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Derivatives of alkylphosphonous and phosphonic acids. VI. Halides and alkylated amides of alkyl(alkoxy)phosphonic acids.

A.I.Razumov, O.A.Mukhacheva and B.A.Markovich (Chem.Tech.Inst., Kazan).

Zhur.Obshchei Khim.27, 2389-94(1957). Cf. A.I.Razumov, Author Certificates 12249(1950) and 102461(1955).

To 139 g. $EtP(O)(OEt)_2$ in 2 L. CCl_4 was added with stirring in small portions 175 g. PCl_5 over 14 hrs. at 26-9°; after stirring 1 hr. the mixture was distd. in vacuo yielding the following ester chlorides: 80% $EtP(O)(OEt)Cl$, b_{10} 73-4°, d_{20} 1.1631, n_D^{20} 1.4838; 80% $EtP(O)(OPr)Cl$, b_{11-12} 85-7°, 1.1303, 1.4400; 45% $EtP(O)(OCHMe_2)Cl$, $b_{9.5}$ 76.5-8.5°, 1.1033, 1.4296; 70% $EtP(O)(OBu)Cl$, b_{10-11} 100-2°, 1.0993, 1.4395; 70% $EtP(O)(OCH_2CHMe_2)Cl$, $b_{13.5}$ 98-9.5°, 1.0898, 1.4355; 60% $MeP(O)(OCHMe_2)Cl$, $b_{0.5}$ 36-7°, 1.2924, 1.4346. In the prepn. of the iso-Pr ester of $EtPO_3H_2$ a difficulty was encountered in both usual methods of synthesis: the Arbuzov reaction gave a contamination of iso-$PrP(O)(OCHMe_2)_2$ from iso-PrI reaction, while the Michaelis reaction gave only the salts, rather than the desired ester. The necessary $EtP(O)(OCHMe_2)_2$, b_{12} 88-90°, 0.9764, 1.4120, was finally prepd. by oxidation of the $EtP(OCHMe_2)_2$ by unstated method. The chloroesters above are readily hydrolyzed by atm. moisture; with H_2O in presence of a base they yield the corresponding pyrophosphonates; on heating they decompose to RCl and RPO_2. The ester chlorides (1 mole) treated with 2 moles of an amine in Et_2O at -15° gave after filtration and distn., the following amide esters, most of which are sol. in H_2O: 58% $EtP(O)(OMe)NEt_2$, b_4 87-7.5°, 1.0043, 1.4381; 56% $EtP(O)(OEt)NEt_2$, $b_{3.5}$ 98-8.5°, 0.9866, 1.4355; [illegible] 33% $EtP(O)(OPr)NEt_2$, b_2 98-9°, 0.9783, 1.4368; 46% $EtP(O)(OCHMe_2)NEt_2$, $b_{0.5}$ 87-8.5°, 0.9650, 1.4381; 76% $EtP(O)(OBu)NEt_2$, b_1 98.5-9.5°, 0.9562, 1.4390; 35% $EtP(O)(OCH_2CHMe_2)NEt_2$, b_1 95.5-7°, 0.9553, 1.4357; 12% $EtP(O)(OC_6H_{13})NEt_2$, $b_{0.5}$ 116.5-8°, 0.9425, 1.4417; 15% $EtP(O)(OC_6H_{11})NEt_2$, $b_{0.5}$ 118-20.5°, 1.0066, 1.4630; 25% $EtP(O)(OCH_2Ph)NEt_2$, b_2 162-3°, 1.0554, 1.4975; 27% $EtP(O)(OEt)NHEt$, $b_{2.5}$ 111.5-2°, 1.0232, 1.4380; 73% $EtP(O)(OCH_2CHMe_2)NHEt$, b_1 129-9.5°, 0.9749, 1.4358; 76% $EtP(O)(OEt)NMe_2$, $b_{0.5}$ 63-4°, 1.0100, 1.4305; 60% $EtP(O)(OEt)N(CH_2)_2$, $b_{1.5}$ 89-92°, 1.0752, 1.4488 (with equimolar mixture of reactants); 52% $EtP(O)(OEt)NHCH_2CH_2Cl$, $b_{0.75}$ 144-5°, 1.1515, 1.4565 (with equimolar mixture); 61% $EtP(O)(OEt)NHCHMe(CH_2)_3NEt_2$, $b_{0.25}$ 153-4°, 0.9594, 1.4530; 55% $EtP(O)(OC_6H_4NO_2\text{-}p)NEt_2$, $b_{0.8}$ 172.5°, 1.1861, 1.5309; 52% $EtP(O)(SEt)NEt_2$, b_2 106-8°, 1.0297, 1.4802. Also were prepd.: 50% $MeP(O)(OMe)NEt_2$, $b_{0.5}$ 71-4°, 1.0214, 1.4355; 50% $MeP(O)(OEt)NEt_2$, $b_{1.5}$ 77-9°, 0.9944, 1.4350; 41% $MeP(O)(OCHMe_2)NEt_2$, $b_{0.1}$ 80-1.5°, 1.0763, 1.4395; 57% iso-$PrP(O)(OEt)NEt_2$, $b_{0.5}$ 74.5-5°, 0.9709, 1.4360. The amides are readily hydrolyzed especially in acid solns and treatment with dil. HCl yields the

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appropriate pyrophosphonate. The ester amides are biologically active and inhibit cholinesterase to extent of 50% at concns. of $1.5X10^{-6}$; with this property, however, their toxicity is low and LD50 intravenously for mice ranges from 2 to 1308 mg/kg. Most of the ester amides produce myosis which may last up to 50 days in cats and humans. Most of the amides are sol. in H_2O and their solns. are stable for not over 25 days. To 47 g. $EtP(O)(OEt)Cl$ in C_6H_6 and 26.2 g. $NaHCO_3$ (or equivalent amount of pyridine) was added 0.6 ml. H_2O (exothermic reaction), yielding after filtration 18% $[EtP(O)(OEt)]_2O$, b_2 139.5-41°, d_{20} 1.1333, n_D^{20} 1.4280. The same formed in 50% yield on addn. to 100 ml. Et_2O, 0.5 g. H_2O and 1.3 g. HCl of 20 ml. Et_2O containing 6 g. $EtP(O)(OEt)NHEt$.

VII. Mixed esters of primary phosphonic acids.

A.I.Razumov, E.A.Markovich and A.D.Reshetnikova. Ibid.2394-6.

