Hydrogen-1 Nuclear Magnetic Resonance Evidence for *trans* Addition in Oxythallation of Acyclic Olefins

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Hydrogen-1 n.m.r. conformational analyses of some stabilised oxythallation products from styrene, *o*-allylphenol, propylene, and oct-1-ene have been performed primarily on the basis of the variation in thallium–proton spin–spin coupling constants. The results have been applied to the oxythallated adduct of *trans*-β-deuteriostyrene to provide the first direct evidence for *trans* addition in the oxythallation of acyclic olefins.

STEREOCHEMICAL studies on the oxymetallation of olefins have received much attention from both synthetic and mechanistic viewpoints.[1] Hydrogen-1 n.m.r. spectroscopy seems to be a particularly useful tool in the study of oxythallation in that large thallium–proton spin–spin coupling constants often provide valuable information for determining the structures of organothallium compounds.[2] Thus, the occurrence of both *trans* and *cis* additions was inferred [3,4] by ^{1}H n.m.r. analyses of the oxythallated adducts of norbornene, norbornadiene, and related olefins. Here we present the first direct evidence for *trans* addition in the oxythallation of acyclic olefins, based on ^{1}H n.m.r. conformational analysis of some oxythallated adducts of alk-1-enes. *trans* Addition in the oxythallation of acyclic olefins has been postulated, but not demonstrated, previously.[1] In the course of the present study, we also found a method of deducing the structures of rather unstable oxythallated adducts of alk-1-enes by forming more stable organothallium derivatives.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were obtained on a Japan Electron Optics JNM-PS-100 spectrometer with tetramethylsilane as internal standard. Thallium(III) acetate was obtained from Tl_2O_3 and acetic acid as the hydrated form, and was used in each experiment without further drying. Each organic solvent used for synthesising the organothallium compounds was of reagent grade. The oxythallated adducts of styrene, (1), and *o*-allylphenol, (2), were prepared according to the methods described in the literature.[5] The compound *trans*-PhCH=CHD was prepared by the reported method.[6]

Alkylthallium Bis(NN-*dimethyldithiocarbamates*), (3) *and* (4).—These were prepared from (1) or (2) and $Na[S_2CNMe_2]$ using a method similar to that [7] for $[TlMe(S_2CNMe_2)_2]$: $[Tl\{CH_2CH(OMe)Ph\}(S_2CNMe_2)_2]$, (3), m.p. 131—132 °C (Found: C, 31.2; H, 4.1. Calc. for $C_{15}H_{23}N_2OS_4Tl$: C, 31.1; H, 4.0%); $[Tl(CH_2CHCH_2C_6H_4O)(S_2CNMe_2)_2]$, (4),

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[1] W. Kitching, *Organometallic Chem. Rev.*, 1968, **A3**, 61.

[2] J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1965, 637.

[3] F. A. L. Anet, *Tetrahedron Letters*, 1964, 3399.

[4] A. McKillop, M. E. Ford, and E. C. Taylor, *J. Org. Chem.*, 1974, **39**, 2434.

[5] H. J. Kabbe, *Annalen*, 1962, **656**, 204.

[6] T. Yoshino, Y. Manabe, and Y. Kikuchi, *J. Amer. Chem. Soc.*, 1964, **86**, 4670.

[7] H. Kurosawa and R. Okawara, *J. Organometallic Chem.*, 1968, **14**, 225.

m.p. 113—114 °C (Found: C, 31.5; H, 3.7. Calc. for $C_{15}H_{21}N_2OS_4Tl$: C, 31.2; H, 3.7%).

