Surface-Active Phosphine Oxides

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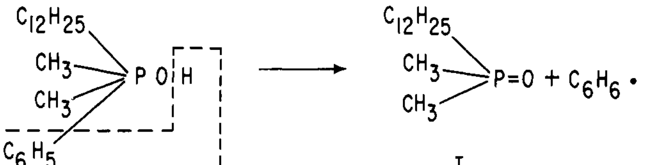
A convenient laboratory procedure is described for the preparation of tertiary phosphine oxides containing one long chain and two short chains, or one long chain and an alicyclic ring. A tertiary phosphine containing a phenyl group is quaternized with a long-chain alkyl halide. The resulting quaternary phosphonium bromide, dissolved in water, is warmed with aqueous alkali to yield the tertiary phosphine oxide.

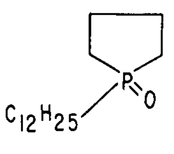
AN ALIPHATIC PHOSPHINE oxide with one long chain and two short chains—e.g., dimethyldodecylphosphine oxide, $C_{12}H_{25}(CH_3)_2PO$—possesses rather unusual surface-active properties which are missing in the short-chain tertiary phosphine oxides or in the long-chain symmetrical compounds, like tridodecylphosphine oxide, $(C_{12}H_{25})_3PO$. Thus, dimethyldodecylphosphine oxide is an outstanding detergent, foam stabilizer, and lime-soap dispersant. A simplified synthesis of unsymmetrical trialkyl phosphine oxides from diethyl phosphite has been reported (*1, 4, 7, 12, 13*), but this method is not satisfactory for compounds with one long chain and two short chains. Unsymmetrical aliphatic phosphine oxides have been synthesized from diphenyl alkylphosphonates and Grignard reagents (*8*).

A more convenient laboratory procedure for the preparation of dimethyldodecylphosphine oxide is described here, based on the work of Meisenheimer (*9*). It consists in quaternizing dimethylphenylphosphine with dodecyl bromide, and treating the aqueous solution of the dimethyldodecylphenylphosphonium bromide with aqueous alkali. The resulting intermediate quaternary phosphonium hydroxide decomposes to give benzene and dimethyldodecylphosphine oxide.



I

This method has also been used to prepare dodecyltetramethylenephosphine oxide, II, from phenyltetramethylenephosphine, and dodecylpentamethylenephosphine oxide, III, from phenylpentamethylenephosphine.



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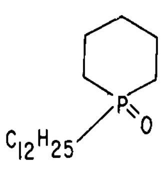

III

EXPERIMENTAL

Dimethyldodecylphosphine Oxide. For the preparation of the dimethylphenylphosphine (*5, 10, 11*), a Grignard was formed from 24 grams of magnesium suspended in 50 ml. of dry ether, and 135 grams of methyl iodide dissolved in 150 ml. of dry ether. The apparatus consisted of a 1-liter three-necked flask, provided with a mercury-sealed stirrer, Dry Ice condenser, and dropping funnel. The reaction was conducted in an atmosphere of nitrogen. After all the methyl iodide solution had been added, the mixture was refluxed for half an hour. The flask was cooled, and a solutuon of 60 grams of dichlorphenylphosphine in 100 ml. of ether was added dropwise, with cooling and stirring, over a period of one hour. The mixture was then refluxed for an hour. The complex was decomposed by the addition of 150 ml. of a saturated ammonium chloride solution. The ether was decanted, and the solid was extracted with 200 ml. of ether. The combined ether portions were dried overnight with anhydrous sodium sulfate. The solvent was removed (nitrogen atmosphere). On distilling the residue (in the presence of nitrogen), most of it passed over at 82° C./15 mm. The yield of dimethylphenylphosphine was 23.5 grams.

A mixture of 23.5 grams of dimethylphenylphosphine and 42.1 grams of dodecyl bromide was heated in an atmosphere of nitrogen at 100°-10° C. for one hour (oil bath). The solid product (*6*) was dissolved in 400 ml. of distilled water and treated with a warm solution (50° C.) of 60 grams of sodium hydroxide in 100 ml. of water. An oil separated out at once. The mixture was heated on the steam bath with vigorous stirring for 15 minutes. The oil was extracted with 500 ml. of ether, and the ethereal solution was washed with 50 ml. of water and then dried with anhydrous sodium sulfate. After removal of the ether, the solid residue (39.0 grams) was recrystallezed from 400 ml. of *n*-hexane. The yield of dimethyldodecylphosphine oxide was 34.3 grams (82%), m.p. 85° C.

Anal. Calcd. for $C_{14}H_{31}OP$ (246.4): C, 68.24; H, 12.68; P, 12.57; O, 6.50. Found: C, 68.3; H, 12.40; P, 12.3; O (direct), 6.81.

