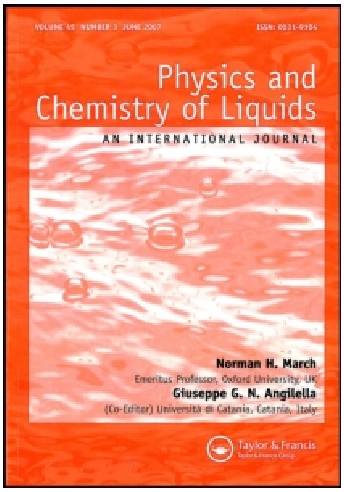

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STUDIES ON THE CATALYSIS OF ENE REACTIONS BY LITHIUM PERCHLORATE IN DIFFERENT SOLVENTS

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The catalytic effect of lithium perchlorate on ene reaction of *cis*-cyclooctene with diethyl azodicarboxylate, 4-phenyl-1,2,4-triazoline-3,5-dione and the metallo-ene reaction of diallyldibutyltin with diethyl azodicarboxylate has been studied in different solvents like acetonitrile, acetone, diethyl ether, dimethylformamide and ethyl acetate.

Keywords: Ene reaction; metallo-ene reaction; lithium perchlorate; kinetic studies

INTRODUCTION

A number of reactions have recently been shown to be surprisingly susceptible to catalysis by lithium perchlorate (typically 5 mol dm^{-3} in ether) [1, 2]. These include the rearrangement of allyl vinyl ethers [2] and of allyl stannanes [3], Diels-Alder reactions [4], the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds [5], and the addition of allylstannanes to aldehydes [6], the ene reaction of some allylic hydrocarbons, and the metalloene reaction of some allyltin compounds, with 1,2,4-triazoline-3,5-dione or with diethyl azodicarboxylate as enophiles [7]. The reaction of cholesterol,

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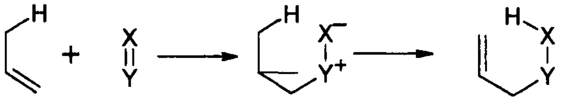
[*] Corresponding author.

cyclopentylidenecyclopentane or of tributylallyltin with singlet oxygen was found to be subject to a similar catalysis [7]. No clear picture of the mechanism of this catalysis has yet emerged, and it has variously been ascribed to a Lewis acid effect, to the ionic stabilization of polar transition states, or to internal pressure created by the lipophobic medium.

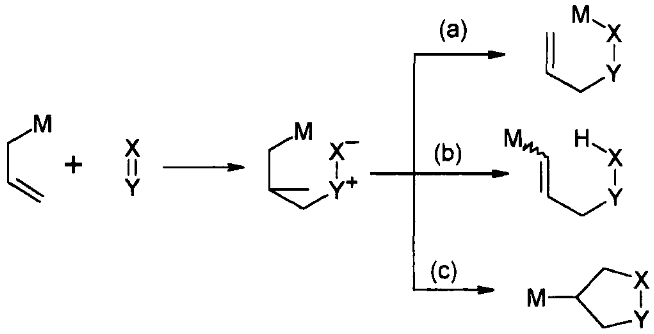
We have been interested in the hydrogen-ene reaction (Scheme 1), and its organometallic equivalent, the metalloene reaction (Scheme 2), particularly when the (homopolar) enophile ($X = Y$) is an azo compound (RN = NR).

There is good evidence from stereochemical and hydrogen isotope studies that the hydrogen-ene reaction proceeds through an intermediate ene-enophile complex, which then undergoes internal hydrogen transfer [8].

It is assumed that a similar complex is formed with allylmetallic compounds [9]. The reaction is then completed by transfer of the metal [Scheme 2(a)], but transfer of hydrogen [Scheme 2(b)], and migration of the metal to the central allylic carbon atom accompanied by ring closure [Scheme 2(c)] may compete.



SCHEME 1



SCHEME 2

EXPERIMENTAL

General – NMR spectra were recorded using a Varian Gemini 200 BP spectrometer, UV spectra were recorded on a Specord spectrometer (Carl Zeiss Jena), 10 mm cells, and mass spectra on a VG 7070 F instrument. Diallyldibutyltin was obtained as described in Ref. [10].

