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Reaction of phosphorus pentachloride with esters of oxamic acid. Amides of alkoxydichloroacetic acids.

A.V.Kirsanov and V.P.Molosnova(Metallurg.Inst.,Dnepropetrovsk). Zhur. Obshchei Khim. 28, 30-5(1958). Cf. this j.27,3075(1957).

Equimolar amounts of $PCl_5$ and aliphatic esters of oxamic acid yield the amides of alkoxydichloroacetic acids, but the aromatic oxamates do not yield the corresponding aryloxydichloroacetamides, yielding only the $ArOCCl_2CON:PCl_3$, possibly owing to the difficulty associated with the addn. of $PCl_4^+$ ion to the O atom. To 25 ml. $CCl_4$ and 0.1 mole Me oxamate there was added at 8-10° 0.1 mole powd.$PCl_5$ and after 3 hrs. when HCl evolution subsided there formed the ppt. of 60-4% $MeOCCl_2CONH_2$, m.95-6°, which is but slowly attacked by $H_2O$ at room temp. In storage this slowly loses MeCl, the process being accelerated by elevated temp. Treated with 2 moles PhONa in $C_6H_6$ this gave 70-3% $(PhO)_2(MeO)CCONH_2$, m.157-9°. Similarly was prepd. 70% $EtOCCl_2CONH_2$, m.81-2°(from $CCl_4$). Similarly was prepd. 90% $BuOCCl_2CONH_2$, m.57-9°(from petr.ether), and 90% iso-$BuOCCl_2CONH_2$, m.76-8°. On heating these amides yield RCl, HCl and solid unidentified products. The ease of decompn. decreases with increased size of the alkoxy group, which fact makes the isolation of Me and Et members a difficult task.

organic

Diesters of aromatic acylamidophosphoric acids.

A.V.Kirsanov and R.G.Makitra (Insecticide Lab., Inst.Organ.Chem. Ukrain. Akad.S.S.R., Kiev). Zhur.Obshchei Khim. 28, 35-40(1958).

Addn. of 0.01 mole $BzNHPOCl_2$ to 0.03 mole MeONa in 15 ml. MeOH with cooling gave after refluxing 15 min., filtration and acidification with HCl 87% $BzNHPO(OMe)_2$, m.116-8°(from 20% EtOH). Similarly p-$MeC_6H_4ONa$ in dioxane gave 26% $BzNHPO(OC_6H_4Me\text{-}p)_2$, m.146-7°(from aq.EtOH). Similarly were prepd.: di-p-chlorophenyl ester, 28.5%, m.131-3°; di-p-nitrophenyl ester, m.151-2°. To 0.01 mole PhONa was rapidly added 0.033 mole $BzN:PCl_3$ in 80 ml. $C_6H_6$ and after refluxing 15 min. with stirring the mixture was refluxed 5 min. with 25 ml. $H_2O$, and the org.layer after washing with $H_2O$ gave 65.1% $BzNHPO(OPh)_2$ m.147-9°; similarly were prepd.: di-p/cresyl ester, 52.4%, m.146-7°(identical with above described); 55.6% di-1-naphthyl ester,m.195-6°; 75.6% di-p-chlorophenyl ester, m.131-3°. Similar reaction gave 34.4% p-$ClC_6H_4CONHPO(OPh)_2$, m.142-3°(the reaction is best run in $Et_2O$ to lessen the formation of p-chlorobenzonitrile); similarly was prepd. 31.3% di-p-cresyl ester,m.139-40°; 74% di-p-chlorophenyl ester, m.155-6°; 89% p-$O_2N$-$C_6H_4CONHPO(OPh)_2$, m.151-2°; 54.6% di-p-cresyl ester, m.165-7°; 70.5% $Et_2O$ di-p-chlorophenyl ester, m.175-6°. Similarly were prepd.: 90.7% $BzNHPO$-

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$(OC_6H_4NO_2\text{-}o)_2$, m.154-5°; 66% di-nitrophenyl ester, m.151-2°; 62% $p\text{-}ClC_6H_4\text{-}CONHPO(OC_6H_4NO_2\text{-}o)_2$, m.179-80°; 57.8% di-p-nitrophenyl ester, m.167-8°; 84.6% $p\text{-}O_2NC_6H_4CONHPO(OC_6H_4NO_2\text{-}o)_2$, m.178-9°; 81.7% di-p-nitrophenyl ester, m.179-80°. Addn. of 0.025 mole $BzNH_2PCl_3$ to 0.1 mole MeONa in MeOH gave after concn. in vacuo and treatment with aq.HCl 56.6% $BzNHPO(OMe)_2$, m.116-8°. Similarly were prepd.: 90.9% $p\text{-}ClC_6H_4CONHPO(OMe)_2$, m.125-6°; and 87.3% $p\text{-}O_2NC_6H_4CONHPO(OMe)_2$, m.153-4°.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 Continuation of old work

Trichlorophosphaseacyls, trichloroisophosphaseacyls and their derivatives. A.V.Kirsanov and G.I.Derkach (Metallurg.Inst., Dnepropetrovsk). Zhur.Obshchei Khim. 27, 3248-54(1957). Cf. this j.27,1080(1957).

It is proposed that substances of type RC(O)N:P$^{V}$ be named phosphaseacyls, and those of type RC(-):NP(O): be named isophosphaseacyls. Heating 0.1 mole $Ph_2CClCONH_2$ and 0.105 mole $PCl_5$ at 85-95° 20-5 min. until HCl evolution ceased, followed by addn. of petr.ether and allowing the mixture to stand 1 day at 0° gave 94% $Ph_2CClCON:PCl_3$ (I), m.60-2° (from petr.ether), which heated to 195-200° gave 90% $POCl_3$ and 91.8% $Ph_2CClCN$, $b_5$ 165-6°. Similarly was prepd. (the reaction is run best in $CCl_4$), 98.8% $Ph_3CCON:PCl_3$, m.123-5° (from petr.ether). I with equimolar amount of dry $HCO_2H$ in $C_6H_6$ gave 99.4% $Ph_2CClCONHPOCl_2$ (IA), m.122-3°. This heated with equimolar amount of $PCl_5$ 15-20 min. at 135-40°, then freed of $POCl_3$ in vacuo and treated at 0° with petr. ther gave after 1 day 87.7% $Ph_2CClC(:NPOCl_2)Cl$ (II), m.81-3° (from petr.ether). Similarly there was prepd. 98% $Ph_3CCONHPOCl_2$, m.128-30° (the reaction with $HCO_2H$ is best run in $CCl_4$), which on melting yields $POCl_3$, $Ph_3CCN$ and metaphosphoric acid; with $PCl_5$ the reaction either yields $Ph_3CCN$ or, at lower temp., fails to take place. Heating $p-O_2NC_6H_4CONHPOCl_2$ with 5% over equimolar amount of $PCl_5$ at 125-30° 20-5 min. gave after removal of $POCl_3$, 76% III) $p-O_2NC_6H_4CCl:NPOCl_2$, m.121-4° (from $C_6H_6$-petr.ether); hydrolysis of this under a variety of conditions gave $p-O_2NC_6H_4CN$ only. I with 3 moles 1-$C_{10}H_7ONa$ in $Et_2O$ gave 57.2% $Ph_2CClCON:P(OC_{10}H_7-1)_3$, m.121-2°, which refluxed 8 min. with $H_2O$ gave 84.2% $Ph_2C(OH)CON:P(OC_{10}H_7-1)_3$, m.148-1°, which is devoid of titratable properties as an acid; heated with bases it yields only tars. II and 1-$C_{10}H_7ONa$ similarly gave 49.7% glassy $Ph_2CClC(OC_{10}H_7-1):NPO(OC_{10}H_7-1)_2$, m.42-7°, after treatment of the crude product in $Et_2O$ with 0.3N NaOH with ice cooling; treatment of the ester with bases yields tars. IA and 1-$C_{10}H_7ONa$ in $Et_2O$ reacted violently yielding 69.4% $Ph_2CClCONHPO(OC_{10}H_7-1)_2$, m.168-70°, soluble in aq.alkalies. IB and 3 moles RONa in $Et_2O$-$C_6H_6$ gave 99.8% $p-O_2NC_6H_4CON:P(OC_{10}H_7-1)_3$ (IV), m.83-6° (boiling with EtOH gave an unidentified substance, m.140-3°) (IB= $pO_2NC_6H_4CON:PCl_3$). Similarly III gave 16.5% $p-O_2NC_6H_4C(OC_{10}H_7-1):NPO(OC_{10}H_7-1)_2$ (V), m.147-8°, the low yield being caused by the need to wash the crude product with aq.NaOH with ice cooling in $Et_2O$ soln. IV kept 2 hrs. with 0.2N NaOH and EtOH gave after concn. and acidification with HCl 80.3% $p-O_2NC_6H_4CONHPO(OC_{10}H_7-1)_2$, m.188-90°, also formed on similar hydrolysis of the isophosphase isomer V.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 phorus; continued old work

Dialkylamides of triarylexyphosphazosulfuric acids and aromatic esters of N,N-dialkylsulfamido-N'-phosphoric acids.

A.V.Kirsanov and Z.D.Nekrasova (Metallurg.Inst.,Dnepropetrovsk). Zhur.Obshchei Khim.27, 3241-8(1957). Cf. this j.27,1253(1957).

To 0.06 mole finely powdered and thoroughly dried PhONa in 50 ml. $C_6H_6$ was added at once 0.02 mole $Me_2NSO_2N:PCl_3$ in $C_6H_6$ (exothermic reaction) and after 0.5 hr. on a steam bath the mixture was filtered and evapd. in vacuo yielding 91% $Me_2NSO_2N:P(OPh)_3$, m.88-90°(from EtOH). Similarly was prepd. the $Et_2N$-analog, 94.6%, which was an oil. With use of some 10% excess RONa there was similarly obtained 100% $Me_2NSO_2N:P(OC_6H_4Cl-p)_3$, m.119-20°(from $CCl_4$) and its $Et_2n$-analog, m.113-5°. The 2 latter esters on boiling with EtOH are hydrolyzed to diaryl esters. Similarly, but in $Et_2O$ soln., there was prepd. 55.2% $Me_2NSO_2N:P(OC_6H_4Cl-o)_3$, m.69-70°(from petr.ether), and its $Et_2N$-analog, m. 40-2°. Similarly (in $C_6H_6$) was prepd. 93.5% $Me_2NSO_2N:P(OC_6H_4NO_2-p)_3$, m.144-6°, and its $Et_2N$-analog, m.148-50°. Similarly were prepd.: $Me_2NSO_2N:P(OC_6H_4NO_2-o)_3$ m.141-2°, and its $Et_2N$-analog, m.115-7°; 70% $Me_2NSO_2N:P(OC_{10}H_7-1)_3$, m.123-4°, and its $Et_2N$-analog, m.110-11°. Heating 0.002 mole of the above esters with 15 ml. EtOH and 4 ml. N NaOH 1 hr. at reflux, removal of EtOH (the resulting aq. soln. should be perfectly clear, indicating complete hydrolysis ) and acidification with aq.HCl gave the following diaryl esters (the Na salts of some of these are sparingly sol. in $H_2O$): $Me_2NSO_2NHPO(OPh)_2$, 94%, m.143-4°; 91% its $Et_2N$ analog, m.122-3°; 75%, $Me_2NSO_2NHPO(OC_6H_4Cl-p)_2$, m.167-8°; its $Et_2N$-analog, m.110-2°; 86% $Me_2NSO_2NHPO(OC_6H_4Cl-o)_2$, m.137-9°; its $Et_2N$-analog, m.110-11°; $Me_2NSO_2NHPO(OC_6H_4NO_2-p)_2$, 97.5%, m.197-8°; its $Et_2N$-analog, m.148-50° (the Na salts of these are sparingly sol. in $H_2O$ in the cold); $Me_2NSO_2$-$NHPO(OC_6H_4NO_2-o)_2$, m.163-4°; its $Et_2N$-analog, m.142-3°; $Me_2NSO_2NHPO(OC_{10}H_7-1)_2$ m.190-1°; its $Et_2N$-analog, m.171-2°. These esters are formed in similarly high yield by reaction of $R_2NSO_2NHPOCl_2$ with 3 moles ArONa in $C_6H_6$

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Reaction of alkyl esters of trichloromethylphosphonic acid with alkylamin
Gil'm Kamai and F.M.Kharrasova (Chem.Technol.Inst.,Kazan). Zhur. Obshchei
Khim. 27, 3064-7(1957).