Alkyl(methyl)thallium Derivatives, (5), (6), *and* (9)—(11).—These were prepared from (1) or (2) and tetramethyltin using methods similar to those[8] for [TlMe(Et)X] (X = O_2CPr^i, Cl, or S_2CNMe_2). In a typical procedure, $SnMe_4$ (0.78 g) and (1) (2.0 g) were allowed to react in methanol (10 cm³) at 20 °C for 2 h. The solvent was removed *in vacuo* and the remaining solids were washed with n-hexane and recrystallised from dichloromethane and n-hexane to give white crystals of [TlMe{$CH_2CH(OMe)Ph$}(O_2CMe)], (5), m.p. 176 °C (Found: C, 34.6; H, 4.0. Calc. for $C_{12}H_{17}O_3Tl$: C, 34.9; H, 4.1%). The compound [TlMe($CH_2\overline{CHCH_2C_6H_4O}$)($O_2CMe$)], (6), was prepared similarly, and recrystallised from methanol, m.p. 178 °C (Found: C, 35.1; H, 3.6. Calc. for $C_{12}H_{15}O_3Tl$: C, 35.0; H, 3.7%). The compounds [TlMe{$CH_2CH(OMe)Ph$}X] [X = Cl (9) or S_2CNMe_2 (10)] were obtained as precipitates on adding an aqueous solution of an excess of NaCl or Na[S_2CNMe_2] to (5) in methanol. Recrystallisation from hot methanol [for (9)] or benzene–n-hexane [for (10)] gave white crystalline products: (9), m.p. >210 °C (decomp.) (Found: C, 30.8; H, 3.6. Calc. for $C_{10}H_{14}ClOTl$: C, 30.8; H, 3.6%); (10), m.p. 104 °C (Found: C, 32.9; H, 4.2. Calc. for $C_{13}H_{20}NOS_2Tl$: C, 32.9; H, 4.3%). The compound [TlMe($CH_2\overline{CHCH_2C_6H_4O}$)Cl], (11), was prepared similarly, and recrystallised from dichloromethane and n-hexane, m.p. 146 °C (Found: C, 30.9; H, 3.0. Calc. for $C_{10}H_{12}ClOTl$: C, 31.0; H, 3.1%). Of these unsymmetrical diorganothallium compounds, (6) and (9) are too insoluble in chloroform for their ^1H n.m.r. spectra to be obtained. When Na[S_2CNMe_2] in water was added dropwise to a methanol solution of (6) or (11) an immediate precipitate of [TlMe(S_2CNMe_2)$_2$] occurred. The presence of *o*-allylphenol in the filtrate was confirmed by g.l.c.

TABLE 1

Hydrogen-1 n.m.r. data[a] for some organothallium compounds in $CDCl_3$ at 23 °C

	δ/p.p.m.				
Compound	H^1	H^2	H^3	Tl–CH_3	Other
(4)[b]	2.65 (635)	2.80 (670)	5.26 (685)		*c*
(7)	2.00 (435)	2.30 (485)	*d*	1.12 (377)	*e*
(8)	2.00 (440)	2.20 (485)	*d*	1.08 (375)	*f*
(11)	2.55 (400)	2.40 (430)	5.85 (680)	1.16 (380)	*g*

[a] Values of *J*(Tl–H) in Hz are given in parentheses. Neither the separation between *J*(^{203}Tl–H) and *J*(^{205}Tl–H) nor proton–proton couplings could be observed because of the broadness of the resonances, except as noted. Proton numbering is as follows: Tl($CH^1H^2CH^3XY$). [b] At −50 °C: *J*(Tl–H^1) 635, *J*(Tl–H^2) 660, *J*(Tl–H^3) 605 Hz. [c] δ(CH_2) 2.9—3.6(m), δ(N–CH_3) 3.28 p.p.m. [d] Not observed due to overlapping with other resonances. [e] δ(C–CH_3) 1.28(d) p.p.m. [*J*(H–H) 6, *J*(Tl–H) 36 Hz], δ(O–CH_3) 3.34, δ($COCH_3$) 1.90 p.p.m. [f] δ(C_6H_{13}) 0.7—1.2(m), δ(O–CH_3) 3.24, δ($COCH_3$) 1.86 p.p.m. [g] δ(CH_2) 2.85—3.5(m) p.p.m.

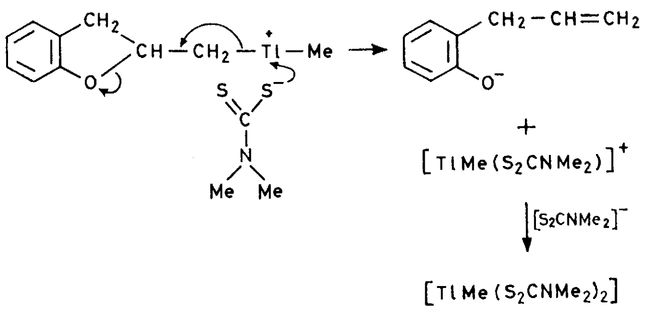
Acetato(2-methoxypropyl)methylthallium, (7).—Propylene gas was passed through an orange-yellow suspension of Tl[O_2CMe]$_3$ (2.0 g) in methanol (20 cm³) at 20 °C for 1 h, whereupon a clear colourless solution formed. To this solution was added $SnMe_4$ (0.94 g), and the reaction mixture was allowed to stand for another hour at 20 °C. The solvent was removed *in vacuo*. The remaining viscous products were triturated with n-hexane, and then filtered off. Recrystallisation from benzene–n-hexane gave white powdery solids (0.76 g). The ^1H n.m.r. spectrum in $CDCl_3$ indicated that the product was contaminated with a small amount of [$TlMe_2(O_2CMe)$] and it was not analysed Acetato(2-methoxyoctyl)methylthallium, (8), was obtained similarly.

