TABLE III
SYMMETRICAL BIS(DIMETHYLPHENYL) DISULFIDES

	M.P., °C	Found[a] C	Found[a] H	Found[a] S
Bis(2,3-dimethylphenyl)disulfide	99.0–99.5	69.86	6.46	23.4
2,4-	Oil	70.18	6.74	22.7
2,5-	46.5–48.0[b]	69.74	6.39	23.3
2,6-	102.5–104.0	70.05	6.66	23.6
3,4-	50–51	69.45	6.60	23.3
3,5-	Oil	69.80	6.84	23.1

[a] Calcd. for $C_{16}H_{18}S_2$: C, 70.02; H, 6.61; S, 23.37. [b] Bis(2,5-dimethylphenyl) disulfide is reported to melt at 46–47°.[5]

DISCUSSION

Although thiophenols are generally believed to show little intermolecular hydrogen bonding,[8] it is evident from an examination of the boiling points in Table I that this phenomenon must exist to a certain extent. The lowest-boiling compound, 2,6-thioxylenol, has a normal boiling point more than four degrees below that of any of the other isomers due to steric interference by the two ortho methyl groups with intermolecular bonding. This behavior is analogous to, although less pronounced than, that of 2,6-xylenol, which boils some 10 degrees below any of the other dimethylphenols.

Infrared spectra of the six thioxylenols were obtained and compared with the spectra of the same compounds in dilute cyclohexane solutions. No clear evidence for or against intermolecular hydrogen bonding could be secured by this method, due to the weak absorption of the SH bond.

Acknowledgment. The authors wish to thank Dr. F. V. Fair and Miss M. J. Alexander for the infrared spectra and assistance in interpreting them.

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[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, London, Methuen, 1954, p. 289.

[CONTRIBUTION FROM THE PENNSYLVANIA SALT MANUFACTURING CO.]

Some Unusual Water Solubility Properties of Alkyl Tetraalkylphosphorodiamidates

BERNARD LOEV AND JOHN T. MASSENGALE

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A number of alkyl tetraalkylphosphorodiamidates have been prepared; some of these have been found to possess unusual water solubility characteristics. A number of other miscellaneous types of phosphorus compounds are described.

During an investigation of the physical properties of a variety of classes of organic phosphorus compounds, the unusual inverse water solubility of the alkyl tetraalkylphosphorodiamidates, $ROP(O)(NR'_2)_2$, prompted us to further investigate these compounds.

Little has appeared concerning the preparation and properties of the phosphorodiamidates, where all substituents are aliphatic,[1] since Michaelis[2] first prepared four of these compounds in 1903.

The compounds of this type which we have prepared are listed in Table I. Except where otherwise indicated in the EXPERIMENTAL, yields were 85% or better.

Most of these compounds were prepared by reacting the appropriate alcohol with phosphoryl chloride to give the alkyl phosphorodichloridate, which was then reacted with excess amine. Under the experimental conditions used, there was never any indication of diester formation. When the amine was readily available, excess amine was used as the acid acceptor. When the amine was of limited availability, triethylamine or pyridine was used. The diamidates prepared from dimethylamine were obtained in higher yield when aqueous rather than anhydrous dimethylamine was used. With all other amines, however, aqueous solutions gave lower or negligible yields. Consequently, except for the preparation of the diamidates of dimethylamine all reactions were carried out under anhydrous conditions.

Compound XVI could not be prepared by this procedure. The reaction of phosphoryl chloride with 2-ethylmercaptoethanol gave only polymeric products, so an inverse synthesis was used for this compound. Phosphoryl chloride was treated with a large excess of diethylamine, and the phosphorodiamidic chloride which was isolated was then allowed to react with the sodium salt of 2-ethylmercaptoethanol to give the desired product.

All attempts to prepare derivatives of diisopropylamine were unsuccessful.

The intermediate acid chlorides were all fuming, lachrymatory liquids; the diamidates were all liquids. The low molecular weight diamidates had pepper-like odors; the higher molecular weight diamidates generally had camphor-like odors.

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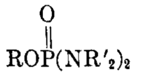
[1] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, New York, 1950.

[2] A. Michaelis, *Ann.*, **326**, 129 (1903).

