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Theory of tautomeric equilibrium. 3. Pseudomerism. Structure and properties of dialkyl thiophosphites.

M.I. Kabachnik and T.A. Mastryukova. Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1953, No. 1, 163-76.

Prototropic tautomeric equil. is a form of protolytic acid-base equil. in which 2 acids with the same anion exist in a solvent or a base which acts as proton carrier. Attempts were made to examine the possible system $(RO)_2P(S)H \rightleftharpoons (RO)_2PSH$ by means of reactions that would involve the latter form (addn. of cuprous halides, S, RX); none of these reactions took place. Only formation of metallic derivs. could be possibly placed in this category; these appear to have the structure $(RO)_2PSM$, but the Na salts in their action on H_2O do not act as salts of a strong acid and are instantly hydrolyzed. Hence in the above system the 1st structure is so predominant that the reactions of the 2nd form do not realize themselves; this fact is contrary to the usual concepts of pseudomerism. Theor. examn. of the kinetics inherent in pseudomerism (Cf. Ingold and Thorpe, New Aspects of Tautomerism) indicates admission of such reaction rates that are not actually realized. It is believed that reactions of this group proceed by transfer of the reactive center without involvement in tautomeric transformation. (K. at this point recants his use of the ideas of resonance in a previous publication (Uspekhi Khimii, 17, 96 (1948)). All properties of dialkyl thiophosphites indicate structure $(RO)_2P(S)H$; these are sol. in org. solvents and aq. EtOH, but insol. in H_2O ; their solns. are neutral. They are insol. in aq. alkalies and are hydrolyzed by acids and alkalies yielding H_3PO_3 . They are vigorously oxidized by HNO_3 . Treatment with standard aq. alc. NaOH they slowly consume alkali because of hydrolysis to $(RO)P(S)(ONa)H$; after this the alkali consumption becomes so slow that it is possible to actually titrate these esters to this endpoint. This is similar to behavior of $(RO)_2POH$. Acidification of these Na salts yields solns. of acidic monoalkyl thiophosphites which are stable for months. The mol. refractions of these esters $(RO)_2P(S)H$ agree very well with exptl.

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 results if the above structure is assumed with refractivity of P taken
 as 4.27 and that of S at 9.70. To 1.54 g. $(EtO)_2PSH$ in 3 ml. EtOH was
 added 2 ml. H_2O , followed by 0.4 g. NaOH and 3 ml. H_2O ; when the alkaline
 reaction disappeared the soln. was evapd. over P_2O_5 yielding colorless
 plates of $(EtO)P(S)H(OH)$. Similarly was obtained the Bu analog, scales.
 $(EtO)_2PSH$ failed to react with S after heating 5 hrs. at 100° . $(EtO)_2PSH$
 (11.6 g.) treated with 5.4 g. Cl_2 at -10° gave $(EtO)_2PSCl$, 45%, $b_{13} 81-2^\circ$,
 $n_D^{20} 1.4711$, $d_4^{20} 1.1918$. $(EtO)_2PSH$ yields the Na deriv. in suspension of
 Na in C_6H_6 and the product forms a crystn. ppt. This is best prepd. as
 follows: Na dust in C_6H_6 is converted to EtONa by addn. of EtOH and this
 is treated with calcd. amount of the ester; finally the Na deriv. can be
 prepd. in EtOH-EtONa soln. The product from 4.62 g. $(EtO)_2PSH$ and 0.69
 g. Na in 12 ml. C_6H_6 was mixed with 0.96 g. S; the reaction was very exo-
 thermic; after 1 hr. the mixture was filtered and the product was
 extd. with H_2O ; addn. of basic Pb acetate to the aq. soln. gave $[(EtO)_2PS_2]_2Pb$,
 $m. 75-6^\circ$. The Na deriv. from 25.1 g. $(EtO)_2PSH$ and 3.44 g. Na in C_6H_6 was
 treated with 22.8 g. EtI and the mixture allowed to stand 4 days; the ppt.
 of NaI was washed out with H_2O and distn. of the org. layer gave 50%
 $EtP(S)(OEt)_2$, $b_{13.5} 82-3.5^\circ$, $d_4^{20} 1.0332$, $n_D^{20} 1.4563$, which is hydrolyzable
 only with great difficulty. Similar reaction with EtCl gave 46.5% of
 the same ester, $b_{13.90} 80-3.5^\circ$, $n_D^{20} 1.4545$, $d_4^{20} 1.0324$. The ester (4 g.) heated
 in sealed tube with 2 vols. 1:1 HCl 3 hrs. at $145-55^\circ$ and evapd. to dryness
 gave $EtPO_2H_2$, $m. 57-8^\circ$. Heating $EtP(S)(OEt)_2$ (4 g.) with 1 vol. EtI to
 $140-50^\circ$ 3 hrs. in sealed tube gave much Et_3SI and 1.3 g. $EtP(O)(OEt)SEt$,
 $b_{476} 6.5^\circ$, $d_4^{20} 1.0709$, $n_D^{20} 1.4730$. To Na deriv. from 7.7 g. $(EtO)_2PSH$ and 1.5
 g. Na in C_6H_6 was added 6.62 g. $PhCH_2Cl$ and the mixture allowed to stand
 2 days, yielding after washing, 5.3 g. $PhCH_2P(S)(OEt)_2$, $b_{5.5} 124-5^\circ$, d_4^{20}
 1.1022 , $n_D^{20} 1.5303$. Similar reaction with $ClCH_2CO_2Et$ gave 72.2% EtO_2CCH_2-
 $P(S)(OEt)_2$, $b_{5105} 6^\circ$, $d_4^{20} 1.1204$, $n_D^{20} 1.4621$, which hydrolyzed with 1:1 HCl at
 130° 3 hrs. in sealed tube to $HO_2CCH_2PO(OH)_2$, $m. 138-9^\circ$. Addn. of equiv. amount
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 of aq. $AgNO_3$ and a little NH_4OH to EtOH soln. of $(EtO)_2PSH$ yields a

