

Review

Catalysis of reactions of allyltin compounds and organotin phenoxides by lithium perchlorate

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Abstract

The effect of increase of polarity of the solvent binary mixture methanol–benzene and acetonitrile–chloroform on the selectivity and the rate of metalloene reaction of different allyltin compounds with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), diethyl azodicarboxylate (DEAD) and singlet oxygen was studied. The more polar solvent favored the production of the M-ene product. Analogous comparative studies were carried out in Et₂O and 4 mol dm⁻³ solutions of LiClO₄ in diethyl ether. All studied reactions were strongly catalysed by LiClO₄. Physicochemical studies were carried out in purpose to explain the catalytic effect of LiClO₄ on the aforementioned reactions. In case of singlet oxygen and diethyl azodicarboxylate it was presumably a result of facilitation of the formation of the polar intermediate by the ionic medium. Whereas, in case of PTAD the mentioned previously effect could be associated with lowering its LUMO by association with lithium. The analogous catalytic effect of LiClO₄ was also observed for reactions of organotin phenoxides with DEAD and bis(trichloroethyl) azodicarboxylate leading to corresponding ring-aminated phenols in excellent yield, and with diethyl acetylenedicarboxylate giving a mixture of corresponding vinyl ethers and ring ethenylated phenols. Organotin phenoxides were distinctly more active than the corresponding phenols.

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Keywords: Metalloene reaction; Lithium perchlorate; Azo enophile; Allyltin compounds; Organotin phenoxides; Diethyl acetylenedicarboxylate

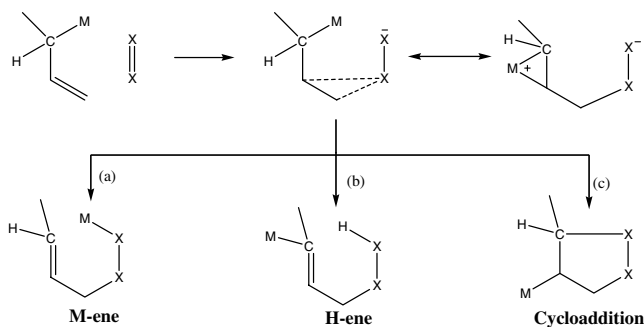
Contents

1. Introduction	1441
2. Results and discussion	1442
2.1. ¹ O ₂ : solvent effects	1444
2.2. ¹ O ₂ : salt effects	1444
3. Conclusions	1450
References	1450

1. Introduction

A number of reactions have recently been shown to be susceptible to catalysis by lithium perchlorate (typically 5 mol dm⁻³ in diethyl ether) [1]. These include the intermolecular [2], intramolecular [3] and hetero-Diels–Alder

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Scheme 1.

reactions [4], [2+2] and [2+3]-cycloadditions [5,6], the [1,3]-sigmatropic rearrangement of allyl vinyl ethers [7], the addition of allylmetals to aldehydes [8], different Mannich-type reactions [9], the chemo- and regioselective isomerization of epoxides to carbonyl compounds [10], substitution reactions of allylic acetates and allylic alcohols [11], and the ene reactions [12,13].

No clear picture of the mechanism of this catalysis has yet emerged.

We have been interested in the metalloene reaction of allyltin compounds (Scheme 1), particularly when the (homopolar) enophile (X=X) is singlet oxygen (O=O) or an azo compound (RN=NR). There is good evidence from stereochemical studies that metalloene reaction proceeds through an intermediate ene-enophile complex [14]. The reaction is then completed by transfer of the metal (Scheme 1(a)), but transfer of hydrogen (Scheme 1(b)), and migration of the metal to the central allylic carbon atom accompanied by ring closure (Scheme 1(c)) may compete.

Previously, Dang and Davies [14] have shown that a polar solvent favors the M-ene reaction. They studied the reaction of allyltricyclohexyltin with $^1\text{O}_2$ and 4-phenyl-1,2,4-triazoline-3,5-dione in CDCl_3 and its mixture with CD_3CN . Also Butler [15] studied solvent effect with (PTAD) and allylsilanes. However, his results indicate a small solvent dependence.

2. Results and discussion

We were interested in investigating the effect on three reaction routes of the ligands about the tin center and the polarity of the solvent. We understood that improvement of the selectivity of these metalloene reactions could affect their usefulness in organic synthesis.

We have studied reactions of different allylmethyl compounds with 4-phenyl-1,2,4-triazoline-3,5-dione in CHCl_3 , CH_3CN , a mixture of CHCl_3 with CH_3CN (1:1 v/v) (see Table 1) [16], MeOH , C_6H_6 and $\text{C}_6\text{H}_6\text{-MeOH}$ solvents [17], and in the absence and presence of LiClO_4 [17]. In case of reactions of all studied allyltin derivatives with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), we have observed a strong increase of the rate of the reaction in CHCl_3 in comparison to CH_3CN as well as in CH_3OH in comparison to

C_6H_6 (1:1, v:v). The reaction of allylstannanes with equimolar amounts of PTAD (0.314 mmol) in all aforementioned solvents was followed visually by fading of the color of the azo compound (times of reactions are shown in Table 1). For more dilute solutions, the rates were followed by UV-Vis spectroscopy ($0.0046 \text{ mol dm}^{-3}$) by measuring half-lives of reactions (times corresponding to the decrease of the initial absorbance by 50%). In MeOH , its mixture with C_6H_6 and in CHCl_3 the reactions were too fast to be monitored spectroscopically, and were followed visually, but the sequence of rates lay in the order allyldibutyltin chloride > diallyldibutyltin \approx tetraallyltin > allyltriphenyltin > allyltricyclohexyltin. This corresponds with the order of values of $\delta(^{13}\text{C})$ for the allylic methylene groups, which provides a measure of the relative Lewis-acid character of the tin. Diallyldibutyltin and tetraallyltin provide an exception to this rule, where, as shown before [14], the presence of more than one allyl group confers a considerably enhanced reactivity.