Ene reactions. Preliminary studies. – Typical examples of the ene reactions were as follows:

(1) Diallyldibutyltin (101 mg, 0.32 mmol) and diethyl azodicarboxylate (55.3 mg, 0.317 mmol) were added to 1 and 2 mol dm^{-3} solutions of $LiClO_4$ in studied solvents (1 cm^3). The progress of the reaction was monitored by TLC and by NMR spectroscopy, which showed that only diethyl N-allyl-N'-allyldibutylstannylhydrazodicarboxylate was formed with a quantitative yield in all studied solvents. Isolation of the product by gradient chromatography (light petroleum-ethyl acetate) gave diethyl N-allylhydrazodicarboxylate as an oil [7a].

(2) *Cis*-cyclooctene (73 mg, 0.66 mmol) and diethyl azodicarboxylate (110 mg, 0.63 mmol) were added to 1 mol dm^{-3} solutions of $LiClO_4$ in studied solvents (2 cm^3). The analogous reaction mixture was also added to the 3 mol dm^{-3} solutions of $LiClO_4$ in Et_2O. The progress of the reaction was only observed in Et_2O and DMF. However, the rate constant, k_2, in DMF was to low for kinetic measurements. After termination of the reaction, the reaction mixtures was washed with water, solvent was removed and the product was isolated by column chromatography using 30% mixture of ethyl acetate in light petroleum ether. The product obtained in a quantitative yield from 3 mol dm^{-3} solutions of $LiClO_4$ in Et_2O was identified by ^{1}H NMR spectroscopy.

(3) 4-Phenyl-1,2,4-triazoline-3,5-dione (35 mg, 0.2 mmol) and *cis*-cyclooctene (24 mg, 0.22 mmol) were added to 1 and 2 mol dm^{-3} solutions of $LiClO_4$ in studied solvents or pure solvents (1 cm^3). The solvent was removed and the product was purified by column chromatography using 25% mixture of ethyl acetate in light petroleum ether and identified by ^{1}H NMR spectroscopy [11]. The yield of the studied reaction varied from quantitative in Et_2O, 95% in acetone, where formation of a small amount of 1-acetonyl-4-

phenyl-1,2,4-triazolidine-3,5-dione [12] was observed, and 90% in all other solvents where 4-phenylurazole was detected in the reaction mixtures.

Details of compounds which have not been reported before are as follows:

Diethyl (cyclooct-2-enyl)hydrazo-1,3-dicarboxylate. – Oil. δ_H ($CDCl_3$) 1.28 (6H, t, *J* 7.1), 1.895 (10H, m), 4.21 (4H, q, *J* 7.1), 5.67 and 5.74 (1H, dm), 6.00 (1H, bs), 6.46 (2H, m).

Kinetic measurements were carried out according to the procedure described by Butler [13]. An alkene solution (1 cm^3) and 2 cm^3 of 4-phenyl-1,2,4-triazoline-3,5-dione of various concentrations, ranging from $5.7 \cdot 10^{-3}$ mol dm^{-3} in pure solvents to $1.14 \cdot 10^{-3}$ mol dm^{-3} in concentrated solutions of $LiClO_4$ in diethyl ether were mixed in a 1 cm, cubic UV cell. The concentration of diethyl azodicarboxylate chosen for studies of rate constants for addition with diallyldibutyltin was equal to $2.54 \cdot 10^{-2}$ mol dm^{-3}. Due to very low value of the rate constant for the reaction of diethyl azodicarboxylate with *cis*-cyclooctene in 3 mol dm^{-3} solutions of $LiClO_4$ the kinetic studies of 0.315 mol dm^{-3} solutions of azo compound were carried. The reaction mixture was stored for several days. The progress of the reactions was monitored by measuring the absorbance at 400 nm of 20 times diluted samples collected each 24 hours from the reaction mixture. The reactions were determined to be second order overall by fitting the data to the given below equation.

$$\log\left(1 + \frac{K}{A_t}\right) = \frac{b-a}{2.30} k_2\, t + \log\frac{b}{a}$$

In this equation, A_t = the absorbance at time *t*, a = the initial concentration of the azo compound, b = the initial concentration of alkene, k_2 = the second order rate constant, and $K = [(b-a)/a]A_0$, where A_0 is the initial absorbance.

