Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

25X1

Page Denied

Next 3 Page(s) In Document Denied

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Useful — the first work in this area to my knowledge

Polarographic study of organophosphorus compounds.

M.K.Saikina. Uchenye Zapiski Kazan.Gosuderst.Univ. im. V.I.Ul'yanova-Lenina Obshcheuniv.Sbornik, 116, No.5, 121-6(1956).

The following values, r sp. are given for polarographic characteristics of organo-P compounds; concn. in moles/l., $E_{0.5}$ in v., i_d in microamps., background electrolyte, shown in order: $MeP(O)(OMe)_2$ ($b_{12.5}$ 67-8°, n_D^{20} 1.4105, d_o^{20} 1.1741), 0.025, -1.36, 151, 0.5M LiCl; ~~[illegible]~~ (at 0.1 M concn. -1.25 v., 669 microamp); $EtP(O)(OEt)_2$ (b_{12} 85°, n_D^{20} 1.4165, d_o^{20} 1.0272), 0.025, -1.35, 38 (at 0.1 M concn., -1.33 v. and 149 microamp.; at 0.2M concn. -1.32 v. and 360 microamp.); $PrP(O)(OPr)_2$ ($b_{9.5}$ 114°, n_D^{20} 1.4245, d_o^{20} 0.9773), 0.05, -1.35, 74 (at 0.1M -1.33 v. and 146 microamp. and at 0.2M, -1.32 v. and 437 microamp.); $MeP(O)(OBu)_2$, 0.05, -1.31, 51 (at 0.1M, -1.30 v. and 102 microamp., and at 0.2M -1.3 v. and 195 microamp.); $CH_2{:}CHCH_2P(O)(OCH_2CH{:}CH_2)_2$, 0.2, -1.34, 247; $AmPO(OAm)_2$ (b_3 144-5°, n_D^{20} 1.4370, d_o^{20} 0.9291), 0.2, -1.32, 11; $Ph_2CHPO(OH)_2$ (m.227-8°), 0.0125, -1.42, 100 (at 0.025 M, -1.32 v. and 200 microamp., and at 0.05M -1.26 v. and 411 microamp.); $EtO_2CCH_2PO(OEt)_2$, 0.1, -1.37, 11 (at 0.5M -1.31 v. and 38 microamp., and at 1M -1.31 v. and 125 microamp.; all above values taken in 0.5M LiCl. In M LiCl: $EtO_2CCHMePO(OEt)_2$ (b_{10} 136.5-7.5°, n_D^{20} 1.4310, d_o^{20} 1.0930), 0.2, -1.36, 7 (at 0.5M, -1.4 and 15); $EtO_2CCMe_2PO(OEt)_2$ (b_8 128-3.5°, n_D^{20} 1.4310, d_o^{20} 1.0774), 0.2, -1.34, 6 (at 0.5M, -0.88 and 108); $AcCH_2P(O)(OEt)_2$ ($b_{1.5}$ 99-102°, n_D^{20} 1.4355, d_o^{20} 1.1232), 0.1, -1.02, 19(at 0.5M,-0.88 and 108); $AcCHMeP(O)(OEt)_2$ ($b_{0.5}$ 92°, n_D^{20} 1.4342, d_o^{20} 1.0820), 0.5, -1.2, 25; $AcCMe_2PO(OEt)_2$ (b_8 112-3.5°, n_D^{20} 1.4360, d_o^{20} 1.0592), 0.5, -1.22, 9. These values were obtained at 25°. For $MeP(OMe)_2$ the temp. coeff. of diffusion current is 1.38% per degree in 15-25° range and 1.74% per degree in 25-50° range; the calcd. number of electrons involved in $Ph_2CHPO_3H_2$ is 2.33, i.e. 2-electron process is probable here, while for $MeP(OMe)_2$ this value is 1. In M LiCl the following values were found for phosphate esters (listed as above): $(EtO)_3PO$, 0.5, -1.4,

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

15; $(EtO)_2PO(OCH_2CH{:}CH_2)$, 0.5, -1.32, 12 (at M concn. -1.26 and 25); $(PrO)_3PO$, 0.5, -1.38, 11. The more negative values of halfwave potentials in this case agrees well with the lower dipole moments of these esters in comparison with those of esters of phosphonic acids. Xamn. of the values obtained for phosphonoacetates and phosphonoacetons derivs. indicates that the reduction involves only the keto form, and no indication of enolic tautomers was secured. The following amides gave good polarographic reduction waves whose heights were proportional to the concns. (notation as above): $(Me_2N)_2POCl$, 0.1, -1.3, 149 (at 0.2M, -1.25, 301); $[(Me_2N)_2P(O)]_2O$, 0.123, -1.24, 3 (at 0.5M, -1.14, 37); $Me_2NP(O)[OPO(NMe_2)_2]_2$ 0.5, -1.24, 13 (at 1M, -1.08, 27); $(EtO)_2P(O)OP(S)(OEt)_2$, 0.025, -1.34, 72 (at 0.1M -1.26, 352); $(EtO)_2P(S)OP(S)(OEt)_2$, 0.1, -1.24, 301. The polarographic analysis of mixtures may be hindered by proximity of the halfwave potentials of the components.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(7)

Imides of acids. Dialkyl phosphoryl-N-phenyltriazines and their salts.

M.I.Kabachnik and V.A.Gilyarov (Inst.Hetero-org.Compounds, Acad.Sci., Moscow). Doklady Akad.Nauk S.S.S.R.114, 781-4(1957).

Cf.this j.106,473(1956).

While $(RO)_2POH$ do not react with PhN_3, the salts (Na and Et_3N) do react yielding $(RO)_2P(ONa):NN:NPh$ (I), which on acidification yield $(RO)_2P(O)N:NNHPh$ (II). The formation of salts of triazines as intermediates above confirms the previous supposition of existence of triazines $(RO)_3P:NN:NPh$ in addn. of $(RO)_3P$ to PhN_3. The Na salts react more rapidly than Et_3N salts. The salts I are yellow crystalline solids, unhydrolyzed in air, sol. in org.solvents and H_2O (aq. solns. decompose on standing); they decompose on melting and lose N_2. The free II are formed from Et_3N salts by vacuum distn., while from the Na salts the recovery of II is done by action of aq.HCl or calcd. amount of AcOH in Et_2O. Dropwise addn. of 11.9 g. PhN_3 in 30 ml.Et_2O to 13.8 g. $(EtO)_2POH$ and 2.3 g.Na in Et_2O, followed by allowing the brown soln. to stand overnight and evapg. the solvent gave 68.5% I (R=Et), m.147.5-8.5°(from $CHCl_3$-petr.ether); similarly were prepd.: 32.5% I (R=Pr), m.142-2.5°; 47.8% I (R=iso-Pr), m.142-3°; 46.7% I (R=Bu), m.145-6°. Addn. of 2.4 g. PhN_3 to 2.2 g. $(MeO)_2POH$ and 2 g. Et_3N in 5 ml. Et_2O and letting the mixture stand 1-2 days gave after concn. 30.4% needles of II, R=Me, m.94.5-5°(from $CHCl_3$-petr.ether); similarly were prepd.: 38.6-57.7% II R=Et, m.84-5°; 17.5-26.3% II R=iso-Pr, m.64-5°; 90% II, R=Bu, oil, n_D^{20}1.5220. II may exist in tautomeric forms $(RO)_2P(OH):NN:NPh$, $(RO)_2P(O)NHN:NPh$ or $(RO)_2P(O)N:NNHPh$; the latter should be least acidic and appears to be the most likely form. II are not basic and do not form picrates or HCl salts; they are sol. in basic solns. and can be recovered by acids. They are stronger acids than $(RO)_2POH$. [redacted]

organophosphorus, new compounds; I and II types. may be toxic

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(3)

Organosilicon phosphates

New methods of synthesis of tris(trialkylsilyl) phosphates.

[illegible] Voronkov and V.N. Zgonnik (Silicate Chem. Inst., Leningrad). Zhur. Obshchei Khim. 27, 1483-6(1957). cf. this j.25,459(1955).

Compounds of type $(R_3SiO)_3PO$ can be prepd. by: reaction of H_3PO_4 with R_3SiOR, reaction of R_3SiCl with H_3PO_4, or reaction of $(RO)_3PO$ with R_3SiCl. The products are colorless liquids stable to 250-300°; they are hydrolyzed by H_2O or aq. acids or bases; they are also cleaved by NaBr. Thus, slow distn. of 58.5 g. Et_3SiOMe from 9.8 g. H_3PO_4 gave 100% MeOH and 74% $(Et_3SiO)_3PO$, b_5 197-200°; redistn. gave b_3 183-6°, d_{20} 0.9668, n_D^{20} 1.4455. Similarly were prepd.: 40% $(MeEt_2SiO)_3PO$, b_1 145-7°, 0.9474, 1.4302, and 50% $(MePr_2SiO)_3PO$, b_{10} 221-4°, 0.9326, 1.4380. Refluxing 66.3 g. Me_3SiCl and 19.1 g. H_3PO_4 6 hrs. gave 35% crude $(Me_3SiO)_3PO$, b. 190-235°, which gave pure product, b_5 91-3°, 0.9650, 1.4082; also obtained was 35 g. $(Me_3Si)_2O$. Distn. of 17.3 g. $(EtO)_3PO$ and 60.5 g. Et_3SiBr gave 70% EtBr and 64% $(Et_3SiO)_3PO$. Heating 22.6 g. Et_3SiCl and 9.1 g. $(EtO)_3PO$ with 0.[illegible] g. dry $FeCl_3$ 9 hrs. gave 41% $(Et_3SiO)_3PO$. Heating 33.7 g. Me_2SiCl_2 and 19.6 g. H_3PO_4 6 hrs. at atm. pressure and 4 hrs. in vacuo gave a viscous polymer, sol. in org. solvents and attacked by H_2O, which had the compn. of $[Me_2Si]_3(PO_4)_2$.

[redacted]

Relatively new class of compounds: some known in US about them, but not much

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(4)

Synthesis of esters of 8-caffeinylmethylphosphonic acid. [illegible] is; new compounds properties unknown

[illegible].Lugovkin (AllUnion Labor Protection Res.Inst., Kazan). Zhur.Obshchei Khim.27, 1524-6(1957).

8-Chloromethylcaffeine (m.215°, from AcOH; cf.Golovchinskaya and Chaman, this j.22,537(1952)) (1.5 g.) heated with 1.4 g. $(EtO)_3P$ 10 min. to 155° and finally to 180° gave after treatment with C in hot EtOH 2.05 g. di-Et 8-caffeinylmethylphosphonate, m.133°; similarly was prepd. 65.2% di-Pr ester, m.70-1°, and 85.6% di-iso-Pr ester, m.121-2°. The di-Bu ester, 88.8%, was a viscous liquid, while the di-iso-Bu ester, 88.7%, m.75-6°. The di-Bu ester heated with 1:1 HCl in sealed tube 5 hrs. at 110-20° gave 8-caffeinylmethylphosphonic acid, m.235-6° (from AcOH), the same being obtained from hydrolysis of the other esters above.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(5)

Organophosphorus; new compounds

Esters of isocyanatophosphoric acid and their derivatives.