Hydrogen-1 n.m.r. data for these compounds are shown in Table 1. In this Table the pairwise selection of components arising from coupling of the H^1 and H^2 protons with thallium nuclei (^{203}Tl and ^{205}Tl, 100% natural abundance) was readily made on inspection of the spectra; thus the upper-field component of the H^1 resonances overlapped that of H^2 in the spectra of (4), (7), and (8), while the lower-field component of the H^1 resonances overlapped that of H^2 in the spectrum of (11).

RESULTS AND DISCUSSION

Derivatisation of Oxythallated Adducts to Stable Organothallium Compounds.—The oxythallated adducts of styrene and *o*-allylphenol,[5] [TlR(O_2CMe)$_2$] [(1) and (2), see below] were converted into the dithiocarbamates, [TlR(S_2CNMe_2)$_2$], (3) and (4), with Na[S_2CNMe_2]. Treatment of (1) and (2) with $SnMe_4$ gave dialkylthallium compounds [TlMeR(O_2CMe)], (5) and (6). It is notable that (3)—(6) are all stable in hot methanol, and thus are much more reluctant to undergo oxidative decomposition[5] than (1) and (2). The methylation of monoalkylthallium compounds with $SnMe_4$ appears to be particularly useful in converting very unstable oxythallated adducts of propylene and oct-1-ene into [TlMeR(O_2CMe)], (7) and (8), possessing reasonable thermal stability.

As expected, the ^1H n.m.r. spectra of (7) and (8) (Table 1) exhibited resonances associated only with the products of Markownikoff addition. It should also be pointed out that Lethbridge *et al.*[9] claimed to have found ^1H n.m.r. evidence for the existence of an oxythallated adduct of oct-1-ene, [Tl{$CH_2CH(OMe)C_6H_{13}$}(O_2CMe)$_2$]; however, their data, which showed no splittings due to large thallium–proton spin couplings, appear to be incorrect when compared to those in Table 1. In particular, the thallium–proton spin coupling constants in monoalkylthallium compounds should be larger than those in dialkylthallium compounds.[2]



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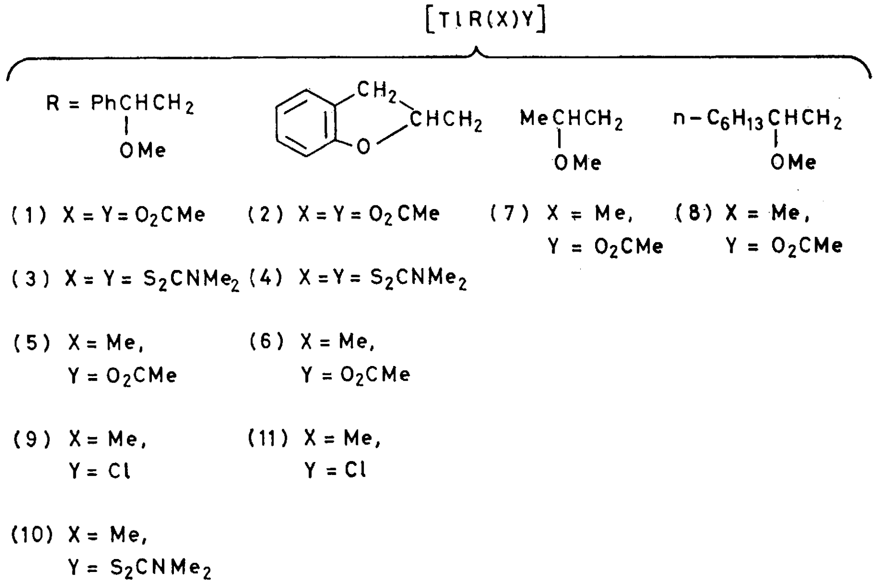
[8] M. Tanaka, H. Kurosawa, and R. Okawara, *J. Organometallic Chem.*, 1969, **18**, 49; 1970, **21**, 41; *Inorg. Nuclear Chem. Letters*, 1967, **3**, 565.

