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OXYTHALLATION AND OXYMERCURATION CARBON-13 NMR EXAMINATION OF SOME NORBORNENE DERIVATIVES

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Summary

Natural abundance ^{13}C NMR spectra of a number of oxythallation adducts of norbornenes have been obtained and assigned by considerations of SFORD spectra, chemical shifts, comparisons of spectra at different frequencies, T_1 values and some aspects of $^{203,205}Tl$—^{13}C couplings The substituent induced shifts (α, β, γ effects) at various carbons have been calculated and compared with those for the analogous mercury(II) compounds ^{203} ^{205}Tl—^{13}C and ^{199}Hg—^{13}C couplings have been measured, and for *vicinal* (^3J) couplings, a dihedral angle dependence (of the Karplus type) is demonstrated

Introduction

Organothallium compounds are very attractive subjects for NMR examination as thallium isotopes (^{203} ^{205}Tl) are 100% magnetically active ($I = \frac{1}{2}$) and large couplings to ^1H and ^{13}C nuclei can be observed [1—8] Our interest in the magnitudes and stereodependencies of ^{13}C—metal couplings [9,10] encouraged examination of alkylthallium compounds ($RTlX_2$) but a suitable variety of uncomplicated types is not available * Fortunately, oxythallation of norbornenes generally leads to isolable adducts [7,12,13] (with *exo* thallium) [5,12] and although ^1H NMR data for some have been reported [5,7], there is essentially no information available on ^{13}C NMR parameters of cycloalkylthallium derivatives [8] In this report, we wish to present the salient features of the ^{13}C spectra of a number of norbornylthallium compounds, and comparisons with the analogous (isoelectronic) mercury(II) derivatives.

(continued on p 355)

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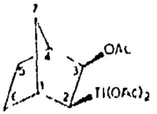
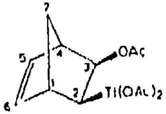
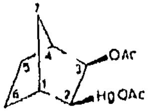
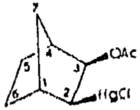
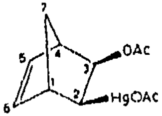
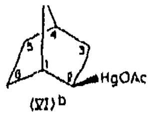
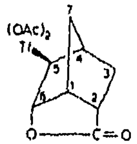
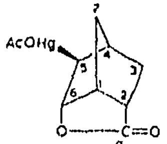
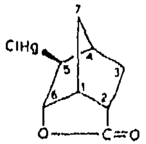
* See ref 11 for the report of $CH_3Tl(OAc)_2$

TABLE 1

CHEMICAL SHIFTS, ^{203,205}Tl—^{13}C AND ^{199}Hg—^{13}C COUPLING CONSTANTS

Compound	Solvent	C(1) ^{c}	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Other
 (I)^a	$CDCl_3$	40 6 (322 3)	76 6 (5701, 5754)	78 9 (683 6)	42 8 (29 3)	23 6 (80 6)	29 5 (1303 7)	35 8 (31 8)	22 7 (CH_3), 179 2 (C=O)
 (II)^a	$CDCl_3$	45 7 (239 3) 5764)	72 0 (5711,	75 2 (427 3)	48 2 ^{c} (17 1)	135 4 (119 7)	146 6 (1069)	47 2 ^{e} ($\sim$ 0)	23 6 (CH_3), 178 8 (C=O)
 (III)^a	$CDCl_3$	40 1 (51 8)	56 3 (1747)	80 2 (142 9)	42 6 (n o)^d	23 7 (n o)	30 0 (254 9)	36 4 (n o)	21 8 (CH_3), 177,0, 170 0 (C=O) 23 3
 (IV)^b	DMSO	40 8 (57 0)	61 7 (1864)	80 0 (147 0)	43,3 (10)	24 6 (n o)^d	30 9 (256)	36 9 (12)	22 4 (CH_3), C=O (folded)
 (V)^a	$CDCl_3$	45 5 (40 3)	52 2 (1735)	77 3 (96,4)	48 3 ^{e} (n o.)	133 3 (17 1)	141 6 (211 2)	48 1 ^{c} (n o)	23 5, 21 6 (CH_3), 170 6, 177 2 (C=O)