A.V.Kirsanov and I.N.Zhmurova. Zhur.Obshchei Khim.27,1002-6(1957). Cf.this j.26,2642, 2285(1956).

Distn. of 18.6 g. $(MeO)_2PONHCO_2Me$ in vacuo gave 80% mixed starting ester and $(MeO)_2P(O)NCO$; redistn. gave 66% latter, b_4 75-6°, d_{20}^{20} 1.3130, n_D^{20} 1.4260(treated with $PhNH_2$ in cold Et_2O this gave 70% $(MeO)_2P(O)NHCONHPh$, m.156-7°). Similarly was prepd. 89% $(PhO)_2P(O)NCO$, b_5 184-6°, 1.2328, 1.5470 (with $PhNH_2$ this gave $(PhO)_2P(O)NHCONHPh$, m.158-56°); while treatment with H_2O gave 96% $(PhO)_2PONH_2$, m.145-50°; use of aq.NH_4OH gave $(PhO)_2P(O)NHCONH_2$, m.199-200°(from EtOH)). Similarly the corresponding urethane deriv. on distn. gave 64% $(p\text{-}BrC_6H_4O)_2P(O)NCO$, b_{10} 250°, m.72-4°(with H_2O this gave 85% $(p\text{-}BrC_6H_4O)_2P(O)NH_2$, m.186-8°(from EtOH); $PhNH_2$ in Et_2O gave 80% $(p\text{-}BrC_6H_4O)_2P(O)NHCONHPh$, m.170-1°(decompn.). Addn. of EtOH to $(MeO)_2P(O)NCO$ gave $(MeO)_2P(O)NHCO_2Et$, a liquid; similarly was prepd. $(MeO)_2P(O)NHCO_2CHMe_2$, a liquid. Addn. of BuOH to $(PhO)_2P(O)NCO$ followed by treatment of the oily product with 40% NaOH and a little MeOH gave a solid Na salt of $(PhO)_2P(O)NHCO_2Bu$, m.161-4° (from C_6H_6-petr.ether); similarly was prepd. Na salt of $(PhO)_2P(O)NHCO_2CH_2CHMe_2$, dec.100-91°. Reaction of 2.2 g. $PhCH_2OH$ with 5.5 g. $(PhO)_2P(O)NCO$, followed by treatment of the product with 5% NaOH and acidification of the alk.soln., gave 6 g. $(PhO)_2P(O)NHCO_2CH_2Ph$, m.79-81°. $(PhO)_2P(O)NCO$ (5.5 g.) and 0.62 g. $(CH_2OH)_2$ gave a glassy solid which treated with 5% NaOH and reprtf. with HCl gave 3 g. $(CH_2O_2CNHP(O)(OPh)_2)_2$ dec.124-6°(from C_6H_6-petr.ether). Similarly were prepd.: 97% $(p\text{-}BrC_6H_4O)_2P(O)NHCO_2Bu$, m.61-3°; and 93% $(p\text{-}BrC_6H_4O)_2P(O)NHCO_2CH_2Ph$, m.113-15°.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(6)

Esters of N-phosphoric acid, trichloroiminoacetic acid and esters of trihydroxyphosphazotrichloroacetyl. II.

V. Mirsunov and G. I. Derkach (Metallurg. Inst., Dnepropetrovsk). Zhur. Obshchei Khim. 27, 1080-3(1957). Cf. this j. 26, 2831(1956).

To a soln. of 0.045 g.at.Na in 0.045 mole 1-$C_{10}H_7OH$ in 70 ml. Et_2O was added 0.015 mole $CCl_3CON:PCl_3$ in Et_2O; after stirring 20 min. the mixture was briefly refluxed and filtered from NaCl; cooling yielded a ppt. of 77.5% $(1\text{-}C_{10}H_7O)_3P:NCOCl_3$ (I), m.114-6° (from petr. ether); it is slowly hydrolyzed by H_2O even on boiling, but rapidly loses one RO group in hot aq.alc.KOH. To soln. of 0.06 mole 1-$C_{10}H_7ONa$ in 60 ml. Et_2O was added with ice cooling 0.03 mole $CCl_3CONH:PCl_2$ in Et_2O; after cooling to 0° the soln. was rapidly washed with cold N NaOH and the org. layer was rapidly filtered through Na_2SO_4 and immediately evapd. yielding 37.1% $(1\text{-}C_{10}H_7O)_2P(O)N:C(OC_{10}H_7\text{-}1)CCl_3$ (II), m.60-4°. Refluxing 0.04 mole 1-$C_{10}H_7ONa$ in Et_2O with 0.02 mole $CCl_3CONH:PCl_2$ 10 min., filtering and evapg. in vacuo gave 66.3% $CCl_3CONHPO(OC_{10}H_7\text{-}1)_2$ (III), m.159-41° (from EtOH), which is hydrolyzed with more difficulty than the analogous h ester. Refluxing 0.001 mole I in 30 ml. EtOH and 2 ml. N NaOH until a soln. formed (1 hr.), concg. in vacuo and adding aq.HCl and cooling gave 60.9% III. Hydrolysis of II with H_2O gives very little III and much tar; aq.alc.NaOH, as above, however gave a green soln. which on acidification gave 30.3% III. Analogously to prepn. of I there was obtained 49.8% $(4\text{-}ClC_{10}H_6\text{-}1\text{-}O)_3P:NCOCl_3$, m.124-5° (from petr. ether) which is very easily attacked by moisture; refluxing this with 95 EtOH 5 min. readily gave 71% $(4\text{-}ClC_{10}H_6\text{-}1\text{-}O)_2P(O)\text{-}NHCOCl_3$ (IV), m.180-2°, which is s l. in basic solns.. Reaction of RONa with $CCl_3COCl:NPOCl_2$, as above, gave very easily hydrolyzable $(4\text{-}ClC_{10}H_6\text{-}1\text{-}O)_2P(O)N:C(O\text{-}1\text{-}C_{10}H_6Cl\text{-}4)CCl_3$, m.36-45° (from Et_2O), which warmed with 95% EtOH gave 74.5% IV, m.180-2°.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2 bounds

Dialkylamides of trichlorophosphazosulfuric acid and chlorides of N,N-dialkylsulfamido-N'-phosphoric acid.

.V.Kirsanov and Z.D.Nekrasova (Metallurg.Inst.,Dnepropetrovsk). Zhur. Obshchei Khim.27, 1253-6(1957). cf. this j.22,88(1952);22,1346(1952). Heating 30 ml. CCl_4, 0.04 mole $Me_2NSO_2NH_2$ and 0.04 mole PCl_5 on a steam bath 1 hr. gave 98.5% HCl and cooling the hot filtrate gave $Me_2NSO_2N:PCl_3$,I, m.73-5°. Similarly was prepd. $Et_2NSO_2N:PCl_3$, oil, d_{20}1.4665, n_D^{20}1.5072. These react vigorously with EtOH and react with H_2O. $Et_2NSO_2NH_2$, m.46-7°, was prepd. from NH_3 and Et_2NSO_2Cl. I in C_6H_6 treated with 1 mole 100% HCO_2H gave after 12 hrs. 93% $Me_2NSO_2NHPOCl_2$,m.110-12°(from CCl_4), which reacts with H_2O much more slowly than the above trichloride. Similarly was obtained 100% $Et_2NSO_2NHPOCl_2$, m.70-2°. Refluxing these in C_6H_6 with equimolar amount of 100% HCO_2H 5 hrs. gave: $Me_2NSO_2NHPOCl(OH)$,dec.74-80°, and $Et_2NSO_2NHPOCl(OH)$, viscous oil (from C_6H_6-petr.ether). If two moles of HCO_2H are used and the reaction is run in refluxing dioxane, there are formed: $Me_2NSO_2NHPO(OH)_2$, 92%, dec.187-9°, and $Et_2NSO_2NHPO(OH)_2$, 81%, m.80-95°, a very hygroscopic solid.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(8)

Synthesis and study of some vinyl esters of acids of phosphorus.

E.L.Gefter and M.I.Kabachnik (Inst.Hetero-org.Compounds, Acad.Sci., Moscow). Doklady Akad.Nauk S.S.S.R.114, 541-4(1957).

A new method of synthesis of vinyl esters of acids of P was developed on the basis of probable formation of 1-chloroalkyl esters of trivalent P in the reaction of chlorides based on P^{III} with aldehydes; it was felt that addn. of a base to a system of aldehyde-P halide should yield a vinyl ester by dehydrohalogenation of the intermediate. This was exptly. verified(Cf. F.F.Faizullin, N.A.Trifonov, Uchen.Zapiski Kasnask.Gos.Univ. 112, No.4, 131, 139, 145(1952)). Chlorides of acids of P were treated with an excess of AcH and Et_3N with cooling and stirring; this yielded a colorless crystalline ppt. which often turned red; distn. gave a low boiling fraction at 20-100 mm., followed by the desired vinyl ester distillable at 2-10 mm. The crystalline ppt. was either filtered off prior to distn. or was left in situ; no effect on the yield was noted. The crude distilled product was freed of traces of Et_3N by contact with few drops of H_3PO_4 and redistn. gave the pure vinyl esters in 30-5% yields; much residue always remains in the distn. app. and strong heating of this leads to decompn. Very pure starting materials and an excess of AcH and Et_3N are essential to obtain the above cited yields. Thus were prepd.: $MeP(O)(OCH{:}CH_2)_2$, b_8 64-5°, d_{20} 1.1097, n_D^{20} 1.4394; $EtP(O)(OCH{:}CH_2)_2$, $b_{5-5.5}$ 60-1°, 1.0707, 1.4409; $ClCH_2P(O)(OCH{:}CH_2)_2$, b_1 66-7°, 1.2458, 1.4636; $CH_2{:}CHP(O)(OCH{:}CH_2)_2$, $b_{1.5-2}$ 49-50°, 1.1020, 1.4530; $MeP(O)(OCH_2CH_2Cl)(OCH{:}CH_2)$, $b_{3.5-4}$ 96-8°, 1.2351, 1.4540; $MeP(O)(OBu)OCH{:}CH_2$, $b_{2.5-3}$ 63-5°, 1.0208, 1.4278; $PhP(O)(OCH{:}CH_2)_2$, $b_{1.5-2}$ 110-11°, 1.1589, 1.5144; $MePhP(O)OCH{:}CH_2$, b_2 102-4°, 1.1166, 1.5224; $o\text{-}C_6H_4O_2POCH{:}CH_2$, $b_{2-2.5}$ 71°, 1.2306, 1.5357; $(CH_2O)_2POCH{:}CH_2$, b_{15} 58-9°, 1.1672, 1.4577; $OP(OCH{:}CH_2)_3$, b_{10} 84-5°, 1.1240, 1.4314. The mechanism of the reaction is believed to be the formation of 1-chloroethyl ester followed by salt formation at the 1-

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

position, such as $(R_2P(O)OCHMeNEt_3)^+Cl^-$, which decomposes to the desired vinyl ester and $Et_3N.HCl$. In expts. with Me_3N such complexes were actually isolated and analyzed. The possibility of isomerization of AcH into vinyl alc. monomer is not probable. All the vinyl esters above were polymerizable at 50-70° with 0.7-1.8% Bz_2O_2. Those with 1 vinyl group gave liquid products of low mol.wt., while those with 2 or 3 vinyl groups gave rapidly tridimensional polymers (usually colored) which were infusible and insoluble, having also a degree of nonflammability. Cf. Allen et al. JACS 78, 3715(1956).

