

LONG-RANGE COUPLING CONSTANTS AND NUCLEAR OVERHAUSER EFFECTS  
IN THE N.M.R. SPECTRA OF ORGANO-THALLIUM COMPOUNDS

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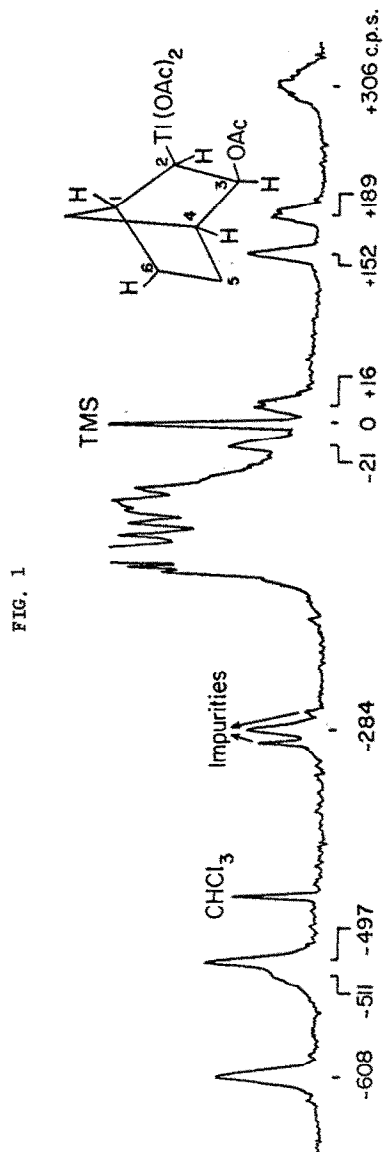
Adducts of thallium (III) acetate to norbornene and norbornadiene have been prepared<sup>(1)</sup> recently, and their structures studied<sup>(1)</sup>. However, the evidence available does not allow unequivocal assignments to the configurations of the  $Tl(OAc)_2$  groups in these compounds.

The proton n.m.r. spectrum (Fig. 1) of the norbornene-thallic acetate adduct (I) shows<sup>(1)</sup> that at least five protons have very large coupling constants<sup>(2)</sup> to thallium, but, because of the lack of fine structure, together with the superposition of some of the bands, it is not possible to pick out directly pairs of bands that correspond to individual protons. We wish to point out that the general nuclear Overhauser effect<sup>(3)</sup> in the double resonance spectrum of such a compound provides a powerful tool for the interpretation of the proton spectrum.

The effect, in the present instance, can be described roughly as follows. Consider a proton that is coupled to a thallium nucleus so that the proton spectrum of the compound is a doublet. One line of the doublet then corresponds to spins of  $+1/2$  and the other to spins of  $-1/2$  for the thallium nuclei. Strong irradiation at a frequency corresponding to one of these bands (say for a thallium spin of  $+1/2$ ) will result in saturation (i.e. a decrease in the population difference between the two proton spin states) for the protons of that band. Because of relaxation, the thallium nuclei continually change their spin states, so that protons corresponding to one component of the doublet become transferred to the other component. If the relaxation time of thallium is shorter than  $T_1$  of protons, as appears to be the case, simultaneous observation of the other proton band (i.e. for a thallium spin of  $-1/2$ ) will show that this band is of much reduced intensity.

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Nuclear Overhauser effects are readily observed<sup>(4)</sup> in the field-sweep double resonance spectra of I. For example, strong irradiation of the band at +306 c.p.s. results in a large decrease in the intensity of the band at -511 c.p.s. (but not of any other band) and vice versa. Other pairs of bands (Table I) can be picked out in a similar fashion. The chemical shifts and the H-Tl coupling constants of five protons are thereby determined (Table I).

TABLE I

Pairs of bands <sup>a</sup>		Assignment	Chemical Shift <sup>b</sup>	$J_{Tl^{205}-H}$ (in c.p.s.) <sup>c</sup>
-497	+152	H1	7.13	$\pm 649$
-608	+189	H2	6.50	$\mp 797$
-608	+16	H3	5.07	$\pm 624$
-284	-21	H4	7.46	263
-511	+306	H6 <sub>exo</sub>	8.29	$\pm 817$

<sup>a</sup> In c.p.s. from tetramethylsilane (positive numbers to high field).

<sup>b</sup> In p.p.m. on the  $\tau$  scale.

<sup>c</sup> Either the top or bottom sign is to be taken throughout.

Because of its chemical shift<sup>(5)</sup>, the proton at  $\tau 5.07$  must be H3. The H3 band at +16 c.p.s. shows a spacing of 6.6 c.p.s. which is even more clearly visible in the spectrum with double irradiation<sup>(6)</sup> at the frequency of Tl<sup>203</sup>, when the remaining band is due solely to coupling to Tl<sup>205</sup>.

When the band at +16 c.p.s. is strongly irradiated, one half of the band at -608 c.p.s. disappears (Overhauser effect), but the remaining band is much sharper than its known partner at +189 c.p.s. This can be ascribed to decoupling involving the disappearance of the 6.6 c.p.s. spacing. It also shows that the low-field component of the pair [-608, +189 c.p.s.] and the high-field component of the pair [-608, +16 c.p.s.] correspond to the same thallium spin; i.e. the two H-Tl coupling constants have opposite signs. Since  $J_{H3-Tl}$  is a vicinal coupling constant, the other is probably a geminal coupling constant (i.e.  $J_{H2-Tl}$ ). Hence, H2 is the proton at  $\tau 6.50$ .

