

## The Oxidation of Organo-phosphines by Aqueous Alkali

By S. M. BLOOM, S. A. BUCKLER, R. F. LAMBERT,\* and E. V. MERRY

(Polaroid Corporation Research Laboratories, Cambridge, Massachusetts 02139)

**Summary** The anaerobic oxidation of several water-soluble t-alkylphosphines by aqueous alkali results in the stoichiometric evolution of hydrogen gas and the formation of the corresponding phosphine oxides.

WHEN aqueous alkaline solutions 0.1 N in tertiary phosphine of compounds (1)–(7)† were heated under reflux in 2N-sodium hydroxide, a stoichiometric quantity of hydrogen gas was collected by water displacement in *ca.* 3 h. Each of these tertiary phosphines are water soluble, solubility being achieved by placing  $\omega$ -carboxy-, hydroxy-, or aminoalkyl groups on phosphorus. (Usually tertiary aliphatic phosphines are extremely insoluble in aqueous media.)



(1) X = CO<sub>2</sub>H, *m* = 0, *n* = 3; (2) X = CO<sub>2</sub>H, *m* = 1, *n* = 2; (3) X = CO<sub>2</sub>H, *m* = 2, *n* = 1; (4) X = CH<sub>2</sub>OH, *m* = 0, *n* = 3; (5) X = CH<sub>2</sub>OH, *m* = 1, *n* = 2; (6) X = CH<sub>2</sub>OH, *m* = 2; *n* = 1; (7) X = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, *m* = 2, *n* = 1.

The predominant organic product isolated in each case was the corresponding tertiary phosphine oxide (Equation 1).



† All new compounds have satisfactory analytical and spectroscopic data.

‡ Hydrogen evolution from (2), (4), and (6) in several alkaline alkyl-diol solvents, *e.g.*, NaO·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>·OH in propane-1,3-diol has been observed. We have also measured the evolution of 2 equivalents of hydrogen gas from the anaerobic alkaline oxidation of bis-3-hydroxypropylphosphine to its phosphinic acid.

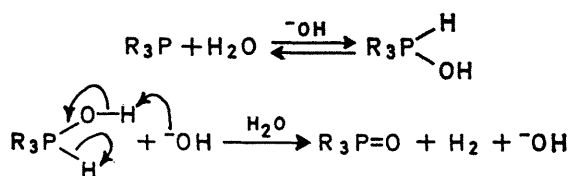
This alkaline oxidation is favoured thermodynamically by the extraordinary stability of the newly formed P=O bond (138 kcal mol<sup>-1</sup>).<sup>1</sup> The dependence of the decomposition reaction on alkali concentration was easily demonstrated. When the hydroxide ion concentration of an aqueous solution, 0.1 N in methylbis-(2-carboxyethyl)phosphine, (2) was lowered from 2N to 10<sup>-5</sup>N, no gas evolution was observed after 48 h reflux. Hydrogen evolution was not noticeably accelerated in the presence of added salt nor noticeably retarded in the presence of radical inhibitors (*e.g.*, hydroquinone and diphenylamine). In all cases the phosphine oxide obtained from the alkaline oxidation reaction was compared with a sample made by the peroxide oxidation<sup>2</sup> of the corresponding phosphine. Sodium ethoxide in ethanol was not an oxidizing medium. No gas evolution was observed for any of the phosphines (5)–(7)† in 2N-sodium ethoxide under reflux for 48 h.‡

The hydrogen evolution, the lack of radical inhibition, and the difficulty in observing any reaction with ethoxide in ethanol indicate that this oxidation differs from the well-known aerial oxidation of phosphines previously described by Buckler<sup>3</sup> and others.<sup>4,5</sup>

A possible mechanism for the oxidation is shown in the Scheme.

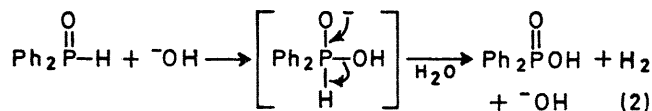
A similar scheme was suggested by Campbell and Stevens<sup>6</sup>

in which a hydride ion was expelled from phosphorus when ethoxide in ethanol was treated with secondary phosphine



SCHEME

oxides. This oxidation was equally effective when aqueous hydroxide was used (Equation 2).



The observation that dimethyl-( $\epsilon$ -aminopentyl)phosphine, (7), reduced 2N-alkali to give a stoichiometric quantity of

hydrogen gas rules out the necessity for an intramolecular nucleophilic-assisted hydride displacement.

In order to deduce the requirements for the decomposition reaction the tertiary phosphine tris-(n-butyl)phosphine, with limited solubility in aqueous media, was tested. It failed to reduce 2N-alkali under reflux for 48 h. § We had assumed that aromatic phosphines might be less prone to attack by alkali as their  $pK_a$ 's are less than 2, in contrast to the strongly basic aliphatic phosphines (1)–(7), with  $pK_a$  values greater than 7. Tris-(*p*-hydroxyphenyl)phosphine and tris-(*o*-hydroxyphenyl)phosphine, however, both reduced alkali under the conditions described previously. The *ortho*-derivative was observed to generate the stoichiometric quantity of hydrogen gas more rapidly than the *para*-derivative. We therefore have been unable to find any singular factor other than solubility in aqueous alkali which is necessary for the anaerobic oxidation of tertiary phosphines.

We thank Mr. A. Hunt of our Analytical Chemistry Laboratory for the gas chromatographic analyses.

(Received, March 26th, 1970; Com. 430.)

§ Although this is a heterogeneous medium,  $\text{Bu}_3\text{P}$  is soluble in water to the extent of 0.1%. Attempted intermittent addition of ethanol or alkyl-diols to alleviate the solubility problem resulted in no observable gas evolution.

<sup>1</sup> R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, 1965, p. 68.

<sup>2</sup> M. M. Rauhut, I. Hechenbleikner, H. A. Currier, F. C. Schaefer, and V. P. Wystrach, *J. Amer. Chem. Soc.*, 1961, **81**, 1103.

<sup>3</sup> S. A. Buckler, *J. Amer. Chem. Soc.*, 1962, **84**, 3093.

<sup>4</sup> A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, New York, 1967, p. 176; J. I. G. Cadogan, *Quart. Rev.*, 1962, **16**, 208.

<sup>5</sup> W. G. Bentrude, J. H. Margis, and P. E. Rusek, jun., *Chem. Comm.*, 1969, 296.

<sup>6</sup> I. G. M. Campbell and I. D. R. Stevens, *Chem. Comm.*, 1966, 505.