this mixture heated at 135°. After several hours some viscosity was noted, and in 24 hr. the tube contents were immobile. Isolation of the polymer revealed a material with an intrinsic viscosity of 0.020 at 30° in 2B alcohol,[17] mol. wt., 692. When this was repeated at one tenth the di-*t*-butyl peroxide level, again a glass was obtained, possessing an intrinsic viscosity 0.025. When the di-*t*-butyl peroxide concentration was decreased again by a factor of ten, the tube contents increased in viscosity only slightly indicating that the chains were too short to allow complete polymerization at that peroxide level.

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[17] Another homopolymer, formed by heating 2.13 g. of the monomer with one drop of di-*t*-butyl peroxide at 135° also had an intrinsic viscosity of 0.02 but a molecular weight of 1350.

[CONTRIBUTION FROM CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Oxidation of Secondary Phosphines to Secondary Phosphine Oxides[1]

M. M. RAUHUT AND HELEN A. CURRIER

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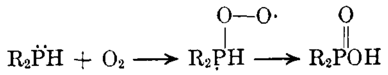
Oxidation of secondary phosphines by air under mild conditions has been found to give secondary phosphine oxides in good yields. Phosphinic acids were not found under the reaction conditions employed.

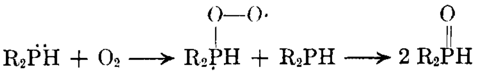
It has been reported that oxidation of secondary phosphines by nitric acid[2] or by air[3] proceeds vigorously[4], and that phosphinic acids are the products of such reactions.[2,3] Although secondary phosphine oxides have been considered possible intermediates in these oxidations, their isolation under the conditions employed has been thought to be impossible.[5]

In view of these results it is conceivable that air oxidation of a secondary phosphine might proceed directly to the corresponding phosphinic acid by an intramolecular oxygen shift.



$$R_2\ddot{P}H + O_2 \longrightarrow R_2\overset{O-O\cdot}{\overset{|}{P}}H \longrightarrow R_2\overset{O}{\overset{\|}{P}}OH$$

Alternatively, a secondary phosphine oxide might be formed as an intermediate, which under the conditions employed could oxidize further in a separate step to the phosphinic acid. If this latter



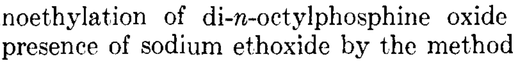
$$R_2\ddot{P}H + O_2 \longrightarrow R_2\overset{O-O\cdot}{\overset{|}{P}}H + R_2PH \longrightarrow 2\,R_2\overset{O}{\overset{\|}{P}}H$$

mechanism is correct, one should be able to isolate the intermediate secondary phosphine oxides, since secondary phosphine oxides, obtained by other means,[6] have been found to be relatively stable toward oxidation.[7]

Accordingly, nine secondary phosphines were oxidized by air at moderate temperatures. In each case, the product obtained was found to be a secondary phosphine oxide (Table I). The reactions were run by simply exposing a small quantity of the phosphine to the atmosphere (Method A) or by passing dry air through a larger quantity of the phosphine dissolved in isopropyl alcohol (Method B). The crystalline oxides were characterized by elemental analysis, by infrared and NMR spectroscopy, and in several cases by the preparation of derivatives.

The oxidations were inhibited by hydroquinone as would be expected for a free-radical process. Unexpectedly, however, oxidation also failed to take place in benzene solution. This latter effect deserves additional study.

Di-*n*-butylphosphine oxide and diisobutylphosphine oxide were characterized by their reactions with chloral hydrate in refluxing isopropyl alcohol to give the corresponding 1-hydroxy-2,2,2-trichloroethylphosphine oxides.



$$R_2\overset{O}{\overset{\|}{P}}H + (HO)_2CHCCl_3 \longrightarrow R_2\overset{O}{\overset{\|}{P}}\overset{OH}{\overset{|}{C}}HCCl_3 + H_2O$$

Cyanoethylation of di-*n*-octylphosphine oxide in the presence of sodium ethoxide by the method of Miller, Bradley and Hamilton[8] gave (2-cyanoethyl)-di-*n*-octylphosphine oxide.

