perature for 15 minutes. The final product contained 19.6% ordinary 2-methylpentane.[21]

2-Methylpentane-5-*d*.—Grignard reagent was prepared, using 10.4 ml. (100 millimoles) of isobutyl chloride (Eastman Kodak Company isobutyl chloride, fractionated in a 30-plate column, b.p. 69.2°, $n^{20}\text{D}$ 1.39811), 30 ml. of ether, 2.5 g. of magnesium turnings and a dry nitrogen atmosphere. At the completion of the reaction the condenser was replaced by a condenser at −30°, and the dropping funnel by a gas inlet tube ending above the surface of the liquid. An iron–constantan thermocouple was inserted directly into the mixture by passage through the condenser. With slow stirring, ethylene oxide (105 millimoles) was introduced at a rate of about 50 ml./min. (indicated by a rotameter between the flask containing the liquid ethylene oxide and the reaction flask). The temperature was maintained below 10° until the addition of reagent was completed, at which time the mixture was refluxed for 30 minutes.

Benzene (30 ml.) was added and the mixture was distilled with stirring until the temperature of the distilling vapor rose to 65°. At that point the condenser was shifted so that the mixture was refluxed for 45 minutes. It was then cooled in ice and ice-water (30 ml.) was added.

After the mixture had stood overnight, it was cooled in ice and a cold solution of 5 ml. of concentrated sulfuric acid in 30 ml. of water was added with stirring. Ether was added and the upper layer was separated, washed with sodium bicarbonate solution, dried and fractionated until the boiling point of the distillate reached 125°.

The hexanol residue was cooled to −30° and 2 ml. of phosphorus tribromide added in portions with stirring. The temperature was allowed to rise to 25° over a period of 48 hours. The product was distilled on the vacuum system twice, and hydrogen bromide was removed by evacuation at 0° until the vapor pressure was less than 10 mm. Any traces remaining were eliminated by distillation through ascarite. The distillate was taken up in ether, washed with sodium bicarbonate solution, and dried with anhydrous potassium carbonate.

The solution was converted to the deuterohydrocarbon in a manner similar to that used for 2-methylpentane-2-*d* above, except that 0.5 g. of magnesium turnings were used. The product distilled from 70% H_2SO_4 was found by mass spectrometric analysis to contain 4.8% benzene, 10.7% ether, 1.7% hexylene, 64% deuteroalkane and 20% ordinary 2-methylpentane. It was treated with 0.2 ml. of bromine and ethanolamine in the usual way, then with 92% sulfuric acid at 0° for five minutes. It was distilled from the latter until the residue had a vapor pressure of 30 mm. at 0°. The product (*ca.* 1 g.) then contained 1.3% ether and 4.0% benzene. It was fractionally distilled in a Podbielniak apparatus, using *n*-heptane as a "chaser." Middle cuts amounting to roughly three-fifths of the total contained no detectable ether and 0.2% benzene.

EMERYVILLE, CALIF. RECEIVED NOVEMBER 12, 1951

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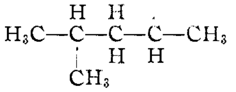
[21] A relatively non-volatile liquid residue left in the fractional distillation analyzed carbon, 84.2%; hydrogen, 15.43%, corresponding well with $C_{12}H_{26}$, for which one should obtain carbon, 84.6%; hydrogen, 15.36%. This material, probably 2,4,5,7-tetramethyloctane, may be formed by combination of the radicals



$$H_3C{-}\underset{\displaystyle CH_3}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{\cdot}{C}}{-}CH_3$$

or by the reaction

$$C_6H_{13}^- + C_6H_{13}Br \longrightarrow C_{12}H_{26} + Br^-$$

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Preparation of Organo-phosphines by the Addition of Phosphine to Unsaturated Compounds

BY A. R. STILES, F. F. RUST AND W. E. VAUGHAN

RECEIVED JANUARY 22, 1952

A series of organo-phosphines has been readily prepared by the free-radical sensitized addition of phosphine to a variety of unsaturated compounds. The products were mixtures of primary, secondary and tertiary phosphines, the relative amounts of each being dependent upon the original ratio of phosphine to unsaturate. Separation was effected by fractional distillation and identification was by the elemental analyses of the phosphines and their products of oxidation with nitric acid.

