SHORT PAPER

Preparation and characterisation of 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane-4,5-dione as standard for an attempt to trap 1,2-dioxetanedione, a possible high-energy intermediate in peroxyoxalate chemiluminescence[†]

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The thermally stable triorganoantimony derivative, 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane-4,5-dione, has been prepared and characterised being then used as a reference in attempts to trap 1,2-dioxetanedione, one of the high-energy intermediates postulated in peroxyoxalate chemiluminescence, by an insertion reaction with triphenylantimony.

Keywords: antimony(V), peroxides, chemiluminescence, 1,3,2-dioxastibolane-4,5-dione

In the course of our investigations on the mechanism of peroxyoxalate chemiluminescence we proposed a simplified mechanistic scheme for the reaction sequence prior to the excitation step,[1] synthesized a peracid key-intermediate of this sequence,[2] and unequivocally demonstrated that this kind of derivative does not act as a high-energy intermediate in the excitation step.[3] Furthermore, direct experimental evidence for an electron exchange between the high-energy intermediate and a fluorescent activator has been obtained.[4] However, the structure of the high-energy intermediate is still unknown,[5] even though several groups have published recent attempts at its identification.[6,7]

Chandross[8] was the first to observe the "volatile" nature of the high-energy intermediate involved in the peroxyoxalate reaction, reporting that vapors evolved from the chemical reaction of oxalyl chloride with hydrogen peroxide (30%) in dioxane "…have the unusual property of inducing the fluorescence of suitable indicators, *e.g.*, a filter paper impregnated with anthracene". Rauhut *et al.*[9] also reported the observation of a volatile high-energy intermediate using a system where a strong flux of Ar, N$_2$ or O$_2$ was passed through a solution containing bis(2,4-dinitrophenyl) oxalate and H$_2$O$_2$ in dimethylphthalate. The evolving gas produced chemiluminescence in the presence of 9,10-diphenylanthracene or rubrene. However, attempts to characterise the volatile high-energy intermediate, using either gas phase infrared spectroscopy or mass spectrometry[10,11] have failed, probably due to the thermal instability of this intermediate.

On the other hand, Baumstark *et al.*[12] report the insertion reaction of triphenylantimony into the O-O bond of tetramethyl-1,2-dioxetane, yielding 4,4,5,5-tetramethyl-2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane (**1**), which proved to be more stable than the corresponding triphenylphosphorous derivative. The addition reaction occurs concomitantly with the catalytic decomposition of tetramethyl-1,2-dioxetane, yielding acetone and triphenylantimony. However, the addition reaction is almost quantitative in conditions of excess tetramethyl-1,2-dioxetane.

We report here our attempts to trap 1,2-dioxetanedione, the possible high-energy intermediate in the peroxyoxalate reaction by insertion reaction of triphenylantimony into the O–O bond of this cyclic peroxide. The expected insertion product, 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane-4,5-dione (**2**), was
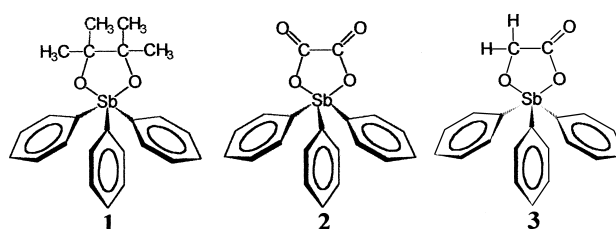
prepared by an independent route and characterised by ^{13}C-NMR, infrared and mass spectrometry.

Results and discussion

The preparation of compound **2** (Scheme 1, Route 1) was performed in analogy to Matsumura's[13] procedure for 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolan-4-one (**3**). Reaction of dibromotriphenylantimony[14] with sodium methoxide followed by addition of anhydrous oxalic acid, results in a white crystalline solid, stable at room temperature, melting at 180–81°C with decomposition and gas evolution. The mass spectrum (direct injection and chemical ionization with methane) shows the expected molecular peak at *m/z* 440/2, in accordance with the natural abundance of ^{121}Sb and ^{123}Sb (57.2% and 42.8%, respectively). The presence of prominent ester carbonyl bands at 1662 and 1685 cm^{-1}, a C–O stretching band at 1438 cm^{-1} and a Sb–O stretching band[15] at 523 cm^{-1} in the infrared spectrum also contribute to confirm the structure (Table 1).

