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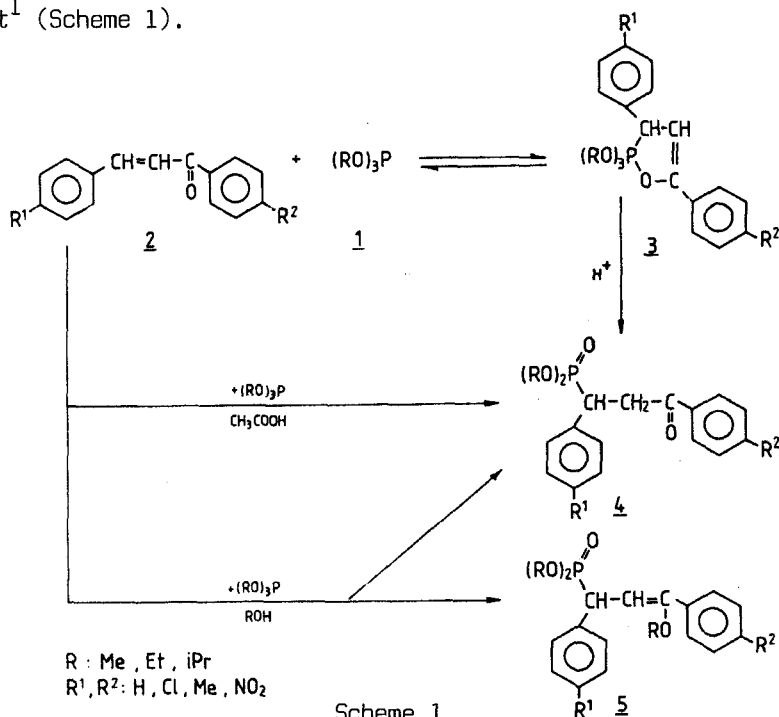
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MECHANISM OF THE REACTION OF TRIALKYL PHOSPHITES WITH CHALCONES

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Abstract According to our kinetic measurements the nucleophilic attack of trialkyl phosphite can occur both on the carbonyl carbon and on the C=C double bond of chalcone producing oxaphospholene ring.

It has previously been shown that the trialkyl phosphites and α,β -unsaturated carbonyl compounds give substituted oxaphospholene in aprotic solvent in an equilibrium reaction. In protic solvent the product is γ -ketophosphonate or the enol ether depending on the solvent¹ (Scheme 1).



Scheme 1

We have investigated the interaction of chalcones (benzalacetophenones) with trialkyl phosphites. In aprotic solvent or without use of any solvent we prepared the oxaphospholene adducts (3) and

identified them by IR, ^1H - and ^{31}P -n.m.r. spectroscopy. The oxaphospholenes (3) are crystalline compounds, which are slowly decomposed to the starting chalcone and trialkyl phosphite. They can be hydrolysed easily in acidic circumstances to the appropriate γ -keto-phosphonate (4). The γ -ketophosphonates are formed in acetic acid quantitatively. Using alcohol as solvent both 4 and its enol ether (5) are formed in an almost equal ratio. The latter can be isolated in pure form by column chromatography.

Ogata and coworkers studied the reaction of α -diketones with trialkyl phosphites which resulted a dioxaphospholene ring². The kinetic data and activation parameters of the reaction have also been measured, and the Hammett and Taft equations have been used for the study of the reaction. A mechanism was assumed by them involving the attack of the phosphite to the carbonyl carbon atom following a phosphoryl migration and a ring closure step.

In our kinetic experiments the chalcone (2) has been reacted with a large excess of trialkyl phosphite (1) without any added solvent in an inert atmosphere at the temperature range of 40–78 °C. The course of the reaction was monitored by measuring the quantity of the chalcone by GC. The reaction was frozen by addition of diluted hydrochloric acid which reacts with both the excess of trialkyl phosphite and with the oxaphospholene in fast reactions to produce dialkyl phosphite and γ -ketophosphonate, respectively.

Table

The pseudofirst order rate constant of 3, yield in the equilibrium and values of the activation parameters at 50 °C

R	R ¹	R ²	k 10 ⁵ (s ⁻¹)	yield (%)	ΔH^* (KJ.mol ⁻¹)	ΔS^* (J. ^o K ⁻¹ .mol ⁻¹)
Me	H	H	1.7	55	61.7	-163
Et	H	H	0.9	60	67.9	-147
iPr	H	H	3.6	30		
Me	Cl	H	2.1	74	47.4	-206
Et	Cl	H	2.1	88		
Me	H	Cl	3.2	82	59.8	-164
Et	H	Cl	2.8	78		
Me	Me	H	0.97	50	55.4	-187
Me	H	Me	0.96	44	47.7	-211

The pseudofirst order rate constants were determined from the initial slope in a diagram of $\log c$ vs. time (Table). According to the measured data the reaction rate depends on the substituents in any of the aromatic rings, namely the electron withdrawing group increases while the electron releasing group decreases the rate.

