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25 YEAR RE-REVIEW

(1) Org phosphorus compounds

Esters of unsaturated phosphonous acids.

M. I. Kabachnik, E. N. Tsvetkov and Chzhan Zhun Yui (Inst. Hetero-org. Compds Moscow). Doklady Akad. Nauk S.S.S.R. 131, 1334-7 (1960).

Addn. of $CH_2{:}CHMgBr$ soln. (from 0.65 at. Mg, 0.67 mole $CH_2{:}CHBr$ and 500 ml. tetrahydrofuran) at -60° to 0.6 mole $(BuO)_2PCl$ in 200 ml. tetrahydrofuran, followed by removal of the solvent in vacuo, addn. of 300 ml. petr. ether and 1.3 moles pyridine (to cleave the complex between Mg halide and the P ester), removal of the ppt. and distn. in the presence of hydroquinone gave $CH_2{:}CHP(OBu)_2$ (I), 71%, b_2 49-51.5°, n_D^{20} 1.4471, d_{20} 0.9039. Similarly, $HC\vdots CMgBr$ (cf. Jones et al., J.Chem.Soc. 1956, 4765) gave 74% $HC\vdots CP(OBu)_2$, b_2 58.8-60°, 1.4520, 0.9289. Reaction of 0.3 mole BuOH and 0.3 mole $PhNEt_2$ added in petr. ether to 0.3 mole $PhPCl_2$ in petr. ether at -30° and stirred 1 hr. gave 62% PhP(OBu)Cl, b_2 77-8°, 1.5352, 1.1049. This with $CH_2{:}CHMgBr$, as above, gave $CH_2{:}CHPPh(OBu)$, 66.4%, b_2 76-7°, 1.5310, 0.9762. Reaction of $(EtO)_2PCl$ with p-$CH_2{:}CHC_6H_4MgCl$ (cf. Leebrick et al. J.Org.Chem. 23, 935 (1958)) gave similarly 33% p-$CH_2{:}CHC_6H_4P(OEt)_2$, b_2 96.5-7°, 1.5398, 1.0251 ($NaNO_2$ was used as the inhibitor during distn.). Treatment of the neutral esters with 1.1 mole H_2O contg. 4% H_2SO_4 in dioxane at room temp. 0.5 hr. gave: 92% $CH_2{:}CHP(O)(H)OBu$, b_2 50-1°, 1.4479, 1.0040; 78% $HC\vdots CP(O)(H)OBu$, $b_{1.5}$ 65-6°, 1.4492, 1.0322. I and S in Et_2O at 0° gave 88.2% $CH_2{:}CHP(S)(OBu)_2$, $b_{2.5}$ 96.2-6.8°, 1.4730, 0.9954. I and MeI in petr. ether in autoclave 4 hrs. at 100-10° in the presence of hydroquinone gave 84% $CH_2{:}CHP(O)(Me)OBu$, b_2 64-4.2°, 1.4452, 0.9862. I heated with cyclopentadiene dimer in sealed tube 13 hrs. at 190-200° gave 55.5% di-Bu bicyclo-(1,2,2)-2-hepten-6-ylphosphonite, $b_{1.5}$ 99.7-101°, 1.4792, 0.9696, which with S at room temp. gave 63.5% corresponding thiophosphonate $RP(S)(OBu)_2$, b_2 139-9.2°, 1.4969, 1.0425. The unsatd. esters of the above series polymerize readily on being heated without inhibitors. The reaction of MeI and I resulted only in polymerization of I if the solvent petr. ether was omitted or replaced by excess MeI or MeCN.

(2)

ditto

Esters of hypophosphorous acid.

M. I. Kabachnik, A. E. Shilov and T. A. Mastryukova (Inst. Hetero-org. Compds. Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 146.

H_3PO_2 reacts smoothly in the cold with diazoalkanes yielding the corresponding esters; onle one mole of diazoalkane reacts regardless of the amt. used. Thus were propd. $(MeO)P(O)H_2$, $b_{2.5}$ 25-5.5°, n_D^{20} 1.4275, d_{20} 1.2177; EtO analog, b_2 31-2°, 1.4250, 1.1120. Both esters decompose rapidly at room temp.; they crystallize at about -20°, and can be stored at -60°. They oxidize in air and are hydrolyzed by H_2O. They show qual. tests typical of H_3PO_2. This confirms the covalent structure of $HOP(O)H_2$.

3

Organolithium compounds in the synthesis of esters of alkyl and aryl phosphonous acids.

M. I. Kabachnik and E. N. Tsvetkov (Inst. Hetero-org. Compds., Moscow). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1960, 133-4. Cf. Doklady Akad. Nauk SSSR 117, 817 (1957).

All reactions were run under N_2. A soln. of PrLi from 35 g. PrBr and 5 g. Li in 150 ml. Et_2O was added dropwise at -60° to 42.5 g. $(BuO)_2PCl$ in 100 ml. Et_2O; Et_2O was then removed in vacuo and the residue was treated with 200 ml. petr. ether and the solid was sepd. Distn. of the liq. portion gave 60% $(BuO)_2PPr$, b_1 59-60°, n_D^{20} 1.4375, d_{20} 0.8836. Similarly BuLi and $(BuO)_2PCl$ gave 81% $(BuO)_2PBu$, $b_{1.5}$ 70.5-1.5°, 1.4421, 0.8814. $(EtO)_2PCl$ and LiPh gave 56.5% $PhP(OEt)_2$, b_1 63-5°, 1.5113, 1.0235. Indenyllithium gave 64.5% di-Et 1-indenylphosphonite, $b_{1.5}$ 99-9.5°, 1.5491, 1.0655; similar reaction with RMgBr gave but 40% yield. 9-Fluorenyllithium (Gilman et al. J. Org. Chem. 23, 550 (1958)) in tetrahydrofuran similarly gave 78% di-Et 9-fluorenylphosphonite, b_2 148.5-9°, m. 67.5-70° (after sublimation at 2 mm). Similar reaction of RMgBr gave only fluorene and a trace of the above ester.

Organic insectofungicides, XIV. Synthesis of alkyl aryl chlorothiophosphates and alkyl aryl thiophosphoramides.

