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41. Organic Phosphorus Compounds 56[1]

The Addition of Hypophosphite Esters to Activated Olefins, a New Method for Preparing 2-Substituted Ethyl Phosphinates [1]

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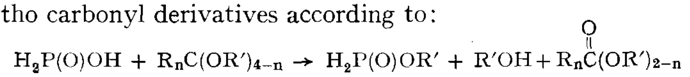
(11. XII. 72)

Summary. The addition of methylhypophosphite, $H_2P(O)OCH_3$, to acrylic acid derivatives, $CH_2{=}CHX$ ($X = CONH_2$, CN, CO_2R), is described and the physical properties of three new 2-substituted ethylphosphinates are reported.

It is known for some time that phosphine, primary phosphines and secondary phosphines [2], primary phosphine oxides [3], secondary phosphine oxides [4] [5], secondary phosphine sulfides [6], and secondary phosphites [7], add to olefins and activated olefins in the presence of basic or radical forming catalysts. Of particular interest is the addition of secondary phosphites to acryl amide [8] because the products produced have achieved technical importance as flame retardants for textiles:

$$(RO)_2(O)PH + CH_2{=}CHCONH_2 \rightarrow (RO)_2(O)PCH_2CH_2CONH_2$$

Surprisingly the corresponding additions of hypophosphite esters to olefins and activated olefins have not been reported, although some addition reactions of hypophosphorous acid to olefins are known[2]. This may be due in part to the fact that hypophosphite esters are relatively unstable at room temperature and are obtainable by a simple procedure only since 1964 [10]. This involves reaction of hypophosphorous acid with ortho carbonyl derivatives according to:



$$H_2P(O)OH + R_nC(OR')_{4-n} \rightarrow H_2P(O)OR' + R'OH + R_n\overset{\overset{O}{\|}}{C}(OR')_{2-n}$$

The also reported formation of hypophosphites from the interaction of hypophosphorous acid with alcohols in the presence of $AlCl_3$ in benzene [11] could not be verified by us. No reaction was observed and only trace amounts of $H_2P(O)OR$ were detected by NMR.-spectroscopy.

Since it has been observed that hypophosphites add to carbonyl compounds [10] [12] and interact with alkylidene diamines and α-amino ethers [13] it is best to prepare hypophosphites by the reaction of H_3PO_2 with orthoformates:

$$H_3PO_2 + HC(OR)_3 \rightarrow H_2P(O)OR + HCO_2R + ROH$$

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[1] Part 55, see [1].

[2] See [7], p. 228 and [9].

After removing the volatile products the crude hypophosphite is directly caused to react with acrylic acid derivatives such as acryl amide, acrylonitrile, and acrylic acid esters in the presence of sodium alkoxide as catalyst. Since the addition reactions with methyl hypophosphite are strongly exothermic, cooling is required during the

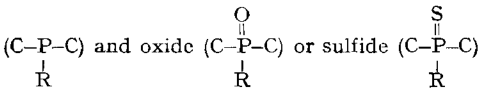
$$H_2P(O)OCH_3 + 2CH_2{=}CHX \xrightarrow{NaOR} (XCH_2CH_2)_2P(O)OCH_3$$

$$\text{I–III, } X = CONH_2,\ CN,\ CO_2R$$

addition. Normally the crude reaction products are contaminated with the corresponding phosphonate of structure $(RO)_2(O)PCH_2CH_2X$. This contamination is due to the fact that the crude methyl hypophosphite always contained some dimethylphosphite which under the reaction condition also adds to the activated olefin to give a substituted phosphonate. It may be removed from the desired phosphinates (I–III) by passing the reaction mixture through a weakly basic ion exchanger.

Attempts to extend the addition reaction to other alkyl hypophosphites or hypophosphorous acid were not very successful. While long chain alkyl hypophosphites did undergo a reaction, thereby producing a mixture which could not be separated, hypophosphorous acid did not react with acrylic acid derivatives or allylamine under the conditions used.

In this connection a related study on the preparation and characterization of polyamides containing phosphine



$$(C\text{–}\underset{R}{P}\text{–}C) \text{ and oxide } (C\text{–}\underset{R}{\overset{O}{\overset{\|}{P}}}\text{–}C) \text{ or sulfide } (C\text{–}\underset{R}{\overset{S}{\overset{\|}{P}}}\text{–}C)$$

groups in their backbone structure is of interest [14]. Bulk polymerization was the preferred method of preparing these materials. The phosphorus polyamides generally were found to be amorphous, relatively low softening materials having an extended solubility range. Most polyamides containing trivalent phosphorus slowly degrade in formic acid solution. A comparison of the thermal stability, adhesive bond strengths, and mechanical behaviour of typical polyamides containing phosphine or phosphine oxide groups in their backbone structure to those of analogous regular nylons disclosed no major differences [14].