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[6] For a recent review of secondary phosphine oxides, see K. D. Berlin and G. B. Butler, *Chem. Revs.*, **60**, 243 (1960).

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[9] Melting points are uncorrected.

TABLE I

SECONDARY PHOSPHINE OXIDES, $R_1R_2\overset{\overset{O}{\|}}{P}H$

R_1	R_2	Method	Yield, %	M.P.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
n-C_4H_9	n-C_4H_9	B	47	66	$C_8H_{19}OP$	59.24	58.61	11.82	11.36	19.08	18.84
i-C_4H_9	i-C_4H_9	B	[a]	[b]	—	—	—	—	—	—	—
n-C_8H_{17}	n-C_8H_{17}	B	88	85–86[c]	—	—	—	—	—	—	—
n-$C_{12}H_{25}$	n-$C_{12}H_{25}$	B	71	99–100	$C_{24}H_{51}OP$	74.53	74.21	13.31	13.15	8.02	8.45
$C_6H_5CH_2CH_2$	$C_6H_5CH_2CH_2$	A	81	69–71	$C_{16}H_{19}OP$	74.40	74.53	7.41	7.55	11.99	11.76
$NCCH_2CH_2$	$NCCH_2CH_2$	B	90	98–99	$C_6H_9N_2OP$	46.15	46.32	5.80	5.95	19.84	19.94
$NCCH_2CH_2$	n-C_8H_{17}	A	[a]	68–69	$C_{11}H_{22}NOP$	61.36	61.40	10.30	10.35	14.39	14.83
$C_2H_5O_2CCH_2CH_2$	n-C_8H_{17}	A	80	50–52	$C_{13}H_{27}O_3P$	59.52	57.58	10.47	10.38	11.81	12.00
C_6H_5	C_6H_5	B	85	53–56[d]	—	—	—	—	—	—	—

[a] Not recorded. [b] The hygroscopic product was characterized as the chloral hydrate addition product, m.p. 175° dec. [c] Lit.[7] m.p. 85°. [d] Lit. m.p. 53–56° [B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957)].

EXPERIMENTAL[9]

Materials. Bis(2-cyanoethyl)phosphine was prepared by the base-catalyzed cyanoethylation of phosphine.[10] Di-n-butylphosphine was distilled from a 10% solution kindly provided by the Westvaco Mineral Products Division, Food Machinery and Chemical Corp. Diphenylphosphine was prepared by the reaction of triphenylphosphine with lithium.[11] (2-Cyanoethyl)-n-octylphosphine and (2-carbethoxyethyl)-n-octylphosphine were obtained by the free radical addition of 2-cyanoethylphosphine and 2-carbethoxyethylphosphine, respectively, to 1-octene.[12] Other secondary phosphines were obtained by the free radical addition of phosphine to the appropriate olefin.[12]

Oxidation of secondary phosphines. Method A. In a typical experiment 4.3 g. of bis(2-phenylethyl)phosphine was spread in a thin layer and exposed to the air for 12 hr. The crystalline product (3.7 g. 81%), m.p. 65–70°, was recrystallized from heptane to obtain the pure oxide, m.p. 69–71°.

Method B. Into a three necked, creased flask equipped with a mechanical stirrer, a thermometer, an efficient reflux condenser, and a gas inlet tube, were placed 1 mole of the secondary phosphine and 500 ml. of isopropyl alcohol. A rapid stream of dry air was passed through the vigorously stirred mixture for 3 to 5 hr. while the temperature was maintained at 45–50° by cooling. Oxidations of di-n-dodecylphosphine and bis(2-cyanoethyl)phosphine were less vigorous and were more conveniently run at 70–80° on a steam bath.