N. N. Mel'nikov, Ya. A. Mandel'baum, Z. M. Bakanova and P. G. Zaks (Res. Inst. Fertilizers and Insectofungicides, Moscow). Zhur. Obshchei Khim. 29, 3286-8 (1959). cf. this j. 28, 2473 (1958); Ger.Pat. 837,603 (C.A. 8446 (1958)). Addn. of $ROPSCl_2$ (0.1 mole) at -10° to 0.1 mole ArOH and 0.11 mole Et_3N in PhCl over 0.5-1.0 hr., stirring 10 min. longer, and quenching in H_2O, gave the following (RO)(ArO)PSCl (R and Ar shown resp.): Et, Ph, 55%, $b_{0.5}$ 94-6°, d_{20} 1.2499, n_D^{20} 1.5390; Et, $p\text{-}ClC_6H_4$, 60%, $b_{0.2}$ 115-6°, 1.3664, 1.5520; Et, $2,4\text{-}Cl_2C_6H_3O$, 58%, $b_{0.4}$ 133-7°, 1.4386, 1.5600; Et, $2,4,5\text{-}Cl_3C_6H_2O$, 50%, $b_{0.7}$ 163-6°, 1.5548, 1.5981; Et, $p\text{-}O_2NC_6H_4$, 54%, $b_{0.2}$ 160°, 1.4543, 1.5740. Similarly (RO)(ArO)PSCl were prepd. by stirring 0.1 mole $ArOPSCl_2$ with 1-4 moles ROH 4-10 hrs. at 20-30°, followed by an aq. treatment; the best yields resulted from the use of 20-30 moles ROH per mole of the chloride; if run in C_6H_6 or PhCl, the reaction also gave good yields with 10:1 molar ratio of reactants; the following were prepd. by this method: Et, Ph; Et, $p\text{-}O_2NC_6H_4$. The products reacted with various amines in 5-10 hrs. at 0-20° in Et_2O or C_6H_6, yielding the following (RO)(ArO)PSNR'R" (R, Ar, R', R" shown resp.): Me, $p\text{-}O_2NC_6H_4$, Et, Et, undistillable, 60%, d_{20} 1.3086, n_D^{20} 1.5700; Et, $p\text{-}O_2N\text{-}C_6H_4$, Et, Et, 68%, $b_{0.1}$ 158-64°, m. 34°; Et, $p\text{-}O_2NC_6H_4$, Me, Me, 52%, $b_{0.2}$ 153-5°, 1.2466, 1.5460; Et, $p\text{-}O_2NC_6H_4$, H, Ph, $b_{0.2}$ 165-70°, 1.3563, 1.5720, 58%; Et, Ph, Et, Et, 70%, $b_{0.4}$ 120-2°, 1.1475, 1.5238. The 2nd, 3rd and 4th of these amides proved to be equivalent to $(EtO)_2POSC_6H_4NO_2\text{-}p$ in insecticidal activity against the rice weevil.

Organic insectofungicides. XLVI. Synthesis of some derivatives of phosphonoacetic acid.

N. N. Mel'nikov, Ya. A. Mandel'baum and V. I. Lomakina (Res. Inst. Fertilizers and Insectofungicides, Moscow). Zhur. Obshchei Khim. 29, 3280-91(1959). cf. preced. abstr. US Pat. 2,701,225(C.A.49, 7180(1955); Swiss Pat. 300,340; Chimia, 9, 47 (1955); Brit. Pat. 723,633 (C.A. 50, 5724(1956); Brit. Pat. 767,225 (C.A. 51, 13456 (1957); Brit.Pat. 785,697 (C.A.52, 8194(1958).

The following compds. were prepd. by interaction of $(EtO)_3P$ with appropriate derivs. of chloroacetic or chlorothioacetic acid, the reaction being completed by 4-10 hrs. at 100-50°: $(EtO)_2P(O)CH_2COSEt$, $b_{0.2}$ 115-20°, d_{20} 1.1382, n_D^{20} 1.4580, 45%; $(EtO)_2P(O)CH_2CO_2Ph$, $b_{0.15}$ 115-20°, 1.1456, 1.4632, 35%; $(EtO)_2P(O)CH_2CO_2C_6H_4Cl$-p, $b_{0.3}$ 152-4°, 1.2572, 1.4980, 50%; $(EtO)_2P(O)CH_2$-OCSC$_6H_4Cl$-p, $b_{0.3}$ 143-6°, 1.2485, 1.5231, 70%; $(EtO)_2P(O)CH_2CO_2C_6H_2Cl_3$-2,4,-5, $b_{0.1}$ 139-41°, 1.3617, 1.5183, 45%; $(EtO)_2P(O)CH_2COSC_6H_2Cl_3$-2,4,5, $b_{0.2}$ 164-6°, 1.4131, 1.5482, 50%; $(EtO)_2P(O)CH_2CONEt_2$, $b_{0.1}$ 123-4°, 1.0988, 1.4586, 20%; $(EtO)_2P(O)CH_2CONHPh$, $b_{0.25}$ 174-7°, 1.1842, 1.5245, 52%. The esters and the amides of phosphonoacetic acid proved to be weak insecticides but the esters of phosphonothioacetic acid were very active contact and systemic insecticides, this being specially true of the aromatic esters.

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method cheaper - This seems useless

6

Organic insectofungicides. XLVIII. Reaction of aryldiazonium salts with dialkyl dithiophosphates.

N. N. Mel'nikov, . F. Grapov and K. D. Shvetsova-Shilovskaya (Res. Inst. Fertilizers and Insectofungicides, Moscow). Zhur. Obshchei Khim. 29, 3291-5 (1959). cf. 27, 1905 (1957); Khim. Nauka i Prom. 2, 264 (1957); this j. 28, 476(1958).