[redacted]

organophosphorus polymers;
general idea well known in U.S.,
but this is a very good new method
to make them.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

8A

Polycyclic compounds. XIV. Synthesis of anthraquinone-1-arsonic and 1-phosphonic acids by the diazo method.

A.M.Lukin and G.S.Petrova. Zhur.Obshchei Khim.27, 2171-4(1957). Cf. this j. 20, 2219(1950).

The paste formed by repptn. of 11.8 g. 95% α-aminoanthraquinone from concd.H_2SO_4 was treated with 40% HBF_4 and the suspension diazotized with 40% aq. $NaNO_2$ (7 g.) at 35-40°, cooled to 0°, the pptd. diazonium fluoborate was filtered off, washed with Et_2O and dried in air; the yield was 87.5% of product containing some 9% undiazotized amine. This (15.5 g.) and 1 g. Cu_2Br_2 were gradually added to 80 ml. abs. EtOAc and 8.4 ml.PCl_3 at room temp. and the mixture was stirred 2 hrs. at 60-5°, allowed to stand overnight, treated with 12 ml. H_2O, 400 ml. 5% NaOH, heated with activated C, filtered and acidified with concd.HNO_3 yielding 60% anthraquinone-1-phosphonic acid, m. above 300°(from 1:1 HNO_3), a yellowish powder; with N NaOH it gave a mono-Na salt, yellow solid; similarly was prepd. the yellow mono-NH_4 salt. If the initial diazonium salt is the chloride or sulfate, the yield of the Schiemann-type reaction above is but 6-9.9%. However in the synthesis of the 1-anthraquinonearsonic acid is best made from the diazonium sulfate (65%), while the chloride gives but 17.5% yield and the fluoborate 23%, in a conventional Bart reaction. 1-Anthraquinonephosphonic acid is effective precipitant, when used as NH_4 salt, for isolation of Th in acetate buffer at pH 3.5-4.4, the sensitivity being 10γ Th in 5 ml. of soln.

[redacted]

organophosphorus → note: thorium

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(9)

A study of the reaction of esters of phosphorous acid with alkyl halides by methods of physico-chemical analysis.

B. . rbuzov and A.V.Fuzhenkova (V.I.Ul'yanov-Lenin State Univ., Kazan).

Doklady Akad.Nauk S.S.S.R.113, 1269-71(1957).

The reaction of $(EtO)_3P$ with EtI, EtBr, $BrCH_2CHBrOEt$ (I), and that of $(PhO)_3P$ with MeI and EtI was examined at various temps. by detn. of n, d, cond. and viscosity. In the system $(EtO)_3P$-EtI the curves of n and d are convex toward the compn. axis and hence do not indicate interaction; cond. and viscosity, as well as natural contraction curves do show an interaction by showing maxima on the property-compn. diagrams; with rise of temp. the location of the maximum shifts toward the ester component. In the system I-$(EtO)_3P$ n and d curves are convex toward the compn. axis and the deviation from additivity is small; specific volume and natural contraction D_n show a max. of contraction at equimolar compn. The viscosity curve in this system even at 20° has S-shape with inflection at equimolar compn. which indicates interaction and association of one of the components. The viscosity curve shows a considerable deviation from additivity especially at equimolar compn. The diagrams are reproduced.

[redacted]

Organophosphorus; reaction study of old problem

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(16)

Radical reactions of pentaphenylphosphorus. IV. Reaction of pentaphenylphosphorus with methyl iodide. Mechanism of radical reactions of pentaphenylphosphorus studied by means of diphenylpicrylhydrazine and diphenylpicrylhydrazyl.

G.A.Razuvaev, N.A.Osanova and I.A.Shlyapnikova (State Univ., Gorkii).

Zhur.Obshchei Khim.27, 1466-9(1957): cf. this j.26,2531(1956).

Reaction of Ph_5P with MeI occurs by radical route. Thus 10 g. Ph_5P and 44 g. MeI after 20 hrs. at 90° in sealed tube gave 0.1 ml. C_2H_6, 6.2 ml. CH_4, 0.19 g. Ph_2, 9.7 g. Ph_4PI, some C_6H_6, MePh, and PhI. The radical nature of the reaction was confirmed by variation of color of solns. of Ph_5P in C_6H_6, pyridine, MeOH, MeI, $CHCl_3$ or AcOH in the presence of 2,4,6-$(O_2N)_3C_6H_2PHNPh_2$ (a) (orange changing to the violet color of the free radical of 2,4,6-$(O_2N)_3C_6H_2\dot{N}NPh_2$ (I) in presence of free radical sources). The ionic nature of the reaction of Ph_5P with AcOH was confirmed by similar means. The reaction with $CHCl_3$ was followed colorimetrically and kinetic curve is shown. The reaction in pyridine appears to proceed intramolecularly. I was prepd. as follows: 0.6 g. A in 9 ml. pure $CHCl_3$ was shaken with 7 g. PbO_2 and 0.5 g. dry Na_2SO_4 1 hr.; evapn. of the filtrate gave violet prisms of I. Reaction of Ph_5P with C_6H_6 in the presence of I failed to fix any radicals on I. Free radical formation was found in reactions with alcs., MeI, C_6H_6 and $CHCl_3$, but none in pyridine.

organophosphorus
interesting theoretically only.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(11)

Derivatives of triphosphoric acid as insecticides.

B.A.Arbuzov, P.I.Alimov and O.N.Fedorova. Izvest.Kazan.Filiala Akad.Nauk S.S.S.R., Ser.Khim.Nauk, No.2, 25-30(1955).

To 50 g. $(EtO)_2POH$ and 54 g. $PhNEt_2$ was added 11.6 g. S at 55-60° and after 1 hr. when the S had reacted the mixture was treated at 20-40° with 29.5 g. $EtOPOCl_2$ and heated 5-6 hrs. at 35-40°; after diln. with petr.ether the amine salt was sepd. and the filtrate evapd. yielding a residue of undistillable $EtOP(O)[OSP(OEt)_2]_2$; the same was prepd. by addn. of 5.8 g. S to 25 g. $(EtO)_2POH$ in petr.ether and passage of dry NH_3 until the reaction was complete, followed by treatment with 14.7 g. $EtOPOCl_2$. The product was 100% effective against grain weevil at 0.05-0.1% concn. by spray application. Similarly was prepd. $EtP(O)[OPS(OEt)_2]_2$ which was 86% effective against the insect at 0.1% concn., and $MeOP(O)[OPS(OEt)_2]_2$, which was as effective as the EtO analog above. Heating 16.2 g. Me_2NPOCl_2 and 36 g. $EtOP(O)(NMe_2)_2$ in xylene finally to 150-5° until EtCl evolution ceased gave a range of fractions from which were obtained: 4.1 g. $(Me_2N)_2P(O)OP(O)(NMe_2)$, b_1 134-5°, and 8.4 g. $(Me_2N)_2P(O)[OP(O)(NMe_2)_2]_2$, b_1 170-1°, which was also a 100% effective agent at 0.2% concn. against the grain weevil; this amide, n_D^{20} 1.4685, d_4^{20} 1.2353. Similar reaction with $(Me_2N)P(S)Cl_2$ gave a range of fractions from which was obtained $Me_2NP(S)[OP(O)(NMe_2)_2]_2$, which was a weak insecticide at even 0.5% concn.; this amide, $b_{1.5}$ 175-6°, n_D^{20} 1.4880, d_4^{20} 1.2072. Similarly were prepd. only in unpurified state: $EtP(O)[OP(O)(NMe_2)_2]_2$, which was 76% effective insecticide at 0.5% concn. and $EtP(O)[OP(NMe_2)_2]_2$ which was a very weak insecticide at 0.5% concn.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Mixed esters of tert-(1,1,1-trichloro)butyl-1-trichloromethylcyclohexyl phosphite. II.

organophosphorus routine

V. S. Abramov and V. Khairullin (S. M. Kirov Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 27, 1365-9(1957). Cf. this j. 27, 444(1957).

To 41.5 g. PCl_3 and 65.3 g. 1-trichloromethylcyclohexanol in 250 ml. Et_2O was added 23.7 g. pyridine at 8°; after stirring 2 hrs. the mixture was filtered and the filtrate yielded 72% viscous fuming $(CH_2)_5C(CCl_3)OPCl_2$, I, b_1 129-30°, d_{20} 1.5091, n_D^{20} 1.5528, which on shock solidified and m. 55-60. Refluxing 158 g. $CCl_3CMe_2OPCl_2$ with 126 g. 1-trichloromethylcyclohexanol and 57.2 g. pyridine in Et_2O 4 hrs. gave 58.5% $(CH_2)_5C(CCl_3)OP(OCMe_2CCl_3)Cl$, (II), b_2 181-2°, 1.5040, 1.5422; when 2 moles of the alc. were used, the same product was formed but in 75% yield. This formed similarly in 30.5% yield from I and CCl_3CMe_2OH; the product, b_3 186-8°, 1.5039, 1.5421. Treatment with H_2O gave $(CH_2)_5C(CCl_3)OP(OCMe_2CCl_3)HO$, m. 67-9° (from cyclohexane). II and ROH in Et_2O with pyridine at 5° gave the following $(CH_2)_5C(CCl_3)O-$

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

$P(OCMe_2CCl_3)OR$ (R shown: Me, 74.8%, $b_2$181-2.5°, d_{20}1.4540, n_D^{20}1.5316, m. 58-60°(after standing); Et, 85.1%, m.86-7.5°; Pr, 76.5%, $b_3$190-2°, 1.3940, 1.5235, m.44-6°; Bu, 76%, $b_1$192-4°, 1.3674, 1.5200; iso-Bu, 63%, $b_2$189-91°, 1.3742, 1.5230. These esters formed monomolecular adducts with CuCl: (R shown) Me, m.143-4.5°; Et, m.159-60°; Pr, m.151°; Bu, m.138-9°; iso-Bu, m. 161-30. Attempts to react the chloride with PhOH failed, while reaction with Me_3COH gave indeterminate results as the product was undistillable and uncrystallizable. No esters with secondary alcs. could be prepd.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Organophosphorus, routine reaction

(13)

New method of synthesis of esters of phosphonic and thiophosphonic acids. VII. Addition of dialkyl phosphites and dialkyl thiophosphites to the ideno derivatives of malonic ester and acetylacetone. Phosphonobarbituric acids.

A. A. Ludovik and T. M. Moshkina (State Univ., Kazan). Zhur. Obshchei Khim. 27, 1611-17(1957). Cf. this j. 22, 267(1952); 22, 2047(1952); Doklady Akad. Nauk SSSR 80, 65(1951); 105, 735(1955). Also cf. Goldhahn and Fiebig, Pharmazie, 9, 964(1954).

