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Solvent and salt effects on the reactions of allyltin (IV) compounds with singlet oxygen, 4-phenyl-1,2,4-triazoline-3,5-dione and diethyl azodicarboxylate

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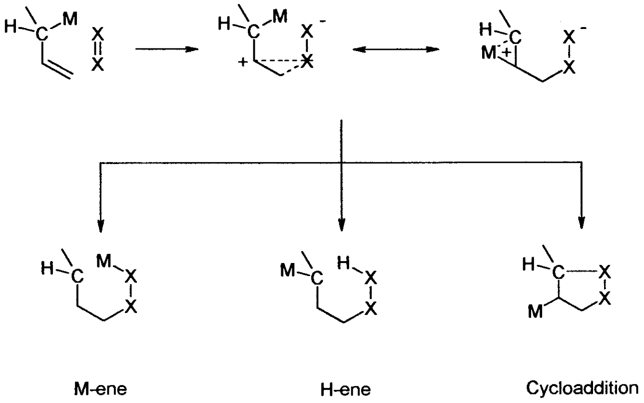
Abstract

The effect of the increase of polarity of the solvent binary mixture methanol–benzene on the selectivity and the rate of metalloene reactions of different allyltin compounds with singlet oxygen, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and diethyl azodicarboxylate (DEAD) was studied. Analogous comparative studies were carried out in Et_2O and 4 mol dm^{-3} solutions of $LiClO_4$ in diethyl ether. In the reaction with PTAD and $^1O_2$ the more polar solvent favoured the production of the M-ene product, whereas the cycloaddition reaction was favoured by a non-polar solvent. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metalloene reaction; Solvent effect; Singlet oxygen; Azo enophile; Lithium perchlorate

1. Introduction

Allyltin compounds react with singlet oxygen or azo enophiles to give the M-ene, H-ene and cycloaddition products as shown in Eq. (1) The relative yields depend on the structural and environmental conditions [1,2].



(1)

It seems likely that the mechanisms of the M-ene and cycloaddition reactions are related to that of the H-ene reactions of allylic hydrocarbons [1]. A reasonable model is that they involve the prior formation of a complex between the ene and the enophile (X=X) (1), which may be represented as an oxirane oxide or an aziridine imine when X=X=O=O or RN=NR respectively. Cyclic transfer of the metal or of hydrogen may then lead to the M-ene or H-ene products respectively, and cyclization with migration of the metal results from β-interaction of the metal with the carbonium ion centre [2]. Different authors have shown that the stereoselectivity of the ene reaction of singlet oxygen with allylic alcohols and amines depends on the polarity of the solvent [3–6]. Davies [7,8] studied the effect of the solvent CH_2Cl_2 and $MeOH–C_6H_6$ on the reaction of allyltin compounds with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and $^1O_2$, and showed that the more polar solvent favoured the M-ene reaction. Recently we have observed a considerable influence of a solvent on the chemoselectivity and the rate of reactions of allyl stannanes with PTAD and $^1O_2$ in $CHCl_3–CH_3CN$ [9], and have also shown that these reactions are strongly catalysed by lithium perchlorate [10].

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We report here a study of the rates and chemoselectivities of the reactions of some allylstannanes with PTAD, (more briefly) with diethyl azodicarboxylate (DEAD), and with $^1O_2$ in MeOH, C_6H_6 and C_6H_6–MeOH solvents, and in Et_2O in the absence and presence of $LiClO_4$.

2. Results

2.1. PTAD and DEAD: solvent effects

The reaction of allyl stannanes with equimolar amounts of PTAD (0.314 mmol) or DEAD (0.159 mmol) in MeOH, C_6H_6 and C_6H_6–MeOH mixtures, was followed visually by the fading of the colour of the azo compound (times of reactions for PTAD are shown in Table 1). For more dilute solutions, the rates were followed by UV–vis spectroscopy (down to 0.0046 mol dm^{-3} for PTAD and 0.0254 mol dm^{-3} for DEAD) by measuring half-lives of reactions (times corresponding to the decrease of the initial absorbance by 50%).

