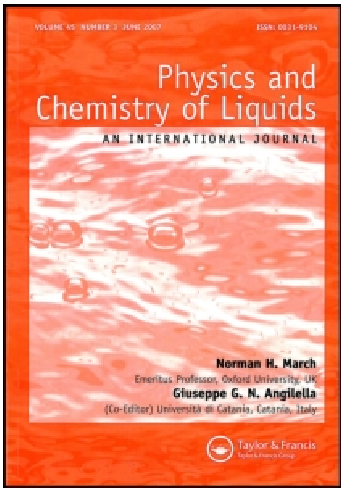

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Studies of the Catalysis of Ene Reactions of 4-Phenyl-1,2,4-triazoline-3,5-dione and Diethyl Azodicarboxylate with Different Olefins by Lithium Perchlorate

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STUDIES OF THE CATALYSIS OF ENE REACTIONS OF 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE AND DIETHYL AZODICARBOXYLATE WITH DIFFERENT OLEFINS BY LITHIUM PERCHLORATE

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The catalytic effect of lithium perchlorate in diethyl ether on ene reaction of 2-hexene, cyclohexene, 1-methylcyclohexene, oleic acid and methyl oleate with 4-phenyl-1,2,4-triazoline-3,5-dione has been studied, as well as on the reaction of diethyl azodicarboxylate with methyl oleate.

Keywords: Ene reaction; Lithium perchlorate; 4-phenyl-1,2,4-triazoline-3,5-dione; Diethyl azodicarboxylate

INTRODUCTION

Many reactions are strongly catalysed by lithium perchlorate. These include the rearrangement of allyl vinyl ethers [1], and allyl stannanes [2], Diels–Alder reactions [3], the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds [4], and the addition of allylstannanes to aldehydes [5]. We have previously shown that ene reaction of allilic hydrocarbons and metallo-ene reaction of

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allyltin compounds, with 4-phenyl-1,2,4-triazoline-2,5-dione (PTAD), diethyl azodicarboxylate (DEAD) or with singlet oxygen as enophiles, in diethyl ether are strongly catalysed by lithium perchlorate [6]. Additionally, we have observed for reactions of different allyltin compounds with PTAD and $^1O_2$ the effect of the polarity of solvent on the chemoselectivity of the reaction [7]. It is known that rates of reaction of PTAD with alkenes depend on the solvent. For example, Greene [8] reported that such rates in benzene are faster than in THF, and they are faster in CH_2Cl_2 than in acetonitrile. Comparison of the *cis–trans* pairs of olefins shows the *cis* isomer to be more reactive than the *trans*.

It is also known that the ratio of isomeric products of PTAD and up to certain extent of $^1O_2$ with trisubstituted olefins such as 1-methylcyclohexene and non-terminal unsymmetrical olefins such as 2-hexene depends on the polarity of the applied solvent [9].

EXPERIMENTAL

General

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.

The NMR spectra of most of the products from the ene reactions of PTAD have been described in other papers [6,9], and provided the basis of the identifications reported in this work. Details of compounds, which have not been reported before, are as follows. Their composition has been confirmed by elemental analysis.

The equimolar mixture of (E)-10 adduct (**1**) and its isomer (**2**) (E)-9-(3,5-dioxo-4-phenyl-[1,2,4]triazolidin-1-yl)-octadec-10-enoic acid – Oil. $\delta_H(CDCl_3)$ 0.879 (3H, t, *J* 7.0 Hz), 1.261 (20H, m), 1.599 (2H, m), 2.017 (2H, m), 2.341 (2H, t, *J* 7.1 Hz), 4.496 (1H, dm, *J* 6.7 Hz), 5.388 (1H, dm, *J* 15.0, 6.7 Hz), 5.600 (1H, dm, *J* 15.0, 6.7 Hz), 7.340 (1H, m), 7.470 (4H, m), 8.620 (1H, br s).

