The m.p. of either product fell about 10° when the sample was allowed to stand in a tightly stoppered vial in the refrigerator. Repeated recrystallization from ethanol or methanol caused rearrangement to the ketone (VI).

Rearrangement of VII.—When 0.500 g. (0.00175 mole) of *trans*-V was brominated in methanol containing 0.30 g. of suspended sodium bicarbonate at −35° and then to the cold solution was added 3.00 g. of freshly prepared silver oxide, an oil was obtained which crystallized from petroleum ether to give 0.42 g. (69%) of **p-methoxybenzhydryl phenyl ketone dimethyl ketal** (VIII), which on further recrystallization from ethanol melted at 77.4–78°.

Anal. Calcd. for $C_{23}H_{24}O_3$: C, 79.3; H, 6.9. Found: C, 79.5; H, 7.0.

When the same conditions were used for *cis*-V, a 66% yield of VIII was obtained as shown by m.p. and mixed m.p.

The structure of VIII was established by its hydrolysis with 2 drops of 10% hydrochloric acid in 5 cc. of 95% ethanol to VI in 70% yield. It also gave VI after standing at room temperature for one month.

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Some Observations on Phosphinic Anhydrides

BY GENNADY M. KOSOLAPOFF

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Some time ago we reported the synthesis of several dialkylphosphinic anhydrides from alkyl dialkylphosphinates and dialkylphosphinyl chlorides, as[1]

$$R_2P(O)Cl + EtOP(O)R_2 \longrightarrow EtCl + R_2P(O)OP(O)R_2$$

At that time we also reported that the reaction of dimethylphosphinyl chloride with ethyl di-*n*-butylphosphinate gave not the expected mixed anhydride but a mixture of the two symmetric anhydrides.

In order to explore the possibly general nature of this observation we attempted the preparation of several mixed phosphinic anhydrides by this reaction. Equimolar mixtures of chlorides and ethyl esters of dimethyl-, diethyl-, di-*n*-propyl- and di-*n*-butylphosphinic acids were heated as described previously[1]; substantially the theoretical amounts of ethyl chloride were obtained from all possible combinations of the above-mentioned compounds at 140–150°. In all instances, however, the distillation of the reaction mixtures, at 0.05–0.1 mm. pressure, gave only the corresponding pairs of the symmetric phosphinic anhydrides, which were characterized by comparison with the known specimens. The work was done in standard Pyrex apparatus. It is conceivable that the transformation of the expected unsymmetrical substances might have been catalyzed by the glass composition and might have been avoided by the use of fused quartz apparatus. However, it appears that the existence of unsymmetric phosphinic anhydrides at moderately elevated temperatures is purely transient. This points out a similarity of behavior to that of mixed carboxylic anhydrides and acetals, which tend to symmetrize during thermal treatment.

After this work was completed there appeared the paper of Todd and co-workers[2] which reports the preparation of unsymmetrical tetraesters of pyrophosphoric acid. Although the unheated crude reaction mixtures indicate the presence of such unsymmetrical esters, the latter could not be isolated by distillation owing to symmetrization similar to the one reported here.

Phosphinic anhydrides are unique among the known anhydrides of various organic acids of phosphorus, in that they have definite boiling points and, therefore, they can be positively identified and purified by conventional techniques of organic chemistry. Tetraesters of pyrophosphoric acid, probably the most studied anhydrides at this time, on the other hand are prone to decomposition and rearrangement reactions at elevated temperatures which make impossible a true fractional distillation of such compounds. These esters are commonly purified by distillation in molecular stills in which boiling points, in the true sense of the word, have very little significance. Identification of individuals in a mixture of closely related substances under such circumstances becomes dubious.

As a result of our work and that reported by Todd, *et al.*,[2] it appears quite possible that at this time no positively characterized unsymmetrical neutral derivatives of phosphorus acid anhydrides are known. While such compounds have been undoubtedly obtained in low temperature reactions, no methods of isolation at low temperatures have been developed and all distillation techniques, used thus far, require thermal treatment which causes the symmetrization discussed above.[3]

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[1] G. M. Kosolapoff and R. M. Watson, THIS JOURNAL, **73**, 4101 5466 (1951).

[2] N. S. Corby, G. W. Kenner and A. R. Todd, *J. Chem. Soc.*, 1234 (1952).

[3] The material was presented at the 121st National Meeting of the A.C.S., March, 1952.

