetricity, and (d) reference to appropriate model compounds.
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10) Ratio of the isomers was not measured directly but taken to be the same as that of the olefin 6 to its deuterated analog (6-2-d_1) in the mixture obtained from these alcohols via the 3-bromide (5), considering a 100% oxo syn stereochemistry[8,9] for the dehydrobromination of 5.

(Received January 31, 1976)