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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 Et_2O and 4 mol dm^{-3} solutions of $LiClO_4$ in diethyl ether. All studied reactions were strongly catalysed by $LiClO_4$. Physicochemical studies were carried out in purpose to explain the catalytic effect of $LiClO_4$ 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 $LiClO_4$ 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.

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

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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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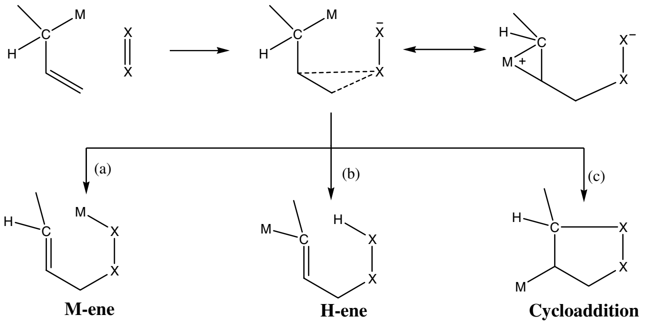

Scheme 1.

reactions [4], [2+2] and [2+3]-cycladditions [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 $^1O_2$ 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 allylmetalic 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 C_6H_6–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 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 ≈ tetraallyltin > allyltriphenyltin > allyltricyclohexyltin. 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. 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-live 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