$(RO)_2P(O)CCl_3$ react with dialkylamines without rupture of the P-C bond and form largely the ester salts. To 5.5 g. $(MeO)_2PHO$ in 7.52 g. $CCl_4$ there was added with cooling 4.5 g. $Me_2NH$; filtration gave 97% $Me_2NH.HCl$ while the filtrate gave 85% $Me_2NPO(OMe)_2$, $b_{11}$72-2.5°, $n_D^{20}$1.4175, $d_0^0$ 1.153; $d_{20}$1.1317. Similarly were prepd.: 66% $Me_2NPO(OEt)_2$, $b_{12}$84°, 1.4180, 1.0678, 1.0469; 91% $Me_2NPO(OCHMe_2)_2$, $b_{12}$84-4.5°, 1.4160, 1.0078, 0.9892; 84% $Me_2NPO(OPr)_2$, $b_{11}$125-6°, 1.4280, 1.0000, 0.9826; 55% $Et_2NPO(OMe)_2$, $b_8$82.5-3°, 1.4265, 1.0885, 1.0664; 86% $Et_2NPO(OEt)_2$, $b_{13}$101°, 1.4242, 1.0297, 1.0113; 70% $Et_2NPO(OCHMe_2)_2$, $b_{20}$115°, 1.4205, 0.9840, 0.9660; 84% $Et_2NPO(OBu)_2$, $b_9$133.5°, 1.4320, 0.9814, 0.9641. To 6.8 g. $CCl_3PO(OMe)_2$ was added 4.5 g. $Et_2NH$ in 10 ml. $Et_2O$, yielding on the following day a ppt. of $CCl_3P(O)(OH)_2.Et_2NH$, m.82-2.5°(from $Me_2CO$-petr.ether), in 99% yield. Heating 11 g. $CCl_3PO(OEt)_2$ and 9.48 g. $Et_2NH$ in sealed tube 6 hrs. at 40-50° and 0.5 hr. at 90-100° gave 14 g. $CCl_3PO(OEt)OH.Et_2NH$, m. 69.5-70°(from $C_6H_6$-petr.ether). Similarly was prepd. 45% $CCl_3PO(OCHMe_2)$-$OH.Et_2NH$, m.100.5-101°. Reactions of $Me_2NH$ or $Et_2NH$ with $CCl_3PO(OR)_2$ where R=Pr, Bu or iso-Bu, gave only uncrystallizable sirups, which were not examined further. Reaction as performed above fails to take place when $Ph_2NH$ is used as the amine; the latter failed to react with $(RO)_2PHO$ in $CCl_4$ also. The results indicate that the amidation of dialkyl phosphites in the presence of $CCl_4$ proceed through formation of $(RO)_2POCl$. Cf. Atherton et al., J.Chem.Soc.1945,660; 1947,674; Kennard et al. JACS 77,1156(1955).

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Salts of dichlorides of arylsulfonamidophosphoric acids.
E.S.Levchenko and A.V.Kirsanov. Zhur. Obshchei Khim. 27,3078-82(1957).
Reaction of $PhSO_2NHPOCl_2$ with $PhNH_2$ in $Et_2O$ yields a ppt. of $[PhSO_2NPOCl_2]^-(PhNH_3)^+$, which can be recrystallized from $CHCl_3$ and which is sol. in $H_2O$, being hydrolyzed by warm $H_2O$. The ability to form such salts was extended to alkali metals. Thus 0.1 mole powd. $ArSO_2NHPOCl_2$ added gradually to sats. aq. soln. of 5 g. $K_2CO_3$ over 10-15 min. at room temp. (no heat evolution) gave solid K salts $ArSO_2NKPOCl_2$, which are washed with ice-$H_2O$, EtOH and recrystallized from MeOH or EtOH; thus were obtained the following salts (Ar shown): 94% Ph, dec.197-8°; 51% p-$MeC_6H_4$, dec.210-3°; 83% p-$ClC_6H_4$, dec.207-8°; 100% o-$O_2NC_6H_4$, dec. 199-200°; 87% p-$O_2NC_6H_4$, dec.190-2°; 100% m-$O_2NC_6H_4$, dec.205-6°. The $PhSO_2NPOCl_2.PhNH_3$ salt, m.107-100°. Addn. of 0.02 moles NaOMe in MeOH to 0.01 mole above K salts gave after distn. of MeOH, soln. of the residue in $H_2O$ and acidification with HCl, the following esters $ArSO_2NH-PO(OMe)_2$ (Ar shown): 93% Ph, m.106-8°; 60% p-$ClC_6H_4$, m.128-9°; 83% m-$O_2NC_6H_4$, m.150-1°. Addn. of $PhSO_2N:PCl_3$ (0.01 mole) to 5 g. $K_2CO_3$ in 10 ml. $H_2O$ (exothermic) and cooling gave 54% $PhSO_2NKPOCl_2$, dec.197-8°, identical with above prepn. Heating 0.1 mole p-$ClC_6H_4SO_2NH_2$ and 0.1 mole $PCl_5$ heated 1.5 hrs. at 100-5° until HCl evolution ceased gave on cooling 100% p-$ClC_6H_4SO_2N:PCl_3$ (I), m.71-3°(from petr.ether). This (0.1 mole) in 20 ml. $C_6H_6$ was treated with 0.15 mole AcOH yielding a ppt. of 90% p-$ClC_6H_4SO_2NHPOCl_2$, m.148-50°(from $C_6H_6$). To 0.025 mole I in $C_6H_6$ was slowly added with cooling NaOMe in MeOH from 0.075 at. Na in 30 ml.MeOH yielding after filtration, evapn. and treatment with $H_2O$, followed by extn. with $Et_2O$ and evapn. of the ext., 41% p-$ClC_6H_4SO_2N:P(OMe)_3$, m. 51-2°(from petr. ether), while the aq. soln. on acidification with HCl gave 20% p-$ClC_6H_4SO_2NHPO(OMe)_2$, m.129-30°(from $C_6H_6$), at first forming thin needles which gradually change in contact with $C_6H_6$ into large prisms.

organophosphorus;
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Organophosphorus polymers. 2. Polycondensation of di-2-chloroethyl esters of alkyl- and arylphosphonic acids.

V.V.Korshak, I.A.Gribova and V.K.Shitikov (Inst.Hetero-org.Compds.,Moscow).

Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1958, 210-6. Cf. 1957,631.

Heating $RP(O)(OCH_2CH_2Cl)_2$ (I) to 220-50° results in elimination of $(CH_2Cl)_2$ and formation of polymeric products in the course of 7-9 hrs., the polymer having generally less than 100 units per chain. Thus I (R=Me) gave a 10-unit polymer at 220°, 20 unit one at 230°, 40 unit one at 240°, but at 250° the free acid of I was formed owing to degradation of I to the free acid and aldehyde. Treatment of 161 g. $ClCH_2CH_2OH$, 202 g. $Et_3N$ in 1.8 l. dioxane at below 5° with 133 g. $MePOCl_2$ gave after 1.5 hrs. on a steam bath 61.2% I (R=Me), $b_1$ 115-6°, $n_D^{20}$ 1.4662, $d_{20}$ 1.3491. This heated as above gave 50-5% polymer an a brown viscous fluid, while the mixture evolved $(CH_2Cl)_2$ and some $MePO(OCH_2)_2$, $b_2$ 110-2°, 1.4590, 1.3545. Heating the reaction mixture with Na several hrs. at 120-40° gave a polymer with mol.wt.622, indicating the presence of the above cyclic ester in the initial reaction mixture; the thermal polymerization yields some AcH as a byproduct. At 250° the products included 23.8% $MePO_3H_2$. Similarly $ClCH_2CH_2OH$, $Et_3N$ and $ClCH_2POCl_2$ in dioxane gave 72% I ($R=ClCH_2$), $b_3$ 158-60°, 1.4845, 1.4637, which in 10 hrs. at 230° gave 88% polymeric viscous product. Similarly was prepd. 43.3% I (R=Ph), $b_1$ 153-4°, 1.5282, 1.3248, which at 250° in 10 hrs. gave 62.4% polymeric fluid with 27 links per chain (mol.wt.). Reaction of 72 g. $POCl_3$ with 106 g. $ClCH_2CH_2OH$ in $C_6H_6$ gave 66.6% $(ClCH_2CH_2O)_3PO$, $b_2$ 168-70°, 1.4728, 1.4289, which at 240° or 280° evolved $(CH_2Cl)_2$ and gave gaseous products and viscous polymeric fluids. The polymers are believed to be repeating units of $-OCH_2CH_2OP(O)R-$ type, formed in part through the initially formed cyclic esters of type $RP(O)(OCH_2)_2$.

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Telomerization of methacrylic acid with trialkyl phosphites.

V.A.Kukhtin, G. Kamai and L.A.Sinchenko (S.M.Kirov Chem.Tech.Inst., Kazan). Doklady Akad.Nauk S.S.S.R.118, 505-8(1958). Cf. Connell and Coover, JACS 78,4453(1956).

Thoroughly purified $(EtO)_3P$ (purified by treatment with Na and careful distn.) undergoes telomerization with $CH_2:CMeCO_2H$ without added catalyst either at room temp. or on being heated. The ester purified by mere distn. does not telomerize. While MeONa or $Et_3N$ do have catalytic effect on this telomerization, they fail to produce high yields of products. The best catalyst is $Bz_2O_2$. Treatment of 1:1 to 1:10 mixtures of $(EtO)_3P$ and $CH_2:CMeCO_2H$ with 0.001-0.2% $Bz_2O_2$ yielded telomers of varying mol. wts. having general formulation $(EtO)_2P(O)(CH_2CMeCO_2)_nEt$, the reaction being performed at 20° with up to 89% yields (0.1% catalyst used). The products are powders which soften and char on heating; they are insol. in the usual solvents except for hot MeOH or AcOH. Mol.wts. range up to 2109. The possibly ionic route of the reaction is discussed, with the $(RO)_3P^+$ and $CO_2^-$ being the polar terminals of the chain initiating and propagating reaction links. Structures of the telomers was not examined. Keeping a 1:1 mixture of $(EtO)_3P$ and $CH_2:CMeCO_2H$ at room temp. until the ester had completely disappeared yielded presumably the initial adduct such as $(EtO)_3\overset{+}{P}CH_2CMeCO_2^-$ (presumably cyclized); this was treated in situ with 8 moles $CH_2:CMeCO_2H$ and 0.01% $Bz_2O_2$, which led to intense formation of the telomer formed in 51% yield (mol.wt.680). Increased proportion of $CH_2:CMeCO_2H$ monomer in the mixture raises the av.mol.wt. of the product; increased concn. of $Bz_2O_2$ also raises the av.mol.wt. of the telomer (0.1% gave 2109, 0.01% gave 752 and 0.001% gave 515 mol.wt.). This is explained by greater probability of chain termination at low catalyst concns.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 ganophosphorus routine

Condensation of dialkyl hydrogen phosphites with derivatives of carboxylic acids.