To equimolar mixture of $CH_2{:}C(CO_2Et)_2$ (cf. Levina and Codovikov, this j. 25, 987(1955)) and $(RO)_2POH$ or $(RO)_2PSH$ was added a satd. soln. of NaOMe in MeOH; after the exothermic reaction the mixture was warmed 15-20 min. on a water bath and distd. yielding: 88% $(MeO)_2P(O)CH_2CH(CO_2Et)_2$, b_{11} 172-3°, n_D^{20} 1.4424, d_{20} 1.2034; 71% di-Et ester analog, b_{10} 179-80°, 1.4355, 1.1278; 46% $(BuO)_2P(O)CH_2CH(CO_2Et)_2$, b_{14} 204-5°, 1.4410, 1.0750; 51% $(EtO)_2P(S)CH_2CH(CO_2Et)_2$, b_{11} 180-2°, 1.4570, 1.1125. Slow addn. of EtONa in EtOH to 10 g. PhCH:CAc_2 and 11 g. $(EtO)_2PSH$ gave after a long induction period a rapid exothermic reaction, which yielded 4.2 g. $PhCH(CH_2Ac)$-$P(O)(OEt)_2$ (I), b_8 190-1°, 1.2005, 1.1264, formed by evident deacylation of the expected product. Similar reactions but using dry EtONa catalyst, gave after 30 min. on a steam bath 6.9 g. $(EtO)_2P(O)CHPhCH(COMe)_2$ (II), b_5 200-2°, 1.5178, 1.1790. Similarly was obtained 40% $(MeO)_2P(O)CHPhCH(COMe)_2$, b_5 198-200°, 1.5338, -. Heating 4 g. II in EtOH with a little EtONa 2 hrs. gave I, b_3 190-2°, 1.5030, 1.1294. Similarly were obtained: $(BuO)_2P(O)$-$CHPhCH(COMe)_2$, 42%, b_4 206-7°, 1.4970, 1.1060; and 50% $(EtO)_2P(O)CHMeCH$-$(COMe)_2$, b_{13} 170-2°, 1.4750, 1.1690. The appropriate phosphonomalonic esters (0.01 mole) treated with soln. of 0.03-0.04 mole EtONa in 20-30 ml. abs. EtOH with 0.07 mole $CO(NH_2)_2$ or $CS(NH_2)_2$ and refluxed 6-7 hrs. gave after soln. in H_2O and acidification the corresponding phosphonobarbituric acids. Thus were prepd. in 60-70% yields: $(MeO)_2P(O)CH_2CH(CONH)_2CO$, m. 97°; di-Et ester, m. 100°; di-Bu ester, m. 109°; $(EtO)_2P(S)CH_2CH(CONH)_2CO$, m. 98-100°;

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

$(MeO)_2P(O)CH_2CH(CONH)_2CS$, m.161°; di-Et ester, m.162-3°; di-Bu ester, m. 168°; $(EtO)_2P(S)CH_2CH(CONH)_2CS$, m.163-4°; $(MeO)_2P(O)CHMeCH(CONH)_2CO$, m.105°; $(EtO)_2P(O)CHMeCH(CONH)_2CO$, m.107°; $(BuO)_2P(O)CHMeCH(CONH)_2CO$, m.110°; $(EtO)_2P(S)CHMeCH(CONH)_2CO$, m.144°; $(MeO)_2P(O)CHMeCH(CONH)_2CS$, m.177°; $(EtO)_2P(O)CHPhCH(CONH)_2CO$, m.109°; $(EtO)_2P(S)CHPhCH(CONH)_2CO$, m.110°; $(EtO)_2P(O)CHPhCH(CONH)_2CS$, m.178°; $(EtO)_2P(S)CHPhCH(CONH)_2CS$, m.179°. Prepn. of $(RO)_2P(O)CH(CO_2R)_2$ was accomplished by 3 different routes all of which giving the same product; hence the Arbuzov reaction is normal with halomalonic esters and the supposition about its abnormality made by Allen and Johnson ((JACS 77,2371(1955)) is incorrect. Heating 16.6 g. $(EtO)_3P$ and 23.9 g. $BrCH(CO_2Et)_2$ 3 hrs. on a steam bath gave 17 g. $(EtO)_2POCH(CO_2Et)_2$, b_{10}160-1°, 1.4430, 1.1660; similarly $ClCH(CO_2Et)_2$ and $(EtO)_3P$ after 3 hrs. on a steam bath gave the same product, $(EtO)_2P(O)CH(CO_2Et)_2$, b_{10}160-1°, 1.4410, 1.1644; reaction of 10 g. $(EtO)_2POCl$ with Na deriv. from 1.2 g. Na and 9.2 g. $CH_2(CO_2Et)_2$ in Et_2O gave after 10 hrs. refluxing 5 g. $(EtO)_2P(O)CH(CO_2Et)_2$, b_{10}159-60°, n_D^{20}1.4458. This (1.4 g.) and 2 g. $CO(NH_2)_2$ as above gave 0.46 g. $(EtO)_2P(O)CH(CONH)_2CO$, m.97°; the phosphonomalonate from alternate route of synthesis gave the same product, m.98°. To Na deriv. from 2 g. Na and 10 g. CH_2Ac_2 was added 15 g. $(EtO)_2POCl$ in Et_2O and after refluxing 12 hrs. the filtrate gave 5.3 g. $(EtO)_2P(O)CHAc_2$, b_{10}161-2°, n_D^{20}1.4328. This (2 g.) with 3 g. $CO(NH_2)_2$ in dioxane with dry EtONa after refluxing 10 hrs., soln. of the ppt. in H_2O, acidification with HCl and concn. gave 0.4 g. $(EtO)_2P(O)C{:}CMeNHCON{:}CMe$, m.115-7°(from EtOH).

[redacted]

(14) XXVIII. Reaction of incomplete esters of acids of phosphorus with α,β-unsaturated cyclic ketones and cyclohexenyl acetate. Ditto

A.N.Pudovik and I.V.Konovalova. Ibid.1617-21.

Addn. of $(RO)_2POH$ or $(RO)_2PSH$ to 2-cyclohexenone and its methylated analogs occurs readily after addn. of catalytic amounts of RONa; after

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

termination of the exothermic reaction, the mixtures were neutralized with AcOH and distd. yielding the following esters: di-Et 3-oxocyclohexylphosphonate, 54%, b_{15}170°, n_D^{20}1.4620, d_{20}1.1210; di-Me ester, 46%, b_{10}160°, 1.4723, 1.2131; ~~[illegible]~~ di-Et 3-oxocyclohexylthiophosphonate, 57%, b_{15}182°, 1.4998, 1.1307; di-Me 3-oxo-2-methylcyclohexylphosphonate, 66%, $b_8$162°, m.96°; di-Et ester, 50%, $b_8$166°, 1.4612, 1.1007; di-Et 3-oxo-2-methylcyclohexylthiophosphonate, 60%, $b_8$165°, 1.4936, 1.1099; di-Me 3-oxo-1-methylcyclohexylphosphonate, 47%, b_{11}162°, 1.4721, 1.1301; di-Et ester, 54%, b_{11}167°, 1.4653, 1.1130; di-Et 3-oxo-1-methylcyclohexylthiophosphonate, 53%, $b_9$172°, 1.4950, 1.1182; di-Et 3-oxo-2,5-dimethylcyclohexylphosphonate, 59%, $b_8$162°, 1.4610, 1.0910; di-Me ester, 60%, $b_8$165°, 1.4780, 1.1499; di-Et 3-oxo-2,5-dimethylcyclohexylthiophosphonate, 66%, $b_9$178°, 1.4921, 1.0940; di-Bu 3-oxo-2,5-dimethylcyclohexylphosphonate, 59%, $b_3$196°, 1.4580, 1.0189; di-Et 3-oxo-2,5,5-trimethylcyclohexylphosphonate, 60%, $b_8$167°, 1.4641, 1.0710. Addn. of satd. EtONa-EtOH dropwise to 10.5 g. $(EtO)_2POH$ and 10.5 g. 1-cyclohexenyl acetate gave a very exothermic reaction which resulted, after cooling and acidification, in isolation of 5 g. cyclohexanone and 13 g. $MeC(OAc)(PO(OEt)_2)_2$ (I), $b_7$174-8.5°, d_{20}1.1511, n_D^{20}1.4308; the latter product formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate. To 19 g. $MeC(O)(OEt)_2$ and 15 g. $(EtO)_2POH$ was added dropwise EtONa-EtOH and after the strongly exothermic reaction there formed 20 g. I, $b_{9.5}$180°, d_{20}1.1535, n_D^{20}1.4300; I heated with BzCl in $PhNMe_2$ 1 hr. at 50° was benzoylated to extent of but 5.3%. Reaction of 0.3 g. 1-cyclohexenyl acetate with 7 g. $(EtO)_2PSH$ in presence of EtONa as above gave 3 g. cyclohexanone and 9.8 g. product, $b_8$159°, 1.1421, 1.4710, identified as $MeC(OAc)(PS(OEt)_2)_2$. The latter, $b_8$168-70°, 1.1410, 1.4710, also formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(15)

Anomalous reaction of α-halo ketones with esters of phosphorous acid. V. Reactions of halogen derivatives of methyl ethyl ketone and acetophenone with triethyl phosphite.

.N.Pudovik and L.G.Biktimirova (State Univ., Moscow). Zhur.Obshchei Khim. 27, 1703-12(1957). Cf. this J.25,2173(1955).

Halokatones having the halogen on a secondary C atom are more prone to the anomalous course of reaction with $(RO)_3P$ than halo ketones with halogen on the primary C atom. To 26.4 g. MeCOCHClMe preheated to 90-100° was added 43.4 g. $(EtO)_3P$ and the mixture gradually heated to 130° gave EtCl and 35.3 g. $(EtO)_2P(O)OCMe:CHMe$ (I), b_{10}110-1.5°, d_{20}1.0598, n_D^{20}1.4274; this heated with EtONa-EtOH gave MeEtCO and $(EtO)_3PO$; ozonolysis of the unsatd. ester gave AcH. Heating 49.8 g. MeCOCHBrMe and 5[illegible].6 g. $(EtO)_3P$ in dry Et_2O gave after 2.5 hrs. refluxing 36 g. I, b_{10}111.5-2°, 1.0578, 1.4[illegible], and 5 g. $AcCHMeP(O)(OEt)_2$ (II), b_{10}123-5°, 1.0975, 1.4340; if the phosphite is added to the bromo-ketone preheated to 110° and the mixture is heated 4 hrs. at 130-40° there was formed 37.9 g. I and 8.8 g. II. Heating I or II at 100° in H_2O, followed by periodic titrations, showed that I is saponified more rapidly than II, as in 20 hrs. 39.8% I was hydrolyzed, while only 14% II was attacked. To 20 g. $(EtO)_3P$ preheated to 130° was added 14.6 g. 2-bromocyclohexanone, yielding 3.1 g. $(EtO)_2POH$ and 13.4 g. di-Et cyclohexenyl phosphate, b_{12}144°, 1.1033, 1.4513; the same products formed on addn. of bromocyclohexanone to refluxing $(EtO)_3P$. Heating the ester with EtONa-EtOH gave cyclohexanone and $(EtO)_3PO$ thus confirming the structure of the former. Addn. of 36.5 g. $(EtO)_3P$ to 48 g. $MeCOCBr_2Me$ at 20-30°, gave on distn. some EtBr and 22.3 g. $(EtO)_2P(O)OCMe:CBrMe$, $b_{10.5}$147-8°(some decompn.),1.3481,1.4655; passage of Cl_2 into this ester in CCl_4 with ice cooling gave $(EtO)_2P(O)$-$OCMeClCBrClMe$, b_{10}164-5°, 1.4677, 1.4760. Addn. of 32.7 g. $(EtO)_3P$ to 55.4 g. $BrCH_2COCHBr_2$ at 60° gave 7.1 g. $(EtO)_2P(O)OCMe:CBr_2$, $b_{2.5-3}$145-8°, 1.6340, 1.4935(with much decompn.) Addn. of 44 g. $(EtO)_3P$ to 50 g. $PhCOCHCl_2$ at 20-30° gave 71 g. $(EtO)_2P(O)OCPh:CHCl$, $b_{0.5}$139-40°, 1.2353,