Absorption spectra of $6-9 \cdot 10^{-5}$ mol dm^{-3} solution of 4-phenyl-1,2,4-triazoline-3,5-dione dissolved in solutions containing various amounts of $LiClO_4$ were recorded in Et_2O and CH_3CN. Additionally the absorption spectra of $2 \cdot 10^{-3}$ mol dm^{-3} solution of (TD) were recorded in all five studied solvents. The analogous spectra of diethyl azodicarboxylate have been recorded for $5.08 \cdot 10^{-4}$ and $1.5 \cdot 10^{-2}$ mol dm^{-3} solutions.

RESULTS AND DISCUSSION

We now report the effect of lithium perchlorate on the reaction of allyl-hydrogen and allyl-tin enes with azo compounds as enophiles in different solvents as: acetonitrile, acetone, diethyl ether, dimethylformamide and ethyl acetate. The reactions involving azo compounds were carried with diethyl azodicarboxylate and N-phenyltriazolinedione. The products obtained in yields close to quantitative were isolated and identified, a compound containing Sn—N bond underwent hydrolysis during work-up, and was characterised as the corresponding protic compound. The reactions were examined by measuring the reaction rates. The reactions of azo compounds with an excess of *cis*-cyclooctene or diallyldibutyltin were carried out in a UV cell using all mentioned above solvents.

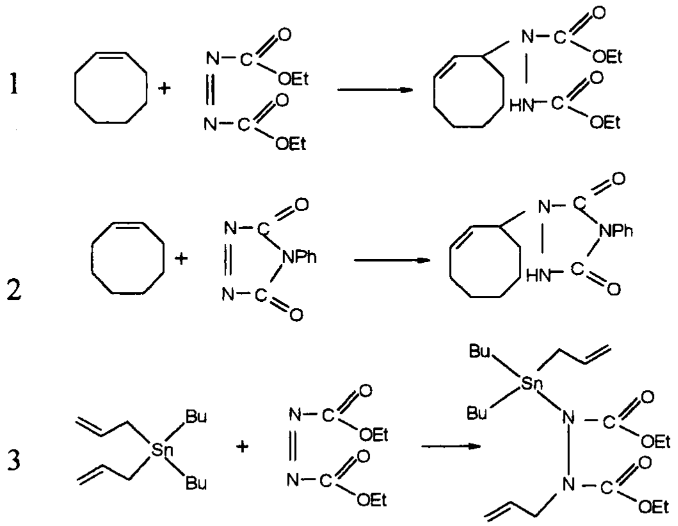
1,2,4-Triazoline-3,5-dione and diethyl azodicarboxylate gave only hydrogen-ene products (Scheme 1) with *cis*-cyclooctene and only metalloene product (Scheme 2(a)) with diallyldibutyltin. The reactions were accelerated by $LiClO_4$, the products, conditions, and rate constants, are given in Table I.

We studied the effect of lithium perchlorate on Reactions 1 – 3 carried in different solvents. Reactions 1 – 3 were treated as a second-order reactions. The second-order rate constants, k_2, are shown in Table I. Due to very small values of k_2 for Reaction 1 it was only possible to examine it in 3 mol dm^{-3} solutions of $LiClO_4$ in diethyl ether. Also, only in this solution the addition product in a quantitative yield was obtained.

In case of the Reaction 2 between 4-phenyl-1,2,4-triazoline-3,5-dione and *cis*-cyclooctene the strongest effect of the addition of $LiClO_4$ was observed for Et_2O. It seems also worth mentioning that the rate constant, k_2, for this reaction achieved the highest value in pure acetonitrile. However, the addition of $LiClO_4$ resulted in a considerable growth of the rate constant only in Et_2O. Thus, the rate constant, k_2, was increased by factor of ca. 39 by 1.9 mol dm^{-3} $LiClO_4$. We studied also the addition of diethyl azodicarboxylate with diallyldi-

TABLE I Reactions of *cis*-cyclooctene and diallyldibutyltin with azo compounds

Reaction



Second-Order Rate Constants ($10^3 \cdot k_2$,dm^3/mol s) at 25° for Reactions 2, 3

Solvent	*Reaction* 2 [*LiClO*$_4$] *mol dm*$^{-3}$			*Reaction* 3 [*LiClO*$_4$] *mol dm*$^{-3}$	
	0	1	1.9	0	1
CH_3CN	15.2	19	19.4	0.13	0.25
Acetone	3.4	3.5	3.7	0.16	0.28
Et_2O	3.5	17.4	129.6	0.29	0.60*
DMF	3.1	2.5	2.6	0.20	0.11
Ethyl Acetate	2.5	3.1	5.2	0.17	0.30