TABLE 1

PROPERTIES OF ALKYL TETRAALKYLPHOSPHORODIAMIDATES



$\mathrm{RO}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{NR'_2})_2$

								Solubility in Water		
No.	R	R'	B.P., °C.	(mm.)	n^t_D	t., °C.	Carbon Atoms	Cold	Room Temp.	Hot
I	Methyl	Methyl	76–82	(10–15)	1.4359	27	5	+	+	+[a]
II	Methyl	Ethyl			1.4519	27	9	+	+	+[b]
III	Ethyl	Ethyl	79–80	(0.8)	1.4380	27	10	+	+	−[c]
IV	Ethyl	Butyl	150–5	(0.5)	1.4455	27	18	−	−	−[d]
V	Ethyl	n-Octyl	d.	(0.1)			34	−	−	−[e]
VI	Butyl	Methyl	123–5	(15)	1.4360	26	8	+	+	−[f]
VII	Butyl	Ethyl	111–13	(0.6)	1.4413	26	12	+	+	−[g]
VIII	Butyl	Butyl			1.4500	21	20	−	−	−[h]
IX	"Isooctyl"	Methyl			1.4440	26	12	+	+	−[i, j, k] [h]
X	*n*-Octyl	Methyl	178–80	(3.5)	1.4414	27	12	+	−	−[l]
XI	*n*-Octyl	Ethyl	168–75	(0.5)	1.4450	26	16	−	−	
XII	*n*-Octyl	Butyl			1.4524	27	24	−	−	−[h]
XIII	"Iso"-tridecyl	Methyl	148–55d.	(0.3)	1.4522	23	17	+5to15	−	−[k]
XIV	"Isotridecyl"	Butyl			1.4551	27	29	−	−	−[h,k]
XV	*n*-Octadecyl	Methyl	240–55	(0.3)	1.4500	26	22	−[n]	−[n]	−[n,m] [p]
XVI	2-Ethylmercapto ethyl	Ethyl			1.4720	27	12	−	−	−[h]

[a] Lit., b.p. 45–46° (1 mm.);[4] n_D^{20} 1.4385.[5] [b] Lit.[6] b.p. 94 (3 mm.). [c] Lit.[1] b.p. 140 (15 mm.); *anal.* calcd.: C 50.9; H 10.7. Found: C 50.9; H 10.6. [d] *Anal.* calcd.: C 62.0; H 11.9; Found: C 61.8; H 12.4. [e] *Anal.* calcd.: P 5.4. Found: P 6.6. [f] *Anal.* calcd.: C 46.2, H 10.2. Found: C 46.2, H 10.2. [g] *Anal.* calcd.: C 53.8, H 11.0, N 10.6, P 11.7; Found C 53.8, H 11.2, N 10.9, P 12.0. [h] Decomposes on attempted vacuum distillation. [i] Milky solution. [j] *Anal.* calcd.: C 54.4, H 11.0. Found: C 54.3, H 11.0. [k] These are made from synthetic mixed branched chain primary octyl or tridecyl alcohols obtained from Enjay Chemical Co. [l] *Anal.* calcd.: C 54.5, H 11.0; Found: C 54.5, H 11.0. [m] *Anal.* calcd.: C 65.3, H 12.2; Found: C 65.5, H 12.4. [n] Hydrate and emulsion, see discussion. [p] M.p. 18.5–20.5°.

The most interesting property of these compounds was their unusual water solubility characteristics. As can be seen by reference to Table I, these vary from being completely soluble (I and II), through materials soluble in cold water and insoluble in hot (III, VI, VII, IX) to materials that are water insoluble (others). The most unusual compound is XIII which is soluble in water over only a 3 degree range, between 5–15°, the exact 3 degrees within which it is water soluble depending on the relative proportion of water to XIII. When mixed with water at room temperature an emulsion occurs; on slow cooling, the solution suddenly becomes homogeneous and transparent; on further cooling, the solution suddenly turns milky again. Another interesting compound is XV which forms a waxy hydrate with water at room temperature and then gradually (more rapidly on warming) forms a milky emulsion.

The water solubility appears to be related to the number of carbon atoms present. An inspection of Table I shows that compounds having 8 or 9 to 12 atoms are soluble in cold but insoluble in warm water, and compounds having 12 or more atoms are insoluble. Branched chain compounds are more soluble than straight chain compounds. In compounds containing the same number of carbon atoms the one having the smaller number of carbons on the amine group is the more soluble.

The high molecular weight compounds are somewhat unstable, and on prolonged standing appear to polymerize, presumably to phosphorodiamidic anhydrides. This reaction is accelerated in many instances by heating, particularly in the presence of strong, concentrated acids, or amine salts. The low molecular weight compounds appear to be more stable.