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

1.5170, which chlorinated in CCl_4 with ice cooling to $(EtO)_2P(O)OCPhCl-CHCl_2$, $b_1$162-3°, 1.5487, 1.5149. Addn. of 39 g. $(EtO)_3P$ to 47.6 g. $PhCOCCl_3$ at 20-30° gave 53.8% $(EtO)_2P(O)OCPh:CCl_2$, $b_2$145-6°, 1.2945, 1.5200. While $(EtO)_3P$ reacted with haloketones such as: dichloro- and dibromobenzalacetone, 3,4-dichloro-2-hexanone, and 3,4-dichloro-4-methyl-2-pentanone on heating to 100-50°, the products could not be distd. or isolated owing to decompn. and tar formation.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(16)

Some glycol esters of pyrophosphorous acid.

B.A.Arbuzov, K.V.Nikonorov, G.N.Vinokurova, O.N.Fedorova and Z.G.Chishova.

Izvest.Kazan.Filiala Akad.Nauk S.S.S.R., Ser.Khim.Nauk No.2, 3-17(1955).

To 41 g. $(CH_2O)_2PCl$ in 100 ml. Et_2O was added at 0° 25.6 g. pyridine and 2.91 g. H_2O; after stirring 5 hrs., the mixture was filtered and the filtrate yielded 40% $[(CH_2O)_2P]_2O$, b_4 100-1°, n_D^{20} 1.4900, d_4^{20} 1.4283. Similarly were prepd.: 44.5% $[OCH_2CH_2CH_2OP]_2O$, b_{2-3} 82-3°, n_D^{20} 1.4625, d_4^{20} 1.2772; 44% $(OCH_2CH(OHCl)OP)_2O$, b_3 144-5°, d_4^{20} 1.5126, n_D^{20} 1.5130; 34.8% $(OCHMeCH_2CH_2OP)_2O$ (A), b_3 118-20°, d_4^{20} 1.2329, n_D^{20} 1.4745. Addn. of -5° of 27 g. $(CH_2O)_2PCl$ to Et_2O soln. of $(EtO)_2PONa$ from 5 g. Na and 30 g. $(EtO)_2POH$, at first at 0° to -5°, finally stirring 2-3 hrs. at room temp. gave 60% $(CH_2O)_2POP(OEt)_2$, b_2 84-5°, n_D^{20} 1.4557, d_4^{20} 1.1890. Similarly were prepd.: 51% $(CH_2O)_2POP(OPr)_2$ (B), b_2 93-4°, n_D^{20} 1.4600, d_4^{20} 1.1446; 47.4% $(CH_2O)_2POP(OCHMe_2)_2$, b_2 90-1°, d_4^{20} 1.1392, n_D^{20} 1.4515; 23.76% $(CH_2O)_2POP(OBu)_2$, b_2 111-2°, d_4^{20} 1.110, n_D^{20} 1.4593 (10.6% byproduct $(BuO)_2POP(OBu)_2$ (I), b_2 136-7°, n_D^{20} 1.4466, d_4^{20} 0.9970, was isolated after prolonged fractionation); 68.1% $OCHMeCH_2OPOP(OEt)_2$, b_3 73-4°, n_D^{20} 1.4520, d_4^{20} 1.1493; 38.46% $OCHMeCH_2OPOP(OPr)_2$, b_2 100°, n_D^{20} 1.4530, d_4^{20} 1.1090; 24.5% $OCHMeCH_2OPOP(OCHMe_2)_2$, b_3 86-8°, n_D^{20} 1.4530, d_4^{20} 1.1070; 19.6% $OCHMeCH_2OPOP(OBu)_2$, b_3 120-1°, d_4^{20} 1.080, n_D^{20} 1.4550 (after much fractionation sepg. about 10% I); 53.3% $OCHMeCH_2CH_2OPOP(OEt)_2$, b_5 113-3.5°, n_D^{20} 1.4563, d_4^{20} 1.1368; 56.4% $OCHMeCH_2CH_2OPOP(OPr)_2$, b_2 110-14°, n_D^{20} 1.4580, d_4^{20} 1.1001; 32.7% $OCHMeCH_2CH_2OPOP(OCHMe_2)_2$, b_2 98-102°, d_4^{20} 1.0645, n_D^{20} 1.4460(after much fractionation from the symmetrical product); 40.1% $OCHMeCH_2CH_2OPOP(OBu)_2$, b_7 152-6°, d_4^{20} 1.0663, n_D^{20} 1.4580; 15% $OCH(CH_2Cl)CH_2OPOP(OEt)_2$, b_{1-2} 110°, d_4^{20} 1.2470, n_D^{20} 1.4660; $OCH(CH_2Cl)CH_2OPOP(OPr)_2$, 20%, $b_{1.5}$ 126-9°, d_4^{20} 1.1990, n_D^{20} 1.4690; 20% $OCH(CH_2Cl)CH_2OPOP(OBu)_2$, $b_{2.5}$ 146-9°, d_4^{20} 1.1986, n_D^{20} 1.473. Heating 2 g.A with 0.25 g. S to 100° gave an undistillable liquid after 40 min. only, but after 3 hrs. at 100° it gave a good yield of $[OCHMeCH_2CH_2OP(S)]_2O$, m.130-5°(from C_6H_6); the ethylene glycol ester analog reacted similarly but gave a viscous undistillable product;

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

heating 4.56 g. $(CH_2O)_2POP(OEt)_2$ with 0.64 g.S 30 min. at 100° gave a product, $C_6H_{14}O_5P_2S$, b_5 139-41°, n_D^{20} 1.4825, d_4^{20} 1.2694 (heating to 150° gave undistillable liquid product). Heating 8.9 g. EtI and 8.3 g. $(OCHMeCH_2CH_2O)POP(OEt)_2$ 5 hrs. at 100-50° in sealed tube gave undistillable residue. Heating 8 g. $(OCHMeCH_2CH_2O)POP(OPr)_2$ and 1.7 g. S finally to 160° also gave an undistillable product, but a reaction with semimolar amount of S without external heating gave a monothio deriv., $C_{10}H_{22}O_5P_2S$, b_5 138-41°, n_D^{20} 1.4680, d_4^{20} 1.1292; the same pyrophosphite reacted readily with CuI giving an adduct, m.108-15° (from EtOH). Treatment of $[(OCHMeCH_2CH_2O)P]_2O$ (3 g.) with 0.21 g. H_2O gave an exothermic reaction yielding 80% $(OCHMeCH_2CH_2O)POH$ (II), b_5 143-5°. Similarly $[(OCH_2CH_2OCH_2CH_2O)P]_2O$ gave a hydrolysis product which however failed to distil in vacuo, but similar hydrolysis of $(OCHMeCH_2CH_2O)POP(OEt)_2$ gave $(EtO)_2POH$ and crude II, b_3 128-30°, n_D^{20} 1.4530, d_4^{20} 1.2485. Similar treatment of $(OCH(CH_2Cl)CH_2O)_2P)_2O$ gave $OCH(CH_2Cl)CH_2OPOH$, b_3 145-6°, n_D^{20} 1.4940, d_4^{20} 1.549.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(17)

Reaction of dialkyl phosphites with aldehydes and ketones. XIII. Esters of α-hydroxy-γ-chloroisopropylphosphonic and 1,2-epoxyisopropylphosphonic acids.

V. A. Abramov and A. S. Kapustina (S. M. Kirov Chem. Tech. Inst., Kazan). Zhur. Obshchei Khim. 27, 1012-15(1957). Cf. this J. 27, 169(1957).

$ClCH_2Ac$ reacts with $(RO)_2POH$ on heating without any catalysts; the best temp. range for the reaction is 100-20°, as decompn. and tar formation occur at higher temps. The reaction is slow and can be followed easily by change of n of the mixture. Thus, 58 g. $(MeO)_2POH$ and 49.5 g. $ClCH_2Ac$ in 20 hrs. at 110-30° gave 58.7% $(MeO)_2P(O)CMe(OH)CH_2Cl$, m. 73-4°, isolated by cooling the mixture and crystallizing from cyclohexane. Similarly were prepd.: 65.3% di-Et ester, m. 47-8° (40 hrs. at 110-30°); 57.9% di-iso-Pr ester, m. 79-80° (120 hrs. at 100°); 50.6% di-Bu ester (38 hrs. at 140-50°), a liquid, n_D^{20} 1.4500, d_{20} 1.0914; and 43.4% di-iso-Bu ester, m. 76-7° (38 hrs. at 14 -50°). The di-Et ester could be distd. with slight decompn., b_4 139-40°, n_D^{20} 1.4500, d_{20} 1.1978, which solidified soon after the distn. These esters were added with cooling to alc. KOH, then briefly refluxed yielding, after sepn. of KCl, the following esters of the epoxy series. Thus ~~xxxxxxx~~ 161 g. di-Et ester with 44 g. KOH in 350 ml. EtOH gave 86.3% KCl and 79.5% $(EtO)_2P(O)CMeCH_2O$, b_6 96-7°, n_D^{20} 1.4305, d_{20} 1.1178; similarly were formed: 41.2% di-iso-Pr ester, b_6 95-7°, 1.4254, 1.0387; 32.1% di-Bu ester, b_5 139-40°, 1.4565, 1.0313; and 58.5% di-iso-Bu ester, b_5 125-7°, 1.4333, 1.0339. The di-Me ester of the epoxy series could not be distd. or isolated.

organophosphorus
routine

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

(18) routine

Action of anhydrides of organic acids on trialkyl phosphites and on dialkyl sodiophosphite.

Gil'm Kamai and V.A.Kukhtin (S.M.Kirov Chem.Technol.Inst.,Kazan). Zhur. Obshchei Khim.27, 949-53(1957). Cf. this j.26,411(1956).

