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NMR SPECTRA OF SOME 2,6-BRIDGED BICYCLO [2.2.1] HEPTANE DERIVATIVES. LONG RANGE SPIN-SPIN COUPLING

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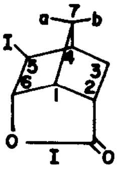
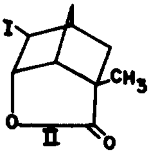
The observation and interpretation of long-range spin-spin coupling has gained increasing importance in structural studies among a wide range of substances[1]. The stereochemical requirements for spin-spin couplings across four saturated bonds of the type H-C-C-C-H have been defined [1-4]. For bicyclo [2.2.1] heptane derivatives such as lactone I, the proton pairs 1-4, 3*en*-7a, 5*en*-7b, 2*ex*-6*ex*, 1-3*ex*, 2*ex*-4 and 6*ex*-4 conform to a nearly zig-zag arrangement and thus are expected to exhibit long-range coupling[1-4].



I



II

We have observed most of these long-range couplings in a number of bicyclo [2.2.1] heptane derivatives bearing a bridged oxygenated unit spanning the 2,6 positions. In this communication we report a fairly detailed analysis of the n.m.r. spectra of iodolactones I and II based on the detection and interpretation of these long range couplings.

Since our chemical shift assignments differ from those made by others for closely related compounds[5], this feature of the spectra will be discussed first.

For compound I two low field resonance peaks at 3.22 and 5.12 p.p.m. equivalent to one proton each appear; these peaks are well separated from the complex additional methylene and methine protons. It appeared reasonable to us, and apparently to others[5], to assign these two low field peaks to protons 2 ex and 6 ex respectively. However, spin-spin decoupling measurements revealed that these two protons were coupled to one another to the extent of 5.4 c.p.s. This value appeared to be suspiciously large for a long range coupling[6]; therefore, confirmation of these assignments was sought. To this end, a methyl group was substituted for the 2 ex proton, and also substitution of deuterium for hydrogen at C_2 in the precursor 2-endo norbornene carboxylic acid was carried out. These substitutions revealed that the 2 ex proton had in fact been assigned incorrectly. The resonance at 3.22 p.p.m. in I and 2.78 p.p.m. in II is due to the C_1 proton. The 2 ex proton occurs at higher field, namely, at 2.54 p.p.m. for I (Table 1). This "reversal" in the expected relative chemical shifts for the 2 ex and C_1 protons may be explained on the basis of a model in which the C_1 proton occupies a position in the deshielding portion of the lactone carbonyl, while the C_2 proton appears in the shielding portion. The assignment of the 6 ex proton was correct and the coupling constant of 5.4 c.p.s.

is the vicinal 1-6 *ex* coupling.

The chemical shift of the C_5 proton on the carbon bearing iodine was readily assigned as the next lowest field proton[7]. The chemical shifts of the C_3 and C_7 protons were apparent from their large geminal coupling constants. Spin decoupling was used in order to distinguish between the 7a and 7b protons, and also confirm the above assignments.

As shown in Table 1, the long range couplings between the 5*en*-7b and 3*en*-7a protons are considerably larger (2-3 c.p.s) than those between the C_1-C_4, 3*ex*-C_1 and C_4-6*ex* protons (0-1 c.p.s.). This trend is in agreement with prediction[8].

Confirmation of the assignments of the C_1, 2*ex*, C_4 protons and differentiation between the 7a-7b protons and 3*ex*-3*en* protons was also accomplished by spin-spin decoupling. The results are depicted in Figure I. Part A shows the normal 100 Mc/sec. spectrum of II.

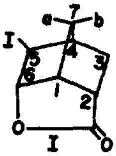
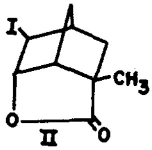
Part B shows the portion of the 100 Mc/sec. spectrum resulting from irradiation at 1.88 p.p.m. (proton 7b). This confirms the assignment of the 7b proton and also reveals the 7b-5*en* long range coupling of 2.10 c.p.s. Part C shows the portion of the spectrum resulting from irradiation at 2.78 p.p.m. (proton 1).

Lastly, part D shows the spectrum resulting from irradiation at 2.66 p.p.m. (proton 4). This causes removal of a large coupling from the resonance at 1.52 p.p.m. and two smaller couplings from the resonances at 1.94 and 1.82 p.p.m. Since it is known that the bridgehead proton is coupled more strongly to the vicinal *exo* proton rather than the *endo* one, the 3 *ex* proton chemical shift is confirmed[9].

These results not only confirm the assignment of the various protons in II, but also

