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Note

The effect of solvent 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 influence on the increase of polarity of the solvent on the selectivity and rate of metalloene reactions of different allyltin compounds with singlet oxygen, 4-phenyl-1,2,4-triazoline-3,5-dione (TD) and diethyl azodicarboxylate has been studied. © 1999 Elsevier Science S.A. All rights reserved.

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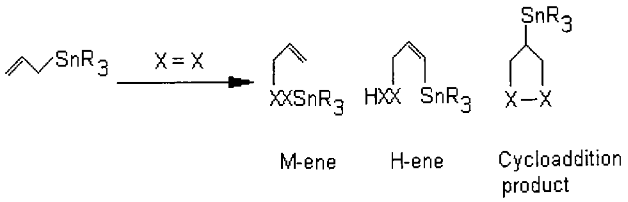
1. Introduction

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



(1)

It seems likely that the mechanism of M-ene and cycloaddition reactions is 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), which may be an aziridineimine when TD is reagent. Peryclic transfer of the metal or of hydrogen may than lead to the M-ene and H-ene product, respectively, and the cyclization with migration of the familiar β-effect of an organometallic group which stabilizes a carbonium ion by forming a bridged intermediate [2]. Previously Dang and Davies [3] have shown that a polar solvent favors the M-ene reaction. They studied the reaction of allyltricyclohexyltin with $^1O_2$ and TD in $CDCl_3$ and its mixture with CD_3CN. Also Butler and co-workers [4] studied solvent effect with TD and allylsilanes. However, their results indicate however a small solvent dependence.

2. Results and discussion

The reactions of allyltin derivatives and allyltriphenylgermane with 4-phenyl-1,2,4-triazoline-3,5-dione (TD) and diethyl azodicarboxylate were followed visually by fading of the color of the azo compound. Additionally these reactions were examined by comparing the ratio of reaction rate constants. They were carried out in a UV cell using different studied solvent mixtures. The reaction of allyltin derivatives with singlet oxygen was studied by NMR spectroscopy. We have carried out the above-mentioned reactions in $CHCl_3$ and a mixture of $CHCl_3$ with CH_3CN (1:1 v/v) (see Table 1).

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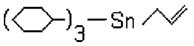
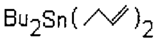
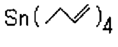
Table 1
Reaction of allyl–Sn compounds and allyltriphenylgermane with singlet oxygen

Compound	Solvent	Product (%)			Yield (%)
		M-ene	H-ene	Cycloaddition	
	$CHCl_3/CH_3CN$	22	46	32	42
	$CHCl_3/CH_3CN$	66	34	0	50
	$CHCl_3/CH_3CN$	100			100
	$CHCl_3/CH_3CN$				0

The yield of the photochemical oxidation of the studied allylmetalic compounds under experimental conditions in $CHCl_3$ was very low and its increase was observed with gradual increase of the concentration of CH_3CN in the solvent mixture.

We suspect that the mechanism of this reaction with singlet oxygen is associated with the formation of the polar intermediate during the metalloene reaction being easier in more polar solvent.

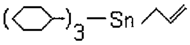
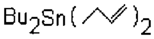
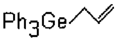
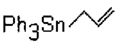
On the other hand, we observed a decrease of rates of reaction with 4-phenyl-1,2,4-triazoline-3,5-dione with different allyltin compounds and allyltriphenylgermane with increase in the concentration of CH_3CN in the solvent mixture. This can be explained by a lowering of the LUMO of the azo compound in pure $CHCl_3$ in comparison to the mixture $CHCl_3$–CH_3CN (2/3 v/v) and pure CH_3CN caused by its association with a molecule of chloroform. It leads to approximately 16–18-fold reduction of the time of the reaction of 0.314 mol dm^{-3} solution of 4-phenyltriazolinedione and the equimolar amount of allylmetalic ene. Values of the ratio of rate constants (k_2) for allyltriphenylgermane, allyltriphenyltin and allyltricyclohexyltin are equal to 1:2.8:3.2, respectively. The reaction of diallyldibutyltin and tetraallyltin in CH_3CN was too fast to be monitored by applied kinetic method similarly to all the reactions shown in Table 2 carried out in $CHCl_3$ and its mixture with CH_3CN. Therefore, our observations regarding the rate of these reactions have been based on visual observations of the time of discharge of the color of 0.314 mol dm^{-3} solutions of TD. We found that the rate of these reactions increases in the following order: allyltriphenylgermane (1) < allyltriphenyltin (2) < allyltricyclohexyltin (3) < diallyldibutyltin (4) < tetraallyltin (5). The analogous order was observed for reactions with diethyl azodicarboxylate. This order corresponds to changes of $\delta(^{13}C)$ values for the allylic methylene group of studied allyltin compounds [3]. Exceptions to this rule are (4) and (5). Allyltriphenylgermane exhibits the lowest reactivity with TD and it seems to be unreactive with diethyl azodicarboxylate at 25°C, which is in agreement with earlier reports that the presence of triphenylgermyl group has less effect on the rate of metalloene reactions than tin as substituent [5]. The change of the solvent from $CHCl_3$ to a $CHCl_3$–CH_3CN mixture (2:3 v/v) and pure CH_3CN caused additionally an increase of the M-ene product at the expense of the cycloaddition and H-ene products for reactions with TD (see Table 2).