The analogous studies of five allyltin compounds have been carried out in Et_2O and 4 mol dm^{-3} solutions of LiClO_4 in Et_2O (see Table 2).

The strong catalytic effect of LiClO_4 has been observed in Et_2O . For example half-life of the reaction was reduced by factor ca. 45 for reactions allyltriphenyltin and allyltricyclohexyltin. Quite interestingly the analogous effect for allyltriphenylgermane was much smaller. The effect of 4 mol dm^{-3} solution of LiClO_4 on the nature of the products was determined by NMR spectroscopy and is shown in Table 2.

We have also analysed the nature of products of studied allyltin derivatives with PTAD in CHCl_3 , CH_3CN , C_6H_6 , CH_3OH and their mixtures. We have observed that the increase of the polarity of the solvent favored the M-ene at the expense of the H-ene and/or cycloaddition reactions. The analogous effect has been observed for adding LiClO_4 to Et_2O .

The solvent and salt effects have been also studied for reaction with diethyl azodicarboxylate (DEAD) [12,17,18]. The results with DEAD were broadly parallel to these with PTAD. However, the DEAD reacted more slowly (see Table 3).

The reactions of allyltriphenyltin and allyltricyclohexyltin 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 M-ene reaction (see Table 4).

Similarly as previously, the studied reactions were faster in methanol, chloroform and 4 mol dm^{-3} solutions of LiClO_4 in Et_2O in comparison to benzene, acetonitrile and pure diethyl ether. We suspect that this is associated with solvation of DEAD by molecules of the solvent. We have also compared the half-lives for reaction of diallyldibutyltin with DEAD in the series of 1 mol dm^{-3} solutions of LiClO_4 in CH_3CN , Et_2O , ethyl acetate and acetone (see Table 5) [19]. The half-lives of reaction, $t_{1/2}$, achieved the shortest value in Et_2O . Further addition of LiClO_4 to all

Table 1

Reactions of allyltin compounds with PTAD (times of the reactions for 0.314 mol dm⁻³ solutions and half-lives of the reactions for 0.0046 mol dm⁻³ solutions)











Compound	Solvent	Relative yields of products (%)			Half-life of the reaction (s)	Time of the reaction (min)
		M-ene	H-ene	Cycloaddition		
Bu ₂ Sn() ₂	CHCl ₃	62	28	10	–	3.5
	CHCl ₃ /CH ₃ CN	100	0	0	–	20
	CH ₃ CN	100	0	0	–	60
	CH ₃ OH	100	0	0	–	25 s
	CH ₃ OH/C ₆ H ₆	93	0	7	–	4.5
	C ₆ H ₆	69	0	31	<10	12
Ph ₃ Sn()	CHCl ₃	47	53	0	–	18
	CHCl ₃ /CH ₃ CN	64	36	0	–	45
	CH ₃ CN	65	35	0	–	300
	CH ₃ OH	100	0	0	–	12
	CH ₃ OH/C ₆ H ₆	75	0	25	–	30
	C ₆ H ₆	36	15	49	213	180
(Cyclohexyl) ₃ Sn()	CHCl ₃	63	0	37	–	15.5
	CHCl ₃ /CH ₃ CN	80	0	20	–	40
	CH ₃ CN	85	0	15	–	260
	CH ₃ OH	100	0	0	–	12
	CH ₃ OH/C ₆ H ₆	66	0	34	–	35
	C ₆ H ₆	28	0	72	320	240
Sn() ₄	CHCl ₃	100	0	0	–	3
	CHCl ₃ /CH ₃ CN	100	0	0	–	10
	CH ₃ CN	100	0	0	–	60
	CH ₃ OH	100	0	0	–	–
	CH ₃ OH/C ₆ H ₆	100	0	0	–	–
	C ₆ H ₆	100	0	0	<5	–
Bu ₂ ClSn()	CHCl ₃	100	0	0	–	2
	CHCl ₃ /CH ₃ CN	100	0	0	–	10
	CH ₃ CN	100	0	0	–	50
	CH ₃ OH	100	0	0	–	15 s
	CH ₃ OH/C ₆ H ₆	100	0	0	–	2
	C ₆ H ₆	100	0	0	<5	7.5

Table 2

Reactions of allyltin derivatives with PTAD in Et₂O (half-lives of reactions for 0.0046 mol dm⁻³ solutions)





Compound	Relative yields of products (%)			[LiClO ₄] (mol dm ⁻³)	Half-life of the reaction (s)
	M-ene	H-ene	Cycloaddition		
Bu ₂ ClSn()	100	–	–	0	15
	100	–	–	4	<5
Bu ₂ Sn() ₂	79	–	11	0	80
	100	–	–	4	<5
Ph ₃ Sn()	69	24	11	0	1140
	93	–	–	4	26
(Cyclohexyl) ₃ Sn()	62	–	38	0	1805
	100	–	–	4	40
Ph ₃ Ge()	53	37	30	0	9000
	56	21	23	4	1500

studied solvents resulted in a considerable decrease of the half-lives particularly in Et₂O and CH₃CN.

