[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

Derivatives of Phosphine Formed with Pyruvic Acid and Benzaldehyde[1]

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Crystalline derivatives of phosphine formed by acid-catalyzed reactions with pyruvic acid and benzaldehyde have been investigated and structural proposals have been made based on chemical and spectroscopic evidence.

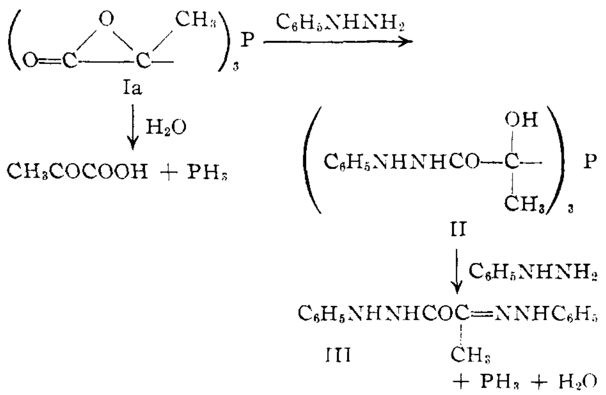
In a survey of the reactions of phosphine with various carbonyl compounds, Messinger and Engels prepared interesting crystalline derivatives with pyruvic acid and benzaldehyde.[2] Although they made some effort to determine the structures of these materials, particularly that of the pyruvic acid derivative, their results appear inconclusive. Because of our general interest in the addition of phosphine to aldehydes and ketones, we have reinvestigated these reactions.

The Phosphine–Pyruvic Acid Derivative (I).—By reaction of phosphine and pyruvic acid in ether in the presence of anhydrous HCl, Messinger and Engels obtained an almost quantitative yield of a compound (I) having the molecular formula $C_9H_9O_6P$, corresponding to the reaction of three molecules of pyruvic acid and one of phosphine with loss of three molecules of water.

$$3CH_3COCOOH + PH_3 \longrightarrow I + 3H_2O$$

These workers further observed: (1) that pyruvic acid and phosphine were recovered in 3:1 molar ratio when compound I was boiled in water, (2) that treatment of I with a limited amount of phenylhydrazine gave a crystalline phosphorus-containing derivative, II, and (3) that reaction of I with an excess of phenylhydrazine gave the phenylhydrazide–phenylhydrazone of pyruvic acid (III), phosphine and water.

From this evidence, Messinger and Engels concluded that the phosphine–pyruvic acid derivative had the tri-α-lactone structure Ia, and proposed the reactions

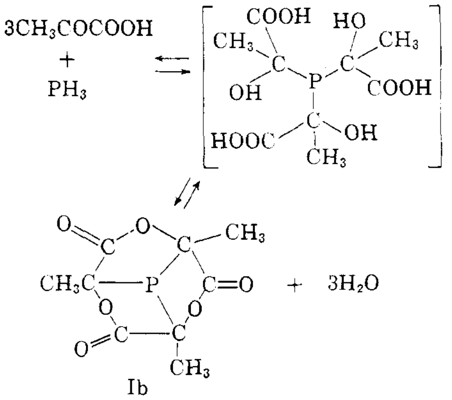


Ia

II

III

Although α-lactones have been postulated as intermediates in chemical reactions,[3] none have ever been isolated, presumably because of the strain associated with this structure.[4] Since there are no obvious features in structure Ia which would tend to stabilize the α-lactone grouping, this structure seems much less likely than that of the alternative formulation Ib, in which the ester groups are part of five-membered rings. This structure could result from normal phosphine–carbonyl addition followed by ring closure between carboxyl and hydroxyl groups attached to different pyruvic acid residues. Study of molecular models indicates that this structure is quite feasible. Furthermore, the evidence which Messinger and Engels adduced in favor of structure Ia supports Ib equally well.



Ib

Some additional evidence has been obtained which supports formulation Ib for the phosphine–pyruvic acid derivative. In the infrared (Fig. 1) a single band was present in the carbonyl region at 1784 cm.$^{-1}$ (5.61 μ). This is about where one would expect to observe the carbonyl absorption due to an ester group which is part of a five-membered ring. For example, γ-lactones give rise to carbonyl bands at 1770–1780 cm.$^{-1}$.[5] The fact that a single peak is observed indicates that the three ester groups are equivalent. The carbonyl absorption of β-propiolactone[5] is observed at 1841 cm.$^{-1}$ and α-lactones, if isolable, would be expected to absorb at still higher frequencies. This can be taken as evidence against structure Ia. The infrared spectrum showed no bands which might be attributed to other possible functional groups, *e.g.*, COOH or OH.