[9] A. Lethbridge, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1974, 1929.

Addition of NaCl or $Na[S_2CNMe_2]$ to (5) in aqueous methanol gave (9) and (10). Compound (11) was obtained similarly from (6). On the other hand, similar treatment of (6) or (11) with either 1 or 2 equivalents of $Na[S_2CNMe_2]$ resulted in ready liberation of *o*-allylphenol and precipitation of $[TlMe(S_2CNMe_2)_2]$. In view of the successful isolation of the related dithiocarbamates, (4) and (10), an apparently base-catalysed deoxythallation of (6) or (11) with the $[S_2CNMe_2]^-$ anion may have been caused by the combined effect of the good leaving ability of the phenoxide anion and the electron-donating property of the methyl group.



Hydrogen-1 *N.M.R. Conformational Analysis of Oxythallation Products and Evidence for* trans *Oxythallation of Styrene*.—The ^1H n.m.r. spectra of the oxythallation products of 1-olefins examined in this study exhibited non-equivalent methylene proton resonances owing to the presence of an asymmetric carbon centre.[10] Uemura *et al.*[11] reported, but did not explain, the considerably large difference in two ^2J(Tl–H) values (760 and 920 Hz) for a pair of diastereotopic methylene protons in (1) and related compounds. In Table 2 are shown the similar ^1H n.m.r. data for compounds derived from (1). The pairwise selection of components arising from coupling of the methylene protons with thallium in the spectra of (1) [11] and (3) is probably correct in view of the fine structure due to proton–proton coupling (see below) and the complete disappearance of one pair of resonances in the spectra of (1D) and (3D) derived from *trans*-PhCH=CHD (see later). Similarly, the spectra of (5) and (10) were assigned on the basis of the spectra of the deuterium analogues prepared from (1D).

We attribute the great difference between the two ^2J(Tl–H) values observed for each compound (Table 2) as originating from the unequal population of the conformers (I) > (II) ≫ (III). First, of the two diastereotopic methylene proton resonances of (3), the resonance with the smaller ^2J(Tl–H) value has vicinal proton coupling constants, ^3J(H–H), of the order of 10 Hz, while the other with the larger ^2J(Tl–H) value shows ^3J(H–H) *ca.* 5 Hz, suggesting that either (I) or (II) is the dominant conformer, although it was difficult to observe temperature-dependent behaviour of ^3J(H–H) because of the broadness of the resonances. Conformer (I) would be more stable than (II) because of the relative size of the phenyl and the methoxy-groups.

TABLE 2

Hydrogen-1 n.m.r. data [a] for some β-methoxy-β-phenylethylthallium compounds in $CDCl_3$

		δ/p.p.m.			
Compound	θ_c/°C	H^1	H^2	H^3	Tl–CH_3
(3)	50 [b]	2.84 (550)	2.80 (675)	4.67 (590)	
	23	2.83 (534)	2.79 (670)	*c* (545 ± 20)	
	−50	2.77 (487)	2.73 (665)	4.52 (460)	
(5)	23	2.20 (360)	2.40 (520)	*d*	1.10 (380)
(10)	50	2.41 (296)	2.56 (455)	5.00 (435)	1.30 (361)
	23	2.39 (275)	2.52 (460)	5.00 (420)	1.29 (360)
	−50	*c* (180 ± 30)	2.50 (470)	*c* (380 ± 30)	1.39 (356)

[a] As in Table 1. [b] $J(H^1–H^2) \simeq J(H^1–H^3) \simeq 10$, $J(H^2–H^3) \simeq 5$ Hz. [c] One half of the doublet resonance split by the thallium coupling is hidden under the strong peaks due to the phenyl protons (δ 7.1—7.5 p.p.m.) in the case of H^3 of (3) and the O–CH_3, N–CH_3, and Tl–CH_3 protons (δ 2.9—3.5 p.p.m.) in the case of H^1 and H^3 of (10). [d] Not observed due to overlapping with other resonances.