In purpose to explain this effect we carried out the comparative studies of both azo compounds in Et₂O and CH₃CN using absorption spectroscopy [19]. Acetonitrile was chosen among other studied solvents, where catalytic

Table 3

Reactions allyltin compounds with DEAD (half-lives of reactions for 0.0254 mol dm⁻³ solutions) in C₆H₆, CH₃OH, CH₃CN and CHCl₃

Compound	Solvent	Half-life of the reaction (s)
Bu ₂ Sn() ₂	CHCl ₃	8840
	CH ₃ CN	30 300
	CH ₃ OH	720
	C ₆ H ₆	12 120
(Cyclohexyl) ₃ Sn()	CH ₃ OH	4500
	C ₆ H ₆	<i>t</i> _{1/100} ≈ 20 min
Ph ₃ Sn()	CHCl ₃	68526
	CH ₃ CN	<i>t</i> _{1/100} = 30 min
	CH ₃ OH	2940
	C ₆ H ₆	<i>t</i> _{1/100} ≈ 15 min
Bu ₂ ClSn()	CH ₃ OH	<20
	C ₆ H ₆	80

activity of LiClO₄ was noticeable, due to its transmittance in the UV region. The solution of PTAD in diethyl ether exhibited two absorption maxima λ_{max} 226 and 258 nm. The increase of the concentration of LiClO₄ in Et₂O resulted in the decrease of the molar absorptivity at 226 nm leading to the decrease of the ratio of molar

Table 4
Reactions allyltin derivatives with DEAD in Et₂O (half-lives of reactions for 0.0254 mol dm⁻³ solutions)






Compound	(LiClO ₄) (mol dm ⁻³)	Half-live of the reaction (s)
Bu ₂ Sn() ₂	0	17420
	4	26
Ph ₃ Sn 	0	<i>t</i> _{1/100} > 900
	4	35
Bu ₂ ClSn 	0	155
	4	<10
 ₃ Sn 	0	<i>t</i> _{1/100} > 1200
	4	50

Table 5
Reaction of diallyldibutyltin with DEAD (half-lives of the reactions for 0.0254 mol dm⁻³ solutions)

Solvent	(LiClO ₄) (mol dm ⁻³)	Half-live of the reaction (s)
CH ₃ CN	0	505
	1	262
Et ₂ O	0	226
	1	109
	3	38
Ethyl acetate	0	386
	1	219
Acetone	0	410
	1	234

absorptivities at 226 and 258 nm. For example, this ratio changed from approximately 2.4 to 1.6 with the increase of the concentration of LiClO₄ from 1.6 up to 3.8 mol dm⁻³ in 9 × 10⁻⁵ mol dm⁻³ solution of 4-phenyl-1,2,4-triazoline-3,5-dione in Et₂O. The increase of the concentration of LiClO₄ caused also a small decrease of the molar absorptivity at 527 nm. In case of 6 × 10⁻⁵ mol dm⁻³ solutions of 4-phenyl-1,2,4-triazoline-3,5-dione in acetonitrile effects associated with the increase of the concentration of LiClO₄ were even more intense. In pure solvent the ratio of molar absorptivities (λ_{\max} 215 and 248 nm) was equal to ca. 4.1, whereas in 1 mol dm⁻³ solution of LiClO₄ it achieved a value equal to ca. 0.6. This change was linked with the decrease of the molar absorptivity at λ_{\max} 226 nm and the increase at λ_{\max} 265 nm. The long wave shift of two mentioned absorption maxima in comparison to pure CH₃CN was also observed. Additionally, the addition of LiClO₄ to CH₃CN resulted in a growth of the molar absorptivity at 530 nm. The absorption spectra of 5.08 × 10⁻⁴ mol dm⁻³ solutions of diethyl azodicarboxylate in Et₂O and CH₃CN exhibited also some differences. Spectra of the studied azo compound in pure Et₂O and 3 mol dm⁻³ solutions of LiClO₄ were similar. Whereas, spectra of 5.08 × 10⁻⁴ mol dm⁻³ solutions of diethyl azodicarboxylate in pure acetonitrile and 1 mol dm⁻³ solution of LiClO₄ exhibited some differences. The addition of LiClO₄ resulted in a small long wave shift of the absorption maximum (λ_{\max} 207 nm) of about 8 nm and the decrease of its molar absorptivity. No effect of the addition of LiClO₄ to studied solvents was observed in case of the second absorp-

tion maximum (λ_{\max} 400 nm). We assume that catalytic properties of LiClO₄ in diethyl ether are linked with: (1) facilitation of the formation of the polar intermediate by ionic medium and (2) lowering LUMO of the azo compound by association with aggregates of LiClO₄. In case of 4-phenyl-1,2,4-triazoline-3,5-dione both mentioned above effects may affect its activity. However, the facilitation of the formation of the polar intermediate seems to be responsible for increased activity of diethyl azodicarboxylate in concentrated solutions of LiClO₄ in Et₂O. No effects associated with changes of electron density of this azo compound with the addition of LiClO₄ were observed in absorption spectra.

2.1. ¹O₂: solvent effects

The reactions involving singlet oxygen in MeOH, C₆H₆ and C₆H₆-MeOH as well as in CHCl₃ and CHCl₃-CH₃CN (1:1, v/v) mixtures were carried out under standard conditions for 3 h and monitored by NMR spectroscopy [12,17]. In C₆H₆ and CHCl₃ the overall yield of products was low but increased as MeOH or CH₃CN were added: yields in pure C₆H₆ and in pure methanol, respectively, were, for allyldibutyltin chloride, 20% and 45% and, for diallyldibutyltin, 0% and 20% (see Table 6). Allyltriphenyltin and allyltricyclohexyltin were unreactive under the experimental conditions, whereas illuminations carried out for more than 8 h led to their decomposition. Also the increase of the yield of the photochemical oxidation of studied allylmetallic compounds in the mixture CHCl₃-CH₃CN was observed with addition of CH₃CN. 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.