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Some Salts of Symmetric Phosphinic Acids

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Many phosphinic acids, *i.e.*, compounds of the general type $R_2P(O)OH$, are known at this time. Qualitative descriptions of a number of metallic salts of a few such acids appear in the literature. However, the only quantitative report dealing with solubility of such salts appears to be that dealing with the copper and lead salts of di-pseudocumylphosphinic acid.[1]

Information about the solubilities of various salts of these acids is of obvious interest for the development of techniques of separation of mixtures of the acids themselves and of mixtures with other substances. We prepared, accordingly, several salts of four phosphinic acids. Two of the latter were aliphatic and two were aromatic, thus encompassing the relatively water-soluble and insoluble acids. Solubilities in water, benzene and 96% ethanol were determined at three temperatures (25, 35 and 45°) by conventional technique.

It is of interest to note the relatively high solu-

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[1] A. Michaelis, *Ann.*, **294**, 1 (1896).

TABLE I

Salt	Procedure	Form and m.p.	Metal, % Calcd.	Metal, % Found
$(Ph_2PO_2)_2Cu$	A	Blue needles	12.77	12.78
$(Bu_2PO_2)_2Cu$	A	Green needles	15.20	15.3
$[(C_{10}H_{21})_2PO_2]_2Cu$	A	Blue needles, m.p. 94°	8.42	8.5
$(Ph_2PO_2)_2Ba$	B	Needles	22.3 for $2.5H_2O$	22.26
$(Bu_2PO_2)_2Ba$	B	Needles	27.93	27.85
$[(p\text{-}ClC_6H_4)_2PO_2]_2Ba$	B	Needles	19.35	19.41
$[(C_{10}H_{21})_2PO_2]_2Ba$	B	Needles, m.p. under 100°	16.58	15.8
$(Ph_2PO_2)_2Mg$	B	Needles	5.3	5.4
$(Bu_2PO_2)_2Mg$	B	Needles	6.42	6.55
$[(C_{10}H_{21})_2PO_2]_2Mg$	C	Needles, m.p. 82–83°	3.4	3.1
$[(p\text{-}ClC_6H_4)_2PO_2]_2Mg$	B	Needles	4.07	4.3
$(Ph_2PO_2)_2Ca$	B	Needles	8.4	8.0
$(Bu_2PO_2)_2Ca$	B	Needles	10.16	10.3
$[(C_{10}H_{21})_2PO_2]_2Ca$	B	Waxy needles	5.47	5.53
$[(p\text{-}ClC_6H_4)_2PO_2]_2Ca$	B	Needles	6.54	6.50
$(Bu_2PO_2)_2Pb$	D	Needles	36.89	36.75
$[(p\text{-}ClC_6H_4)_3PO_2]_2Pb$	D	Needles	26.58	26.58
$[(C_{10}H_{21})_2PO_2]_2Pb$	D	Needles	23.07	22.92
$(Ph_2PO_2)_2Pb$	D	Needles	32.2	42.7[a]
$(Ph_2PO_2)_2Pb$	A	Powder	32.2	34.15

[a] The product obtained was substantially the basic salt. Procedure A gave a product that had an admixture of the basic salt, which could not be removed by repeated crystallization.