The equimolar mixture of (E)-10 adduct (**3**) and its isomer (**4**) (E)-9-(3,5-dioxo-4-phenyl-[1,2,4]triazolidin-1-yl)-octadec-10-enoic acid methyl ester. M.p. 165–170°C. $\delta_H(CDCl_3)$ 0.873 (3H, t, *J* 7.0 Hz), 1.277 (22H, m), 2.021 (2H, m), 2.287 (2H, t, *J* 7.3 Hz), 3.662 (3H, s), 4.598

(1H, dm, *J* 7.1 Hz), 5.420 (1H, dm, *J* 15.0, 7.1 Hz), 5.748 (1H, dm, *J* 15.7, 7.1 Hz), 7.350 (2H, m) 7.489 (3H, m), 8.600 (1H, br s).

δ_C(CDCl$_3$) 14.12, 22.68, 24.84, 28.98, 29.08, 29.12, 29.24, 31.84, 33.99, 51.45, 58.81, 60.43, 119.87, 125.41, 128.93, 136.00 (C = C), 153.94, 171.24 (C = O).

The equimolar mixture of (E)-10 adduct (**5**) and its isomer (**6**) (E)-9-[1,2-bis(ethoxycarbonyl)hydrazin-1-yl]octadec-10-enoic acid methyl ester Oil. δ_H(CDCl$_3$) 0.845 (3H, t, *J* 7.0 Hz), 1.147 (28H, m), 2.022 (2H, m), 2.310 (2H, t, *J* 7.3 Hz), 3.667 (3H, s), 4.199 (4H, q, *J* 7.2 Hz), 4.529 (1H, q, *J* 6.3 Hz), 5.392 (1H, m), 5.561 (1H, m), 6.279 (1H, br s).

Separation of above pairs of isomers was impossible by column chromatography.

Ene Reactions

Typical examples of the ene reactions were as follows: (**1**) methyl oleate (93.1 mg, 0.314 mmol) and 4-phenyl-1,2,4-triazolin-3,5-dione (55 mg, 0.314 mmol) were added to a 4 mol dm^{-3} solution of LiClO$_4$ in diethyl ether (1 cm^3). The colour of the azo compound was discharged within few hours. The product was isolated by column chromatography on silica using a mixture of ethyl acetate and petroleum ether (v : v 2 : 3).

(**2**) Diethyl azodicarboxylate (189 µl, 1.2 mmol) was added to a solution of methyl oleate (343.9 mg, 1.16 mmol) to 4 mol dm^{-3} solution of LiClO$_4$ in diethyl ether (1 cm^3). The colour of the azo compound was discharged within four days. The product was isolated in the same way as previously.

Kinetic measurements with PTAD were carried out in a 1 cm^3, UV cell. The concentration of PTAD and olefin chosen was equal to 0.0046 mol dm^{-3}. 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% and assume that their ratio corresponds to a certain degree with the ratio of the reaction rate constants.

RESULTS AND DISCUSSION

We were anxious to compare the reactivity of different olefins with PTAD in diethyl ether and 4 mol dm^{-3} solutions of LiClO$_4$ in Et$_2$O.

Additionally we planned to check the influence of $LiClO_4$ on the selectivity of reactions of 1-methylcyclohexene and 2-hexene with PTAD.

The reaction of olefins with equimolar amounts of PTAD (0.314 mmol) in Et_2O and 4 mol dm^{-3} solutions of $LiClO_4$ in Et_2O was followed visually by fading of the colour of the azo compound. Products were purified by column chromatography and identified by NMR spectroscopy. For more dilute solutions (0.0046 mol dm^{-3}), the rates were followed by measuring half-lifes of reactions (times corresponding to the decrease of the initial absorbance by 50%). The results with PTAD are shown in Table I.

We have also compared products of the reaction of PTAD with 1-methylcyclohexene (see Reaction 1 and Table II) and a mixture of *cis* and *trans*-2-hexene (see Reaction 2) carried in different solvents.

