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REACTION KINETICS OF TRIETHYL PHOSPHITE WITH p-PHENACYLCHLORIDES

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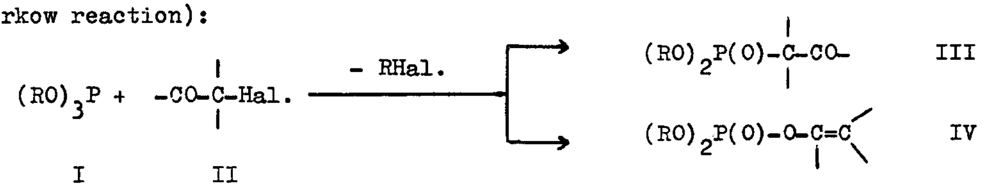
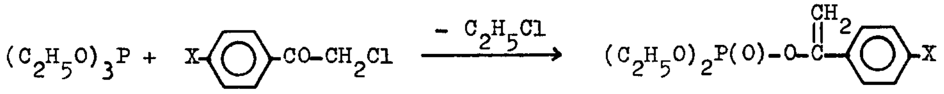
The reactions of trialkyl phosphites I with α-halo ketones II lead to β-ketophosphonates III (Michaelis-Arbuzov reaction) and enol phosphates IV (Perkow reaction):



Michaelis-Arbuzov reaction mechanism is clear and has been widely investigated kinetically (1); on the contrary for the Perkow reaction several mechanisms have been proposed (2).

In previous works (3), the experimental results obtained lead us, in agreement with other Authors (4), to postulate as initial reaction step the attack of phosphorus atom at carbonyl carbon, followed by rearrangement to the enol phosphate.

A kinetic study of reaction of triethyl phosphite with para-substituted phenacylchlorides in benzene at 40°C, which was found to yield exclusively enol phosphate (3), has been undertaken by us:



X = H, CH_3, OCH_3, Cl, NO_2

The reaction was followed in sealed tube by determining the chloride ion concentration resulting from the hydrolysis of the unreacted phenacylchloride.

At definite time intervals the tubes were rapidly cooled in an acetone-solid carbon dioxide mixture and then broken under a solution composed by 20 ml water, 20 ml 95 per cent ethyl alcohol and 1 g NaOH.

The mixture was refluxed for 15 minutes, cooled and acidified with dilute nitric acid; chloride ion, following Volhard, was titrated (ferric ammonium sulfate, as indicator, in the presence of nitrobenzene).

The pseudo first-order reaction with the isolation method respect to phenacylchloride and global reaction order with equal initial concentrations of reactants were calculated (TABLE 1).

TABLE 1

PSEUDO FIRST-ORDER AND SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF TRIETHYL PHOSPHITE AND PHENACYLCHLORIDE IN BENZENE AT 40 ± 0.01°

Run No	Pseudo 1st order rate const. sec^{-1} x 10^4	Second order rate const. 1/mole sec x 10^5
1	1.88	7.61
2	1.81	7.37
3	1.87	7.36

Results obtained indicate that reaction follows a second order kinetic, first order respect to each reactant. The reaction was followed to approximately 75% of completion; the average error of the measured concentration is ± 3% and the reaction temperature was kept constant within ± 0.01°.

Second order rate constants of para-substituted phenacylchlorides are given in TABLE 2.

TABLE 2

Substituent	Second order rate const. 1/mole sec x 10^5
p-CH_3O	2.14
p-CH_3	3.68
p-H	7.45
p-Cl	16.79
p-NO_2	227.44

The kinetic data follow a straight line with σ_p values,the slope of the regression line being +1.89 (Fig.1).