The n.m.r. spectrum of I dissolved in dimethylformamide was consistent with structure Ib in both the phosphorus and proton regions. The phosphorus spectrum showed a single peak with a chemical shift of +21 p.p.m. (relative to 85% H_3PO_4) which is in the range observed for tertiary phosphines. For example, triphenylphosphine, triethyl-

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(1) Presented in part at the 134th Meeting of the American Chemical Society in Chicago, Ill., September, 1958.

(2) J. Messinger and C. Engels, *Ber.*, **21**, 326, 2919 (1888).

(3) C. M. Bean, J. Kenyon and H. Philips, *J. Chem. Soc.*, 303 (1936).

(4) A recent paper describes an attempt to prepare an α-lactone by oxidation of ethylene oxide with the interesting oxidizing agent ruthenium tetroxide (L. M. Berkowitz and P. N. Rylander, THIS JOURNAL, **80**, 6682 (1958)).

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 186–188.

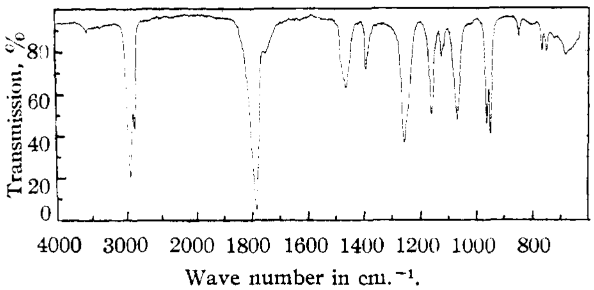
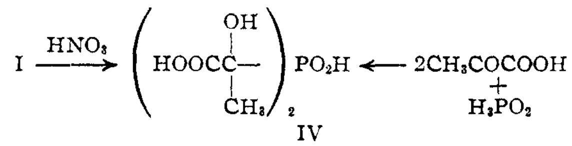


Fig. 1.—The infrared spectrum of the phosphine-pyruvic acid derivative, I (Nujol mull, Beckman IR 4 spectrophotometer).

phosphine and trimethylphosphine have chemical shifts of +8,[6] +20.4[7] and +62 p.p.m.,[6] respectively. The 40 mc. proton spectrum consisted of two sharp lines of equal intensity at +210 and +223 c.p.s. to the high field side of an external benzene reference. The two peaks arise from the methyl protons split by the P^{31} nucleus (spin $^1/_2$) and demonstrate the equivalence of all the hydrogens in this molecule. Furthermore, the splitting of 13 c.p.s. is consistent with the splitting observed between the phosphorus and β-hydrogens in several model compounds in this Laboratory.[8]

Additional chemical evidence also has been obtained in support of structure Ib for the phosphine–pyruvic acid derivative. Treatment with nitric acid gave an oxidative degradation product, bis-(1-carboxy-1-hydroxyethyl)-phosphinic acid (IV).

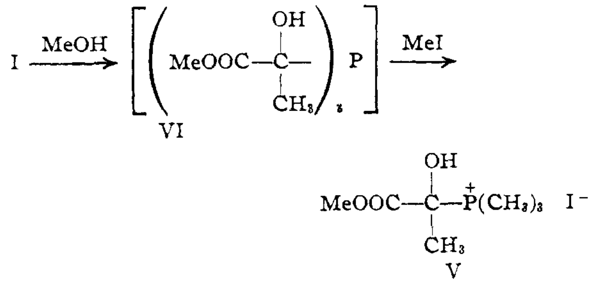


$$\mathrm{I} \xrightarrow{\mathrm{HNO_3}} \left(\mathrm{HOOC}\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\right)_2\mathrm{PO_2H} \longleftarrow \begin{matrix}2\mathrm{CH_3COCOOH}\\ +\\ \mathrm{H_3PO_2}\end{matrix}$$

IV

The structure of this material was established *via* independent synthesis by the reaction of pyruvic acid with hypophosphorous acid. This observation indicates that at least two of the pyruvic acid residues in I were formed by normal addition of phosphine to the carbonyl group. Since the spectroscopic data point to equivalence of the ester groups as well as the methyl groups in I, all three residues can be considered to be bonded in this fashion.