Derivatives of *N*-allyl-*N′*-stannylhydrazodicarboxylate were formed as sole products in reactions of diethyl azodicarboxylate with allyltin compounds. We have not observed here the analogous effect of the solvent on reactions with TD. Rates of reactions with diethyl azodicarboxylate in CH_3CN have not differed considerably in $CHCl_3$.

3. 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. IR spectra were recorded using a Specord 75 IR spectrometer (Carl Zeiss Jena). Allyltin compounds and triphenyl(prop-2-enyl)germane were prepared by a modified Gringard method [3] in which a solution of trialkyltin chloride and allyl bromide (five molar equivalents) in ether was added to magnesium (equivalent to the allyl bromide) with vigorous stirring under argon at such a rate to maintain gentle refluxing.

Table 2
Reaction of allyl–Sn compounds and allyltriphenylgermane with 4-phenyl-1,2,4-triazoline-3,5-dione (TD)

Compound	Solvent	Product (%)		
		M-ene	H-ene	Cycloaddition
	$CHCl_3$	63		37
	$CHCl_3/CH_3CN$	80	0	20
	CH_3CN	85	0	15
	$CHCl_3$	62	28	10
	$CHCl_3/CH_3CN$	100		
	CH_3CN	100		
	$CHCl_3$	100		
	$CHCl_3/CH_3CN$	100		
	CH_3CN	100		
	$CHCl_3$	33	37	30
	$CHCl_3/CH_3CN$	67	24	9
	CH_3CN	73	23	4
	$CHCl_3$	47	53	
	$CHCl_3/CH_3CN$	64	36	
	CH_3CN	65	35	

3.1. Metalloene reactions

Typical examples of metalloene reactions were as follows: — A solution of tetra(prop-2-enyl)tin (92 mg, 0.325 mmol) and methylene blue (3 mg) in $CHCl_3$ 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 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 diethyl azodicarboxylate (27.7 mg, 0.1585 mmol) were added to $CHCl_3$ (1 cm^3). The progress of the reaction was monitored by TLC and by NMR spectroscopy, which showed that only diethyl *N*-allyl-*N′*-tricyclohexylstannylhydrazodicarboxylate was formed with a quantitative yield in all solvents. Isolation of the product by gradient chromatography (light petroleum-ethyl acetate) gave diethyl *N*-allylhydrazodicarboxylate as an oil.

4-Phenyl-1,2,4-triazoline-3,5-dione (55 mg, 0.314 mmol) and allyltricyclohexyltin (133 mg, 0.325 mmol) were added to $CHCl_3$. The progress of the reaction was monitored by TLC. The solvent was removed and the product was identified by 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. Products from H-ene and cycloaddition reactions of singlet oxygen decomposed on silica gel, and were identified in the reaction mixture by high resolution NMR.

In the case of the reactions with TD 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*-metallotriazolidines underwent hydrolysis on the column to give the corresponding protic compound. The characteristics of the products was analogous to this described in the literature [1–3].

Kinetic measurements with TD and diethyl azodicarboxylate were carried out in a 1 cm^3 UV cell. The concentration of diethyl azodicarboxylate and allyltin derivative chosen for studies was equal to 0.012 mol dm^{-3}. The progress of the reaction at 298 K was monitored by measuring the absorbance at 400 nm. The analogous studies with TD were carried 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 530 nm. We have measured times corresponding to decrease of the initial absorbance by 50% for reactions of TD and diethyl azodicarboxylate with chosen allyltin derivatives assuming that their ratio agrees up to certain degree with the ratio of the reaction rate constants.

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