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colorless ppt. of the Ag salt, which darkens in light; it dissolves slowly in C_6H_6 forming a sol of Ag. The results are held to be the evidence for the structure of the Na deriv. as $(RO)_2PSNa$ with trivalent P. Their formation is ascribed to transfer of the reactive center during reaction of formation, yielding ions $(RO)_2PS^-$. Alkylation with RX appears to occur by attack of RX on unshared electron pair at P atom with elimination of Na which forms NaX, although it is possible that the anion $(RO)_2PS^-$ can also participate similarly.

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The dialkyl dithiophosphates obtained from ROH and either P_4S_7 or P_4S_{10} are completely identical. The products are titrated in aq. or alc. media as strong monobasic acids and are oxidized with I_2 in alkaline medium yielding the corresponding disulfides $(RO)_2P(S)SSP(S)(OR)_2$, which are solids, insol. in H_2O . To 24 g. MeOH was gradually added 33.3 g. P_4S_{10} , the mixture was warmed on a steam bath until H_2S evolution ceased and the filtered mixture was distd. yielding 73% $(MeO)_2PS_2H$, $b_4 56.2-3^\circ$, $n_D^{20} 1.5343$, $d_4^{20} 1.2888$, $\delta_{20} 38.87$; to neutralized soln. of 3.16 g. of this ester was added 1.29 g. $NiCl_2$ and the evapd. soln. gave 3.5 g. $[(MeO)_2PS_2]_2Ni$, lilac, m. 124-5° (from petr. ether). Reaction of 50.8 g. P_4S_{10} with 69 g. EtOH gave 3.2 g. solid residue and 76.5% $(EtO)_2PS_2H$, $b_5 81.5-2.5^\circ$, $n_D^{20} 1.5076$, $d_4^{20} 1.1654$, $\delta_{20} 31.7$; its Pb salt, m. 75-6°. Reaction of 11.1 g. P_4S_{10} with 12 g. PrOH gave 75% $(PrO)_2PS_2H$, $b_2 81.5-2.5^\circ$, $n_D^{20} 1.4986$. P_4S_{10} (5.6 g.) and 6 g. iso-PrOH gave 60% $(iso-PrO)_2PS_2H$, $b_3 71-2^\circ$, $n_D^{20} 1.4918$, $d_4^{20} 1.0911$. This (4.28 g.) neutralized to phenolphthalein with NaOH and treated with 3.79 g. $Pb(OAc)_2$ gave $[(iso-PrO)_2PS_2]_2Pb$, m. 130-1° (from EtOH). Reaction of 11.1 g. P_4S_{10} with 14.8 g. BuOH gave an undistillable product; this, neutralized with 10% NaOH and extd. with Et_2O , was treated with 12 g. $HgCl_2$ yielding an oily Hg salt, which extd. with Et_2O and evapd. gave the pure $[(BuO)_2PS_2]_2Hg$, m. 60-1° (from MeOH). To 4.8 g. $(MeO)_2PS_2H$ in equiv. amount of aq. NaOH was added aq. soln. of 3.8 g. I_2 in KI, yielding 74.3% $(MeO)_2P(S)SSP(S)(OMe)_2$, m. 51-2° (from hexane). The tetra-Et analog, $[(EtO)_2PS_2]_2$ (m. not given), the tetra-iso-Pr analog, 82.75%, m. 91-2° (from EtOH).