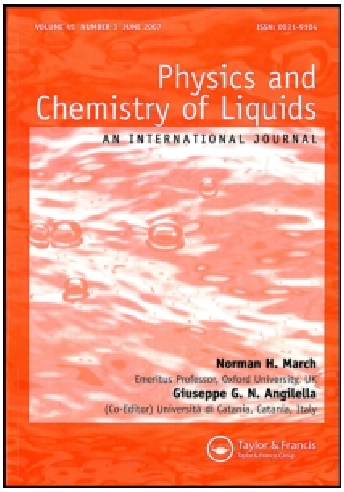

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EFFECT OF SOLVENT ON RATE OF REACTIONS OF DIFFERENT OLEFINS WITH 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE

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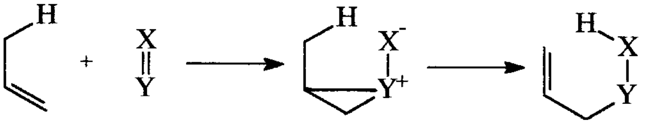
The effect of the influence of the properties of the solvent on the rate of the ene reaction of different olefins with 4-phenyl-1,2,4-triazoline-3,5-dione carried out in CH_3CN, $CHCl_3$ and C_6H_6 has been studied.

Keywords: Ene reaction; Solvent; 4-phenyl-1,2,4-triazoline-3,5-dione

INTRODUCTION

Olefins react with azo enophiles to give addition products as shown in Eq. (1). There is good evidence from stereochemical and hydrogen isotope studies that the ene reaction proceeds through an intermediate ene–enophile complex, which then undergoes internal hydrogen transfer [1].



(1)

Previously, we have compared the influence of CH_3CN, $CHCl_3$ and their mixture on the rates and selectivity of reactions of allyltin compounds with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) [2]. The increase in rates of these reactions in pure $CHCl_3$ in comparison to CH_3CN and the $CHCl_3$–CH_3CN (2/3 v/v) mixture was explained by the association of a molecule of the azo enophile with a molecule of chloroform.

Butler [3] carried out kinetic measurements for the reaction of 4-substituted -1,2,4-triazoline-3,5-diones including PTAD with different olefins.

It was found that the reactivity of alkenes was markedly dependent on their structure. He explained observed solvent effects as a result of a strong donor–acceptor complex

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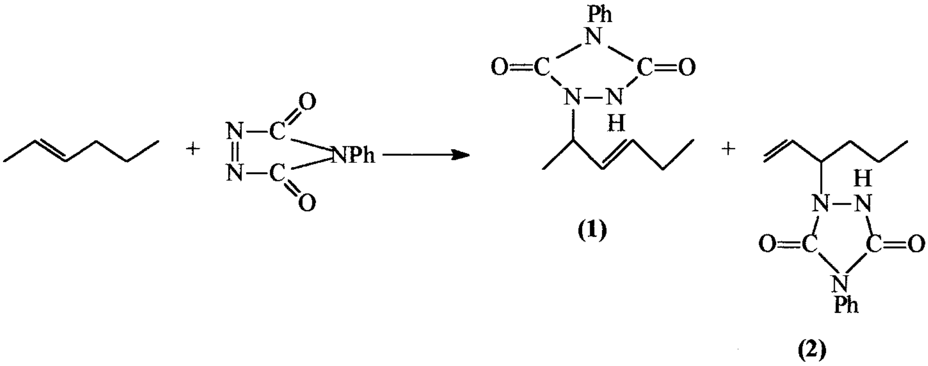
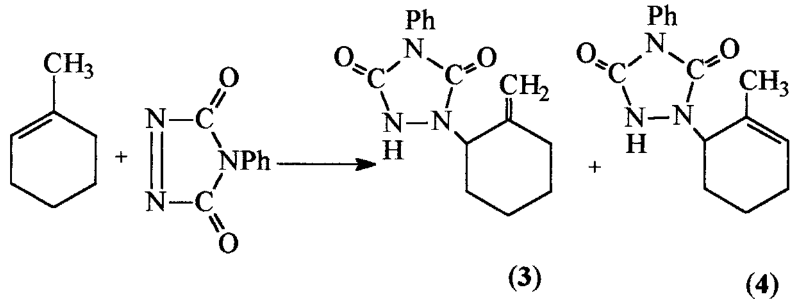
interaction between PTAD and solvent. Also Greene [4] carried out analogous studies. He observed for several olefins that the rates of reactions with PTAD in benzene are faster than in THF, and the rates in CH_2Cl_2 are faster than in CH_3CN. Greene additionally noted that some olefins (as tetramethylethylene and indene) show a stronger response to solvent polarity. Butler [5] also observed the possibility of formation of two different addition products both for the reaction with *trans*-2-hexene (see Eq. (2)) and 1-methyl-l-cyclohexene (see Eq. (3)).



(2)



(3)

Trans-2-hexene gave a slight excess of the internal olefin in CH_2Cl_2 at room temperature (**1** : **2** ratio of 3 : 2), whereas, 1-methyl-l-cyclohexene under analogous conditions was attacked exclusively at the 2-position and the ratio between the two isomers **3** and **4**, was 1 : 1.

We observed only small variations of the ratio of products **3** and **4** with increase in solvent polarity for reactions carried out in diethyl ether, $CHCl_3$, C_6H_6, CH_3CN, CH_3OH and 4 M solutions of $LiClO_4$ in Et_2O [6].