Products were identified by NMR spectroscopy. The results with PTAD are shown in Table 1.

In MeOH, the reactions were too fast to be monitored spectroscopically, and were followed visually, but the sequence of rates lay in the order **1** > **2** > **3** > **4**. This corresponds with the order of values of $\delta(^{13}C)$ for the allylic methylene groups, which provides a measure of the relative Lewis-acid character of the tin. Compound **2** provides an exception to this rule, where, as shown before [8], the presence of more than one allyl group confers a considerably enhanced reactivity.

Table 1
Reactions of allyl–Sn compounds with PTAD

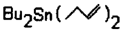
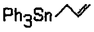
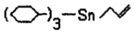
			M-ene	H-ene	Cycloaddition		
		MeOH	100	-	-	15 s	
1		MeOH/C_6H_6	100	-	-	2 min	
		C_6H_6	100	-	-	7.5 min	< 5 s
		MeOH	100	-	-	25 s	
2		MeOH/C_6H_6	93	-	7	4.5 min	
		C_6H_6	69	-	31	12 min	< 10 s
		MeOH	100	-	-	12 min	
3		MeOH/C_6H_6	75	-	25	30 min	
		C_6H_6	36	15	49	180 min	213 s
		MeOH	100	-	-	27 min	
4		MeOH/C_6H_6	66	-	34	65 min	
		C_6H_6	28	-	72	270 min	320 s

Table 2
Reactions of allyl–Sn compounds with DEAD

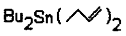
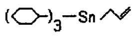
	Compound	Solvent	Half-life of the reaction
1		MeOH	< 20 s
		C_6H_6	80s
2		MeOH	12 min
		C_6H_6	202 min
3		MeOH	49 min
		C_6H_6	$t_{1/100} \sim$ 15 min
4		MeOH	75 min
		C_6H_6	$t_{1/100} \sim$ 20 min

Table 3
Reactions of allyltin derivatives with PTAD in Et_2O

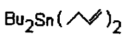
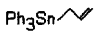
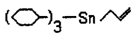
	Compound	Relative Yields of Products			[$LiClO_4$] mol dm^{-3}	Half-life of the Reaction
		M-ene	H-ene	Cycloaddition		
1		100			0	15 s
		100			4	«5 s
2		79	-	11	0	80 s
		100	-	-	4	< 5 s
3		69	24	11	0	1140 s
		93	-	-	4	26 s
4		62	-	38	0	1805 s
		100	-	-	4	40 s

Table 4
Reactions of allyltin derivatives with DEAD in Et_2O (0.0254 mol dm^{-3})

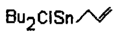
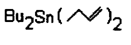
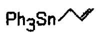
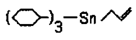
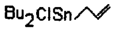
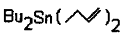
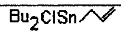
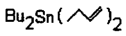
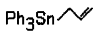
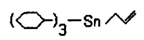
1		0	155 s
		4	< 10 s
2		0	290 min
		4	26 s
3		0	$t_{1/100}$ > 20 min
		4	35 s
4		0	$t_{1/100}$ > 20 min
		4	50 s

Table 5
Reactions of allyltin derivatives with singlet oxygen in MeOH and C_6H_6

	Compound	Solvent	Relative Yields of Products			Yield of the reaction [%]
			M-ene	H-ene	Cycloaddition	
1		MeOH	100	-	-	45
		C_6H_6	100	-	-	20
2		MeOH	100	-	-	20
		C_6H_6	-	-	-	0
		C_6H_6	82	18	-	20*

* *The illumination was carried out for 6 hours*

Table 6
Reactions of allyltin derivatives with singlet oxygen in 4 mol dm^{-3} solutions of $LiClO_4$

	Compound	Relative Yields of [%]		Products	[$LiClO_4$] mol dm^{-3}	Yield of the Reaction [%]
		M-ene	H-ene	Cycloaddition		
1		100	-	-	4	100
2		66	34	-	4	50
3		100	-	-	4	40
4		47	53	-	4	40

The chemoselectivity between the M-ene, H-ene, and cycloaddition paths is shown in Table 1. The H-ene reaction (15%) was observed only with allyltriphenyltin (**3**) in benzene. Compound **1** showed only the M-ene reaction whatever the solvent composition. Compounds **2**, **3** and **4** showed both the M-ene and cycloaddition routes in pure C_6H_6, but in pure MeOH, all four compounds gave only the M-ene reaction.

