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Esters of phosphoric and thiophosphoric acid containing heterocyclic radicals. 1. Compounds with pyrimidine and imidomethyluracil radicals. B. A. Arbuzov and V. M. Zoroastrova (State Univ., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1958, 1331-39. Cf. Mel'nikov et al. Zhur. Obshchei Khim. 26, 808 (1956); Gasser, C. A. 10167(1953).

A series of phosphates and thiophosphates contg. pyrimidine and imidouracil radicals as one of the ester grouping was prepared. Treatment of 2,4-dimethyl-6-hydroxypyrimidine with theoretical amount of NaOH and evapn. gave after drying at 130° the corresponding anhydrous Na salt (I). Treatment of the pyrimidine above with $AgNO_3$ in aq. NH_4OH soln. gave the Ag salt (II). Reaction of equimolar amounts of benzamidine HCl salt and $AcCH_2CO_2Et$ in the presence of 10% NaOH gave 2-phenyl-4-methyl-6-hydroxypyrimidine, m. 215-16.5°, which gave the Na salt (III) and the Ag salt (IV). Refluxing 23.09 g. II in MePh 6 hrs. with 17.25 g. $(EtO)_2POCl$ gave after filtration and repeated distn. a P-free product, b_5 65-67°, n_D^{20} 1.4780, d_o^{20} 1.0141, whose structure was not detd., and 18% yellowish di-Et 2,4-dimethylpyrimidyl-6-phosphate, $b_{5.5}$ 153-57° (some decompn.), n_D^{20} 1.4720, d_o^{20} 1.1561; similar reaction of I in refluxing xylene (2 hrs.) gave after centrifuging and distn. a very low yield of the impure product, $b_{4-4.5}$ 147-50°, 1.4875, 1.1348, and much tar. Stirring 12 g. II in xylene with 9.8 g. $(EtO)_2PSCl$ (heat evolution on mixing) with heating 6 hrs. (temp. not indicated) gave 28% di-Et 2,4-dimethylpyrimidyl-6-thiophosphate, b_4 152-54°, 1.5060, 1.1507, sparingly sol. in cold water, in contrast to the O analog which is sol. in H_2O. Similarly 18 g. IV and $(EtO)_2POCl$ in toluene gave in 10 hrs. of refluxing 2 g. 2-phenyl-4-methyl-6-hydroxypyrimidine as a ppt. on cooling the filtrate; the residual soln. after evapn. and rubbing with petr. ether gave 50% di-Et 2-phenyl-4-methylpyrimidyl-6-phosphate, m. 69-70° (from petr. ether), sparingly sol. in cold H_2O. This heated with 1:1 HCl 2 hrs. gave the original hydroxypyrimidine. Reaction of III run as above in xylene 1.5 hrs. gave 78.3% same ester as above, m. 69-71°. IV and $(EtO)_2PSCl$ in MePh gave in 6 hrs. an

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unstated but low yield of di-Et 2-phenyl-4-methylpyrimidyl-6-thiophosphate, m. 46-48° (from petr. ether), sparingly sol. in H_2O, and obtained in not very pure state; the ester distils with much decompn., $b_{3.5-4}$ 180-82°, 1.5433, 1.1470. The crudely distd. liquid ester yields the original hydroxypyrimidine on being heated with 1:1 HCl, as does the more pure solid ester. III and $(EtO)_2PSCl$ in xylene gave 70% crude ester, identical with the above, m. 46-48° III and $(iso\text{-}BuO)_2PSCl$ in xylene (0.5 hr. reflux) gave 72.6% di-iso-Bu 2-phenyl-4-methylpyrimidyl-6-phosphate, m. 64-65° (from petr. ether or H_2O); with 1:1 HCl it gave the original hydroxypyrimidine. Treatment of hot aq. soln. of imidomethyluracil in the presence of NH_4OH with hot soln. of $AgNO_3$ gave the corresponding Ag salt (V), which was dried at 130°. This (8.1 g.) and 6 g. $(EtO)_2PSCl$ refluxed 0.5 hr. in xylene gave after filtration 51.6% di-Et 2-imido-4-methyluracil-6-phosphate, m. 110-11°(from C_6H_6-petr. ether), sol. in hot H_2O; heated with 1:1 HCl it gave the original imidomethyluracil, dec. 290°. Similar reaction of V with $(BuO)_2PSCl$ in MePh gave 57.6% di-Bu 2-imido-4-methyluracil-6-phosphate, m. 106-107° (from C_6H_6-petr. ether); with hot 1:1 HCl it gave the original imidomethyluracil. Azeotropic removal of H_2O with MePh from 7.2 g. imidomethyluracil and 7.55 g. K_2CO_3 in 2 hrs. gave the crude Na salt which was directly treated with 13.16 g. $(BuO)_2PSCl$ and refluxed 27 hrs.; the org. layer after quenching in H_2O gave 2.7 g. product, $b_{0.02}$ 84-85°, 1.4290, 0.9837, whose analysis indicated proximity to a mono-Bu ester analog of the above. V and $(iso\text{-}BuO)_2PSCl$ in xylene gave 54.7% di-iso-Bu 2-imido-4-methyluracil-6-phosphate, m. 114-16° (from petr. ether). V and $(EtO)_2PSCl$ in xylene (15 min. reflux) gave 57% di-Et 2-imido-4-methyluracil-6-thiophosphate, m. 107-108° (from C_6H_6-petr. ether), sol. in hot H_2O. Attempts to prepare phosphates and thiophosphates from Na salts of other uracils (4-methyluracil and thio-4-methyluracil) failed to yield any definite products; since the Ag salts of these uracils could not be obtained in pure form, no attempts were made to use them in the syntheses. The esters above were relatively toxic to grain weevil generally giving 100% kill at 0.05-0.1%

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concn. In mouse toxicities, the first 2 esters showed little toxicity while LD_{100} of 2.5 mg./kg. was obtained for the most toxic member, di-Et 2-imido-4-methyluracil-6-phosphate.

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Reaction of trialkyl phosphites with nitrosyl chloride and NO_2Cl.

B. A. Arbuzov and E. N. Ukhvatova (State Univ., Kazan). Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk 1958, 1395-96.

To 26.6 g. $(EtO)_3P$ was added 10.5 g. NOCl (exothermic reaction) and after finally heating on a steam bath 1 hr. the mixture yielded 49.1% $(EtO)_3PO$ (colored yellow) and about 2 g. product, b_1 131°, n_D^{20} 1.4182, d_o^{20} 1.2576, identified as crude $Et_4P_2O_7$. Similarly 13 g. $(EtO)_3P$ and 6.3 g. NO_2Cl gave 63.3% $(EtO)_3PO$ and a little $Et_4P_2O_7$. Reaction of 60.4 g. $(PrO)_3P$ with 19 g. NOCl gave 62.4% $(PrO)_3PO$, $b_{1.5}$ 87.5-88°, 1.4173, 1.0091. $(BuO)_3P$ and NOCl gave 55.2% $(BuO)_3PO$, $b_{0.5}$ 105.5-106°, 1.4265, 0.9835. Reaction of 18.2 g. NO_2Cl with 55.8 g. $(BuO)_3P$ gave 50.9% $(BuO)_3PO$. Owing to decompn. during distn., the pyrophosphates with higher alkyl groups could not be isolated. The formation of the pyrophosphates is explained by partial conversion of $(RO)_3P$ into $(RO)_2POCl$ by oxidation and chlorination, after which the product reacts with $(RO)_3PO$, formed by the direct oxidation of $(RO)_3P$, yielding the pyrophosphate by elimination of RCl.

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3-C CP

Structure of products of reaction of some -halo ketones of carbocyclic series with triethyl phosphite and diethyl sodiophosphite.

B. . rbuzov, V. .Vinogradova and N. .Polezhaeva (Ul'yanov-Lenin State Univ., Kazan). Doklady Akad.Nauk . . . .R.121, 641-3(1958).

Reaction of $(EtO)_3P$ with 2-chlorocyclohexanone yields di-Et 1-cyclohexenyl phosphate (cf. Ludovik, Zhur.Obsh.Khim.25,2173(1955)) and not the expected phosphonate. The result is the same when $(EtO)_3P$ is replaced by $(EtO)_2PONa$ and 2-bromocyclohexanone is employed, as confirmed by chemical constants and Raman spectra of the product. The Na salt however reacts with 2-chlorocyclohexanone to yield neither the phosphonate nor the unsatd.phosphate but a product which did not react with EtOH nor formed carbonyl derivs. and whose spectrum did not show the carbonyl group; this product was identified as di-Et 1,2-epoxycyclohexyl-phosphonate, $b_{2.5}$ 112-4°, n_D^{20} 1.4571, d_{20}^{20} 1.1193, which was alternatively prepd. by addn. of $(EtO)_2PHO$ to 2-chlorocyclohexanone yielding the di-Et 1-hydroxy-2-chlorocyclohexylphosphonate which with alc.KOH gave the above epoxy deriv. Reaction of either $(EtO)_3P$ or $(EtO)_2PONa$ with 2-chloro-2-methylcyclohexanone gave the same products; both treated with EtOH gave $(EtO)_3PO$ and methylcyclohexanone, which fact showed them to be di-Et 2-methyl-1-cyclohexenyl phosphate. $MeCOCBrMe_2$ and $(EtO)_3P$ or $(EtO)_2PONa$ also gave the same product: $(EtO)_2P(O)OCMe:CMe_2$. Previously reported product of reaction of $(EtO)_2PONa$ and 2-chlorocyclopentanone(this J.111,107) is di-Et 1,2-epoxycyclopentylphosphonate. Reaction of $(EtO)_2PONa$ with α-bromocamphor also gave the unsatd. phosphate, and the product from similar reaction of bromopyruvic ester turned out to be $(EtO)_2P(O)OC(:CH_2)-COCO_2Et$.

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3-d

CP

Esters of propylene glycol phosphite and their transformations. A.E.Arbuzov and N.A.Razumova (S.M.Kirov Chem.Tech.Inst., Kazan). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 1061-9. Cf. this j.1956,4877. Heating 14.7 g. $MeCHCH_2OP(OEt)O$, (I), with 10.8 g. EtBr in sealed tube 7 hrs. at 130-5° gave 49% $BrCH_2CHMeOP(O)(Et)OEt$, b_{14} 133.5-4.5°, d_o^0 1.3396, d_o^{20} 1.3184, n_D^{20} 1.4558. Similarly $MeCHCH_2OP(OBu)O$ and BuBr at 150-65° gave 10% $MeCHCH_2OP(O)(Bu)O$, $b_{0.2}$ 121.5-3°, d_o^{20} 1.1300, n_D^{20} 1.4482. Reaction of $MeCHCH_2OP(OMe)O$ with MeBr in 4 hrs. at 100° gave 38% $MeCHCH_2OP(O)(Me)O$, b_{13} 140.5-2°, d_o^{20} 1.2389, n_D^{20} 1.4415. I and $PhCH_2Cl$ in 10 hrs. at 120-30° and 3 hrs. at 170° gave [illegible] g. crystalline product, m.122-[illegible]°, identified as $MeCHCH_2OP(O)(CH_2Ph)O$, and 30% $ClCH_2CHMeOP(O)(CH_2Ph)OEt$, b_1 148-50°, d_o^0 1.1949, d_o^{20} 1.1775, n_D^{20} 1.5044. I and EtBr in 2.75 hrs. at 150-60° gave 23% $MeCHCH_2OP(O)(Et)O$, $b_{0.15}$ 101°, d_o^{20} 1.1941, n_D^{20} 1.4444. I and EtBr in 7 hrs. at 140-5° gave 25% $BrCH_2CHMeOP(O)(Et)OEt$, b_{15} 135-6.5°, n_D^{20} 1.4558, d_o^{20} 1.3180, and 10% $MeCHCH_2OP(O)(Et)O$, b_{12} 143.5-4.5°, n_D^{20} 1.4450, d_o^{20} 1.1946. $MeCHCH_2OP(OMe)O$ (9.8 g.) and 8.5 g. MeBr in 10 hrs. at 40-5° gave 11% $BrCH_2CHMeOP(O)(Me)(OMe)$, b_{13} 133.5-5°, d_o^{20} 1.4130, n_D^{20} 1.4535, and some $MeCHCH_2OP(O)(Me)O$, b_{11} 134-6°, d_o^{20} 1.2383, n_D^{20} 1.4422. Heating 14.9 g. $BrCH_2CHMeOP(O)(Et)OEt$ 3 hrs. to 140-50° in sealed tube gave 2.9 g. EtBr and $MeCHCH_2OP(O)(Et)O$, b_{16} 147-50°, d_o^{20} 1.1951, n_D^{20} 1.4450, in 6 g. yield. Similarly $BrCH_2CHMeOP(O)(Me)OMe$ in 3 hrs. at 100° gave MeBr and 62% $MeCHCH_2OP(O)(Me)O$, b_{14} 140-3°, n_D^{20} 1.4415, d_o^{20} 1.2389. I and 16% excess EtBr in 2.75 hrs. at 150-60° in sealed tube gave 30% $MeCHCH_2OP(O)(Et)O$, b_{11} 140-2°. Heating 20 g. $MeCHCH_2OP(OMe)O$ and 19 g. $PhCH_2Cl$ 10 hrs. at 135-40° gave 35.5% $MeCHCH_2OP(O)(CH_2Ph)O$, m.1[illegible]2-2.5°. Heating 12 g. $MeCHCH_2O$-$P(OMe)O$ with 2 g. MeBr 4 hrs. at 100° gave 50% $MeCHCH_2OP(O)(Me)O$, b_{16} 145-50°, n_D^{20} 1.4422. The results suggest that the haloalkyl esters formed initially and were transformed then into the cyclic esters. If I and its analogs are treated with alkyl iodides at 100-50°, the products are undistillable and often decompose violently with loss of iodine.