Into a soln. of $EtP(O)H(OEt)$, b_{15} 77.5°, d_{20} 1.0779, n_D^{20} 1.4262, (13.4 g.) was passed Cl_2 at -15° until yellowish color appeared; after blowing with N_2 there was obtained 36% $EtP(O)(OEt)Cl$. This (204.5 g.) added to 181 g. $p\text{-}O_2NC_6H_4OH$ and 1.5 l. dry Et_2O and stirred 45 min., then slowly treated with 132 g. Et_3N in Et_2O, and refluxed 40 min., gave after filtration and distn.(not over 0.2 mm.pressure to avoid decompn.) 61% $EtP(O)(OEt)\text{-}OC_6H_4NO_2\text{-}p$, $b_{0.2}$ 163-5°, 1.2545, 1.5242. Similarly were prepd.: 44% $EtP(O)(OMe)OC_6H_4NO_2\text{-}p$, $b_{0.33}$ 159-60°, 1.3018, 1.5294; 44% $EtP(O)(OEt)OC_6H_4\text{-}NO_2\text{-}o$, $b_{0.15}$ 140-2°, 1.2487, 1.5115; 60% $EtP(O)(OEt)OC_6H_4NO_2\text{-}o$ (apparently a misprint; cf. one directly above), $b_{0.15}$ 145-8°, 1.2482, 1.5110; 50% $EtP(O)(OPr)OC_6H_4NO_2\text{-}p$, $b_{0.2}$ 158-8.5°, 1.2231, 1.5210; 15% $EtP(O)(OCHMe_2)\text{-}OC_6H_4NO_2\text{-}p$, $b_{0.24}$ 161-4°, 1.2286, 1.5233; 57% $EtP(O)(OBu)OC_6H_4NO_2\text{-}p$, $b_{0.5}$ 181.5-2.5°, 1.1968, 1.5180; 22% $EtP(O)(OCH_2CHMe_2)OC_6H_4NO_2\text{-}p$, $b_{0.5}$ 163.5-4°, 1.1971, 1.5174; 60% $EtP(O)(OEt)OC_6H_4Cl\text{-}p$, $b_{0.17}$ 117-8°, 1.2122, 1.5050; 32% $EtP(O)(OEt)OC_6H_4Cl\text{-}o$, $b_{0.06}$ 106-7°, 1.2065, 1.5045. The esters are slightly sol. in H_2O and are stable in aq. soln. for several years, but are hydrolyzed in alkaline solns. All are strong myotics and inhibitors of cholinesterase. The Et panitrophenyl ester is most active giving myosis at 1:200,000 diln. and having anticholinesterase activity at $2X10^{-9}$ concn. This substance, named "Armin" is used clinically for glaucoma treatment

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... continued work by Razuma ... biologically active ...

Derivatives of alkylphosphonous and phosphonic acids. IX. Some alkylated amide esters of phosphorous acid and their ability to isomerize.

A.I.Razumov. Trudy Kazan.Khim.Tekhnol.Inst. im.S.M.Kirova,23, 201-4(1957). Cf.Kabachnik et al. Doklady Akad.Nauk SSSR 96,991(1954); Razumov et al. Khimiya i Primenenie Fosfororgan.Soedinenii, 1957.

To 29.5 g. Et_2NH in Et_2O was added at -10° 26.5 g. $(EtO)_2PCl$ and after refluxing 45 min. the mixture was filtered and distd. yielding 52% $(EtO)_2PNEt_2$, $b_8$63.5-4.5°, d_{20}0.9268, n_D^{20}1.4314. Similarly were obtained: 63% $(PrO)_2PNEt_2$, $b_{8.5}$88-91°, 0.9214, 1.4355; 50% $(iso\text{-}PrO)_2PNEt_2$, $b_{7.5}$62-4°, 0.8798, 1.4257; 80% $(BuO)_2PNEt_2$, $b_{9.5}$109-11°, 0.9111, 1.4382; 50% $(iso\text{-}BuO)_2PNEt_2$, b_{15}110-2°, 0.9065, 1.4322; 67% $(PrO)_2PN(CH_2)_5$, $b_8$116-8°, 0.958 1.4588. Keeping 12 g. $(EtO)_2PNEt_2$ and 9.5 g. EtI overnight gave some solid ppt. and heating 5 hrs. at 95° in sealed tube gave 1.5 g. solid and 18.5 g. liquid product; reheating 3 hrs. at 125° gave 3 g. solid product and 11 g. liquid product; distn. of the latter gave EtI and 29% $EtP(O)(OEt)NEt_2$, $b_{3.5}$98-100.5°, d_{20}0.9938, n_D^{20}1.4338; the same formed from Et_2NH and $EtP(O)(OEt)Cl$, the product having $b_3$98-8.5°, d_{20}0.9866, n_D^{20}1.435 Addn. of 1.6 g. S to 12.5 g. $(BuO)_2PNEt_2$ led to exothermic reaction yielding 71% $(BuO)_2P(S)NEt_2$, $b_{0.25}$101.5-2°, d_{20}0.9789, n_D^{20}1.4618. ~~Thm~~

X. Mixed esters and amide esters of alkylphosphonic acids and a certain biological characterization of them.

Ibid.205-14.

A number of biologically active ester amides and mixed esters of alkylphosphonic acids are reported; the products have anticholinesterasic actic and most of the products have myotic activity also. The mixed esters are more active than the ester amides in block of cholinesterase, but the latter compounds produce more durable myosis. The mixed esters are stable in aq. soln. even on heating, but ester amides are slowly hydrolyzed and in 20-30 days their activity is impaired. The mixed esters are hydrolyzed in alkaline solns. while the ester amides are best hydrolyzed in acid media. The following esters are listed (b.pt., d_{20}, n_D^{20} , sely. in H_2O, minimum concn. causing myosis in rabbits, toxicity to white mice in mg/kg. subcutaneously and intravenously, anticholinesterase activity against true cholinesterase and pseudocholinesterase, are shown resp. for each substan