Some unanticipated observations were made when typical tertiary phosphine reactions were attempted with the phosphine–pyruvic acid derivative. Compound I failed to react with methyl iodide, sulfur or anhydrous peroxides in non-hydroxylic solvents. It also failed to display basic properties when titration was attempted with perchloric acid in nitromethane solution.[9] On the other hand, a reaction did occur when the phosphine–pyruvic acid derivative was treated with methyl iodide in methanol solution. The product obtained in 82% yield was 1-carbomethoxy-1-hydroxyethyltrimethylphosphonium iodide (V).



$$\mathrm{I} \xrightarrow{\mathrm{MeOH}} \left[\left(\mathrm{MeOOC}\text{—}\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\right)_3\mathrm{P}\right] \xrightarrow{\mathrm{MeI}}$$

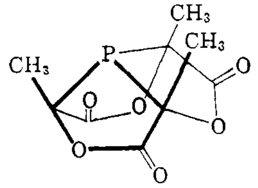
VI

$$\mathrm{MeOOC}\text{—}\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\text{—}\overset{+}{\mathrm{P}}(\mathrm{CH_3})_3\ \mathrm{I}^-$$

V

This phosphonium salt could arise from Ib by initial methanolysis of the γ-lactone groupings to give the trimethyl ester VI followed by successive quaternization with methyl iodide and elimination of methyl pyruvate until the stable iodide V is formed. It is evident that methanolysis precedes quaternization, since compound I was recovered nearly quantitatively when reaction with methyl iodide was attempted in 2-propanol and since only I and V were detected in a reaction in methanol which was interrupted before completion.

The absence of tertiary phosphine chemical properties in the phosphine–pyruvic acid derivative in non-hydroxylic solvents is not incompatible with structure Ib, since little is known about the reactivity of phosphines in which the phosphorus atom is part of a rigid, polycyclic system. The most favorable geometrical isomer of Ib is one in which the pyramidal phosphorus atom and the methyl groups are on the same side of a boundary defined by the lactone rings.



The methyl groups surrounding phosphorus would be expected to offer steric hindrance to attacking groups. Another possible explanation of this lack of phosphine properties takes into account the difference in geometry between trivalent and tetravalent forms of phosphorus derivatives.[10] The triply connected phosphorus compounds exhibit bond angles which tend to be more acute than those of the tetravalent compounds, which are more nearly tetrahedral. Thus, the lack of phosphine chemical properties in a rigid structure such as Ib could be due to the inability of phosphorus to change its bond angles. The fact that latent phosphine properties were uncovered by reaction with methyl iodide in the presence of methanol, a solvent which could cleave the rings at the ester linkages, tends to support this argument.

The Phosphine–Benzaldehyde Derivative (VII).—As in the case of the pyruvic acid derivative, a phosphine–benzaldehyde derivative was prepared by Messinger and Engels in ether solution con-

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[6] J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, THIS JOURNAL, **78**, 5715 (1956).

[7] N. Muller, P. C. Lauterbur and J. Goldenson, *ibid.*, **78**, 3557 (1956).

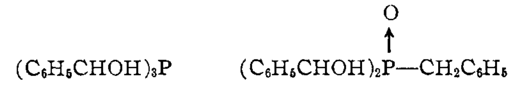
[8] J. E. Lancaster and W. G. Hodgson, unpublished observations. Protons on a carbon atom bonded directly to phosphorus were found to have a much smaller splitting.

[9] The author wishes to thank Dr. C. A. Streuli of this Laboratory for carrying out this experiment. The K_b of I is estimated to be $<10^{-16}$.

[10] J. R. Van Wazer, "Phosphorus and Its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, Vol. 1, pp. 14–15.

taining anhydrous HCl.[2] Their analytical data indicated that their product was formed from benzaldehyde and phosphine in 4:1 molar ratio. Further characterization was not attempted and no structural formula was given.