V. [illegible]bramov ([illegible] Kirov Chem.Tech.Inst., Kazan). Doklady Akad.Nauk S.S.S.R. 117, 311-3(1957).

$CS(NH_2)_2$ reacts with $(RO)_2PHO$ after being heated to a critical temp., when the reaction becomes vigorous; The di-Me ester reacts at 60°, others require heating in sealed tubes. Since the products do not add S, the reaction apparently proceeds by addn. at the C:S bond. Thus were obtained: 20.5% $(MeO)_2P(O)C(SH)(NH_2)_2$, m.113-4°; 49.8% di-Et ester, m.109-10°; 52% di-Pr ester, m.1[illegible]-4°; 30% di-Bu ester, m.114-5°; and 21% di-iso-Bu ester, m.144-5°. The products are sol. in org.solvents and $H_2O$ and are best crystallized from dioxane. Preliminary exts. showed reaction of $(RO)_2PHO$ with urea, formamide and other derivs. of carboxylic acids. $PhP(O)H(OR)$ also reacts with $CS(NH_2)_2$.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 Phosphorus continue

Trichlorophosphazosulfonenitroaryls and products of their hydrolysis. [illegible] Kirsanov and N.G.Feshchenko, Zhur.Obshchei Khim.27,2817-20(1957). Heating 0.05 mole powd. $O_2NC_6H_4SO_2NH_2$ (X) and 0.035 mole $PCl_5$ under a reflux condenser to 135° for o-isomer or 160-70° for p-isomer, gave an exothermic reaction with loss of HCl, completed in 15 min. After evacuation at 150° to remove residual HCl, the mixture was cooled yielding yellow prisms of $O_2NC_6H_4SO_2NiPCl_3$, which on recrystallization from inert solvents become colorless, but do not change their melting points: o-isomer, m.73-5°; m-isomer, m.82-84°; p-isomer, m.118-9°. Treatment of these in $C_6H_6$ with equimolar amount of $HCO_2H$, finally at 50° [illegible] hr. gave by standing at room temp. 1 day, the corresponding $O_2NC_6H_4SO_2NHPOCl_2$: o-isomer, m.149-51°; m-isomer, m.145-7°; p-isomer, m.143-5° (all with decompn.), which are less readily attacked by moisture than the trichlorides. All react with alcs., amines and phenols. Treatment of the dichlorides with equimolar amount of $HCO_2H$ in $C_6H_6$ at reflux 1.5 hrs. gave after standing at room temp. the corresponding $O_2NC_6H_4SO_2NHPO(OH)Cl$: o-isomer, dec.125-5°; m-isomer, dec. 71-3°; p-isomer, dec. 45-6°. Treatment of these with small amount of $H_2O$ and drying over $H_2SO_4$ and solid KOH gave corresponding $O_2NC_6H_4SO_2NHPO_3H_2$, o-isomer, dec.188-90°; m-isomer, dec.159-61°; p-isomer, dec.173-5°. These boiled in aq. soln. are totally hydrolyzed to $H_3PO_4$. In cold aq. alkalies the acids form sol. salts. The acids titrate as dibasic acids to phenolphthalein; the p-isomer is more sol. in $H_2O$ and EtOH and less in $Me_2CO$ than the o-isomer, a fact explained by hydrogen bonding in the o-isomer.

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N-Thiazolyl- and N-pyridyl derivatives of carbamido-N'-phosphoric acid.

A.V.Kirsanov and E.S.Levchenko. Zhur.Obshchei Khim.27,2588-90(1957).

Cf. this j.26,2285(1956), and 27,1002(1957).

To $Et_2O$ soln. of 0.01 mole $Cl_2PCONCO$ was added dropwise equimolar amount of the desired amine in $Et_2O$ yielding a ppt. of the corresponding $Cl_2P(O)NHCO-NHR$: R shown: 2-benzothiazolyl, dec.152-4°; 2-thiazolyl, very hygroscopic solid; 2-pyridyl, decomposes in air(in hot $H_2O$ this yields after neutralization 2-pyridylurea,m.176-7°). The chlorides treated with $H_2O$ at room temp. gave ppts. of the acids $RNHCONHPO(OH)_2$: 2-benzothiazolyl, dec.306-10°; 2-thiazolyl, dec.156-8°; 2-pyridyl, dec.160-2°. If the reaction mixture in the prepn. of the phosphoryl chlorides is treated with MeONa in MeOH there are formed $(MeO)_2P(O)NHCONHR$: 75% 2-benzothiazolyl, m.157-8°; 90% 2-thiazolyl, m.129-30°; 88% 2-pyridyl, m.154-5°; 3-pyridyl, m.160-1°; 2-methyl-6-benzothiazolyl, m.154-6°. Similarly was prepd. di-Et ester of the 2-benzothiazolyl member, 18%, m.153-4°.Reaction of $(MeO)_2P(O)NCO$ with the amines in $Et_2O$ gave the same products as above. Reaction of $(PhO)_2P(O)NCO$ with the amines gave $(PhO)_2P(O)NHCONHR$: 99% benzo-2-thiazolyl, m.165-6°; 2-methyl-6-benzothiazolyl, 85%, m.194-5°; 89% 2-pyridyl, m.111-3°. I with $Me_2SO_4$ in 0.5 hr. at 130° gave 63% $(PhO)_2P(O)NHCONA$ (A-N-methyl-2-benzothiazolilydine), m.196-200°, which formed on mixing $Et_2O$ solns. of $(PhO)_2P(O)NCO$ and 3-methyl-2-benzothiazoleneimine. The latter with $(MeO)_2P(O)NCO$ similarly gave di-Me N(3-methyldihydrobenzothiazolyl-2-idene)carbamido-N'-phosphate, m.197-8°, which heated 2 hrs. with $Me_2SO_4$ gave 3-methyl-2-benzothiazolonimine,m.120° . Heating di-Pr N(2-methyl-6-benzothiazolyl)carbamido-N'-phosphate with $Me_2SO_4$ at 120° gave the 3-methylmethosulfate, m.196-7°.

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 Si on phosphorus

Reaction of organosilicon compounds with phosphorus chlorides.

A.P.Kreshkov and D.A.Karateev (D.I.Mendeleev Chem.Tech.Inst.,Moscow). Zhur.Obshchei Khim.27, 2715-20(1957). Cf.Stokes, Ber.24,933(1891) and Am. Chem.J. 14,545(1892); Friedel et al. Ber.3,15(1870); Frisch et al. JACS 75,4076(1953); Brit.Pat.706,781(1954); US Pat.2,488,449, CA 44,2287. Refluxing 0.2 mole $(MeO)_4Si$ or $(EtO)_4Si$, or 0.1 mole $(BuO)_4Si$, with 0.1 mole $POCl_3$ 15 min. to 4 hrs. depending on the size of alkyl group, gave the corresponding RCl, distillable substances and undistillable residues of organosilicophosphorus compounds, thermolyses for which are cited; These appear to be polyesters of silanols with partly hydrolysed phosphate esters. Thus were identified $Si_4P_3C_3H_{13}O_{19}$, $Si_2P_2C_2H_{10}O_{12}$, and $Si_3P_2C_4H_{16}O_{15}$ obtained from reactions with $(MeO)_4Si$, $(EtO)_4Si$ and $(BuO)_4Si$, resp. Refluxing equimolar amounts of $(PhO)_4Si$ with $PCl_3$ or $POCl_3$ 15 hrs. gave, resp. $(PhO)_3P$ or $(PhO)_3PO$ in 20-30% yields. Similarly was prepd. $(o\text{-}MeC_6H_4\text{-}O)_3PO$. The substances were characterized by infra-red spectra.

organophosphorus; routine

Allylic rearrangements. XIX. Reactions of organomagnesium compounds with diethyl sodio phosphite with isomeric isoprene hydrochlorides and methoxychloroisohexenes.

A.N.Pudovik and I.V.Shorgina (State Univ.,Kazan). Zhur.Obshchei Khim.27, 2750-5(1957). Cf. this j.26,398, 1635(1956).

Reaction of PhMgBr from 7.8 g. Mg with 40 g. 1-methoxy-3-methyl-5-chloro-3-pentene (I) gave in 4 hrs. 18 g. 1-methoxy-3-methyl-5-phenyl-3-pentene, $b_8$ 121-2°, $n_D^{20}$ 1.5100, $d_{20}$ 0.9420(ozonolysis gave $PhCH_2CHO$). Similarly 1-methoxy-3-methyl-3-chloro-4-pentene gave the same product. EtMgBr treated with I ~~xxxxxxxxxxxxxx~~gave 1-methoxy-3-methyl-3-heptene, $b_{740}$ 162-3°, 1.4300, 0.8151 (ozonolysis gave PrCHO). BuMgBr and I gave 1-methoxy-3-methyl-3-nonene, $b_{11}$ 86-7°, 1.4390, 0.8233. PhMgBr and 1-chloro-3-methyl-2-butene(II) gave 1-phenyl-3-methyl-2-butene, $b_8$ 79-80°, 1.5110, 0.8971, while the use of 3-methyl-3-chloro-1-butene also gave the same product. EtMgBr and II gave 2-methyl-2-hexene. $(EtO)_2PONa$ from 31 g. ester in $Et_2O$ and 30 g. II gave in 3 hrs. 29 g. $Me_2C{:}CHCHP(O)(OEt)_2$, $b_{13}$ 117-8°, 1.4450, 1.0080 (ozonolysis gave $Me_2CO$); the same product, $b_8$ 111-2°, 1.4430, 1.009, formed in similar reaction of 3-chloro-3-methyl-1-butene, the reaction being run either in $Et_2O$ or in $C_6H_6$. Reaction of $(EtO)_2PONa$ with I gave a low yield of $MeOCH_2CH_2CMe{:}CHCH_2P(O)(OEt)_2$, $b_8$ 140-2°, 1.4530, 1.031.

