Notes A department for short papers of immediate interest.

Phosphine Oxides. VI. Formation of Disubstituted Phosphine Oxides by Hydrolysis of Disubstituted Phosphinous Halides

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Received January 5, 1959

Disubstituted phosphine oxides (I), $R_2P(O)H$, have been prepared by the reaction of Grignard reagents[2,3] or organolithium compounds[4] with disubstituted phosphonates. Recently, two methods utilizing trivalent phosphorus reagents have been reported: the air oxidation of disubstituted phosphines in isopropyl alcohol solution[5] and the reaction under Friedel-Crafts conditions of highly methylated benzenes with phosphorus trichloride and aluminum chloride followed by hydrolysis.[6] This work reports the preparation of two examples of I by the hydrolysis of disubstituted phosphinous halides in the absence of air.

Since it has been shown that low molecular weight disubstituted phosphine oxides are unstable,[7] the previously unknown di-*n*-octylphosphinous bromide (II) was synthesized as the starting reagent. The treatment of phosphorus trichloride with two moles of *n*-octylmagnesium bromide followed by dry distillation of the solid product gave II in poor yield. Rather surprisingly, the use of

$$2n\text{-}C_8H_{17}MgBr + PCl_3 \longrightarrow \xrightarrow{\Delta\Delta} (n\text{-}C_8H_{17})_2PBr$$

phosphorus tribromide instead of phosphorus trichloride gave much smaller amounts of II. Treatment of I in refluxing benzene with water and triethylamine gave a 73% yield of the pure di-*n*-octylphosphine oxide (IA).

A similar treatment of diphenylphosphinous chloride (III) with water gave diphenylphosphine oxide, $(C_6H_5)_2P(O)H$, in fair yield. The crude deliquescent product was characterized by its known benzaldehyde addition product, $(C_6H_5)_2P(O)CH(OH)C_6H_5$.[8]

A possible path of the hydrolysis reaction would involve displacement of the halogen from the trivalent phosphorus atom by water followed by a rapid tautomerization of the phosphinous acid formed.

$$R_2P\text{—}X + H_2O \longrightarrow R_2P\text{—}O\text{—}H \rightleftarrows R_2P(O)H$$

The nature of this reaction appears to be similar to that observed by Sallmann[9] and Michalski[10] when diethyl chlorophosphite was treated with hydrogen sulfide to yield *O,O*-diethyl thiophosphonate.

$$(C_2H_5O)_2PCl + H_2S \xrightarrow[\text{amine}]{\text{tertiary}} (C_2H_5O)_2P\text{—}S\text{—}H \rightleftarrows (C_2H_5O)_2P(S)H$$

Certain partially oxygenated phosphorus compounds have shown themselves prone to disproportionation upon heating with or without base. Phenylphosphinic acid, $C_6H_5P(O)(H)OH$, has been reported easily converted to phenylphosphine and benzenephosphonic acid at temperatures of 100° and higher.[11] Previous workers have treated III with aqueous strong base to obtain the salt of diphenylphosphinic acid and diphenylphosphine. It was presumed that a disproportionation reaction had taken place[12] which is now proposed as involving the then unknown diphenylphosphine oxide as an intermediate.

$$\begin{array}{l}2(C_6H_5)_2PCl + 2H_2O \longrightarrow \\ \qquad\qquad [2(C_6H_5)_2P\text{—}O\text{—}H \rightleftarrows 2(C_6H_5)_2P(O)H] \\ \qquad\qquad\qquad\qquad\qquad \text{NaOH}\big\downarrow \\ \qquad\qquad\qquad (C_6H_5)_2P(O)ONa \quad (C_6H_5)_2PH\end{array}$$

To ascertain if such a reaction could involve $R_2P(O)H$ as an intermediate, IA was refluxed with sodium hydroxide under nitrogen to give a 68% yield of di-*n*-octylphosphine (IV) and, after acidification, 110% of di-*n*-octylphosphinic acid. The separation of the distillable liquid phosphine from small amounts of sublimed unreacted IA was made more difficult by the great reactivity of IV with the oxygen in air. This oxidation probably accounts for

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[2] R. H. Williams and L. A. Hamilton, *J. Am. Chem. Soc.*, **74**, 5418 (1952); **77**, 3411 (1955).

[3] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).

[4] J. L. Willians, *Chem. and Ind.* (*London*), 235 (1957).

[5] M. M. Rauhut, I. Hechenbleikner, H. A. Currier, and V. P. Wystrach, *J. Am. Chem. Soc.*, **80**, 6690 (1958).