Table 1   Assigned IR frequencies for **2**

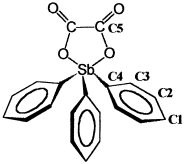| Frequency (cm^{-1})[a]	Assignment	Frequency (cm^{-1})[a]	Assignment
1685 m	ν(C=O)	1021 w	ν(C-O)
1662 s	ν(C=O)	996 w	ν(C=C) ring breath
1613 vw	ν(C=C)	904 vw	CH rock
1573 vw	ν(C=C)	828 vw	CH rock
1480 w	δ(CH)	817 vw	CH rock
1462 m	δ(CH)	765 m	CO$_2$ scissoring
1438 m	ν(C-O)	731 m	CO$_2$ scissoring
1338 w	CH wag	686 m	ν(Sb-C)
1318 w	CH wag	614 vw	δ(CH)
1271 w	CH wag	523 vw	Sb-O stretching[15]
1212 s	ν(C-O)	458 m	CO$_2$ rock
1069 w	ν(C-O)		

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Further support is provided by INVGATE ^{13}C-NMR spectroscopy, which allows integration of the peaks. The chemical shifts and the relative integrated intensities are in agreement with structure **2** (Table 2, Figure 1). The two carbonyl carbons are equivalent and appear at 160.1 ppm and, since only one set of peaks is observed for the three phenyl groups, it appears reasonable to assume that these are attached to the antimony forming a distorted trigonal pyramid, orthogonal to the plane of the oxalic acid moiety, in agreement with the structure proposed for the similar triphenylantimony glycolate **3**.[13]

Table 2 INVGATE ^{13}C-NMR peak assignments and integrals obtained for **2**

	C1	C2	C3	C4	C5
Shift (ppm)^a	130.3	128.9	133.6	141.1	160.1
Carbon Integrals	(3.2)	(6.8)	(6.7)	(3.1)	(2.0)

^{a}relative to TMS at 25°C, DMSO-d$_6$ and 50 MHz.

Attempts were made to trap possible volatile intermediates formed in the peroxyoxalate reaction, which consists in a base catalysed reaction of activated oxalate esters with hydrogen peroxide in the presence of a polyaromatic hydrocarbon. From the high-energy intermediates postulated in this reaction,[16] the only structure expected to show high volatility is the peroxidic CO_2 dimer, 1,2-dioxetanedione (**4**),[5] which should yield **2** by an insertion reaction of triphenylantimony (Scheme 1, Route 2). The peroxyoxalate reaction was performed in the absence of an activator, passing dry and cooled N_2 through the peroxyoxalate solution and leading the gas stream into a solution of triphenylantimony in CH_2Cl_2 kept at low temperature. After warming to room temperature this solution was analysed for the content of **2**. However, having used various experimental reaction conditions (reagent concentrations, solvents, temperatures), we were not able to identify the presence of **2**, after purification of the solid obtained by chromatographic techniques. Only a yellowish solid with a melting point (275°C) quite similar to that reported for poly(triphenylstibine) oxide (280°C) was isolated.

This compound may have been formed by reaction of triphenylantimony with hydrogen peroxide,[17] carried by the gas stream to the flask containing triphenylantimony.

Although it was not possible to detect the trapping product of 1,2-dioxetanedione (**4**) by triphenylantimony, this does not mean that **4** is not formed as a volatile high-energy intermediate in the peroxyoxalate reaction. This intermediate might not be stable enough to persist the time to reach the flask containing triphenylantimony, or the main reaction of this cyclic peroxide might be catalytic decomposition.[12] Alternatively, the reaction may occur by addition of $(C_6H_5)_3Sb$ to one of the peroxidic oxygen atoms, forming $(C_6H_5)_3Sb^+$-O-CO-COO$^-$, which can fragment to $(C_6H_5)_3SbO$, CO and CO_2, rather than cyclise.[18]