 (XI)[b]	CDCl$_3$	43 1 (41)	48 7 (1660)	38 8 (43)	38 3 (93)	30 8 (n o)	33 1 (276)	41 5 (9)	24,4 (CH$_3$), 177 5 (C=O)
 (XII)[a]	Pyridine	39 4 (75 7)	47 5 (70 8)	37 3 (1289)	42 6 (219 7)	67 7 (6592, 6655)	85 5 (61 0)	39 1 (131 8)	22,8 (CH$_3$), 177 (C=O)
 (XIII)[a]	Pyridine	39 1 (17 1)	47 2 (n o)	40 4 (437)	42 2 (39 1)	52 7 (1798)	86 1 (n o)	36 8 (36 6)	22,2 (CH$_3$), 176 7, 181 7 (C=O)
 (IX)[a]	Pyridine	39 5 (nr)[d]	47 5 (nr)	40 6 (440)	43 0 (36 6)	56 6 (1938)	87 0 (n o)	37 3 (nr)	181 2 (C=O)

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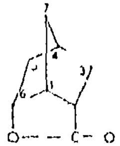
[a] Chemical shifts relative to internal TMS [b] Relative to internal dioxan δ(TMS) = δ(dioxane) + 67 4 ppm [c] Numbers in parentheses are thallium—carbon or mercury—carbon coupling constants Only for the large one bond couplings are separate couplings to ^{203}Tl and ^{205}Tl resolved (γ ratio 1 0097) [d] n o , not observed, nr, not resolved [e] Possible assignment interchange

TABLE 2

CHEMICAL SHIFTS OF PARENT COMPOUNDS AND IS (Δδ) OF COMPOUNDS I–IX

Compound	Solvent	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	Other
	$CDCl_3$ [a]	35 8	40 0	77 6	41 9	24 7	27 6	35 6	21 3 (CH_3), 170 2 (C=O)
	Dioxan [a]	36 8	30 1	30 1	36 8	30 1	30 1	38 7	
	$CDCl_3$ [a]	41 1	35 0	75 2	47 7	133 1	141 4	46 6	21 1 (CH_3), 170 5 (C=O)
	$CDCl_3$ [b]	39 1	46 5	38 1	37 9	34 5	80 9	36 5	C=O (not recorded)
I		4 8	36 6	1 3	0 9	−1 1	1 9	0 2	
II		4 6	37 0	0 0	0 5	2 3	5 2	0 6	
III		4 3	16 3	2 6	0 7	−1 0	2 4	0 8	
IV		5 0	21 7	2 4	1 4	−0 1	3 3	1 3	
V		4 4	17 2	2 1	0 6	0 2	0 2	1 5	
VI		6 3	18 6	8 7	1 5	0 7	3 0	2 8	
VII		0 3	1 0	−0 8	4 7	33 2	4 6	2 6	
VIII		0 0	0 7	2 3	4 3	18 2	5 5	−0 1	
IX		0 4	1 0	2 5	5 1	22 1	6 1	1 2	

[a] Referenced to internal dioxan (δ(TMS) = δ(dioxan) + 67 4 ppm) [b] Referenced to internal TMS

Results and discussion

Spectra were obtained for the oxythallation and oxymercuration adducts of norbornene, norbornadiene, norborn-2-ene-5-*endo* carboxylic acid (providing a lactone-type adduct), 2-acetoxynorbornane, 5-acetoxynorbor-2-ene and the parent lactone from the 5-endo acid [12].