Since the demonstration by Kharasch and Mayo that hydrogen bromide will add "abnormally" to olefins by a free radical chain mechanism, a considerable number of compounds have been shown to follow an analogous path of addition.[1] It has now been found that phosphine can be added by photo- or peroxide-sensitization to unsaturated compounds. The reaction appears to parallel the addition of hydrogen sulfide to unsaturates[2] and affords an apparently generally applicable method for the synthesis of organo-phosphines. The sequence of steps, which can be initiated by radiation of certain frequencies, by organic peroxides and by other free radical sources, may be summarized as

$$R_2PH + (h\nu \text{ or } R') \longrightarrow R_2P + (H \text{ or } R'H)$$

$$R_2P + RCH{=}CH_2 \longrightarrow R_2PCH_2\overset{|}{C}HR$$

$$R_2PCH_2\overset{|}{C}HR + R_2PH \longrightarrow R_2PCH_2CH_2R + R_2P$$

$$R = \text{H, alkyl or substituted alkyl}$$

Photochemical initiation of these reactions is possible because phosphine absorbs radiation below about 2300 Å. and the primary step, which is reversible, is the formation of PH_2 and a hydrogen atom with a quantum efficiency of approximately 0.5.[3] Light of longer wave length is effective if a photosensitizer such as acetone is included in the reaction mixture. Di-*t*-butyl peroxide will also promote the addition of phosphine to olefins when the reaction is carried out at an elevated temperature.

Experimental

Phosphine was prepared in a vacuum line by heating anhydrous phosphorous acid at 200 to 210°, at which temperature the gas is smoothly evolved

$$4\ H_3PO_3 \xrightarrow{\text{heat}} 3\ H_3PO_4 + PH_3$$

The gas was passed through a trap immersed in Dry Ice to remove water vapor and collected by freezing with liquid nitrogen. The phosphine was then degassed several times

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[1] See F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[2] W. E. Vaughan and F. F. Rust, *J. Org. Chem.*, **7**, 472 (1942).

[3] W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 383–384.

to remove hydrogen and then stored in bulbs at approximately atmospheric pressure.

Method.—All manipulative operations involving phosphine were conducted on a vacuum line. Measured amounts of purified phosphine and unsaturate were successively withdrawn from calibrated reservoirs and condensed into small quartz or Pyrex bomb tubes. After the tubes were sealed off they were allowed to warm to room temperature in a screen for protection against explosion. Temperature was maintained approximately constant by flowing a stream of tap water over the tubes which were irradiated from a 360-watt General Electric Uviarc at a distance of about 25 cm. The progress of the reactions was followed by the decrease in liquid volume; runs were terminated when the rate of decrease became very slow and the tubes were then frozen in liquid nitrogen before opening.

TABLE I

SPEED OF ADDITION REACTION OF PHOSPHINE AND UNSATURATES

Unsaturated compound	Mole ratio of phosphine to unsaturate	Time of ultraviolet irradiation, hr.[a]	Volume change, %
1-Butene	1.0	2.5	22
1-Butene	0.33	6.5	24
Isobutene[b]	0.33	5.5	16
Cyclohexene	1.0	7.0	9
Allyl alcohol	1.0	1.3	23
Allylamine	0.5	5.0	22
Allyl chloride	0.5	6.0	9

[a] Time required for incremental volume change to become less than 1% per half hour. [b] This reaction was carried out in a Pyrex tube using 2.5 mole per cent. acetone as the sensitizer.