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$EtP(O)(OMe)OC_6H_4NO_2$-p, $b_{0.93}$159-60°, 1.3018, 1.5294, 1:200, 1:75000, 1.15, 0.65, 5.5×10^{-9}, 6.5×10^{-8}; $EtP(O)(OEt)OC_6H_4NO_2$-p, $b_{0.2}$163-5°, 1.2545, 1.5242, 1:300, 1:200,000, 0.54, 0.39, 2×10^{-9}, 2.2×10^{-9}; $EtP(O)(OEt)OC_6H_4$-NO_2-o, $b_{0.15}$140-2°, 1.2487, 1.5115, 1:200, 1:10,000, 7.5, 5, 5×10^{-8}, 5×10^{-8}; $EtP(O)(OEt)OC_6H_4NO_2$-m, $b_{0.15}$145-9°, 1.2482, 1.5110, 1:300, 1:30,000 2.5, 2.2, 1×10^{-8}, 2×10^{-8}; $EtP(O)(OPr)OC_6H_4NO_2$-p, $b_2$158-8.5°, 1.2231, 1.5210 1:700, 1:150,000, 0.5, 0.3, $a\times10^{-9}$, 3.3×10^{-8}; $EtP(O)(OCHMe_2)OC_6H_4NO_2$-p, $b_{0.24}$161-4°, 1.2286, 1.5233, 1:600, 1:75,000, 1.5, 0.75, 2×10^{-9}, 2.2×10^{-8}; $EtP(O)(OBu)OC_6H_4NO_2$-p, $b_{0.5}$181.5-2.5°, 1.1968, 1.5180, 1:1500, 1:75,000, 0.8, 0.4, $a\times10^{-9}$, 2.2×10^{-8}; $EtP(O)(OCH_2CHMe_2)OC_6H_4NO_2$-p, $b_{0.5}$163.5-4°, 1.1971, 1.5174, 1:1200, 1:100,000, 0.8, 0.4, 2×10^{-9}, 2.2×10^{-8}; $EtP(O)(OEt)$-OC_6H_4Cl-p, $b_{0.17}$117-8°, 1.2122, 1.5050, 1:800, none, 30, 25, 2×10^{-7}, 1×10^{-6} $EtP(O)(OEt)OC_6H_4Cl$-o, $b_{0.06}$106-7°, 1.2065, 1.5045, 1:500, none, 75, 60, 2×10^{-6}, 3×10^{-6}. The following amide esters are described: $EtP(O)(OMe)NEt_2$, $b_4$87-7.5°, d_{20}1.0043, n_D^{20}1.4381; $EtP(O)(OEt)NEt_2$, $b_{3.5}$98-8.5°, 0.9866, 1.4355; $EtP(O)(OPr)NEt_2$, $b_2$98-9°, 0.9783, 1.4368; $EtP(O)(OCHMe_2)NEt_2$, $b_{1.5}$81-2°, 0.9849, 1.4335; $EtP(O)(OBu)NEt_2$, $b_1$98.5-9.5°, 0.9562, 1.4390; $EtP(O)(OCH_2CHMe_2)NEt_2$, $b_1$95.5-7°, 0.9553, 1.4357; $EtP(O)(OC_6H_{13})NEt_2$, $b_{0.5}$ 116.5-8°, 0.9425, 1.4417; $EtP(O)(OC_6H_{11})NEt_2$, $b_{0.5}$118-20.5°, 1.0066, 1.4630; $EtP(O)(OCH_2Ph)NEt_2$, $b_2$162-3°, 1.0554, 1.4975; $EtP(O)(OEt)NHEt$, $b_{2.5}$111.5-2°, 1.0232, 1.4380; $EtP(O)(OCH_2CHMe_2)NHEt$, $b_1$129-9.5°, 0.9749, 1.4358; $EtP(O)(OEt)NMe_2$, $b_{0.5}$63-4°, 1.0100, 1.4385; $EtP(O)(OEt)N(CH_2)_2$, $b_{1.5}$89-92°, 1.0752, 1.4488; $EtP(O)(OEt)CHCH_2CH_2Cl$, $b_{0.75}$144-5°, 1.1515, 1.4565; $EtP(O)(OEt)NHCHMe(CH_2)_3NEt_2$, $b_{0.25}$153-4°, 0.9594, 1.4530; $EtP(O)$-$(SEt)NEt_2$, $b_2$106-8°, 1.0297, 1.4892; $EtP(O)(NEt_2)OC_6H_4NO_2$-p, $b_{0.8}$172.5°, 1.1801, 1.5309; $MeP(O)(OMe)NEt_2$, $b_{0.5}$71-4°, 1.0264, 1.4355; $MeP(O)(OEt)NEt_2$, $b_{1.5}$77-9°, 0.9944, 1.4150; $MeP(O)(OCHMe_2)NEt_2$, $b_{0.1}$80-1.5°, 1.0763, 1.4395; iso-$PrP(O)(OEt)NEt_2$, $b_{0.5}$74.5-5°, 0.9709, 1.4360. The above group produced pyosis in cats and rabbits in aq. soln. applied to the eye. The most active compounds were $EtP(O)(OCHMe_2)NEt_2$, $EtP(O)(OEt)NEtH$ and $EtP(O)(OCH_2CHMe_2)$-$NHEt$, which required less than 1% soln. for the effect. Anticholinesterase activity of these compounds did not exceed the activity at 10^{-6} concn.

XI. Synthesis of dicarbethoxymethyl esters of ethyl- and carbethoxymethylphosphonic acids.

A.I.Razumov and E.I.Korobkova. Ibid.215-18.

To 30 g. EtO_2CCH_2OH and 26.2 g. pyridine in C_6H_6 there was added at -12° an unstated amount of PCl_3; after 2 hrs. the mixture was filtered and distd. yielding 32% $(EtO_2CCH_2O)_3P$, $b_1$176-7°, d_4^{20}1.2104, n_D^{20}1.4491. To 40 g. EtO_2CCH_2OH in Et_2O was added 17.6 g. PCl_3 with ice cooling in N_2 stream.

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and after refluxing 45 min. the mixture yielded 66% $(EtO_2CCH_2O)_2PNO$, $b_{0.15}$150-2°, d_4^{20}1.2485, n_D^{20}1.4422; this treated with Cl_2 with ice cooling gave 30.4% $(EtO_2CCH_2O)_2POCl$, $b_{0.3}$163°, d_4^{20}1.3182, n_D^{20}1.4451. Heating 15 g. $(EtO_2CCH_2O)_3P$ and 7.5 g. $BrCH_2CO_2Et$ in sealed tube 3 hrs. at 160° and 2hrs. at 170°, gave 63.3% $EtO_2CCH_2P(O)(OCH_2CO_2Et)_2$, $b_{0.015}$167-8°, d_4^{20} 1.2399, n_D^{20}1.4470; similar reaction with EtBr in 5 hrs. at 150° gave $EtP(O)(OCH_2CO_2Et)_2$, $b_{0.02}$145-7°, d_4^{20}1.1974, 1.4420; the same formed in 26.6% yield from 20.8 g. EtO_2CCH_2OH, 20.2 g. Et_3N and 15 g. $EtPOCl_2$. The two phosphonates shown above showed biological activity(unspecified). Cf.Gerrard et al.J.Chem.Soc.1953,1920.

Structure and insecticidal activity of anhydrides of some acids which contain phosphorus.

A.I.Razumov, N.N.Sankevskaya and I.D.Noklesova. Trudy Kazan.Khim.Tekhnol. Inst. im. S.M.Kirova, 23, 219-27.

Heating 25 g. $(EtO)_2POCl$ and 24 g. $EtP(O)(OEt)_2$ to 114° gave in 40 min. 7.5 g. EtCl and 35% $(EtO)_2P(O)OP(O)Et(OEt)$, $b_{0.3}$120-2°, d_4^{20}1.1664, n_D^{20} 1.4280. Reaction of 20 g. Et_2POCl with 25.9 g. $(EtO)_3PO$ at 140-58° gave in 1 hr. 35% $(EtO)_2P(O)OP(O)Et_2$, $b_{0.3}$128-9°, 1.1469, 1.4414. Reaction of 21.3 g. $EtP(O)(OEt)_2$ and 20 g. $EtP(O)(OEt)Cl$ at 106-28° gave 42% (EtO)-$EtP(O)OP(O)Et(OEt)$, $b_{0.5}$120.5-1°, 1.1457, 1.4365. Reaction of 23.3 g. Et_2POCl with 27.5 g. $EtP(O)(OEt)_2$ in 1 hr. at 130° gave 23% $(EtO)EtP(O)$-$OP(O)Et_2$, $b_{0.3}$124-6°, 1.1194, 1.4502.Heating 20 g. $Et_2P(O)OEt$ and 18.7 g. Et_2POCl ay 86-112° 1.75 hrs. gave 43% $Et_2P(O)OP(O)Et_2$, $b_{0.3}$142-3°, 1.1042, 1.4648. The pH values of aq. solns. of the anhydrides were recorded over a period of time (shown graphically) and the rates of their hydrolysis were estd.(shown graphically). In both symmetric and unsymmetric anhydrides the rate of hydrolysis decreases with decreased number of ester groups. Thus 50% hydrolysis is reached in 12 hrs. for $[(EtO)EtP(O)]_2O$, in 22 hrs. for $(Et_2P(O))_2O$, in 1.25 hrs. for $(EtO)_2P(O)OP(O)Et(OEt)$, in 2.5 hrs. for $(EtO)_2P(O)OP(O)Et_2$, and 3.6 hrs. for $(EtO)EtP(O)OP(O)Et_2$. The greatest insecticidal activity against Calandra granaria was shown by $(EtO)_2P(O)OP(O)Et(OEt)$ and $[(EtO)EtP(O)]_2O$; the other anhydrides showed much weaker activity, being least in the phosphinic anhydride. Generally, insecticidal activity decreased with increased stability to hydrolysis. Cf. Kosolapoff and Watson,JACS 73,4101(1951).

