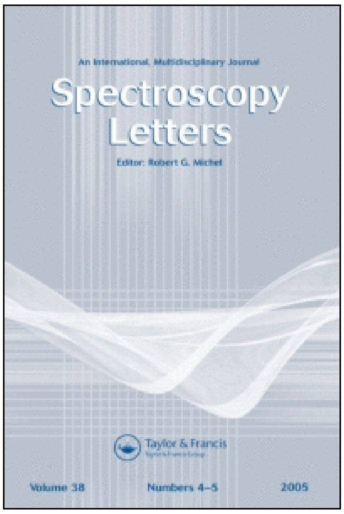

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Carbon-13 Chemical Shift Assignment of 3,3-Dihalogenotricyclo[4.2.1.0^{2,4}]Nonane Derivatives by Two-Dimensional NMR Techniques

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CARBON-13 CHEMICAL SHIFT ASSIGNMENT OF 3,3-DIHALOGENOTRICYCLO[4.2.1.$0^{2,4}$]NONANE DERIVATIVES BY TWO-DIMENSIONAL NMR TECHNIQUES

Key Words : 3,3-dihalogenotricyclo[4.2.1.$0^{2,4}$]nonanes, Carbon-13 NMR, Chemical shift assignment, 2D NMR, INADEQUATE, XHCORR.

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ABSTRACT : We describe therein the Carbon-13 NMR spectra of six dihalogenotricyclo[4.2.1.$0^{2,4}$]nonane derivatives. The complete assignment of carbon chemical shifts has been made using 2D NMR techniques.

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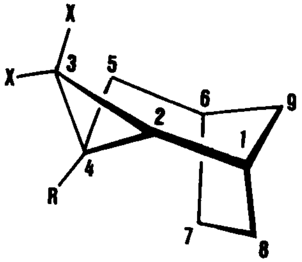
TABLE 1
Carbon Chemical Shift Assignment of Compounds 1–6

	1	2	3	4	5	6
1	33.2	33.0	33.1	32.2	32.0	32.1
2	35.4	41.6	45.1	34.4	40.1	43.8
3	40.1	49.3	43.4	68.0	73.5	70.1
4	25.1	24.2	46.3	24.0	24.5	46.5
5	31.8	38.6	42.7	30.2	37.2	41.3
6	30.2	30.8	30.6	30.4	31.1	30.8
7	27.7	26.5	26.3	27.6	26.6	26.3
8	32.8	32.3	32.1	32.8	32.4	32.0
9	31.4	29.8	29.3	31.7	30.4	29.8
Me		29.5			26.6	

INTRODUCTION

Dihalogenotricyclo[4.2.1.$0^{2,4}$]nonanes are useful intermediates for the synthesis of functionnalyzed bicyclo[4.2.1]nonane derivatives (1). The spectroscopic data analysis of these compounds is quite difficult and, although a few Carbon-13 NMR spectra are described, the complete chemical shift assignment of carbons has been reported for none of them (2–4). Practically, the carbon chemical shift values are too close to allow an unambiguous assignment by comparison with other cyclopropanic compounds (5,6), or by taking into account the substituent induced steric and electronic effects.

In this paper, we describe the carbon chemical shift assignment for two 3,3-dihalogenotricyclo[4.2.1.$0^{2,4}$]nonanes 1,4 and four derivatives 2, 3, 5 and 6



1 : X = Br, R = H

2 : X = Br, R = CH_3

3 : X = Br, R = Cl

4 : X = Cl, R = H

5 : X = Cl, R = CH_3

6 : X = Cl, R = Cl

FIG.1 Structure of 3,3-dihalogenotricyclo[4.2.1.$0^{2,4}$]nonane derivatives 1–6.

(Table 1, FIG.1) which has been achieved using two dimensional NMR techniques : carbon–carbon (INADEQUATE) and proton–carbon (XHCORR) correlations.

EXPERIMENTAL

Compounds 1–6 have been prepared by dibromo or dichlorocarbene addition on the corresponding bicyclo[3.2.1]oct-2-ene, following known procedures (4, 7–10).

All NMR spectra were recorded on a Bruker AC 200 Fourier transform spectrometer operating at 200.132 MHz for ^1H and 50.323 MHz for ^{13}C, in deuteriated chloroform (1D NMR, XHCORR) or hexadeuteriated benzene (INADEQUATE), with all shifts referenced to internal tetramethylsilane (TMS). Carbon and proton NMR spectra were recorded respectively with the following parameters : pulse width (PW) : 3 μs (flip angle 45°) and 2 μs (flip angle 25°) ; acquisition time : 1.3 and 2.3 s for 32K and 16K data table with a spectral width (SW) of 250 and 15 ppm. Carbon–13 spectra were recorded with broad band decoupling and a digital resolution of 0.763 Hz/pt. Exponential multiplication of the free induction decay (FID) with the line broadening of 1.0 Hz was used before Fourier transformation.