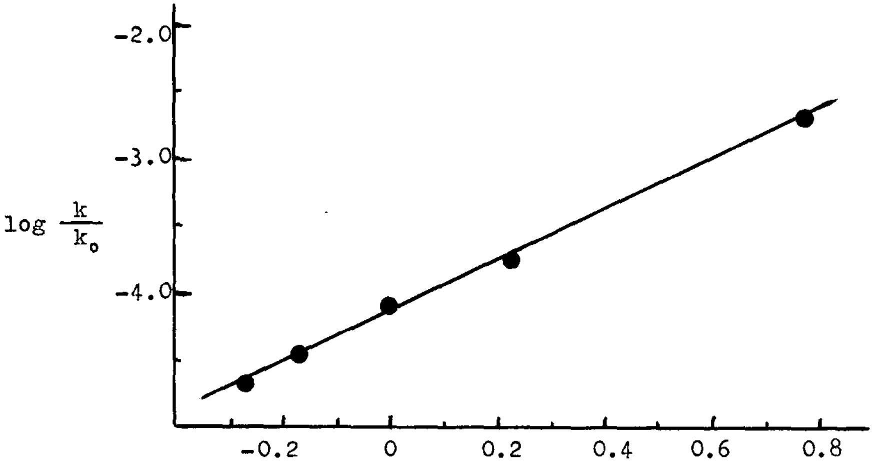
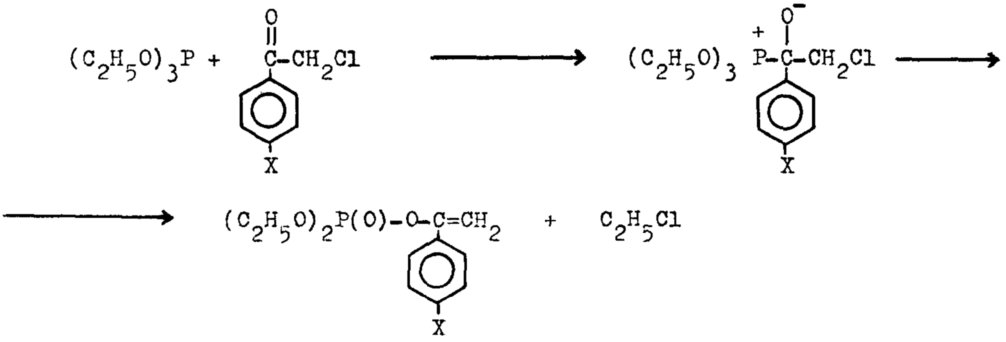


Figure 1

The kinetic data are consistent with a mechanism which involves initial attack of triethyl phosphite on carbonyl carbon followed by rearrangement of the phosphorus to carbonyl oxygen:



This is supported by the effect of para-substitution in the phenacylchloride which parallels the effect observed in other carbonyl addition reactions and by the observed ρ value,which is of the same order of magnitude with that found for other similar reactions (5).

REFERENCES

1. G.Aksnes and D.Aksnes, *Acta Chem.Scand.*, **18**, 38 (1964); *ibidem*, **19**, 898 (1965); G.Aksnes and R.Eriksen, *ibidem*, **20**, 2463 (1966).
2. F.W.Lichtenthaler, *Chem.Rev.*, **61**, 607 (1961); N.L.Paddock, *Quart.Rev.*, **18**, 168 (1964); R.F.Hudson, "Structure and Mechanism in Organo-phosphorus Chemistry", Acad.Press, London, 1965.
3. A.Arcoria and S.Fisichella, *Ann.Chim.* (Italy), **57**, 1228 (1967).
4. J.F.Allen and O.H.Johnson, *J.Am.Chem.Soc.*, **77**, 2871 (1955); M.S.Kharasch and I.S.Bengelsdorf, *J.Org.Chem.*, **20**, 1356 (1955); N.Kreutzkamp and H.Kayser, *Chem.Ber.*, **89**, 1614 (1956); P.A.Chopard, V.M.Clark, R.F.Hudson and A.J.Kirby, *Tetrahedron*, **21**, 1961 (1965); I.J.Borowitz, M.Anschel and S.Firstenberg, *J.Org.Chem.*, **32**, 1723 (1967).
5. A.J.Speziale and D.E.Bissing, *J.Am.Chem.Soc.*, **85**, 3878 (1963); D.P.Evans, J.J.Gordon and H.B.Wilson, *J.Chem.Soc.*, 1430 (1937); C.K.Ingold and W.S. Nathan, *ibidem*, 222 (1936).