We carried out a reaction in ether saturated with HCl and obtained a material having a similar melting point, but our phosphine-benzaldehyde derivative (VII) was formed from the aldehyde and phosphine in 3:1 molar ratio. On the assumption that carbonyl addition had taken place in the normal way, we at first thought that this substance was tris-(α-hydroxybenzyl)-phosphine (VIIa); however,

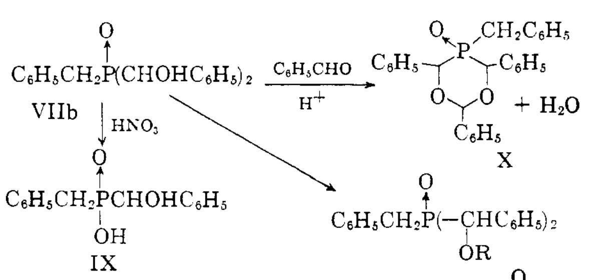


$(C_6H_5CHOH)_3P$ VIIa $\quad (C_6H_5CHOH)_2\overset{O\uparrow}{P}—CH_2C_6H_5$ VIIb

it soon became apparent that this was not the case. The evidence presented below demonstrates that this phosphine-benzaldehyde derivative is benzyl-bis-(α-hydroxybenzyl)-phosphine oxide (VIIb), the formation of which requires a transfer of oxygen from carbon to phosphorus.

The infrared spectrum of VII (Fig. 2) showed intense absorption at 1145 cm.$^{-1}$ which is in the region characteristic of the P→O group in tertiary phosphine oxides. For comparison, we prepared the closely related compound dibenzyl-α-hydroxybenzylphosphine oxide, $(C_6H_5CH_2)_2P(O)CHOHC_6H_5$ (VIII).[11] This material was found to have absorption at 1150 cm.$^{-1}$. The hydroxyl region of VII showed the presence of both hydrogen-bonded and non-bonded absorption. Miller, Miller and Rogers have found that the hydroxyl absorption in molecules having the part structure $P(O)C(OH)R_2$ occurs at 3050–3100 cm.$^{-1}$ indicating that hydrogen bonding is taking place.[12] The presence of both bonded and non-bonded forms in a molecule such as VIIb would not be surprising since two hydroxyl groups are present. The n.m.r. spectrum of VII dissolved in dimethylformamide showed a single peak with a chemical shift of −43 p.p.m. in the phosphorus region (relative to 85% H_3PO_4). By comparison, the phosphine oxide VIII showed a chemical shift of −41 p.p.m.

Chemical evidence favoring structure VIIb was obtained by oxidation and by preparation of hydroxyl derivatives. Treatment of the phosphine-benzaldehyde derivative with boiling 35% nitric acid led to the formation of benzyl-α-hydroxybenzylphosphinic acid (IX) in an oxidative cleavage reaction not unlike that observed with the phosphine-pyruvic acid derivative. Reaction of VII with benzaldehyde under conditions suitable for acetal formation gave a product in which a molecule of benzaldehyde had been incorporated with loss of a molecule of water. The cyclic structure X was assigned to this material, which was obtained as a mixture of stereoisomers, two of which were isolated in pure form by fractional crystallization. The diacetate XI and bis-(phenylurethan) XII derivatives were prepared by standard procedures.



XI, $R = CH_3\overset{O}{\overset{\|}{C}}-$
XII, $R = C_6H_5NH\overset{O}{\overset{\|}{C}}-$

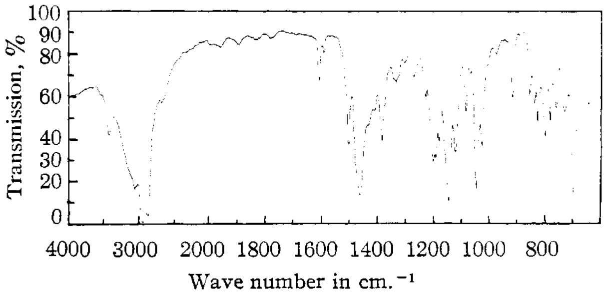
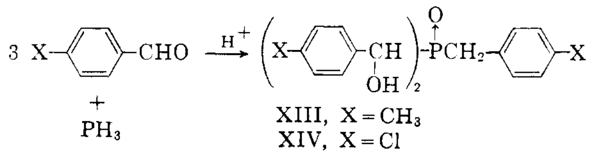


Fig. 2.—The infrared spectrum of the phosphine-benzaldehyde derivative, VII (Nujol mull, Beckman IR 4 spectrophotometer).