Experimental

Dibromotriphenylantimony[14] (90%, m.p. 210–212°C) and anhydrous oxalic acid[19] were prepared by literature procedures. Anhydrous ethyl acetate and a stock solution of anhydrous hydrogen peroxide in ethyl acetate were prepared as previously described.[1] IR spectra were obtained on a Perkin-Elmer FT-IR 1750 and mass spectrometry was performed on a Finnigan Mat INCOS 50 Mass Spectrometer. ^{13}C-NMR analyses were acquired in a Bruker AC 200-F (50 MHz for ^{13}C) using DMSO-d$_6$ as solvent and the standard Bruker program INVGATE.AU (recycle delay: 5 s; acquisition time: 1.3 s; pulse duration: 2.0 μs [34°]; 32 k data points). The data were then zero filled to 64 k data points and Fourier transformed under matched filter conditions (digital resolution *ca.* 0.4 Hz per data point).

Preparation of 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane-4,5-dione (**2**): A benzene solution of dibromotriphenylantimony (1.95 mmol, 10 ml) was added at room temperature to a stirred solution of sodium methoxide in methanol (90 mg of Na dissolved in 2 ml of methanol). After 30 min a white precipitate of sodium bromide was filtered off and 10 ml of an anhydrous ethereal solution of oxalic acid (2.22 mmol) were added at 0°C. After 30 min stirring, the temperature was allowed to rise to room temperature and the solution was stirred an additional 30 min. After removing the solvent, a finely divided white solid was obtained, being then dried at 100°C/ 1.0 mmHg for 3h [93%, m.p. (decomp.) 180–181°C]. TLC on SiO_2 using ether showed only one spot with R_F = 0.33, revealed with I_2. The molecular peak was detected at *m/e* 440/2 [M$^+$, $(C_6H_5)_3Sb(OOC-COO)$] as well as fragments at 352/4 [$(C_6H_5)_3Sb^{+·}$] and 275/7 [$(C_6H_5)_2Sb^+$] in the mass spectrum, using direct injection and chemical ionisation with methane. The ^{13}C-NMR spectrum of **2** was acquired using chromium (III) 2,4-pentanedionate as the relaxation agent. In this condition integration is possible and relative integral values are given in parenthesis. ^{13}C-NMR (DMSO-d$_6$, 50 MHz, ppm): 128.9 (6C, 6.8), 130.3 (3C, 3.2), 133.6 (6C, 6.7), 141.1 (3C, 3.1), 160.1 (2O–C=O, 2.0).
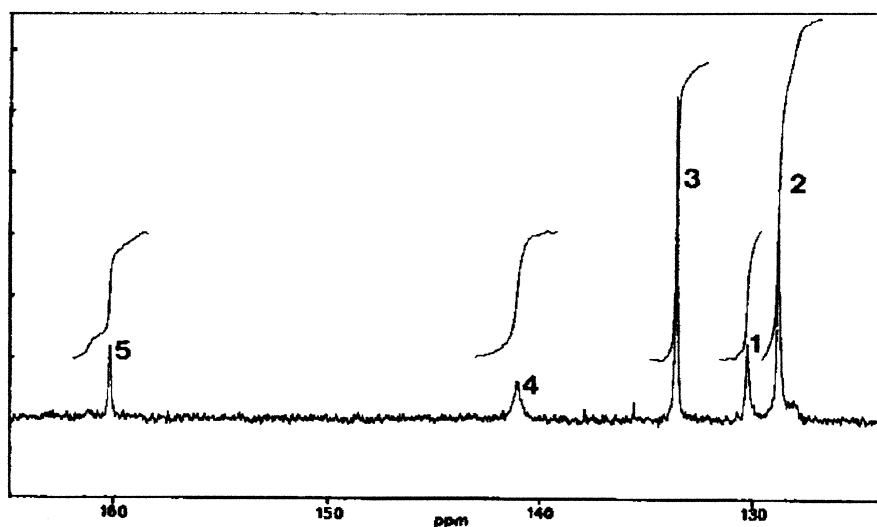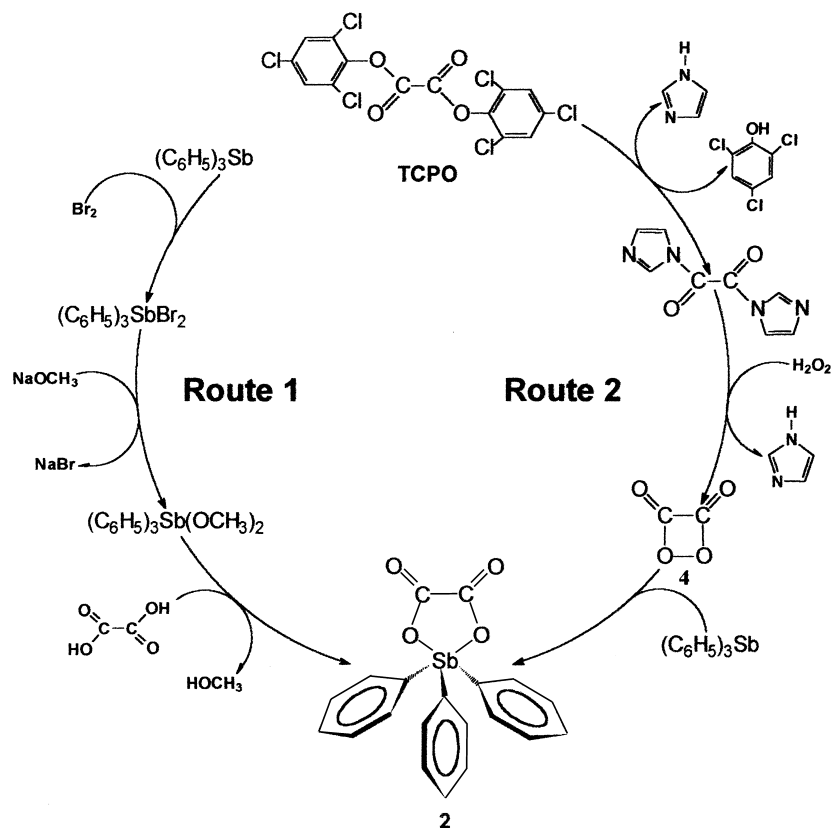
Fig. 1 INVGATE ^{13}C-NMR spectrum of 2,2,2-triphenyl-2λ^5-1,3,2-dioxastibolane-4,5-dione (**2**)