The protons at  $\tau 7.13$  and 7.46 are assigned to H1 and H4 on the basis of chemical shifts. The proton at  $\tau 7.13$  has a much larger coupling constant to thallium than the other and is therefore assigned to H1.

Decoupling experiments show that neither H1 nor H4 are appreciably coupled to H2 or H3. In conjunction with the previously established coupling constant of 6.6 c.p.s. between H2 and H3, these results establish<sup>(7)</sup> the stereochemistry of the substituents at C2 and C3 as exo.

The proton at  $\tau$ 8.29 is assigned to H6exo on the basis of its chemical shift and of H-H coupling constants. The bands of this proton are very broad, being consistent with coupling constants of 10 to 12 c.p.s. to H6endo and to H4exo. A coupling to H1 was revealed by the following quadruple resonance experiment. The band of H1 at +152 c.p.s., with strong irradiation at about -103 c.p.s. (to decouple protons on C7) and at the frequency of Tl<sup>203</sup>, becomes a doublet (spacing 4 c.p.s.) which collapses to a singlet by additional strong irradiation at +306 c.p.s. (i.e. at a frequency corresponding to one of the bands of the proton at  $\tau$ 8.29). The 4 c.p.s. coupling is consistent<sup>(7)</sup> only with the assignment made above. The experiment also proves that the signs of the coupling constants of H1 and H6exo to thallium are the same. In Table I,  $J_{H1-Tl}$  and  $J_{H3-Tl}$  are assumed to have the same signs, since they are both large vicinal coupling constants.

Protons other than those mentioned in Table I occur over a region of about 80 c.p.s., so that this must be an upper limit to the absolute values of their coupling constants to thallium.

The most interesting aspect of the proton-thallium coupling pattern is the strong stereochemical dependence and the very large sizes of the long-range coupling constants<sup>(8)</sup>. Of the five protons  $\gamma$  to the thallium, H6exo and H4 show coupling constants of 817 and 263 c.p.s. respectively; the other three protons have coupling constants of less than 80 c.p.s.

The spectrum of the norbornadiene-thallic acetate adduct was interpreted in the same general way as that of I. A coupling constant of  $5.9 \pm 0.3$  c.p.s. between H2 and H3 again indicates that the substituents on C2 and C3 are cis to one another. Although no extremely large long-range coupling constants are present, the thallium nucleus is coupled by about 112 c.p.s. to H4 and by 76 and 92 c.p.s. to H5 and H6 (not necessarily respectively). The coupling constants to H1 (410 c.p.s.) and to H2 (581 c.p.s.) are distinctly smaller, in absolute values, than the corresponding coupling constants found in I. Further discussion of these spectra will be presented in a full paper.

Acknowledgements: I wish to thank Professor S. Winstein for bringing this problem to my attention.

## REFERENCES

- (1) S. Winstein and K. C. Pande, Tetrahedron Letters, accompanying communication.
- (2) From the work of J. P. Maher and D. P. Evans (Proc. Chem. Soc., 176 (1963)) on the di-n-propylthallium cation, together with the established correlation of coupling constants in the  $R_2Tl^+$  and  $RTl^{++}$  ions, the following H-Tl coupling constants (in c.p.s.) are anticipated: Tl-C-H,  $\pm 800$ ; Tl-C-C-H,  $\pm 1,000$ ; Tl-C-C-C-H,  $\pm 50$ . Because of possible geometric effects, the last two values may not be applicable when rigid molecules are considered. Thallium actually possesses two isotopes,  $Tl^{205}$  and  $Tl^{203}$ , both of spin 1/2, and with natural abundances of 70.5 and 29.5% respectively. The H- $Tl^{205}$  coupling constants are about 1% higher than the corresponding H- $Tl^{203}$  values (J. V. Hatton, J. Chem. Phys., 40, 933 (1964)).
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- (6) An N.M.R. Specialties Model SD60 decoupler was used. Because the thallium resonances of  $Tl^{203}$  (or  $Tl^{205}$ ) occur in the present compound over a region of several thousand c.p.s., complete decoupling does not take place. Sufficient power is available, however, to spread the proton spectrum more or less uniformly over the base line.
- (7) The coupling constants (in c.p.s.) between pairs of protons are expected<sup>(5)</sup> to be as follows: H2 and H3, 5.8-7.7 (cis-endo), 8.9-11.4 (cis-exo), 2.2-5.8 (trans); H1 and H2, 3-5 (H2exo), ca. 0 (H2endo); H2 and H6, 1-2 (both exo), ca. 0 (other than both exo); H1 and H7  $< 1$ .
- (8) Cf. the long-range coupling constants between exo-protons on C2 and C6 in bicycloheptane derivatives<sup>(7)</sup>. For a discussion of proton-thallium coupling constants, see W. G. Schneider and A. D. Buckingham, Disc. Farad. Soc., 34, 147 (1962).