Mechanisms of Stannyl-Carbon Bond Cleavages by Reactions with Benzoyl Peroxide

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The mechanism for the process giving trimethyl(benzoyloxy)stannane by the reaction of benzoyl peroxide with trimethylphenylstannane or tetramethylstannane has been investigated. The kinetic results exclude the possibility that the decomposition of the peroxide is induced by the stannanes. The addition of dicyclohexylcarbodiimide as a trapping agent for benzoic acid markedly depressed the yield of the benzoyloxystannane by the reaction of trimethylphenylstannane, suggesting that the benzoyloxystannane is mainly or exclusively produced by the protodestannylation reaction of trimethylphenylstannane with benzoic acid. In the reaction of tetramethylstannane with benzoyl peroxide, trimethyl(benzoyloxy)stannane was formed only when a large excess of the stannane was used, and dicyclohexylcarbodiimide showed no significant effect upon the formation of the benzoyloxystannane. A homolytic process has been suggested for the reaction giving the benzoyloxystannane from tetramethylstannane.

There are many reactions which have been established to involve homolytic cleavages of the stannyl–carbon bond caused by free-radical attack.[1] An example is the reaction of diacyl peroxide with tetraalkylstannane or trialkylarylstannane.[2] The thermal decomposition of benzoyl peroxide in trimethylphenylstannane was examined by Razuvaev *et al.*; they found carbon dioxide, benzene, biphenyl, and trimethyl(benzoyloxy)stannane as the products. Since the formation of carbon dioxide and the hydrocarbons was thought to strongly suggest the generation of the benzoyloxyl radical through the thermolysis of the benzoyl peroxide, the formation of trimethyl(benzoyloxy)stannane was explained in terms of the attack of the benzoyloxyl radical on the stannane.[2a,b] However, there was no definite evidence

$$(PhC(=O)-O-)_2 \longrightarrow PhC(=O)-O\cdot \xrightarrow{Me_3SnPh} PhC(=O)-O-SnMe_3 + Ph\cdot$$

in support of their mechanism for the process giving trimethyl(benzoyloxy)stannane from trimethylphenylstannane. Some other mechanisms are possible; for example, the reaction of diacyl peroxide with the stannane by way of the coordination of the tin atom to the carbonyl oxygen of the peroxide, analogous to the Lewis acid-catalyzed decomposition,[3] may produce the benzoyloxystannane. A somewhat modified cyclic coordination process has been suggested for the reaction of allyltrimethylstannane with benzoyl peroxide giving allyl benzoate and trimethyl(benzoyloxy)stannane; this suggestion was based on the observations that the rate of the decomposition was apparently dependent on the concentration of the stannane, a large negative entropy value, and that only 1-methylallyl benzoate was formed from 2-butenyltrimethylstannane.[4]

Secondly, since carboxylic acid has been known to be formed by the thermolysis of diacyl peroxide in a hydrocarbon solvent,[5] protodestannylation of organostannane with the carboxylic acid is also a possible route to give acyloxystannane,[6] as has been suggested preliminarily.[7]

Such a tetraalkylstannane as tetraethylstannane has also been known to give trialkyl(benzoyloxy)stannane by means of a reaction with benzoyl peroxide.[2a] A stannane not bearing a phenyl group would resist the protodestannylation process,[8] though; hence a different mechanism would be expected for the process giving triethyl(benzoyloxy)stannane in the reaction of tetraethylstannane with benzoyl peroxide. In this paper we wish to discuss the mechanisms of the processes giving trialkyl(benzoyloxy)stannane from trialkylphenyl- and tetraalkylstannanes by means of reactions with benzoyl peroxide.

