Approved For Release 1999/09/10 : CIA-RDP83-00423R001200820003-5

3

Glycol esters of pyrophosphorous acid.

B.A.Arbuzov, K.V.Nikonorov, O.N.Fedorova, G.M.Vinokurova and Z.G.Shishova (A.E.Arbuzov Chem.Inst.,Kazan). Doklady Akad. Nauk S.S.S.R. 91, 817-20(1953).

CPYRGHT

Slow addn. of the calcd. amount of H_2O and a base (pyridine, Me_2NPh, or Et_3N) to 2 moles CH_2CH_2OPClO dild. with 2-3 parts Et_2O at about -5° with stirring, followed by 3 hrs. at room temp. gave after filtration and distn. of the filtrate 40% $(CH_2O)_2POP(OCH_2)_2$, $b_4$100-1°, d_{20}1.4293, n_D^{20}1.4900. Similarly were obtained: [illegible] 44.5% $OCHMeCH_2OPOPOCH_2$-$CHMeO$, b_{2-3}82-3°, d_{20}1.2772, n_D^{20}1.4625; 44% $OCH(CH_2Cl)CH_2OPOPOCH_2CH$-$(CH_2Cl)O$, $b_3$144-5°, d_{20}1.5126, n_D^{20}1.5130; 34.8% $OCHMeCH_2CH_2OPOPOCH_2$-CH_2CHMeO, $b_2$118-20°, d_{20}1.2329, n_D^{20}1.4745. These esters readily add Cu_2X_2 and S; they react violently with H_2O. Treatment of OCH_2CH_2OPCl with $(RO)_2PONa$ with cooling in Et_2O gave after sepn. of pptd. NaCl the corresponding $(CH_2O)_2POP(OR)_2$, (R shown): di-Et, 60%, $b_2$84-5°, d_{20}1.1890, n_D^{20}1.4557; di-Pr, 51%, $b_2$93-4°, d_{20}1.1446, n_D^{20}1.4600; di-iso-Pr, 47.4%, $b_2$90-1°, d_{20}1.1392, n_D^{20}1.4515; di-Bu, 10.2%, $b_1$104-5°, d_{20}1.136, n_D^{20}1.4626. Similarly were formed: 68.1% $OCHMeCH_2OPOP(OEt)_2$, $b_3$73-4°, d_{20}1.1493, n_D^{20}1.4520; di-Pr analog, 33.4%, $b_2$110°, d_{20}1.1090, n_D^{20}1.4530; di-iso-Pr analog, 24.5%, $b_3$86-8°, d_{20}1.1070, n_D^{20}1.4530; di-Bu analog, 19.6%, $b_3$120-1°, d_{20}1.080, n_D^{20}1.4550; 53.3% $OCHMeCH_2CH_2OP$-$OP(OEt)_2$, $b_5$113-3.5°, d_{20}1.1368, n_D^{20}1.4563; di-Pr analog, 56.4%, $b_4$110-11°, d_{20}1.1001, n_D^{20}1.4580; 32.7% di-iso-Pr analog, $b_2$98-102°, d_{20}1.0645, n_D^{20}1.4460; 40.1% di-Bu analog, $b_7$152-6°, d_{20}1.0663, n_D^{20}1.4580; 15% $OCH(CH_2Cl)CH_2OPOP(OEt)_2$, b_{1-2}110°, d_{20}1.2470, n_D^{20}1.4660; 20% di-Pr analog, b_{1-2}125-9°, d_{20}1.1990, n_D^{20}1.4690; 23% di-Bu analog, $b_3$147-50°, d_{20}1.1986, n_D^{20}1.473. These esters possess the usual properties of the phosphites. The yields of the higher unsym.esters are reduced by the symmetrization reaction during distn.

Approved For Release 1999/09/10 : CIA-RDP83-00423R001200820003-5