The products were transferred to a small distilling flask under an atmosphere of nitrogen gas, to prevent oxidation by air, and then fractionated through a small glass-spiral packed column. In most cases the various fractions were identified by elemental analysis as well as by analyses of the products obtained by oxidation with nitric acid. This was done stepwise, the organo-phosphine was first treated with cold 70%w. nitric acid and then with an excess of white, fuming nitric acid (96%w.), as otherwise the oxidation of the phosphine with fuming nitric acid is quite violent, usually resulting in flames and considerable spattering. Finally the mixture was cautiously heated on a steam-bath and the solid products isolated by evaporating the excess nitric acid and crystallizing the residue from alcohol, alcohol–water or heptane.

Results

The data of a number of experiments are summarized in Tables I, II and III. In the first the

TABLE II

THE PREPARATION OF ORGANIC PHOSPHINES BY THE PHOTO-SENSITIZED ADDITION OF PHOSPHINE TO UNSATURATED COMPOUNDS

Unsaturated compound, moles		Phosphine moles	Conversion[a] of PH_3, %	Products, phosphine	Yield, %	B.p., °C.	B.p., Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus % Calcd.	Phosphorus % Found
1-Butene	0.5	0.5	64	Butyl-	38	86.2–7.8		53.4	55.3	12.2	12.2	34.4	31.0
				Dibutyl-	10	181–5[b]		65.8	65.0	13.0	13.1	21.2	21.2
				Tributyl-	2	240.4–2.2[c]		71.3	62.7	13.4	12.4	15.3	15.4
1-Butene	0.28	0.09	100	Tributyl-	67	135–44	43[c]	71.3	70.6	13.4	13.5	15.3	15.3
Cyclohexene	0.15	0.15		Cyclohexyl-	34	146.8–9.4		62.1	58.8	11.2	10.7	26.7	25.8
Allyl alcohol	0.32	0.33	66	3-Hydroxypropyl-	26	79–85	32	39.1	38.6	9.8	10.2	33.7	32.2
				Bis-(3-hydroxypropyl)-	5	123–30	1	48.0	47.2	10.0	10.3	20.7	20.4
				Tris-(3-hydroxypropyl)-	3	196–8	1	51.9	51.6	10.1	10.4	14.9	15.6
Allylamine	0.16	0.08	83	3-Aminopropyl-	28	58.5–62	52	39.6	37.9	11.0	10.6	34.1	32.5
				Bis-(3-aminopropyl)-	20	162–8	36	48.7	46.4	11.5	11.2	20.9	20.5
				Tris-(3-aminopropyl)-	..	Bottoms		52.6	52.3	11.7	11.9	15.1	15.3

[a] Based upon the recovery of phosphine after the reaction had ceased. [b] B.p. 180–186°, C. Walling, U. S. Patent 2,437,795 (1948). [c] B.p. 149.5° (50 mm.), W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929). Tributylphosphine was also prepared in about 70% yield by heating in a sealed tube 0.15 mole of butene, 0.05 mole of phosphine and 2.5 mole per cent. of di-*t*-butyl peroxide at 122° for 16 hours. B.p. 144–146° (54 mm.); the carbon disulfide addition product had m.p. 65–66°; Davies and Jones, above, found m.p. 65.5°.