* $k_2 = 1.74 \cdot 10^{-3} dm^{-3}$/mol s for Reaction 3 carried in 3 mol dm^{-3} solution of $LiClO_4$ in Et_2O. (Further addition of $LiClO_4$ to four other solvents did not result in the increase of rate constants). $k_2 \approx 7 \cdot 10^{-6} dm^3$/mol s for Reaction 1 carried in 3 mol dm^{-3} solutions of Et_2O.

butyltin. The rate constant, k_2, for the Reaction 3 in the series of five studied solvents in 1 mol dm^{-3} $LiClO_4$ solution achieved the highest value in Et_2O. Further addition of $LiClO_4$ to all studied solvents resulted in a considerable growth of the rate constant only in Et_2O. Thus the rate constant, k_2, was increased by factor ca. 6 by 3 mol dm^{-3} $LiClO_4$ in Et_2O.

The ene reactions of *cis*-cyclooctene and diallyldibutyltin with azo enophiles were accelerated by lithium perchlorate in Et_2O (Tab. I). All measured rate constants achieved the highest values in concentrated solutions of $LiClO_4$ in Et_2O. The reaction between diethyl azodicarboxylate and *cis*-cyclooctene, which were unreactive under normal conditions, occurred in 3 mol dm^{-3} $LiClO_4$ in Et_2O. However, the examination of rate constants, k_2, for Reaction 2 and 3 indicates that catalytic activity of $LiClO_4$ in Et_2O is stronger in case of 4-phenyl-1,2,4-triazoline-3,5-dione in comparison with diethyl azodicarboxylate. In purpose to explain this effect we carried out the comparative studies of both azo compounds in Et_2O and CH_3CN using absorption spectroscopy. Acetonitrile was chosen among other studied solvents, where catalytic activity of $LiClO_4$ for Reactions 1–3 was inconsiderable, due to its transmittance in the UV region. The solution of 4-phenyl-1,2,4-triazoline-3,5-dione in diethyl ether exhibited two absorption maxima λ_{max} 226 and 258 nm. The increase of the concentration of $LiClO_4$ in Et_2O resulted in the decrease of the molar absorptivity at 226 nm leading to the decrease of the ratio of molar 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 $LiClO_4$ from 1.6 up to 3.8 mol dm^{-3} in $9 \cdot 10^{-5}$ mol dm^{-3} solution of 4-phenyl-1,2,4-triazoline-3,5-dione in Et_2O. The increase of the concentration of $LiClO_4$ caused also a small decrease of the molar absorptivity at 527 nm. In case of $6 \cdot 10^{-5}$ 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 $LiClO_4$ 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 $LiClO_4$ 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 CH_3CN was observed. Additionally the addition of $LiClO_4$ to CH_3CN resulted in a growth of the molar absorptivity at 530 nm. The absorption spectra of $5.08 \cdot 10^{-4}$ mol dm^{-3} solutions of diethyl azodicarboxylate in Et_2O and CH_3CN exhibited also some differences. Spectra of the studied azo compound in pure Et_2O and 3 mol dm^{-3} solutions of $LiClO_4$ were similar. Whereas, spectra of $5.08 \cdot 10^{-4}$ mol dm^{-3} solutions of diethyl azodicarboxylate in pure acetonitryle and 1 mol dm^{-3} solution of $LiClO_4$ exhibited some differences. The addition of $LiClO_4$ 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 $LiClO_4$ to five studied solvents was observed in case of the second absorption maximum (λ_{max} 400 nm). We assume that specific catalytic properties of $LiClO_4$ in diethyl ether are linked with: (1) facilitation of the formation of the polar intermediate by the ionic medium (Scheme 1) and (2) lowering HOMO of the azo compound by association with aggregates of $LiClO_4$. In case of 4-phenyl-1,2,4-triazoline-3,5-dione both mentioned above effects may affect its activity. However facilitation of the formation of the polar intermediate seems to be responsible for increased activity of diethyl azodicarboxylate in concentrated solutions of $LiClO_4$ in Et_2O. (No effects associated with changes of electron density of the azo compound with the addition of $LiClO_4$ were observed in absorption spectra.) The properties of solutions of $LiClO_4$ in Et_2O observed presently by us were also discussed previously by several authors [14].

Acknowledgements

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