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A method of synthesis of esters of alkylphosphonous acids.

A.I.Nabechnik and E.N.Tsvetkov (Inst.Hetero-org.Compounds, Moscow). Doklady Akad.Nauk [illegible].117, 217-20(1957).

A soln. of Grignard reagent (0.11 mole RX, 0.11 at.Mg in 50 ml. Et_2O) is added dropwise to 0.1 mole $(RO)_2PCl$ in 50 ml. Et_2O at -60° to -65°; the liquid is decanted from the solid, the latter being washed with petr.ether and the soln. is distd., all operations being done in N_2. Thus are obtained $(RO)_2PR'$ in a convenient procedure and satisfactory yields. In case of use of MeMgI, the removal of MgI_2 must be performed by removal of Et_2O from the reaction mixture and extn. of the residue with petr.ether. If the atomic refraction for P of 7.74 is used for calcn. of molar refraction of the products, an exaltation of 0.41 is found for alkyl members and 1.8 for the aryl members. (Cf.Razumov et al., Zhur.Obsh.Khim.26,1436(1956)). The reported products are: $MeP(OBu)_2$, 69.5%, $b_1$39-40°, n_D^{20}1.4348, d_{20}0.8902; $EtP(OPr)_2$, 64.3%, $b_7$36-8.5°, 1.4318, 0.8935; $EtP(OBu)_2$, 70%, $b_1$47-8°, 1.4370, 0.8871; $PrP(OBu)_2$, 66.4%, $b_1$39.3-40.3°, 1.4393, 0.8851; $BuP(OBu)_2$, 68.4%, $b_1$68-9°, 1.4420, 0.8830; $PhCH_2P(OBu)_2$, 54.5%, $b_1$103-4°, 1.4972, 0.9742; $PhP(OBu)_2$, 67%, $b_1$97.5-8.5°, 1.4993, 0.9769; $PhP(OPr)_2$, 61.5%, $b_1$73-4°, 1.5072, 1.0000; $PhP(OEt)_2$, 53.7%, $b_1$62.5-3°, 1.5131, 1.0252; $(CH:CH)_2CHP(OBu)_2$, unstated yield, $b_2$81.5-3°, 1.4827,-. Addn. of S to these gave: 87% $MeP(S)(OBu)_2$, $b_1$69-70°, 1.4622, 0.9872; $EtP(S)(OBu)_2$, 85%, $b_1$75-7°, 1.4628, 0.9795; 93.[illegible] $EtP(S)(OPr)_2$, $b_1$55-6°, 1.4630, 1.0007; 87.5% $PrP(S)(OBu)_2$, $b_1$84-5°, 1.4623, 0.9702. Cuprous salt adducts: $PhP(OEt)_2.CuI$, m.122.5-3.5°; $PhP(OPr)_2$-CuI, m.129.5-30.5°; $PhP(OBu)_2.CuI$, m.88-9°.

organophosphorus,
rather routine
but all substances
reported are usable
as G intermediates
Same type as Razumov's work

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Alkylphosphonous and phosphonic acids. Synthesis and properties of some alkylated amides of alkylphosphonic chlorides.

A.I.Razumov, O.A.Mukhacheva and B.A.Markovich (Chem.Technol.Inst.,Kazan).

Zhur.Obshchei Khim.28, 194-7(1958). Cf. this j.27,2389(1957).

Organo-P, almost every compound described is a G intermediate

Heating 14 g. $Et_2NH.HCl$ and 60 g. $EtPOCl_2$ at reflux 6 hrs. at 235° gave 35% $EtP(O)(NEt_2)Cl$, $b_{3.5}$101.5°, d_{20}1.0964, n_D^{20}1.4643; this method requires a large excess of $RPOCl_2$ and gives but 30-5% yields. Treatment of $RPOCl_2$ in Et_2O with 2 moles R_2NH at -5°, followed by refluxing 30-50 min.gave after sepn. of the amine HCl salt (generally found to be in excess over the theory owing to attack by moisture) the more satisfactory yields of the partial amides; thus were obtained: 50% $MeP(O)(NEt_2)Cl$, $b_9$115-5.5°, 1.1274, 1.4648; 65% $EtPO(NEt_2)Cl$, 45% $PrP(O)(NEt_2)Cl$, $b_4$112-3°, 1.0706, 1.4642; 40% iso-$PrP(O)(NEt_2)Cl$, $b_1$90-1°, 1.0707, 1.4627; 50% $BuP(O)(NEt_2)Cl$, $b_3$113-5°, 1.0526, 1.4641. On cooling $MeP(O)(NEt_2)Cl$ solidified and m.42-3°. All the above chlorides are rapidly attacked by moisture yielding pyro derivs. isolable however only in low yields owing to extreme hydrolyzability by moisture. The necessary $RPOCl_2$ were prepd. by the action of PCl_3-Cl_2 on corresponding di-Bu esters; thus were obtained: 90% $MePOCl_2$, $b_{11.5}$59-9.5°; $EtPOCl_2$, 75%, b_{15}133.5-4.5°; 75% $PrPOCl_2$, $b_{12.5}$141°; 70% iso-$PrPOCl_2$, $b_3$113-4°; 75% $BuPOCl_2$, b_{15-16}96-8°. Treatment of 46 g. $EtP(O)(NEt_2)Cl$ at 0-10° with calcd. amount H_2O in N_2 stream gave despite a rapid distn. in vacuo much $Et_2NH.HCl$ and but 9% $(EtP(O)(NEt_2))_2O$, which formed in 50% yield if $NaHCO_3$ was used to bind the resulting HCl; the product, $b_2$163.5-4.5°, 1.0619, 1.4607. Heating $RP(O)(NEt_2)Cl$ with calcd. amount of $NaBF_4$ to 110-175° gave: 33% $MeP(O)(NEt_2)F$, b_{19}101°, 1.0735, 1.4195; 38% $EtP(O)(NEt_2)F$, b_{15}103°, 1.0036, 1.4130; 25% $PrP(O)(NEt_2)F$, b_{12}110.5°, 1.0301, 1.4238; 34% iso-$PrP(O)(NEt_2)F$, b_{17}82°, 1.0263, 1.4231; 30% $BuP(O)(NEt_2)F$, b_{16}128-30°, 1.0380, 1.4258; 10% $MePOF_2$, b_{27}22°, 1.3838, 1.3277; 25% $EtPOF_2$, b_{25}44-5°, 1.2510, 1.3410; 34% $PrPOF_2$, b_{13}30.5°, 1.1791, 1.3541; 10% iso-$PrPOF_2$, $b_{17.5}$25°, 1.1736, 1.3512; 33% $BuPOF_2$, $b_{17.5}$51.5-2°, 1.1342, 1.3709. Attempts at fluorination with NaF were unsuccessful.