Reaction of ArN_2X salts with $(RO)_2PS_2H$ yields mixed esters of dithiophosphoric acid if run in neutral medium, or disulfides if run in an acid medium, provided that the original dithiophosphate is a K salt. Other salts tend to yield the mixed dithiophosphate esters. Diazotization of 13 g. $p-ClC_6H_4NH_2$ with 8 g. $NaNO_2$ in 50 ml. concd. HCl and 1.5 l. H_2O was followed by addn. of 15.8 g. $(MeO)_2PS_2H$ and 1 g. Cu_2Cl_2 and heating to 50°; after cessation of N_2 evolution, the mixt. was extd. with Et_2O yielding $(p-ClC_6H_4N:)_2$ which sepd. in unstated yield from a fraction, $b_{0.3-0.6}$ 120-35° on cooling; the filtrate from this gave 35% $(MeO)_2PS_2C_6H_4Cl-p$, $b_{0.15}$ 115.5-6°, d_{20} 1.3255, n_D^{20} 1.5948. Diazotization of 5.15 g. $p-MeOC_6H_4NH_2$ in 50 ml. concd. HCl and 30 ml. H_2O with 3.5 g. $NaNO_2$ in 20 ml. H_2O was followed by addn. of 12.6 g. $(iso-PrO)_2PS_2K$ in 50 ml. H_2O and 1 g. Cu_2Cl_2; after heating to 40°, the cooled mixt. gave 8 g. $[(iso-PrO)_2PS_2]_2$, m. 90-1°; the filtrate from this was steam distd. yielding MeOPh. Similar reaction with $p-ClC_6H_4N_2Cl$ gave 74% above disulfide; PhN_2Cl gave 90%; $p-O_2NC_6H_4N_2Cl$ gave 15%. A soln. of 3.22 g. $PhNH_2.HCl$ in 25 ml. EtOH was diazotized with 3 g. iso-AmONO in the presence of 0.1 g. HCl at 0-2°; the soln. was dild. with 50 ml. Et_2O yielding a ppt. of PhN_2Cl which was washed with Et_2O, taken up in H_2O and treated with 6 g. $(iso-PrO)_2PS_2K$ in 35 ml. H_2O and 0.5 g. Cu_2Cl_2; usual treatment gave 65% $(iso-PrO)_2PS_2Ph$, $b_{0.08}$ 102.5-4°, 1.1174, 1.5487. To 5 g. $p-ClC_6H_4NH_2.HCl$ diazotized with 6 g. iso-AmONO, as above, was added 10.1 g. $(iso-PrO)_2PS_2K$ in 75 ml. H_2O; on cooling there pptd. $p-ClC_6H_4N_2S_2P(C[illegible])_2$, m. 53-5°, which warmed in aq. medium with Cu_2Cl_2 gave 33% $(iso-PrO)_2PS_2C_6H_4Cl-p$, $b_{0.12}$ 121.5-2.5°, 1.1904, 1.5612. Similarly were prepd.: 28% $(EtO)_2PS_2C_6H_4OCH_3-p$, $b_{0.15}$

120.5-30°, 1.2003, 1.5680; 33% $(EtO)_2PS_2C_6H_4CO_2Me$-o, $b_{0.2}$ 144-5°, 1.2330, 1.5648; 32% $(iso\text{-}PrO)_2PS_2C_6H_4OMe$-p, $b_{0.1}$ 125-7°, 1.1367, 1.5451; 40% $(PrO)_2PS_2Ph$, $b_{0.28}$ 125.5-7.5°, 1.1262, 1.5467. Usually $(PrO)_2PS_2K$ gave mixts. of products which were unseparable. Similarly, PhS_2Cl and $(MeEtCHO)_2PS_2K$ gave unseparable mixt. of $(MeEtCHO)_2PS_2Ph$ and $[(MeEtCHO)_2PS_2]_2$, whose absorption spectrum was shown. The above disulfide, an oil, d_{20} 1.1267, n_D^{20} 1.5372, was prepd. from the K salt and aq. $KI-I_2$. The spectrum of this product is shown. On the basis of these infrared spectra, it was shown that the above reaction yielded mainly the mixed ester with a minor amount of the disulfide.

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Organic insectofungicides. L. Synthesis of some mixed esters of dithiophosphoric acid.

K. D. Shvetsova-Shilovskaya, N. N. Mel'nikov and V. A. Glushenkov (Res. Inst. Fertilis. and Insectofungic., Moscow). Zhur. Obshchei Khim. 29, 3593-4 (1959). Cf. Agric. Chem. 13, 32 (1958).

Refluxing an appropriate alkylene dihalide 2-4 hrs. with $(RO)_2PS_2K$ in ROH gave after an aq. treatment and extn. with C_6H_6, the following esters, which were only very weak insecticides, were prepd.: $[(EtO)_2PS_2]_2CH_2$, 35% $b_{0.3}$ 164-5°, d_{20} 1.2277, n_D^{20} 1.5478; tetra-Pr ester, 49%, $b_{0.1}$ 175-6°, 1.1630, 1.5276; tetra-iso-Pr ester, 58%, undistillable, 1.1539, 1.5258; tetra-Bu ester, 45%, undistillable, 1.1084, 1.5153; tetra-iso-Bu ester, 41%, undistillable, 1.0919, 1.5103; $[(EtO)_2PS_2]_2(CH_2)_2$, 35%, $b_{0.25}$ 187°, 1.2188, 1.5427; tetra-Pr ester, 34%, $b_{0.2}$ 185-6°, 1.1638, 1.5265; tetra-iso-Pr ester, 72%, undistillable, 1.1790, 1.5268; tetra-Bu ester, 73%, undistillable, 1.1045, 1.5156; tetra-iso-Bu ester 28%, undistillable, 1.1006, 1.5143; $[(EtO)_2PS_2]_2(CH_2)_3$, 69%, $b_{0.35}$ 192°, 1.1922, 1.5402; $[(EtO)_2PS_2]_2(CH_2)_3$, 59%, $b_{0.22}$ 204°, 1.1783, 1.5335.

⑧

New method of synthesis of esters of phosphonic and thiophosphonic acids. XXXII. Reaction of partial esters of phosphonous acids with ketene. A. N. Pudovik, V. I. Nikitina and G. P. Krupnov (State Univ., Kazan). Zhur. Obshchei Khim. 29, 4019-21 (1959). cf. 29, 1219(1959); Kennedy et al. C.A. 4933e(1957); McConnell et al. J. Org. Chem. 830(1958).