Results and Discussion

Trialkyl(benzoyloxy)stannane from Trialkylphenylstannane.[9] In order to elucidate the mechanism for the process giving trimethyl(benzoyloxy)stannane, the thermal decompositions of benzoyl peroxide were carried out under several different conditions. Reactions were carried out in evacuated sealed tubes except for that analyzing the amount of carbon dioxide formed by the thermolysis of benzoyl peroxide. Although the formations of other products such as benzene, benzoic acid, and biphenyl were observed, only the yields of carbon dioxide and trimethyl(benzoyloxy)stannane will be noted in the present study since a detailed product analysis of the reaction had been reported by Razuvaev *et al.*[2]

The rate of the thermal decomposition of benzoyl peroxide was measured in the presence and in the absence of trimethylphenylstannane. Although cyclohexane has often been used as the solvent for the thermolysis,[5] a cyclohexane–chloroform mixed solvent was used for the present kinetic study because of the poor solubility of the other additives in the hydrocarbon solvent. The rate of the decomposition was substantially depressed in the presence of styrene, while the presence of the stannane was found neither to depress nor enhance the rate of the decomposition of benzoyl peroxide. The results, given in Table 1, suggest that trimethylphenylstannane does not take a part in the decomposition of benzoyl peroxide. The possibility of the reaction giving the benzoyloxy stannane directly from trimethylphenylstannane and benzoyl peroxide can thus be ruled out.

Table 1. Rate constants for the decomposition of benzoyl peroxide (0.01 mol/dm³) in chloroform–cyclohexane (1: 1 v/v) at 80 °C with or without an additive[-1]

Additive	Mole ratio Add./BPO	Rate constant $k_1 \times 10^5/s^{-1}$
None		4.91±0.15
$PhCH=CH_2$	10	3.05±0.10
Me_3SnPh	10	4.34±0.29
Me_4Sn	10	4.69±0.18
DCC[a)]	2[b)]	5.92±0.28
PhCOOCOPh	10	4.92±0.30
DCU[c)]	2[b)]	3.43±0.33

a) Dicyclohexylcarbodiimide. b) Experiments with higher concentrations could not be performed because of the limited solubility of the additive. c) *N,N'*-Dicyclohexylurea.

Dicyclohexylcarbodiimide (DCC) was added to the reaction system in order to trap the benzoic acid formed by the thermolysis of benzoyl peroxide in the hydrocarbon solvent. *N,N'*-dicyclohexylurea (DCU) was isolated by the TLC separation of the reaction mixture. The yield of trimethyl(benzoyloxy)stannane was depressed by the addition of DCC in a cyclohexane–chloroform solution. The themolysis of benzoyl peroxide in a cyclohexane–tetrahydrofuran solution in the presence of DCC gave no detectable amount of trimethyl(benzoyloxy)stannane. The amount of carbon dioxide formed by the thermolysis, however, was not affected by the addition of DCC, suggesting that DCC does not intercept the benzoyloxyl radicals during the thermolysis, although a carbodiimide has been known to intercept radicals.[10] The results shown in Table 2 indicate that the decomposition of benzoyl peroxide was not affected by the addition of DCC, they also suggest that benzoic acid might be an intermediate to give trimethyl(benzoyloxy)stannane.

In a control experiment, benzoic acid was heated with trimethylphenylstannane at 85—90 °C for 16 h.

Table 2. Reaction of benzoyl peroxide (BPO) with trimethylphenylstannane (TPSn) at 85—90 °C for 16 h

Initial concentration mol/dm³			Solvent[a)]	Product yield/%[b)]	
BPO	TPSn	DCC		CO_2	$Me_3SnOCOPh$
0.03	0	0	C_6H_{12}–$CHCl_3$	58	—
0.03	0	0.03	C_6H_{12}–$CHCl_3$	55	—
0.03	0.06	0	C_6H_{12}–$CHCl_3$	55	34
0.03	0.06	0.03	C_6H_{12}–$CHCl_3$	54	20
0.03	0	0	C_6H_{12}–THF	27	—
0.03	0	0.03	C_6H_{12}–THF	27	—
0.03	0.06	0	C_6H_{12}–THF	26	15
0.03	0.06	0.03	C_6H_{12}–THF	27	0
0.21	4.2	0	$CHCl_3$	—[c)]	103
0.21	4.2	0.21	$CHCl_3$	—[c)]	30

a) 1: 1 v/v mixture, C_6H_{12}=cyclohexane, THF=tetrahydrofuran. b) Based on mole of BPO. c) Not analyzed.