The values of the enthalpy and entropy of activation were calculated and are shown in the Table.

The observed small value of ΔH^* and the large negative value of ΔS^* are characteristic for a series of the reaction of carbonyl compounds with nucleophiles. In general, a large negative value of ΔS^* is observed in the reaction in which the total number of species decreases or a strongly polarized and/or crowded transition states are involved. Therefore the concerted onestep cycloaddition of chalcone with trialkyl phosphite may be excluded.

Beside the attack on the carbonyl carbon there is an other possibility for the attack of the phosphite nucleophile, namely this site is the C=C double bond in the β position. From the measured thermodynamic data it seems to be difficult to differentiate between a nucleophilic attack on the C=C bond from the attack on the carbonyl carbon by the trialkyl phosphite. This difficulty can be overcome using the Hammett equation which method had been used in our earlier work to elucidate the mechanism of Perkow-Arbuzov reaction³.

Thus the $\log k$ vs. σ_p was plotted in the case of some chalcones having substituents on the aromatic rings (Fig. 1. and Fig. 2.).

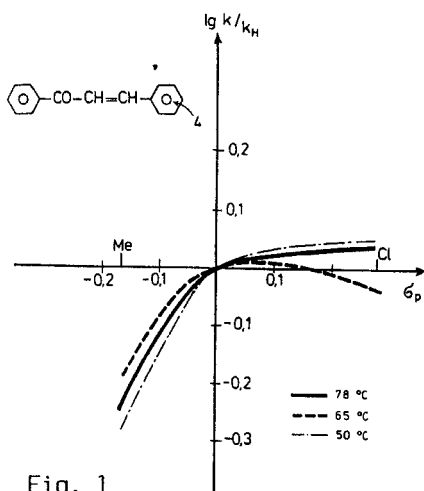


Fig. 1

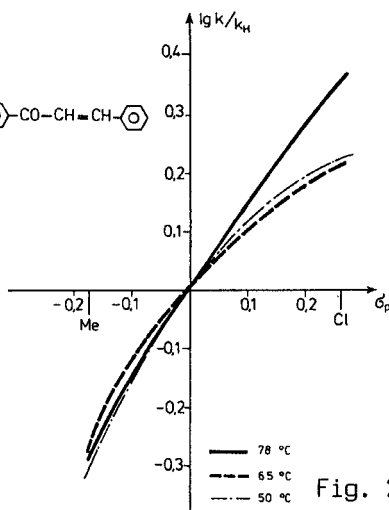
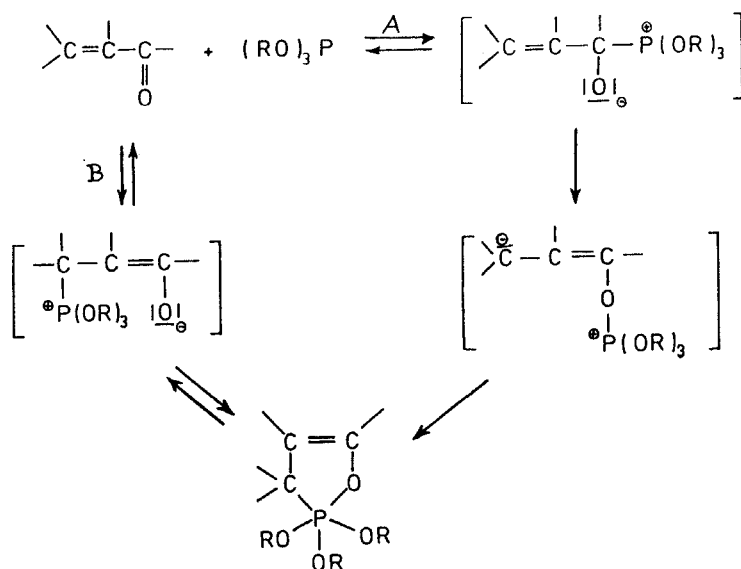


Fig. 2

As it can be seen from the Figures the Hammett plots became curved especially in the case when the substituents are situated on the aromatic ring next to the C=C double bond (Fig. 1.). It means that more than one complex are formed in the rate determining step, namely the trialkyl phosphite can attack both on the carbonyl carbon (route A in Scheme 2) and on the C=C double bond (route B).



Scheme 2

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