The results with DEAD were broadly parallel to those with PTAD, the DEAD reacting more slowly (see Table 2).

The reactions of allyltriphenyltin (**3**) and allyltricyclohexyltin (**4**) in benzene were very slow. Therefore, times corresponding to the decrease of the initial absorbance by 1% ($t_{1/100}$) were measured for them in benzene. All four compounds gave only the M-ene reaction.

2.2. PTAD and DEAD: salt effects

The salt effect on the rates (0.0046 mol dm^{-3}) and chemoselectivities of the reactions were studied with $LiClO_4$ added to diethyl ether, the reactions being monitored by absorbance at 536 nm. The results with PTAD as the enophile are given in Table 3.

The results with DEAD were parallel to those with PTAD, again the DEAD reacting more slowly (see Table 4).

Again the reactions of allyltriphenyltin (**3**) and allyltricyclohexyltin (**4**) in Et_2O were very slow and times corresponding to the decrease of the initial absorbance by 1% ($t_{1/100}$) were measured for them. All four compounds gave only the M-ene reaction.

The effect of 4 mol dm^{-3} $LiClO_4$ on the nature of the products was determined by NMR spectroscopy and is shown in Table 3. With each compound, the effect of adding $LiClO_4$ is parallel to that of adding MeOH to C_6H_6 solvent: an increase in the rate of reaction and a chemoselectivity favouring the M-ene at the expense of the H-ene and/or cycloaddition reactions.

2.3. $^1O_2$: *solvent effects*

The reactions involving singlet oxygen in MeOH, C_6H_6 and C_6H_6–MeOH mixtures were carried out under standard conditions for 3 h and monitored by NMR spectroscopy. In C_6H_6 the overall yield of products was low but it increased as MeOH was added: yields in pure C_6H_6 and in pure methanol respectively were, for allyldibutyltin chloride, 20 and 45% and for diallyldibutyltin, 0 and 20% (see Table 5). Allyltriphenyltin and allyltricyclohexyltin were ureactive under the experimental conditions, whereas illuminations carried out for more than 8 h led to their decomposition.

2.4. $^1O_2$: *salt effects*

The effect of added salt was studied with all four allyltin derivatives in ether under standard conditions. The results are given in Table 6.

In pure ether, the yields of compounds **2**, **3**, and **4** after 3 h was less than 5%. The yield for allyldibutyltin chloride was equal to 30%. Illuminations carried out for a longer time led to decomposition.

The addition of 4 mol dm^{-3} $LiClO_4$ gave a considerable increase in the yield of the reaction; no cycloaddition products were detected, and the ratio of the M-ene and H-ene reactions varied from ca. 1:1 for allyltricyclohexyltin to 1:0 for allyltriphenyltin.

As observed with the azo enophiles, an increase in polarity of the medium resulted in an increase in the overall rate of the reaction, and a chemoselectivity favouring the M-ene reaction.

3. Discussion

The general picture which emerges is that as the medium is made more polar, either by varying the solvent or by adding a salt, the overall rate of the reaction increases, and the chemoselectivity becomes biased towards the M-ene reaction, so that it is often the only product.

If the formation of the polar ene–enophile complex as shown in (1) is rate determining, the effect of an increasingly polar medium can be seen to result in stabilization of the transition state to this intermediate, in which the charges are developing. The chemoselectivity will then depend on the partition of this intermediate between the three possible paths of intermolecular S_N2 reaction at the metal (the M-ene reaction), or at hydrogen (the H-ene reaction), or at carbon (the cycloaddition reaction). Presumably a polar medium has the effect of reducing the activation energy of the first process more than that of the latter pair, and the M-ene reaction becomes dominant. From an experimental point of view, this work shows that a polar solvent such as methanol, and/or a salt such as lithium perchlorate should be added, if an ene–enophile reaction is to be selective for the metalloene process.