Table 3. Reaction of benzoic acid (BA) with trimethylphenylstannane (TPSn) or tetramethylstannane (TMSn) at 85—90 °C for 16 h

Initial concentration/(mol/dm³)				Solvent[b)]	Yield/%[a)]
BA	TPSn	TMSn	DCC		$Me_3SnOCOPh$
0.03	0.06	0	0	C_6H_{12}–$CHCl_3$	26
0.03	0.06	0	0.03	C_6H_{12}–$CHCl_3$	0
0.03	0.06	0	0	C_6H_{12}–THF	11
0.03	0.06	0	0.03	C_6H_{12}–THF	trace
0.3[c)]	0	6.0[c)]	0	none	0

a) Based on mole of BA. b) 1: 1 v/v mixture, C_6H_{12}=cyclohexane, THF=tetrahydrofuran. c) Millimoles used for neat reaction.

Trimethyl(benzoyloxy)stannane was formed in yields comparable with those obtained by the reactions with benzoyl peroxide in both the solvents examined. Here again, the presence of DCC completely depressed the formation of trimethyl(benzoyloxy)stannane. These results are shown in Table 3. No serious effect of these additives, *i.e.*, DCC, DCU, and benzoic anhydride, on the rate of the decomposition of benzoyl peroxide was observed, although a slight acceleration and a little depression of the rate of the decompositions were observed in the presence of DCC and DCU respectively. The kinetic results are summarized in Table 1. These results also reveal that the thermolysis of benzoyl peroxide was not seriously affected in the presence of DCC.

On the basis of these observations, the mechanism for the process giving trimethyl(benzoyloxy)stannane may be concluded to involve the protodestannylation reaction of trimethylphenylstannane with benzoic acid, at least partially in a cyclohexane–chloroform solution or a high-concentration reaction in chloroform, and exclusively in a cyclohexane–tetrahydrofuran solution. In the reactions carried out in chloroform-containing solutions, it is not clear whether another competing process (for example, the radical process suggested by Razuvaev *et al.*[2)]) was also operative concurrently or whether DCC could not effectively trap all the benzoic acid.

The mechanism for the formation of trimethyl(benzoyloxy)stannane by means of the reaction of benzoyl peroxide with trimethylphenylstannane in a cyclohexane–tetrahydrofuran solution (and the main process in the other solvent) is shown below. The observation that only the aryl–Sn bond is cleaved by

$$(PhCOO)_2 \longrightarrow 2PhCOO\cdot$$

$$PhCOO\cdot + R\text{–}H \longrightarrow PhCOOH + Ph\text{–}H,\ CO_2,\ Ph\text{–}Ph\ \textit{etc.}$$

$$PhCOOH + Me_3SnPh \xrightarrow{\text{Protodestannylation}} Me_3SnOCOPh + Ph\text{–}H$$

the reaction of trimethylphenylstannane with benzoyl peroxide, giving trimethyl(benzoyloxy)stannane as the sole benzoyloxystannane, is also in accordance with the proposed mechanism.[8)]

Trialkyl(acyloxy)stannane from Tetraalkylstannane. Tetraethylstannane has been known to give triethyl(benzoyloxy)stannane by the reaction with benzoyl peroxide, along with such other products as carbon dioxide, ethane, ethene, butane, and benzoic acid.[2b,d] In our present study, tetramethylstannane instead of tetraethylstannane was chosen as the tetraalkylstannane for two reasons: 1) the recovered tetramethylstannane can easily be removed from the reaction mixture by evaporation, and 2) both the starting stannane and the product, trimethyl(benzoyloxy)stannane, exhibit sharp singlet methyl signals in the NMR spectra and so can conveniently be detected.

Table 4. Reaction of benzoyl peroxide (BPO) with tetramethyl stannane (TMSn) at 85—90 °C for 16 h

Initial concentration mol/dm³			Solvent[a]	Yield/%[b] $Me_3SnOCOPh$
BPO	TMSn	DCC		
0.03	0.06	0	C_6H_{12}–$CHCl_3$	0
0.03	0.06	0	C_6H_{12}–THF	0
0.03	0.24	0	C_6H_{12}–$CHCl_3$	0
0.21	4.2	0	$CHCl_3$	20
0.21	4.2	0.21	$CHCl_3$	18
0.3[c]	6.0[c]	0	none	24
0.3[c]	6.0[c]	0.3[c]	none	23

a) C_6H_{12}=cyclohexane, THF=tetrahydrofuran. Mixed solvents are 1:1 v/v mixtures. b) Based on mol of BPO. c) Millimoles used for neat reactions.