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Dealkylation of isomeric tributenyl phosphites by hydrogen chloride.
A.N.Pudovik (State Univ.,Kazan). Zhur.Obshchei Khim.27,2755-60(1957).
Cf. Doklady Akad.Nauk SSSR 84,519(1952), and Abramov et al. this j.24,1823.
Polemical discussion of previous article and its criticism by Abramov.
It is now shown that $(RO)_3P$ are intermediate products in the reaction of $PCl_3$ with isomeric butenols; the initial dealkylation of these occurs along the lines of Arbuzov rearrangement by the attack of HCl. Further attack by HCl may pursue $S_N1$ or $S_N2$ routes. Since $(RO)_2POH$ are attacked by dry HCl at -10° only very slowly if the radicals in the esters are primary and secondary, the rapid dealkylation of dicrotyl and diisobutenyl esters may be explained by direct action of HCl on the quinquevalent form of the ester through four-center reaction at the PO group, with electron supply provided by induction of alkyl groups aiding the reaction. Reaction of 64.8 g. crotyl alc., 109 g. $PhNMe_2$ and 41.3 g. $PCl_3$ in $Et_2O$ gave 45.5 g. $(MeCH:CHCH_2O)_3P$, $b_1$ 98-9°, $d_{20}$ 0.9757, $n_D^{20}$ 1.4680; this (10 g.) treated with dry HCl at -10° gave 6.5 g. mixed chlorobutenes (86% 1-chloro-2-butene and 14% 2-chloro-3-butene) and 3.2 g. $H_3PO_3$. Addn. of 37 g. $PCl_3$ to 50 g. crotyl alc. at -15° gave after 0.5 hr. stirring and quenching in ice 59.5 g. mixed chlorobutenes of same compn. as above. Similarly $PCl_3$ and $MeCH(OH)CH:CH_2$ gave the same mixture of chlorides. Reaction of $PCl_3$ with BuOH under these conditions gave 84% $(BuO)_2PHO$, while allyl alc. gave 42% $(CH_2:CHCH_2O)_2PHO$ (on distn. the residue tends to explode violently if heated unduly). Passage of dry HCl into $(BuO)_3P$ at -10° and stirring 0.5 hr. gave 1 mole BuCl and $(BuO)_2PHO$. Similarly $(CH_2:CHCH_2O)_3P$ and HCl gave allyl chloride and $(RO)_2PHO$, $b_8$ 97-8°, $n_D^{20}$ 1.4430, with much residue. Reaction of HCl similarly with ~~[illegible]~~ $(CH_2:CHCHMeO)_3P$ gave $H_3PO_3$ and mixed butenyl chlorides (50-3% 1-chloro-2-butene and 47-50% 2-chloro-3-butene). Keeping $(RO)_3P$ in $Et_2O$ in presence of dry HCl at room temp. and following the reaction by periodic analysis for labile Cl showed that in 3 days the Bu ester lost 0.96 mole alkyl radical, allyl ester lost 1.7, crotyl ester lost 2.3 and methallyl ester lost 2.2 ester groups.

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Synthesis of aminoalkylphosphonic acids. Reaction of some heterocyclic ketones with dialkyl phosphites and ammonia.

T.Ya.Medved and M.I.Kabachnik (Inst.Hetero-org.Compounds, Acad.Sci.,Moscow Izvest.Akad.Nauk SSSSR., Otdel.Khim.Nauk 1957, 1357-62. Cf. 1954,314. Into 18 g. 1,2,5-trimethyl-4-piperidone and 17.5 g. $(EtO)_2PHO$ there was introduced dry $NH_3$ (exothermic) and the mixture was heated 3 hrs. at 50° and 2 hrs. on a steam bath in a continued stream of $NH_3$; on cooling the mixture was treated with dry $Et_2O$ yielding a ppt. mainly of $NH_4$ salt of Et phosphite, which was sepd. and the filtrate distd. yielding 43% (I) yellow hygroscopic di-Et 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonate, $b_{0.1}$ 81-3°, $n_D^{20}$ 1.4784, $d_{20}$ 1.0601; picrate, m.165-6°, $C_{24}H_{33}N_8PO_{17}$ (type error?). Similarly 2,2-dimethyltetrahydro-4-pyranone gave 56% di-Et 2,2-dimethyl-4-aminotetrahydropyranyl-4-phosphonate, (II) $b_{0.01}$ 79-81°, 1.4691, 1.1088; thus were also prepd.: 52% di-Bu 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonate, $b_{4x10^{-4}}$ 108-9°, 1.4693, 1.0240; 42% di-Et 1,2,5-trimethyl-4-aminopiperidyl-4-thionophosphonate, $b_3$ 120-3°, 1.4952, 1.0720. I warmed with PhNCO on a steam bath gave di-Et 1,2,5-trimethyl-4-(N-phenylureido)-piperidyl-4-phosphonate, m.198° (from $C_6H_6$). I with AcCl in petr.ether at 20-5° gave very hygroscopic 4-acetamido analog of I, dec.104° as the HCl salt, which with $Na_2CO_3$ in $Et_2O$ gave 33% free ester, $b_{2x10^{-4}}$ 127°, m.115-7° also formed in 56% yield from I heated 10 min. with $Ac_2O$, neutralized and distd. ($b_2$ 164°). I and EtCOCl in petr.ether gave 4-propionamido analog of I, as HCl salt, hygroscopic solid, dec.99°, which gave the free ester on treatment with EtONa; the free ester, 53%, $b_{3x10^{-4}}$ 109-11°, m.105° (from petr.ether). I and BzCl in petr.ether gave 4-benzamido analog of I, 35%, m.131-2°, whose HCl salt, dec.94°, is very hygroscopic. Similarly II and EtCOCl in $C_6H_6$ in presence of pyridine at 50-60° gave 4-propionamido analog of II, m.97° (from $Et_2O$). To 7.05 g. 1,2,5-trimethyl-4-piperidone and 7 g. $(EtO)_2PHO$ was added dropwise EtONa-EtOH (exothermic); after heating 0.5 hr. on a steam bath the low boiling materials were distd. leaving 32% di-Et 1,2,5-trimethyl-4-hydroxypiperidyl-4-phosphonate, m.82-3° (from $Et_2O$). Similarly was obtained 56% di-Et 2,2-dimethyl-4-hydroxytetrahydropyranyl-4-phosphonate, m.75-6° (from petr.ether).

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**Substitution reactions of phosphonoacetic ester and phosphonoacetone.**
A.N.Pudovik, L.P.Shebelkina and L.A.Bashirova (State Univ.,Kazan). Zhur. Obshchei Khim.27, 2367-71(1957). Cf. this J.25,1920(1955); 27,1708(1957).
To a soln. of 3.4 g. Na in 35 g. $EtO_2CCH_2PO(OEt)_2$ in 150 ml. $Et_2O$ was added 20 g. 1-methoxy-5-chloro-3-pentene, yielding after heating and sepn. of NaCl 12 g. $MeOCH_2CH_2CH{:}CHCH_2CH(CO_2Et)PO(OEt)_2$, $b_4$ 167-9°, $n_D^{20}$ 1.4526, $d_{20}$ 1.0718, which oxidized with $KMnO_4$ to methoxypropionic acid, $b_9$ 105-6°. Similar reaction of 1-chloro-2-butene gave $MeCH{:}CHCH_2CH(CO_2Et)PO(OEt)_2$, $b_{10}$ 156-7°, 1.4453, 1.0617, which also formed in similar yield from 3-chloro-3-butene, which thus underwent an allylic shift. Similarly $BrCH_2CO_2Et$ gave $EtO_2C$-$CH_2CH(CO_2Et)PO(OEt)_2$, $b_{3.5}$ 165-6°, 1.4402, 1.1355. The use of $MeCHBrCO_2Me$ gave a moderate yield of Et $MeO_2CCHMeCH(CO_2Et)PO(OEt)_2$, $b_{2.5}$ 151-3°, 1.4432, 1.1434. Similarly $BuOCH_2Cl$ gave $BuOCH_2CH(CO_2Et)PO(OEt)_2$, $b_3$ 177-8°, 1.4415, 1.0612. The soln. from 1.77 g. Na, 15 g. $MeCOCH_2PO(OEt)_2$, and 100 ml. $Et_2O$ was treated with 20 g. $BrCH_2CO_2Et$ yielding after 8 hrs. 6.5 g. $MeCOCH$-$(PO(OEt)_2)CH_2CO_2Et$, $b_3$ 148-9°, 1.4430, 1.1351; similarly $MeCHBrCO_2Et$ gave after 4 hrs. on a steam bath in $C_6H_6$ a modest yield of $MeCOCH(PO(OEt)_2)$-$CHMeCO_2Et$, $b_3$ 151-3°, 1.4556,-. Similar reaction with $AcCH_2Br$ gave a low yield of $MeCOCH(PO(OEt)_2)CH_2COMe$, $b_9$ 125-6°, 1.4510, 1.1415. The Na deriv. of $MeCOCH_2PO(OEt)_2$ reacted with $EtOCH_2Cl$ and $BuOCH_2Cl$ but the products could not be isolated owing to decompn. and tar formation. The reaction of Na deriv. of $EtO_2CCH_2PO(OEt)_2$ with $Me_2CBrCO_2R$ proceeded very slowly even in hot $C_6H_6$ and only traces of higher boiling products were obtained.

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**Addition of complete esters of phosphorous acid and phosphonous acids to conjugated systems. I. Addition of trialkyl phosphites to acrylic and methacrylic acids.**
Gil'm Kamai and V.A.Kukhtin (Chem.Tech.Inst.,Kazan). Zhur.Obshchei Khim.27, 2372-6(1956). Cf. Doklady Akad.Nauk SSSR 102, 283(1955).
To 12 g. $(MeO)_3P$ was added dropwise 7 g. $CH_2{:}CHCO_2H$, producing an exothermic reaction (temp.rise to 125°), after which 2 hrs. at 120° gave 10 g. $MeO_2C$-$CH_2CH_2PO(OMe)_2$, $b_3$ 122°, $n_D^{20}$ 1.4370, $d_4^{20}$ 1.2010 (52%). Similarly were prepd.: 39.4% tri-Et ester, $b_3$ 123-4°, 1.4310, 1.0941; 26.2% tri-Bu ester, $b_4$ 147-9°, 1.4382, 1.0024; 42% tri-iso-Bu ester, $b_6$ 163-5°, 1.4360, 1.0020. To 12 g. $(MeO)_3P$ was added 8.6 g. $CH_2{:}CMeCO_2H$, with slight exothermic effect; after 3 hrs. at 120-30° there was obtained 56.8% $(MeO)_2P(O)CH_2CHMeCO_2Me$, $b_5$ 126-7°, 1.4372, 1.1681; 34.1% tri-Et ester, $b_5$ 123-5°, 1.4335, 1.0761; 31.2% tri-Bu ester, $b_3$ 153-5°, 1.4390, 1.0019; 62.1% tri-iso-Bu ester, $b_5$ 155-7°, 1.4375,

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1.0011; were prepd. similarly. Hydrolysis of $EtO_2CCH_2CH_2P(OEt)_2$ with 15% HCl 3 hrs. at 120-30° gave the free acid, m.168°. Keeping 16.6 g. $(EtO)_3P$ 1 month in sealed ampul with $CH_2:CMeCO_2H$ (8.6 g.) gave an a reaction mixture with $n_D^{20}$1.4310, $d_4^{20}$0.9961; after 2 months these became $n_D^{20}$1.4320, $d_4^{20}$0.9957; treatment of this with $Cu_2Cl_2$ failed to produce an exothermic reaction and the mixture was devoid of typical odor of the phosphite. The material(10.4 g.) was treated with 2 g. MeOH (slight heat evolution) and kept 2 days yielding 5.3 g. $(EtO)_2P(O)CH_2CHMeCO_2Me$, $b_3$120-1°, 1.4346, 1.1021. (Cf. Fudovik, Uspekhi Khim.23,547(1954)). It is suggested that the addn. of the $(RO)_3P$ to the unsatd. acids proceeds with formation of a bipolar ion $(RO)_3P^+CH_2CH:C(OH)O^-$, which may cyclize, then rearrange to the final product. The formation of an intermediate adduct is confirmed by the above described room temp. reaction and by the fact that the thus obtained reaction mixture reacts exothermically with $H_2O$, while the final phosphonocarboxylates do not react with $H_2O$ at room temp. The above reaction is a special form of the Arbuzov rearrangement.