2.2. ¹O₂: salt effects

The effect of added LiClO₄ was studied with five allyltin derivatives in ether under standard conditions [12,20]. The results are given in Table 7. In pure ether, the yields of studied compounds after 3 h were 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 LiClO₄ gave a considerable increase in the yield of the reaction; no cycladdition 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.

We suspect that the mechanism of this catalytic reaction with singlet oxygen is associated with the formation of the polar intermediate during the metalloene reaction being easier. To prove this assumption we have carried out photo-oxygenations of 1.48 × 10⁻² mol dm⁻³ solutions of 1,3-diphenylisobenzofuran in Et₂O and 4 mol dm⁻³

Table 6
Reactions of allyltin compounds with singlet oxygen in CHCl₃, CHCl₃–CH₃CN, MeOH and C₆H₆

Compound	Solvent	Relative yields of products (%)			Yield of the reaction (%)
		M-ene	H-ene	Cycloaddition	
Sn($\text{CH}_2=\text{CH}-\text{CH}_3$) ₄	CHCl ₃ /CH ₃ CN	100	–	–	100
	CHCl ₃	100	–	–	67
Bu ₂ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$) ₂	CHCl ₃ /CH ₃ CN	66	34	–	50
	CHCl ₃	–	–	–	<5
	CH ₃ OH	100	–	–	20
	CH ₃ OH/C ₆ H ₆	–	–	–	0
Ph ₃ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$)	CHCl ₃ /CH ₃ CN	42	53	5	20
	CHCl ₃	–	–	–	<5
(C ₆ H ₅) ₃ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$)	CHCl ₃ /CH ₃ CN	22	46	32	42
	CHCl ₃	–	–	–	0
Bu ₂ ClSn($\text{CH}_2=\text{CH}-\text{CH}_3$)	CH ₃ OH	100	–	–	45
	CH ₃ OH/C ₆ H ₆	100	–	–	30
	C ₆ H ₆	100	–	–	20

Table 7
Reactions of allyltin derivatives with singlet oxygen in 4 mol dm⁻³ solution of LiClO₄

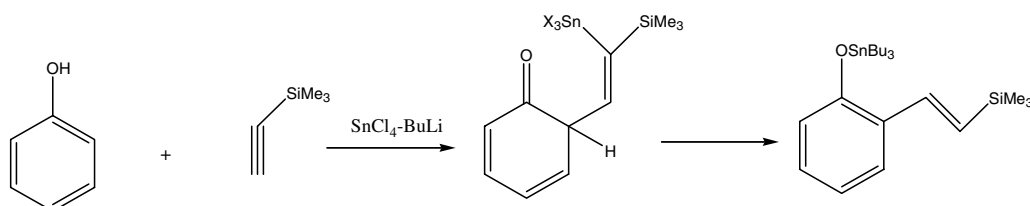
Compound	Relative yields of products (%)			[LiClO ₄] (mol dm ⁻³)	Half-life of the reaction (s)
	M-ene	H-ene	Cycloaddition		
Bu ₂ ClSn($\text{CH}_2=\text{CH}-\text{CH}_3$)	100	–	–	4	100
Bu ₂ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$) ₂	66	34	–	4	50
Ph ₃ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$)	100	–	–	4	40
(C ₆ H ₅) ₃ Sn($\text{CH}_2=\text{CH}-\text{CH}_3$)	47	53	–	4	40
($\text{CH}_2=\text{CH}-\text{CH}_3$) ₄ Sn	100	–	–	4	90

solutions of LiClO₄ in Et₂O [20]. The yields of the reactions measured after 90 and 240 s in both solutions were nearly the same (12% and 80%, respectively). It has been shown by other authors that the above reaction is solvent sensitive [21]. β values [the ratio of the rate of decay of singlet oxygen (k_d) and the rate of reaction of ¹O₂ (k_{rx}) with 1,3-diphenylisobenzofuran] have usually been measured. The solvent may affect either or both values of k_{rx} and k_d . Therefore, assuming that the yield of this reaction reflects in a quantitative way changes in the β value, we expect that the catalytic role of LiClO₄ in case of studied photo-oxygenations cannot be explained by possible variations in the concentration of ¹O₂ under heterogenous conditions, of ¹O₂, or of its lifetime.



Scheme 2.

Being aware of the aforementioned results and making use of the principles that (a) metals frequently act as surrogates for hydrogen with an increase in reactivity and (b) many reactions are accelerated in the presence of high concentrations of lithium perchlorate, we have decided to work out some useful from practical point of view synthetic strategies. The use of O-metallation of alcohols or enols to enhance their reactivity towards electrophiles such as aldehydes or alkyl or acyl halides has been reported by Davies [22]. He also reported the reaction of tin alkoxides with other polar multiply bonded acceptors (Scheme 2) where A=B is RNC=O, RNC=S, O=CO, S=CS, RN=C=NR, EtO₂C–C=C–CO₂Et, etc., but he did little on phenoxides. We suspected that the O-metallation of phenols could be exploited to enhance the rate of electrophilic substitution in the ring. The polarity of the M^{δ+}O^{δ-}–Ar bond would be expected to promote the reaction with enophiles such as DEAD, bis(trichloroethyl) azodicarboxylate and diethyl acetylenedicarboxylate, whatever the detailed structure of the metal phenoxide (which may be associated in solution), or the mechanism of the substitution (see below). Organotin phenoxides (Bu₃SnOAr) are very useful reagents because it is easy to introduce or remove the organotin



Scheme 3.