These reactions indicate that the phosphine-benzaldehyde derivative has two hydroxyl groups and that an unsubstituted benzyl group is present. A further indication that VII is not the ordinary type of phosphine-carbonyl derivative VIIa is its relative stability in alkali. This substance can be dissolved in 15% NaOH at room temperature and regenerated upon acidification. It is known that hydrogens on a carbon atom adjacent to a P→O group are somewhat acidic.[13] On the other hand, phosphine-carbonyl derivatives in which oxygen has not transferred from carbon to phosphorus are reported to be unstable in alkali,[2,14] the addition reaction tending to reverse under these conditions. However, when VII was boiled in alcoholic KOH solution, decomposition did occur. Benzaldehyde was liberated and the phosphorus was recovered in a mixture of organophosphorus acids. No phosphine was formed. This behavior is reminiscent of that reported for the related compound VIII in hot alkali.[11]

Two substituted benzaldehydes also have been treated successfully with phosphine to give the same type of dihydroxyphosphine oxide as is formed with benzaldehyde. It was found more convenient



to carry out these reactions in aqueous mineral acid solution rather than under anhydrous conditions. Yields of about 60% of the phosphine oxides VIIb, XIII and XIV were obtained from benzaldehyde, *p*-tolualdehyde and *p*-chlorobenzaldehyde. *p*-Ni-

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(11) R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, THIS JOURNAL, **79**, 424 (1957).

(12) C. D. Miller, R. C. Miller and W. Rogers, Jr., *ibid.*, **80**, 1562 (1958).

(13) L. Horner, H. Hoffmann and H. G. Wippel, *Ber.*, **91**, 61 (1958).

(14) A. Hoffman, THIS JOURNAL, **43**, 1684 (1921); **52**, 2995 (1930).

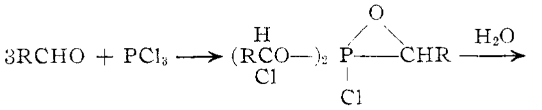
trobenzaldehyde, *p*-hydroxybenzaldehyde and 1-naphthaldehyde also reacted with phosphine under these conditions, but the only products isolated were amorphous solids from which no pure components could be obtained.

There are numerous examples of the transfer of oxygen[15] from carbon to phosphorus in the course of chemical reactions. Apparently the driving force in these reactions is the formation of the strong P→O bond. Some of these observations involve reactions with aldehydes and ketones. Litthauer found that heating benzaldehyde and phosphonium iodide in a sealed tube led to a mixture of tribenzylphosphine oxide, dibenzylphosphinic acid and benzylphosphonic acid.[16]

$$PH_4I + C_6H_5CHO \longrightarrow (C_6H_5CH_2)_3PO + (C_6H_5CH_2)_2PO_2H + C_6H_5CH_2PO_3H_2$$

Kosolapoff has pointed out that these products might have been formed by reduction of the hydroxyl groups formed from carbonyl addition by HI with subsequent air oxidation of the benzylphosphines.[17] Thus, this reaction may not involve the same type of oxygen transfer as the phosphine-benzaldehyde reaction.

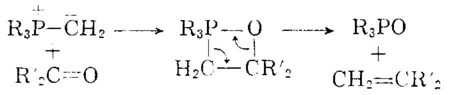
Phosphorus trichloride reacts with aldehydes to give 1:3 adducts,[18,19] but this reaction probably has only a superficial similarity to the phosphine-aromatic aldehyde reaction since apparently only one carbon-to-phosphorus bond is formed. Upon treatment with water, two moles of the aldehyde are recovered along with the hydroxyalkylphosphonic acid. Page[19] proposed XV as the structure of the phosphorus trichloride-aldehyde adduct.