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Also reported are: $BrCH_2CHMeOP(O)(Pr)OPr$, b_1 121°, d_4^{20} 1.2188, n_D^{20} 1.4520; $BrCH_2CHMeOP(O)(OCHMe_2)OCHMe_2$, b_6 125-7°, 1.2490, 1.4545; $BrCH_2CHMeOP(O)$-(Me)OPh, $b_{0.07}$ 187°, 1.3641, 1.5188.

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3-2 CP

Anomalous reaction of -halo ketones with esters of phosphorous acid. VII. Reactions of esters of phosphorous acid with chloro derivatives of -diketones.

A.N.Pudovik and L.G.Biktimirova (State Univ., Kazan). Zhur.Obshchei Khim. 28, 1496-1500(1958). Cf. this j.26,2238(1956).

Addn. of $(RO)_3P$ to equimolar amount of monochloro or dichloro-acetylacetone or benzoylacetone led to exothermic reaction with distn. of RCl; after 1 hr. on a steam bath the products were distd. Thus were obtained: $R'C(OPO(OR)_2):CXCOR''$ (R, R', R'', X shown resp.): Me, Me, Me, H, $b_2$103-4°, d_{20}1.2040, n_D^{20}1.4572; Bu, Me, Me, H, $b_1$125-7°, 1.0503, 1.4510; Me, Me, Me, Cl, $b_2$115°, 1.3065, 1.4710; Bu, Me, Me, Cl, $b_2$133-9°, 2.1202, 1.4618; Me, Ph, Me, H, $b_1$138-9°, 1.2278, 1.5262; Et, Ph, Me, H, $b_2$170-2°, 1.1611, 1.5135; Me, Ph, Me, Cl, $b_{2.5}$156-7°, 1.2969, 1.5223; Et, Ph, Ph, H, $b_3$208°, -, 1.5490. The yields of these anomalous products were 60-80% and their structures were confirmed by bromination and hydrolysis to the initial diketone. Except for the last specimen above, the unsatd. esters were sterable without decompn. Heating I to 160° 2 hrs. gave benzoylacetone and tar. Reaction of $(EtO)_3P$ with 2-chloro-5,5-dimethylcyclohexane-1,3-dione (II) in C_6H_6 at reflux 2 hrs. gave a low yield of 5,5-dimethyl-1,3-cyclohexanedione; 2,2-dichloro-5,5-dimethylcyclohexane-1,3-dione treated similarly gave some II and a low yield of 2-chloro-5,5-dimethyl-1-cyclohexen-3-enyl diethyl phosphate, $b_{2.5}$160-1°, n_D^{20}1.4818. Thermograms are shown for the typical reactions of $(RO)_3P$ with the halodiketones and for thermal decompn. of the unsatd. phosphate esters shown above.

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3-f CP

Anomalous reaction of phosphites with -halo ketones. VIII. Reaction of mixed phosphites with chloro- and dichloroacetone.

A.N.Pudovik and E.G.Chebotareva (State Univ.,Kazan). Zhur.Obshchei Khim. 28, 2492-6(1958). Cf. this j.26,1431(1956).

To 30-40 g. $(RO)_2POR'$ preheated to 120-40° there was gradually added equimolar amount of $ClCH_2Ac$ or Cl_2CHAc; after 1 hr. at 120-30° the mixture was distd. yielding the following products. $(iso\text{-}BuO)_2POEt$ and Cl_2CHAc gave 63.3% $(iso\text{-}BuO)_2P(O)OCMe{:}CHCl$, $b_9$139.5-40°, d_{20}1.0855, n_D^{20}1.4402; $(EtO)_2POPh$ gave 51.5% $(EtO)_2P(O)OCMe{:}CHCl$, $b_1$130-1°, 1.2446, 1.4972; $(BuO)_2POPh$ gave 61.4% $(BuO)_2P(O)OCMe{:}CHCl$ (A), $b_3$155-6°, 1.1800, 1.4917. $(isoBuO)_2POEt$ and $ClCH_2Ac$ gave 69.3% $(iso\text{-}BuO)_2P(O)OCMe{:}CH_2$ (I), $b_9$122-3°, 0.9960, 1.4245; $(EtO)_2POPh$ gave 58.3% $(EtO)(PhO)P(O)OCMe{:}CH_2$, b_{10}151.5-2°, 1.1423, 1.4845, and 17% $(EtO)(PhO)P(O)CH_2Ac$ (II), $b_8$178-9°, 1.1883, 1.5005. $(BuO)_2POPh$ gave 49.2% $(BuO)(PhO)P(O)OCMe{:}CH_2$, $b_9$166-7°, 1.1005, 1.4825 and 13.5% $(BuO)(PhO)P(O)CH_2Ac$ (III), $b_4$176-7°, 1.1276, 1.4944. $(PhO)_2POBu$ gave 57.4% $(PhO)_2P(O)OCMe{:}CH_2$, $b_{1.5}$186°, 1.2271, 1.5483. $(Et_2N)_2POEt$ gave 40% $(Et_2N)_2P(O)OCMe{:}CH_2$, $b_8$124-5°, 0.9920, 1.4520, and 8.3% $(Et_2N)_2P(O)CH_2Ac$, $b_8$149-50°, 1.0413, 1.4709. Heating I with EtONa-EtOH gave Me_2CO. Hydrolysis of II with 30% H_2SO_4 was vigorous on heating and gave a distillate of Me_2CO. Ozonolysis of III gave CH_2O. Chlorination of A in CCl_4 gave $(BuO)(PhO)P(O)$[redacted]$MeClCHCl_2$, $b_4$180-1°, 1.2837, 1.5020. Thus the reaction of mixed phosphites invariably involves the ester group of the lowest mol.wt.

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3-9

Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XVIII. Phenyl esters of α-hydroxyalkylphosphonic acids.

V. S. Abramov and N. A. Semenova (S. M. Kirov Chem. Tech. Inst., Kazan).

Zhur. Obshchei Khim. 28, 3056-58 (1958).cf. 22, 647 (1952).

Esters of general form $(PhO)_2P(O)C(OH)RR'$ (I) were prepd. as shown below by simultaneous hydrolysis of $(PhO)_3P$ and coupling of the resulting $(PhO)_2PHO$ with carbonyl compds. in situ. To a mixture of equimolar amounts of $(PhO)_3P$ and an aldehyde or a ketone there was added the equimolar amount of H_2O and the whole was shaken (exothermic effect). In case of AcPh external heating was required. Then the mixture was either set aside or was heated on a steam bath to complete the action. After removal of PhOH by washing with H_2O, the products crystallized. The following compds. were prepd. thus (temp. in parentheses indicates the conditions used for reaction proper): I (R,R' shown resp.): Et, H, (spontaneous), 20%, m. 87-87.5° (from aq. EtOH); Pr, H, (spontaneous), 32%, m. 63-64° (from cyclohexane); CCl_3, H, (spontaneous), 80%, m. 131-31.5° (EtOH-cyclohexane); Ph, H, (spontaneous), 84%, m. 147-48° (96% EtOH); 3-cyclohexyl, H, 88%, m. 112-14° (cyclohexane); m-$O_2NC_6H_4$, H, (spontaneous), 20%, m. 98.5-100° (cyclohexane); Me, Me, (spontaneous), 32%, m. 116-17° (from cyclohexane); Me, CH_2Cl (spontaneous), 22%, m. 122-23° (from aq. EtOH); CH_2Cl, CH_2Cl, (spontaneous), 18%, m. 112-14° (from aq. EtOH); Ph, Me, (steam bath), 20%, m. 126-27.5° (from cyclohexane-EtOH); $(CH_2)_4$, (spontaneous), 25%, m. 126-27° (from cyclohexane); $(CH_2)_5$, (steam bath), 30%, m. 127-28° (from cyclohexane). Many other such products were not crystallizable and are not listed in the publication.

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3-n CP

Reaction of aryl(alkyl)phosphinic acids with aldehydes and ketones.

XIX. Esters of α-hydroxyalkylphenylphosphinic acids.

V. S. Abramov and M. I. Kashirskii (S. M. Kirov Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 28, 3059-61 (1958). cf. 22, 257 (1952); and Hamilton et al. JACS 79, 424 (1957).

Equimolar mixtures of PhP(O)(OR)H and an aldehyde or a ketone were either kept at room temp. for several days or, mainly with ketones, were heated on a water bath 1.5-2 days, to yield crystalline products of general type: PhP(O)(OR)CR'R"OH (R, R', R" shown resp.) as follows: Me, CCl_3, H, 23%, m. 122-23° (from aq. Me_2CO); Me, m-$O_2NC_6H_4$, H, 20%, m. 155-56° (from abs. EtOH); Et, Pr, H, 15%, m. 122-23.5° (from abs. EtOH); Et, Ph, H, 25%, m. 182-82.5° (from 96% EtOH); Et, m-$O_2NC_6H_4$, H, 20%, m. 120-21° (from Me_2CO); Bu, Ph, H, 25%, m. 76-78° (from aq. Me_2CO); Bu, m-$O_2NC_6H_4$, H, 23%, m. 120-21.5° (from abs. EtOH); Iso-Bu, Ph, H, 58%, m. 100-101° (from abs. EtOH); iso-Bu, m-$O_2NC_6H_4$, H, 66%, m. 142-43° (from abs. EtOH); iso-Bu, Me, Me, 16%, m. 94-95.5° (from Me_2CO); iso-Bu, Ph, Me, 28%, m. 150-51° (from 96% EtOH). The completion of reaction was judged by the formation of crystals in the reaction mixture. Since the crude yields of the products were 70-90%, it is possible that the loss of yield in purification may be caused by partial dissocn. of the products into the starting materials.

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Synthesis of octaalkyltetramidopyrophosphates and octaalkyltetramido-thiopyrophosphates.

A.V.Nikonorov and [illegible]peranskaya ([illegible]rbuzov Inst., Kazan). Izvest. Akad. Nauk [illegible], Otdel. Khim. Nauk 1958, 964-7.

Heating $(R_2N)_2PCl$ and $(R_2N)_2P(OEt)$, or their corresponding thiono analogs, 12-16 hrs. at 130-70° gave the following pyro derivs.: 32% $(Me_2N)_2P(O)OP(O)(NMe_2)(NEt_2)$, $b_{0.04}$ 138-3°, d_{20} 1.1067, n^{20}_D 1.4625; 47.5% $(Me_2N)_2P(O)OP(O)(NEt_2)_2$, b_2 150-7°, 1.0851, 1.4640; (xx 54% $(Me_2N)(Et_2N)P(O)OP(O)(NEt_2)_2$, $b_{1.5}$ 159-60°, 1.0827, 1.4645; 43 48.4% $(Me_2N)_2P(O)OP(O)(NMe_2)(NEt_2)$, b_2 150-2°, 1.1178, 1.4912; $(Me_2N)_2P(O)OP(O)(NEt_2)_2$, 30%, $b_{0.05}$ 128-31°, 1.0951, 1.4928; 46% $(Me_2N)(Et_2N)P(O)OP(O)(NEt_2)_2$, $b_{1.5}$ 171-2°, 1.0754, 1.4910; 48.3% $(Et_2N)_2P(O)OP(O)(NEt_2)_2$, $b_{0.02}$ 159-61°, 1.0611, 1.4900. Reaction of $(R_2N)_2PCl$ with H_2O in presence of Et_3N gave; after 6-7 hrs. at 80-90°, the folowing: 40.9% $(Me_2N)(Et_2N)P(O)OP(O)(NMe_2)(NEt_2)$, b_2 153-5°, 1.0831, 1.4630, and 30.4% $(Et_2N)_2P(O)OP(O)(NEt_2)_2$, b_1 174-6°, 1.0444, 1.4650. The pyrophosphate derivs. showed 1.7-1.8 units negative exaltation of molar refraction, while the thio derivs. showed a 1.5 unit negative exlatation; it is suggested that new values for P or N must be found in this group of substances.

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Synthesis of some esters of α-(dialkylphosphono)-β,β,β-trichloroethyl phosphoric acid and α-(dialkylphosphono)-β,β,β-trichloroethyl esters of carboxylic acids and their derivatives.

K. V. Nikomorov (A. E. Arbuzov Chem. Inst., Acad. Sci., Kazan). Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1958, 1340-44. Cf. Barthel et al. JACS 76, 4186 (1954) and 77, 2424 (1955).