Reaction of ketene with $RP(OR)_2$ evidently occurs with initial formation of $RP(O)(OR)C(OH):CH_2$ which is then acetylated by ketene. Passage of excess ketene at 35-45° into 10-20 g. appropriate ester in 50-75 ml. dioxane gave the following products: $EtP(O)(OEt)C(OAc):\overset{(I)}{CH_2}$, b_{10} 127°, n_D^{20} 1.4510, d_{20} 1.1010(30%); $\overset{Ac}{\ }EtP(O)(OBu)$, b_{10} 134-6°, 1.4471, 1.0598 (30%); $EtP(O)$-$(OBu)C(OAc):CH_2$, b_{10} 145-6°, 1.4512, 1.0737 (53%); $PhP(O)(OMe)Ac$, 36%, b_{10} 142-3°, 1.4891, 1.1698; $PhP(O)(OMe)C(OAc):CH_2$, 6%, b_{10} 165-6°, 1.5001, 1.1802; $PhP(O)(OEt)Ac$, 30%, b_{10} 146-7°, 1.4968, 1.1376; $PhP(O)(OEt)C(OAc)$-$:CH_2$, 15%, b_{10} 172-3°, 1.5078, 1.1621; $PhP(O)(OEt)Ac$, 53%, b_{10} 155°, 1.5028, 1.1095. Ozonization of I gave CH_2O, thus confirming the structure. Passage of ketene 6 hrs. at 30-5° into 6.5 g. $AcEtP(O)OBu$ in dioxane gave 3.8 g. $EtP(O)(OBu)C(OAc):CH_2$, b_{10} 145-6°, 1.4512, 1.0737..

Pudovik back at usual location
organophosphorus

9

Addition of lithium dialkylphosphides to vinylacetylenic hydrocarbons. [illegible]etrov and V. [illegible] Kormer (Lensovet Technol. Inst., Leningrad). Doklady Akad. Nauk [illegible] 132, 1095-6 (1960).

Reaction of 0.08-0.1 mole LiBu in 75 ml. Et$_2$O was treated with 0.08 mole R$_2$PH in 25 ml. Et$_2$O and after 0.5 hr. the vinylacetylenic hydrocarbon was added dropwise (0.08 mole) with somewhat exothermic reaction. After 0.5 hr. the mixt. was treated with ice and the org. layer distd. Reaction of Bu$_2$PLi with HC:CCH:CH$_2$ gave 1.6 g. (10%) 1-dibutylphosphino-3-butyne, b$_5$ 95-6°, d$_{20}$ 0.8448, n_D^{20} 1.4830 (infrared spectrum shown; this has 210 and 3318 cm^{-1} bands of the terminal acetylenic group and 1590-1300, 3083 cm^{-1} lines of 1,3-diene grouping as well as 1960 and 805 cm^{-1} of allenic group), which apparently contained admixtures of all 3 possible adduct orientations. Et$_2$PLi and MeC:CCH:CH$_2$ gave 4.5 g. 1-diethylphosphino-2,3-pentadiene, b$_5$ 60-1°, 0.8697, 1.5050, whose infrared spectrum showed strong allenic bands, while the acetylenic bands were nearly absent and the bands of the conjugated double bond system were very weak. Et$_2$PLi and EtC:CCH:CH$_2$ gave 4.6 g. 1-diethylphosphino-2,3-hexadiene, b$_5$ 78-9°, 0.8569, 1.5025; Bu$_2$PLi gave 8 g. 1-dibutylphosphino-2,3-hexadiene, b$_5$ 125-6°, 0.8584, 1.4952. Both were quite pure allenic derivs. Reaction of BuCl in Et$_2$O with Et$_2$PLi gave 80% Et$_2$BuP, b$_5$ 41-2°, b$_{100}$ 106-7°, 0.8094, 1.4300. Similarly was prepd. Bu$_3$P, b$_{22}$ 135.5-6°, b$_{50}$ 146-7°, 0.8191, 1.4632. This indicates the need for a total absence of excess RX in the RLi used to form R$_2$PLi. Cf. [illegible]aier et al. Z. Naturforsch. 12, 263 (1957); Tzschach et al. Ber. 92, 1118 (1959) and 92, 1397 (1959).

Organophosphorus -
connected with synthetic
rubber

10

Addition of phosphorus pentachloride to vinylethylacetylene.

A. A. Petrov, Yu. I. Porfir'eva and V. I. Savchenko (Lensovet Technol. Inst., Leningrad). Zhur. Obshchei Khim. 29, 4096-7 (1959).

cf. Nauch. Doklady Vyssh. Shkol., 1958, 335; also this j. 24, 380 (1954).

Addn. of PCl_5 to vinylethylacetylene yields 30% adduct, which treated with SO_2, gave EtC($POCl_2$):CClCH:CH_2, b_3 132-3°, d_{20} 1.3374, n_D^{20} 1.5560. Low boiling products, free of P are also formed. Hydrolysis of the above chloride with H_2O gave the free acid $C_6H_{10}O_3PCl$, m. 123°, whose aniline salt, m. 166°. The chloride shows an infra red band at 1575 and 1624 cm^{-1} indicative of a chloro-substituted double bond, and 936 and 986 cm^{-1} indicative of a vinyl group. The allenic bands are absent. The product may contain some product of the 3,4-addn. (acetylenic chloride) since there is observed the 2213 cm^{-1} band indicative of this. The PO bond has a strong band at 1264 cm^{-1}. The above reaction of PCl_5 differs from the reaction with vinylacetylene or isopropenylacetylene in which one H atom is also replaced by Cl yielding $C_nH_{2n}Cl_2POCl_2$ products after treatment with SO_2 (cf. above ref.)

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organophosphorus

Diaryl esters of N-phosphoric acid of amidines of the aromatic series. G. I. Derkach and A. V. Kirsanov (Inst. Org. Chem., Kiev). Zhur. Obshchei Khim. 29, 3424-8 (1959). cf. 29, 241(1959).