4. Experimental

NMR spectra were recorded using a Varian Gemini 200 BP spectrometer. UV spectra were recorded on a Specord spectrometer (Carl Zeiss Jena) using 10 mm cells. Allyltin compounds were prepared by a modified Grignard method [8] in which a solution of trialkyltin chloride and allyl bromide (5 mol equivalent) in ether was added to magnesium (equivalent to the allyl bromide) with vigorous stirring under argon at such a rate as to maintain gentle refluxing.

Details of the NMR spectra of the products from reactions of singlet oxygen and PTAD were described before [8].

In the case of the reactions of allyl stannanes (**1**–**4**) with PTAD the soluble product was chromatographed using light petroleum (b.p. 30–40°C)-diethyl ether (1/1 v/v) as eluent, and the products were purified by recrystallization from benzene–hexane, or by further chromatography. The *N*-metalotriazolidines underwent hydrolysis on the column to give the corresponding protic compound.

Products from the H-ene and cycloaddition reactions of singlet oxygen decomposed on silica gel, and were identified in the reaction mixture by high resolution NMR.

The allylperoxytin compounds produced by M-ene reactions were converted to allyl hydroperoxide during chromatography on silica gel; this was reduced by triphenylphosphine to allyl alcohol.Isolation of the products from the reactions with DEAD by gradient chromatography gave diethyl *N*-allylhydrazodicarboxylate as an oil [10a].

Typical examples of metalloene reactions were as follows:

- A solution of tricyclohexyl (prop-2-enyl)tin (133 mg, 0.325 mmol) and tetraphenylporphin (3 mg) in diethyl ether (5 cm^3) and a 4 mol dm^{-3} solution of

$LiClO_4$ in Et_2O, or Rose Bengal (in CH_3OH), was vigorously stirred under oxygen while being irradiated with light from a 400 W sodium lamp for 3 h. The solvent was removed and the product was identified by NMR. All illuminations of the allyltin compounds were carried out under the same conditions (pressure of oxygen above the solution, intensity of irradiation of the sample, temperature (298 K) etc. were constant).

- Tricyclohexyl(prop-2-enyl)tin (66 mg, 0.1615 mmol) and DEAD (27.7 mg, 0.1585 mmol) were added to CH_3OH (1 cm^3). The progress of the reaction was monitored by TLC (using light petroleum-ethyl acetate (7/3 v/v) as eluent) and by NMR spectroscopy, which showed that only diethyl *N*-allyl-*N′*-tricyclohexylstannylhydrazodicarboxylate was formed in quantitative yield. Isolation of the product by gradient chromatography (light petroleum–ethyl acetate) gave diethyl *N*-allylhydrazodicarboxylate as an oil.
- PTAD (55 mg, 0.314 mmol) and allyltricyclohexyltin (133 mg, 0.325 mmol) were added to C_6H_6 (1 cm^3). After discharge of the colour of the azo compound, the solvent was removed and the product was identified by NMR.

Kinetic measurements with PTAD and DEAD were carried out in a 1 cm^3, UV cell. The concentration of DEAD and allyltin derivative chosen was equal to 0.0254 mol dm^{-3}. The progress of the reaction at 298 K was monitored by measuring the absorbance at 410 nm. The analogous studies with PTAD were carried out with 0.0046 mol dm^{-3} solutions of the azo compound and allyltin derivative. The progress of the reaction at 298 K was monitored by measuring the absorbance at 536 nm. We measured times corresponding to the decrease of the initial absorbance by 50% for reactions of PTAD and DEAD with chosen allyltin derivatives and assume that their ratio corresponds to a certain degree with the ratio of the reaction rate constants.

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