II. Addition of trialkyl phosphites to acrolein and crotonaldehyde. Ibid.2374-80. Cf. Kamai, Kukhtin and Sarogova, Trudy Kazansk.Khim.Tekh.Inst., No.21,155(1956).

To 10 g. $(MeO)_3P$ in dioxane was added 4.5 g. $CH_2:CHCHO$ (exothermic reaction) and the mixture after 2.5 hrs. at 80-90° was distd. with much decompn.; if prior to distn. the mixture is treated with 2.6 g. MeOH and the mixture kept 1 day at room temp., the yield of distd. product rises to 30% of $(MeO)_2P(O)CH_2CH:CHOMe$, $b_3$125-6°, $n_D^{20}$1.4432, $d_4^{20}$1.1570. Similarly were prepd. 19.2% $(EtO)_2P(O)CH_2CH:CHOEt$, $b_3$132-4°, 1.4442, 1.0603; 11% $(PrO)_2P(O)CH_2$-$CH:CHOPr$, $b_5$153-5°, 1.4426, 1.0089; 40.6% $(BuO)_2P(O)CH_2CH:CHCHOBu$, $b_3$156-7°, 1.4460, 0.9806; 17.4% $(iso\text{-}BuO)_2P(O)CH_2CH:CHOCH_2CHMe_2$, $b_3$150-1°, 1.4430, 0.9750. Treatment of the undistd. original reaction mixture of $(EtO)_3P$ above with MeOH and distn. after 2 days at room temp. gave 34.5% $(EtO)_2P(O)CH_2$-$CH:CHOMe$, $b_3$123-4°, 1.4435, 1.0985. Treatment of the Bu member of the above series with 2% $H_2SO_4$ at 70-80° gave after neutralization and distn. a low yield of $(BuO)_2P(O)CH_2CH_2CHO$, $b_5$150-1°, 1.4406, 1.0129; treatment of the reaction product of $(EtO)_3P$ similarly with $H_2O$ gave 31% $(EtO)_2P(O)CH_2CH_2CHO$, $b_4$128-30°, 1.4480, 1.1320. To 17 g. $(EtO)_3P$ was added 7 g. $MeCH:CHCHO$ and the mixture after 2 hrs. at 110° gave 4.7 g.(17.1%) $(EtO)_2P(O)CHMeCH:CHOEt$, $b_1$136-8°, 1.4506, 1.0436. Similarly was prepd. 12.9% $(PrO)_2P(O)CHMeCH:CHOPr$, $b_3$152-4°, 1.4496, 1.0046. The addn. is believed to proceed through a dipolar ion, which cyclizes to an intermediate $(RO)_3PCH_2CH:CHO$. Thus trialkyl phosphites are capable of adding to α,β- and γ-δ conjugated

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Mixed esters of tertiary-1,1,1-trichlorobutyl phosphorous acid.
V.S.Abramov and V.K.Khairullin (Chem.Tech.Inst.,Kazan). Zhur.Obshchei Khim. 27, 2381-86(1957). Cf. this j.27,444 and 1365(1957).
To 0.2 mole glycol or 0.4 mole ROH and 0.4 mole pyridine in 300-400 ml.$Et_2O$ there was added with ice cooling 0.2 mole $CCl_3CMe_2OPCl_2$; after stirring at room temp., and finally at reflux, the mixture was filtered and distd. yielding the following esters: 62.5% $CCl_3CMe_2OP(OCH_2)_2$, $b_5$104°, $d_{20}$1.4226, $n_D^{20}$1.4980; 60% $CCl_3CMe_2OPOCH_2CHMeO$, $b_1$97°, 1.3665, 1.4891; 56.2% $CCl_3CMe_2O$-$P(OCMe_2)_2$, $b_3$122-3°, d 1.2635, 1.4830, m.60-1°; 95% $CCl_3CMe_2OPO_2C_6H_4$-o, $b_6$151°, m.62-3°; 79.2% $CCl_3CMe_2OP(OMe)_2$, $b_9$106°, 1.3346, 1.4779; 75% $CCl_3$-$CMe_2OP(OEt)_2$, $b_1$90°, 1.2898, 1.4700; 62.2% $CCl_3CMe_2OP(OBu)_2$, $b_1$123-4°, 1.1611, 1.4675; 85.6% $CCl_3CMe_2OP(OCHMe_2)_2$, $b_{1.5}$98°, 1.1872, 1.4612; 58% $CCl_3CMe_2OP(OCH(CH_2Cl)_2)_2$, $b_3$194-7°, 1.4730, 1.5132; 70% $CCl_3CMe_2OP(OC_6H_{11})_2$, $b_3$183-4°, 1.2105, 1.4985; & 78% $CCl_3CMe_2O$-$P(OPh)_2$, $b_2$189-90°, 1.3130, 1.5640; 61.4% $CCl_3CMe_2OP(OCMe_2CN)_2$, $b_1$163°, 1.2533, 1.4776. The esters formed adducts with $Cu_2Cl_2$ of type ester.CuCl; these were crystalline solids in the following examples of the R radicals: $(CMe_2)_2$, m.174-5°; o-$C_6H_4$, m.146°(dec.); Me, dec.157-8°; iso-Pr, m.144-4.5°; $C_6H_{11}$ m.160-1°; Ph, m.121-2°; $CMe_2CN$, m.148°. The reaction of the above chlorophosphite with benzpinacol failed even at 100° in the presence of pyridine. The reaction with tert.alcs. did proceed in cases of $Me_3COH$, $Ph_3COH$ and 1-trichloromethylcyclohexanol; the 1st of these gave (RO)(R'O)PHO, the 2nd gave $Ph_3CCl$, while the third gave (RO)-(R'O)PCl (cf. above refs.)..

Reaction of dialkyl phosphites with aldehydes and ketones. XIV. Tertiary 1,1,1-trichloromethylcyclohexyl esters of substituted α-hydroxymethylphosphonic acid.
V.S.Abramov and V.K.Khairullin (Chem.Tech.Inst.,Kazan). Zhur.Obshchei Khim. 27, 2387-9(1957). Cf.this j.26,811(1956);27,2381(1957).
Brief heating of equimolar mixtures of appropriate carbonyl compounds and $(CCl_3CMe_2O)[(CH_2)_5CCl_2O)PHO$ in ampul to 50-60°, followed by standing at room temp. gave the following $(CCl_3CMe_2O)[(CH_2)_5CCl_2O]P(O)CRR'OH$:(R,R', shown, resp.): H, Me m.179-81°; H, Et, m.172-80°; H, Pr, m.156-8°; H, iso-Bu m.177-8°; H, $CCl_3$, m. 162.5°; H, Ph, m.144-6°; H, p-$MeOC_6H_4$, m.150-2°; H, m-$O_2NC_6H_4$, m.154-6°; Me, Me, m.145-7°; $CH_2Cl$, $CH_2Cl$, m.168-8.5°; $(CH_2)_4$, m.190°(dec.); $(CH_2)_5$, m.166-7.5°. These were crystallized from EtOH or $CHCl_3$-MeOH; they are substantially insol.in $H_2O$. The reaction was complete in 24-318 hrs. at room temp. as evidenced by crystallization.

Osmophosphorus routine

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Preparation and some properties of intermediate products of the Arbuzov rearrangement.

A.I.Razumov and N.N.Bankovskaya (S.M.Kirov Chem.Tech.Inst.,Kazan). Doklady Akad.Nauk S.S.S.R. 116, 241-3(1957). Cf. Kamai and Nukhtin, this j.112,868 (1957).

In order to decrease the probability of decompn. of the intermediates in the Arbuzov rearrangement by the necessarily elevated temp. of the reaction, the authors selected $R_2POR$ as the initial ester, owing to their ease of entry into the Arbuzov reaction without heating. (Addn. of MeI to $Et_2POEt$ at room temp. leads to explosive reaction and liberation of $I_2$). Addn. of MeI to $Et_2POEt$ at -6° results in complete reaction in 0.5 hr. and formation of crystalline product, $Et_2MeP(OEt)I$, m.56-8°(after washing with dry $Et_2O$). This kept in desiccator over $P_2O_5$ decomposed spontaneously in 24-5 days at 18°, the reaction commencing rather abruptly; at 45° the formation of the complex is terminated in 20 min. and the reaction proper is complete in 5.75 hrs., while at 55° the complex formation is complete in 10 min. and the reaction is complete in 2 hrs. Similarly, EtI and $Et_2POEt$ react in 22-3 hrs. at 21° yielding $Et_3P(OEt)I$,m.79-81°, which over $P_2O_5$ decomposed after 15 days at 21°. PrI and $Et_2POEt$ in 42-4 hrs. at 18° gave $PrEt_2P(OEt)I$, m.73-5°, which decomposed over $P_2O_5$ in 10 days at 18°. The adducts are sol.in polar solvents and $C_6H_6$, insol. in $CCl_4$. The decompn. of the adducts yields $R_3PO$ and RX; owing to hygroscopicity of the phosphine oxides they were isolated as chloroaurates; thus chloroaurate of $Et_3PO$, m.53-4°(cf.Pickard and Kenyon, J.C.S. 89,262(1906)). The dipole moment of $PrEt_2P(OEt)I$ was 5.0D; the value for this compares with $(PhO)_3PMeI$ (Cf. B.A.Arbuzov et al.,Khimiya i Primen.Fosfororgan.Soedinenii, 1957,p.69). Thus the bond in the quasiphosphonium compound is not purely covalent or purely ionic.

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**Bis-trialkylsilylphosphonates.**

M.G.Voronkov, V.A.Kaleneva and V.N.Egorenik (Silicate Chem.Inst.,Leningrad).

Izvest.Akad.Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1363-7.