Satn. of C_6H_6 soln. of $RCCl{:}NP(O)(OR')_2$ with NH_3 over 3 hrs. at 20-30° and keeping the closed vessel 10-12 hrs. at room temp. gave after removal of the solvent and washing the residue with warm H_2O, 65-100% $RC(NH_2){:}NPO(OR')_2$ (I) which may be crystd. from EtOH. Thus were prepd.:(R and R' shown resp.): Ph, Ph, m. 99-101°; p-ClC_6H_4, Ph, m. 147-9°; p-$O_2NC_6H_4$, Ph, m. 168-70°; m-$O_2NC_6H_4$, Ph, m. 128-30°; 3,5-$(O_2N)_2C_6H_3$, Ph, m. 182-3°; Ph, 1-$C_{10}H_7$, m. 119-21°. Similar reaction with Et_2NH in Et_2O gave $RC(NEt_2){:}PO(OR')_2$: Ph, Ph, m. 77-9°; p-ClC_6H_4, Ph, m. 69-71°; p-$O_2NC_6H_4$, Ph, m. 102-4°; m-$O_2NC_6H_4$, Ph, m. 100-2°; 3,5-$(O_2N)_2C_6H_3$, Ph, m. 99-100°. Similar reaction with $PhNH_2$, completed by refluxing the C_6H_6 or PhCl soln.(latter used for the nitro substituted members) gave $RC(NHPh){:}PO(OR')_2$ (II): Ph, Ph, m. 153-5°; p-ClC_6H_4, Ph, m. 192-3°; p-$O_2NC_6H_4$, Ph, m. 195-6°; m-$O_2NC_6H_4$, Ph, m. 204-6 ; 3,5-$(O_2N)_2C_6H_3$, Ph, m. 164-5°; Ph, p-$O_2NC_6H_4$, m. 153-5°; p-ClC_6H_4, p-O_2N-C_6H_4, m. 225-8°; p-$O_2NC_6H_4$, p-$O_2NC_6H_4$, m. 232-3°; m-$O_2NC_6H_4$,, p-$O_2NC_6H_4$, m. 172-4°; 3,5-$(O_2N)_2C_6H_3$, p-$O_2NC_6H_4$, m. 210-12°. Pyrolysis of I at 270-80° in vacuo gave 72% $(PhO)_2PONH_2$, which distils and solidifies; m. 144-6°; 58% PhCN also formed. Similarly II gave 91% PhCN and 88% $(PhO)_2PONHPh$, m. 127-9°. Compds. of type I and the N,N-diethyl analogs form oily HCl salts on being treated with dry HCl; these salts regenerate the original materials on being treated with alc. NaOH.

[redacted]

10-11 insecticides

(12)

Derivatives of nitrobenzenesulfonamido-N-phosphoric acids.

A. V. Kirsanov and N. G. Foshchenko (Inst. Org. Chem., Kiev). Zhur. Obshchei Khim. 29, 4085-91 (1959). cf. 28,339(1958).

Treatment of $O_2NC_6H_4SO_2N{:}PCl_3$ in C_6H_6 with Me_2NH with ice cooling gave after the uptake of 6 moles of the amine, evapn. of the solvent and washing the residue with a little H_2O, and crystn. of the residue from small vol. of EtOH, the following amides; similar reaction with Et_2NH was performed at reflux over 8 hrs.: o-$O_2NC_6H_4SO_2N{:}P(NMe_2)_3$, 86%, m. 160-3°; m-isomer, 76%, m. 66-8°; p-isomer, 79%, m. 109-11°; o-$O_2NC_6H_4SO_2N{:}P(NEt_2)_2Cl$ 99%, m. 84-6°; p-isomer, 98%, m. 58-60°; the m-isomer was an unpurifiable oil. The Et_2N derivs. could not be converted to the triamides even after 40 hrs. of refluxing with the amine, nor could the Cl atom be hydrolyzed with alkali. Refluxing the Me members with aq. alc. NaOH gave some 20-5% starting materials, 61-3% $O_2NC_6H_4SO_2NHPO(NMe_2)_2$ and 3% nitrobenzenesulfonamides. The o-nitro member failed to hydrolyze at all even after many hrs. Reaction of $O2NC_6H_4SO_2NHPOCl_2$ with 33% aq. Me_2NH in dioxane at 25°, followed by evapn. in vacuo and treatment with 5N HCl gave: 82% o-$O_2NC_6H_4SO_2NH$-$PO(NMe_2)_2$, m. 161-4°; m- isomer, 82%, m. 145-7°; p-isomer, 84%, m. 169-70°. Similarly were prepd.: p-$O_2NC_6H_4SO_2NH$ $O(NEt_2)_2$, 83%, m. 109-11°; m-isomer, 79%, m. 125-7°. The o-isomer could not be obtained in the pure state. These amides are sol. in aq. alkalies and are titrated as monobasic acids. Reaction of 0.06 mole MeONa in 35 ml. MeOH with 0.02 mole $O_2NC_6H_4SO_2NHPOCl_2$ followed by evapn. and either leaching with H_2O or extn. with hot EtOH, gave: 70% o-$O_2NC_6H_4SO_2NNaPO(OMe)_2$, 70%, m. 156-8°; m-isomer, dihydrate, 79%, m. 195-8°; p-isomer dihydrate, 83%, m. 188-90°. Similar reaction with ArONa in dioxane gave: 76% o-$O_2NC_6H_4SO_2NNaPO(OPh)_2$, m. 164-7° (trihydrate); m-isomer, 82%, trihydrate, m. 137-40°; p-isomer, 94%, anhydrous, m. 210-12°; analogous di-p-chlorophenyl ester of: o-isomer, 64%, trihydrate, m. 182-4°; of m-isomer, 59%, trihydrate, m. 153-5°; of p-isomer, 87%, anhydrous, m. 221-2°; analogous o-nitrophenyl ester of: o-isomer, 92%, anhydrous (as are all remaining in this list), m. 200-2°; of m-isomer, 90%, m. 172-4°; of p-isomer, 88%, m. 202-5°; analogous p-nitrophenyl esters of: o-isomer, 87%, m. 210-3°; of m-isomer, 87%, m. 216-8°; of p-isomer, 83%, m. 220-2°. These Na salts readily pass into the Et_2O layer during extn. of aq. soln. with Et_2O, they also dissolve in CCl_4 and C_6H_6, provided that the esters is based on the p-chlorophenyl residue; the others are insol. in org. solvents.

[redacted]

(13)

Ammonolysis of phenyldichlorophosphazosulfonaryls.

V. I. Shevchenko and V. T. Stratienko (Metallurg. Inst., Dnepropetrovsk). Zhur. Obshchei Khim. 29, 3757-60 (1959). cf. 29, 3458 (1959).