Di-n-dodecylphosphine oxide and bis(2-cyanoethyl)phosphine oxide separated from their reaction mixtures on cooling and were recrystallized from isopropyl alcohol. The other phosphine oxides were obtained by evaporating the solvent under reduced pressure. Diisobutylphosphine oxide and diphenylphosphine oxide were obtained initially as oils. Diisobutylphosphine oxide was crystallized by cooling a heptane solution in a Dry Ice–acetone bath. The product was highly deliquescent and became semiliquid on even brief exposure to moist air. Diphenylphosphine oxide was crystallized by shaking with ether and cooling the mixture in Dry Ice–acetone.

Melting points, yields, and analyses are presented in Table I. The oxide structures of the products were substantiated by their infrared and NMR spectra. In the infrared spectra a strong P=O absorption band appeared at 1655 cm.$^{-1}$ to 1670 cm.$^{-1}$, and a generally weak P=H absorption band appeared at 2300 cm.$^{-1}$ to 2340 cm.$^{-1}$ In the NMR spectra the secondary phosphine oxides gave a 1-1 doublet centered near -28 ppm. (referred to 85% phosphoric acid) with the exceptions of diphenylphosphine oxide, which centered at -18 ppm. and (2-carbethoxyethyl)-n-octylphosphine oxide which centered at -39 ppm. The splittings (p=H coupling) varied from 19 ppm. to 31 ppm. This is significantly greater than the corresponding coupling in secondary phosphines, which has been observed to be 12 ppm. in a large number of compounds.

Diisobutyl(1-hydroxy-2,2,2-trichloroethyl)phosphine oxide. A solution of 6.5 g. (0.04 mole) of crude diisobutylphosphine oxide and 6.7 g. (0.04 mole) of chloral hydrate in 25 ml. of isopropyl alcohol was refluxed for 2 hr. A white solid separated from the reaction mixture and was collected to obtain 10.4 g. (79%) of the tertiary oxide, m.p. 175° dec. Recrystallization from methanol gave an analytical sample, m.p. 175° dec.

Anal. Calcd. for $C_{10}H_{20}Cl_3O_2P$: P, 10.00; Cl, 34.35. Found: P, 10.07; Cl, 34.56.

Di-n-butyl(1-hydroxy-2,2,2-trichloroethyl)phosphine oxide. A solution of 8.1 g. (0.05 mole) of dibutylphosphine oxide, 8.3 g. (0.05 mole) of chloral hydrate and 25 ml. of isopropyl alcohol was refluxed for 2 hr. and cooled to 0°. After several minutes the product crystallized and was washed onto a filter with ether. The white solid (7.4 g.) melted at 134°. The ether was evaporated from the filtrate and the residue was diluted with water and filtered to obtain an additional 6.4 g. of the product. The total yield was 13.8 g. (89%) m.p. 129–132°. Recrystallization from benzene provided an analytical sample, m.p. 132–133°.

Anal. Calcd. for $C_{10}H_{20}Cl_3O_2P$: P, 10.00. Found: P, 9.78.

(2-Cyanoethyl)di-n-octylphosphine oxide. A mixture of 14.0 g. (0.051 mole) of di-n-octylphosphine oxide, 5.4 (0.102 mole) of acrylonitrile, and 25 ml. of absolute ethanol was treated with 13 drops of alcoholic sodium ethoxide solution, and refluxed on the steam bath for 2 hr. The reaction mixture was evaporated under reduced pressure to obtain an orange oil which solidified upon cooling in an ice bath. Recrystallization from petroleum ether (b.p. 30–60°) gave 10.5 g. (63%) of the product, m.p. 50.5–53°. A second recrystallization provided a sample melting at 51–51.5° (lit.[8] m.p. 53.4–54.2°).