To $(MeO)_2P(O)CH(OH)CCl_3$ or the di-Et ester analog in Et_2O or Et_2O-C_6H_6 there was added Et_3N and the calcd. amount of $(RO)_2POCl$ and the mixture was stirred 12 hrs. at room temp. After filtration and distn at 0.02 mm in a molecular still there were obtained the following $(RO)_2P(O)CH(CCl_3)OP(O)(OR')_2$ (R and R' shown resp.): Me, Me, 55.2%, $b_{0.05}$ 118-20°, n_D^{20} 1.4592, d_{20} 1.4798; Me, Et, 55.5%, $b_{0.05}$ 119-21°, 1.4590, 1.4128; Me, Pr, 50.5%, $b_{0.02}$ 120-22°, 1.4506, 1.3228; Me, iso-Pr, 41.5%, $b_{0.05}$ 116-17°, 1.4540, 1.2880; Me, Bu, 52%, $b_{0.05}$ 132-33°, 1.4515, 1.2608; Me, iso-Bu, 52.5%, $b_{0.02}$ 129-31°, 1.4608, 1.3047; Et, Et, 63.1%, $b_{0.05}$ 126-28°, 1.4642, 1.3551; Et, Pr, 58.2%, $b_{0.02}$ 139-40°, 1.4580, 1.2904; Et, iso-Pr, 57%, $b_{0.02}$ 129-31°, 1.4606, 1.3040; Et, Bu, 66.6%, $b_{0.02}$ 145-48°, 1.4422, 1.2140; Et, iso-Bu, 53.5%, $b_{0.05}$ 140-42°, 1.4635, 1.2657; also prepd. was $(EtO)_2P(O)CH(CCl_3)OP(S)(OEt)_2$, 41.1%, $b_{0.02}$ 136-39°, 1.4572, 1.3036. Similar reaction with RCOCl in 2-3 hrs. gave the following $(RO)_2P(O)CH(CCl_3)O_2CR'$: Me, Me, 80.8%, $b_{0.05}$ 83-84°, 1.4730, 1.4724; Me, Et, 72.5%, $b_{0.015}$ 92-93°, 1.4730, 1.4251; Me, Pr, 65%, $b_{0.05}$ 112-14°, 1.4740, 1.3998; Me, iso-Pr, 64.5%, $b_{0.05}$ 110-12°, 1.4725, 1.3957; Me, CHMeEr, 59%, $b_{0.04}$ 130-31°, 1.4925, 1.6290; Et, Me, 70%, $b_{0.027}$ 90-93°, 1.4650, 1.3651; Et, Et, 72.5%, $b_{0.05}$ 96-97°, 1.4658, 1.3269; Et, Pr, 75%,

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$b_{0.05}$ 124-25°, 1.4685, 1.3141; Et, iso-Pr, 58%, $b_{0.02}$ 115-19°, 1.4660, 1.3033; Et, CHMeBr, 66.2%, $b_{0.05}$ 136-37°, 1.4846, 1.5074; Et, NEt_2, 44.2%. $b_{0.04}$ 120-21°, 1.4740, 1.2964. The above reactions run with pyridine instead of Et_3N are very much more slow. The above products showed some systemic insecticidal activity (no details).

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3-h CP

Some new forms of the Arbuzov rearrangement.

V.A.Kukhtin (AllUnion Sine-Photo Res.Inst.Kazan Branch, Kazan). Doklady Akad.Nauk S.S.S.R.121, 466-9(1958).

It was shown that $(RO)_3P$ react readily with Ac_2 yielding $(RO)_2P(O)OCMe:CMeOR$. Thus were obtained: 23.3% $(EtO)_2P(O)OCMe:CMeOEt$, b_{10} 127-30°, n_D^{20} 1.4250, d_{20} 1.1061; 46.7% $(PrO)_2P(O)OCMe:CMeOPr$, b_{10} 140-2°, 1.4230, 1.0752; 42.6% $(BuO)_2P(O)OCMe:CMeOBu$, b_{10} 145-50°, 1.4240, 1.0192. It is suggested that the reaction proceeds by nucleophilic attack by P on a carbonyl C atom, the resulting adduct (bipolar ion) rearranging rapidly to the bipolar ion $(RO)_3\overset{+}{P}OCMe:CMe\overset{-}{O}$, which passes to a cyclic intermediate $(RO)_3P(OCMe:)_2$, which then yields the final product (Cf. Bengelsdorf, J.Org.Ch.21,475(1956), Kamai et al. this j.109,91(1956) and 112,867(1957)). Careful hydrolysis of the products with 2% HCl gave $(RO)_2P(O)OCHMeCOMe$: 30.7% $(EtO)_2P(O)OCHMeAc$, b_{12} 132-4°, 1.4230, 1.1122. Drastic hydrolysis gave H_3PO_4. If the original reaction is run in mild conditions (20-30° in Et_2O) it is possible to isolate the intermediates which are similar to intermediates in the reaction of phosphites with unsatd. acids (cf. Kamai ref. above): 47.2% $(EtO)_3P(OCMe:)_2$, b_{10} 104-5°, 1.4290, 1.0825, and 37.1% $(PrO)_3P(OCMe:)_2$, b_{10} 127-30°, 1.4305, 1.0256. These react with H_2O with exothermic effect and yield the keto ester shown above; on heating or prolonged standing the unsatd. phosphate is formed; addn. to acrylic acid results in energetic telomerization reaction. The stability of these cycles is attributed to the ionic character: pos. charge at P and neg. charge at one O atom, this being distributed among 2 O atoms for stabilization. The reaction is considered as a new form of Arbuzov reaction.

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3-X CP

Addition of complete esters of phosphorous and phosphonous acids to conjugated systems. VI. Combined action of alkyl halides and , -unsaturated acids on trialkyl phosphites.

V. A. Kukhtin and K. M. Orekhova (S. M. Kirov Chem. Technol. Inst., Kaza...). Zhur. Obshchei Khim. 28, 2790-97 (1958). Cf. this j. 28, 1196 (1958).

To 15 g. $(EtO)_3P$ and 11.1 g. PrBr was added 7.78 g. $CH_2:CMeCO_2H$ and heated 6 hrs. at 95-6°, yielding among other products 8 g. $(EtO)_2P(O)CH_2CHMeCO_2$..., b_8 139-40°, n_D^{20} 1.4350, d_{20} 1.068. Similarly were prepd.: 17.8% $(EtO)_2P(O)$-$CH_2CHMeCO_2CH_2CHMe_2$, b_9 144-46°, 1.4360, 1.052; 15.6% $(EtO)_2P(O)CH_2CHMeCO_2$-$CH_2CH_2CHMe_2$, b_8 146-48°, 1.4310, 1.001; 79% $(EtO)_2P(O)CH_2CH_2CO_2CHMe_2$, b_8 150-51°, 1.4335, 1.071; 52% $(EtO)_2P(O)CH_2CH_2CO_2Pr$, b_{12} 154-56°, 1.4330, 1.070; 53.5% $(PrO)_2P(O)CH_2CHMeCO_2CH_2CHMe_2$, b_9 164-65°, 1.4370, 1.007; 42.6% $(BuO)_2P(O)CH_2CHMeCO_2Pr$, b_8 178-80°, 1.4410, 1.023; 8.4% $(BuO)_2P(O)CH_2CHMe$-CO_2Et, b_{10} 180°, 1.4420, 1.033; 55% $(BuO)_2P(O)CH_2CH_2CO_2Et$, b_4 190-92°, 1.4385, 1.026. To 25 g. $(BuO)_3P$ was added dropwise 9.6 g. $CH_2:CMeCO_2H$ and after 3 days at room temp. no $(RO)_3P$ remained in the mixture (test with Cu_2X_2); the mixture was treated with 12.1 g. EtBr and refluxed 3 hrs. yielding 20 g. $(BuO)_2P(O)CH_2CHMeCO_2Et$, 58.5%, b_9 180-81°, 1.4420, 1.034. Keeping 20 g. $(EtO)_3P$, 23.8 g. iso-AmI and 10.3 g. $CH_2:CMeCO_2H$ 2 days at room temp. gave 11.6 g. colorless solid ppt., dec. 240-50°, generally insol. except in MeOH, identified as $(EtO)_2P(O)(CH_2CHMeCO_2)_3$-$CH_2CHMeCO_2CH_2CH_2CHMe_2$; distn. of the liquid portion gave 2 g. EtI, 3 g. $(EtO)_2PHO$, 1 g. iso-$AmP(O)(OEt)_2$ and 5 g. $(EtO)_2P(O)CH_2CHMeCO_2CH_2CH_2CHMe_2$. Similarly were run expts. with RI, $CH_2:CMeCO_2H$ and $(RO)_3P$, which gave: from $(EtO)_3P$, $CH_2:CMeCO_2H$ and PrBr - 20% $CH_2:CMeCO_2Et$, 55.6% $(EtO)_2PHO$, and 27.8% $(EtO)_2P(O)CH_2CHMeCO_2Pr$, b_8 139-40°, 1.4350, 1.068 (run at 95°); from $(EtO)_3P$, RCO_2H and PrBr at 16° - 88% PrBr, 19% $(EtO)_2PHO$ and 57.5% $(EtO)_2P(O)CH_2CHMeCO_2Et$, b_8 140-42°, 1.4340, 1.081; from $(BuO)_3P$, RCO_2H and PrBr at 95° - 27% BuBr, 17% $CH_2:CMeCO_2Bu$, 36% $(BuO)_2PHO$ and 42.6% $(BuO)_2$-$P(O)CH_2CHMeCO_2Pr$, b_8 178-80°, 1.4410, 1.023; from $(PrO)_3P$, RCO_2H and iso-

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BuBr at 95° - 12% PrBr and 53.5% $(PrO)_2P(O)CH_2CHMeCO_2CH_2CHMe_2$, b_9 164.5-65°, 1.4370, 1.007; from $(EtO)_3P$, $CH_2:CHCO_2H$ and iso-PrBr at 85° - 79% $(EtO)_2P(O)CH_2CH_2CO_2CHMe_2$, b_8 150-51°, 1.4335, 1.071; from $(EtO)_3P$, iso-PrBr and $CH_2:CHCO_2H$ at 20° - 52% $(EtO)_2P(O)CH_2CH_2CO_2CHMe_2$, b_{12} 154.6°, 1.4330, 1.070; from $(EtO)_3P$, $CH_2:CMeCO_2H$ and iso-BuI at 15° - 39.2% solid $(EtO)_2P(O)(CH_2CHMeCO_2)_{11}CH_2CHMe_2$, 10.6% EtI, some $CH_2:CMeCO_2Et$, 19% $(EtO)_2PHO$ and 17.8% $(EtO)_2P(O)CH_2CHMeCO_2CH_2CHMe_2$, b_9 144-46°, 1.4360, 1.0520; from $(EtO)_3P$ and $CH_2:CMeCO_2H$ and iso-AmI at 16° (described above). $(BuO)_3P$, $CH_2:CMeCO_2H$ and EtI at 16° - 20% BuI, 6.8% $(BuO)_2P(O)(CH_2CHMeCO_2)_4Et$, solid, 10% $EtP(O)(OBu)_2$, and 8.4% $(BuO)_2P(O)CH_2CHMeCO_2Et$, b_{10} 180°, 1.4430, 1.033; from $(BuO)_3P$, $CH_2:CHCO_2H$ and EtI at 20° - 20% BuI, 24% $(BuO)_2PHO$, 55% $(BuO)_2P(O)CH_2CH_2CO_2Et$, b_4 190-92°, 1.4385, 1.024, and from evidently cyclic adduct of $(BuO)_3P$ and $CH_2:CMeCO_2H$ prepd. at room temp. and EtBr at 80° - 58.5% $(BuO)_2P(O)CH_2CHMeCO_2Et$. The telomeric products were colorless infusible and generally insol. solids. The probable mechanisms of the addns. described above are discussed.

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4-a

β-Ethylmercaptoethyl phosphites and some of their properties.

T.Ya.Medved and M.I.Kabachnik (Inst.Hetero-org.Compds.,Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 1212-18.