[6] A. W. Frank, *J. Org. Chem.*, **24**, 966 (1959).

[7] R. H. Williams, Ph.D. thesis, Temple University, 1953.

[8] R. C. Miller, C. D. Miller, W. Rogers, and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957).

[9] R. Sallmann (Ciba Ltd.), U. S. Patent **2,805,241** (1957).

[10] J. Michalski and Cz. Krawiecki, *Chem. & Ind.* (*London*), 1323 (1957).

[11] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, 1950, p. 12.

[12] G. M. Kosolapoff, *Organophosphorus Compounds*, p. 52.

the discrepancy in the product balance from that expected from the following equation:

$$2R_2P(O)H + NaOH \longrightarrow R_2PH + R_2P(O)ONa$$

In the absence of base, IA can be heated to 200–250° for several hours with only a negligible loss of starting material. On the other hand, sodium di-*n*-octylphosphinate is stable under similar thermal conditions in the presence or absence of sodium hydroxide. The identity of the di-*n*-octylphosphine was ascertained by an independent two-step synthesis from IA by (1) chlorination with *N*-chlorosuccinimide and (2) reduction of the crude phosphinyl chloride in refluxing ether with lithium aluminum hydride. These two reactions have been previously used to yield IA from di-*n*-octylphosphinic acid when the reduction is carried out at lower temperatures,[2] but at higher temperatures, greater reduction to the substituted phosphine occurs. Both the disproportionation reaction and the reduction method represent reasonable route of synthesis of disubstituted phosphines.

EXPERIMENTAL

Preparation of di-n-octylphosphinous bromide from n-octylmagnesium bromide and phosphorus trichloride. A solution of *n*-octylmagnesium bromide from 164.2 g. (0.851 mol.) of *n*-octyl bromide and 21.3 g. (0.877 g.-atom) of magnesium powder in 640 ml. of anhydrous diethyl ether was added over a 2-hr. period to a mixture of 68.5 g. (0.50 mol.) of phosphorus trichloride and 200 ml. of ether at 0°. A heavy white solid which was sufficiently immobile to stop the electric stirrer was formed. This mixture was heated for 1 hr. on a steam bath, stripped of ether, and the remaining solid was heated at 1 mm. by an oil bath (maximum temperature 278°). A moderate quantity (64.7 g.) of an opaque orange oil was collected through a condenser. Two redistillations through a Vigreux column gave a 24.8 g. cut, boiling at 138.5–140.0° at 0.15–0.19 mm. The colorless liquid reacted immediately with moist air to form a white solid and was therefore always handled under nitrogen. The refractive index at 25.0° was 1.4856.

Anal. Calcd. for $C_{16}H_{34}BrP$: C, 56.97; H, 10.16; P, 9.18; Br, 23.69. Found: C, 57.30; H, 10.34; P, 9.33; Br, 23.36.

The over-all yield from the *n*-octyl bromide run was 17.2%. Most of the solid product did not decompose at the oil bath temperature. Since the crude orange product upon distillation left an easily ignited yellow-orange residue upon the condenser walls, it was found advisable to allow the column to cool to room temperature and to flush the apparatus with nitrogen before exposing the Vigreux column to the air. A similar reaction utilizing phosphorus tribromide yielded only 4.6% of the pure desired product, as the solid complex failed to markedly decompose even at oil bath temperatures of 290–300°.

Conversion of di-n-octylphosphinous bromide to di-n-octylphosphine oxide. A mixture of 4.50 g. (0.0133 mol.) of di-*n*-octylphosphinous bromide, 5.0 g. (0.27 mol.) of water, and 4.0 g. (0.040 mol.) of triethylamine in 100 ml. of benzene was refluxed under nitrogen for 2 hr. After the excess water was removed from the system by distilling it with benzene (as a benzene water azeotrope), 1.90 g. of triethylamine hydrobromide was filtered from the mixture. Upon evaporation of the filtrate, 3.45 g. of white product, melting at 81.5–83.5° was obtained.[13] A benzene solution of the crude product was washed with several portions of cold 25% aqueous potassium carbonate solution and, after evaporation of solvent and recrystallization from *n*-hexane, 2.65 g. (72.5% yield) of di-*n*-octylphosphine oxide, melting at 85.0–86.0°, was obtained. The melting point of a sample mixed with an authentic sample of IA[2] was not depressed, and the infrared spectra were identical.

