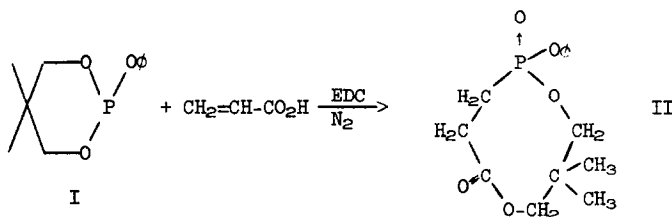


REACTION OF PHENYLNEOPENTYLENE PHOSPHITE WITH ACRYLIC ACID

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When phenylneopentylene phosphite I was reacted with acrylic acid in chlorinated solvents, better than 50% yields of a nine-membered ring phosphonate, II, were obtained.

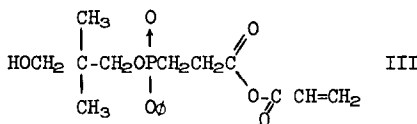


II is a white crystalline solid having, m.p. 97°C, mass number 298, vapor osmometry mol. wt., 325, and elemental analysis

	C	H	P
Calc.	56.4	6.38	10.4
Found	54.7	6.47	10.6

The carbonyl group is slightly strained as evidenced by its IR absorption at 1760-1765 cm⁻¹ (5.68-5.67μ).

When the reaction was followed by infrared, an intermediate was observed to buildup and disappear. The data are consistent with the γ-hydroxyarhydride structure III.



a) III has two carbonyl absorptions, one at 1740 cm⁻¹ (5.75μ) and one at 1790-1820 cm⁻¹ (5.59-5.49μ).

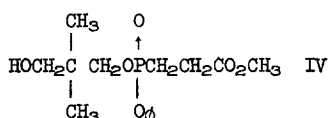
b) III has a strong -OH peak at 3.2μ.

c) III has only weak C=C absorption and no carboxylic acid proton absorption.

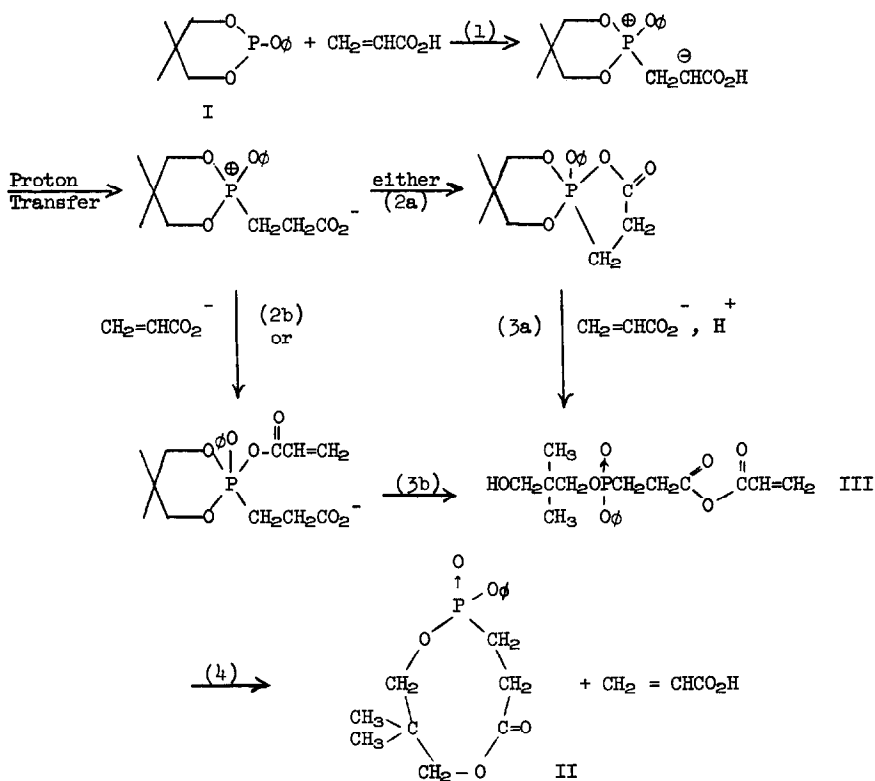
d) At the maximum concentration of III, an acid number of 57.5 (the 50% solids reaction solution gives an initial AN of 94) was obtained in alcoholic KOH and 69.0 in aqueous acetone.

e) The hydroxyl group and the anhydride group are observed to increase and decrease in concentration simultaneously.

f) Methanolysis of the reaction solution at the maximum concentration of III gave a compound having a normal ester carbonyl absorption at 5.75μ , a strong -OH absorption at 3.1μ and the expected phosphonate absorption. These data are consistent with the structure IV, the methanolysis product of III.



