

V. Abramov and G. Karp (Kazan State Univ.). Doklady Akad. Nauk S.S.S.R.
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The existence of the previously hypothetical addn. product of $(RO)_3P$ and RX in the Arbuzov reaction has been proven by isolation of such adducts between several $(RO)_3P$ and $EtOCHBrCH_2Br$. The adducts could not be crystallized and were obtained as viscous masses which on heating gave the expected RBr and the corresponding phosphonates; treatment of these adducts with H_2O also gave the same phosphonates. Thus were obtained:

64.4% $(MeO)_2P(O)CH(OEt)CH_2Br$, $b_{13} 137-8^\circ$, $n_D^{20} 1.4648$, $d_4^{20} 1.4402$; 74.1% di-Et ester, $b_{9-9.5} 140-40.5^\circ$, $n_D^{20} 1.4570$, $d_4^{20} 1.3180$; 52.3% di-Bu ester, $b_{12-13} 176-8^\circ$, $n_D^{20} 1.4548$, $d_4^{20} 1.1909$; 53.2% di-iso-Bu ester, $b_{14-14.5} 170-1^\circ$, $n_D^{20} 1.4523$, $d_4^{20} 1.1839$; and unstated yield of di-Ph ester, $m. 40-2^\circ$. The temp. necessary for decompn. of the intermediate $(RO)_3PR'Br$ rises with increase of the mol. wt. of the ester used. The results suggest that the Arbuzov reaction proceeds through the addn. step which goes by the bimolecular mechanism, after which the adduct decomposes by either intramolecular mechanism or by ionization and a bimolecular loss of RX .

Cf. Pudovik, Doklady Akad. Nauk SSSR 84, 519(1952).

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