Anal. Calcd. for $C_{16}H_{35}OP$: C, 70.02; H, 12.86; P, 11.29. Found: C, 69.82; H, 12.80; P, 11.62.

Hydrolysis of diphenylphosphinous chloride. A mixture of 17.0 g. (0.077 mol.) of diphenylphosphinous chloride prepared from diphenylphosphinodithioic acid,[14,15] 6.0 g. (0.33 mol.) of water, and 75 ml. of benzene was refluxed for 16 hr. under nitrogen. After removal of the excess water by azeotropic distillation and evaporation of the benzene, the remaining oil was stored under nitrogen at 0° for 4 days. A 16.5 g. crop of deliquescent needles, melting at 45–53°, was obtained which contained some halide impurity. Recrystallization from ether gave 3.0 g. of colorless needles, melting at 51–54°. The melting point was not depressed when this compound was mixed with an authentic sample of $(C_6H_5)_2P(O)H$,[3] and the infrared spectra, showing a strong P—H peak at 4.25μ, were also in agreement. A 2.50-g. quantity of the product in 5 ml. of ethanol and 2.00 g. of benzaldehyde was treated with a trace of sodium ethoxide in ethanol to yield, after standing overnight, an initial crop of 1.52 g. of white needles. After recrystallization from 2:1 aqueous ethanol, the product melted at 182.5–183.7° and was shown by mixed melting point and infrared spectrum to be identical to an authentic sample of $(C_6H_5)_2P(O)CH(OH)C_6H_5$.[8]

Disproportionation of di-n-octylphosphine oxide. A mixture of 54.8 g. (0.200 mol.) of di-*n*-octylphosphine oxide was heated with 6.0 g. (0.15 mol.) of sodium hydroxide in sealed tubes at 245° for 24 hr. On cooling, the semisolidified white mixture was transferred to a distillation flask in a nitrogen atmosphere and distilled under vacuum. The first distillation yielded a main cut of 23.1 g. of a colorless liquid, boiling at 138–145° at 0.80 mm. This product contained some solid which had initially sublimed into the condenser and was washed down into the receiver. A redistillation gave a 17.6 g. main cut boiling at 140–142° at 1.1 mm. This material had a refractive index of 1.4629 at 25.1°. The rather sweet smelling colorless liquid reacted with air and solidified immediately; it could be maintained only under nitrogen. The infrared spectrum of a sample in chloroform showed a strong P—H band at 4.43μ.

Anal. Calcd. for $C_{16}H_{35}P$: C, 74.36; H, 13.66; P, 11.99. Found: C, 74.42; H, 13.71; P, 12.05.

The pot residue of the initial distillation was acidified with dilute hydrochloric acid and the white solid obtained after evaporation of the aqueous layer was crystallized from *n*-hexane. The 31.9 g. of white solid melted at 83.5–84.7° and failed to depress the melting point of an authentic sample of di-*n*-octylphosphinic acid.[2]

Anal. Calcd. for $C_{16}H_{35}O_2P$: neut. equiv., 290. Found: neut. equiv., 288, 289.

These yields represent 68.2% and 110% of di-*n*-octylphosphine and di-*n*-octylphosphinic acid, respectively. Failure to completely separate the phosphine by distillation and oxidation of the residue by air during the work-up of the acid could account for the high yield of the phosphinic acid obtained.

Two-step reduction of di-n-octylphosphine oxide. A stirred solution of 87.4 g. (0.319 mol.) of di-*n*-octylphosphine oxide in 400 ml. of chloroform was treated with 43.5 g. (0.327 mol.) of *N*-chlorosuccinimide during 1 hr. After standing for 2 hr., the solvent was evaporated and 29.2 g. of succinimide was removed by filtration. The crude di-*n*-octylphosphinyl chloride, a yellow oil, was taken up in 200 ml.

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[13] All melting points uncorrected.

[14] W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).

[15] C. Steube, W. M. LeSeur, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 3526 (1955).

of anhydrous ether and added to a slurry of 27.5 g. (0.725 mol.) of lithium aluminum hydride in 200 ml. of ether. After the mixture was refluxed for 1 hr., the excess hydride was hydrolyzed by adding an ethanol ether mixture followed by 100 ml. of water. The voluminous precipitate was filtered under nitrogen and washed with 300 ml. of ether. The combined filtrate and washings were distilled under nitrogen to obtain a 43.5 g. main cut (53% yield), boiling at 143–146° at 1.3 mm. The refractive index was 1.4626 at 26.2°, and the infrared spectrum was in complete agreement with the product previously obtained by disproportionation of IA.