Assignments were arrived at by orthodox procedures, and SFORD spectra, comparisons of 22.63 MHz and 67.89 MHz spectra, chemical shift comparisons with the parent compounds, some ^{13}C T_1 values and aspects of ^{203,205}Tl—^{13}C coupling [3,4] were considered. In particular, the carbon bearing thallium was characterised by a large (5—6 KHz) coupling to ^{203,205}Tl [3], and other patterns in long range couplings quickly emerged. The well-established shielding effect [14] of the acetate oxygen at γ- and *anti*-periplanar carbons is also in evidence, and provides strong evidence where appropriate, for the listed assignments. Although the SFORD spectra distinguish the secondary and tertiary carbons, it was considered that the T_1 values * should be characteristically different also, with smaller T_1's for the secondary carbons. The adduct of norbornene (i.e. 3-acetoxy-2-norbornylthallium diacetate, compound I in Table 1) was examined and the tertiary carbons (C(1), C(3), C(4)) exhibited T_1's ranging from 0.52 sec to 0.67 sec, while the secondary carbons (C(5), C(6), C(7)) had T_1's in the range 0.31 sec to 0.43 sec. These values separate the secondary and tertiary carbons, in agreement with the SFORD spectra. (The T_1's for C(2), bearing thallium were not determined, as this carbon signal consists of four lines (resolved coupling to both ^{203,205}Tl), of overall low intensity.) If any doubt exists between closely resonating carbons, this is indicated in Table 1. The chemical shifts and coupling constants are located in Table 1, and the substituent induced shifts (*IS*) in Table 2.

There are several features of the results that warrant emphasis. Regarding chemical shifts, the α-effects (Table 2) of $Tl(OAc)_2$, HgOAc and HgCl are large and positive, but the effect is much greater (ca. a factor of two) for the $Tl(OAc)_2$ group. Some discussion of the α-effects in a series of organostannanes has recently been presented [16], and the influence of metal electropositivity outlined. In the present case, it is reasonable that increased nuclear charge at the metal in these thallium(III) and mercury(II) derivatives will result in a transfer of electron density from the carbon orbitals to the metal (σ-polarisation) causing α-carbon deshielding. In this connection, it seems consistent that α-effects in phenylthallium(III) derivatives [3,17] are ca. one-half of those in the norbornyl series, as polarisation of the sp^2C—Tl bond would be less favorable. Strong coordination to thallium would be expected to reduce the electronegativity of the $Tl(OAc)_2$ group (and also the α-effect) and in pyridine solvent (compared with $CDCl_3$) the α-effect is ca. 5 ppm less positive. α-Effects of the thallium group may also be influenced by "ponderal effects" associated with the ligands on the metal, but the long Tl—C bond may minimise such contributions. β-Effects (Table 2) of both $Tl(OAc)_2$ and HgOAc are positive, but oxygenation (at C(3) in I—V and C(6) in VII—IX) at a β-carbon appears to have variable influences depending on the *endo* or *exo* nature of the C—O linkage. In

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* See ref. 15 for the procedure employed.

compounds I—V, note the greater β-effect (ca 4—5 ppm) at the tertiary C(1), compared with the effect at the *exo*-oxygenated C(3) (ca. 1—2 ppm) whereas in VII—IX, the effects at the tertiary C(4) and *endo*-oxygenated C(6) are very similar indeed (4—5 ppm) In *exo*-2-norbornylmercuric acetate itself, the β-effect is greater (8 7 ppm) at the secondary C(3) than at the bridgehead tertiary C(1) (6 3 ppm) Positive β-effects for metal groups (e g Hg, Tl, Sn, Pb, etc) appear to be the general rule, but it is apparent that a number of effects are contributory The γ-effects (Table 2) of TlX_2 and HgX in these systems are of particular interest in view of our recent report [18] for the Group IVB $M(CH_3)_3$ cases. For the saturated systems (I, III, IV—VI) positive γ-effects of ca. 2 ppm at the remote C(6) position and at C(3) in VIII and IX, are recorded These shifts are in the same direction as those previously determined for Group IVB systems, and positive γ-effects (in the absence of "steric compression") may also be a general result for alkyl derivatives of the main group metals exhibiting acceptor properties