The rate of the thermal decomposition of benzoyl peroxide was measured in both the presence and absence of tetramethylstannane. The results are summarized in Table 1. Neither the acceleration nor the retardation of the rate in the presence of tetramethylstannane was observed. The results suggest that the stannane does not take part in the decomposition of benzoyl peroxide. On the other hand, no detectable amount of trimethyl(benzoyloxy)stannane was formed by the thermolysis of the peroxide in the presence of tetramethylstannane under the same reaction conditions as those used for the thermolysis of benzoyl peroxide in the presence of trimethylphenylstannane. The benzoyloxystannane was formed in a moderate yield only when a large excess and a high concentration of tetramethylstannane were used. The reaction of benzoyl peroxide with tetramethylstannane without the use of the solvent gave trimethyl(benzoyloxy)stannane in a similar yield.[11] Under these conditions, DCC showed no significant effect upon the formation of trimethyl(benzoyloxy)-stannane. These results are given in Table 4. Furthermore, the heating of benzoic acid with tetramethylstannane gave no detectable amount of trimethyl(benzoyloxy)stannane under any reaction conditions used for the thermal decomposition of benzoyl peroxide in the presence of the stannane. This result, together with the lack of any effect of DCC on the formation of trimethyl(benzoyloxy)stannane and the lack of any effect of tetramethylstannane on the rate of the decomposition of benzoyl peroxide, rules out the possibility that the benzoyloxystannane was formed by the decomposition of the peroxide by way of the coordination mechanism. The same results would also rule out the possibility of the benzoyloxystannane being given by the protodestannylation reaction of tetramethylstannane with benzoic acid under the reaction conditions examined. A possible mechanism for the formation of the benzoyloxystannane is a radical attack, as has been suggested by Razuvaev *et al.*[2] The formation of butane by the reaction of benzoyl peroxide with tetraethylstannane[2b,d] is clear evidence in support of the generation of the ethyl radical through the radical attack on the stannane.

$$PhCOO\cdot + Me_4Sn \longrightarrow Me_3SnOCOPh + Me\cdot$$

$$2Me\cdot \longrightarrow C_2H_6 \text{ or } \xrightarrow{R\text{-}H} CH_4 + R\cdot$$

The reactions of benzoyl peroxide with trialkylphenylstannane and with tetraalkylstannane, both giving trialkyl(benzoyloxy)stannane, have thus been found to be quite different in their mechanisms. The formation of trialkyl(benzoyloxy)stannane from trialkylphenylstannane is a more facile reaction than that from tetraalkylstannane. The reaction of tetraalkylstannane with benzoyl peroxide gives trialkyl(benzoyloxy)stannane in a moderate yield only when a high concentration of the stannane is used. The difference is undoubtedly due to the different reactivities of tetraalkyl- and trialkylphenylstannanes to a protodestannylation reaction. The phenyl–Sn bond is reactive enough to be cleaved by the reaction with benzoic acid under the conditions used for the thermolysis of benzoyl peroxide. The alkyl–Sn bond, on the other hand, is stable enough in the reaction with benzoic acid under the same conditions and is cleaved by radical attack only when a high concentration of the stannane is used.

The reaction of benzoyl peroxide with allyltrimethylstannane[4] seems to be an exception, since the stannane has two coordination centers, *i.e.*, the tin atom and the double bond, and can form a cyclic complex with the peroxide. Although trimethylphenylstannane also bears an unsaturated moiety, the interaction of the phenyl group with the electrophile might be weaker than that of the allyl group, and the formation of a cyclic complex of trimethylphenylstannane with the peroxide would not be conformationally favored. Thus, trimethylphenylstannane does not promote the decomposition of benzoyl peroxide.