Experimental

(with Miss *H. Muntwyler*)

1. $\underset{b}{CH_3}OP(O)(\underset{a}{CH_2}CH_2\underset{c}{CONH_2})_2$ (*I*). To 20.68 g (0.26 mol) of crude $CH_3OP(O)H_2$ (containing CH_3OH, HCO_2CH_3, and some $(CH_3O)_2P(O)H$) are added 36.96 g (0.52 mol) of $CH_2{=}CHCONH_2$ and then slowly 4.32 g of CH_3ONa with cooling. A strong exothermic reaction ensues. The temperature rises to 85°. After all CH_3ONa is added the mixture is refluxed for 3 h, and then diluted with CH_3OH, neutralized with HCl, NaCl filtered off, washed with methanol, and the filtrate evaporated. There is obtained 29.8 g (51.8%) crude I, a yellow oil, which shows in the ^{31}P-NMR.-spectrum peaks at –51 ppm (in CH_3OH, 80%, I), –28 ppm (15% $(CH_3O)_2P(O)CH_2CH_2CONH_2$) and –6 ppm (5%, unknown).

^1H-NMR. (in CD_3OD): a) 1.6–2.9 (*m*, 7.25 H); b) 3.3 (*d*, 3.06 H); c) 5.14 (*s*, 4.7 H).

$C_7H_{15}N_2O_4P$ (222.2) Calc. 37.83 H 6.80 N 12.60% Found C 34.73 H 6.67 N 11.38%

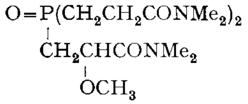
2. $\underset{b}{CH_3}OP(O)(\underset{a}{CH_2CH_2}CN)_2$ *(II)*. From 20.68 g (0.26 mol) of crude $CH_3OP(O)H_2$, 27.6 g (0.52 mol) $CH_2{=}CHCN$, and 4.4 g of CH_3ONa as in 1. Reaction is exothermic. After 4 h reflux the mixture is diluted with methanol, neutralized with HCl, NaCl filtered off, and the filtrate evaporated to give 40 g (82.6%) of a slightly colored liquid which according to the ^{31}P-NMR.-spectrum contains 70% II at -53.0 ppm (in CH_3OH) and about 30% of $(CH_3O)_2P(O)CH_2CH_2CN$ at -38 ppm (in CH_3OH). The product cannot be distilled; on heating for 2 h to 205° in the hiogh vacuum, the product turned black. Therefore to obtain an analytically pure sample, 3 g were passed through a weakly basic ion exchanger to give 1.8 g of an yellow oil, which now seems to be pure II, ^{31}P -53 ppm, ^1H-NMR. (in CD_3OD): a) 1.7–3.1 (*m*, 8.1 H); b) 3.77 (*s*, J_{POCH} 10.6 Hz, 2.9 H).

$C_7H_{11}N_2O_2P$	Calc.	C 45.16	H 5.95	N 15.05	P 16.65%
(186.16)	Found	,, 44.91	,, 5.76	,, 14.87	,, 16.45%

3. $CH_3OP(O)(CH_2CH_2CO_2CH_2CH_3)_2$ *(III)*. From 20.68 g (0.26 mol) of $CH_3OP(O)H_2$, 52.06 g (0.52 mol) of $CH_2{=}CHCO_2Et$ and 4.4 g CH_3ONa as in 1. The crude product (66 g = 91%) shows in the ^{31}P-NMR.-spectrum two signals at -57 ppm (60%) and at -50 ppm (40%) (in CH_3OH). On attempted distillation only a small part distilled between 70–115°/0.1 Torr. The distillate still showed two peaks at -54 ppm (90%) and at -48 ppm (10%). By far the greatest part remained as a residue which showed signals in the ^{31}P-NMR. at -57 ppm (20%) and -51 ppm (80%).

4. $\underset{c}{CH_3}OP(O)(\underset{a}{CH_2CH_2}CON\underset{b}{(CH_3)_2})_2$ *(IV)*. From 2.63 g (0.0328 mol) $CH_3OP(O)H_2$, 6.5 g (0.0656 mol) $CH_2{=}CHCONMe_2$ and 0.55 g CH_3ONa as in 1. Reaction is exothermic. After 3 h reflux some CH_3ONa is added to make the solution basic. The mixture is kept for another hour at 110°, then neutralized with HCl, NaCl filtered off, and the filtrate evaporated. The residue dissolved in methanol shows in the ^{31}P-NMR.-spectrum peaks at -61 ppm (40%) and -44.5 ppm (60%); ^1H-NMR. (in CD_3OD): a) 1.6–2.75 (*m*, 8.9 H); b) 2.92 and 3.05; c) 2.95 (J_{POCH} 11 Hz), b+c 14.1 H; impurity at 3.3–3.8.

The methoxy-groups attached to phosphorus have mainly been lost. The product has possibly the following structure:



$$\begin{array}{l} O{=}P(CH_2CH_2CONMe_2)_2 \\ \quad | \\ \quad CH_2CHCONMe_2 \\ \qquad | \\ \qquad OCH_3 \end{array}$$

Microanalysis were carried out by *W. Manser*, ETH Zürich. ^{31}P- and ^1H-NMR.-spectra were run on an HA60IL *Varian* spectrometer using H_3PO_4 or TMS as reference. Shifts are given in ppm.

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