The following parameters were used for spin-echo experiments (JMODXH Bruker microprogram) : PW : (90°) : 6.0 μs; relaxation delay (RD) : 4s ; 1/J(C,H) delay : 7 ms ; SW : 12500 Hz.

The proton-carbon chemical shift correlation utilized the XHCORR sequence with delays optimized for J(C,H) values of 140 Hz. The spectra were acquired with 2K x 256 data points and a data acquisition of 64 x 256 increments in t_1 and a zero filling in the F_1 dimension. The spectral widths were 1500 Hz in the F_2 domain and 400 Hz in the proton F_1 domain. The fixed delays were a 5.0 s relaxation delay, 4.0 ms polarization transfer delay and 2.0 ms refocusing delay. A 5 s delay was used between pulse, for each value of t_1 256 transients were accumulated. The data were processed with a sine bell squared window fonction in each dimension.

The carbon-carbon correlated 2D spectra (INAD2D) were acquired with a spectral width of 1500 Hz in the F_2 domain and a 32-step phase cycling and data acquisition of 128 x 256 increments of t_1 to provide after zero filling in the F_1 dimension, a matrix of 2048 X 512. Data files were processed using unshifted sine-bell squared window function in both dimensions prior to Fourier transformation. The delay for the creation of double quantum coherence was 6.5 ms and the relaxation delay was 10 s.

RESULTS AND DISCUSSION

The unambiguous chemical shift assignment of all carbons of compounds 1-6 was achieved using the following methodology. The carbon-carbon correlation spectrum (INADEQUATE) was run for two compounds which were then used as models. The combination of chemical shift values of signals in the

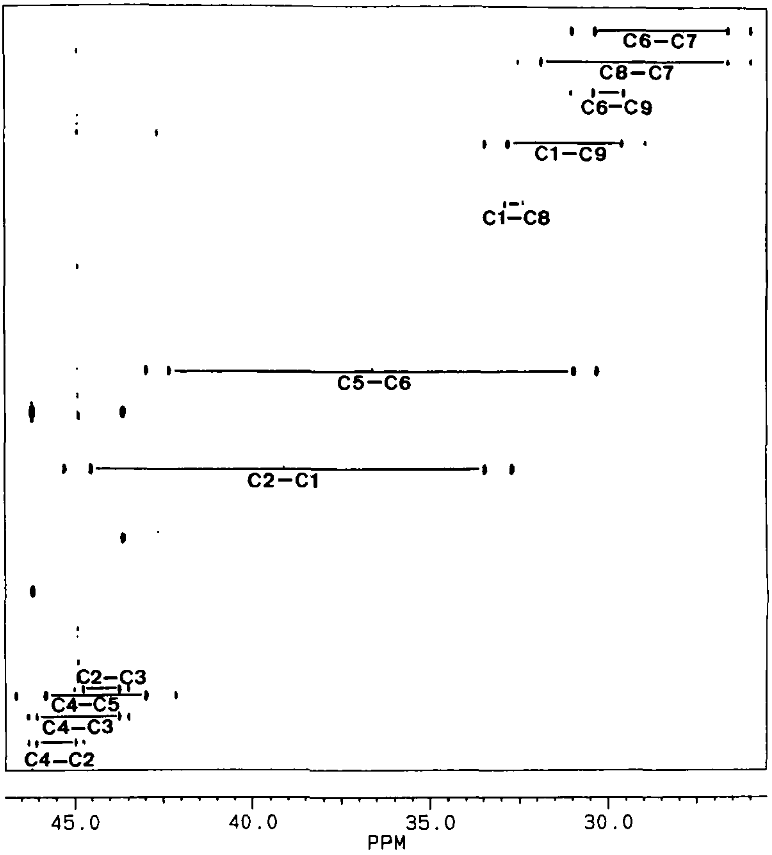


FIG. 2 2D INADEQUATE Spectrum of Compound 3.

proton spectra and the proton–carbon correlation (XHCORR) allowed the identification of all carbons in the other compounds.

Compounds 3 and 5

The carbon–carbon correlation spectrum was run for 3 and 5. The expanded diagramm for 3 is shown in FIG.2.

Compounds 2 and 6

The identification of quaternary carbons C3 and C4 and methyl group is straightforward on the basis of their multiplicities and chemical shift.