Reaction of $(RCO)_2O$ with $(RO)_3P$ yields RCO_2R and $RCOP(O)(OR)_2$. Thus, heating 33.2 g. $(EtO)_3P$ and 20.4 g. Ac_2O 6 hrs. at 120-40° gave 72.7% EtOAc and 3.9 g. $AcP(O)(OEt)_2$, b_{44}84-6°, n_D^{20}1.4126, d_o^{20}1.0979(this gave intense color with sodium nitroprusside and formed 2,4-dinitrophenylhydrazone, m.152-3°; it gives color with fuchsine-SO_2). In addition there formed an unstated yield of material, $b_2$156-7°, 1.4325, 1.1579, which does not have an active carbonyl group and which was identical with a product isolated by Arbuzov and Azanovskaya (Doklady Akad.Nauk SSSR 58, 1961(1947)); this substance is $MeC(OAc)(PO(OEt)_2)_2$. Reaction of 10 g. $(MeO)_3P$ and 7 g. Ac_2O in 6 hrs. at 110-20° gave 3.1 g. MeOAc and unstated yield of $AcPO(OMe)_2$, $b_4$78-9°, 1.4206, 1.2109. Reaction of 20 g. $(EtO)_3P$ and 19 g. $(PrCO)_2O$ in 8 hrs. at 150° gave 7.1 g. EtO_2CPr, 4.5 g. $PrCOP(O)(OEt)_2$, $b_4$124-5°, 1.4418, 1.0580, and 5 g. $PrCOP(O)(O_2CPr)OEt$, $b_2$143-5°, 1.4385, 1.0547. $(EtO)_3P$ and Bz_2O similarly gave $BzP(O)(OEt)_2$, $b_4$157-8°, 1.5050, 1.1591, and $BzP(O)(OBz)OEt$, $b_3$194-6°, 1.5168, 1.1401. $(iso\text{-}BuO)_3P$ and Ac_2O gave $AcP(O)(OCH_2CHMe_2)_2$, $b_4$144-6°, 1.4305, 1.0018 and $MeC(OAc)(PO(OCH_2CHMe_2)_2)_2$, $b_2$174-8°, 1.4375, 1.0481. $(MeO)_3P$ and Bz_2O gave $BzP(O)(OMe)_2$, $b_4$146-8°, 1.5254, 1.2405. Addn. of 15.5 g. Ac_2O to $(EtO)_2POMa$ from 20 g. $(EtO)_2POH$ and 3.5 g. Na in Et_2O gave a ppt. of NaOAc and after 30 min. on a steam bath and filtration, there was obtained 50.7% $MeC(OAc)(PO(OEt)_2)_2$, $b_3$157°, 1.4318, 1.1597. Similarly $(iso\text{-}PrO)_2POMa$ gave $MeC(OAc)(PO(OCHMe_2)_2)_2$, $b_3$159-62°, 1.4312, 1.0823.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19

Action of carbon tetrachloride on mixed alkyl esters of phosphorous acid. Gil'm Kamai and F.M.Kharrasova (S.M.Kirov Chem.Technol.Inst.,Kazan). Zhur. Obshchei Khim.27, 953-60(1957). Cf.this J.20,1487(1950).

To 20 g. MeOH and 68 g. Me_2NPh was added 40 g. $EtOPCl_2$ in Et_2O at 5-10°; after 1 hr. at 30-5° the mixture was filtered and the filtrate yielded $(MeO)_2P(OEt)$, b_{14}28-9°, b_{759}122-4°, d_{20}1.0259, n_D^{20}1.4110. Similarly were prepd.: $(iso\text{-}PrO)_2POEt$, b_{18}65.5-6.5°, n_D^{20}1.4150, d_o^o0.9471; $(PrO)_2POEt$, b_{17}85-7°, 1.4215, 0.9720; $(iso\text{-}BuO)_2POEt$, $b_5$86-9°, 1.4258, 0.9462; $(BuO)_2$-POEt, b_{10}120.5-22°, 1.4285, 0.9510; $(iso\text{-}AmO)_2POEt$, b_{10}110-2°, 1.4315, 0.9311; $(MeO)_2POBu$, b_{18}65-6°, 1.4215, 1.0010; $(iso\text{-}PrO)_2POBu$, b_{10}76-8°, 1.4170, 0.9405; $(iso\text{-}AmO)_2POBu$, $b_4$114-4.5°, 1.4350, 0.9303. To 68.5 g. PCl_3 in 700 ml. Et_2O was added with ice cooling 37 g. BuOH in 60.5 g. Me_2NPh, followed by 46 g. EtOH in 121.2 g. Me_2NPh; after refluxing 1 hr. on a steam bath the mixture was filtered and distd. yielding $(EtO)_2POBu$, b_{13}72-4°, d_o^o 0.9749, d_{20}0.9551, n_D^{20}1.4262. Similarly was prepd. $(iso\text{-}AmO)_2$-POBu, $b_5$91-2°, n_D^{20}1.4283, d_o^o-, d_4^{20}0.9050. The yields of the phosphites were 30-69%. Heating $(MeO)_2POEt$ in Et_2O with S 1 hr. gave 88.3% $(MeO)_2$-PS(OEt), b_{17}79.5-80.5°, d_o^o1.1841, d_{20}1.1631, n_D^{20}1.4530. Similarly were prepd.: $(iso\text{-}PrO)_2PS(OEt)$, 85%, b_{23}106-8°, n_D^{20}1.4425, d_o^o1.0376, d_{20}1.0176; $(PrO)_2PS(OEt)$, 83.3%, b_{13}105-7°, 1.4475, 1.0579, 1.0388; $(iso\text{-}BuO)_2PS(OEt)$, 75.5%, b_{16}134-5°, 1.4450, 1.0116, 0.9942; $(BuO)_2PS(OEt)$, 81.3%, b_{13}135-7°, 1.4486, 1.0146, 0.9969; $(iso\text{-}AmO)_2PS(OEt)$, 88.7%, $b_5$127-9°, 1.4530, 1.0084, 0.9881; $(MeO)_2PS(OBu)$, 31%, b_{15}100-2°, 1.4545, 1.1342, 1.1144; $(EtO)_2PS$-(OBu), 77.1%, b_{14}116-7°, 1.4502, 1.0540, 1.0354; $(iso\text{-}AmO)_2PS(OBu)$, 50.6%, $b_9$126-7°, 1.4544, 0.9860, 0.9695. Heating 9 g. $(EtO)P(OMe)_2$ and 10.4 g. CCl_4 at reflux 4 hrs. gave 60.1% $(EtO)(MeO)P(O)CCl_3$, b_{10}116-8°, n_D^{20}1.4620, d_o^o1.4602, d_{20}1.4368. Similarly were prepd.: 94.9% $(iso\text{-}PrO)_2P(O)CCl_3$, $b_4$9[illegible] 1.4560, 1.3094, 1.2883; 35.6% $(PrO)_2P(O)CCl_3$, $b_7$123-5°, 1.4625, 1.3310, 1.3098; 70% $(iso\text{-}BuO)_2P(O)CCl_3$, b_{10}141-3°, 1.4585, 1.2804, 1.2406; 45.2% $(BuO)_2P(O)CCl_3$, b_{10}150-3°, 1.4600, 1.2690, 1.2454; 45.1% $(iso\text{-}AmO)_2P(O)C$[illegible]

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

$b_3$133-5°, 1.4615, 1.2204, 1.2016 (if prepd. from $(RO)_2POEt$), or 35%, b_{10}163-4°, 1.4590, 1.1920, 1.1728(if prepd. from $(RO)_2POBu$); 30.8% (I) $(MeO)(BuO)P(O)CCl_3$, $b_7$125-6°, 1.4625, 1.3476, 1.3264; 44.5% $(EtO)(BuO)P(O)CCl_3$, $b_5$105-7°, 1.4602, 1.3351, 1.3180; 50.1% $(iso\text{-}BuO)(BuO)P(O)CCl_3$, $b_3$105-9°, 1.4545, 1.2715, 1.2528; 33.6% $(iso\text{-}AmO)(BuO)P(O)CCl_3$, b_{11}150-1°, 1.4575, 1.-, 1.2084. Heating I with 15% HCl 4 hrs. at 145-50° and evapn. gave ,eCl, BuCl and $CCl_3PO_3H_2$, m.95-6° (cf. Yakubovich et al. this j.24, 1465, 2250(1954); Doklady Akad.Nauk S.S.S.R. 82,273(1952). Also cf. Kyhon et al. JCS 1954, 2224.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19A.

Tautomerism of diphenyl phosphite. Theoretical Organophosphorus

M.I.Kabachnik and Yu.M.Polikarpov (Inst.Hetero-Org.Compounds, Acad.Sci., Moscow). Doklady Akad.Nauk S.S.S.R.115, 512-15(1957). Cf.Noack, Ann.218, 93(1883) and Milobendzki and Szulgin, Chem.Polsk.15,66(1917).

$(PhO)_2PHO$ (I) was prepd. in 100% yield by careful hydrolysis of $(PhO)_2PCl$ in Et_2O by addn. of equivalent amount of H_2O, with subsequent removal of HCl and solvent in vacuo; the product, $b_{3\times10^{-4}}$ 100-1°, n_D^{20} 1.5590, d_{20} 1.2318. Infra-red spectrum of the ester shows sharp absorption bands characteristic of the P-H bond (2420 cm^{-1}) and P=O bond (1230 cm^{-1}), without noticeable absorption in the region of the HO group; the molar refraction is 61.57 which agrees with the 61.46 calcd. for $(PhO)_2P(O)H$ structure. However the chemical properties indicate a detectable amount of the tervalent form $(PhO)_2POH$ in equilibrium. ~~xxx~~ Thus, I reacts in the cold with PhN_3 yielding $(PhO)_2P(O)NHPh$; kept in sealed tube the equimolar mixture of the reactants gave in 4 months at room temp. 83% $(PhO)_2P(O)NHPh$, m.126-9°; in 5 hrs. at 100° the yield was 50%. Heating I with equimolar amount of [illegible] yields $(PhO)_2P(O)Cl$; in 6 hrs. at 120° some 77% of [illegible] reacted; the ethereal soln. of the reaction mixture was treated with aq. NaOH and the alkaline ext. acidified, yielding $(PhO)_2PSOH$, characterized as the cyclohexylamine salt, needles, m.127-9°(from aq. EtOH), obtained in 6% yield(cf. Lecocq and Todd, J.Chem.Soc.1954,2361). The above addn. of I takes place with evolution of some H_2S, and considerable amount of $(PhO)_3P$ is also formed. I dissolves Cu_2Cl_2, forming a complex I.CuCl; after brief heating, soln. in Et_2O, sepn. of unreacted Cu_2Cl_2 (considerable amount) and addn. of MeOH, the complex was pptd. and analyzed; the product, decl20°(from dioxane-petr. ether). I reacts with CH_2N_2 in Et_2O with evolution of N_2, yielding 58% $(PhO)_2POMe$, b_2 101-3°, n_D^{20} 1.5575, d_{20} 1.1663; this readily forms a complex $(PhO)_2(MeO)P.CuCl$, viscous syrup. The results indicate the presence of considerable enolic form of I in equilibrium.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19B

Organic insectofungicides. XXVI. New method of synthesis of mixed esters of dithiophosphoric acid.

N.N.Mel'nikov, A.F.Grapov and K.D.Shvetsova-Shilovskaya (Sci.Inst.Fertilizers and Insectofungicides, Moscow). Zhur.Obshchei Khim.27, 1905-7(1957). Cf. this j.26,2569(1956).