Dodecyltetramethylenephosphine Oxide. Phenyltetramethylenephosphine was prepared from 1,4-dibromobutane, magnesium, and dichlorophenylphosphine, using the procedure described above for the dimethylphenylphosphine. The reaction product was decomposed with ammonium chloride solution and not distilled, as directed in the literature (*2*). From 8 grams of magnesium, 36 grams of 1,4-dibromobutane, and 20 grams of dichlorophenylphosphine, there were obtained 3.4 grams of phenyltetramethylenephosphine, b.p. 125° C./13 mm. (oil bath temp., 210° C.).

For the preparation of the quaternary compound, a mixture of 3.4 grams of phenyltetramethylenephosphine and 5.2 grams of dodecyl bromide was heated for 2 hours at 100°-20° C. The solid dodecylphenyltetramethylenephosphonium bromide was washed with ether; it melted at 60° C.

Four grams of the phosphonium bromide were dissolved in 40 ml. of distilled water, and treated with 40 ml. of a 10% aqueous sodium hydroxide solution. The mixture was heated on the steam bath for 30 minutes, with vigorous stirring. It was then cooled, and the oil extracted with 200 ml. of ether. The extract was dried over anhydrous sodium sulfate. After removal of the ether, the residue weighed 2.3 grams. It was recrystallized from 25 ml. of

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n-hexane. The yield of purified dodecyltetramethylenephosphine oxide was 1.0 gram, m.p. 62° C.

Anal. Calcd. for $C_{16}H_{33}OP$ (272.4): C, 70.50; H, 12.21; P, 11.37%. Found: C, 70.77; H, 11.98; P, 11.40%.

Dodecylpentamethylenephosphine Oxide. The starting product, pentamethylenephenylphosphine, is known (*3*). Here, again, the reaction product was not distilled, but decomposed with ammonium chloride solution. From 8 grams of magnesium, 38 grams of 1,5-dibromopentane, and 20 grams of dichlorophenylphosphine, the yield of pentamethylenephenylphosphine was 5.24 grams, b.p. 140° C./13 mm. (oil bath temp., 240° C.).

To 5.24 grams of the cyclic phosphine there were added 7.32 grams of dodecyl bromide, and the homogeneous mixture was heated for 3 hours at 100°-10° C., in an atmosphere of nitrogen. The product (which could not be brought to crystallization) was dissolved in 70 ml. of distilled water and treated with a solution of 27 grams of sodium hydroxide in 70 ml. of water. The mixture was heated for one hour at 90° C., with rapid stirring. The oil was extracted with 200 ml. of ether, and the extract washed with 20 ml. of water and dried over anhydrous sodium sulfate. The yield of crude dodecylpentamethylenephosphine oxide amounted to 7.0 grams. This was recrystallized from 100 ml. of n-hexane, giving 4.5 grams of pure phosphine oxide, m.p. 78° C.

Anal. Calcd. for $C_{17}H_{35}OP$ (286.4): C, 71.28; H, 12.32; P, 10.81. Found: C, 71.54; H, 12.26; P, 10.57.

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Synthesis of Some Chloro- and Iodoacetanilides

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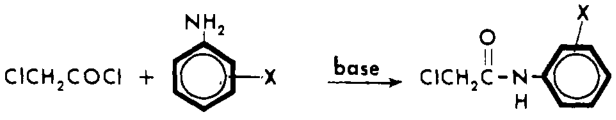
Sixteen acetanilides were prepared and characterized. These included principally chloro- and iodoacetanilides having halogen or alkoxy substituents on the aromatic ring.

A WELL known method to characterize carboxylic acids (*1*) is the preparation of anilides, haloanilides, or toluides by reaction of the acid halide with the corresponding aromatic amine. The derivatives obtained are usually solids which are easily purified and serve as a quick and accurate identification of the carboxylic acid. Recently, the authors prepared in their laboratory several chloro- and iodoacetanilides in which the aromatic ring was substituted with chlorine, bromine, or iodine or with methoxyl or ethoxyl groups. In addition, they prepared 2′-chloro-5′-trifluoromethyl-2-(2,4-dichlorophenoxy)acetanilide, p-chloroacetoxy-2-chloroacetanilide, and p-iodoacetoxy-2-iodoacetanilide. The chloroacetanilides were prepared from the corresponding aniline derivative and chloro- or dichloroacetyl chloride. The iodo analogs were then prepared from these materials by reaction with potassium or sodium iodide in acetone.



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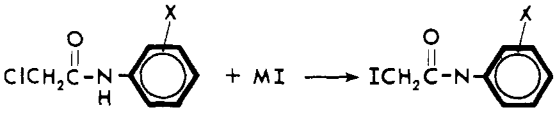

(2)

where X is Cl, Br, I, OMe, OEt, and M is Na or K

All compounds exhibited characteristic NH stretching vibrations at 2.99 to 3.11 microns (unbonded) and in some cases bonded NH stretching at 2.95 microns. Aliphatic C—H stretch occurred at 3.30 to 3.56 microns with a few as low as 3.21 microns while aromatic C—H stretch was seen at 3.20 to 3.25 microns with a few as high as

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