Experimental

Materials. The tetramethylstannane and trimethylphenylstannane were prepared in according to the literature.[12] Commercial benzoyl peroxide was recrystallized from chloroform–ethanol before use. The solvents were purified by usual procedures

Kinetics. Six evaporated sealed tubes, each containing 2 ml of the peroxide solution (0.01 mol/dm³), were prepared for each run. The tubes were dipped in a constant-temperature bath (80 °C) and then taken up at intervals. The rate of the decomposition was calculated by measuring the remaining amount of the peroxide, which was obtained by iodometry. Experiments in the presence of additives were carried out similarly. The results are given in Table 1.

Reaction of Benzoyl Peroxide with Trimethylphenylstannane or Tetramethylstannane. Benzoyl peroxide (72.7 mg, 0.3 mmol) and trimethylphenylstannane (145 mg, 0.6 mmol) were dissolved in a chloroform–cyclohexane mixed solvent (1 : 1 v/v mixture; total, 10 ml) and sealed in an evacuated tube with or without addition of DCC.

The tube was then heated for 16 h at 85—90 °C. After heating, the solvent and volatile products were evaporated. The residue was weighed and dissolved in chloroform-*d*. A known amount of dichloromethane was added to the solution, and the whole solution was submitted to NMR analysis. The amount of trimethyl(benzoyloxy)stannane was determined by the integration of the trimethyl signal (δ 0.62 ppm) relative to that of dichloromethane (δ 5.21 ppm). A substantial amount of trimethyl(benzoyloxy)stannane (34, 15, and 103% yields in C_6H_{12}–$CHCl_3$, C_6H_{12}–THF, and $CHCl_3$ respectively) was detected by the reaction with trimethylphenylstannane, though the yield was markedly affected by the addition of DCC. The formation of trimethyl(benzoyloxy)-stannane was not observed at all in the reaction with tetramethylstannane under the same conditions as that of trimethylphenylstannane. Trimethyl(benzoyloxy)stannane was formed from tetramethylstannane in a 20% yield when an excess of the stannane (1 g, 4.2 mmol) in a high concentration was allowed to react with benzoyl peroxide (51 mg, 0.21 mmol) in chloroform (10 ml); it was also formed in an 18% yield in the presence of DCC (39 mg, 0.21 mmol). The neat reaction of benzoyl peroxide (73 mg, 0.3 mmol) with tetramethylstannane (1.45 g, 6.0 mmol) gave trimethyl(benzoyloxy)stannane in a 24% yield; the yield was not affected by the addition of DCC (55 mg, 0.3 mmol). The NMR signal of trimethyl(benzoyl-oxy)stannane was confirmed by examining the spectrum of the authentic sample prepared from bromotrimethylstannane and silver benzoate.[13] The amount of carbon dioxide formed during thermolysis (reflux, 16 h) was measured by bubbling a nitrogen stream into the reaction solution, which was then introduced into aqueous barium hydroxide (0.1 mol/dm^3, 10 ml). After the decomposition of the peroxide, the aqueous solution was titrated by dil HCl (0.1 mol/dm^3), and the amount of carbon dioxide was obtained from the comsumption of barium hydroxide. The results are shown in Tables 2 and 4.

Reaction of Benzoic Acid with Trimethylphenylstannane or Tetramethylstannane. The acid (37 mg, 0.3 mmol) and trimethlyphenylstannane (145 mg, 0.6 mmol) were dissolved in chloroform–cyclohexane (1 : 1 v/v, total, 10 ml), and then the solution was allowed to react at 85—90 °C for 16 h. The amount of trimethyl(benzoyloxy)stannane was determined by the method as described above. Trimethyl(benzoyloxy)stannane was obtained by the reaction with trimethylphenylstannane in a 26% yield, with a 74% recovery of the starting stannane. No reaction of tetramethylstannane with benzoic acid was observed, even without the use of the solvent. For example, both the starting materials were recovered nearly quantitatively after the heating of benzoic acid (37 mg, 0.3 mmol) with tetramethylstannane (1.45 g, 6.0 mmol) for 16 h at 85—90 °C. The results are given in Table 3.

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