TABLE 1

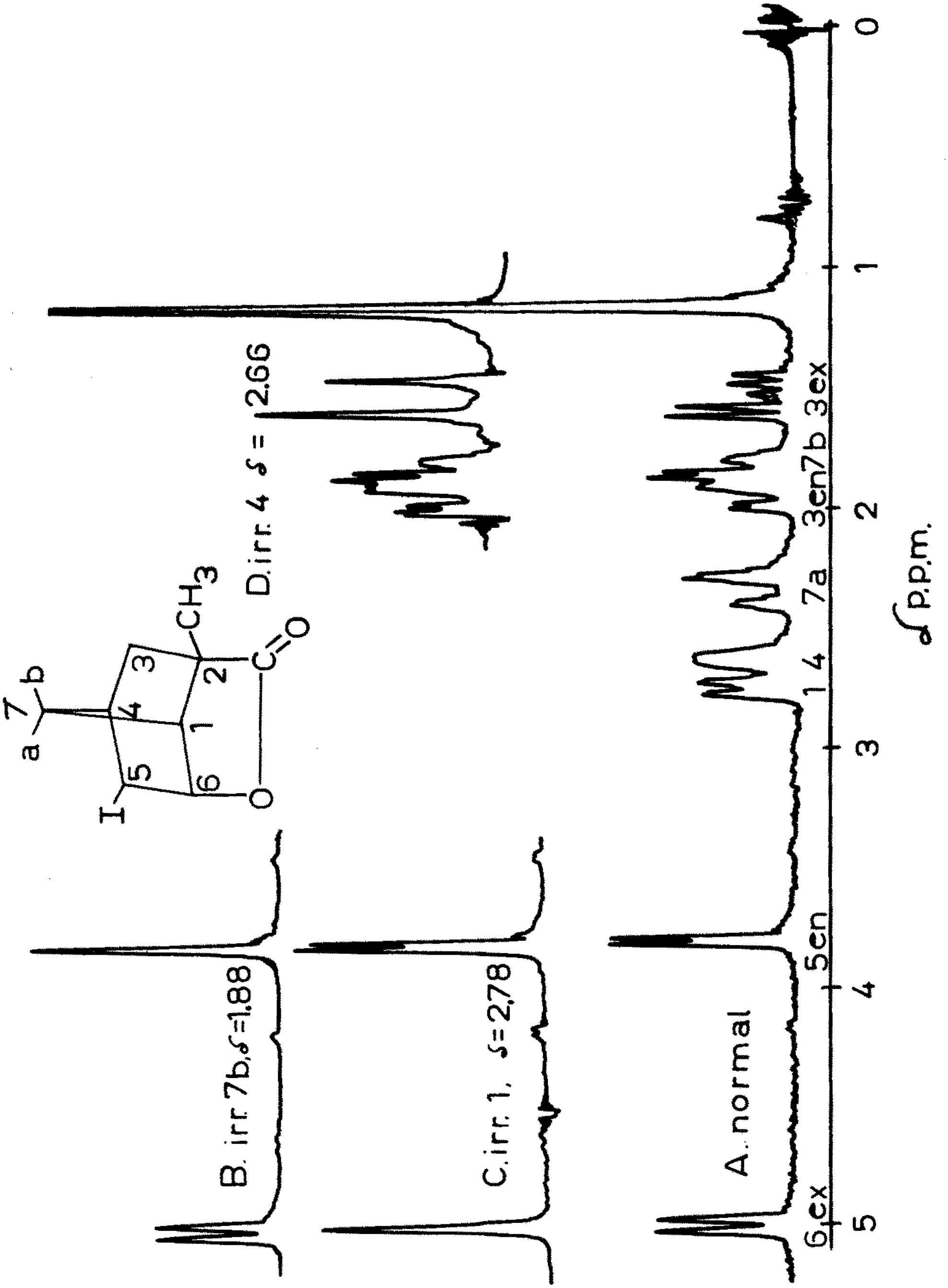
NMR PARAMETERS FOR IODOLACTONES I AND II[a]

Compound	Proton Chemical Shifts (p.p.m.) 1	2ex	3ex	3en	4	5en	6ex	7a	7b
 I	3.22	2.54	2.06	1.52	2.70	3.92	5.12	2.32	1.82
 II	2.78	1.17 (CH_3)	1.52	1.94	2.66	3.85	5.07	2.36	1.88

Coupling Constants (c.p.s.)

Compound	Geminal	Vicinal	Long range
I	$J_{3ex-3en}$ = 13.4 J_{7a-7b} = 11.2	J_{1-2ex} = 5.0 $J_{2ex-3ex}$ = 10.6 $J_{2ex-3en}$ = 3.0 J_{3ex-4} = 3.6 J_{3en-4} = 0.5 J_{4-5en} = 0.5 J_{6ex-1} = 5.4 J_{7a-1} = 1.6 J_{7a-4} = 1.8 J_{7b-1} = 1.6 J_{7b-4} = 1.5	J_{4-6ex} = 1.0 J_{1-3ex} = 0.5 J_{7b-5en} = 2.6 J_{7a-3en} = 1.3 $J_{2ex-6ex}$ = 1.2 J_{2ex-4} = 0.5 J_{1-4} = 1.4
II	$J_{3ex-3en}$ = 13.6 J_{7a-7b} = 11.2	J_{1-6ex} = 5.1 J_{3ex-4} = 4.1 J_{3en-4}= 0.7 J_{7a-1} = 1.4 J_{7a-4} = 1.6 J_{7b-1} = 1.6 J_{7b-4} = 1.6	J_{7b-5en} = 2.1 J_{7a-3en} = 2.1 J_{1-3ex} = 0.8 J_{1-4}=1.4

(a) Chemical shifts refer to dilute $CDCl_3$ solutions relative to TMS as internal standard


a
7
b
I
5
6
4
1
3
2
CH3
C=O
O
B. irr. 7b, δ=1.88
C. irr. 1, δ=2.78
D. irr. 4 δ = 2.66
A. normal
6ex
5en
1 4
7a
3en 7b
3ex
5
4
3
2
1
0
δ p.p.m.

prove the existence of several unique stereochemical long range couplings. Finally, these results complement closely related work by others on the n.m.r. spectra of bridged bicyclics.[10, 11, 12, 13, 14]

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14. Dr. P. Laszlo, Institut de Chimie des Substances Naturelles, Gif-Sur-Yvette, Paris, France, has informed us of his interest in the n.m.r. studies of bridged lactones such as I and II. We gratefully acknowledge the exchange of information and hope to publish a fully elaborated account of our joint studies in the future.