TABLE II

SOLUBILITY OF THE SALTS, IN GRAMS PER 100 ML. OF SOLUTION

Salt	Water 25°	Water 35°	Water 45°	96% Ethanol 25°	96% Ethanol 35°	96% Ethanol 45°	Benzene 25°	Benzene 35°	Benzene 45°
$(Bu_2PO_2)_2Pb$	0.0654	0.066	0.0662	0.452	0.542	0.588	0.032	0.030	0.158
$[(ClC_6H_4)_2PO_2]_2Pb$	.0076	.0178	.0216	.068	.084	.112	.094	.092	.090
$[(C_{10}H_{21})_2PO_2]_2Pb$	.0008	.0012	.0016	.036	.042	.056	.034	.052	.572
$(Ph_2PO_2)_2Cu$	.0400	.0424	.0430	.006	.020	.000	.000	.000	.000
$(Bu_2PO_2)_2Cu$	.0172	.0186	.0220	.246	.250	.324	.080	.248	.816
$[(C_{10}H_{21})_2PO_2]_2Cu$	.0034	.0038	.0039	.026	.060	.108	.110	2.758	25.418
$(Ph_2PO_2)_2Ba$	.112	.111	.110	.112	.114	.152	.138	.198	0.240
$(Bu_2PO_2)_2Ba$	Over 188	Not detd.		13.38	14.05	21.24	.000	.000	.000
$[(ClC_6H_4)_3PO_2]_2Ba$	1.128	1.056	1.018	0.430	0.538	0.916	.018	.022	.024
$[(C_{10}H_{21})_1PO_2]_2Ba$	0.0036	0.0016	0.001	.326	.327	0.334	.000	4.208	4.366
$(Ph_2PO_2)_2Mg$	3.554	3.350	2.616	.290	.288	....	.000	0.000	0.000
$(Bu_2PO_2)_2Mg$	6.570	4.714	3.168	.178	.266	0.728	.168	2.438	Gel.
$[(ClC_6H_4)_2PO_2]_2Mg$	0.382	0.342	0.302	.400	.286	.196	.006	0.002	Gel.
$[(C_{10}H_{21})_2PO_2]_2Mg$	.0012	.0010	.0008	.030	.048	.076	.144	.200	15.774
$(Ph_2PO_2)_2Ca$	.704	.698	.694	1.224	1.196	1.199	.000	.004	0.004
$(Bu_2PO_2)_2Ca$	4.636	4.362	4.318	0.314	0.418	0.712	.002	.002	.002
$[(ClC_7H_4)_2PO_2]_2Ca$	0.114	0.114	0.114	.636	.760	2.970	.118	.180	.334
$[(C_{10}H_{21})_1PO_2]_2Ca$	0.0029	0.0036	0.0036	.024	.038	0.062	.028	.066	080

bilities in water of the magnesium, barium and calcium salts of dibutylphosphinic acid and of the magnesium salt of diphenylphosphinic acid. The high solubility of barium dibutylphosphinate in 96% ethanol, and that of copper di-*n*-decylphosphinate, barium di-*n*-decylphosphinate, magnesium di-*n*-butyl- and di-*n*-decylphosphinates in warm benzene should be noted. The tendency of the salts of barium, calcium and magnesium to have higher solubility in cold water than in hot water is also of interest. The inverse solubility–temperature relation is also seen in alcoholic solutions of magnesium and calcium diphenylphosphinates and magnesium bis-*p*-chlorophenylphosphinate.

Experimental Part

Preparation of the Salts.—The following typical procedures were used.

Procedure A.—Five grams of diphenylphosphinic acid, suspended in 50 ml. of water, was neutralized with *N* sodium hydroxide (phenolphthalein indicator). The filtered solution was treated with a slight excess (0.012 mole) of *M* cupric chloride. The product, in the form of light-blue tiny needles, was washed with water and ethanol, and dried in air.

The procedure failed with the bis-*p*-chlorophenylphosphinic acid. The product consisted of two components neither of which had the properties of the desired salt. The free acid could not be regenerated from it by treatment with mineral acids, indicating a formation of a complex at the halogen atom.

Procedure B.—Five grams of diphenylphosphinic acid, suspended in 50 ml. of water, was neutralized directly with *M* barium hydroxide. The filtered solution was evaporated to dryness and the residue was crystallized from 96% ethanol. The air-dried product contains 2.5 molecules of water which are lost by heating in vacuum at 120°; the anhydrous product is extremely hygroscopic.

Procedure C.—An intimate mixture of 5 g. of di-*n*-decylphosphinic acid (m.p. 87–88°) with 1.5 g. of magnesium acetate tetrahydrate was heated under an infrared lamp until all odor of the eliminated acetic acid was removed. The product was washed with hot water, followed by ethanol. It forms tiny needles, m.p. 82–83°.

Procedure D.—A mixture of five grams of di-*n*-butylphosphinic acid and 3.4 g. of lead oxide was refluxed in 200 ml. of xylene with collection of the evolved water in a Starke–Dean moisture trap. The reaction was complete in 30 minutes. The hot solution was filtered rapidly and cooled. The product precipitated in the form of felted needles which were recrystallized from water. The product was anhydrous after air-drying.

This procedure when used with diphenylphosphinic acid gave a product that was largely the basic salt, containing 42.74% of lead.

The procedures used in the preparation and the properties of the products are listed in Table I.

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Rates of Hydrolysis of Fructose-6-phosphoric Acid[1]

BY S. L. FRIESS

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In studies concerned with the acid-catalyzed cleavage of a terminal phosphate group from the

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[1] Presented in part before the Second International Congress of Biochemistry, Paris, France, July 21–27, 1952.