Reaction of PCl_3 with 3 moles $EtSCH_2CH_2OH$ (I) failed to yield $(RO)_2PHO$ and gave only $ClCH_2CH_2SEt$. However, addn. of 47.7 g. $EtSCH_2CH_2OH$ to 20.7 g. PCl_3, 400 ml. Et_2O and 54.5 g. $PhNMe_2$ at -5°, stirring 1 hr. at 0° and 0.5 hr. at room temp., gave after filtration and distn. 64% $(EtSCH_2CH_2O)_3P$ (A), $b_{0.0007}$ 87-90°, n_D^{20} 1.5213, d_{20} 1.1184 (b_2 181-3° with decompn.). Reaction of PCl_3 (6.8 g.) in C_6H_6) at 7-8° with 12.1 g. $PhNMe_2$ and 10.6 g. I, stirred 0.5 hr., the treated with addnl. 5.3 g. I, stirred 0.5 hr., filtered, washed with H_2O, 5N NH_4OH and H_2O, gave on distn. 49% $(EtSCH_2CH_2O)_2PHO$ (II), $b_{0.0007}$ 110-2°, 1.5048, 1.1551; the same product formed in 53% yield ($b_{0.0004}$ 112.5-3°, 1.5057, 1.1573) when 6.9 g. PCl_3 in C_6H_6 was treated at 10° with 10.6 g.I and 12.1 g. $PhNMe_2$ in C_6H_6, stirred 20 min., treated dropwise with 15 ml. H_2O, and the org.layer sepd. and washed as above. Reaction of $EtOPCl_2$ with I in the presence of $PhNMe_2$ as above gave 34% $(EtSCH_2CH_2O)(EtO)PHO$, b_2 104-5°, 1.4688, 1.1284. For satisfactory isolation of II, the reaction mixture must be freed of all acidic material prior to distn. Treatment of 5.2 g. II with 0.46 g.Na in C_6H_6 1.5 hrs. at 40-5° and addn. of 0.65 g. S to the soln. and heating 1 hr. at 50° gave 48.5% $(EtSCH_2CH_2O)_2POSNa$, needles, m.109-10° (from Et_2O-petr.ether). Reaction of II with Na, as above, followed by MeI, followed by refluxing 3 hrs. in Et_2O gave $MeP(O)(OCH_2CH_2SEt)_2$ (III), 65%, $b_{0.0008}$ 108-9°, 1.5020, 1.1404; the same formed in 57% yield from 6.9 g.A and 2.8 g.MeI heated carefully on a steam bath 1 hr.(2 layers formed; only the upper layer was investigated), the product, $b_{0.0004}$ 108°, 1.5027, 1.1448; the same ester, $b_{0.001}$ 111°, 1.5030, 1.1412, formed in 59% yield from $MePOCl_2$ and I in the presence of $PhNMe_2$. Refluxing 5 hrs. 7.45 g. $MePSCl_2$, 10.1 g. Et_3N, 10.6 g. I and 50 ml. C_6H_6 gave after aq.treatment 21% $MePS(OCH_2CH_2SEt)_2$, $b_{0.001}$ 123-4°, 1.5362, 1.1497. III forms dimethiodide, a sirup;

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and a mono-Me Me sulfate, a sirup. To 0.42 g. BzH and 1.04 g. II was added 2 drops MeONa soln. (spontaneous reaction) and after 5 min. at 80°, the mixture was washed with aq. $NaHSO_3$ and NaCl, yielding 50% colorless sirupy $PhCH(OH)P(O)(OCH_2CH_2SEt)_2$. Into 15.5 g. II and 5.2 g. Me_2CO there was passed dry NH_3, then the mixture was heated 15 min. at 50-60°, and 1 hr. at 100°, cooled, extd. with Et_2O, the ext. washed with H_2O, dried and evapd. in vacuo leaving a liquid residue of $Me_2C(NH_2)PO(OCH_2CH_2SEt)_2$, n_D^{20} 1.5056, d_{20} 1.1167; it decomposes on attempted distn.; it forms a monopicrate, m. 99-100°, which with NaOH regenerates the original ester. Similar reaction of $(EtSCH_2CH_2O)(EtO)PHO$ gave 33.8% $Me_2C(NH_2)PO(OEt)(OCH_2CH_2SEt)$, b_3 131-2°, n_D^{20} 1.4778, d_{20} 1.0886; monopicrate, m. 114-5°. Passage of dry NH_3 into 7.1 g. 1,2,5-trimethyl-4-piperidone and 9.9 g. $(EtSCH_2CH_2O)(EtO)PHO$ and heating in a stream of NH_3 1.5 hr. at 60° and 2 hrs. at 100°, gave after addn. of Et_2O, washing the ext. and distg., 18% Et 2-ethylmercaptoethyl 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonate, $b_{0.0001}$ 128-32°, n_D^{20} 1.5008, d_{20} 1.0952.

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Synthesis and evaluation of complex forming ability of some organophosphorus compounds.

M.I.Kabachnik, T.Ya.Medved, G.K.Kozlova, V.S.Balabukha, M.M.Senyavin and L.I.Tikhonov(Inst.Hetero-org.Compds.,Acad.Sci.,Moscow). Izvest.Akad.Nauk U.S.S.R., Otdel.Khim.Nauk 1958, 1070-5.

Reaction of $(RO)_2PHO$ with diamines and aldehydes or ketones resulted in formation of compounds of type $(CH_2NHCRR'P(O)(OR)_2)_2$, which were hydrolyzed to the free acids, which were ested for complex forming ability by the chromatographic method of Senyavin and Tikhonova (Zhur.Neorg.Khim.1,12, 2772(1956)). It was found that the 3 diphosphonic acids reported here form relatively stable complexes with ions of Yb and Y; aminoalkylphosphonic acids also form such complexes but these are much less stable.

To 13.8 g. $(EtO)_2PHO$ and 3 g. $(CH_2NH_2)_2$ was added dropwise 5.8 g. Me_2CO and after 15 min. at 80-5°, the mixture was stirred with Et_2O, decanted from a syrup and treated with picric acid, yielding 61% $[CH_2NHCMe_2PO(OEt)_2]_2 \cdot 2C_6H_2(NO_2)_3OH$, m.151. If the ethereal soln. is refluxed with concd.HCl 7 hrs. there is formed 25% $[CH_2NHCMe_2PO(OH)_2]_2 \cdot 2H_2O$, m.230-1° (from dil.HCl). Similar reaction with $(MeO)_2PHO$ run in C_6H_6 gave on evapn. of the solvent 43% $[CH_2NHCMe_2P(O)(OMe)_2]_2$, m.96-7°, whose dipicrate, m.164-5°; the free acid, m.230-1°, as above. Use of $(EtO)_2PHO$ and $MeEtCO$ similarly gave 40% $[CH_2NHCMeEtPO(OEt)_2]_2 \cdot 2C_6H_2(NO_2)_3OH$, m.125-6° (whose dipicrate, m.156°). $(EtO)_2PHO$ and EtCHO gave the corresponding ester which was directly hydrolyzed to $[CH_2NHCHEtPO(OH)_2]_2$ m.240°, in 21% yield. Use of BzH gave 47% $[CH_2NHCHPhPO(OEt)_2]_2 \cdot 2C_6H_2(NO_2)_3OH$ m.193-4°; free acid, m.236°, contains $2.5H_2O$.

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4- C

CP

Reaction of trialkyl phosphites with phosgene.

M. I. Kabachnik and P. A. Rossiiskaya (Inst. Hetero-org. Compds., Moscow).

Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1958, 1398.

A retraction. Although it was reported previously (this j. 1957, 48) that $(RO)_3P$ and $COCl_2$ yield ~~[illegible]~~ $(RO)_2P(O)COCl$, a repetition of the expts. showed that such compds. are not formed and the reaction yields RCl, CO and $(RO)_2POCl$. Hence all derivs. given in the previous paper are incorrectly characterized; their structure is now undetd. Passage of dry Cl_2 at -5° into 24.8 g. $(MeO)_3P$ gave 17.6 g. $(MeO)_2POCl$, b_{11} 65-67°, n_D^{20} 1.4167, d_{20} 1.3286; with $PhNH_2$ it gave $(MeO)_2PONHPh$, m.88-89°. [redacted]

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Organophosphorus insecticides. Some derivatives of methylthiophosphonic and methyldithiophosphonic acids.

M.I.Kabachnik, N.N.Godovikov, D.M.Paikin, M.P.Shabanova, N.M.Gamper and L.P. Fimova. Zhur.Obshchei Khim.28, 1568-73(1958).

Reaction of MeCl with PCl_3 and $AlCl_3$, followed by H_2O, gave $MePOCl_2$ which with P_2S_5 gave $MeP(S)Cl_2$(cf. Doklady Akad.Nauk SSSR,110,217(1956)), which with equimolar amounts of ROH and Et_3N in Et_2O, finally at reflux 0.5 hr., gave: MeP(S)(OMe)Cl, b_{21}54-5°, n_D^{20}1.5085, d_{20}1.2574, MeP(S)(OEt)Cl, $b_8$55-55.5°, 1.4958, 1.1992; MeP(S)(OPr)Cl, $b_7$66-7°, 1.4890, 1.1549, in 70-80% yields. These treated with equimolar amount of p-$O_2NC_6H_4OH$ in EtOH with equimolar amount of EtONa gave after filtration of NaCl and distn. the following: MeP(S)(OMe)$OC_6H_4NO_2$-p, (I) m.52-3°, 71%; MeP(S)(OEt)$OC_6H_4NO_2$-p, m.35-6°, 84%. Similarly the chloride with equimolar amount of NaOEt in EtOH with 4-methyl-7-hydroxycoumarin gave after heating to complete the reaction 90% O-ethyl O-7(4-methylcoumaryl) methylthiophosphonate, m.72-3°. Heating the ester chloride with equimolar amount of an ester of mercaptosuccinic acid in the presence of equivalent amount of Et_3N in Et_2O 1 hr. gave: 38% MeP(S)(OMe)SCH(CO_2Me)CH_2CO_2Me, $b_{3.5}$155-6°, n_D^{20} 1.5269, d_{20}1.2765; MeP(S)(OEt)SCH(CO_2Me)CH_2CO_2Me, $b_2$166-7°, 1.5065,1.1818 (41%). Similarly the ester chloride heated 1 hr. with equivalent amount of $HOCH_2CH_2CH$ and NaOH in dry C_6H_6 gave: 59% MeP(S)(OMe)OCH_2CH_2SEt, undistd., 1.5204, 1.1861, and 52% MeP(S)(OEt)OCH_2CH_2SEt, $b_1$78°, 1.5050, 1.1124. Of all the compds. above only I was more active contact insecticide than its ester analog: parathion Me ester; all others were less active than their ester analogs among thiophosphates.

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4-2 CP

Derivatives of unsaturated phosphonic acids. 21. Esters and amides of -isooctyloxyvinylphosphonic acid.

K.N.Anisimov and B.V.Raisbaum (Inst.Hetero-org. Compounds, Moscow). Izvest. Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 1208-11. Cf. 1954, 610.

To 166.5 g. PCl_5 suspended in 150 ml. C_6H_6 was added 61 g. $BuEtCHCH_2OCH:CH_2$ and on the following day the mass was treated with SO_2 and distd. yielding 85.5% $BuEtCHCH_2OCH:CHPOCl_2$, $b_3$151-2°, n_D^{20}1.4363, d_{20}1.087. This treated with slight excess of EtOH in C_6H_6 in the presence of pyridine, finally on a steam bath 2 hrs., gave after filtration and aq. washing, 85.4% $BuEtCHCH_2OCH:CHP(O)(OEt)_2$, $b_0$143-4°(Note: the paper has O for vacuum indication- GMK), 1.4553, 1.0084. Similarly were prepd.: 77% di-Pr ester, $b_2$168-70°, 1.4530, 0.9782; 69% di-Bu ester, $b_{2.5}$182-3°, 1.4540, 0.9631; 69% di-iso-Bu ester, $b_{0.5}$174-5°, 1.4514, 0.9821; 79% di-iso-Am ester, b (high vacuum) 159°, 1.4540, 0.9547; 63% di-n-hexyl ester, b (high vacuum) 210°, 1.4556, 0.9425; 50% di-2-ethylhexyl ester, b (high vacuum) unstated temp., 1.4563, 0.9289; 85% di-2-methoxyethyl ester, b high vacuum unstated temp., 1.4578, 1.0410; 90% di-2-ethoxyethyl ester, b high vacuum unstated temp., 1.4560, 1.0372. Reaction of the phosphonic dichloride with 4 moles of Me_2NH in ligroin gave after filtration and washing with aq.Na_2CO_3 79% $BuEtCHCH_2OCH:CHP(O)(NMe_2)_2$, $b_2$171-2°, 1.4748, 0.9831; similarly was prepd. 69% tetra-Et diamide, $b_2$181-2°, 1.4720, 0.9526; and 43% di-piperidide, b 0.02 191°, 1.5060, 1.0348.

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4-f CP

Action of trialkylaluminum on phosphorus trichloride.

G.Yu.Okhlobystin and L.I.Zakharkin (Inst.Hetero-org.Compds., Moscow).

Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 1006-8.