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novel compounds

these novel compounds could be pre-toxic materials

Reaction of halogen derivatives of some β-disulfones with diethyl sodiophosphite and triethyl phosphite.

B.A.Arbusov and N.P.Bogonostseva (Chem.Res.Inst., State Univ.,Kazan). Zhur. Obshchei Khim.27, 2356-60(1957). Cf. A. and B., Izvest.Akad.Nauk SSSR, otdel khim.nauk 1954,837; Kreutzkamp, Naturwiss. 42,415(1955).

Careful heating of 76 g. $CS(NH_2)_2$, 100 ml. 96% EtOH, 156 g. EtI or 109 g. EtBr until soln. formed, followed by rapid addn. of 50 g. NaOH in 150 ml. H_2O, followed by distn. from a water bath, gave 97.4% crude or 92.2% pure EtSH in 2.5-3 hrs. To a soln. of 1g. Na in 6 g. $(EtO)_2PHO$ and 100 ml. Et_2O was added 6.8 g. $CBr_2(SO_2Et)_2$ in C_6H_6, yielding a ppt. of 100% NaBr, while the filtrate gave 3 g. $(EtSO_2)_2CH_2$, m.102-4°; the filtrate from this gave 3.17 g. $(EtO)_3PO$ and 2.5 g. $CH_2(P(O)(OEt)_2)_2$, $b_{0.5}$132-5°, d_{20}^{20}1.1878, n_D^{20}1.43-00. Reaction of 17 g. $Br_2C(SO_2Et)_2$ with 20 g. $(EtO)_3P$ (exothermic) gave in 2 hrs. on a steam bath 3.7 g. $(EtO)_3PO$, and 6 g. propylidenediethyl-sulfone, $C_7H_{16}O_4S_2$, m.77-8°. Reaction of 4.6 g. methyldiethylsulfonomethane bromide (cf.Escales and Baumann, Ber.18,2815(1884)) with $(EtO)_2PONa$ from 2.5 g. ester, in Et_2O, was vigorous and gave in 2 hrs. NaBr, $(EtO)_3PO$ and some $MeCH(PO(OEt)_2)_2$ (I), m.75-8°; same reaction with $(EtO)_3P$ required cooling and gave $(EtO)_3PO$ and I, b$_5$166-72°, m.75-8°, and a liquid, $b_9$166-7°, n_D^{20}1.4500, d_{20}^{20} 1.2060, containing 12.5-13% P. Reaction of $CCl_2(SO_2Et)_2$ with $(EtO)_2PONa$ in Et_2O gave NaCl, $(EtO)_3PO$ and $CH_2(SO_2Et)_2$, m.102-4°; similar reaction with $(EtO)_3P$ run under N_2 gave $CH_2(SO_2Et)_2$ and $EtCH(SO_2Et)_2$, m.73-5°. The obviously oxidation-reduction course of the above reactions is not dependent on air or H_2O for the supply of O, and occurs intermolecularly. $CH_2(PO(OEt)_2)_2$ was devoid of insecticidal properties.

Synthesis of some phosphonosulfides and phosphonosulfones.

B.A.Arbusov and N.P.Bogonostseva (Chem.Inst.,State Univ.,Kazan). Zhur. Obshchei Khim.27, 2360-2(1957).

EtSH (6 g.) treated with 1.85 g.Na in Et_2O followed by 15 g. $ClCH_2PO(OEt)_2$ and refluxed 2 hrs. gave after further 2 hrs. at 100° 4.7 g. NaCl and 85.6% $EtSCH_2PO(OEt)_2$, $b_7$127-7.5°, d_{20}^{20}1.1052, n_D^{20}1.4650; this (2 g.) with 10 ml. Et_2O soln. of AcO_2H contg. 0.5 g. active O at 2° gave after 2 days 1.9 g. $EtSO_2CH_2PO(OEt)_2$, $b_{11.5}$194°, 1.2271, 1.4560. Similarly was prepd. a low yield of $PhSCH_2PO(OEt)_2$, $b_7$177-9°, $b_2$167-8°, 1.1736, 1.5483, which with AcO_2H gave $PhSO_2CH_2PO(OEt)_2$, m.145-8° (from H_2O). Heating 5 hrs. 4 g. dry Na_2S and 19 g. $ClCH_2PO(OEt)_2$ in Me_2CO 5 hrs. gave 2 g. $S(CH_2PO(OEt)_2)_2$, $b_{2.5}$191-2°, 1.1947, 1.4675, which oxidized to the sulfone, m.76-8°

as above

organo phosphorus, novel compounds

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Possible [illegible] consideration organophosphorus novel compounds

Cyano substituted dialkyl phosphites.

Gil'm Kamai, E.V.Kuznetsov and R.K.Valetdinov (S.M.Kirov Chem.Tech.Res.Inst. Kazan). Doklady Akad.Nauk S.S.S.R.118, 965-8(1957).

Reaction of PCl_3 with cyanohydrins yields mixtures of $ROPCl_2$, $(RO)_2PCl$ and $(RO)_3P$, which appear to form a reversible system. The $(RO)_3P$ members do not suffer degradation to $(RO)_2PCl$ as is common for alkyl derivs. (Cf. Kuznetsov and Valetdinov, Trudy Kazan.Khim.Tekhnol.Inst.im.S.M.Kirova, 21, 167(1956). Thus were obtained: $MeCH(CN)OPCl_2$, b_{11} 67-8°, d_4^{20} 1.3509, n_D^{20} 1.4808; $(MeCH(CN)O)_2PCl$, b_{10} 140-2°, 1.1844, 1.4575; $(MeCH(CN)O)_3P$, b_2 152-4°, 1.1188, 1.4470; $Me_2C(CN)OPCl_2$, b_{11} 78-80°, 1.2760, 1.4775; $(Me_2C(CN)O)_2PCl$, b_{11} 139-40°, 1.1417, 1.4587; $(Me_2C(CN)O)_3P$, b_4 133-4°, 1.0740, 1.4442; $EtCH(CN)OPCl_2$, b_8 70-9°, 1.2068, 1.4800; $(EtCH(CN)O)_2PCl$, b_{11} 152-5°, 1.1470, 1.4612; $(EtCH(CN)O)_3P$, b_2 162-4°, 1.0810, 1.4515; iso-$PrCH(CN)OPCl_2$, b_2 83-4°, 1.2410, 1.4780; (iso-$PrCH(CN)O)_2PCl$, b_2 127-8°, 1.1080, 1.4620; (iso-$PrCH(CN)O)_3P$, b_2 163-4°, 1.0475, 1.4545; $PrCH(CN)OPCl_2$, b_{10} 92-4°, 1.2095, 1.4765; $(PrCH(CN)O)_2PCl$, b_2 138-40°, 1.1176, 1.4650; $(PrCH(CN)O)_3P$, b_2 168-9°, 1.0433, 1.4530; iso-$BuCH(CN)OPCl_2$, b_{10} 96-6°, 1.2020, 1.4770; (iso-$BuCH(CN)O)_2PCl$, b_1 138-40°, 1.0808, 1.4625; (iso-$BuCH(CN)O)_3P$, b_2 162-8°, 1.0138, 1.4550; $(CH_2)_5C(CN)OPCl_2$, b_{10} 124-6°, 1.2210, 1.5118; $[(CH_2)_5C(CN)O]_2PCl$, b_{10} 205-7°, 1.1810, 1.5050; $[(CH_2)_5C(CN)O]_3P$, m.73°. Treatment of the chlorides in Et_2O with calcd. amount of H_2O in the presence of pyridine gave $(RO)_2PHO$, which unlike the dialkyl analogs, are true members of the class of P^{III} derivatives. Thus were obtained: $(MeCH(CN)O)_2PHO$, $b_{0.2}$ 112-5°, 1.1605, 1.4400; $(Me_2C(CN)O)_2PHO$, $b_{0.2}$ 118-20°, 1.1128, 1.4420; (iso-$PrCH(CN)O)_2PHO$, $b_{0.2}$ 125-4°, 1.0995, 1.4460; $(PrCH(CN)O)_2PHO$, $b_{0.2}$ 134-5°, 1.0846, 1.4426; (iso-$BuCH(CN)O)_2PHO$, $b_{0.1}$ 133-5°, 1.0529, 1.4505; $(Me_2C(CN)O)(ClCH_2CH_2S)PHO$, $b_{0.5}$ 115-7°, 1.2964, 1.4622. These react with CuX with heat evolution forming glassy masses; they react with PhN_3 yielding N_2 and amides (thus was prepd. $(Me_2C(CN)O)_2PCHNPh$, m.87°). $(RO)_2PHO$ in this group do not tend to disproportionate on heating if the radical is tertiary; those with secondary radicals yield $RSPO_2H_2$ and $(RO)_3P$.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520002-1 of interest possibly this were new compounds all the way through.