Passage of dry NH_3 into a benzene soln. of $ArSO_2N{:}PPhCl_2$ at 10-15° gave $ArSO_2N{:}PPh(NH_2)_2$ (Ar shown): 90.7% Ph, m. 151-2°; 94.9% o-MeC_6H_4, m. 140-2 92.6% p-isomer, m. 130-1°; 91.6% p-ClC_6H_4, m. 162-4°; 94.5% 1-$C_{10}H_7$, m. 149-51°; 97.2% 2-$C_{10}H_7$, m. 148-52°. Heating these with 0.2N aq. NaOH 0.5 hr. on a steam bath gave $PhP(O)(NH_2)ONa$, needles, m. 164-5° (from aq. EtOH). Similar hydrolysis in acid medium gave the corresponding $ArSO_2NH_2$, and the P-contg. component was not examined. The above diamides are not attacked by hot neutral H_2O. It is suggested that the diamides, like the similar triamides, have a chelated or hydrogen bonded ring structure at the NH_2 and SO_2 groups; in the compds. described above the P-N dipole is disseminated in the Ph ring, explaining the relative hydrolytic stability; the triamides do not have such a dissipation of the dipole and are very readily hydrolyzed.

Continuation of Kirsanov's work in organophosphorus insecticides anor's work

(14) Arylaminolysis of phenyldichlorophosphazosulfonaryls.

V. I. Chevchenko and V. T. Stratienko (Metallurg. Inst., Dnepropetrovsk). Zhur. Obshchei Khim. 29, 3458-62 (1959). cf. 29, 1005(1959).

Refluxing 0.003 mole $ArSO_2N:PPhCl_2$ with 0.015 mole $PhNH_2$ in C_6H_6 5-8 hrs., followed by sepn. of $PhNH_2.HCl$ and washing with H_2O and N NaOH, gave the residue of $ArSO_2N:PPh(NHPh)_2$ in 70-96% yields: (Ar shown): Ph, m. 191°; o-MeC_6H_4, m. 196°; p-isomer, m. 182°; 1-$C_{10}H_7$, m. 207°; 2-$C_{10}H_7$, m. 215°; o-$O_2NC_6H_4$, m. 212°; m-isomer, m. 214°; p-isomer, m. 176°. The wash liquors gave, on being acidified, some $ArSO_2NHPO(Ph)(NHPh)$ (I) formed by the hydrolysis of intermediate $ArSO_2N:PPh(NHPh)Cl$ (II) which were not isolated. I (Ar shown): Ph, m. 167°; 1-$C_{10}H_7$, m. 160°; o-$O_2NC_6H_4$, m. 165°; m-isomer, m. 169°; p-isomer, m. 166°. If $ArSO_2N:PPhCl_2$ reacts with but 2 moles $PhNH_2$ in C_6H_6 (2-3 hrs. at reflux), the monochlorides II appear in the resulting ppt. and on treatment with aq. NaOH are hydrolyzed as above to the anilides. The derivs. with Ph and 1-$C_{10}H_7$ radicals are sol. in C_6H_6 and remain in soln. The replacement of the 2nd Cl atom in II is difficult and even after prolonged reflux, some II remains unreacted in mixts. with $PhNH_2$; this lack of reactivity is ascribed to steric effects. Refluxing $ArSO_2N:PPh(NHPh)_2$ with aq. alc. NaOH 8 hrs. gave some unreacted insol. material and acidification gave the expected I (Ar shown) in 37-67% yields: Ph, m. 167°; 1-$C_{10}H_7$, m. 160°; o-MeC_6H_4, m. 164°; p-isomer, m. 160°; 2-$C_{10}H_7$, m. 164°. The o-tolyl and 1-naphthyl members require 2N NaOH for this hydrolysis, while the others are formed by 0.2N NaOH; while the nitrophenyl members evidently undergo such alkaline hydrolysis readily, the anilides could not be isolated as tar formation intervened. The relative stability to hydrolysis shown by o-substituted tolyl member is explained by possible hydrogen bonding of the Me group with the SO_2 group.

15

Preparation and properties of dialkylphosphato alkyl xanthates.

M. S. Malinovskii and S. F. Solomko (State Univ., Dnepropetrovsk). Zhur. Obshchei Khim. 30, 652-3 (1960).

cf. U.S.Pat. 2668826-32 (1955), C.A. 49, 5517 (1955).

Heating equimolar mixt. of $ROCS_2K$ with $(R'O)_2POCl$ in Et_2O 2-3 hrs. gave the following products after sepn. of KCl, $(R'O)_2P(O)S_2COR$ (R' and R shown resp.): 86.4% Et, Me, b_5 51°, n_D^{20} 1.4915, d_{10} 1.1792; Et, Et, 84.5%, b_4 59-60°, 1.4715, 1.1043; Et, Pr, 89.5%, b_4 79-80°, 1.4860, 1.1072; Pr, Me, 99.6% (this and the following esters were undistillable), n_D^{20} 1.4520, d_{20} 1.0949; Pr, Et, 1.4665, 1.1080; Pr, Pr, 1.4729, 1.0873; Pr, iso-Pr, 1.4575, 1.0590; Pr, Bu, 1.4620, 1.0655; Pr, iso-Bu, 1.4602, 1.0363; Pr, Am, 1.4508, 1.0070; Pr, iso-Am, 1.4360, 0.9680; iso-Pr, Me, 1.4490, 0.965; iso-Pr, Et, 1.4565, 1.0892; iso-Pr, Pr, 1.4615, 1.0695; iso-Pr, iso-Pr, 1.4470, 1.0531; iso-Pr, Bu, 1.4605, 0.9895; iso-Pr, iso-Bu, 1.4555, 1.0125; iso-Pr, Am, 1.4465, 1.0312; iso-Pr, iso-Am, 1.4337, 1.0078. Saponification with alc. NaOH or KOH in 24 hrs. yields K or Na phosphate and K or Na xanthate.

⑯

Synthesis of acyl derivatives of 0,0-dibutyl thiophosphate.

S. P. Olifirenko, N. I. Zemlyanskii and A. M. Lylyk (State Univ., Lvov). Zhur. Obshchei Khim. 30, 579-80 (1960). cf. Michalski et al., Rocz. Chem. 27, 482 (1953).

To 10.5 g. Na in C_6H_6 was added 82 g. $(BuO)_2PHO$ and after 20 hrs. the excess Na was removed and the mixt. treated with 14.7 g. S and heated 0.5 hr. to 60°; partial evapn. gave $(BuO)_2PSONa$, hygroscopic solid. This treated with appropriate acyl chlorides in Bt_2O and refluxed briefly gave the following: $(BuO)_2PSOBz$, 41%, n_D^{21} 1.5015, d_{21} 1.066; $(BuO)_2PSOCO(CH_2)_2CO_2P(S)(OBu)_2$, 35 d_{21} 1.466; $(CH_2)_3[CO_2P(S)(OBu)_2]_2$, 78%, d_{21} 1.158; $(CH_2)_4[CO_2P(S)(OBu)_2]_2$, 26.5%, d_{21} 1.1192. The products were distd. at 0.4 mm. but b.pts. are not shown.