EXPERIMENTAL

NMR spectra were recorded using a Varian Gemini BP spectrometer, UV spectra were recorded on a Specord spectrometer (Carl Zeiss Jena) using 10 mm cells.

The NMR spectra of all products of the ene reactions of PTAD have been described previously [5,6], and have provided the basis of identifications reported in this work.

Ene Reactions

Typical examples of the ene reactions were as follows: methyl oleate (93.1 mg, 0.314 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (55 mg, 0.314 mmol) were added to acetonitrile (1 cm^3). The colour of the azo compound was discharged within a few hours. The product was isolated by column chromatography on silica using a mixture of ethyl acetate and petroleum ether (2/3 v/v).

Kinetic measurements with PTAD were carried out in a 1 cm^3 UV cell. The concentration of PTAD and chosen olefin 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

The aim of the present study was to compare the response of different olefins to properties of three chosen solvents (CH_3CN, $CHCl_3$ and C_6H_6) for their reaction with PTAD. The rates of reactions were followed by UV–Vis spectroscopy by measuring half-lives of reactions (times corresponding to the decrease of the initial absorbance by 50%). The obtained results are given in Table I.

TABLE I Reactions of olefins with PTAD in CH_3CN, $CHCl_3$ and C_6H_6 carried at 298 K

Compound	*Solvent*	*Half-live of the reaction*	*The ratio of half-lives in CH_3CN and $CHCl_3$*	*The ratio of half-lives in CH_3CN and C_6H_6*
Methyl oleate	CH_3CN	2700		
	$CHCl_3$	240	11.25	2.62
	C_6H_6	1030		
Oleic acid	CH_3CN	2340		
	$CHCl_3$	130	18.00	3.84
	C_6H_6	610		
Cyclohexene	CH_3CN	7200		
	$CHCl_3$	2400	3.00	0.83
	C_6H_6	8700		
1-Methyl-l-cyclohexene	CH_3CN	3000		
	$CHCl_3$	250	12.00	1.92
	C_6H_6	1560		
Trans-2-hexene	CH_3CN	8760		
	$CHCl_3$	1050	8.34	1.58
	C_6H_6	5540		
Cyclopentene	CH_3CN	2800		
	$CHCl_3$	1750	1.60	0.30
	C_6H_6	9420		
1-Hexene	CH_3CN	24240		
	$CHCl_3$	7590	3.19	0.28
	C_6H_6	86780		
Trans-3-hexene	CH_3CN	11320		
	$CHCl_3$	790	14.33	1.71
	C_6H_6	6620		

For all olefins studied by us the rate of reaction was the highest in $CHCl_3$. A considerable decrease of half-lives in $CHCl_3$ in comparison to CH_3CN and C_6H_6 seem to be linked with the association of molecules of PTAD with $CHCl_3$, leading to a decrease of LUMO of the azo enophile. Additionally, for methyl oleate, oleic acid, 1-methyl-1-cyclohexene, *trans*-2-hexene and *trans*-3-hexene, the studied additions were faster in benzene than in more polar acetonitrile.

The half-lives of reactions of cyclohexene, cyclopentene and 1-hexene exhibited a less pronounced effect on the change of solvent from CH_3CN to $CHCl_3$. The ratio of half-lives in both solvents varied from 1.6 for cyclopentene to 3.19 for 1-hexene. Also, in comparison to other olefins, reactions carried out in acetonitrile for the three above-mentioned olefins were faster than in benzene. It seems to prove the conclusion that a response on the ene reaction to solvent polarity depends on the structure of the olefin.

The reaction of *trans*-2-hexene with PTAD carried out in CH_3CN, $CHCl_3$ and C_6H_6 gave a mixture of two isomeric adducts mainly (*E*)-2-(3,5-dioxo-4-phenyl-[1,2,4]triazolidin-1-yl)-3-hexene (**1**) and a small amount of 3-(3,5-dioxo-4-phenyl-[1,2,4]-triazolidin-1-yl)-1-hexene (**2**). The ratio of **1** and **2**, in all three studied solvents was close to 2 : 1, but differed only slightly in $CHCl_3$ and CH_3CN. In CH_3CN, a small increase of the yield of product **1** has been observed. As described previously, solvent effects on the ratio of products for reactions of 1-methyl-1-cylohexene were small [6].

References

[1] M. Orfanopoulous, I. Smonou and C.S. Foote (1990). *J. Am. Chem. Soc.*, **112**, 3607; H.S. Dang and A.G. Davies (1991). *J. Chem. Soc. Perkin Trans.*, **2**, 2011; H.S. Dang and A.G. Davies (1991). *Tetrahedron Lett.*, **32**, 1745.

[2] W.J. Kinart, C.M. Kinart and I. Tylak (1999). *J. Organomet. Chem.*, **590**, 258.

[3] S. Ohashi and G.B. Butler (1980). *J. Org. Chem.*, **45**, 3472.

[4] C.C. Cheng, C.A. Seymour, M.A. Petti and F.D. Greene (1984). *J. Org. Chem.*, **49**, 2910.

[5] S. Ohashi, K. Leong, K. Matyjaszewski and G.B. Butler (1980). *J. Org. Chem.*, **45**, 3467; J. Cai and A.G. Davies (1992). *J. Chem. Soc. Perkin Trans.*, **2**, 1743.

[6] W.J. Kinart, C.M. Kinart and I. Tylak (2002). *Phys. Chem. Liq.*, **40**, 405.