Secondly, the smaller value of ^2J(Tl–H^1) than ^2J(Tl–H^2) assigned to conformation (I) is understandable if the theory [12] of β-substituent effects on ^2J(H–H) applies in

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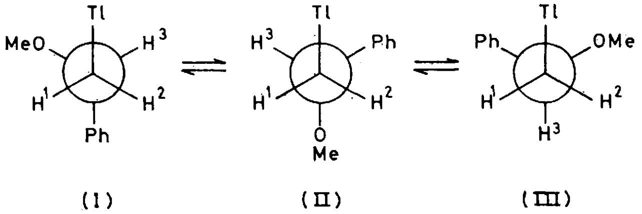
[10] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 368.

[11] S. Uemura, K. Zushi, A. Tabata, A. Toshimitsu, and M. Okano, *Bull. Chem. Soc. Japan*, 1974, **47**, 920.

[12] J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 1965, **42**, 1339.

the case of ${}^2J$(Tl–H). It was shown previously[2] that values of ${}^2J$(Tl–H), like ${}^2J$(H–H), are negative in sign and dominated by the Fermi contact term. Thus, in conformation (I), the strongly electron-withdrawing methoxy-group located *gauche* to Tl and H^1, but *trans* to H^2, may cause a positive shift of ${}^2J$(Tl–H^1) but a negative shift of ${}^2J$(Tl–H^2) relative to ${}^2J$(Tl–H) of unsubstituted β-phenylethylthallium compounds, leading to different values of these two ${}^2J$(Tl–H). On the other hand, (II) would cause negative shifts in both ${}^2J$(Tl–H^1) and ${}^2J$(Tl–H^2) of similar magnitudes and therefore give rise to approximately similar values of the two ${}^2J$(Tl–H), provided that the phenyl group has very little influence on ${}^2J$(Tl–H) compared to the methoxy-group; ${}^2J$(Sn–H) of $Ph_3SnCH_2CH_2Ph$ (55.5 Hz) is almost the same as that of $Ph_3SnCH_2CH_3$ (56.5 Hz), but smaller than that of $Ph_3SnCH_2CH_2OPh$ (63.5 Hz).[13] In addition, at lower temperatures the increased contribution of (I) to the spectra at the expense of that of (II) would result in a decrease of ${}^2J$(Tl–H^1) but very little change in ${}^2J$(Tl–H^2), as is actually observed for (3) and (10) (Table 2). The almost temperature-independent behaviour of ${}^2J$(Tl–CH$_3$) for (10) is also consistent with the suggestion that the change of ${}^2J$(Tl–H^1) with temperature is primarily due to a conformational effect, not to a change in electronic configuration around the thallium atom. However, it is difficult at present to explain more fully all the aspects of the temperature-dependent ^{1}H n.m.r. data, particularly the change in ${}^3J$(Tl–H^3) and, to a lesser extent, ${}^2J$(Tl–H^2). One possible explanation for the former is that only a slight decrease in the concentration of (III) at the lower temperature is enough to cause a decrease in ${}^3J$(Tl–H^3), since this coupling is expected to be much more configuration dependent in view of the reported ratio, ${}^3J$[Hg–H(*trans*)] : ${}^3J$[Hg–H(*gauche*)] $\geqslant$ 6 : 1 in organomercury compounds.[14]



(I) (II) (III)

Thirdly, for compounds in Table 1 where the difference in the steric bulk of two β substituents is not as large as those in (1) and its derivatives, the contributions of the conformations corresponding to (I) and (II) to the observed spectra are expected to be approximately equal, and hence the difference between the two ${}^2J$(Tl–H) values in these compounds may not be as large as those in Table 2 [*cf.* (4) and (3), or (7) or (8) and (5) in Table 1]. Moreover, ${}^2J$(Tl–H^1) and ${}^2J$(Tl–H^2) of (4) exhibited almost no temperature dependence, in contrast to those of (3) (see above).

In the ^{1}H n.m.r. spectra of (1D) and (3D) derived from *trans*-PhCH=CHD, the pair of methylene proton resonances having the smaller ${}^2J$(Tl–H) disappeared completely. This indicates that H^1 of (I)—(III) was replaced by deuterium, and that, within experimental error, oxythallation of styrene was 100% *trans*.

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[13] B. de Poorter, *J. Organometallic Chem.*, 1977, **128**, 361.

[14] M. M. Kreevoy and J. F. Schaefer, *J. Organometallic Chem.*, 1966, **6**, 589.