The following method was used to prepare mixed esters of dithiophosphoric acid. To an aq. soln. of an aryl diazonium salt, freed of excess HNO_2 by air-blowing, was added an aq. soln. of equimolar amount of $(RO)_2PS_2H$ in the form of a slat, such as K, and 0.1 g. powd. Cu per 0.1 mole reactants. The mixing was done at 0-2° and the mixture was warmed to 40-50° until N_2 evolution terminated. After cooling to 10-15°, the mixture was extd. with Et_2O and the dried ext. was distd. Thus were obtained: $PhSPS(OMe)_2$, 54%, $b_{0.1}$95-7°, d_{20}1.2466, n_D^{20}1.5927 (gives 50% kill of Calandra oryzae at 0.021% in 50 hrs.); $PhSPS(OEt)_2$, 48%, $b_{0.1}$102.5-4.5°, 1.1823, 1.5629 (0.03%); o-$MeC_6H_4SPS(OMe)_2$, 46.5%, $b_{0.1}$101-2.5°, 1.1644, 1.5660 (-%); m-isomer, 40%, $b_{0.1}$102.5-2.8°, 1.1729, 1.5682 (-%); p-isomer, 27.5%, $b_{0.15}$104.5-5°, 1.2136, 1.5829 ((0.03%); o-$MeC_6H_4SPS(OEt)_2$, 47.5%, $b_{0.2}$ 118-8.5°, 1.1696, 1.5642 (0.07%); m-isomer, 42%, $b_{0.09}$105-7°, 1.1781, 1.5624 (0.042%); p-isomer, 51%, $b_{0.12}$110-2°, 1.1779, 1.5639 ((0.035%); m-$ClC_6H_4SPS(OEt)_2$, 45%, $b_{0.08}$104.5-6.5°, 1.2538, 1.5730 (-%); p-isomer, 51.3%, $b_{0.2}$122-3°, 1.2627, 1.5750(-%); p-$O_2NC_6H_4SPS(OEt)_2$, 41.5%, $b_{0.1}$ 137-9°, m.45.5-6.5°,(0.004%). If the soln. of the diazonium salt is not freed of N oxides the $(RO)_2PS_2H$ is oxidized to the disulfide and the products are badly contaminated.

19C

XXVII. New method of preparation of esters of chlorothiophosphoric acid. N.N.Mel'nikov, Ya.A.Mandel'baum, E.I.Sventsitskii and Z.M.Bakanova. Ibid. 1908-10.

Partial or complete esterification of $PSCl_3$ is conveniently attained by the use of $(RO)_2Mg$ as the alkylating agent. To Mg covered with dry ROH was added a crystal of I_2 and 3-3 drops CCl_4; after the reaction had

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

been initiated (H_2 evolution) the remainder of the requisite ROH was added; the ROH is taken in 2.5-3 fold excess over theoretical amount. The mixture was refluxed 1.5-2 hrs. until Mg dissolved; This soln. was used directly below. To well stirred 34 g. $PSCl_3$ was gradually added $(EtO)_2Mg$ from 5.3 g. Mg at 30-45° over 45 min. The mixture was stirred 2 hrs. at 45°, dild. with cold H_2O acidified with HCl, and the sepd. oil was dried and distd. yielding 77% $(EtO)_2PSCl$, b_{25} 96-8°, d_{20}-, n_D^{20}-. Under these conditions 17.8 g. $EtOPSCl_2$ and $(EtO)_2Mg$ from 1.4 g. Mg gave 82% $(EtO)_2PSCl$, the addn. requiring 20 min. at 25-30°, and heating 1 hr. at 35-45°. Similarly were obtained: (MeO)(EtO)PSCl, 75.5%, b_{17} 79-80°, 1.2506, 1.4740; (iso-PrO)(EtO)PSCl, b_{10} 84-5°, 1.1561, 1.4620, 70%; (EtO)(BuO)PSCl, 70%, b_{22} 126-7°, 1.1432, 1.4660; 70% (EtO)(iso-AmO)PSCl, b_{20} 131-2°, 1.0885, 1.4620. The best yields result from $(RO)_2Mg$ which contains 2 moles ROH. If the ROH is removed, the Mg salt has a grey color and is unreactive, giving low yields of the desired products.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19P

Organophosphorus

Organophosphorus derivatives of ethylenimine. 2 Addition of halogen derivatives of hydrocarbons and of halogens to ethylenamides of dialkyl phosphates. N.P.Grechkin (A.E.Arbuzov Chem.Inst.,Kazan). Izvest.Akad.Nauk S.S.S.R., Otdel. Khim.Nauk 1957, 1053-8. Cf. this j.1956,538.

Heating in sealed tube 10 g. $(EtO)_2P(O)NCH_2CH_2$ and 7.1 g. $PhCH_2Cl$ 4 hrs. at 135-45° and 2 hrs. at 185° gave 55% $(EtO)_2P(O)N(CH_2Ph)CH_2CH_2Cl$, $b_{1.7}$151-1.5°, d_{20}1.1621, n_D^{20}1.5013, which hydrolysed with HCl to $PhCH_2NHCH_2CH_2Cl$ HCl salt, m.191-2°. Similar reaction with 9.9 g. $1\text{-}C_{10}H_7CH_2Cl$ in 4 hrs. at 165-85° gave 9.5 g. starting materials and 10 g. undistillable residue, which on hydrolysis with HCl gave $1\text{-}C_{10}H_7CH_2NHCH_2CH_2Cl.HCl$, m.196-8°; evidently the expected $(EtO)_2P(O)N(CH_2C_{10}H_7)CH_2CH_2Cl$ could not be distd at 1 mm. Treatment of 6.6 g. $(iso\text{-}BuO)_2P(O)NCH_2CH_2$ in 50 ml. CCl_4 with calcd. amount (2 g.) Cl_2 in 50 ml. CCl_4 at 0° and allowing the mixture to stand overnight gave 67% $(iso\text{-}BuO)_2P(O)NClCH_2CH_2Cl$, $b_3$132-3°, d_{20}1.1416, n_D^{20}1.4539. Similarly were prepd.: $(EtO)_2P(O)NClCH_2CH_2Cl$, 80%, $b_1$99-100°, 1.2710, 1.4574; di-iso-Pr ester, 64%, $b_2$101-2°, 1.1867, 1.4513; di-Am ester, 79%, $b_2$149-50°, 1.1144, 1.4586; di-n-hexyl ester, 40%, $b_2$160-2°, 1.0827, 1.4590. Addn. of 6.4 g. $(EtO)_3P$ to 9.7 g. $(EtO)_2P(O)NClCH_2CH_2Cl$ at 35-50° (cooling with acetone-Dry Ice was necessary) gave 2 g. $EtP(O)(OEt)_2$ and 9.5 g.(74% pure) $ClCH_2CH_2\text{-}N[P(O)(OEt)_2]_2$, $b_1$133-5°, 1.2114, 1.4467. Heating 10.5 g. $(EtO)_2P(O)NClCH_2CH_2Cl$ in sealed tube with 7.5 g. $(EtO)_2P(O)NCH_2CH_2$ 6 hrs. at 120-30° gave 8 g. starting materials and about 65% $[ClCH_2CH_2NP(O)(OEt)_2]_2$, a hydrazine deriv., $b_{1.3}$109°, 1.1912, 1.4484.

19E

Synthesis of mixed ester amides of monothio- and dithiopyrophosphoric acid. K.V.Nikonorov and Z.G.Speranskaya (A.E.Arbuzov Chem.Inst.,Kazan). Izvest.Akad. Nauk S.S.S.R., Otdel.Khim.Nauk 1957, 1059-63.

Organophosphorus

To $(RO)_2POSH$ prepd. by heating $(RO)_2PHO$ with S in presence of Et_3N 1 hr. at 60° was added $(Me_2N)_2POCl$ and heated 4-5 hrs. at 40°, the mixture was dild. with gasoline, the pptd. amine salt was sepd. and the product distd. Thus were obtained: 58% $(Me_2N)_2P(O)OP(S)(OPr)_2$, $b_{3.5}$159-60°, d_{20}1.1186, n_D^{20}1.4700; 48% $(Me_2N)_2P(O)OP(S)(OCHMe_2)_2$, $b_3$150-2°, 1.1237, 1.4665; 31.7% $(Me_2N)(Et_2N)P(S)O\text{-}P(S)(OPr)_2$, $b_{1.5}$149-52°, 1.0950, 1.4710; 45% $(Me_2N)_2P(O)OP(S)(OBu)_2$, $b_1$154-7°, 1.0883, 1.4695; $(Me_2N)_2P(O)OP(S)(OCH_2CHMe_2)_2$, $b_{2.5}$159-60°, 1.082, 1.4652; The $(RO)_2POSH$, prepd. as above was treated at 40° with $(Et_2N)_2PCl$ and calcd. amount of powd.S and the mixture heated 8-10 hrs. at 60°, gave the following products, isolated after dilm. with gasoline, filtration and distn.: 44.8% $(Et_2N)_2P(S)OP(S)(OEt)_2$, b_{1-2}153-6°, 1.1097, 1.500; 49.5% $(Et_2N)_2P(S)OP(S)(OPr)_2$ b_{2-3}167-70°, 1.0890, 1.4970; 36.5% $(Et_2N)_2P(S)OP(S)(OCHMe_2)_2$, b_{2-3}165-8°, 1.0746, 1.4912; 25% $(Et_2N)_2P(S)OP(S)(OBu)_2$, $b_2$172-5°, 1.0670, 1.4960; 30% $(Et_2N)_2P(S)OP(S)(OCH_2CHMe_2)_2$, b_{2-3}173-7°, 1.0567, 1.4880. The products had some insecticidal activity.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19.7

Thermographic study of the reaction of esters of ethylene glycol phospherous acid with alkyl halides.

B.A.Arbuzov, M.K.Saikina and V.M.Zoroastrova (V.I.Ul'yanov-Lenin State Univ., Kazan). Izvest.Akad.Nauk S.S.S.R., Otdel. Khim. Nauk 1957,1046-52. Cf. Doklady Akad.Nauk SSSR 114, 89(1957) and N.A.Razumova, Dissertation, Kazan, 154.