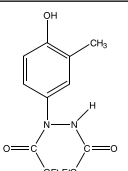

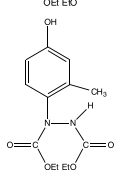

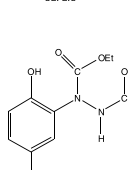

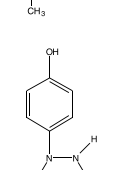

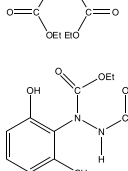

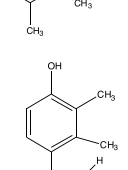

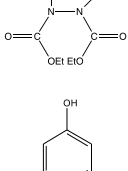

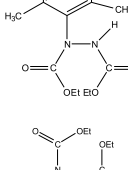

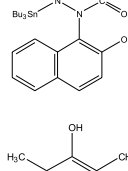

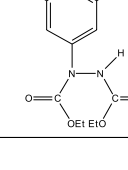


group and because of the pronounced polarity of the Sn–O bond. Previously, Kobayashi and Yamaguchi [23] found that the reaction of phenol with trimethylsilylacetylene at the *ortho*-position is catalysed by SnCl₄–BuLi. They believe that the reaction occurs through the tin phenoxide and this can be written as Scheme 3.

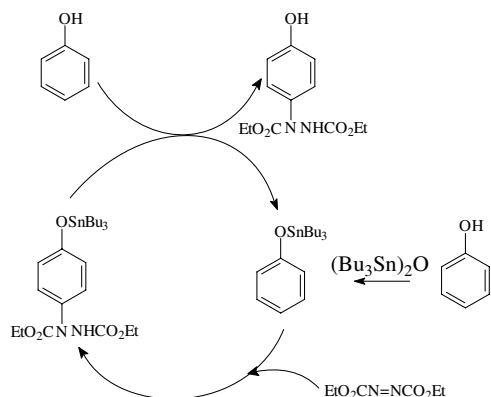
The tributyltin phenoxides were prepared by azeotropic dehydration of a mixture of phenol and tributyltin oxide (TBTO) in toluene [24]. In our recent studies [25,26] the tin phenoxides and DEAD were added to 4 mol dm⁻³ solutions of LiClO₄ in diethyl ether at 298 K. For measuring the half-lives of the reactions, the concentrations of the reagents were equal to 0.0254 mol dm⁻³ and the absorbance of DEAD at 410 nm was monitored. On a preparative scale, the reaction was followed by TLC or NMR and the products were isolated by chromatography, which also served to remove the Bu₃Sn group. Table 8 shows the half-lives of the reactions and the structure of products, which are obtained, in essentially quantitative yields. Exceptionally, the yield of the reaction of tributyl-(3,4-dimethylphenoxy)tin was equal to 30%, and this seems to be associated with the fact that its substitution was exclusively possible in the *ortho* position. Additionally, we have observed that tributyl-(2,6-dimethoxyphenoxy)tin was completely inactive, and no product with DEAD has been formed. Also, no reaction occurred between the parent phenols and DEAD under these conditions; the presence of LiClO₄ reduces the half-lives of the reactions of tin phenoxides by factor 7–27. Many of the reactions that depend on the enhanced reactivity of the SnOR group over that of the HOR group (e.g., the addition to isocyanates) can be carried out using HOR and a catalytic amount of TBTO or other equivalent reagent that will stannylate the alcohol or phenol [23]. It, therefore, appeared likely that these ring aminations could similarly be carried out catalytically and indeed the reactions occur equally well when alcohol and DEAD are used together with 10 mol% of TBTO, thus avoiding the need to prepare the tin phenoxide. Indeed, our results show that the reactions of 1- and 2-naphtols with DEAD are strongly catalysed by TBTO. (1-Hydroxy-4-naphtyl)-hydrazine-*N,N'*-dicarboxylic acid diethyl ester and (2-hydroxy-1-naphtyl)-hydrazine-*N,N'*-dicarboxylic acid diethyl ester were, respectively, formed with excellent yields and half-lives of reactions were similar to that of tributyltin naphthoxides [25]. The cycle of reactions that is involved is shown in Scheme 4 and examples of the reaction in Table 8.

The mechanism of the reaction when amination occurs in the *para*-position to the stannyloxy group may well be a simple electrophilic substitution via a Wheland intermediate (see Scheme 5).

The reaction of 1-naphtylamine, however, has been written in the form of an ene reaction [27] and two reasonable mechanisms, apart from the above electrophilic substitution, can be proposed for the *ortho*-amination of 2-(tributylstannyloxy)naphthalene. First, it could follow a metalloene mechanism (see Scheme 6).

Table 8
Amination of phenols with DEAD catalysed by LiClO₄ (half-lives of the reaction for 0.0254 mol dm⁻³ solutions)

Compound	[LiClO ₄] mol/dm ³	Half-life of the reaction [s]	Product
	0	1520	
	4	200	
	0	2200	
	4	240	
	0	7500	
	4	270	
	0	1050	
	4	135	
	0	> 60 min	
	4	> 20 min	
	0	720	
	4	130	
	0	920	
	4	200	
	0	5760	
	4	609	
	0	470	
	4	60	



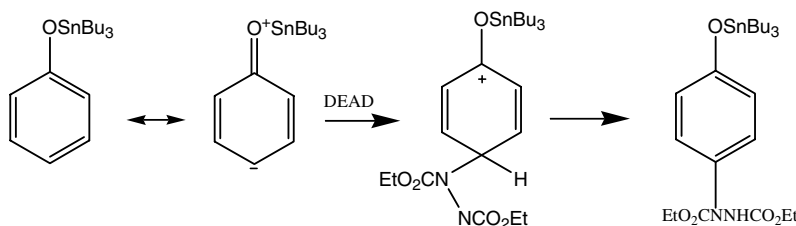
Scheme 4.