Slow distn. of 28.3 g. $Et_3SiOMe$ from 5.2 g. crystalline $H_3PO_3$ gave 4 g. MeOH and 67% $(Et_3SiO)_2PHO$, $b_3$152-3°, $d_{20}$0.9584, $n_D^{20}$1.4402 (increase of proportion of reactants to 4:1 failed to alter the yield or the product); Raman spectrum in $cm^{-1}$: 254(1), 303(3), 393(0), 564(10), 623(2), 671(0), 733(2), 753(2), 973(8), 1008(5), 1018(5), 1110(1), 1232(4), 1267(1), 1382 (1), 1412, 1465(10), 2423(1), 2884(12), 2917(7), 2942(2), 2965(10). Thus were obtained 40% $(MeEt_2SiO)_2PHO$, $b_6$138-45°, 0.9498, 1.4299, whose Raman spectrum wasandetd., and 50%$(MePr_2SiO)_2PHO$, $b_{17}$185-6°, 0.9373, 1.4385, whose Raman spectrum was: 173(2), 196(2), 232(2), 265(2), 351(1), 436(0), 520(0), 591(1), 644(1), 700(1), 753(2), 800(2), 873(1), 897(6), 1032(7), 1069(5), 1103(1), 1206(5), 1259(2), 1300(2), 1341(0), 1410(8), 1454(10), 2429(2), 2735(1), 2874(12), 2911(12), 2935(3), 2968(12). Refluxing 48.9 g. $Me_3SiCl$ and 12.3 g. $H_3PO_3$ in 25 ml. $C_6H_6$ until HCl evolution stopped gave 57% $(Me_3SiO)_2PHO$, $b_{763}$196°, $b_3$74-5°, 0.9661, 1.4145, whose Raman spectrum was:171(8), 198(10), 229(1), 262(7), 286(1), 321(0), 367(1), 439(0), 507(0), 521(1), 566(3), 593(8), 610(8), 656(10), 700(10), 765(8), 851(6), 930(0), 991(3), 1006(3), 1039(1), 1093(1), 1134(4), 1259(10), 1322(2), 1383(1), 1416 (10), 2426(3), 2887(12), 2970(12); similarly was prepd. 73% $(Et_3SiO)_2PHO$, $b_5$162-4°, -,1.4412. The 560-593 $cm^{-1}$ region is assigned to Si-C vibrations, 610-671 to Si-O, 700-765 to P-O, 873-1069 to H-P-O and C-C, 1093-1206 to P-O, 1232-1275 to P=O and CH; 1320-1465 to CH, 2423-9 to P-H, and higher bands to CH vibrations. Refluxing 32.2 g. $Et_3SiOMe$ and 5.6 g. $H_3PO_3$ in a stream of dry air 8 hrs. gave 80% MeOH and 58% $(Et_3SiO)_3PO$, $b_{10}$208°,0.9668, 1.4452; similarly was prepd. $(Me_3SiO)_3PO$, $b_6$98-104°, -,1.4082, whose Raman spectrum was:170(10), 190(5), 220(1), 246(4), 258(5), 330(1), 345(1), 460(1), 589(7), 614(10), 652(5), 697(7), 760(5), 846(5), 1200(1), 1257(5), 1275(2), 1320(1), 1372(1), 1414(7), 2907(10), 2970(10). $(R_3SiO)_2POH$ are hydrolysed by $H_2O$ and alcs. yielding $H_3PO_3$. They do not add CuX; they react with MeMgX yielding $CH_4$, but only the Et member gave 100% yield, the others giving much lower yields of methane. Cf. Voronkov, Zhur.Obsh.Khim.27,1483(1957), 25,469(1955).

organosilicon phosphorus

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Condensation of nitroparaffins with ketones and a study of the action of halogen compounds of phosphorus on the resulting nitro alcohols. L.M.Kozlov, E.F.Fink and D.G.Liertar. Trudy Kazan. Khim.Tekhnol.Inst. im. S.M.Kirova, 25, 148-60(1957).

To 30 g. $EtNO_2$ and 250 ml. $Me_2CO$ was added 0.5 g. Na in 25 ml. abs.MeOH and the mixture was shaken 30 hrs. at room temp. yielding after neutralization with 6N HCl, 21% $Me_2C(OH)CHMeNO_2$, $b_{12-13}$ 87-8°, $d_D^{15}$ 1.0739, $n_D^{15}$ 1.4460. Similarly were obtained: 37% $Me_2C(OH)CH_2NO_2$, $b_{12}$ 81-2°, 1.0749, 1.4043; 20% $Me_2C(OH)CHEtNO_2$, $b_{12}$ 96-7°, 1.0724, 1.447; 19% $Me_2C(OH)CMe_2NO_2$, $b_{12-13}$ 89-90°, 1.0715, 1.451; 24% $MeEtC(OH)CH_2NO_2$, $b_{12}$ 90-2°, 1.1099, 1.4504; 42.1% $(CH_2)_4C(OH)CH_2NO_2$, $b_{14}$ 110-11°, 1.1780, 1.4810; 85% $(CH_2)_5C(OH)CH_2NO_2$, $b_{14}$ 120-1°, 1.1665, 1.4901; 53% $(CH_2)_5C(OH)CHMeNO_2$, $b_{14}$ 123-4°, 1.1121, 1.4850; 45% $(CH_2)_5C(OH)CMe_2NO_2$, $b_{14}$ 128-30°, 1.1025, 1.4810; 39% $(CH_2)_5C(OH)CHEtNO_2$, $b_{14}$ 133-4°, 1.0964, 1.4740. To 20 g. 1-nitro-2-propanol and 15.2 g. pyridine in $Et_2O$ was added with cooling 9.6 g. $PCl_3$ in $Et_2O$, yielding after 2 hrs. at room temp., followed by filtration, 0.75 g. $MeCH:CHNO_2$, 1.5 g. mixed original ROH and the nitro-olefin, and a polymerized undistillable residue. Similar reaction of 1-nitro-2-propanol with $EtOPCl_2$ in the presence of pyridine at 5° gave 32% $MeCH:CHNO_2$ and a polymerized residue. Similarly $EtOPCl_2$ and 1-nitro-2-methyl-2-propanol gave 54.7% $Me_2C:CHNO_2$ and a polymerized residue; the use of 1-nitro-2-pentanol in this reaction gave 46% $PrCH:CHNO_2$ and a polymerized residue. 1-Nitro-2-methylp2-propanol and $EtOPCl_2$ gave 46.3% 1-nitro-2-methyl-1-propene and a small amount of unidentified material, $b_{13}$ 107-15°. 1-Nitro-2-methyl-2-propanol and $AsCl_3$ gave some original ROH and a fraction, $b_{18}$ 39-67.5°. Reaction of 1-nitro-2-methyl-2-propanol under these conditions with $POCl_3$ gave some unreacted ROH and 40% 1-nitro-2-methyl-1-propene. Reaction of $(EtO)_2PONa$ from 3 g. Na and $(EtO)_2PHO$ in $Et_2O$ with 17.15 g. $MeCHBrNO_2$ gave only $(EtO)_2PO$. Reaction of 1-nitro-2-propanol with $(EtO)_2PCl$ in the presence of pyridine as above gave some 1-nitro-1-propene and some $(EtO)_2PHO$. Similarly $(EtO)_2PCl$ and 1-nitro-2-methyl-2-propanol gave 1-nitro-2-methyl-1-propene and $(EtO)_2PHO$. Addn. of a little MeONa-MeOH to 10 g. 1-nitro-2-methyl-1-propene and 14 g/ $(EtO)_2PHO$ gave an exothermic reaction and after 1 hr. on a steam bath the mixture gave only the starting materials. It is suggested that the reactions of nitro alcs. with P halides did yield the expected esters, but that these suffered thermal decompn. to the olefins during the distn. Cf. U.S.Pat.2,177,757.

organophosphorus routine

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Reaction of chloro-substituted tertiary alcohols with phosphorus trichloride. V.S.Abramov and V.K.Khairullin. Trudy Kazan. Khim.Tekhnol.Inst. im. S.M. Kirova, 23, 65-76(1957).

To 1 mole $PCl_3$ and 1 mole ROH in dry $Et_2O$ was added with ice cooling 1 mole dry pyridine and after stirring 1-2 hrs. at room temp., then 0.5 hr. at reflux, the mixture was filtered and distd. yielding: 71% $Me_2C(CCl_3)OPCl_2$, $b_{16}$118°, $d_{20}$1.3280, $n_D^{20}$1.5254; 80% $(CH_2CH_2)_2C(CCl_3)OPCl_2$, $b_3$127°, 1.5215, 1.5425; 72% $CH_2(CH_2CH_2)_2C(CCl_3)OPCl_2$, $b_1$129-30° (m.35-6°), 1.5091, 1.5528. The dichlorides (1 mole) with 1 mole dry pyridine in $Et_2O$, treated with 1 mole R'OH at 0° as above, then refluxed 0.5 hr., similarly gave the monochlorides: 78.5% $[Me_2C(CCl_3)O]_2PCl$, $b_3$171°, 1.5192, 1.5268; 58.5% $CH_2(CH_2CH_2)_2C(CCl_3)OPClOCMe_2CCl_3$, $b_2$181-2°, 1.5067, 1.5421; 77% $(CH_2CH_2)_2C(CCl_3)OPClOCMe_2CCl_3$, $b_4$178-9° (m.39-40.5°), 1.5152, 1.5565; 52% $[(CH_2CH_2)_2C(CCl_3)O]_2PCl$, $b_3$198-4°, (m.57-8°), 1.4968, 1.5450. Use of 2 moles of R'OH resulted in 60-70% yields of the monochlorides and recovery of unreacted R'OH. Attempts to form tertiary esters in this family were fruitless. Treatment of the monochlorides with theoretical amount of $H_2O$ with cooling and drying the products in vacuo gave the following $(RO)_2PHO$: $[Me_2C(CCl_3)O]_2PHO$, m.45-6°; $[(CH_2CH_2)_2C(CCl_3)O]_2PHO$, liquid, $d_{20}$1.4770, $n_D^{20}$1.5255; $(CH_2CH_2)_2C(CCl_3)OP(HO)OCMe_2CCl_3$, liquid, 1.4900, 1.5180; $CH_2(CH_2CH_2)_2C(CCl_3)OP(HO)OCMe_2CCl_3$, m.67-9°; $[CH_2(CH_2CH_2)_2C(CCl_3)O]_2PHO$, m.138-9°. It was shown on molecular models that phosphites with R groups shown above exhibit much steric hindrance and are incapable of free group rotation. To 810 g. $CHCl_3$ and 500 g. cyclopentanone was added with ice cooling 75 g. powd. KOH over 4 hrs.; after stirring 2 hrs. at room temp., the mixture was quenched in 1 kg. ice, acidified with $H_2SO_4$ and the aq. layer was extd. with $Et_2O$; the combined org.layers gave 18.5% 1-trichloromethylcyclopentanol, $b_{13}$97-8°, $d_{20}$1.3854, $n_D^{20}$1.5085. Cf. Gerrard et al. J.Chem.Soc.1952,914;1955,1920

organophosphorus
routine

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Mixed esters of tertiary-(1',1',1'-trichloro)butyl-1-trichloromethylcyclopentyl phosphorous acid. IV.

V. S. Abramov and V. K. Khairullin. Trudy Kazan. Khim. Tekhnol. Inst. im. S. M. Kirova, 23, 77-82(1957).

To 0.05 mole ROH and 0.05 mole dry pyridine in 250 ml. $Et_2O$ was added with ice cooling 0.05 mole $(CH_2CH_2)_2C(CCl_3)OPCl(OCMe_2CCl_3$ (I) in 50 ml. $Et_2O$ and after stirring 1-2 hrs. at room temp. and refluxing briefly, the mixture was filtered and distd. yielding the following esters $(CH_2CH_2)_2C(CCl_3)$-$O(OR)OCMe_2CCl_3$ (R shown): 66.6% Me, $b_3$176-7°, $d_{20}$1.4490, $n_D^{20}$1.5185 (CuCl adduct, white solid); 81% Et, $b_3$179-80°, 1.4152, 1.5152 (CuCl adduct, m.169°) 70% Pr, $b_3$186-8°, 1.3860, 1.5120 (CuCl adduct, m.168°); 74.5% Bu, $b_3$196-6°, 1.3633, 1.5085 (CuCl adduct, m.147-8°); 73.6% iso-Bu, $b_{2.5}$185-4°, 1.3687, 1.5080 (CuCl adduct, m.178° with decompn.); 67.5% Ph, $b_3$210-15°, 1.4243, 1.5450 (CuCl adduct, a sirup). The iso-Pr ester could not be distd., but the crude product formed a CuCl adduct, m.179°. Reaction with $Me_3COH$ gave a crude ester, $d_{20}$1.5010, $n_D^{20}$1.5180, which appeared to be the free acid corresponding to I. The adducts with CuCl were prepd. at 100-40° and were pptd. by careful addn. of MeOH to the reaction mixtures. The inability of I to react with tertiary alc. is explained on steric grounds. Cf. this j. 23, 65(1957).

organophosphorus routine

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Rearrangement of mixed esters of bis-tert-trichlorobutyl phosphorous acid. V.S.Abramov and V.K.Khairullin. Trudy Kazan. Khim.Tekhnol.Inst. im.S.M. Kirova, 23, 85-90(1957). Cf. Zhur.Obshch.Khim.27,444(1957).