Anal. Found: C, 74.64%; H, 13.88%; P, 11.85%.

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The Basicity of 4,4'-Bis(dimethylamino)-Azobenzene

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Received February 10, 1959

Although the pKa of a host of 4-aminoazobenzene derivatives has been measured,[1-3] there are no data on the basicity of 4,4'-bis(dimethylamino)-azobenzene [$4'$-$N(CH_3)_2$-DAB]. This dye shows an unusual behavior in dilute acids inasmuch as it gives a green color[4] and only on increasing the acidity presents the red color shown by 4-dimethylaminoazobenzene (DAB) derivatives in acid media.

The pKa of this dye in 50% aqueous ethanol corresponding to the first proton addition has now been determined spectrophotometrically and found to be 3.2. This value merely represents the over-all basicity because a mixture of conjugate acids is formed on protonation.[2,3,5-7]

The observed pKa value makes $4'$-$N(CH_3)_2$-DAB one of the most basic 4-aminoazobenzene derivatives.

This relatively high basicity is in part due to the presence in this dye, but not in monodimethylaminoazobenzenes, of a centre of symmetry; the positions of proton capture are doubled and this statistical factor, log 2, rises the pKa of 0.30 pH units. Yet it is possible that these positions of proton capture are more than four—*i.e.*, a third monoprotonated dye coexists besides the dimethylammonium (I) and azonium (II) cations.

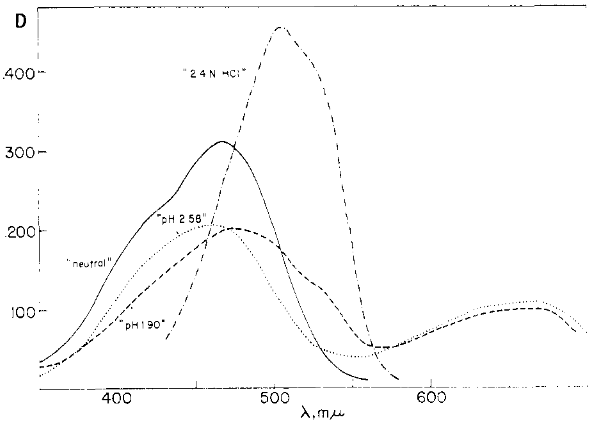
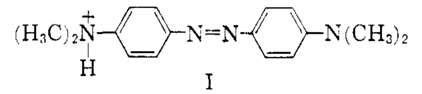
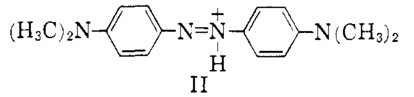


Fig. 1. Visible spectrum of $4'$-$N(CH_3)_2$-DAB at different acidities. (Only a few curves are shown: ——— neutral; ······ pH = 2.58; - - - - pH = 1.90; - · - · - 2.4N HCl.)

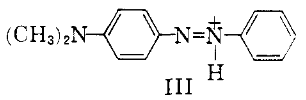


I



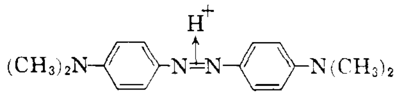
II

The evidence is mainly spectral. In the acid spectrum, λ_{max} of the longer transition is at 670 mμ (Fig. 1). This band cannot of course be due to the cation I. Sawicki[8] ascribed it to the cation II and interpreted the enormous shift with respect to the β-azonium cation of DAB (III) (λ_{max} 516 mμ) to extrachromophoric resonance.



III

This explanation is by no means convincing.[9] We propose that the 670 mμ transition is due to the cation IV, a π-complex resulting from incorporation of the π-electrons of the azo group in the vacant 1s orbital of the proton. In such a cation the positive charge can be efficiently distributed over the



IV

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(6) A. Hantzsch and A. Burawoy, *Ber.*, **63**, 1760 (1930).

(7) E. Sawicki, (a) *J. Org. Chem.*, **21**, 605 (1956); (b) *J. Org. Chem.*, **22**, 365 (1957).

(8) E. Sawicki, *J. Org. Chem.*, **22**, 1084 (1957).

(9) This point has also been stressed by a referee who reports that "structure IIIa-IIIb in reference (8) for the monocation should absorb at about 500 mμ, because of its aza-amidinium system; and its p-dimethylaminophenyl substituent would lengthen its absorption some but not up to 660 mμ, as Sawicki proposes."