Second, the tin could act as a Lewis acid in stabilising the Wheland intermediate by coordination to anionic nitrogen (see Scheme 7).

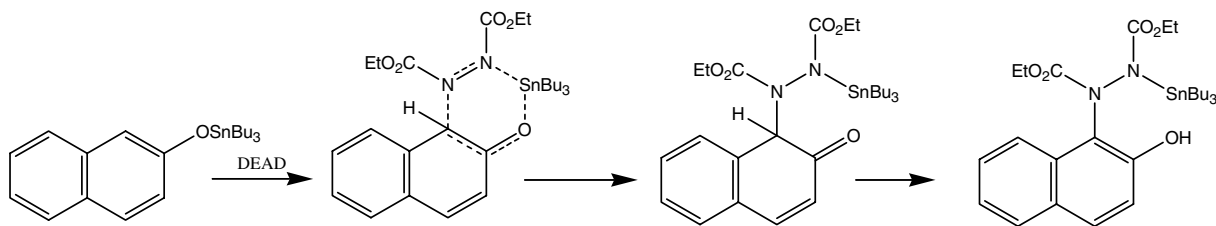
In an attempt to obtain further evidence of the mechanism, we studied the behaviour of 2-methoxynaphthalene and 2-trimethylsiloxynaphthalene under standard conditions, neither compound would be expected to take part in an ene reaction nor involve a Lewis acid-stabilised transition state, and if reaction did occur it would argue in favour of a conventional electrophilic aromatic substitution. However, neither compound showed any reaction

with DEAD in the presence of LiClO_4 at room temperature for some weeks and the mechanism of the reaction must still be regarded as an open question. Hydrazocarboxylate esters can readily be hydrolysed and then reduced to amines, hence our reaction provides a means for introducing the amino group and its derivatives into a phenolic ring under very mild conditions.

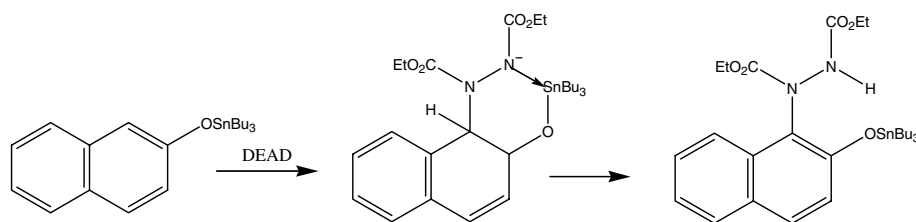
Previously, Leblanc [28] has shown that reactions of electron-rich arens with bis(2,2,2-trichloroethyl) azodicarboxylate in diethyl ether and acetone are strongly catalysed by lithium perchlorate (3 mol dm^{-3} solutions of LiClO_4 in Et_2O and acetone). Although it is more expensive and less stable than DEAD, it is also more reactive in reactions with electron-rich arens. Therefore, we assume that its application may sometimes be an alternative to DEAD. Previous studies with this azo enophile were carried out at elevated temperatures [28]. However, it is known that heating of solution of LiClO_4 in Et_2O or acetone may be hazardous. We wanted to prove that the use of organotin phenoxides instead of pure phenols and more concentrated solution of LiClO_4 would enable to carry out reactions with bis(trichloroethyl) azodicarboxylate with quantitative yield at room temperature (see Table 9) [29]. We have compared the yields of the reactions of five phenols and obtained from them tributyltin phenoxides in 5 mol dm^{-3} solutions of LiClO_4 in Et_2O at room temperature. The aryl



Scheme 5.

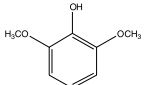
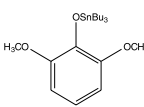
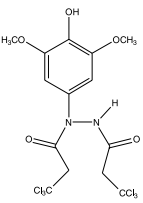

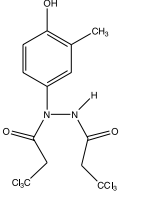

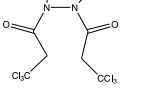

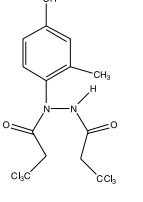

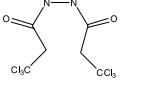

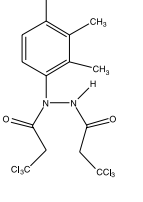

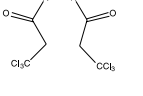

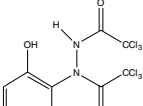
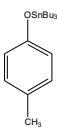
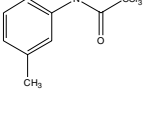


Scheme 6.



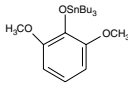
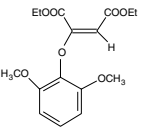
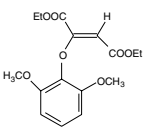

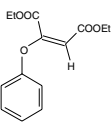
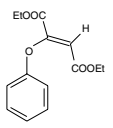
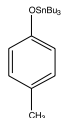
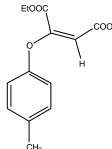
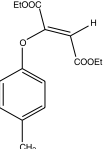

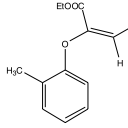
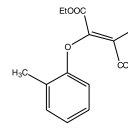

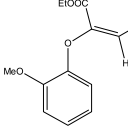
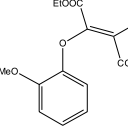
Scheme 7.