Aspects of ^{203} ^{205}Tl—^{13}C coupling in some phenylthallium(III) compounds have been reported [3,4], are large one-bond couplings [3,17] of ca 8—10 KHz were noted In compounds I, II and VII such couplings (^1J) are still large (5—7 KHz) but significantly smaller than in the phenyl series. We believe the main factors responsible are the altered s-content in the carbon-bonding orbital to thallium as well as larger promotional energies to excited states in the alkyl compounds For compound I, a solvent change from $CDCl_3$ to the more strongly coordinating pyridine induces a small change (~10%) in ^1J from 5754, 5701 Hz to 6306; 6245 Hz, presumably reflecting a minor hybridisation change at thallium [19] [*]. The two-bond couplings are much smaller, but still show considerable variation For example, in I, coupling to C(1) (322 3 Hz) is less than to C(3) (683 6 Hz) and the effect of *exo*-oxygenation at C(3) is thus considerable, but in line with observations for the mercury compounds (cf C(3) in IV and VI) Most intriguing is the astoundingly small two-bond coupling to C(6) in VII, VIII and IX (with *endo*-oxygenation) being 61 0 Hz in VII, and unresolvably small in VIII and IX This (two-bond) coupling clearly has a pronounced stereochemical dependence on the adjacent C—O bond Although the exact nature of this dependence is unclear, it may result partially from cancellation effects of dual pathway coupling. Vicinal couplings (^3J) were of particular interest to us, as Karplus-type dependencies have been established for analogous ^{119}Sn [9] and ^{199}Hg [10] coupling and appears very probable for ^{207}Pb [20] In I, the largest ^3J (1303 Hz) is to C(6) with a dihedral angle of ~170°, while much smaller couplings to C(7) (31 8 Hz) and C(4) (29 3 Hz) occur If the dihedral angle was the strongly dominant factor regulating ^3J, coupling to C(7) ($\theta \sim 85°$) would be smaller than to C(4) ($\theta \sim 120°$), as for example, in 2-norbornylmercuric acetate (VI). Similar *vic*-couplings to C(4) and C(7) are manifested in all compounds I—V, despite the differences in θ, and we believe the small C(7) coupling is expected, but some other factor(s) is assuming importance and depressing the coupling to C(4) The precise structural features in these norbornyloxymetallic compounds are unknown and different torsional angles (relative to VI, say)

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[*] Some discussion of coordination systems for monoalkylthallium species is given in ref 10c

could be present * Oxygenation at the adjacent C(3) in I—V, could also be responsible for some electronic changes at C(4), resulting in a reduced coupling In the lactone adducts (VII—IX) the largest *vic*-coupling is to C(3), again with the favorable (~170°) θ, whereas coupling to C(7) (in both VII, VIII) exceeds that to C(1) While it is clear that dihedral angle is a strong regulator of ^3J, examination of compounds lacking complicating oxygenation would be necessary, but the lability of $RTlX_2$ (R = unsubstituted cycloalkyl) pose some problems for the synthesis of suitable types [11] Efforts in this direction are continuing

Nevertheless, the present data should provide a firm base for assignment of the spectra of cycloalkyl-mercury and -thallium systems

Experimental

(*a*) Compounds I—IX listed in Table 1 and 2 are well known [12] and our samples had physical and spectroscopic properties in agreement with the indicated structures and literature values [12]

(*b*) ^{13}C NMR spectra were recorded on Bruker spectrometers operating at either 22 625 MHz or 67 89 MHz in the FT mode. Chemical shifts are referenced to internal TMS

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* There is evidence that in *cis* hydroxymercurials O—Hg interactions occur so that the IR spectra (ν(OH) provide a means of distinguishing *cis* and *trans* isomers [21]

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