TABLE III

NITRIC ACID OXIDATION PRODUCTS OF ALIPHATIC PHOSPHINES

Product fractions, phosphine	B.p., °C.	Nitric acid oxidation product	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Equiv. wt. (strong acid) Calcd.	Equiv. wt. (strong acid) Found
Butyl-	86.2–87.8	Butanephosphonic acid	104–105[b]	34.8	34.7	8.0	8.1	22.5	22.4	138	140
Dibutyl-	181–185	Dibutanephosphinic acid	66–67[c]	54.0	53.5	10.7	10.8	17.4	16.4	178	179
Disobutyl-	78.0–79.6[a]	Isobutanephosphonic acid	123–124[d]	34.8	34.7	8.0	8.1	22.5	22.5	138	139
Isobutyl	169.6–171.8[a]	Diisobutanephosphinic acid	41–44[e]	54.0	53.8	10.7	10.7	17.4	17.4	178	177
Triisobutyl-	Residue of distillation	Triisobutylphosphine oxide	123–125	66.0	65.1	12.3	12.3	13.6	13.2	...	...
Cyclohexyl-	146.8–149.4	Cyclohexanephosphonic acid	160–161[f]	43.9	43.7	7.9	8.0	18.7	19.0	164	165
Dicyclohexyl-	Residue of distillation	Dicyclohexanephosphinic acid	140–141.5	62.6	62.0	10.0	10.0	13.5	12.6	230	233
3-Hydroxypropyl-	79–85 (32 mm.)	2-Carboxyethanephosphonic acid	160–161[g]	23.4	22.2	4.6	4.6	20.1	22.3	154	153
		3-Hydroxypropanephosphonic acid	Liquid	25.7	25.4	6.4	5.9	22.1	24.5	140	146
3-Chloropropyl-	Sublimate 125	3-Chloropropanephosphonic acid	95–97.5	22.7	22.8	5.1	5.3	19.6	19.5	161	158

[a] W. A. Hofmann, *Ber.*, **6**, 292 (1873), gives b.p. 62° for isobutylphosphine and b.p. 153° for diisobutylphosphine. [b] M.p. 103.5–104.0°, G. M. Kosolapoff, THIS JOURNAL, **67**, 1180 (1945). [c] M.p. 70.5–71°, G. M. Kosolapoff, *ibid.*, **71**, 369 (1949). [d] M.p. 124°, F. Guichard, *Ber.*, **32**, 1572 (1899). [e] Obtained as a liquid by W. A. Hofmann, *ibid.*, **6**, 303 (1873). [f] M.p. 166–167°, J. D. Clayton and W. L. Jensen, THIS JOURNAL, **70**, 3880 (1948). [g] M.p. 178–180°, P. Nylen, *Ber.*, **59**, 1119 (1926).

total volume changes for the reactions are tabulated, the time shown is the duration of illumination until the incremental volume change was less than 1% in a half hour. The only generalization which perhaps may be made is that the higher the ratio of phosphine to unsaturate, the faster the addition reaction takes place.

In Table II the reactant proportions for the various preparations and the products obtained together with the elemental analyses are summarized. The experiments with isobutene and allyl chloride are not included as no analytical data were obtained with the products of addition but only with the oxidation products. The figures given for the yields of the various products should be construed as indicating the order of the yields since handling losses were quite variable. The yield of 3-chloropropylphosphine was low even though the conversion of phosphine was 55%, as the main product was a hard insoluble phosphorus-containing polymer.

Table III summarizes the results of oxidizing the various phosphines with 96% nitric acid. In all cases but one, crystalline derivatives were prepared. It was found that nitric acid oxidized the carbon atom in the 3 position in 3-hydroxypropylphosphine to a carboxy group as well as oxidizing the phosphorus to a phosphonic acid group. However when this phosphine was treated with 30%w. hydrogen peroxide at 100° only the phosphorus atom was oxidized and 3-hydroxypropanephosphonic acid was obtained. The titration curves obtained during the course of the equivalent weight determinations gave further proof of the structures of the acids as all phosphonic acids gave two end-points, except 2-carboxyethanephosphonic acid which gave three, and all phosphinic acids gave one end-point.