R_3Al reacts with PCl_3 yielding all possible substitution products depending on the conditions used. Even with excess R_3Al, however, the yield of R_3P reaches only 30%. With excess PCl_3, good yields of $RPCl_2$ may be obtained; since R_3P and R_2PCl form stable complexes with Al halides, the distn. yields only $RPCl_2$; the yields of $RPCl_2$ are raised by using R_3Al as a complex with Et_2O or pyridine. The alkyl radical is not isomerized in the reaction. R_2PCl could not be isolated as such, for above given reason, and must be isolated in the form of acidic derivs. Reaction of PCl_3 with $Me_3Al.Et_2O$ gave products from which $MePCl_2$ could not be isolated, however. A soln. of 20 g. Et_3Al in 25 ml. Et_2O was added under N_2 to 110 g. PCl_3 at 50-5°; distn. into a chilled receiver gave PCl_3 mixed with $EtPCl_2$ and after fractionation gave 61.5% $EtPCl_2$, b.112°, n_D^{25}1.4930, d_{20}1.2000. Similarly 23 g. $Pr_3Al.Et_2O$ and 55 ml. PCl_3 gave 50.6% $PrPCl_2$, b.1[illegible]°, n_D^{20}1.4880, d_{20}1.1854; this with [illegible] in presence of $AlCl_3$ gave in 2 hrs. $PrPOCl_2$, $b_9$62-3°, n_D^{20}1.5290, d_{20}1.2332, which gave dianilide, m.133° (cf. Kabachnik et al. Doklady Akad.Nauk S.S.S.R 110, 216 (1956)). Reaction of 22.5 g. iso-$Pr_3Al.Et_2O$ and 63 ml. PCl_3 gave 43.1% iso-$PrPCl_2$, b_{745}130°, n_D^{20}1.4880, d_{20}1.1922, which with [illegible] gave iso-$PrPOCl_2$, b_{10}63-4°, n_D^{20}1.5322, d_{20}1.2956, which gave dianilide, m.114°. Reaction of 32.5 g. iso-Bu_3Al added at 60-70° to 120 ml. PCl_3 gave 17.6% iso-$BuPCl_2$, b_{50}59-60°, $b_9$35-6°, b_{740}148-9°, n_D^{20}1.4810, d_{20}1.1268; reaction of 94 g. iso-Bu_3Al in 50 ml. Et_2O and 300 g. PCl_3 at 65-70° gave 33% iso-$BuPCl_2$, while 26.5 g. iso-Bu_3Al and 11 ml. pyridine with 71.0 ml. PCl_3 gave 36% iso-$BuPCl_2$. Similarly was obtained 57.4% $BuPCl_2$, b.153-5°, $b_9$38.5-9°, n_D^{20}1.4868, d_{20}1.1416. Reaction of 38 g. $(C_6H_{13})_3Al$ and 80 ml. PCl_3 gave 42.5% $C_6H_{13}PCl_2$, $b_9$83-4°, n_D^{20}1.4820, d_{20}1.0670. To 30.5 g. Et_3Al was added 33.2 g. PCl_3 and the mixture stirred 3 hrs. at 80° gave a viscous

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complex; 35.5 g. of this was treated with excess aq.NaOH and extd.with Et_2O yielding after fractionation under N_2 30% Et_3N, b.129-30°, n_D^{16} 1.4575; CS_2 adduct, red, m.121° (from EtOH). To 45 g. iso-Bu_3Al in 50 ml. heptane was added 23 g. $AlCl_3$ in heptane, at 60-70°; after concn. in vacuo the residual complex was decomp. with NaOH and the mixed products treated with 30% H_2O_2 with cooling; after extn. with 20% NaOH, the ext.was filtered, washed with C_6H_6 and acidified yielding 13.2 g. iso-Bu_2AlO_2H, $b_{0.4}$ 140-1°, m.43-5° (from pentane).

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4-8 CP

Organophosphorus polymers. 4. Polyesters of some phosphonic acids and hydroquinone.

V. [illegible] Korshak, I. [illegible] Gribova and [illegible] Andreeva (Inst. Heteroorg. Compds., Moscow). Izvest. Akad. Nauk [illegible], Otdel. Khim. Nauk 1958, 880-5. Cf. 1957, 631.

Heating appropriate chlorides with hydroquinone under N_2 finally at 200° gave the following series of polyesters: $(-MePO_2C_6H_4O-)_n$, m.63-5°, brittle solid, forms threads at 7[illegible]-4°; $(-PhPO_2C_6H_4O-)_n$, m.83-5°, brittle solid, forms threads at 94-5°; $(-(PhO)PO_2C_6H_4O-)_n$, m.50°, rubbery solid; $(-(p-O_2N-C_6H_4O)PO_2C_6H_4O-)_n$, m.3[illegible]-2°, brittle solid, forms threads at 41-2°; $(-(p-MeO-C_6H_4O)PO_2C_6H_4O-)_n$, m.3[illegible]-8°, brittle solid. A series of mixed polyesters were prepd. from hydroquinone and mixed $PhPOCl_2$ and $PhOPOCl_2$; the intermediate compns. were elastic and showed good adhesion to glass; similar series was prepd. with $MePOCl_2$ and $PhOPOCl_2$. All such mixed polyesters have a minimum m.pt. in the compn. diagram. $PhOPOCl_2$, from $POCl_3$ and PhOH, b_2 10[illegible]-4o, n_D^{20} 1.5[illegible], d_{20} 1.4145; $p-O_2NC_6H_4OPOCl_2$, 53%, b_3 179-80°, m.42-3° (supercooled, d_{20} 1.5745, n_D^{20} 1.5585); $p-MeOC_6H_4OPOCl_2$, 55.[illegible]%, b_{5-6} 175-6°, n_D^{20} 1.5355, d_{20} 1.4210. In prepn. of the above polyesters it was advantageous to add catalytic amount of [illegible]n to the reaction mixture when the temp. reached 170°.

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5-a C P

Organic insectofungicides.XXXIV. New method of synthesis of trialkyl phosphites.

N.N.Mel'nikov, Ya.A.Mandel'baum and Z.M.Bakanova. Zhur.Obshchei Khim. 28, 2473-4(1958). Cf. this j.27,1908(1957).

To $(EtO)_2Mg$ from 5.5 g. powd.Mg and 27 ml. abs.EtOH in 75 ml. dry Et_2O was added 13.7 g. PCl_3 and after refluxing 1.5 hrs. the filtered soln. gave 56-60% $(EtO)_3P$. If 5.5 g. Mg is allowed to react with 70 ml. EtOH, the excess EtOH being then removed in vacuo, and the resulting salt treated as above with PCl_3, there is formed 55% $(EtO)_3P$. Lower yields result from the use of C_6H_6 or petr.ether as the solvent. $(MeO)_3P$ is preparable in this manner but in low yield. $(EtO)_3P$, 55-50%, b.154-5°, d_{20}0.9665, n_D^{20}1.4136; $(PrO)_3P$, 41%, b_{10}83°, 0.9223, 1.4290; $(BuO)_3P$, 55%, b_{26}137°, 0.9267, 1.4320; $(iso\text{-}BuO)_3P$, 60%, b_{14}112°, 0.9060, 1.4330, were prepd. similarly from $(RO)_2Mg$. Prepn. of $ROPCl_2$ and $(RO)_2PCl$ is said to be feasible by this technique also.

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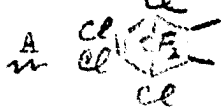
Organic insectofungicides. XXXV. Reaction of 1,1-difluorotetrachlorocyclopentadiene with some unsaturated compounds.

S. D. Volodkovich, N.N. Mel'nikov, A. F. Plate and M. A. Pryanishnikova (Res. Inst. Fertliz. and Insectofungicides, Moscow). Zhur. Obshchei Khim. 28, 3123-26 (1958).

Cf. Doklady Akad. Nauk SSSR 105, 1252 (1955).

Heating 1,1-difluorotetrachlorocyclopentadiene, b_{20} 70-71°, d_{20} 1.7382, n_D^{20} 1.4990 (Cf. Riemschneider et al. Monats. 86, 58 (1955)) with equimolar amount of appropriate unsatd. compound 1-6 hrs. on a steam bath gave the following products most of which showed very weak insecticidal activity. Thus were prepd. A (substituents shown):



$(CH_2)_3$, 25%, b_{19} 143-45°, m. 43-44°; 3,5-(1-cyclohexen)ylene, 60%, b_{20} 163-65°, m. 38-39°; 1,3-cyclohexylene, 81%, m. 47-48°; 1,3-(4-amylcyclohexylene), 46%, b_5 182-83°, n_D^{20} 1.5080, d_{20} 1.3158; 1,3-(4-methyl-4-carboxy cyclohexylene), 71%, m. 205-206°; Me ester of above, 48%, b_8 186-87°, 1.5210, 1.4906; di-carbomethoxy, 26%, b_{10} 155-57°, m. 75-76°; di-carbethoxy, 44%, b_7 165-68°, 1.4990, 1.5054; di-carbobutoxy, b_5 187-89°, 1.4825, 1.3440; also were prepd.: 1,2,3,4-tetrachloro-1,4-endodifluoromethylene-5-cyano-2-cyclohexene, 65%, b_{12} 135-38°, 1.5118, 1.6215; 1,2,3,4-tetrachloro-1,4-endodifluoromethylene-5carbomethoxy-2-cyclohexene, 44%, b_{10} 130-32°, 1.4970, 1.5680.

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Organic insectofungicides. XXXVI. Reaction of tetra- and pentachlorocyclopentadienes with some unsaturated compounds.

N. N. Mel'nikov and S. D. Volodkovich (Res.Inst. Fertilizers and Insectofungicides, Moscow). Zhur. Obshchei Khim. 28, 3317-19(1958). Cf. this j. 28, 3123 (1958).

Reduction of hexachlorocyclopentadiene with Zn-AcOH gave 2,3,4,5-tetrachlorocyclopentadiene, m. 61-62°. Fractionation of com. hexachlorocyclopentadiene gave 1,2,3,4,5-pentachlorocyclopentadiene, b_{25} 104-106°, d_{20} 1.6642, n_D^{20} 1.5615. These dienes were heated at 120-30° with the desired unsatd. compds.(bicyclo-[2,2,1]-heptene, bicyclo-[2,2,1]-2,5-heptadiene, esters of maleic acid and other unsatd. compds. Thus were obtained: A, 70%, b_{10} 172-3°, n_D^{20} 1.5752, d_{20} 1.4970 (some product with 63.5% Cl, m. 82-3°, was also formed); B, 60%, m. 93-94°. C (substituents shown): CO_2Me, H, 70%, b_4 135-36°, 1.5375, 1.5912; CO_2Me, CO_2Me, 39%, b_4 184-85°, m. 88-89°; CO_2Et, CO_2Et, 34%, b_4 168-69°, 1.5410, 1.5292; CO_2Bu, CO_2Bu, 34%, b_4 175-76°, m. 122-23°. D, 43%, b_4 142-43°, 1.5620, 1.4278; E, 47%, b_4 140-41°, 1.5630, 1.4170; F, 54%, b_{24} 208-10°, 1.5442, 1.4160; G (substituents shown) CO_2Me, H, 50%, b_{20} 146-47°, 1.5300, 1.4947; CO_2Me, CO_2Me 43%, m. 105-106°; CO_2Et, CO_2Et, 37%, b. 163-94°, 1.5349, 1.4534; CO_2CHMe_2, CO_2CHMe_2, 31%, b. 174-76°, 1.5210, 1.3644; CO_2Bu, CO_2Bu, 32%, b. 188-90°, 1.5060, 1.3141. The most active insecticide in the group was 1,2,3,4,10-pentachloro-1,4,5,8-diendomethylenehexahydronaphthalene; its 1,2,3,4-tetrachloro analog was almost inactive.

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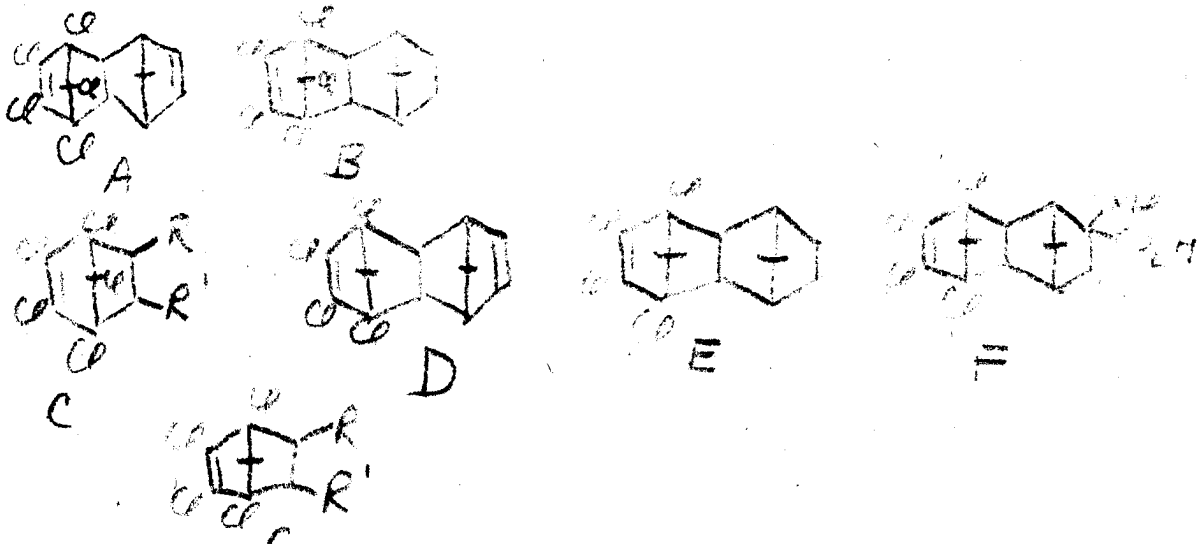

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6-a CP

Reaction of phosphorus pentachloride with amides of phosphoric acid. A.V.Kirsanov and I.N.Zhmurova (Inst.Org.Chem., Acad. Sci., Kiev). Zhur.Obshchei Khim.28, 2478-84(1958). Cf. this j.26,2009(1956).