Compound III was used for a more thorough investigation of certain physical properties. Hydrolysis experiments carried out on III showed it to be quite resistant to aqueous hydrolysis. III was recovered unchanged after an 8 hr. refluxing of a 12.5% aqueous solution. Solutions of 5% III in 0.1*N* H_2SO_4 and in 0.1*N* NaOH were refluxed 8 hr. III was recovered in 95% yield in each case.

Samples of III were heated at 100°, 150°, and 200°C. After 7 hr., the 100° sample was unchanged, the 150° material was yellow-brown in color and slightly acidic. The 200° material was dark brown and strongly basic. However, III was recovered in 93% yield on distillation. In both the 150° and 200° materials diethylamine could be detected above the samples.

III is only slightly volatile with steam. It is

TABLE II

PROPERTIES OF MISCELLANEOUS PHOSPHORUS COMPOUNDS

No.	Compound	B.P. °C.	B.P. Mm.	n^t_D	t_2°C.	
XVII	$2,4\text{-}Cl_2C_6H_3OCH_2CH_2OP(O)[N(C_2H_5)_2]_2$			1.5240	27	[a]
XVIII	$2\text{-}CH_3C_6H_4OP(O)[N(C_2H_5)_2]_2$	153–5	2	1.4990	26	[b]
XIX	$CH_3CH_2OP(O)[N(CH_3)C_6H_5]_2$			1.5545	27	[a]
XX	$(CH_3CH_2O)_2P(O)N(C_2H_5)_2$	113–14	18	1.4212	27	[c,d]
XXI	$C_6H_5P(O)[N(C_2H_5)]_2$			1.5215	24	[g]
XXII	$(C_6Cl_5O)_2P(O)N(C_4H_9)_2$					[e,f]
XXIII	$C_2H_5SCH_2CH_2OP(S)[N(C_2H_5)_2]_2$			1.5130	21	[g,a]
XXIV	$(C_2H_5SCH_2CH_2O)_3PO$			1.4968	28	[a]

[a] Decomposed on attempted vacuum distillation. [b] *Anal.* Calcd. C 60.5, H 10.9; Found: C 59.9, H 9.1. [c] Lit.[1] b.p. 114–17 (25 mm.). [d] Soluble in cold water, insoluble in hot. [e] *Anal.* Calcd.: C 34.0, H 2.5, Cl 50.4; Found: C 35.3, H 2.5, Cl 49.7. [f] M.p. 144–5° C. [g] *Anal.* Calcd.: C 46.1, H 9.3; Found: C 44.7, H 9.0.

miscible with most organic solvents and readily dissolves such diverse materials as sugar, succinic acid, and Tygon, and attacks butadiene polymers. It readily extracts succinic acid from an aqueous solution. It is miscible with glycerine at room temperature, but separates into two phases on warming.

Most of the phosphorodiamidates are soluble in dilute hydrochloric acid; all are insoluble in dilute nitric acid and sodium hydroxide. Acetylene has an appreciable solubility in III only.

A variety of miscellaneous compounds were synthesized for comparison with these alkyl phosphorodiamidates. These compounds are: 2,4-dichlorophenoxyethyl tetraethylphosphorodiamidate (XVII), 2-methylphenyl tetraethylphosphorodiamidate (XVIII), ethyl *N*,*N'*-dimethyl-*N*,*N'*-diphenylphosphorodiamidate (XIX), diethyl diethylphosphoroamidate (XX), tetraethyl benzenephosphonic diamide (XXI), bis(pentachlorophenyl) dibutylphosphoroamidate (XXII), 2-ethylmercaptoethyl tetraethylphosphorodiamidothionate (XXIII), and 2-ethylmercaptoethyl phosphate (XXIV). The physical properties of these compounds are listed in Table II.

In the preparation of XVIII the conversion of *o*-cresol to the phosphorodichloridate was improved by the addition of a small amount of magnesium chloride[3] to the reaction mixture.

XXIII is the thiono analog of XVI, prepared by using thiophosphoryl chloride in place of phosphoryl chloride.

Attempts to prepare pentachlorophenyl phosphorodichloridate by reaction of phosphoryl chloride with pentachlorophenol or its sodium salt led to the diester as the major product, even when a large excess of phosphoryl chloride was used. The bispentachlorophenyl ester was converted to the amide, XXII.

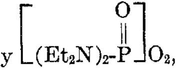
XX, which is the reverse of III in having two ester groups and one amide group, was the only compound in Table II showing water solubility. It exhibited the same inverse solubility as did III, although it is more water soluble than III.

The reaction of ethyl phosphorodichloridate with *p*-phenylenediamine gave an insoluble, high melting polymer.