Scheme 1
Strategies to prepare compound 2,2,2-triphenyl-2λ⁵-1,3,2-dioxastibolane-4,5-dione (**2**) – Route 1 –
and to trap 1,2-dioxetanedione (**4**) – Route 2.

Attempt to trap 1,2-dioxetanedione with triphenylantimony: Two three-neck round-bottom flasks (Flask A and Flask B of 125 and 50 ml, respectively) were connected by a Teflon tube (17 × 0.5 cm), introduced into the solution of Flask B, but not of Flask A, which also contained a gas inlet. To Flask A, containing bis(2,4,6-trichlorophenyl) oxalate (0.44 mmol) in 20 ml of dichloromethane, under magnetic stirring and a strong flux of dry and cold N_2, 10 ml of an ethereal imidazole/H_2O_2 solution (50 μmol and 0.85 mmol, respectively) were added. The gas outlet of Flask A entered the solution of Flask B containing triphenylantimony (0.85 mmol) in 20 ml of dichloromethane at –60°C. After 30 min with a strong flux of dry and cold N_2 (passed through a column containing silica gel and anhydrous $CaCl_2$, and through a metal coil kept at –70°C), the content of Flask B was allowed to reach room temperature and the obtained solution was evaporated, obtaining a yellowish solid (m.p. 275–9°C). Infrared analysis of this solid in KBr showed a carbonyl band at 1643 cm⁻¹. TLC on SiO_2 plates (ethyl ether/hexane, 3:1) revealed three substances with R_f = 0.0, 0.33 and 0.56, which were separated by two subsequent column chromatographies [neutral Al_2O_3 (activity II), ether/hexane (3:1) and neutral Al_2O_3 (activity II), $CHCl_3$/ether (10:1)]. However, none of the compounds isolated was spectroscopically identical to the standard **2**. Therefore, their identification was pursued no further.

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