Keeping an equimolar mixture of $(PhO)_2PONH_2$ and PCl_5 5-6 hrs., followed by 0.5 hr. at 50-60° gave 99.4% $(PhO)_2P(O)N{:}PCl_3$ (I), a viscous fluid. Similarly was prepd. 99.5% liquid $(PhO)_2P(S)N{:}PCl_3$ (II). The former refluxed 5 hrs. with 6 moles $PhNH_2$ in C_6H_6 gave 76% $(PhO)_2P(O)N{:}P(NHPh)_3$, m.195-7°(from EtOH). Heating equimolar mixture of I and 100% HCO_2H 1 hr. at 100° and finally at 120-5° (1.5-2 hrs.) gave 99.5% very viscous liquid $(PhO)_2P(O)NHPOCl_2$ (III). Similarly II in 3 days at 35° gave 30% $(PhO)_2P(S)NHPOCl_2$ (IV), m. 102-4°(from CCl_4). These chlorides with 4 moles $PhNH_2$ in refluxing C_6H_6 gave in 5 hrs. resp. 54% $(PhO)_2P(O)NHP(O)(NHPh)_2$, m.197-8° (from MeOH), and 98% $(PhO)_2P(S)NHP(O)(NHPh)_2$, m.198-200°(from EtOH). Treating 0.[illegible]mole I with 5 ml. H_2O overnight gave 83% $(PhO)_2P(O)NHPO(OH)_2$, m.170-2°(from dioxane-Et_2O). Reaction of I with 6 moles PhONa in C_6H_6, finally at reflux 1 hr., gave 76% $(PhO)_2P(O)N{:}P(OPh)_3$, m.72-4°(from C_6H_6-petr.ether). Similarly was prepd. from II 69% $(PhO)_2P(S)N{:}P(OPh)_3$, m.96-8°(from MeOH). Refluxing I with 3 moles $p\text{-}O_2NC_6H_4ONa$ in dioxane 2 hrs. gave 78% $(PhO)_2P(O)N{:}P(OC_6H_4NO_2\text{-}p)_3$, m.132-4° (from C_6H_6); similarly was prepd. 70% $(PhO)_2P(S)N{:}P(OC_6H_4NO_2\text{-}p)_3$, m.154-6°(from C_6H_6). With $p\text{-}ClC_6H_4ONa$ there was prepd. 36% $(PhO)_2P(O)N{:}P(OC_6H_4Cl\text{-}p)_3$, m.69-71°(from MeOH). The reaction of III with 3 moles MeONa in cold MeOH-C_6H_6 gave a viscous liquid $(PhO)_2P(O)NHP(O)(OMe)_2$. The use of PhONa in C_6H_6, completed at reflux in 1 hr. gave after an aq.treatment with HCl 13% $(PhO)_2P(O)NHP(O)(OPh)_2$, m. 110-2°(from C_6H_6-petr.ether), the same being formed in 57% yield from I and 6 moles PhONa in C_6H_6 after a similar aq.treatment. Similarly IV and MeONa gave 90% $(PhO)_2P(S)NHPO(OMe)_2$, m.115-7°(from C_6H_6-petr.ether); EtONa gave 81% $(PhO)_2P(S)NHPO(OEt)_2$, m.67-9°(from CCl_4-petr.ether); PhONa gave 87% $(PhO)_2P(S)NHPO(OPh)_2$, m.100-2°(from C_6H_6-petr.ether), also prepd. in 53% yield from $(PhO)_2P(O)N{:}PCl_3$. II and $p\text{-}ClC_6H_4ONa$ in C_6H_6 gave 34%

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$(PhO)_2P(S)NHP(O)(OC_6H_4Cl\text{-}p)_2$, m.144-6° (from EtOH). Reaction of $(PhO)_2P(S)N{:}P(OC_6H_4NO_2\text{-}p)_3$ with 2N NaOH 10 min. at reflux resulted on acidification in 12% $(PhO)_2P(S)NHP(O)(OC_6H_4NO_2\text{-}p)_2$, m.174-6°, the same being formed in the reaction of IV with 3 moles RONa in refluxing dioxane, followed by an aq. treatment. $(PhO)_2P(O)NHP(O)(OEt)_2$ does not hydrolyze even on boiling in H_2O 5-10 min., this phenomenon being evidently explained by internal hydrogen bonding of the acidic group with the adjacent P(O) group. The thiono analog is accordingly slowly hydrolyzed by H_2O, and therefore $(PhO)_2P(S)N{:}PCl_3$ on treatment with H_2O yields only H_3PO_4 and $(PhO)_2PSNH_2$.

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Bis-triaryloxyphosphazosulfones and tetra-aryl esters of sulfamido-bisphosphoric acid.

..V.Kirsanov and I.L.Matveenko (Metallurg.Inst.,Dnepropetrovsk). Zhur. Obshchei Khim.28, 1892-901(1958). Cf. this j.22,2346(1952).

In the following prepns. the purity of Na salts used is most important these must be prepd. with precise amounts of NaOH and must be dried under N_2 to eliminate oxidative changes during drying at 150-80°. To 0.05 mole $SO_2(N:PCl_3)_2$ in C_6H_6 was added at once 0.31 mole PhONa and after 30 min. on a steam bath the colorless soln. was sepd. and evapd. yielding after adun. of 50 ml. H_2O to the residue, 95-8% $SO_2(N:P(OPh)_3)_2$ m.131-2°; m.132-3°(from C_6H_6). similarly were prepd.: hexa-o-cresoxy analog, m.105-15°(contains C_6H_6 of crystallization), m.127-9°(solvent free); hexa-m-cresoxy analog, m.54-6°; hexa-p-cresoxy analog, m.80-1°; hexa-1-naphthoxy analog, best prepd. in Et_2O, m.205-6°; 2-isomer,m.133- hexa-p-chlorophenoxy analog, m.111-3°; hexa-p-nitrophenoxy analog,m. 198-200°. These treated with aq.alc.NaOH until dissolved, then acidified with alc.HCl, gave $SO_2(NHP(O)(OR)_2)_2$ (R shown): Ph, dec.188-9°(I); o-tolyl, dec.173-6°; m-tolyl, dec.170-2°; p-tolyl, dec.184-5°; 1-$C_{10}H_7$, best prepd. with alc.NaOH in pyridine with heating 1.5-2 hrs., dec. 213-5°; 2-isomer, dec.195-8°; p-ClC_6H_4, dec.188-9°; p-$O_2NC_6H_4$,m. 218-21°. I refluxedwith 96% EtOH 0.5 hr. gave $(PhO)_2PONH_2$, m.148-9°, and an acidic product; MeOH gave a similar result. I with aq.Na_2CO_3 gave $SO_2(NHP(O)(OPh)_2)Na_2$, dec.252-4° (decahydrate,plates from H_2O, m.44-57°); di-K salt, and its heptahydrate,m.52-4°, were prepd, similarly; di-NH_4 salt and its tetrahydrate, m.65-7°, are also reported.

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6-C

CP

Trichloroisophosphazoacyls of aromatic series.

A.V.Kirsanov (Inst.Org.Chem.,Acad.Sci.,Kiev). Zhur.Obshchei Khim.28,1887-92(1958). Cf.this j.27,3246(1957).

Heating 0.05 mole $RCONH_2$ and 0.051 mole PCl_5 at 125-35° 80-25 min. gave about 95% HCl after which $POCl_3$ was distd. in vacuo and the residue on chilling gave nearly 100% corresponding trichloroisophosphazoacyls. These are sol. in C_6H_6, sparingly in CCl_4 and petr.ether. Thus were prepd.: $RCCl:NPOCl_2$(R shown): Ph, oil; p-tolyl, oil; 1-$C_{10}H_7$, oil; 2-$C_{10}H_7$, oil; o-ClC_6H_4, oil; p-isomer, oil; 2,4-$Cl_2C_6H_3$, oil; o-$O_2NC_6H_4$, oil; m-isomer, oil; p-isomer, m.121-4°; 3,5-$(O_2N)_2C_6H_3$, m.82-4°; 2,4-$Cl(O_2N)C_6H_3$, oil; m-$C_6H_4(CCl:NPOCl_2)_2$, oil. Heated to 135-210° these readily cleaved into $POCl_3$ and corresponding RCN, the latter being obtained in 90-100% yields. The $RCCl:NPOCl_2$ are also preparable in case of negatively substituted org.radicals(cf.26,2009(1956)). Refluxing 0.03 mols $RCONH_2$ with 0.031 mole PCl_5 in CCl_4 20-5 min. gave on evapn. of the residue nerely 100% RCON:PCl_3 (R shown): p-tolyl, glassy solid; 1-$C_{10}H_7$, m.66-8°; 2-isomer, m.-40°; 2,4-chloronitrophenyl, m.62-4°. The same reaction applied to isophthalic diamide gave m-$C_6H_4(CON:PCl_3)_2$, m.96-9°(from petr.ether). These on heatir reacted exothermically and yielded $POCl_3$ and RCN, generally at 90-135°, at lower temps. than required by the isophosphazo analogs above. RCON:PC treated with HCO_2H gave good yields of the $RCONHPOCl_2$(R shown): p-tolyl, m.99-101°; 1-$C_{10}H_7$, m.99-101°; 2-$C_{10}H_7$, m.111-3°; m-$C_6H_4(CONHPOCl_2)_2$, m. 130-1°. These were converted to free acids (cf. this j.27,450(1957)): $RCONHPO(OH)_2$ (R shown): p-tolyl, m.153-9°; 1-$C_{10}H_7$, m.139-41°; 2-isomer, m.155-7°. The isophthalic deriv. could not be isolated owing to ready loss of the P-N bond.

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6-a CP

Diphenylamide of trichlorophosphazocarbonic acid and its derivatives. A.V.Kirsanov and Z.S.Nekrasova (Metallurg.Inst.,Dnepropetrovsk). Zhur. Obshchei Khim.28, 1595-1601(1958). Cf. this j.26,909(1956).

Heating 0.01 mole dry Ph_2NCONH_2, 0.01 mole PCl_5 and 50 ml. CCl_4 at 70-80° 45 min., filtration of hot soln. after HCl evolution had stopped, concn. in vacuo and cooling gave 100% $Ph_2NCON{:}PCl_3$ (I), m.112-4°, sparingly sol. in Et_2O and petr.ether. Treated with equimolar amount of HCO_2H in C_6H_6 it vigorously gave CO and HCl and gave a ppt. of 95% $Ph_2NCONHPOCl_2$ (II), dec.136-7°, insol. in hot Et_2O or petr.ether (previously reported m.pt. for this compound should read 136-7°, not 113-4°, and m.pt. for $PhEtNCONHPOCl_2$, should read 113-4°, not 136-7°, as previously reported in this j.26,2286). Equimolar mixture of isocyanatophosphoryl dichloride and Ph_2NH in C_6H_6 in the cold gave 91% of the above substance,m.136-7°(from CCl_4). Keeping a soln. of I in an org.solvent in a desiccator contg. some H_2O for 3 hrs. also gave the same product,m.136-7°, if the solvent used is CCl_4; with C_6H_6 or dioxane, the product,m.171-4°, was identified as $Ph_2NCONHPO(OH)Cl$, III. Treatment of I with 3 moles HCO_2H in C_6H_6 gave after refluxing 4 hrs. 63.7% $Ph_2NCONHPO(OH)_2$, dec.110°, a very hygroscopic solid. Similarly equimolar amounts of II and HCO_2H in C_6H_6 in 1 hr. gave 61.9% III, dec.172-6°, decomposed by warm H_2O. Reaction of I with 3 moles powd.NaOPh in C_6H_6 in 0.5 hr. at reflux, followed by rapid shaking with aq.NaOH in the cold, rapid filtration of org.layer through Na_2SO_4 and evapn. in vacuo gave 90% $Ph_2NCON{:}P(OPh)_3$, m.83-4°, which with warm alc.-aq. soln. gave $Ph_2NCONHPO(OPh)_2$. Similarly were obtained: 80% $Ph_2NCON{:}P(OC_6H_4Cl\text{-}p)_3$, m. 128-30°; 80% $Ph_2NCON{:}P(OC_6H_4Cl\text{-}o)_3$, m.40-3°; 83.9% $Ph_2NCON{:}P(OC_6H_4NO_2\text{-}p)_3$, yellow oil; 91.4% $Ph_2NCON{:}P(OC_6H_4NO_2\text{-}o)_3$, yellow oil; $Ph_2NCON{:}P(OC_{10}H_7\alpha)_3$, m.47-50°,70%. These refluxed with 96% EtOH gave in 0.5-2 hrs.: 74.3% $Ph_2CONHPO(OPh)_2$, m.147-9°; 55.2% di-p-chlorophenyl ester,m.151-2°; 41.4% di-o-chlorophenyl ester, m.63-5°; 82.1% di-p-nitrophenyl ester,m.148-50°; 31.8% di-o-nitrophenyl ester,m.182-3°. These are titrated by NaOH as monobasic acids. $PhPhNCON{:}P(OAr)_2$ and 2 moles N NaOH in 2 hrs. gave 100% Ph_2NH.

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6-x

Salts of fluorides of arylsulfonamidophosphoric acids.

A.V.Kirsanov and S.S.Levchenko (Inst.Org.Chem.,Acad.Sci.,Kiev). Zhur. Obshchei Khim.28, 1589-94(1958). Cf. this j.27,3078(1957).