Table 9
Amination of phenols and tributyltin phenoxides with bis(trichloroethyl) azo-dicarboxylate carried out in 5 mol dm⁻³ solution of LiClO₄ in Et₂O

Compound	Product	Yield [%]
	—	0
		60
		60
		100
		70
		100
		40
		100
		50
		100

hydrazides prepared during this study were easily converted to their corresponding anilines by reduction with zinc dust in acetic acid. They were identified by comparison with the literature ¹H NMR data for corresponding aminophenols. We believe that LiClO₄ plays two roles in the present reaction, i.e., the activation of the azo compound and stabilisation of the intermediate complex. The 1.42 × 10⁻³ mol dm⁻³ solution of bis(2,2,2-trichloroethyl) azodicarboxylate in diethyl ether exhibits an absorption maximum at 243 nm. An increase in the concentration of LiClO₄ in Et₂O results in the decrease in the molar absorptivity at 243 nm. For example, its ratio in the solution of LiClO₄ in Et₂O changes from approximately 1.1 to 1.6 with

Table 10
Catalytic vinylation of different organotin phenoxides

Organotin phenoxide	Product	Yield [%]
	 	60%
	(1) : (2) = 1 : 1	
	 	60%
	(3) : (4) : (5) : (6) = 1 : 1 : 1 : 1	
	 	100%
	(7) : (8) : (9) : (10) = 1 : 1 : 1 : 1	
	 	80%
	(11) : (12) : (13) : (14) = 1,5 : 1,5 : 1 : 1	
	 	80%
	(15) : (16) : (17) : (18) = 2 : 2 : 1 : 1	

increasing concentration of LiClO_4 in the range 1–1.9 mol dm^{-3} . This seems to reflect the decreasing of LUMO of the azo enophile by association with aggregates of LiClO_4 .

In 1908, pure *o*-vinylphenol was synthesised for the first time by decarboxylation of *o*-hydroxycinnamic acid [30]. Since then, a number of methods have been developed for the synthesis of vinylphenols. Electrophilic acylation of phenol followed by reduction and dehydration was employed in the commercial production of *p*-vinylphenol by Maruzen Petrochemicals Co. [31]. Halophenol derivatives could be vinyliated by the Heck reaction [32]. Yamaguchi [23] reported the ethenylation reaction of phenol using the $\text{SnCl}_4\text{-Bu}_3\text{N}$ reagent system. 2-Phenoxy-fumaric acid diethyl ester as well as *o*- and *p*-tolylxy-fumaric acid diethyl esters were obtained for the first time by Ruhemann and Beddow [33] using chloro-fumaric acid diethyl ester and the appropriate phenol salt. Recently, Strazisar and Wolczanski [34] studied the possibility of application of vinyl ethers (including phenyl vinyl ethers) for production of commercially important polymers generated using single-site Ziegler–Natta catalysts. Due to the importance of both vinylphenols and phenyl vinyl ethers, we have decided to apply the analogous as previously strategy used for amination of phenols in purpose of their vinylation [35]. The tributyltin phenoxides and diethyl acetylenedicarboxylate were added to 5 mol dm^{-3} solutions of LiClO_4 in diethyl ether at 298 K. They were stored at room temperature for 2 days. The progress of the reaction was monitored by TLC (using petroleum-ethyl acetate mixture; 7:3 v/v as eluent). The yields of the reactions and products of studied additions of different tributyltin phenoxides with diethyl acetylenedicarboxylate carried in 5 mol dm^{-3} solutions of LiClO_4 in diethyl ether at 298 K are collected in Table 10.

We believe that the reaction between studied organotin phenoxides and diethyl acetylenedicarboxylate proceeds according to two possible mechanisms, which may compete. As the result, a mixture of a pair of *o*-vinylphenols

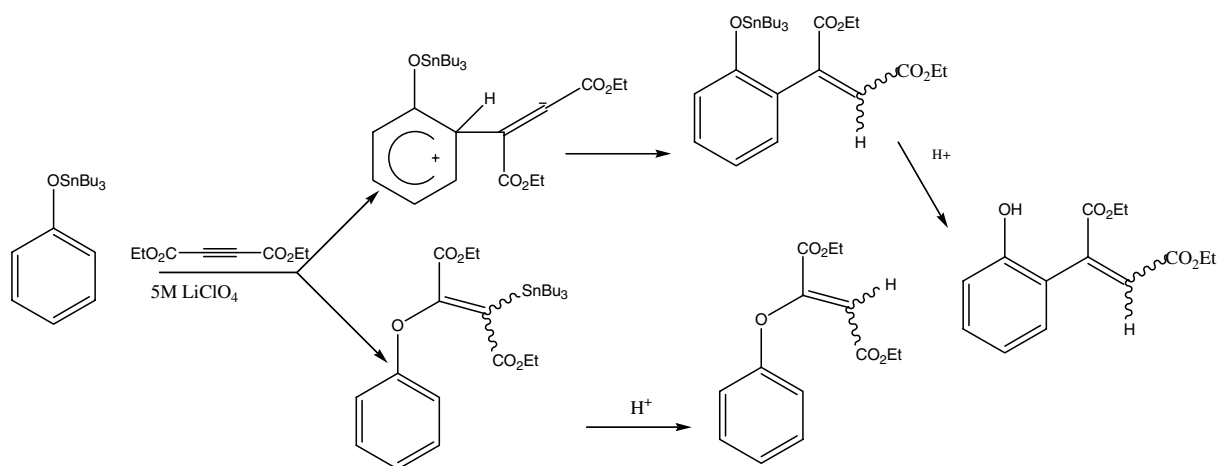
and the analogous pair of phenyl vinyl ethers can be obtained, as shown below.