Acknowledgment. The authors wish to thank Dr. V. P. Wystrach for his continuing interest and encouragement. The authors are also indebted

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[CONTRIBUTION FROM CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Reactions of Bis(2-cyanoethyl)phosphine Oxide

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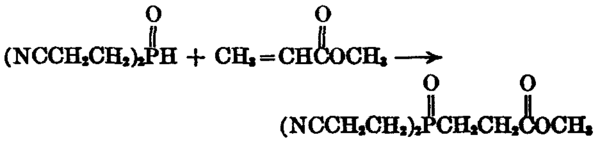
Bis(2-cyanoethyl)phosphine oxide reacted with α,β-unsaturated carbonyl compounds in the presence of strong organic bases, and with aldehydes and acetone without catalyst or in the presence of tertiary amines to give good yields of unsymmetrical tertiary phosphine oxides. Bis(2-cyanoethyl)phosphine oxide also reacted with *p*-chlorophenyl isocyanate and with 2,4-dichlorobenzyl chloride to give corresponding tertiary phosphine oxides. Reaction with isopropyl alcohol and carbon tetrachloride gave isopropyl bis(2-cyanoethyl)phosphinate. Additional reactions are described.

Secondary phosphine oxides can be prepared by the reaction of Grignard reagents[1,2] or aryl lithium compounds[3] with dialkyl phosphites, by reduction of phosphinyl chlorides with lithium aluminum hydride,[1] by hydrolysis of dialkyl[4] or diaryl[5] halo phosphines, and by controlled oxidation of secondary phosphines.[6] The latter method appears best suited for the preparation of secondary phosphine oxides containing reactive substituents. Thus bis(2-cyanoethyl)phosphine oxide was prepared in 90% yield by the air oxidation of bis(2-cyanoethyl)phosphine.[6] Reactions of secondary phosphine oxides had received little study at the time the work described here was in progress, and the chemistry of bis(2-cyanoethyl)phosphine oxide was studied in some detail. Recently, Hamilton and co-workers have reported the sodium ethoxide-catalyzed addition reactions of di-*n*-octylphosphine oxide and dibenzylphosphine oxide to unsaturated nitrile and carbonyl compounds[7] and to aldehydes and ketones.[8]

RESULTS AND DISCUSSION

Bis(2-cyanoethyl)phosphine oxide reacted with α,β-unsaturated carbonyl compounds in the presence of the strong organic bases pentamethylguanidine (PMG) or heptamethylbiguanide (HMB) to give unsymmetrical tertiary phosphine oxides (Table I). The reactions were carried out under mild conditions and generally provided good yields.



$$(NCCH_2CH_2)_2\overset{\overset{O}{\|}}{P}H + CH_2{=}CH\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow (NCCH_2CH_2)_2\overset{\overset{O}{\|}}{P}CH_2CH_2\overset{\overset{O}{\|}}{C}OCH_3$$

TABLE I

ADDITION OF BIS(2-CYANOETHYL)PHOSPHINE OXIDE TO α,β-UNSATURATED CARBONYL COMPOUNDS

Unsaturated Compound	Catalyst	Solvent	Yield, %
$CH_3O\overset{\overset{O}{\|}}{C}CH{=}CH_2$	PMG	Isopropyl alcohol	99
$n\text{-}C_{12}H_{25}O\overset{\overset{O}{\|}}{C}CH{=}CH_2$	PMG	Isopropyl alcohol	98
$cis\text{-}C_2H_5O\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{O}{\|}}{C}OC_2H_5{}^{a}$	HMB	None	40
$H_2N\overset{\overset{O}{\|}}{C}CH{=}CH_2$	HMB	Isopropyl alcohol	100
$CH_3\overset{\overset{O}{\|}}{C}CH{=}C(CH_3)_2{}^{a}$	PMG[b]	Methanol	40

[a] The molar ratio of oxide to unsaturated carbonyl compound was 1:2. [b] When PMG was replaced by triethylamine, no reaction took place.

Pentamethylguanidine did not catalyze the addition of di-*n*-octylphosphine oxide to acrylonitrile. The reactivity of bis(2-cyanoethyl)phosphine oxide under these conditions is evidently a consequence of its greater acidity, which results from the inductive effect of the nitrile substituents.

The free radical addition of bis(2-cyanoethyl)phosphine oxide to octene-1 was initiated by α,α-azobisisobutyronitrile and gave *n*-octylbis(2-cyanoethyl)phosphine oxide in 48% yield.

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