EMERYVILLE, CALIFORNIA

[CONTRIBUTION FROM THE BUREAU OF MINES, PETROLEUM AND OIL-SHALE EXPERIMENT STATION]

Thermal Decomposition of Sulfur Compounds. I. 2-Methyl-2-propanethiol

BY C. J. THOMPSON, R. A. MEYER AND J. S. BALL[1]

RECEIVED NOVEMBER 19, 1951

2-Methyl-2-propanethiol was thermally decomposed in a quartz tube utilizing a flow method. The conditions (300–500° with exposure times of 10–120 seconds) employed in this study resulted in decompositions ranging from 0 to 97%. The predominant sulfur-containing decomposition product was hydrogen sulfide. In addition small amounts of elemental sulfur and residual sulfur were found. Isobutylene and isobutane were the major gaseous hydrocarbons produced. A free radical chain type decomposition mechanism is proposed.

2-Methyl-2-propanethiol was decomposed in a quartz tube under various conditions of time and temperature. The temperatures employed were 300, 350, 400, 450 and 500°, with residence times of 10 to 120 seconds. These conditions resulted in decompositions ranging from 0 to 97%. The decomposition at temperatures above 500°, where secondary reactions become preponderant, was not studied. Satisfactory sulfur balances were obtained, and results were found to be reproducible. Hydrogen sulfide, elemental sulfur, and residual sulfur (compounds unreactive to ordinary reagents) were found as decomposition products in addition to the gaseous hydrocarbons, isobutylene and isobutane. The amount of decomposition increased with each rise in temperature and/or time of exposure. Based on experimental evidence and supported by similar known reactions, a free radical decomposition mechanism is proposed.

Apparatus and Procedure

Materials.—The 2-methyl-2-propanethiol was 99.92 mole % pure, as determined by the freezing point method of Rossini.[2] All other reagents were C.P. grade or better.

Apparatus.—The decompositions were made in a 25-mm. o.d. quartz tube heated by a 3-unit Hevi Duty organic combustion furnace. The heated section of the furnace was 560 mm. in length and contained a 27-mm. i.d. copper tube which acted as a heat distribution jacket and also as a support for the reaction tube. The entire furnace was covered with an asbestos blanket 3 mm. in thickness. Individual temperature control on each of the 3 furnace units was achieved by the use of a 3-point Celectray controller employing chromel–alumel thermocouples located in recesses in the copper tube. The thermocouples were protected from the direct heat of the furnace elements by thin pads of asbestos. The entire furnace and reaction tube were inclined at an angle of 7.5° from the horizontal. The sample was fed into the upper end of the decomposition tube by a positive feed mechanism. This feed device consisted of a hypodermic syringe and an eccentric and rachet drive, the shaft of which pushed on the plunger of the syringe. The hypodermic needle attached to the syringe was inserted into the reaction tube through a neoprene stopper. The speed of the motor, the number of teeth engaged per revolution, and the size of the syringe were all variable. Feed rate was, therefore, variable from 0.04 to 1.75 g./min. A 125-mm. section of the reaction tube extending from the lower end of the furnace was packed with glass wool. Two slant-tube gas scrubbers (Fig. 1) were used in series at the exit end of the decomposition tube. These scrubbers each contained 100 ml. of 33% sodium hydroxide, which removed any hydrogen sulfide or thiol. This apparatus was designed to give complete gas scrubbing with very little back pressure. Test runs proved its ability to quantitatively remove hydrogen sulfide and thiol from the exit gases. Low-boiling hydrocarbons in the exit gases from the scrubbers were condensed in a trap cooled with a mixture of Dry Ice, carbon tetrachloride and chloroform. An A.S.T.M. Lamp Sulfur Apparatus, a Beckman Laboratory Model *p*H Meter, and a Consolidated Model 21-102 Mass Spectrometer were also used.

Procedure. (a) Temperature Calibration.—The temperature of the reaction tube was determined by a thermocouple placed equidistant from the walls of the tube. Readings were taken at 1-inch intervals and averaged to find the reported decomposition temperature. Temperature surge at any one point within the reaction tube was not greater than ±1.5°. All calibrations were made in an empty tube,

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[1] To whom inquiries regarding this article should be sent.

[2] F. D. Rossini, *Anal. Chem.*, **20**, 110 (1948).