was obtained a quantitative yield of 3,5-diiodo-4-thiopyridone, m.p. 197–199°. Purification may be effected by dissolving in sodium carbonate or ammonia solution, filtering and reprecipitating with acid. The purified product melts at 204–205°.[6]

Thiobenzanilide.—Benzanilide (41 g., 0.071 mole) and phosphorus pentasulfide (17 g., 0.076 mole) were refluxed 40 minutes in 70 ml. of pyridine and poured into water. The resulting gum turned crystalline when made weakly alkaline with potassium hydroxide. The product can be crystallized from dilute methanol or purified by dissolving in alkali and precipitating with hydrochloric acid. There was obtained 11 g. (73%), m.p. 96–96.5°.[7] Methylation with dimethyl sulfate and alkali gave the S-methyl ether, m.p. 65.5–66°.[8]

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(7) Bernthsen, *Ber.*, **11**, 503 (1878).

(8) May, *J. Chem. Soc.*, **103**, 2272 (1913).

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Preparation of Some Mixed Dialkyl Phosphites

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There is a very considerable body of literature concerning the symmetric dialkyl phosphites, but not a single example of a mixed dialkyl phosphite, containing two unlike radicals, can be found.

In order to secure some information about such compounds, their preparation was examined. Although, theoretically, one may expect to obtain such compounds by the reaction of phosphorus trichloride with a mixture of alcohols, such a reaction yields complex mixtures which contain relatively small amounts of the mixed derivatives. Another possible method is exchange esterification with symmetric dialkyl phosphites. This method gives the desired mixed esters in moderate yields and can be made to proceed without difficulty at reflux conditions without added catalysts.

TABLE I

Ester	Ref.	R.I.	Density	*MR*obsd.	*MR*calcd. with: *AR* = 3.75	*AR* = 4.44
$(EtO)_2POH$	2	n^{20}_D 1.4080	d^{20}_0 1.0742	31.69	31.02	31.71
$(PrO)_2POH$	2	1.4172	1.0184	41.03	40.25	40.94
$(BuO)_2POH$	2	1.4240	0.9888	50.10	49.49	50.18
$(C_6H_{13}O)_2POH$	2	1.4325	0.9486	68.75	67.96	68.65
$(C_7H_{15}O)_2POH$	2	1.4382	0.9363	77.95	77.19	77.88
(EtO)(BuO)POH		n^{27}_D 1.4139	d^{27}_0 1.0120	40.98	40.25	40.94
(EtO)(AmO)POH		1.4189	0.9935	45.71	44.87	45.56

In the course of characterization of the products it was desirable to evaluate their molecular refractions. It was found that the values of *MR* that are found experimentally are significantly higher than the calculated values, when the reasonable assumption is made that the esters possess the "keto" structure, *i.e.*, $(RO)_2P(O)H$. This formulation calls for a value of atomic refraction of phosphorus that is probably close to the value suggested by Kabachnik[1] for the phosphates, *i.e.*, for phosphorus in the higher state of oxidation: $AR = 3.75$. The use of a value in the vicinity of the above is reasonable since the dialkyl phosphites do not display the chemical properties of trivalent phosphorus. The truly trivalent derivatives, such as $(RO)_3P$ and $ROPX_2$, give very good correlation of *MR* values when *AR* for phosphorus is taken as 7.04. Trials of the latter value in calculations involving the dialkyl phosphites leave no doubt that this value cannot be applied at all. This confirms the non-trivalence of phosphorus in these compounds. The use of the 3.75 value in calculations with the compounds described in this paper, along with a number of previously prepared symmetric esters, reveals a need for a new *AR* value for phosphorus for compounds having the structures of the type found in dialkyl phosphites. The table below gives the results of calculations using the "phosphate" *AR* of 3.75, and the newly proposed value of 4.44, derived on empirical basis from the calculations with Kabachnik's value. The magnitude of this constant appears to indicate that the phosphorus atom in these esters is much closer to the tetra-(or penta)-valent state of the phosphates, than it is to the trivalent state found in other phosphites in which the trivalency is clearly demonstrable.

Experimental

Ethyl Butyl Phosphite.—A mixture of 27.6 g. (0.2 mole) of diethyl phosphite and 14.8 g. (0.2 mole) of *n*-butanol was slowly heated in a distillation apparatus up to bath temperature of 150°, when a brisk reaction started and ethanol began to distil. The bath was kept at 150–155° for 55 minutes, at which time 5.8 ml. of ethanol was collected. Distillation of the mixture under reduced pressure gave 8 g. of unchanged diethyl phosphite, 16 g. of crude ethyl butyl phosphite, b.p. 103–105° at 13 mm., and 3 g. of crude dibutyl phosphite, b.p. 110–115° at 11 mm.; the residue showed signs of decomposition on attempts at further distillation. Redistillation of the middle cut gave pure ethyl butyl phosphite (15.0 g., 45%), b.p. 99–100° at 13 mm., n^{27}_D 1.4139, d^{27}_0 1.0120. Found: P, 18.6, 18.8. Calcd. for (EtO)(BuO)POH: P, 18.7. Treatment with warm water, acidified with hydrochloric acid, rapidly yielded phosphorous acid which was detected by the calomel test. This showed that no isomerization to a phosphonate took place during the reaction, thus confirming the above formula.

Ethyl *n*-Amyl Phosphite.—The procedure described above, using 27.6 g. of diethyl phosphite and 17.6 g. of *n*-amyl alcohol, gave 11.5 g. of unreacted diethyl phosphite and 12 g. of pure (after two distillations) ethyl *n*-amyl phosphite (33%), b.p. 109–110° at 13 mm., n^{27}_D 1.4189, d^{27}_0 0.9935. Found: P, 17.2, 17.25. Calcd. for (EtO)(AmO)POH: P, 17.25. Behavior on hydrolysis was as described above.

Reaction with *n*-Decanol.—When diethyl phosphite (27.6 g.) was heated as above with 31.6 g. of *n*-decanol, the reaction took place briskly at 150–155° bath temperature with distillation of ethanol. Attempted distillation of the mixture gave only 9 g. of unreacted diethyl phosphite, further distillation leading to considerable decomposition of the mixture even at 1 mm. Thus, the probably formed ethyl decyl phosphite could not be isolated.

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(1) Kabachnik, *Isvestiya Akad. Nauk S.S.S.R., otdel. khim. nauk*, 219 (1948); *C. A.*, **42**, 5736*g* (1948).

(2) Arbuzov and Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, **55**, 31 (1947); *Isvestiya Akad. Nauk S.S.S.R., otdel, khim. nauk*, 617 (1947); *C. A.*, **42**, 5844*h* (1948).