Reductant-induced Homolysis of the Thallium–Carbon Bond: Novel Oxygenation of Alkylthallium(III) Compounds with Ascorbic Acid

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Summary The oxygenation of monoalkylthallium(III) salts to give alcohols and their reductive conversion into dialkylthallium(III) compounds with ascorbic acid and hydrazine both proceed through reductant-induced homolysis of the thallium–carbon bond.

IN contrast to recent interest in the ready homolysis of metal–carbon bonds of organometallic compounds through photochemical activation[1] or initial interaction with oxidants,[2] homolysis induced by reducing agents has not been widely investigated except for the free radical mechanism in reductive demercuration by $NaBH_4$[3] or the symmetrisation by other reductants[4] of organomercury(II) salts. Similar treatment of organothallium(III) salts with $NaBH_4$,[5] however, resulted in quite different reactions from those in the $NaBH_4$ reduction of organomercurials, providing no convincing evidence for a radical mechanism. We describe here the first clear evidence for the occurrence of reductant-induced homolysis of thallium–carbon bonds† in alkylthallium(III) salts brought about by ascorbic acid and hydrazine, and possibly also $NaBH_4$.

Reaction of the diacetate (**1**) (3 mmol) with hydrazine (9 mmol) in methanol (20 cm^3) under nitrogen at room temperature for 3 h gave the acetate (**2**), m.p. 113—114 °C (60%, based on the alkyl), PhCH(OMe)Me (16%), and styrene (10%), with the remaining thallium components being converted into thallium(I) salts. Compound (**1**) and ascorbic acid under similar conditions likewise gave (**2**) (44%). Comparison of the ^1H n.m.r. spectra of [$^2H_1$]-(**2**) obtained from the stereospecifically deuterium labelled compound [**3a**, X = $Tl(OAc)_2$][7] with the spectra of (**2**) and [**3a**, X = $Tl(OAc)_2$] indicated that the formation of [$^2H_1$]-(**2**) was accompanied by 55% (for hydrazine) or 63% (for ascorbic acid) racemisation at the α-carbon atom. A

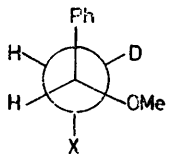
† Free alkyl radicals have recently been trapped as spin adducts in the bromodethallation of $PhCH(OMe)CH_2Tl(OAc)_2$ with CuBr,[6] but neither the precise role of CuBr nor the way by which the compound decomposed in this reaction were elucidated.

recovered sample of [**3a**, X = $Tl(OAc)_2$] at 40% completion of the reaction with hydrazine was contaminated by *ca.* 10% of [**3b**, X = $Tl(OAc)_2$] (20% racemisation), while the stereochemistry of [**3a**, X = $Tl(OAc)_2$] was unchanged under similar conditions in the absence of added reductants. In addition, the same ^1H n.m.r. method showed that $[PhCH(OMe)CHD]_2TlOH$, a minor product from reduction with $NaBH_4$[5a] of [**3a**, X = $Tl(OAc)_2$], contained 56% of the racemised alkyl. This reductive conversion of alkylthallium(III) salts into dialkylthallium(III) compounds with racemisation is analogous to that[4] of alkylmercury(II) salts under reducing conditions, suggesting occurrence of reductant-induced homolysis of the thallium–carbon bond [reaction (1)].

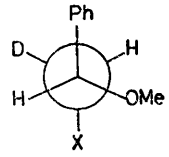
$$RTl^{2+} \xrightarrow{e^-} RTl^{+} \longrightarrow R\cdot + Tl^{+} \qquad (1)$$

$PhCH(OMe)CH_2Tl(OAc)_2$ (1)

$[PhCH(OMe)CH_2]_2TlOAc$ (2)



(3a)



(3b)

In confirmation of the generation of an alkyl radical species, the e.s.r. spectra of a solution in acetonitrile of (**1**), perdeuterionitrosodurene, and hydrazine or ascorbic acid exhibited resonances identical with those of $PhCH(OMe)CH_2N(O\cdot)C_6H(CD_3)_4$.[6] The e.s.r. parameters (g = 2·006, a_H = 1·59, a_H' = 0·48, a_N = 1·39 mT at 17 °C) for a similar solution in methanol–benzene (1 : 1) were also identical with those for $PhCH(OMe)CH_2N(O\cdot)C_6H(CD_3)_4$ generated independently in methanol–benzene by the method reported.[6] (The differences between the e.s.r. parameters for acetonitrile[6] and methanol–benzene solutions can be ascribed to a solvent effect.)

The reaction of various compounds of type $RTl(OAc)_2$, which were prepared either by oxythallation or by metathesis between $Tl(OAc)_3$ and $K_2[RSiF_5]$, with several reductants was also investigated in methanol at room temperature under oxygen at atmospheric pressure. Ascorbic acid was found to be particularly suitable for selectively converting the diacetates $RTl(OAc)_2$ into the alcohols ROH under very mild conditions; % yields for the alcohols ROH isolated [reaction (2)] are as follows: R = n-octyl, 70; $MeO_2C[CH_2]_{10}$, 85; $PhCH(OMe)CH_2$, 67; $PhCH(OEt)CH_2$, 59; $PhMeC(OMe)CH_2$, 55; $Me_2C(OMe)CH_2$, 32.

$$R\cdot + O_2 \longrightarrow ROO\cdot \xrightarrow{\text{Reductant}} ROH \qquad (2)$$

Of particular relevance to the mechanistic aspects of this oxygenation are the following: (i) ROH is not produced in the absence of ascorbic acid, nor from $RTl(OAc)_2$ and H_2O_2; (ii) ROAc is not a precursor of ROH since it is stable under the reaction conditions; (iii) a 1 : 1 mixture of (**3a**, X = OH) and (**3b**, X = OH) was obtained from [**3a**, X = $Tl(OAc)_2$] as shown by ^1H n.m.r. spectroscopy. In contrast, hydrazine and $NaBH_4$ with $RTl(OAc)_2$ under O_2 afforded only very low yields (trace—20%) of ROH, larger amounts of R_2TlOAc (30—80%) being produced in the case of hydrazine reduction. Catechol, *o*-aminophenol, and hydroquinone were even less effective for the oxygenation of $RTl(OAc)_2$.

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[1] P. W. N. M. van Leeuwen, C. F. Roobeek, and R. Huis, *J. Organometallic Chem.*, 1977, **142**, 233; J. R. Sheats and H. M. McConell, *J. Amer. Chem. Soc.*, 1977, **99**, 7091.
[2] J. Y. Chen and J. K. Kochi, *J. Amer. Chem. Soc.*, 1977, **99**, 1450, and references therein.
[3] R. P. Quirk and R. E. Lea, *J. Amer. Chem. Soc.*, 1976, **98**, 5973, and references therein.
[4] F. R. Jensen and B. Rickborn, 'Electrophilic Substitution of Organomercurials,' McGraw-Hill, New York, 1968, p. 137.
[5] (a) S. Uemura, A. Tabata, and M. Okano, *J.C.S. Chem. Comm.*, 1972, 517; (b) R. B. Herbert, *Tetrahedron Letters*, 1973, 1375.
[6] S. Uemura, A. Toshimitsu, M. Okano, T. Kawamura, T. Yonezawa, and K. Ichikawa, *J.C.S. Chem. Comm.*, 1978, 65.
[7] H. Kurosawa, R. Kitano, and T. Sasaki, *J.C.S. Dalton*, 1978 ,234.