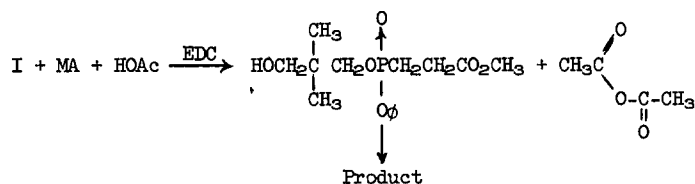
The following mechanism is advanced to explain the formation of both II and III.



No attempt is made to distinguish between steps 2a and 2b.

The product forming step involves the rather daring preference of formation of a nine-membered ring as opposed to polymerization. The yield of the phosphonate is certainly not quantitative and some low molecular weight acrylic compounds are no doubt formed.

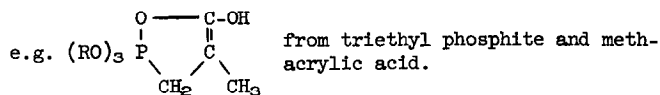
In support of the proposed mechanism is the fact that when I was reacted with methyl acrylate and acetic acid (six months at room temperature), the infrared spectrum showed the expected anhydride carbonyl and hydroxyl absorptions while the overall spectrum was very similar to those seen from reaction solutions of I and acrylic acid. GLC analysis revealed a compound with a retention time identical to acetic anhydride. EDC, MA, and HOAc were also identified and methyl acetate was shown to be absent (acidolysis product from reaction of MA and HOAc).



The formation of the carboxylate Zwitterion was shown not to revert to starting material since reaction of acrylic acid -O-D with I gave no scrambling of deuterium in the unreacted acrylic acid.

One very interesting but completely unexplained result is that the reaction shows an induction period which depends on the concentration of added water but is not affected by degassing or by the monomethyl ether of hydroquinone. Kinetic analysis would be difficult but might reveal an ionic chain mechanism that is H₂O inhibited and possibly involves addition of I to the double bond of the acrylate anion.

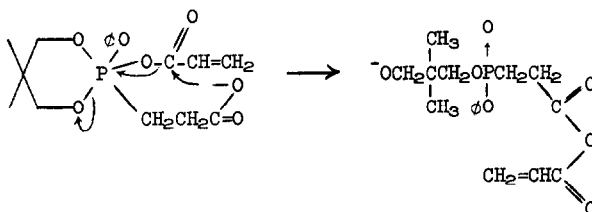
The general reaction of phosphites with α,β -unsaturated acids and esters is well known.^{1,2} Intermediates have been reportedly observed that neither correspond to nor are compatible with III.



The proposed mechanism deviates significantly from the normal Arbusov rearrangement in that it takes place on pentavalent phosphorus instead of the usual phosphonium salt. (In actual fact distinction between these two bonded forms of phosphorus probably becomes quite difficult and one should be able to control the course of the Arbusov with a proper choice of basicity and

nucleophilicity of the reactants.)

The phosphonate cannot be formed from the usual phosphonium salt since the phosphoryl oxygen of the γ -hydroxyanhydride must come from the pentacovalent intermediate.



One question that must be dealt with is why the Arbusov rearrangement would occur with ring opening to an alkoxide ion. If the pentacovalent intermediate is accepted, then the highly exothermic character of the rearrangement (P \rightarrow O bond formation) means that the transition state (for the phosphonate formation) will resemble reactants, i.e., the pentacovalent intermediate, much more than it will the products. The feature determining the site of attack by the anionic species is then not the nature of the leaving group but the susceptibility of the various centers to nucleophilic attack. Viewed in this somewhat oversimplified manner, the carboxylate attack should occur at the carbonyl rather than at the neopentyl carbon.

REFERENCES

¹Topics in Phosphorus Chemistry, Vol. I, Interscience Publishers, 1964, pp. 92-94

²Structure and Mechanism in Organo-Phosphorus Chemistry, R. F. Hudson, Academic Press, 1965, pp. 192-196