To 10 g. $KF.2H_2O$ in satd.aq. soln. there was added 0.01 mole powd.$ArSO_2N:PCl_3$ which gave an exothermic reaction which after a few minutes yielded a crystalline ppt. of $K^+(ArSO_2NPOF_2)^-$ (plates or needles) which after sepn. and crystn. from EtOH, MeOH or aq.EtOH resulted in 41-61% pure products (Ar shown): Ph, (I) m.230-2°, p-tolyl, m.232-5°; $p-ClC_6H_4$, m.265-8°; $p-FC_6H_4$, m.225-8°; $o-O_2NC_6H_4$, m.181-2°; $m-O_2NC_6H_4$, m.217-20°; $p-O_2NC_6H_4$, m.225-8°. Heating a suspension of 0.01 mole $ArSO_2NHPOCl_2$ (Ar=Ph or p-tolyl) in satd. soln. of 10 g. KF in H_2O at 30-40° resulted in several minutes in a distinct change in the form of the ppt., which was sepd. and crystd. from EtOH yielding the products identical with above described, in 31-40% yields. Similar reaction of 0.01 mole $PhSO_2NHPOCl_2$ with satd.aq.KF (10 g.) 20 min. run without heating gave a ppt. of $K^+(PhSO_2NPOCl_2)^-$, 48%, m.197-8°(from EtOH), which indicates that the formation of K salts of the difluorides above proceeds through this intermediate. This heated carefully to 40-50° with KHF_2 in satd.aq.soln. until dissolved, than cooled, gave 86% I. The K salts of the difluorides treated with 2 moles MeONa in MeOH 1 hr. gave after distn. of MeOH, treatment with H_2O and acidification of filtered aq.soln. with HCl gave the following esters $ArSO_2NHPO(OMe)_2$ (Ar shown): Ph, 46%, m.100-8°; $p-ClC_6H_4$, 68%, m.128-9°; $m-O_2NC_6H_4$, 63%, m.148-50°; $p-O_2NC_6H_4$, 68%, m.177-9°. To satd. aq. soln. of 10 g.$KF.2H_2O$ was added 0.01 mole $ArSO_2N:PCl_3$ or $ArSO_2NHPOCl_2$ and the mixture was warmed on water bath until a soln.formed;then heating to 80-5° for few minutes and cooling gave ppts. of di-K salts: $K_2^+(ArSO_2NPO_2F)^{--}$ (Ar shown): 46% $p-ClC_6H_4$, dec. 312-6°; $o-O_2NC_6H_4$, 77%, dec.235-7°; m-isomer, 73%, dec.302-6°; p-isomer, 37%, dec.299-302°(all from aq.EtOH). The Ag salts are less sol.in H_2O than are the K salts. The stability of the above salts to hydrolysis in aq.media may be explained by the neg.character of the sulfonamido group.

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CP

Anilides of alkylsulfonamidophosphoric acids.

A.V.Kirsanov and N.L.Agorova (Metallurg.Inst.,Dnepropetrovsk). Zhur.Obshchei Khim.28, 1587-9(1958). Cf. this j.25,187(1955).

Regardless of proportions of reactants it was impossible to isolate any $RSO_2N:PCl_2NHPh$ from reaction of $PhNH_2$ with $RSO_2N:PCl_3$, but the reaction readily yields $RSO_2N:PCl(NHPh)_2$,(I), if run in CCl_4; I are colorless solids of neutral character, readily saponified to $RSO_2NHPO(NHPh)_2$,(II), on heating with 96% EtOH or H_2O; I and aq.alkalies yield sol.salts of II and on acidification yield free II, which are solids with very bitter taste and not attacked after prolonged refluxing with H_2O or alkalies; dil.acids slowly hydrolyze them on heating and yield amides of alkanesulfonic acids and phosphoranilides. II are monobasic acids of considerable strength. To 0.01 mole $EtSO_2N:PCl_3$ in 15 ml. CCl_4 was added 0.05 mole $PhNH_2$ in 15 ml CCl_4 with ice cooling to 5-15°(higher temp. leads to trisubtituted product) and after 2 days at room temp. the mixture was filtered and extd. with hot C_6H_6 which on cooling gave60.2% $EtSO_2N:PCl(NHPh)_2$, m.88-9°. Similarly was prepd. 63.3% more soluble $BuSO_2N:PCl(NHPh)_2$, m.176-8°. Heating the former (0.01 mole) to reflux with 40 ml. N NaOH, filtering and addn. of 5N HCl to Congo red endpoint gave 62.2% $EtSO_2NHPO(NHPh)_2$, m.127-30°, a monohydrate; heated to 100° it gave anhydrous product,m.158-60°(from C_6H_6). Similarly was prepd. 59.9% $BuSO_2NHPO(NHPh)_2$, m.188-9°(from H_2O). Reaction of 0.01 mole $EtSO_2N:PCl_3$ in C_6H_6 with 0.08 mole $PhNH_2$ in C_6H_6 with cooling and refluxing 10 hrs. gave after washing the isolated ppt. with C_6H_6, H_2O, N HCl and 0.5N NaOH and H_2O, gave 79% $EtSO_2N:P(NHPh)_3$, m.251-2°(from EtOH). Thus was prepd. $BuSO_2N:P(NHPh)_3$, m.232-3°(from EtOH); these have bitter taste and are insol.in H_2O or aq.bases or acids. They dissolve in hot Me_2CO, dioxane, EtOH or EtOAc. These are remarkably stable to attack by hot alkalies,even to hot alc.NaOH.

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6 7

Triaryloxyisophosphazoacyls of the aromatic series.

A.V.Kirsanov and G.I.Derkach (Inst.Org.Chem.,Acad.Sci.,Kiev). Zhur. Obshchei Khim.28, 2247-52(1958). Cf. this j.28,1887(1958).

To 0.02 mole RCCl:NPOCl$_2$ in dry C_6H_6 was added 0.0604 mole dry R'ONa in dioxane and after stirring until the mixture becomes neutral (10-15 min.) the mixture was washed with H_2O, dried and evapd. yielding the following RC(OR')N:PO(OR')$_2$ (R'and R^{m} shown resp.): 84.3% Ph, Ph, m. 100-2°; 65.5% Ph, 1-$C_{10}H_7$, m.97-8°; 95% Ph, o-ClC_6H_4, m.119-20°; 78.4% Ph, 2,4-$Cl_2C_6H_3$, m.99-101°; 82.5% Ph, m-$O_2NC_6H_4$, m.122-3°; 80% Ph, p-$O_2NC_6H_4$, m. 139-41°; 89.2% Ph, 3,5-$(O_2N)_2C_6H_3$, m. 105-8°; 81.6% Ph, 2,4-$Cl(O_2N)C_6H_3$, m.112-4°; 50% m-MeC_6H_4, p-$O_2NC_6H_4$, m.113-5°; 68.3% 1-$C_{10}H_7$, Ph, m.146-8°; 55.3% 2-$C_{10}H_7$, p-ClC_6H_4, m.~~[illegible]~~ 115-7°; 63.4% p-ClC_6H_4, Ph, m.107-9°; 85% p-ClC_6H_4, o-ClC_6H_4, m.161-3°; 82.4% p-Cl-C_6H_4, 2,4-$Cl_2C_6H_3$, m.107-9°; 68.3% p-ClC_6H_4, m-$O_2NC_6H_4$, m.119-21°; 78.7% p-ClC_6H_4, p-$O_2NC_6H_4$, m.152-3°; 84.5% p-ClC_6H_4, 3,5-$(O_2N)_2C_6H_3$, m.151-5°; 79.9% o-$O_2NC_6H_4$, 2,4-$Cl_2C_6H_3$, m.107-9°; 95.3% o-$O_2NC_6H_4$, p-$O_2NC_6H_4$, m.162-5°; ~~[illegible]~~ 92.3% p-$O_2NC_6H_4$, p-$O_2NC_6H_4$, m.220-2°; 79% p-$O_2NC_6H_4$, 2,4-$Cl_2C_6H_3$, m.147-9°; 82.2% p-$O_2NC_6H_4$, m-$O_2NC_6H_4$, m.167-9°, 63.8% Me, 3,5-$(O_2N)_2C_6H_3$, m.96-8°. The naphthoxy derivs. were best prepd. in Et_2O medium, as were the p-chlorophenoxy derivs. The nitrophenoxy derivs. required refluxing 1.5-3.5 hrs. for completion of the reaction in C_6H_6. The methoxyderiv. was prepd. in MeOH soln. The products refluxed 1 hr. with 0.2N NaOH in aq.EtOH, concd. and treated with aq.HCl to Congo red gave RCONHPO(OR')$_2$ (R' and R given resp.): 50% Ph, Ph, m.147-9°; 52% Ph, 1-$C_{10}H_7$, m.127-9°; 61.6% Ph, o-ClC_6H_4, m.102-4°; 66.4% Ph, 2,4-$Cl_2C_6H_3$, m.136-8°; 71.7% Ph, m-$O_2NC_6H_4$, m.166-7°; 75.2% Ph, p-$O_2NC_6H_4$, m.151-2°; 90.4% Ph, 3,5-$(O_2N)_2C_6H_3$, m.197-9°; 93.4% Ph, 2,4-$Cl(O_2N)C_6H_3$, m. 107-9°; 70.1% m-MeC_6H_4, p-$O_2NC_6H_4$, m.13[illegible] 8°; 84.1% 1-$C_{10}H_7$, Ph, m.195-6°; 85.5% 2-$C_{10}H_7$, p-ClC_6H_4, m.166-7°;

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81% p-ClC_6H_4, Ph, m.131-3°; 87% p-ClC_6H_4, o-ClC_6H_4, m.179-80°; 89.9% p-ClC_6H_4, 2,4-$Cl_2C_6H_3$, m.152-4°; 91.4% p-ClC_6H_4, m-$O_2NC_6H_4$, m.171-5°, 73.3% p-ClC_6H_4, p-$O_2NC_6H_4$, m.175-6°; p-ClC_6H_4, 3,5-$(O_2N)_2C_6H_3$, m.216-7°; 84.2% o-$O_2NC_6H_4$, 2,4-$Cl_2C_6H_3$, m.170-1°; 83.1% o-$O_2NC_6H_4$, p-O_2N-C_6H_4, m.178-9°; 83.4% p-$O_2NC_6H_4$, 2,4-$Cl_2C_6H_3$, m.160-2°; 92.4% p-O_2N-C_6H_4, p-$O_2NC_6H_4$, m.178-9°; 86.2% p-$O_2NC_6H_4$, m-$O_2NC_6H_4$, m.176-8°; 95% Me, 3,5-$(O_2N)_2C_6H_3$, m.189-91°.

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6-N

CP

Reaction of phenylphosphorus tetrachloride with diazomethane.

L. M. Yagupol'skii and P. A. Yufa (Inst. Org. Chem., Acad. Sci., Kiev). Zhur. Obshchei Khim. 28, 2853-56 (1958). Cf. Yakubovich et al. this j. 22, 1534 (1952).

To 25 g. $PhPCl_4$ in 150 ml. dry Et_2O was added at -40° over 1 hr. 9.7 g. CH_2N_2 in 300 ml. Et_2O cooled to -2° and dried over KOH and Na; a ppt. formed a midpoint of the addn.; after stirring 0.5 hr. at -40°, the mixtur was left overnight at 0°, freed of Et_2O by distn. without sepn. of the ppt., and the residue was added to 500 ml. H_2O (exothermic). After 1 day the product was filtered off and washed with H_2O; there was formed 31.4% $PhP(O)(CH_2Cl)_2$, m. 141-42° (from MeOH). This (5.58 g.) added at 0° to 19.9 g. HNO_3 (d 1.5) and 16.1 g. H_2SO_4 (d 1.83), then heated 45 min. on a steam bath and poured on ice, gave 93% $m\text{-}O_2NC_6H_4P(O)(CH_2Cl)_2$, yellow m. 155-56° (from MeOH or C_6H_6). This (5.36 g.) in 50 ml. EtOH was treated at 70° dropwise over 0.5 hr. with 15.9 g. $SnCl_2.2H_2O$ in 10 ml. concd. HCl and after 1 hr. at 70°, followed by refluxing 15 min., the solvent was distd. in vacuo, the residue treated with 30% NaOH and extd. with Et_2O, yielding 56% yellowish $m\text{-}H_2NC_6H_4P(O)(CH_2Cl)_2$, m. 110-11° (from C_6H_6); acetyl deriv., prisms, m. 163-64° (from H_2O). This diazotized conventionally in 20% HCl and treated with Cu_2Cl_2-HCl gave 52% $m\text{-}ClC_6H_4P(O)(CH_2Cl)_2$ (I), m. 129-30° (from H_2O). To 57 g. $HgCl_2$ in 75 ml. concd. HCl and 75 g. ice, cooled with ice-NaCl, there was added 25.5 g. (22.5 g.) $m\text{-}ClC_6H_4NH_2$ in 100 ml. Et_2O yielding in 15 min. the double salt ppt., which after washing was added to 20 g. powd. Cu in 100 ml. Me_2CO, yielding after treatment with NH_4OH and H_2O, 23% $(m\text{-}ClC_6H_4)_2Hg$, m. 148-49° (from EtOH). This (0.5 g.) and 25 g. PCl_3 in sealed tube 24 hrs. at 230-50° gave after extn. with petr. ether 6.8 g. $m\text{-}ClC_6H_4PCl_2$, b_5 101-103°, which with Cl_2 gave $m\text{-}ClC_6H_4PCl_4$, m. 46-47°, which (2.14 g.) with 1.1 g. CH_2N_2 in Et_2O, as above, gave 100% I. Refluxing 2.23 g. $PhP(O)(CH_2Cl)_2$, 4.4 g. KI and 18 ml. $(CH_2OH)_2$ 6 hrs. gave after quenching in ice a ppt. of 61.5% $PhP(O)(CH_2I)_2$, m. 172-73° (from aq. EtOH).