Heating equimolar amount of MeI with $(CCl_3CMe_2O)_2PCR$ (I) in glass ampuls until the mixture formed a solid crystalline mass (10-87 hrs. with heating or some 3 months at room temp.) yielded the same product, regardless of the nature of R; the product was $MeP(O)(OCMe_2CCl_3)_2$, m.88-90°. The yields were 89-96.5% with R ranging through: Me (40° reaction temp.), Et (100°), Pr (100°), iso-Pr (80°), Bu (100°), iso-Bu (80°), MeEtCH (155°). Heating I (R=Et) with $PhCH_2Br$ at 155° 7.5 hrs. gave 84% $PhCH_2P(O)(OCMe_2CCl_3)_2$, m.99-101°(from $Et_2O$-petr.ether). The same product formed from I with R-iso-Pr or iso-Bu, the yieldinds being 88-6%, the reaction requiring 36-40 hrs. at 155°. The reaction rate decreases with increased size of R and the radical lost in the Arbuzov reaction is the smallest one present; attempts to isolate the intermediate adducts were unsuccessful. Reaction of I with R=Ph failed to give an isolable product containing P; similar results were obtained from reaction of MeI with $(PhO)_2POCMe_2CCl_3$ or $o\text{-}C_6H_4O_2POCMe_2\text{-}CCl_3$; the only identified product was trichloroisobutylene.

organophosphorus
routine

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Approved For Release 2008/11/25 : CIA-RDP80T00246A003800520003-0 non-phosphorus routine

Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XV. Esters of α-hydroxy-α-acetoethylphosphonic acid.

V. S. Abramov and L. Sh. Belokon. Trudy Kazan. Khim. Tekhnol. Inst. im. S. M. Kirova, 23, 91-6(1957). Cf. Zhur. Obshchei Khim. 23, 1013(1953).

Heating equimolar mixture of $Ac_2$ and $(RO)_2PHO$ in sealed ampul on a steam bath 10-12 hrs. until the values of d and n became stable gave after distn. the following esters: 51% $(MeO)_2P(O)CHMeAcOH$, $b_4$ 116°, $n_D^{20}$ 1.4530, $d_{20}$ 1.2391; 55% di-Et ester, $b_4$ 120°, 1.4450, 1.1408; 86.5% di-iso-Pr ester, $b_3$ 115°, 1.4410, 1.1211; 84% di-Bu ester, $b_4$ 142°, 1.4480, 1.0641; 86% di-iso-Bu ester, $b_3$ 131°, 1.4430, 1.0513. Addn. of RONa to the mixture failed to show any catalytic effect, and for this reason the reactions were run without a catalyst. Use of 2 moles $(RO)_2PHO$ in this reaction resulted in recovery of 50% of the latter and gave 67-78% esters identical with the above; a small undistillable residue remained, but it was impossible to isolate any products of addn. of 2 moles of the ester to the dicarbonyl compound.

XVI. Esters of 2-hydroxy-4-oxo-2-pentylphosphonic acid.

V. S. Abramov and F. I. Makhmutova. Ibid. 97-101. organophosphorus routine

Heating equimolar mixtures of $Ac_2CH_2$ and $(RO)_2PHO$ in sealed ampuls on a steam bath 20-60 hrs. until the values of d and n became constant, yielded the following esters (RONa failed to show any catalytic effect on the reaction): 8% $(MeO)_2P(O)CMe(OH)CH_2Ac$, $b_3$ 107°, $n_D^{20}$ 1.4550, $d_{20}$ 1.1677; 27% di-Et ester, $b_3$ 114-5°, 1.4450, 1.1019; 14% di-iso-Pr ester, $b_3$ 115-6°, 1.4400, 1.0542; 18% di-Bu ester, $b_3$ 139-40°, 1.4490, 1.0278; 21% di-iso-Bu ester, $b_4$ 137-8°, 1.4470, 1.0153. The molar refractions of the products approached the calcd. values for the enolic form $(RO)_2P(O)CMe(OH)CH{:}CMeOH$, and titration with bromide-bromate soln. showed unsatn. of 30-40%. The products gave uncrystallizble products with $PhNHNH_2$; hence the existence of carbonyl groups was uncertain. The esters showed signs of some decompn. during distn.

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Reaction of dialkyl hydrogen phosphites with aldehydes and ketones. XVII. Tertiary-trichlorobutyl 1-trichloromethylcyclopentyl esters of substituted α-hydroxymethylphosphonic acid.

V.S.Abramov and V.K.Khairullin. Trudy Kazan.Khim.Tekhnol.Inst. im. S.M. Kirova, 23, 102-4(1957). Cf. this j. 23,90(1957).

Keeping equimolar mixture of $(CH_2CH_2)_2C(CCl_3)OP(OH)OCMe_2CCl_3$ (I) and an aldehyde or ketone in sealed ampul up to 424 hrs. results in addn. yielding the following esters which were purified by crystn. from EtOH: $(CH_2CH_2)_2C(CCl_3)OP(O)(OCMe_2CCl_3)CRR'OH$ (R and R' shown resp.): H, Me, 60%, m.123-5°; H, Et, 55.6%, m.136-7°; H, Pr, 76.2%, m.125-6°; H, iso-Bu, 54.5%, m.134-5.5°; H, Ph, 78%, m.133-3.5°; H, p-$MeC_6H_4$, 98%, m.142-4°; H, p-$HOC_6H_4$, 52.8%, m.150-1°; Me, Me, 79.2%, m.134-6°; $(CH_2)_4$, 66.6%, m.160-1°; $(CH_2)_5$, 72.5%, m.166-7°. The reaction was most rapid with BzH and p-$MeC_6H_4CHO$, most slow with $Me_2CO$ and cyclopentanone.

Mechanism of the Arbuzov rearrangement. V. Reaction of esters of bromo substituted carboxylic acids with phosphites. Routine organophosphorus

V.S.Abramov and Shara Pall. Trudy Kazan.Khim.Tekhnol.Inst. im. S.M.Kirova, 23, 105-10(1957). Cf. Zhur.Obshchei Khim.26,2014(1956).

Keeping $BrCH_2CH_2CO_2Et$ with $(RO)_3P$ (R= Et or Bu), or $PhCHBrCO_2Et$ and $(RO)_3P$ (R=Et, Bu, iso-Bu, Ph) in ampuls at room temp. until the values of n and d became constant resulted in reaction of the 2nd ester only; the 1st bromo ester required heating to 130-50°. Thus were obtained: 50% $(EtO)_2P(O)CH_2CH_2CO_2Et$, $b_{16}$188-9°, $n_D^{20}$1.4308, $d_{20}$1.0942; 51% $(BuO)_2P(O)CH_2CH_2CO_2Et$, $b_1$139-41°, 1.4337, 1.0310; 70% $(EtO)_2P(O)CHPhCO_2Et$, $b_3$120-1°, 1.4632, 1.1332; 51% di-Bu ester, $b_2$197-8°, 1.4246, 1.0821; 34% di-iso-Bu ester, $b_2$189-90°, 1.4826, 1.0641; 70% di-Ph ester, m.103-4°. Heating was necessary to complete the prepn. of the latter group of products. $(EtO)_3P$ (22.8 g.) and 16.8 g. $PhCHBrCHBrCO_2Et$ gave an exothermic effect on mixing and after 6 days gave 61% Et cinnamate; $(BuO)_3P$ gave a similar result. $(CHBrCO_2Me)_2$ (from di-Me maleate) and $(EtO)_3P$ gave 92% di-Me fumarate; $(BuO)_3P$ gave the same result

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while $(CHBrCO_2Et)_2$ (from di-Et maleate) and $(EtO)_3P$ also gave only EtBr and a non-P contg. product, $b_{13}$104-5°, $n_D^{20}$1.4879, $d_{20}$1.0915. Reaction of $(EtO)_3P$ with $(CHBrCO_2Me)_2$ (from di-Me fumarate) gave di-Me fumarate; $(BuO)_3P$ also gave the same product; $(CHBrCO_2Et)_2$ (from di-Et fumarate) and $(EtO)_3P$ gave EtBr and a non-P contg. product, $b_9$97-8°, 1.4414, 1.0565, while $(BuO)_3P$ gave BuBr and a product, $b_{11}$120-1°, 1.4418, 1.0560. These reactions were decidedly exothermic and fail to yield organo-P derivs. Attempts to isolate the intermediate products of Arbuzov reaction were unsuccessful.

Action of carbon tetrachloride on mixed alkyl aryl esters of phosphorous acid. G. Kamai and F.M.Kharrasova. Trudy Kazan. Khim.Tekhnol.Inst. im. S.M.Kirova, 23, 122-6(1957).

Routine organophosphorus

Reaction of $PhOPCl_2$ or $(PhO)_2PCl$ with desired ROH in $Et_2O$ in the presence of $PhNMe_2$ or pyridine gave: 36.6% $PhOP(OMe)_2$, $b_{12}$86°, $n_D^{20}$1.4940, $d_0^0$ -, $d_{20}$1.1218; 23.3% $PhOP(OEt)_2$, $b_{11}$111-12°, 1.4885, 1.0848, 1.0630; 45% $(iso\text{-}PrO)_2POPh$, $b_{10}$117-8°, 1.4825, 1.0365; 25.1% $PhOP(OPr)_2$, $b_7$122-3°, 1.4865, 1.0530; 47% $(PhO)_2POMe$, $b_{11}$169.5-70.5°, 1.5568, 1.1825; 1.1645; 69.3% $(PhO)_2POCH_2CH{:}CH_2$, $b_{10}$186-7°, 1.5515, 1.1497, 1.1321; 61.5% $(PhO)_2POCH_2Ph$, $b_{14}$197.5-8°, 1.5836, 1.2086, 1.1674.. Heating 4.8 g. $(iso\text{-}PrO)_2POPh$ with 0.64 g. S at 100° gave $(iso\text{-}PrO)_2P(S)OPh$, $b_{12}$151-1.5°, $n_D^{22}$1.4995, $n_D^{20}$1.5006, $d_0^0$ 1.1104, $d_{20}$1.0952; similarly were prepd.: 82% $(PrO)_2P(S)OPh$, $b_{66}$147-8°, $n_D^{20}$1.5052, $d_0^0$1.1212, $d_{20}$1.1040; 45% $(PhO)_2P(S)OCH_2CH{:}CH_2$, $b_3$82-3°, 1.5651, 1.2270, 1.2095; 91% $(PhO)_2P(S)OCH_2Ph$, m.62.5-3.5°. Refluxing 7.6 g. $(EtO)_2POPh$ with 7 g. $CCl_4$ 7 hrs. gave 100% EtCl and 44% $CCl_3P(O)(OEt)(OPh)$, $b_8$155-6°, $d_0^0$ 1.3670, $d_0^{20}$ 1.3460, $n_D^{20}$ 1.5163. Heating 10 g. $(PhO)_2POMe$ and 7 g. $CCl_4$ in ampul 10 hrs. at 160-80° gave $(PhO)_2POCl$. Heating 24.5 g. $(PhO)_2POCH_2Ph$ and 15 g. $CCl_4$ 32 hrs. at 160-5° gave 13 g. product, $b_5$219-45°, which gave unstated yield of $PhCH_2P(O)(OPh)_2$, $b_5$219-21°, m.67-8°, which hydrolyzed to the free acid, m.165-6°. Similarly $(PhO)_2POCH_2CH{:}CH_2$ gave crude $CH_2{:}CHCH_2P(O)(OPh)_2$, $b_5$178-80°

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Action of carbon tetrabromide on acid and neutral esters of phosphorous acid G. Kamai and F.M.Kharrasova. Trudy Kazan. Khim. Tekhnol.Inst. im. S.M. Kirova, 23, 127-32(1957).