17

Arbuzov rearrangement of vinyl esters of phosphorous and phenylphosphonous acids.

I. F. Lutsenko and Z. S. Kraits (M.V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 132, 612-4 (1960). cf. this J. 124, 1251 (1959). Refluxing 8.2 g. $(EtO)_2POCH:CH_2$ with 7.7 g. MeI 4 hrs. gave 65% EtI and 89% $MePO(OEt)(OCH:CH_2)$, b_{25} 82-3°, n_D^{20} 1.4265, d_{20} 1.0775. $(BuO)_2POCH:CH_2$ (10.6 g.) and 10 g. BuI in 8 hrs. at 150° in sealed tube gave 85% $BuPO(OBu)(OCH:CH_2)$, b_1 83.5-4°, 1.4369, 0.9786. $(CH_2:CHO)_2POEt$ (10 g.) and 12 g. MeI in 8 hrs. at 110° gave 88% $MePO(OCH:CH_2)_2$, $b_{6.5}$ 62.5-3°, 1.4388, 1.1030. $EtOP(OCMe:CH_2)_2$ and EtI in 8 hrs. at 130° gave 82% $EtPO(OCMe:CH_2)_2$, b_2 69.5-70°, 1.4470, 1.0392. $(EtO)_2POCH:CH_2$ and AcCl kept 2 days gave 63% $AcPO(OEt)(OCH:CH_2)$, b_2 76.5°, 1.4352, 1.1310. BzCl and $BuOP(OCH:CH_2)_2$ in 8 hrs. at 120° gave 50% $BzPO(OCH:CH_2)_2$, b_1 135-7°, 1.5315, 1.1961. The following are also reported as prepd. similarly at 100-40°: $MePO(OPr)(OCH:CH_2)$, 90%, b_8 79-9.5°, 1.4290, 1.0447; $MePO(OBu)(OCH:CH_2)$, 86%, $b_{3.5}$ 79.5-80°, 1.4320, 1.0232; $EtPO(OBu)(OCH:CH_2)$, 50%, $b_{7.5}$ 95-6°, 1.4335, 1.0070; $EtPO(OEt)(OCH:CH_2)$, 80%, b_6 69-9.5°, 1.4291, 1.0485; $EtPO(OCH:CH_2)_2$ 82%, b_7 66.5°, 1.4398, 1.0714; $PrPO(OCH:CH_2)_2$, 65%, $b_{1.5}$ 71-1.5°, 1.4408, 1.0435; $BuPO(OCH:CH_2)_2$, 74%, b_2 71-2°, 1.4430, 1.0224. Reactions at 20° gave: 58% $AcPO(OPr)(OCH:CH_2)$, b_1 67-8°, 1.4361, 1.0940; 76% $AcPO(OBu)(OCH:CH_2)$, b_1 91-2°, 1.4390, 1.0739; and 83% $BzPO(OPr)(OCH:CH_2)$ (I), b_3 147-8°, 1.5108, 1.1483. To 60 g. mercuribisacetaldehyde and 20.2 g. Et_3N in 300 ml. isopentane was added under N_2 35.8 g. $PhPCl_2$ in isopentane; after addn. of 50% of the chloride, the mixt. was treated with 60 g. I and 20.2 g. Et_3N, after which the addn. of $PhPCl_2$ was resumed; after stirring 1.5 hrs. and filtration, there was obtained 43% $PhP(OCH:CH_2)_2$, b_2 76-8°, 1.5385, 1.0633. This and MeI in Me_2CO kept overnight gave 58% solid, m. 37-8°, identified as an adduct of reactants; heating yields I_3 and tar. Thus isomerization of vinyl esters of P^{III} acids occurs less readily than does that of satd. esters; the divinyl esters are even less reactive.

Reaction of $ROP(OCH:CH_2)_2$ with R'X gave a mixt. of phosphonates contg. R and R' radicals. $P(OCH:CH_2)_3$ failed to react with MeI, while heating to 120° in sealed tube led to decompn. In no case was the vinyl group replaced in the Arbuzov reaction.

⑱ Phosphorylated chlorovinyl ketones. Primary reaction products of phosphorus pentachloride with enol acetates.

I. F. Lutsenko and M. Kirilov (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 132, 842-5 (1960). cf. 128, 89 (1959).

To filtered soln. of 41.6 g. PCl_5 in 250 ml. CCl_4 was added dropwise 8.6 g. CH_2:CHOAc at 7-8°; after stirring 6 hrs. at 7°, the ppt. was filtered off with cooling by means of Dry Ice, and after washing with CCl_4 and isopentane, the vacuum dried product was shown to be $AcOCHClCH_2PCl_4.PCl_5$, a very hygroscopic solid, unstable at room temp. If the unisolated product is treated directly with SO_2 at 5-7°, there is formed 85% $AcOCHClCH_2POCl_2$ (A), $b_{1.5}$ 99-100°, n_D^{20} 1.4855, d_{20} 1.5035. With equimolar ratio of the reactants, the yield drops to 50%. Addn. of 20 g. $AcOCMe:CH_2$ to 83.5 g. PCl_5 in CCl_4 at -24° and, after 2 hrs., treatment with SO_2 at -25° gave a product which decomposed on attempted distn. at 60-70° and, after the reaction was complete, there was isolated 60% $AcCH_2POCl_2$ (I) (evidently formed from $AcOCMeCl$-CH_2POCl_2 which formed from the original adduct), $b_{1.5}$ 89.5-90°, m. 39-40°; use of 1:1 molar ratio of reactants gave a 37% yield. If the above mixt. after treatment with SO_2 at -20-5° is freed of volatiles at room temp. in vacuo and chilled, there is formed 70% $AcOCMeClCH_2POCl_2$ (II), m. 45.5-6.5° (from isopentane), which at 95-105° loses AcCl and yields the above shown I (83.6%). Treatment of A with 2 moles EtOH in the presence of pyridine in Et_2O at 0°, finally at reflux 1 hr., gave on filtration and cooling to -10° a ppt. of pyridine.HCl and a phosphonate ester; this extd. with hot Et_2O gave on cooling 79% $AcOCHClCH_2PO(OEt)_2$ (III), m. 64-5°, which slowly loses AcCl in air. Reaction of II in Et_2O with EtOH in the absence of pyridine without cooling (0.5 hr. at 30° to complete the reaction), gave 60% $AcCH_2PO(OEt)_2$, $b_{2.5}$ 101-2°, n_D^{20} 1.4364, d_{20} 1.1117; the same formed in 47% yield in the presence of pyridine; the same ester formed similarly in 76.6% yield from I and EtOH in the presence of pyridine; the product, b_1 94-5°, 1.4370, 1.1131. Keeping 6 g. III in 10 ml. Me_2CO and 1 ml. H_2O 4 days gave after removal of solvent and AcOH, 66.6% $HCOCH_2PO(OEt)_2$, b 92-3°, 1.4383, 1.1476; this also