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Synthesis of ferrocene derivatives with the aid of N,N-dimethylaminomethylferrocene methiodide.

A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva and Yu. S. Ustynyuk (M. V. Lomonosov State Univ., Moscow). Dokladty Akad. Nauk S.S.S.R. 124, 331-34 (1959). Cf.Lindsay et al. J.Org.Chem. 22,355(1957).

Heating 1.1 g N,N-dimethylaminomethylferrocene methiodide (I) and 1.5 g. $Na_2SO_3.7H_2O$ in 60 ml. H_2O 7 hrs. at 70-80°, followed by treatment with $Ba(OH)_2$, removal of excess Ba with CO_2, and evapn. gave 77% ferrocenylmethane sulfonic acid, isolated as Na salt, does not m. 230°; a monohydrate (from EtOH). I (0.36 g.) refluxed with aq. soln. of 0.3 g.KSCN 3 hrs. gave on cooling and acidification with HCl 46% yellow ferrocenylmethyl thiocyanate, m. 59-61° (from petr. ether). Heating 0.3 g. I with 0.1 g. PhOH and 0.05 g. NaOH in aq. soln. 5 hrs. at 90° gave after extn. with Et_2O 80% Ph ferrocenylcarbinyl ether, m. 129-30° (from petr. ether). Similarly was prepd. 40% 2-naphthyl ferrocenylcarbinyl ether, dec. 121-23° (from petr. ether). Addn. of aq. soln. of 1 g. I to 0.5 g. p-hydroxyazibenzene in 5% NaOH and heating 20 hrs. at 90-100° gave 80% p-(ferrocenylmethoxy)-azobenzene, dec. 135.5-37.5° (from C_6H_6).

To 20.8 g. Et_2NH in 50 ml. AcOH was added 6.4 g. paraformaldehyde and the mixture was warmed until a soln. formed; to this was added 18.6 g. ferrocene and the mixture was kept 16 hrs. at 80-100°, dild. with H_2O, filtered from pptd. ferrocene (16.8 g.) and the aq. soln. was extd. with Et_2O, made alkaline and again extd. with Et_2O. The last ext. gave 2 g. oil from which some diethylaminomethylferrocene was isolated by steam distn.; soft yellow crystals; methiodide, dec. 159-62°(from EtOH). Heating 30 g. methylferrocene, 15.3 g. N,N,N',N'-tetramethyldiaminomethane, 4.5 g. paraformaldehyde, 30 g H_3PO_4 (d. 1.73) and 200 ml. AcOH 7 hrs. at 90° gave after distn. of the reaction products in vacuo from Zn 80% (N,N-dimethylaminomethyl)methylferrocene (II), b_1 115-18°, b_5 138-40°, n_D^{20} 1.5812, d_{20} 1.2150 (infra red spectrum reported) and 19% bis-(N,N-dimethylaminomethyl)methylferrocene, b_1 130-31.5°, 1.5622, 1.1260 (infra red spectrum reported).

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II yields the methiodide, dec. above 185°. If the aminomethylation is run without added H_3PO_4 the yield of II is 60% (70% if isolated as the methiodide). If tetramethyldiaminomethane is used, and the reaction run 10 hrs. at 115°, the yield of the disubstituted deriv. is 32% and that of II is 42%. Reduction of II methiodide with Na-Hg gave 75% dimethylferrocene, b_4 77°, b_{13} 119°, 1.6007, 1.2458 (n_D^{35} 1.5922); its infra red spectrum is reported. Dimethylferrocene and ~~the~~ II are homoannular products with substituents probably in 1,3-positions.

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CP

Synthesis of organophosphorus compounds from hydrocarbons and their derivatives. VII. Oxidative chlorophosphonation with alkoxy and dialkylamidodichlorophosphines.

Yu. . inov'ev, V.N.Kulakova and L.. oborovskii. Zhur.Obshchei Khim.28, 1551-4 (1958). Cf.this j.26,303(1956) and Doklady Akad.Nauk SSSR 109, 98(1956).

Into 21 g. cyclohexane and 180 g. $EtOPCl_2$ was bubbled O_2 until the reaction ceased; distn. gave 11 g. product, $b_3$106-112°, d_{20}1.2576, which dissolved completely in H_2O and on evapn. gave cyclohexanephosphonic acid, m.160-1°. Into 200 g. CH_2:CHCl and 128.2 g. $MeOPCl_2$ was passed O_2 at -20° yielding 25 g.(12.3) product, $b_5$110-8°, which on redistn. gave $C_3H_6O_2PCl_3$, $b_5$105-10°, d_{20}1.5220, n_D^{20}1.4693, identified as $C_2H_3Cl_2P(O)(OMe)Cl$; this with MeOH at 10° gave $C_2H_3Cl_2P(O)(OMe)_2$, $b_4$105-9°, d_{20}1.4060, n_D^{20}1.4508, which was identical with previously reported product(2nd ref.above). Reaction of CH_2:CHCl and PCl_3 with O_2 gave $C_2H_3Cl_2POCl_2$ which (21.6 g.) added to 48 g. MeOH at -10° gave 87.5% $C_2H_3Cl_2PO(OMe)_2$, $b_4$110-2°, d_{20} 1.4039, n_D^{20}1.4510. Into 90 g. CH_2:CHCl and 82 g. Me_2NPCl_2 (b.146-8°, d_{20}1.2624) was passed O_2 at -30° yielding 30.2 g. Me_2NPOCl_2, 72 g.CH_2:CHCl and 14.4 g.(23%) product, $b_{1.5}$114-5°, d_{20}1.4036, n_D^{20}1.4780, identified as $C_2H_3Cl_2PO(NMe_2)Cl$; this also formed from $C_2H_3Cl_2POCl_2$ and Me_2NH and this specimen $b_{2.5}$118°, d_{20}1.3997, n_D^{20}1.4775. The chloride and EtONa gave $C_2H_3Cl_2P(O)(NMe_2)OEt$, b_{10-5}85-90°, d_{20}1.2191, n_D^{20}1.4495. The products from vinyl chloride appeared to be isomer mixtures.

VIII. Oxidation of phosphorus trichloride by oxygen.

.K.Baranaev, Yu.V.Zinov'ev, T.K.Skripach and L.Z.Soborovskii.Ibid.1628-31. Kinetic curves of oxidation of PCl_3 by O2 are shown. The initial stage of reaction is heterogeneous and its rate is detd. by rate of soln. of O_2. The rate of oxidation in initial and final stages is almost independent of the temp. The energy of activation of the reaction is very small,which fact supports the hypothesized free radical course of the reaction, with intermediate Cl_3POO biradical. Small amount of I_2 blocks the reaction.

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1-C

CP

Synthesis of P-amino acid derivatives of adenylic acid.

E. A. Shabarova, L. G. Satarova and M. A. Prokof'ev (M. V. Lomonosov State Univ., Moscow). Doklady Akad. Nauk S.S.S.R. 123, 864-67 (1958).

Two types of amino acid derivs. of adenosine-5'-phosphate were prepd. To 0.08 g. dry 2',3'-isopropylidene-adenosine-5'-(benzyl phosphite) (I) (cf. Corby et al. J. Chem. Soc. 1952, 3669) in CCl_4 was added 0.1 g. Et phenylalanine ester and the soln. was kept overnight, evapd., dissolved in $CHCl_3$, washed with H_2O, aq. HCl and $NaHCO_3$, and evapd. yielding 62.5% Et ester of N-(2,3-isopropylidene-adenosine-5-(benzyl phospho))phenylalanine, $C_{31}H_{37}O_8N_6P.3H_2O$, dec. 88-90° (from C_6H_6-petr. ether), Rf 0.91 ($BuOH-H_2O-AcOH$). The product has abs. max. 259-260 m . Boiled with 0.1N H_2SO_4 0.5 hr. it began to show the formation of phenylalanine; no cleavage of N-P bond took place on boiling with 0.1N NaOH 2 hrs., but in 2N NaOH phenylalanine is cleaved in 30 min.. Similar prepn. using Me ester of glycine gave 52% Me ester of (2,3-isopropylidene-adenosine-5(benzyl phospho)-glycine, $C_{23}H_{29}O_8N_6P.3H_2O$, dec. 60-63°, abs. max. 260 m ; its hydrolytic behavior was as above. Me ester of leucine gave Me ester of (2,3-isopropylidene-adenosine-5-(benzyl phospho)leucine, 44%, dec. 68-72°, whose hydrolytic behavior was similar to the above. To 0.2 g. I in dry C_6H_6 was added 3 ml. abs. MeCN and 0.1 g. $(CH_2CO)_2NCl$; after 2 hrs. the mixture was filtered and the filtrate treated with 0.07 g Ag salt of carbobenzozyleucine in 5 ml. dioxane. After standing overnight, filtration, evapn. and treatment with 0.1 g. Me ester of glycine there was isolated by paper chromatography an indication of formation of a substance with Rf 0.93 corresponding to Me ester of carbobenzoxyleucylglycine. Thus a mixed anhydride of 2,3-isopropylidene-adenosine-5-(benzyl phosphate) and carbobenzoxyleucine was formed. Similarly was prepd. the mixed anhydride of carbobenzoxyglycine from Ag salt of glycine; it was detected by formation of Me ester of carbobenzoxyglycylphenylalanine in the reaction with Me ester of phenylalanine.

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Synthesis of phosphorylaminopyrimidines.

Yu.P.Shvachkin and M.A.Prokof'ev (State Univ., Moscow). Zhur.Obshchei Khim.1617-21(1958).

It was found that the prepn. of diphenylphosphorylguanidine described in Ger.Pat.556,145(1932) cannot be duplicated. To 11.2 g. guanidine in 50 ml. dry EtOH was added with cooling 25.6 g. $(PhO)_2POCl$ and after 0.5 hr. stirring and 5 hrs. at room temp. the mixture was poured on ice yielding 73% $(PhO)_2P(O)NHC(NH_2):NH$, m.118° (from C_6H_6). This (1.45 g.) refluxed with NaOEt soln. from 0.58 g.Na and 35 ml. dry EtOH and treated with 3.25 g. $AcCH_2CO_2Et$ and refluxed 4 hrs. gave, after concn. in vacuo, soln.of the residue in least vol. of H_2O, acidification with 5% HCl and cooling, 28% colorless 2(diphenylphosphorylamido)-4-hydroxy-6-methylpyrimidine, (A) m.182-3° (from BuOH), which does not have NH_2-N and has abs.max. 268 m and 253 m ; treated with dil.NaOH this reacts with 1 equiv. of base. Similar reaction of 2.9 g. amide with 8 g. $CH_2(CO_2Et)_2$ and 1.15 g.Na in 40 ml. EtOH gave 54% 2-(diphenylphosphorylamido)-4,6-dihydroxypyrimidine, (I) m.159-60° (from $CHCl_3$), which does not contain NH_2-N and titrates with 1 equiv.of NaOH; abs.max. 258 m . Similarly the use of $MeCH(CO_2Et)_2$ gave 59% 2(diphenylphosphorylamido)-4,6-dihydroxy-5-methylpyrimidine, m.169-70°, which reacts with 1 equiv.of NaOH; use of $EtCH(CO_2Et)_2$ gave 46.5% 2(diphenylphosphorylamido)-4,6-dihydroxy-5-ethylpyrimidine, m.209-10° (from BuOH), which reacts with 1 mole NaOH. Refluxing 1 1 hr. in H_2O gave $(PhO)_2PO_2H$ (in aq.soln. abs.max.262 and 231 m ; its aniline salt, m.165°) and 2-amino-4,6-dihydroxypyrimidine and guanidine; no PhOH or H_3PO_4 was detected. I refluxed with N NaOH was 97% hydrolyzed at P-N bond in 20 min.; after 3 hrs. H_3PO_4 began to appear. I boiled 1 hr. in N HCl was 68.7 hydrolyzed at P-N bond. A was not attacked in 1 hr. by boiling H_2O but was cleaved with N NaOH and N HCl, as was I. The lack of free amino groups in the above pyrimidines indicates the correctness of the proposed structures, eliminating an alternative course of the condensation.

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Synthesis of di- , -chloroethyl ester of vinylphosphonic acid.

E.L.Gefter (Plastics Res.Inst.,Moscow). Zhur.Obshchei Khim.28,2500-2(1958).

The following prepn. of $CH_2:CHPO(OCH_2CH_2Cl)_2$ gives better yields than the previous procedures: 1080 g. $ClCH_2CH_2PO(OCH_2CH_2Cl)_2$, 412 g. Et_3N and 1 l. C_6H_6 stirred 3 hrs. at 30-40°, 2 hrs. at 50-60° and 80-8° 3 hrs. followed by standing overnight, filtration of pptd. salt, washing the filtrate with H_2O and distn. gave 70% $CH_2:CHPO(OCH_2CH_2Cl)_2$, b_3 131-2°, b_4 135-7°, n_D^{20} 1.4787, d_{20} 1.3233. If the reaction is run rapidly, the same proportions of reactants give 10-12% lower yield. Attempts to use an excess of Et_3N also lowered the yield. Evidently the amine forms a quaternary salt at the phosphonate Cl position, which then decomposes. However at 80-90° evidently similar complexes form at the ester Cl atoms, these being relatively stable and sparingly sol. and thus being lost during filtration of the amine salt.

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