REACTIONS OF ETHYLENEAMIDES OF PHOSPHORUS ACIDS
WITH SOME UNSATURATED ACIDS AND WITH ALLYLAMINE

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Unsaturated phosphorus-containing compounds have recently attracted the attention of many investigators as
monomers. The introduction of phosphorus into macromolecular compounds endows them with considerable flame
resistance and other useful properties. Phosphorated polymers are usually prepared by the copolymerization of un-
saturated phosphorus-containing compounds with other monomers, and more rarely by homopolymerization. It
was of interest to prepare derivatives of \( \alpha,\beta \)-unsaturated acids and some other compounds. Such compounds are
not readily available. Kamai and Kukhtin [1] were unable to isolate \( \text{CH}_2=\text{C} \rightleftharpoons \text{PO(OCH}_3\text{)z} \) in the pure state,
because the reaction product polymerized when distilled. Hall and Stephens [2] also gave an incomplete char-
acterization of the diethyl acryloylphosphonate that they prepared.

In [3] a method was proposed for the preparation of phosphorus-containing polymers and monomers with
the aid of the "phosphonaminoethylation" of compounds containing a mobile hydrogen or halogen (amines,
carboxylic acids, chloromethyl derivatives, etc.), e.g.,

By the phosphonaminoethylation of acrylic, methacrylic, and maleic acids and of allylamine we succeeded
in preparing some phosphorus-containing unsaturated compounds. The reactions of dialkyl N-ethylenephosphor-
amidates with \( \alpha,\beta \)-unsaturated acids proceed on mixture of the reactants, but for increased yield and reaction
rate it is necessary to heat the reactants in sealed tubes at 80-90° for 5-6 hr. There has been a previous detailed
study of the reaction between dialkyl N-ethylenephosphoramidates with carboxylic acids [4]; hence, on the basis
of analogy, the proposed structures of the reaction products may be regarded as correct.

On reaction between diethyl N-ethylenephosphoramidate and allylamine in equimolecular amounts, the
process appears to proceed stagewise at the two hydrogen atoms of the amino group

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\begin{align*}
\text{(C}_2\text{H}_5\text{O})_2\text{PN} & \quad \text{CH}_2 + \text{H}_2\text{NCH}_2\text{CH} = \text{CH}_2 \rightarrow \text{(C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2 = \text{CH}_2 \\
\text{(C}_2\text{H}_5\text{O})_2\text{PN} & \quad \text{CH}_2 + \text{CH}_2 = \text{CHCH}_2\text{NHCH}_2\text{CH}_2\text{NHP(OC}_3\text{H}_5)_2\rightarrow \\
& \quad \rightarrow \text{(C}_2\text{H}_5\text{O})_2\text{PNHCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2 = \text{CH}_2 .
\end{align*}
\]
Actually, the yield of the expected reaction product (I) was relatively low and, judging from the elementary analysis, the substance remaining in the flask was (II). The product of the reaction of dibutyl N-ethylenephosphoramidate with maleic acid could not be purified by distillation. The unsaturated phosphorus-containing derivatives which we obtained from acrylic and methacrylic acids were able to polymerize and also to copolymerize with methyl methacrylate, methyl acrylate, styrene, and other monomers when heated with radical-polymerization initiators. Derivatives of maleic acid and allylamine are able only to copolymerize with other monomers. The properties of the polymers obtained will be described elsewhere. Some information about the monomers obtained is given in the table.

**EXPERIMENTAL**

**Reaction of Diethyl N-Ethylenephosphoramidate with Methacrylic Acid.** A hard-glass tube was charged with 10.2 g of diethyl N-ethylenephosphoramidate, 5 g of methacrylic acid, 50 mg of hydroquinone, and 20-30 mg of ammonium chloride (catalyst for the opening of the ethylenimine ring). The tube was then sealed and heated in a tube furnace for 5-6 hr at 80-90°C. When cool, the tube was opened, and the contents were distilled into an Arbuzov flask. Two distillations gave 10.2 g (67.1%) of a substance having the following constants: b.p. 138-139°C (0.015 mm); n_20^20 1.4542, d_20^20 1.1315. Found: C 46.41, 46.11; H 7.89, 7.96; P 11.69, 11.99%; MR 63.45. C_{10}H_{20}O_{5}PN. Calculated: C 45.28; H 7.54; P 11.69%; MR 63.77.

**Reaction of Diethyl N-Ethylenephosphoramidate with Acrylic Acid.** The conditions for the reaction and the isolation of the products were similar to those described above. We took 17.9 g of diethyl N-ethylenephosphoramidate, 7.5 g of acrylic acid, 80 mg of hydroquinone, and 20-30 mg of ammonium chloride. We obtained 17.9 g (71.3%) of a substance having the following constants: b.p. 139°C (0.5 mm); n_20^20 1.4526; d_20^20 1.1502. Found: C 42.97; H 7.40; P 12.35%; MR 59.02. C_{8}H_{18}O_{5}PN. Calculated: C 43.02; H 7.01; P 12.35%; MR 59.14.

**Reaction of Dipropyl N-Ethylenephosphoramidate with Acrylic Acid.** The conditions for the reaction and the isolation of the products were similar to those described above. We took 15.2 g of dipropyl N-ethylenephosphoramidate, 5.3 g of acrylic acid, 50 mg of hydroquinone, and 20-30 mg of ammonium chloride. We obtained 15.0 g (73.1%) of a substance having the following properties: b.p. 147-148°C (0.4 mm); n_20^20 1.4518; d_20^20 1.0997. Found: C 46.92, 46.89; H 8.17, 8.20; P 10.84, 10.79%; MR 68.41. C_{11}H_{22}O_{5}PN. Calculated: C 47.31; H 7.88; P 11.11%; MR 68.38.