Cyano substituted esters of acids of phosphorus. 2. Neutral cyano substituted esters of phosphorous and phosphoric acids.

E.V.Kuznetsov and R.K.Valetdinov. Trudy Kazan.Khim.Tekhnol.Inst. im. S.M.Kirova, 23, 161-6(1957). Cf. this j.XI,167(1956).

To the desired cyano alc. in Et_2O was added pyridine and the mixture was treated with ice cooling with equimolar amount of PCl_3 in Et_2O (S.N.K.- probably 3:1 ratio rather than 1:1 is meant) at 5°; after refluxing 15 min. the mixture was filtered and distd. yielding the following esters: $(NCCH_2O)_3P$, could not be distd.; 78.7% $(NCCHMeO)_3P$, $b_2$152-4°, d_{20}1.1188, n_D^{20}1.4470; $(NCCH_2CH_2O)_3P$, could not be distd.; 79.5% $(NCCMe_2O)_3P$, $b_4$153-4°, 1.0749, 1.4462; 82.5% $(NCCHEtO)_3P$, $b_2$162-4°, 1.0810, 1.4515; 79.3% $(NCCH(CHMe_2)O)_3P$, $b_2$163-4°, 1.0475, 1.4545; 76.1% $(NCCHPrO)_3P$, $b_2$168-9°, 1.0433, 1.4530; 79.9% $(NCCH(CH_2CHMe_2)O)_3P$, $b_2$182-5°, 1.0138, 1.455; 51.6% $[(CH_2)_5C(CN)O]_3P$, m.75°; Similar all these reacted with CuCl but the adducts even after being heated to 115° formed only uncrystallizable sirups. Passage of O_2 through the phosphites at 76° (in CCl_4 thereafter) 6-16 hrs. gave the corresponding phosphates: 94% $(NCCHMeO)_3PO$, $b_{0.4}$170-2°, 1.1844, 1.4352; 90% $(NCCMe_2O)_3PO$, $b_{0.6}$145-8°, m.33° (d_{33}1.1153, n_D^{33}1.4395); 80.5% $(NCCHEtO)_3PO$, $b_{0.5}$163-5°, 1.1230, 1.4430; 96% $(NCCH(CHMe_2)O)_3PO$, $b_{0.1}$144-5°, 1.0786, 1.4445; 91% $(NCCHPrO)_3PO$, $b_{0.15}$155-8°, 1.0797, 1.4430; 81.1% $(NCCH(CH_2CHMe_2)O)_3PO$, $b_{0.2}$169-71°, 1.0469, 1.4455. None of the $(RO)_3P$ listed above could be induced to undergo the Arbuzov reaction with MeI, PrI or CCl_4 even after prolonged heating. In the prepn. of cyanoalkyl phosphites, the reaction evidently took place but the products could not be distd. if the cyano alc. used was a primary alc.

3. Reaction of cyano substituted alcohols with phosphorus trichloride. Ibid.167-73.

Addn. of 5.7 g. $NCCH_2OH$ to 13.7 g. PCl_3 at 45° yielded some HCl and gave only some PCl_3 and unreacted alc. in addn. to a viscous resin. Addn. of 35.5 g. $NCCH_2CH_2OH$ to 68.7 g. PCl_3 at 40° gave after 1 hr. at 40° a colorless solid which was sepd. and the liq. portion yielded some $ClCH_2CH_2CN$, b_{10}66-7°, and some $NCCH_2CH_2OPCl_2$, $b_7$110-5°, d_{20}1.3919, n_D^{20} 1.4971. Addn. of 53.2% $NCCHMeOH$ at 59° to 102.8 g. PCl_3 gave after 15 min. at 65° 39.1% $NCCHMeOPCl_2$, b_{11}67-8°, 1.3359, 1.4885, some $(NCCHMeO)_2PCl$, b_{10}140-5°, 1.1844, 1.4575, and some $(NCCHMeO)_3P$, $b_2$165-8°, n_D^{22}1.4465, d_{20}1.1150 . To 137 g. PCl_3 at 70° was added 85 g. $NCCMe_2OH$ over 1 hr. and after 0.5 hr. at 70° the mixture gave 72 g. $NCCMe_2OPCl_2$, b_{11}78-80°, d_{20}1.2760, n_D^{20}1.4773, 64.2 g. $(NCCMe_2O)_2PCl$, b_{11}139-40°, 1.1417, 1.4557, and 15.1 g. $(NCCMe_2O)_3P$. Similarly were obtained:

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$NCCMe_2OPCl_2$, b_8 78-9°, 1.2868, 1.4800; iso-$PrCH(CN)OPCl_2$, b_8 83-4°, 1.2410, 1.4780; $NCCHPrOPCl_2$, b_{10} 93-4°, 1.2395, 1.4765; iso-$BuCH(CN)OPCl_2$, b_{10} 95-6°, 1.2020, 1.4770; $(CN)_3C(CN)OPCl_2$, b_{10} 124-6°, 1.2818, 1.5115; $(NCCMe_2O)_2PCl$, b_{11} 152-3°, 1.1470, 1.4612; $(iso\text{-}PrCH(CN)O)_2PCl$, b_3 127-8°, 1.1089, 1.4620; $(NCCHPrO)_2PCl$, b_3 138-40°, 1.1176, 1.4630; $(iso\text{-}BuCH(CN)O)_2PCl$, b_1 128-40°, 1.0808, 1.4623; and $[(CN)_3C(CN)O]_2PCl$, b_{10} 203-7°, 1.1810, 1.5050.