The reaction of a mixture of *cis* and *trans*-2-hexene with PTAD carried in 4M solution of $LiClO_4$ in Et_2O gave a mixture of two isomeric adducts mainly (E)-2-(3,5-dioxo-4-phenyl-[1,2,4]triazolidin-1-yl)-3-hexene(**9**) and a small amount of 3-(3,5-dioxo-4-phenyl[1,2,4]-triazolidin-1-yl)-1-hexene (**10**). The ratio of (**9**) : (**10**) was equal to 77 : 23.

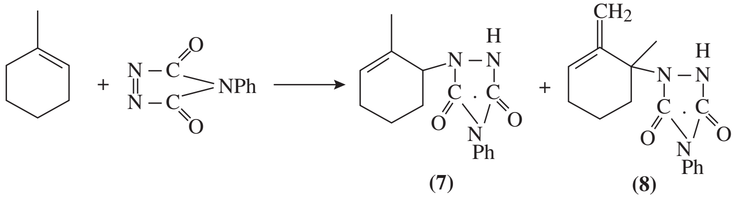
For the Reaction 2 carried in pure Et_2O the ratio of products (**9**) : (**10**) was equal to 64 : 36. Obtained results seem to indicate the growth of selectivity of Reaction 1 and 2 with addition of $LiClO_4$. This may be presumably explained by stabilisation of the transition state by the polar medium. A considerable decrease of half-lifes of the reaction (see Table I) in 4 mol dm^{-3} solutions of $LiClO_4$ in Et_2O

TABLE I Reactions of olefins with PTAD in Et_2O

Compound	*[$LiClO_4$]* mol dm^{-3}	*Half-life of the Reaction* [s]
oleic acid	0	4624
	4	507
methyl oleate	0	4800
	4	555
Cyclohexene	0	48600
	4	1466
1-methylcyclohexene	0	8817
	4	300
mixture of *cis* and *trans*-2-hexene	0	
	4	

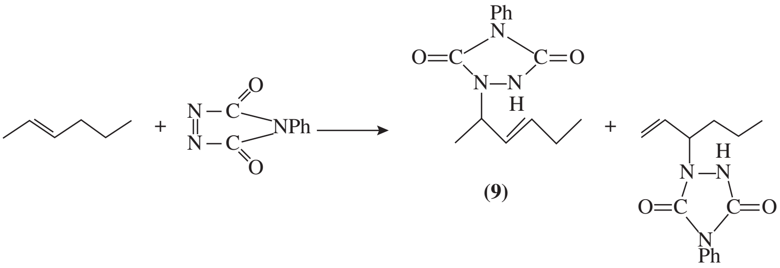
TABLE II Reaction of 1-methylcyclohexene with PTAD in different solvents

Solvent	*Yield of* *(7)* [%]	*Yield of* *(8)* [%]
$CHCl_3$	45	55
C_6H_6	52	48
CH_3CN	59	41
CH_3OH	82	18
Et_2O	48	52
4 M $LiClO_4$ in Et_2O	100	–



(7) **(8)**

REACTION 1



(9)

(10)

REACTION 2

seem to be linked with the association of molecules of azo enophile with lithium cation leading to decrease of its LUMO.

Recently Shimada [10] has shown that adduct of PTAD is suitable for the identification of D_3 – fatty acid ester in biological fluids. The kinetic studies carried in this work (see Table I) indicate that reactivity of oleic acid and its methyl ester is very similar in Et_2O as well as in 4M solutions of $LiClO_4$ in Et_2O. A mixture of *trans* 9- and

10-monoadducts has been obtained from both reactions (see Experimental).

Finally we compared the effects of $LiClO_4$ on the reaction of diethyl azodicarboxylate with methyl oleate. An equimolar mixture of (**5**) and (**6**) was obtained after four days only from 4 mol dm^{-3} solution of $LiClO_4$ in Et_2O.

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