The mechanism of the reaction of vinylation in the *ortho*-position to the stannyloxy group of different organotin phenoxides must still be regarded as an open question, whether it is an ene reaction or the simple aromatic substitution (see Scheme 8).

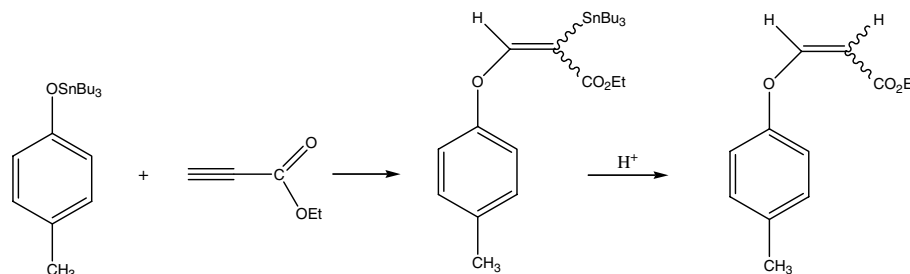
The studied reaction of tin phenoxides with diethyl acetylenedicarboxylate gives a mixture of products. Additionally, we have found that the yield of vinylphenols obtained as products of the discussed reaction of studied tributyltin phenoxides increases in the following order: tributyl-(2-methoxyphenoxy)tin < tributyl-(*o*-tolylxy)tin \approx tributylphenoxytin < tributyl-(*p*-tolylxy)tin. Although the kinetic studies have not been carried out for the studied reactions, the comparison of their yields seems to indicate that tributyl-(*p*-tolylxy)tin is the most reactive out of four mentioned above phenoxides. The yields and the ratio of obtained ethers and vinylphenols from each reaction have been given in Table 10. Again as it was observed for amination, tributyl-(2,6-dimethoxy)tin exhibited different behavior in comparison to other phenoxides. Its reaction with diethyl acetylenedicarboxylate gave only an equimolar mixture of 2-(2,6-dimethoxyphenoxy)maleic acid diethyl ester and 2-(2,6-dimethoxyphenoxy)fumaric acid diethyl ester with 80% yield (see Table 10).

Further extension of this method for the reaction of the less active ethyl propiolate with tributyl-(*p*-tolylxy)tin carried out in 5 mol dm^{-3} solution of LiClO_4 in the sealed glass tube exposed to the ultrasonic irradiation for several hours led to formation of the corresponding phenyl vinyl ether [36] (see Scheme 9).

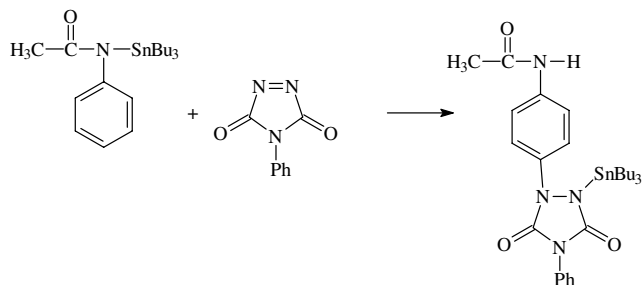
Finally, our preliminary results show that the strategy which has been worked out by us for tributyltin phenoxides can be extended to other groups of compounds (e.g., aromatic amines). In purpose to prove it, we have obtained *N*-tributylstannylacetanilide by azeotropic dehydration of a mixture of acetanilide and tributyltin oxide in toluene, and we have identified its product with 4-phenyl-1,2,4-



Scheme 8.



Scheme 9.



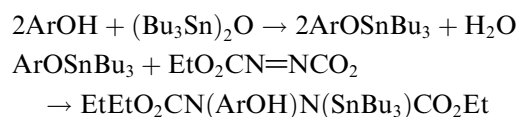
Scheme 10.

triazoline-3,5-dione from the reaction carried in benzene at room temperature as *N*-[4-(2-tributylstannyl-3,5-dioxo-4-phenyl-[1,2,4]triazolidin-1-yl)-phenyl]-acetamide, which was obtained with 30% yield [36] (see Scheme 10). Quite interestingly acetanilide and aniline do not give the analogous addition products with PTAD under standard conditions.

3. Conclusions

Metalloene reactions of allyltin compounds (which are considerably more active than the simple olefins) with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), diethyl azodicarboxylate (DEAD) and singlet oxygen are strongly catalysed by LiClO_4 . Additionally, the general picture emerges from our studies that as the medium is made more polar, either by varying the solvent or by adding a salt, the chemoselectivity of these reactions 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 Scheme 1 is rate determining, the effect of the increasing polar medium can be seen to result in stabilisation 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 $\text{S}_{\text{N}}2$ 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 of the latter pair, and the M-ene reaction becomes dominant. We have also observed that tributyltin oxide catalyses the reaction of phenols with

diethyl azodicarboxylate, bis(2,2,2-trichloroethyl) azodicarboxylate and diethyl acetylene-dicarboxylate. For DEAD this can be represented by the sequence of the reactions:



The final product undergoes hydrolysis at silica to: $\text{Et}_2\text{OCN}(\text{ArOH})\text{NHCO}_2\text{Et}$.

This reaction is also subject to discussed previously salt effect. We have also observed that stannylation of nitrogen in acetanilide leads to increase of its activity in reaction with PTAD.

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