4. Cyano substituted mixed esters of phosphorous acid.
Ibid. 174-86.
Reaction of $ClCH_2CH_2OPCl_2$ with $NCCH_2CN$ in the presence of pyridine gave a range of products, b_{11} 163-200° which could not be resolved into individual products. Passage of 10 g. ethylene oxide into 15.7 g. $MeCH(CN)OPCl_2$ gave 15.3 g. $(ClCH_2CH_2O)(MeCH(CN)O)P$, b_{10} 166-8°, d_{20} 1.2773, n_D^{20} 1.4735. Reaction of 14.8 g. $BuOH$ with 17.2 g. $NCCH_2CH_2OPCl_2$ in the presence of 15.8 g. pyridine gave 4.2 g. $(BuO)_3P$, 9.5 g. $(BuO)_2POCH_2CH_2CN$, b_8 150-3°, 1.0002, 1.4435, and 5.2 g. $BuOP(OCH_2CH_2CN)_2$, b_8 190-2°, 1.0837, 1.4475. Addn. of 93 g. $NCCMe_2OPCl_2$ at 5° to 74 g. $BuOH$ and 79 g. pyridine in Et_2O gave after refluxing 15 min., followed by filtration, 73% $(BuO)_2POCMe_2CN$, b_{14} 134-5°, 0.9629, 1.4328, which percolated with dry O_2 9 hrs. at 76° gave 87.1% $(BuO)_2P(O)OCMe_2CN$, b_{11} 163-4°, b_4 144-5°, 1.0152, 1.4265. Heating $(NCCMe_2O)_2POBu$ with PrN failed to produce any reaction at even 150°; the result was the same with $(BuO)_2POCMe_2CN$. The following esters were prepd. by method described above: $(EtO)_2POCH_2CH_2CN$, b_{10} 119-20°, 1.0579, 1.4352; $(BuO)_2POCH_2CH_2CN$, b_8 150-3°, 1.0002, 1.4435; $(NCCH_2CH_2O)_2POBu$, b_8 190-2°, 1.0837, 1.4475; $NCCH_2CH_2OP(OCH_2CH{:}CH_2)_2$, $b_{0.5}$ 140-5°, 1.0691, 1.4636; $(NCCH_2CH_2O)_2POCH_2CH{:}CH_2$, $b_{0.5}$ 165-70°, 1.0989, 1.4580; 57% $NCCMe_2OP(OMe)_2$, b_{11} 78-80°, 1.0489, 1.4240; 58% $MeOP(OCMe_2CN)_2$, b_9 139-41°, 1.0653, 1.4382; 49% $NCCMe_2OP(OEt)_2$, b_{10} 89-91°, 1.0188, 1.4190; 39.6% $(NCCMe_2O)_2POEt$, b_8 136-9°, 1.0471, 1.4320; 60% $(iso\text{-}PrO)_2POCMe_2CN$, b_{11} 99-101°, 0.9731, 1.4221; 55% $iso\text{-}PrOP(OCMe_2CN)_2$, b_{12} 142-3°, 1.0241, 1.4360; 50 $NCCMe_2OP(OPr)_2$, b_{10} 103-4°, 0.9845, 1.4290; 34.5% $(NCCMe_2O)_2POPr$, b_{10} 147-9°, 1.0342, 1.4371; 39.4% $(iso\text{-}BuO)_2POCMe_2CN$, b_{11} 115-7°, 0.9412, 1.4241; 36.8% $iso\text{-}BuOP(OCMe_2CN)_2$, b_7 143-4°, 1.0190, 1.4380; 73% $NCCMe_2OP(OBu)_2$, b_{14} 134-5°, 0.9629, 1.4328; $(NCCMe_2O)_2POBu$, b_{11} 155-6°, 1.0150, 1.4371(76%); 66% $(iso\text{-}AmO)_2POCMe_2CN$, b_{11} 145-7°, 0.9378, 1.4320; 87% $iso\text{-}AmOP(OCMe_2CN)_2$, b_9 154-5°, 1.0021, 1.4405; 72% $NCCMe_2OP(OCH_2CH{:}CH_2)_2$, b_7 114-6°, 1.0230, 1.4425; 36% $(NCCMe_2O)_2POCH_2CH{:}CH_2$, b_{10} 151-6°, 1.0546, 1.4490; 98% $NCCMe_2OP(OPh)_2$, b_3 172-4°, 1.1448, 1.5341; 71% $(NCCMe_2O)_2POPh$, b_{11} 186-7°, 1.1035, 1.4852; 58% $NCCMe_2OP(OC_6H_{11})_2$, b_3 160-2°, 1.0488, 1.4735; 74%

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$(NCCMe_2O)_2POC_6H_{11}$, $b_7$165-6°, 1.0556, 1.4588; $NCCMe_2OP(O)OCH_2CH_2Cl$, b_{13}135-7°, 1.3215, 1.4835; 62.1% $NCCMe_2OP(OCH_2CH_2Cl)_2$, b_{11}160-3°, 1.2350, 1.4685; 90% $(NCCMe_2O)_2POCH_2CH_2Cl$, b_{10}165-7°, 1.1980, 1.4525; 81.3% $(CH_2O)_2POCMe_2CN$, b_{10}101-5°, 1.1642, 1.4515; $(iso\text{-}PrCH(CN)O)_2POCH_2CMe_2$, b_{10}167-70°, 1.0039, 1.4452; 36.5% $(CH_2)_5C(CN)OP(OCH_2CMe_2)_2$, $b_7$160-2°, 1.0034, 1.4580; 41.7% $[(CH_2)_5C(CN)O]_2POCH_2CMe_2$, $b_1$182-6°, 1.0781, 1.4805; 67% $[(CH_2)_5C(CN)O]_2POBu$, $b_{0.4}$160-2°, 1.0735, 1.4815; 47.2% $NCCMe_2OP(O)(OCH_2CH_2Cl)_2$, $b_{0.3}$185-70° (apparently should be 165-70°, GMK), 1.3147, 1.4572; 87.1% $NCCMe_2OP(O)(OBu)_2$, $b_4$144-5°, 1.0152, 1.4865; 83.5% $(NCCMe_2O)_2P(O)OBu$, $b_4$164-5°, 1.0761, 1.4330; 73% $(NCCMe_2O)_2P(O)OCH_2CMe_2$, b_{14}165-9°, 1.0690, 1.4300; 75% $(NCCMe_2O)_2P(O)OCH_2CH_2CMe_2$, b_{12}175-80°, 1.0549, 1.4323; 95% $NCCMe_2OP(O)(OCH_2CH_2Cl)_2$, $b_{0.2}$138-40°, 1.3713, 1.4555; 95% $(NCCMe_2O)_2P(O)OCH_2CH_2Cl$, $b_{0.2}$142-4°, 1.2017, 1.4459; 81% $(NCCMe_2O)_2P(O)OPh$, m.35°; 79% $(NCCMe_2O)_2P(O)OC_6H_{11}$, m.34°; $[(CH_2)_5C(CN)O]_2P(O)OCH_2CMe_2$, $b_{0.15}$165-7°, 1.1148, 1.4733; 55.7% $[(CH_2)_5C(CN)O]_2P(O)OBu$, $b_{0.15}$172-5°, 1.1206, 1.4752. The results indicate that generally phosphites with primary and secondary radicals suffer a ready radical exchange, but phosphites based on tertiary radicals are quite stable to heat and suffer no significant group exchange.