The carbons C2 and C5 were differenciated from the other methynes and methylenes on the basis of their chemical shift values and electronic β effect of the substituent. The chemical shift assignment of bridgehead carbons C1 and C6 in one hand, as well as C7, C8 and C9 on the other, was obtained by comparison with 3 or 5 (for each carbon, $\Delta\delta \leq 0.6$ ppm)

Compounds 1 and 4

In the spectra of these compounds, the lack of the substituent led to a more difficult interpretation. The chemical shift assignment of methynes C1 and C6 was achieved again by comparison with 3 and 5 ($\Delta\delta \leq 0.7$ ppm). It is noteworthy that, in the overall series, the more deshielded of two methynes C1 and C6 correlates with the more deshielded signal in the proton spectra. The C4 has an upfield chemical shift which fits very well with the slight shift induced on carbon α by the introduction of a methyl group on a dihalogeno-cyclopropanic framework (5,11). C2 is the remaining resonance.

The chemical shift of C7 was attributed with respect to its relative shielding for all compounds 1–6. The XHCORR sequence was used to assign the resonances of methylenes C5, C8 and C9. More precisely, one could observe in the proton–carbon correlation spectra of the four sustituted compounds 2, 3, 5 and 6 that (i) one of the two hydrogens bonded to C9 is shielded at $\delta = 0.95$–1.00 ppm (ii) the two protons bonded to C5 have a different chemical shift, conversely the signals of those bonded to C8 are overlapped. The same correlations have been observed on the XHCORR spectra of 1 and 4 and allowed the chemical shift assignment of carbons C5, C8 and C9.

CONCLUSION

The combination of the heteronuclear correlation for all compounds 1–6 and carbon–carbon sequence for two molecules 3 and 5 used as models was found to be an efficient approach to assign the carbon chemical shifts of 3,3–dihalogenotricyclo[4.2.1.$0^{2,4}$]nonanes. It is noticeable that the introduction of a substituent on carbon C4 does not affect significally the chemical shift values of most carbons excepted those on position α and β. Consequently, these molecules could be used as models for other derivatives bearing the tricyclo[4.2.1.$0^{2,4}$]nonane framework.

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REFERENCES

1. Casanova J., Koukoua G., Waegell B. Le Squelette bicyclo[4.2.1] nonanique : Analyse conformationnelle, Synthèses, Réactivité. Bull. Soc. Chim. F. 1990; 127: 528–552.
2. Kraus W., Klein G., Sadlo H., Rothenwöhrer W. Addition von Dihalocarbenen and bicyclische Olefine ; Herstellung von Bicyclo[3.2.1]octan– und exo–Tricyclo [4.2.1.$0^{2,4}$]nonan–derivativen. Synthesis 1972; 485–487.
3. Klein G. Synthese, Stereochemie und Solvolyse von Bicyclo[4.2.1]nonen–2–yl–4– und Bicyclo[4.2.1]nonanyl–3– Derivaten. Thesis, Eberhard–Karls Universität, Tubingen, 1975.
4. Sadlo H. Darstellung, Stereochemie und Solvolyse von Bicyclo[4.2.1]non–3–en–2–yl– und Bicyclo[4.2.1]nonan–2–yl Derivaten. Thesis, Eberhard–Karls–Universität, Tubingen, 1976.
5. Brun P., Casanova J., Hatem J., Zahra J.P., Waegell B. Détermination Directe de la Stéréochimie de l'Addition de Carbènes aux Oléfines Bicycliques par RMN du carbone–13. Org. Magn. Reson. 1979; 12: 537–541.
7. Jefford C.W., Mahajan S.N., Medary R.T., Wojnarowski W., Waegell B., Ramey K.C. Entry to the Bicyclo[4.2.1]nonane System. Chem. Commun. 1967; 310–311.
8. Jefford C.W., Burger U., Delay F. Synthesis of Bridged Bicyclic Molecules using Halocarbenes Derivatives of Bicyclo[4.2.1]nonane. Helv. Chim. Acta 1973; 56: 1093–1096.

9 Brun P., Casanova J., Leprince C.,Waegell B. Synthèse Régiosélective d'alcools Allyliques Secondaires et Tertiaires en Série Bicyclo[4.2.1] nonénique. Tetrahedron Lett. 1974; 3979–3981.

10. Sadlo H., Kraus W. Die Isomeren Bicyclo[4.2.1]nonen-3-ole-2 und Bicyclo [4.2.1]nonanole-2. Tetrahedron 1978; 34: 1965–1969.

11. Brun P., Casanova J., Hatem J., Vincent E.-J., Waegell B., Zahra J.P. Etude par RMN du Carbone-13 de quelques dérivés bicyclo[n.1.0]alcaniques. Comptes Rendus Acad.Sci. Paris. 1979; 288: 201–204.

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