To 9 g. $(MeO)_2PHO$ in 10 ml. $Et_2O$ was added with cooling 33.1 g. $CBr_4$ in $Et_2O$ (exothermic reaction) and the mixture was distd. yielding some 20 g. $CHBr_3$ as the sole distillable product; presumably the reaction also gave $(MeO)_2POBr$. Similarly $CBr_4$ and $(EtO)_2PHO$ gave $CHBr_3$ as the sole identifiable product. Addn. of 21.9 g. $CBr_4$ to 16.6 g. $(EtO)_3P$ (vigorous reaction) gave 10.9 g. EtBr and considerable amount of undistillable material; $(BuO)_3P$ reacted similarly. Heating 15.5 g. $(PhO)_3P$ with 15.6 g. $CBr_4$ in sealed tube under $CO_2$ 6 hrs. at 100-20° gave 42.5% $(PhO)_2POBr$, $b_3$198-200°, m.46-7°, which must be stored under an inert gas. Addn. of 12.9 g. $CBr_4$ in $Et_2O$ to 7.25 g. $(MeO)_2POPh$ with cooling gave MeBr, $CHBr_3$ and crude $(MeO)(PhO)POBr$, $b_3$115-25°, $n_D^{20}$1.5050, $d_4^{20}$1.2162, in 8.6% yield. Similarly 14 g. $MeOP(OPh)_2$ and 18.5 g. $CBr_4$ in sealed tube 7 hrs. at 120° gave a low yield of $(PhO)_2POBr$, $b_3$191-200°, $n_D^{20}$1.5705, $d_4^{20}$1.5042, m.42-7°(after prolonged standing). Similarly $EtOP(OPh)_2$ and $CBr_4$ gave EtBr and some crude $(PhO)_2POBr$; $CBr_4$ and $PhCH_2OP(OPh)_2$ gave $PhCH_2Br$ and $(PhO)_2POBr$. The necessary phosphites were prepd. by reaction of the respective chlorides with ROH in the presence of pyridine. $PhOP(OMe)_2$, $b_{12}$86°, $n_D^{20}$1.4940, $d_{20}$1.1248; $(PhO)_2POMe$, $b_{11}$169.5-70.5°, 1.5568, 1.1645; $(PhO)_2POEt$, $b_{12}$169.5-70°, 1.5485, 1.1542; $(PhO)_2POCH_2Ph$, $b_{14}$197.5-8°, 1.5856, 1.1674.

Routine organophosphorus

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Addition of neutral esters of phosphorous acid and phosphonous acids to conjugated systems. III. Reaction of trialkyl phosphites with cinnamic, maleic and pyruvic acids.

G. Kamai and V.A.Kukhtin. Trudy Kazan.Khim.Tekhnol.Inst.,im.S.M.Kirova, 23, 133-7(1957). Cf. Doklady Akad.Nauk SSSR 109,91(1956).

Heating 10 g. $(EtO)_3P$ with 8 g. $PhCH{:}CHCO_2H$ 4 hrs. at 120° gave 9.1 g.(50.5%) $(EtO)_2P(O)CHPhCH_2CO_2Et$, $b_7$189-90°, $n_D^{20}$1.4906, $d_4^{20}$1.1199. No reaction took place at room temp. after even very prolonged period. Similarly were prepd.: 51% $(PrO)_2P(O)CHPhCH_2CO_2Pr$, $b_4$196-7°, 1.4868, 1.0819; 57.1% $(BuO)_2P(O)CHPhCH_2CO_2Bu$, $b_2$208-9°, 1.4856, 1.0682. To 11 g. maleic acid in dioxane there was added dropwise 16 g. $(EtO)_3P$ in $Et_2O$ with cooling at 50° or below; after distn. there was obtained 4.7 g. (17.5%) $(EtO)_2P(O)CH(CO_2H)CH_2CO_2Et$, $b_{0.5}$143-6°, 1.4590, 1.1446; similarly was prepd. 19.2% $(PrO)_2P(O)CH(CO_2H)CH_2CO_2Pr$, $b_1$137-8°, 1.4548, 1.0485. If cooling is omitted in this reaction, the temp. rises to 90° and violent evolution of $CO_2$ takes place, yielding a thoroughly decomposed mass. Even in dioxane-$Et_2O$ soln. as above, some decompn. and loss of $CO_2$ takes place; the products suffer some decompn. during distn. Reaction of $(RO)_3P$ with Et H maleate is similarly violent and it was impossible to isolate any definite reaction products. To 32 g. $(EtO)_3P$ in $Et_2O$ there was added 17 g. pyruvic acid (exothermic effect); distn. of the mixture gave 23.5 g. $(EtO)_2PO$. It is suggested that $(RO)_3P$ and unsatd. monobasic acids yield intermediates such as $(RO)_3P^+CHRCR{:}C(OH)O^-$ and $(RO)_3POC(O)CHRCHR$, while unsatd. dibasic acids react similarly at one carboxyl group. Pyruvic acid reacts so violently with $(MeO)_3P$ that the decompn. sets in directly. $(EtO)_3P$ failed to react with $CH_2{:}CHCOAc$ even after 20 hrs. at 120°.

Continued old work on organophosphorus

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Propargyl esters of alkylphosphonous acids.

G. Kamai and Z.A.Gerasimova. Trudy Kazan. Khim. Tekhnol.Inst. im. S.M. Kirova, 23, 138-42(1957).

To 19.9 g. dry pyridine, 14.1 g. $HC\equiv CCH_2OH$ and 100 ml. $Et_2O$ was added with cooling 20 g. $BuPCl_2$ in $Et_2O$; after gradual heating to reflux for 3 hrs. the mixture was filtered and distd. under $CO_2$ yielding $BuP(OCH_2C\equiv CH)_2$, $b_6$ 146-7°, $d_o^{12}$ 1.0406, $n_D^{12}$ 1.4949; similarly were prepd.: $EtP(OCH_2C\equiv CH)_2$, $b_6$ 126-7°, 1.0801, 1.5015; $PrP(OCH_2C\equiv CH)_2$, $b_6$ 136-4.5°, 1.0898, 1.5001. All these esters readily react with atm. $O_2$. Treatment of the Pr member with $CCl_4$ resulted in exothermic reaction which gave $HC\equiv CCH_2Cl$ as the sole identifiable product. Similarly, 18.2 g. $CH_2{:}CHCH_2OH$, 49.6 g. pyridine and 25 g. $BuPCl_2$ in $Et_2O$ gave 64% $BuP(OCH_2CH{:}CH_2)_2$, $b_{11}$ 98-100°, $d_o^{20}$ 0.9340, $n_D^{20}$ 1.4550 (this reacted readily with $CCl_4$ yielding $CH_2{:}CHCH_2Cl$ and unidentified substance, $b_{10}$ 145-55°). The esters of $P^{III}$ readily add CuX. The necessary $RPCl_2$ were prepd. from $R_2Cd$ and $PCl_3$; $EtPCl_2$, $b_{33}$ 26°, $d_o^{20}$ 1.2485, $n_D^{20}$ 1.4930; $PrPCl_2$, $b_{15}$ 43°, 1.1664, 1.4942; $BuPCl_2$, $b_{20}$ 56°, 1.1341, 1.4838.

Structure of phosphorous acid and its derivatives.

S.D.Troitskaya. Trudy Kazan.Khim.Tekhnol.Inst. im. S.M.Kirova, 23,228-42(1957

It is suggested that $(RO)_2PHO$ in aq. soln. exist largely in the $P^V$ tautomeric form and that both such esters and $H_3PO_3$ in aq. medium suffer a form of Arbuzov rearrangement yielding the $(HO)_2P(O)H$ or $(RO)_2P(O)H$ forms from the normal $P^{III}$ structures. Heating 0.5 g. $K_2[PtCl_4]$ and 1.1 g. $(MeO)_2PHO$ in sealed ampul with direct flame followed by cooling of the soln. and addn. of $H_2O$, gave colorless $[Pt(P(OMe)_2HO)_2(P(OMe)_2O)_2]$, m.168°. Similarly was prepd. $[Pt(P(OEt)_2HO)_2(P(OEt)_2O)_2]$, m.84-5°; $[Pt(P(OPr)_2HO)_2(P(OPr)_2O)_2]$, m.36-7°; $[Pt(P(OBu)_2HO)_2(P(OBu)_2O)_2]$, viscous oil. Heating 0.5 g. $K_2[PtCl_4]$ in 3-4 ml. $H_2O$ with 1.4 g. $(EtO)_2PHO$ as above gave $[Pt(P(OEt)_2HO)_2(P(OEt)_2O)_2]$, m.94.5-5°; similarly was prepd. $[Pt(P(OPr)_2HO)_2Cl_2]$ from $(PrO)_2PHO$, and $[Pt(P(OBu)_2HO)_2Cl_2]$ and more sol. $[Pt(P(OBu)_2HO)_2(P(OBu)_2O)_2]_2$ from

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$(BuO)_2PO$. Evidently the reactions performed under anhydrous [redacted]ditions and those run in presence of $H_2O$ yield substances which [redacted]ic with each other, as their physical constants differ, but compa[redacted]ame. Heating 0.6 g. $H_3PO_3$ with 0.5 g. $K_2[PtCl_4]$ in open flame ([redacted] compn. point) gave much HCl and after 0.5 hr. gave a yellow produ[redacted] of [redacted]d on cooling gave unreacted $K_2PtCl_4$ and 2 products: a s[redacted] of alc.sol. colorless ~~[redacted]~~ $[Pt(P(OH)_3)_3P(OH)_2O]Cl$, [redacted]low substance, insol. in EtOH, which was $[Pt(P(OH)_3)_4]Cl_2$. Use of [redacted] the amount of $H_3PO_3$ fails to produce any of the yellow product [redacted]ve and only the colorless product is obtained; allowing a melt [redacted]$_4$ and $H_3PO_3$ to stand 2-3 weeks yields a cream colored soli[redacted]$_3)_2P(OH)_2)_2]$. To 0.5 g. $K_2[PtCl_4]$ in 1-1.5 ml. $H_2O$ was added 1[redacted]$_3$; heating resulted in decolorization of the soln. and af[redacted] and addn. of EtOH there was isolated colorless $[Pt(P(OH)_3)_2(P(OH)_2O[redacted]$.

organophosphorus
santine

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