EXPERIMENTAL

Alkyl phosphorodichloridates. One mole of the appropriate anhydrous alcohol was added dropwise to phosphoryl chloride, the temperature being maintained below 20°. On completion of the addition, the cooling bath was removed and the solution was stirred at room temperature for 2 hr. Then the solution was placed under 100 mm. vacuum and warmed to 60° to remove unreacted phosphoryl chloride and dissolved HCl. In two instances the product was distilled; in the others, the crude phosphorodichloridate was used. In every instance the product, $ROP(O)Cl_2$, was obtained in 85–100% yield. When R = ethyl, b.p. 67–68° (18 mm.), n^{28}_D 1.4300; (lit.[7] b.p.$_{19}$ 63°); R = butyl, b.p. 80–82° (10 mm.), n^{28}_D 1.4372 (lit.[8] b.p.$_{13}$ 85°, n^{31}_D 1.4453).

Preparation of alkyl tetraalkylphosphorodiamidates by reaction of amine with alkyl phosphorodichloridates. A solution of one mole of the alkyl phosphorodichloridates in ether was gradually added to a cold ethereal solution containing 4–5 moles dialkylamine. When the dialkylamine was available in only limited quantities, the reaction was carried out using 1 mole of dialkylamine and 3–4 moles of pyridine or triethylamine. The mixture, which was viscous with precipitated amine hydrochloride, was stirred overnight and filtered. The solvent and excess amine were distilled off. When the phosphorodiamidate was thermally stable, it was distilled, usually as a colorless or pale yellow oil. Those compounds which could not be distilled were freed of solvent and amine by heating in vacuum.

During one distillation of III, decomposition occurred and a pale yellow, moderately viscous liquid distilled, b.p. 150–160° (2 mm.), n^{27}_D 1.4625 (possibly  $\left[(Et_2N)_2\text{-}\overset{\overset{\displaystyle O}{\|}}{P}\right]O_2$, lit.[9] b.p.$_{<1mm}$ 95–110°, n^{25}_D 1.4668).

Preparation of tetramethylphosphorodiamidates by reaction with aqueous dimethylamine. One mole of alkyl phosphorodichloridate was added dropwise with stirring to 5 moles of

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(3) S. L. Bass, U. S. Patent 2,117,283 (1938).

(4) J. D. Dickey, T. E. Stanin, H. W. Coover, U. S. Patent 2,487,859 (1948); *Chem. Abstr.*, 44, 2456 (1950).

(5) H. Tolkmith, U. S. Patent 2,654,783 (1953); *Chem. Abstr.*, 48, 10051 (1954).

(6) W. A. L. David and B. A. Kilby, *Nature*, 164, 522 (1949).

(7) B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

(8) W. Gerrard, *J. Chem. Soc.*, 1464 (1940).

(9) A. D. F. Toy and J. R. Costello, U. S. Patent 2,717,249 (1955).

chilled 40% aqueous dimethylamine. After the addition was complete the solution was heated until the excess dimethylamine had been distilled off. The oily product was separated hot, dried, and when the product was thermally stable, distilled.

Preparation of alkyl tetraethylphosphorodiamidate by reaction of the phosphorodiamidic chloride with the sodium alcoholate. A solution of 4 moles diethylamine in chloroform was slowly added to a solution of one mole of phosphoryl chloride (or thiophosphoryl chloride) in dry chloroform at 0°. The solution was stirred 2 hr. at room temperature and then heated to distill out most of the chloroform. A large volume of petroleum ether was then added and the precipitated amine salt was filtered. The solvent was then removed and the phosphorodiamidic chloride was distilled.

The sodium alcoholate was prepared by reaction of sodium sand with the alcohol in toluene. To the dispersion of the sodium alcoholate in toluene was slowly added the phosphorodiamidic chloride. The mixture was warmed for several hours, then filtered. The organic layer was washed with water, dried, and distilled. Thermally unstable compounds were treated with a decolorizing carbon, and last traces of solvent were removed by mild heating in vacuum.

o-Cresyl tetraethylphosphorodiamidate (XVIII). *o*-Cresol (1.5 moles) was added to 3.25 moles phosphoryl chloride containing 1 g. anhydrous magnesium chloride and maintained at 90°, and then refluxed overnight. The excess chloride was distilled off and the *o*-cresyl phosphorodichloridate distilled, b.p. 110° (7 mm.), n_D^{30} 1.5170–80 (51% conversion). When the magnesium chloride was not present, the conversion dropped to 33%.