5. Hydrolysis of chlorides of dialkyl phosphorous acids.

Ibid. 187-9.

$(RO)_2PCl$ are hydrolyzed with H_2O in the presence of pyridine to bind the resulting HCl. The procedure yields $(RO)_2PHO$. To 36 g. $(BuO)_2PCl$ in 100 ml. Et_2O was added at 5° 3.3 g. H_2O, 13.4 g. pyridine and 50 ml. Et_2O; after refluxing 15 min. the mixture was filtered and distd. yielding 70% $(BuO)_2PHO$, b_{14}119-21°, d_{20}^{0}0.9908, n_D^{20}1.4241. To 24.3 g. $(PhO)_2PCl$ in Et_2O was added 1.74 g. H_2O and 7.6 g. pyridine in Et_2O, yielding similarly 73.5% $(PhO)_2PHO$, $b_{0.15}$145-8°, d_{20}1.2159, n_D^{20}1.5599, which rapidly acquires the odor of free PhOH after contact with moist air; it hydrolyzes with H_2O with heat evolution and cannot be distd. except in high vacuum. Similarly 13.2 g. $[(ClCH_2)_2CHO]_2PCl$, 0.73 g. H_2O and 3.2 g. pyridine in Et_2O gave 61.5% $[(ClCH_2)_2CHO]_2PHO$, $b_{0.4}$145-7°, d_{20}1.4855, n_D^{20}1.5010.

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Cyano substituted esters of acids of phosphorus. 6. Di-α-cyanoalkyl phosphites.

G.Kh.Kamai, E.V.Kuznetsov and R.K.Valetdinov. Trudy Kazan.Khim.Tekhnol. Inst. im. S.M.Kirova, 23, 190-6(1957).

To 44 g. $(NCCMe_2O)_2PCl$ in 150 ml. Et_2O was added with cooling at 0° 3.15 g.H_2O and 13.8 g. pyridine in 50 ml. Et_2O; after filtration and distn. there was obtained 62.1% $(NCCMe_2O)_2POH$, $b_{0.15}$118-20°, d_{20}1.1128, n_D^{20}1.4420, (I). Heating $(NCCMe_2O)_3P$ 7.5 hrs. at 165° gave a distillate of evidently MeCH(CN):CH_2, b.50-3°, d_{20}0.7649, and a residue of 78.5% I, b_{11}165-8°, n_D^{20}1.4415, d_{20}1.1115. Hydrolysis of $(NCCHMeO)_2PCl$ as above gave 33.3% $(NCCHMeO)_2POH$, $b_{0.15}$112-5°, n_D^{20}1.4400, d_{20}1.1605, obtained only in crude state. Similarly was prepd. 55% $(NCCHPrO)_2POH$, $b_{0.15}$134-5°, d_{20}1.0846, n_D^{20}1.4486, and some $(NCCHPrO)_3P$, $b_{0.15}$140-5°, 1.0421, 1.4530. Similarly was prepd. 64.5% (iso-PrCH(CN)O)$_2$POH, $b_{0.15}$123-4°, 1.0903, 1.4460, and some (iso-PrCH(CN)O)$_3$P, $b_{0.15}$135-40°, 1.048, 1.4540. The $(RO)_2POH$ shown above readily and exothermally react with CuCl and yield sirupy or glassy adducts. I reacts with PhN_3 yielding N_2 and $(NCCMe_2O)_2P(OH):NPh$, m.87°. The esters with secondary radicals react readily with PhN_3 but the products fail to crystallize. Keeping I in moist air gave $NCCMe_2OPO_2H_2.H_2O$, m.112° (from EtOH or MeOH); this in EtOH was treated with alc.$AgNO_3$ in the presence of NH_4OH yielding light-unstable colorless $NCCMe_2OP(OAg)_2.H_2O$. Reaction of 10.3 g.I and 3.7 g. pyridine in Et_2O with 12 g. $(NCCMe_2O)_2PCl$ at 0° gave 9.3% $[(NCCMe_2O)_2P]_2O$, $b_{0.2}$165-71°, d_{20}1.1370, n_D^{20}1.4555, which slowly solidified and m.28° (needles). Thus this group of esters shows evidence of true hydroxyl group at P^{III} atom; thus the above $(RO)_2POH$ are derivs. of trivalent P. $(RO)_2POH$ based on cyano substituted secondary radicals behave as other mixed esters of phosphorous acid, being capable of ready radical exchange. This is shown by formation of $(RO)_3P$ during hydrolysis of $(RO)_2PCl$ described above; such exchange also yields $ROPO_2H_2$. The feeble additive function of these $(RO)_2POH$ evidently hinders the usual course of Arbusov-type rearrangement which is common among other esters of this type and thus the trivalency of P is preserved.

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Tris(trialkylsilyl) phosphites. organosilicon phosphorus

M.G.Voronkov and Yu.I.Skerik (Silicate Chem.Inst.,Leningrad). Izvest. Akad. Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 119.

Simple distn. of a mixture of PBr_3 with an excess of R_3SiOH containing 0.5-0.6 mole % $ZnCl_2$, $FeCl_3$, $SnCl_2$ or other metallic halide yields 75-100% ~~[illegible]~~ RBr and about 30% $(R_3SiO)_3P$. Analogous reaction of PBr_3 with $(R_3Si)_2O$ gives 25-30% yields of the same products. The products are to be described in a later paper.

organosilicon phosphorus

Synthesis of some silicoorganophosphorus compounds.

E.A.Chernyshev (N.D.Zelinskii Inst.Org.Chem.,Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 96-8. Cf. Doklady Akad. Nauk SSSR 105,282 (1955).

Passage of dry O_2 at 4 l./hr. into 177.5 g. $PrSiCl_3$ and 374 g. PCl_3 at 50-70° 2 hrs. gave 24.2 g. $Cl_3SiC_3H_6POCl_2$, b_4 134-42°, n_D^{20} 1.5003; d_{20} 1.5208. This treated with H_2O and evapd. gave a polymer which after drying at 150° gave a water insoluble resin. Similarly $MePrSiCl_2$ gave 12.8% $Cl_2SiMeC_3H_6$-$POCl_2$, b_4 137-45°, 1.4978, 1.4118; $MeCH:CHSiCl_3$ gave 1.8% $Cl_3SiC_2H_3ClPOCl_2$, b_4 135-40°, 1.5068, 1.6328; $ClCH_2CH_2SiCl_3$ gave 2.1% $Cl_3SiC_2H_3ClPOCl_2$, b_4 141-6°, 1.5125, 1.6612; $Et_3SiCH:CH_2$ gave 8% $Et_3SiC_2H_3ClPOCl_2$, b_3 130-1°, 1.4948, 1.1844. The resins formed from hydrolysis of the above do not support combustion.

Compounds probably of interest for making new polymers

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