Reactions of the following esters of ethylene glycol phospherous acid with alkyl halides were studied thermographically with a differential thermocouple, by heating 1:1 mixtures at 4-5° per minute, completing the process in 1 hr. Under these conditions the esters gave a single exothermic effect (typical heating curves shown) except for the iso-Pr and iso-Bu esters which gave 2 effects. Since esters of propylene phosphite react with alkyl halides at low temp. to yield haloesters of phosphonic acids with open chain structure, which at higher temp. lose a mole of alkyl halide and form cyclic esters of phosphonic acids (cf. 1957 ref. above), the open chain ester may be regarded as an intermediate in the overall high temp. Arbuzov reaction of cyclic phosphites. When the above listed expts. were repeated with heating rate of 0.4-0.5° per min., two exothermic effects were clearly evident. The mixture formed at the 1st effect from $EtOPOCH_2CH_2O$ was examined, yielding after several distns. $EtP(O)(OCH_2CH_2Br)OEt$, $b_{1.5}$98-102°, n_D^{20}1.4600, d_{20}^{20}1.3891, along with higher and lower boiling substances. The product formed at the 2nd exothermic effect was $EtP(O)(OCH_2CH_2)_2$, $b_2$118-22°, n_D^{20}1.4480, d_e^{20} 1.2633. The former ester on thermographic examn. gave only 1 effect which corresponded to the 2nd transformation and gave the latter ester as the result. The thermal effect expected for the primary addn. of RX to the cyclic phosphite cannot be detected thermographically. The initiation temp. for this reason was detd. thermographically by drawing a tangent at 45° to the differential record curve at the point of its deviation from zero order location and subsequent projection of the point of tangency on a direct recording of temperature. The ratios of the areas under the peaks were calcd. The results show that the Arbuzov reaction proceeds most readily with cyclic esters having the smallest third ester groups on the P atom, as shown by low initiation temp. and large thermal effect; the 2nd process of cyclization produces less heat than the 1st process. With increase of the alkyl group in the ester the ratio of the area under the 2 peaks increases owing to less facile transformation of the halealkyl ester into the cyclic product. Iodides react more readily than the bromides and produce largers thermal effects. The following esters were used: $MeOP(OCH_2)_2$, b_{14}44.5°, d_e^{20}1.2159, n_D^{20}

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

1.4440; $EtOP(OCH_2)_2$, b_{15}51-1.5°, 1.1317, 1.4395; $PrOP(OCH_2)_2$, b_{12}64-6°, 1.1026, 1.4445; iso-$PrOP(OCH_2)_2$, $b_{10-10.5}$53.5-4°, 1.0829, 1.4348; $BuOP(OCH_2)_2$, $b_{8.5}$71-2°, 1.0819, 1.4470; iso-$BuOP(OCH_2)_2$, $b_{4-4.6}$54°, 1.0652, 1.4420; $CH_2{:}CHCH_2OP(OCH_2)_2$, b_{10-11}69.5-70°, 1.1553, 1.4635. The curves showing the thermal effects are reproduced. The following data are tabulated for various reactant pairs (for the rapid heating rate, the following information is given, resp. temp. of initiation of isomerization reaction, magnitude of thermal effect, time for completion of reaction, area under the peak in sq.cm.) as follows: $MeOP(OCH_2)_2$ + MeBr 86°, 17°, 8 ~~xxxx~~ min., 53.53; $MeOP(OCH_2)_2$ + MeI 68°, 17°, 8 min., 55.8; $EtOP(OCH_2)_2$ + EtBr 175°, 10°, 11 min., 43.47; EtI + $EtOP(OCH_2)_2$ 126°, 23°, 10 min.20 sec., 50.97; $PrOP(OCH_2)_2$ + PrBr 184°, 12°, 9 min., 36.48; iso-$PrOP(OCH_2)_2$ + iso-PrBr 225 or 250°, 9 or 8°, 5 min.10 sec. or 1 min.15 sec., 15.53 or 13.47, resp.; $BuOP(OCH_2)_2$ + BuBr 202°, 5°, 12 min. 15 sec., 34.2; iso-$BuOP(OCH_2)_2$ + iso-BuBr 235 or 302°, 10 or 19°, 5 min. or 1 min. 15 sec., 14.9 or 11.3, resp.; $CH_2{:}CHCH_2OP(OCH_2)_2$ + $CH_2{:}CHCH_2Br$ 128°, 7°, 9 min.15 sec., 45.07; $CH_2{:}CHCH_2OP(OCH_2)_2$ + $CH_2{:}CHCH_2I$ 82.5°, 15°, 8 min.45 sec., 63.07; $BrCH_2CH_2OP(O)Et(OEt)$ 220°, -,-,-; $EtP(O)(OCH_2)_2$ no effect observed and decompn. took place; $(CH_2O)_2POEt$ + NaI 195°, 16°, 6 min.45 sec., 33.65; $PrOP(OCH_2)_2$ + NaI 262°, 14°, 5 min., 21.2. In the above and the following listings the substances were taken in equimolar amounts, with 0.0094 moles of each being used. Repetition with the slow heating rate gave the following data (formation temp. for primary product, same for 2nd product, and ratio of peak areas shown resp.); $MeOP(OCH_2)_2$ + MeBr 48°, 145°, 5.22; EtBr + $EtOP(OCH_2)_2$ 100°, 295°, 7.64; $PrOP(OCH_2)_2$ + PrBr 115°, 225°, 9.43; iso-PrBr + iso-$PrOP(OCH_2)_2$ 120°, 190°, 5.21; $BuOP(OCH_2)_2$ + BuBr 118°, 210°, 15.24; iso-$BuOP(OCH_2)_2$ + iso-BuBr 130°, 225°, 7.2; iso-$PrOP(OCH_2)_2$ + MeI 50°, 125°, 6.25; $CH_2{:}CHCH_2OP(OCH_2)_2$ + $CH_2{:}CHCH_2Br$ 80°, 178°, 5.12.

Organophosphorus, theoretical interest only

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

19C

Reaction of intermediate products of Arbuzov rearrangement with amines. A.E.Arbuzov and N.N.Sazonova. Doklady Akad.Nauk S.S.S.R.115,1119-21(1957). The intermediate Arbuzov complexes $(ArO)_3PRX$ were treated with Me_2NH or Et_2NH in an extension of the previously known reaction with H_2O or ROH. The following complexes were used (shown resp. are duration of formation, the temp. used and yield): $(PhO)_3PMeI$, 8-10 hrs., 100°, m.130°, 100%; ~~[illegible]~~ $(o\text{-}MeC_6H_4O)_3PMeI$, 4 hrs., 100°, 100%, m.135-6°; $(o\text{-}ClC_6H_4O)_3PMeI$, 7 hrs., 100-10°, 75%, m. 49°; $(p\text{-}ClC_6H_4O)_3PMeI$, 13 hrs., 100°, 100%, m.104°; $(o\text{-}MeC_6H_4O)_3PEtI$, 16 hrs., 110-20°, 70%, m.107-8°; $(o\text{-}C_6H_4O)_3PMeI$, 36 hrs., 110-20°, an oil. The complexes above when treated with EtOH gave the following phosphonates: $(o\text{-}MeC_6H_4O)_2P(O)Me$, 74.6%, b_{16}215°, d_4^{20}-, n_D^{20}-, m.64°; $(o\text{-}C_6H_4O)_2P(O)Et$, 38.8%, b_{12}213-4°, 1.1410, 1.5415; $(o\text{-}ClC_6H_4O)_2P(O)Me$, 30%, $b_3$176-7°, 1.3350, 1.5560; $(o\text{-}MeC_6H_4O)_2P(O)Bu$, 30.2%, b_{11}216-7°, 1.1071, 1.5321. The reaction of the complexes with the amines gave phenols and a product which was either a liquid or a crystallizable solid. All, on standing in air, hydrolyzed and yielded the amine HI salts. Thus were obtained: 56% $(PhO)_2PMe{:}NEt_2I$, m.126°; 26% $(PhO)_2PMe{:}NMe_2I$, m.109°; 41.1% $(o\text{-}MeC_6H_4O)_2PMe{:}NEt_2I$, m.141°; and 28.8% $(o\text{-}MeC_6H_4O)_2PMe{:}NMe_2I$, m.136.5-7°. Reaction of $(PhO)_2PCl$ with 2 Et_2NH gave $(PhO)_2PNEt_2$, 62.8%, $b_4$176-8°, 1.0902, 1.5532, which on being heated with MeI gave a product identical with that formed from $(PhO)_3PMeI$ and Et_2NH. Treatment of $(PhO)_2PNEt_2$ with Cu_2I_2 gave the complex, m.111°, with mol. wt. of 1443, indicating a trimeric substance. The products obtained from the reaction of the complexes with amines gave after hydrolysis the products which prove their structures. Thus the 1st product gave $MeP(O)(OH)_2$, m.102° and $Et_2NH.HI$; treatment of the product with $AgNO_3$ gave AgI indicating the ionic binding of the halogen and supporting the proposed reaction course which is that of formation of ArOH and $(ArO)_2PRNR_2I$ salt, which passes to $(ArO)_2PR{:}NR_2I$. Esters of amidophosphorous acid appear to react with alkyl halides to yield undistillable masses and amine salts, while esters of diamidophosphorous acid are isomerizable normally by the action of alkyl halides

organophosphorus, rather routine

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2

organophosphorus sonture

194

Anomalous reaction of α-halo ketones with esters of phosphorous acid. VI. Reaction of esters of phosphorous acid with halides of halosubstituted carboxylic acids.

A.N.Pudovik and L.G.Biktimirova (State Univ.,Kazan). Zhur.Obshchei Khim. 27, 2104-8(1957). Cf. this j.27,1708(1957).

To $(RO)_3P$ was added the desired RCOCl in which R is a halogen bearing radical. The reactions were exothermic, requiring cooling. After termination of evolution of alkyl halide, the products were distd. Reaction of $(MeO)_3P$ with $ClCH_2COCl$, with heating 0.5 hr. at 100° gave 84% product identified as $(MeO)_2P(O)OC(:CH_2)P(O)(OMe)_2$, b_1 141°, d_{20} 1.3214, n_D^{20} 1.4420; similar reaction with $(EtO)_3P$ gave the tetra-Et analog, 86.4%, $b_{0.5}$ 125-6°, 1.1827, 1.4396. The same reaction run in Et_2O gave a low yield. Ozonolysis of the products in CCl_4 gave CH_2O, thus confirming the structure. $(MeO)_3P$ and $Me_2CBrCOBr$ similarly gave 92.3% product, identified as $Me_2C:C(PO(OMe)_2)OP(O)(OMe)_2$, $b_{0.5}$ 131-2°, 1.2756, 1.4580, while $(EtO)_3P$ gave 90% corresponding tetra-Et ester, $b_{1.5}$ 134-5°, 1.1602, 1.4503. $(MeO)_3P$ and CCl_3COCl at below 30° gave 78.3% $CCl_2:C(PO(OMe)_2)OP(O)(OMe)_2$, $b_{0.75}$ 134-5°, 1.4901, 1.4770, while the $(EtO)_3P$ reaction gave 78.6% tetra-Et ester, $b_{0.5}$ 132-3°, 1.3219, 1.4660. If the last reaction is run in Et_2O, there was obtained the above tetra-Et ester and a somewhat greater amount of $CCl_3COP(O)(OEt)_2$, b_2 95°, 1.3916, 1.4632, which is evidently the intermediate in the formation of the di-phosphorus esters. The phosphonate is formed also if the phosphite is used in less than the theoretical amount for the reaction with the acyl halide. Reaction of $(EtO)_3P$ with $MeCHBrCOBr$ at 100° (final temp.) gave 78.6% $MeCH:C(PO(OEt)_2)OP(O)(OEt)_2$, $b_{1.5}$ 128-9°, 1.1690, 1.4450. Thus, halosubstituted acyl halides react with phosphites predominantly by the anomalous route.

Approved For Release 2008/11/26 : CIA-RDP80T00246A003200030001-2