The reaction with diethylamine was carried out in a manner similar to that already described.

Bis(pentachlorophenyl) dibutylphosphoroamidate (XXII). One hundred grams (0.376 mole) pentachlorophenol in warm chlorobenzene was added to 111 g. (0.724 mole) $POCl_3$ at 70°. Refluxing for 2 hr. gave only a small quantity of evolved HCl, so the solution was cooled to 100° and 29.7 g. (0.376 mole) pyridine was added, causing formation of a heavy precipitate of amine hydrochloride. The mixture was stirred at 100° for 1 hr., cooled, and filtered. The filtrate was concentrated *in vacuo* leaving 130 g. of a brown oil which soon crystallized. This bis(pentachlorophenyl)phosphorochloridate was taken up in toluene and added to 185 g. cold dibutylamine. The solution was refluxed 3 days and cooled, and the amine salt was filtered. Volatile materials were removed in vacuum leaving a semi-crystalline brown oil which was treated with ligroin and filtered. The precipitate was recrystallized from benzene, 33 g., m.p. 144–145°, white solid, soluble in most organic solvents.

Tetraethyl benzenephosphonic diamide (XXI). Benzenephosphonic dichloride (Victor Chemical Co.) was treated with diethylamine in the same manner that was employed with the amides already described.

Diethyl diethylphosphoroamidate (XX). Diethylphosphorochloridate (Victor Chemical Co.) was reacted with 2 moles diethylamine in the manner previously described.

Polymeric material from ethyl phosphorodichloridate and p-phenylenediamine. Four grams of *p*-phenylenediamine (Eastman Technical, purple crystals) were dissolved in a solution of chloroform containing 20 cc. pyridine. Ethyl phosphorodichloridate (6.1 g.) was slowly added. The reaction was quite exothermic. No attempt was made to prevent contact with air. The thick purple precipitate was filtered and washed with petroleum ether, dried, triturated with water, then with acetone, and then dried in vacuum at 110°. The resulting hard solid was powdered, giving beautiful purple crystals (under microscope), insoluble in acetone, dimethyl formamide, and other organic solvents. On heating it turns white at 190°, starts melting at 235°, and chars at 320°. It is readily decomposed by acids and bases.

Anal. Calcd. for $C_8H_{11}N_2O_2P$: C, 48.5, H, 5.6, N, 14.1. Found, C, 45.4, H, 5.2, N, 12.5. Mol. wt. 1250 (approx.) determined cryoscopically in acetic acid.

Solubility of acetylene in various phosphoramidates. A weighed amount of phosphoramidates was saturated with acetylene and the gain in weight was determined. III absorbed 8% of its own weight, IV and XIII absorbed nothing. By comparison hexamethylphosphoramide absorbed 14% of its weight.

PHILADELPHIA 18, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. XII. Ketone Cleavage of Acetoacetic Esters by Pyrolysis[1,2]

WILLIAM J. BAILEY AND JOHN J. DALY, JR.[3]

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The pyrolysis of acetoacetic esters is shown to be an excellent procedure for the ketone cleavage. For example, in the pyrolysis of ethyl α-isopropylacetoacetate at 525° the ester portion decomposes to give ethylene and the resulting acetoacetic acid almost simultaneously loses carbon dioxide to give an 82% yield of methyl isobutyl ketone, more than double the yield obtained by conventional basic hydrolysis. In many cases the saving of time and material as well as adaptability to large quantities recommend the pyrolysis of acetoacetic ester rather than hydrolysis. The ketone cleavage by pyrolysis is particularly advantageous if the acetoacetic ester contains a branched group or if the resulting ketone has a moderately high solubility in water.

Previous work[1,4–6] in this laboratory has shown that the pyrolysis of esters is an excellent method for the preparation of strained or sensitive olefins provided that charring is eliminated. Since the products from the pyrolysis of an ester are an olefin and an acid, it seemed logical that this reaction would be useful also in the synthesis of acids and

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(1) Previous paper in this series, *J. Org. Chem.*, 22, 1076 (1957).

(2) Presented in part before the Division of Organic Chemistry at the 126th National Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y., September 1954.

(3) Office of Naval Research Fellow, 1950–52; Union Carbide Fellow, 1952–53; Du Pont Fellow, 1953–54.

(4) W. J. Bailey and W. A. Klein, *J. Am. Chem. Soc.*, **79**, 3124 (1957).

(5) W. J. Bailey and J. Economy, *J. Am. Chem. Soc.*, **77**, 1133 (1955).

(6) W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).