19 Addition of neutral esters of phosphorous and phosphonous acids to conjugated systems. VIII. Reaction of esters of ethylphosphonous acid to acrylic and methacrylic acids.

V. A. Kukhtin and L. A. Khismatullina (Section of Cine-photo Res. Inst., Kazan). Zhur. Obshchei Khim. 29, 3276-8 (1959). cf. this j. 27,2372(1957) and 28, 939 (1958).

To 9.4 g. $EtP(OEt)_2$ (I) was added 5.1 g. $CH_2:CHCO_2H$ with cooling and, after 3 hrs. on a steam bath, the mixt. yielded 36.7% $EtP(O)(OEt)CH_2CH_2CO_2Et$, b_2 114-5°, n_D^{20} 1.4450, d_0^{20} 1.0810; the reaction is best run in Et_2O as the initial mixing results in strong exothermic effect. Similarly 12.5 g. I was treated dropwise with 8 g. $CH_2:CMeCO_2H$ (after the addn. of 1 g. the mixt. was gently warmed and when the temp. reached 110°, the flask was chilled with ice and the rest of the addn. was done with ice cooling) and after 1.5 hr. at 80-90° the mixt. gave 40.5% $EtP(O)(OEt)CH_2CHMeCO_2Et$, b_5 139-40°, 1.4440, 1.0575. The reactions of $RP(OR)_2$ were all run under CO_2 atm. Similarly were prepd.: 35% $EtP(O)(OPr)CH_2CH_2CO_2Pr$, b_3 143-5°, 1.4455,-; 27% $EtP(O)(OPr)CH_2CHMeCO_2Pr$, b_3 141°, 1.4470, 1.0417; 46% $EtP(O)(OBu)CH_2$-CH_2CO_2Bu, b_3 157-9°, 1.4510, 1.0199; 50% $EtP(O)(OBu)CH_2CHMeCO_2Bu$, b_3 151-2°, 1.4510, 1.0094.

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Copolymerization of poly(1,3-butanediol fumarate) with allyl esters of acids of phosphorus.

S. S. Spasskii and M. E. Mat'kova (Ural Section of Acad. Sci. USSR). Zhur. Obshchei Khim. 29, 3438-42(1959).

Kinetic data are reported for polymerization of mixts. of poly(1,3-butanediol fumarate) with $(EtO)_2P(O)CH_2CO_2CH_2CH:CH_2$ and $(EtO)(CH_2:CHCH_2O)PHO$ at 80^0 uner N_2. The copolymerization constants for the 1st system were found to be r_1 10.0, r_2 0.075; for the 2nd system r_1 5.5, r_2 0.035, i.e. the P-contg. components were only weakly active. Thermomechanical properties of the copolymers are shown graphically.

[redacted]

routine organophosphorus -
polymers containing phosphorus -
flame resistant polymers

21

Radiational method of synthesis of phosphonitrilic chloride derivatives.

V.I.Spitsyn, N. A. Afanas'eva, A. K. Pikaev, I. D. Kolli and P. Ya. Glazunov (M.V.Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 131, 1106-8 (1960).

Irradiation of 80 ml. 5% soln. of $(PNCl_2)_4$ in BuOH 6 hrs. with 0.6 m.e.v. electrons from a linear accelerator while air was passed through the soln. at 30° gave after evapn. of BuOH a brown residue of 45% $(NP(OBu)_2)_x$. The Cl content in the material drops steadily with prolonged irradiation. The viscosity of the soln. undergoes pos. and neg. changes during the process with much loss of viscosity and Cl content in the early stages. A radical mechanism for the reaction is suggested, in which monomer or dimer units may participate in the reaction with BuOH (PNCl is a suggested unit). Since the reaction is reversible, the minima appear on the overall curve. Similar irradiation of $(NPCl_2)_3$ in dioxane gave a residue of $(NPClC_4H_8O_2)_x$, which is resistant to hot alc. KOH.

organophosphorus polymers

Reaction of di- and trifunctional alkylalkoxysilanes with phosphoric anhydride.

A. P. Kreshkov and D. A. Karateev (D.I.Mendeleev Chem. Technol. Inst., Moscow). Zhur. Obshchei Khim. 29, 4082-5 (1959).cf. 27,2715(1957).

Refluxing 0.15 mole $Me_2Si(OEt)_2$ (or $Me_2Si(OBu)_2$) with 0.05 mole P_2O_5 3 hrs. gave some ROR and starting silane; at 170° the mixt. formed a glue-like substance while at 260-70° foaming occurred and a sticky solid resulted; after extn. with C_6H_6 and vacuum drying there was obtained a rather poorly sol.$[(Me_2Si)_3(PO_4)_2]_7$; it is hydrolyzed by H_2O and heating with P_2O_5 yields $Si(PO_4)_4$. It decomposes at about 250°. Similarly 0.06 mole $Et_2Si(OEt)_2$ with 0.02 mole P_2O_5 gave Et_2O and , at 190°, resulted in $[(Et_2Si)_3(PO_4)_2]_4$, which is somewhat more sol. in org. solvents than the Me analog. Reaction of $MeSi(OEt)_3$ or $EtSi(OEt)_3$ with P_2O_5 similarly gave polymers of the type$[(RSi(OEt)_2OPO_{1.5})_2O]_n$, the mol. wt of which could not be detd. owing to low soly. in org. solvents.

organo phosphorus & silicon polymers –
fall apart in water – impractical