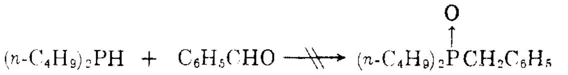
XV

$$\longrightarrow RCHOHPO_3H_2 + 2RCHO + 3\ HCl$$

Another example of transfer of oxygen from carbon to phosphorus in which a carbonyl group is involved is the Wittig reaction. In this reaction a phosphorus ylide is treated with an aldehyde or ketone to give an olefin and tertiary phosphine oxide. An intramolecular transfer of oxygen has been postulated.[20]



In the phosphine-aromatic aldehyde reaction we are not only faced with the problem of the mechanism of oxygentr ansfer but also with the stage of aldehyde substitution at which this transfer occurs. The reaction of dibutylphosphine with benzaldehyde was carried out in the hope that the oxidation-reduction phenomenon would be observed in a simpler system.



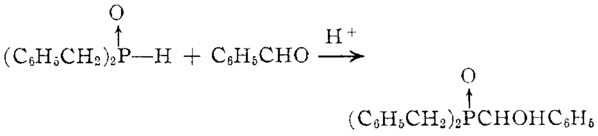
$$(n\text{-}C_4H_9)_2PH + C_6H_5CHO \not\longrightarrow (n\text{-}C_4H_9)_2\overset{O\atop\uparrow}{P}CH_2C_6H_5$$

This reaction did not occur. Instead, a quaternary phosphonium salt was formed of the type reminiscent of the phosphine-*n*-alkylaldehyde reactions.[2,14]

$$(n\text{-}C_4H_9)_2PH + 2C_6H_5CHO + HCl \longrightarrow (n\text{-}C_4H_9)_2\overset{+}{P}(CHOHC_6H_5)_2\ Cl^-$$

This suggests that a secondary phosphine may not be an intermediate in the phosphine-benzaldehyde reaction.

If the oxygen transfer step occurred at the first or second stage of benzaldehyde substitution, the secondary phosphine oxide, $C_6H_5CH_2\overset{O\ \ H}{\overset{\uparrow\ /}{P}}CHOHC_6H_5$, would be an essential intermediate. This would then have to react further with benzaldehyde under acidic conditions to give the observed product VIIb. However, only base-catalyzed reactions of aldehydes and secondary phosphine oxides have been reported in the literature. Accordingly, a model compound, dibenzylphosphine oxide, was treated with benzaldehyde in acidic solution. A 98% yield of the tertiary phosphine oxide VIII was obtained, somewhat higher than that reported under



$$(C_6H_5CH_2)_2\overset{O\atop\uparrow}{P}\text{—}H + C_6H_5CHO \xrightarrow{H^+} (C_6H_5CH_2)_2\overset{O\atop\uparrow}{P}CHOHC_6H_5$$

VIII

basic conditions.[11] Thus, a secondary phosphine oxide could well be an intermediate in the formation of the phosphine-benzaldehyde derivative. Further evidence bearing on this problem will be presented in a forthcoming publication.

Acknowledgment.—The author wishes to express his sincere appreciation to Drs. J. E. Lancaster and W. G. Hodgson for their assistance with n.m.r. studies, to Mr. S. E. Polchlopek for the infrared spectra, and to Mrs. E. C. Grim and associates for the microanalyses reported in this paper.

Experimental[21]

Preparation of the Phosphine-Pyruvic Acid Derivative (I).—The procedure employed was much the same as that described by Messinger and Engels,[2] with the major modifications being the apparatus and source of phosphine. The apparatus consisted of a phosphine generator and a reaction flask. The former was composed of a 3-necked flask fitted with a sealed stirrer, condenser and a dropping funnel. The latter consisted of a Morton flask fitted with a stirrer, a gas-inlet tube connected to the top of the condenser of the generator with an additional T-tube connection for an HCl inlet and an outlet tube leading to a trap filled with dry xylene. The trap outlet was connected to a tube leading to the hood exit. The generator was charged with 33 g. (0.57 mole) of aluminum phosphide and 100 ml. of dioxane in the flask and 150 ml. of water in the dropping funnel. A solution of 50 g. (0.57 mole) of commercial pyruvic acid in 350 ml. of anhydrous diethyl ether was placed in the reactor. The apparatus was swept thoroughly with nitrogen,

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[15] The phrase "transfer of oxygen" is a simple description of the oxidation-reduction phenomenon which occurs in the reaction of phosphine and benzaldehyde and in certain related reactions. It is not implied here that all these reactions occur by direct intramolecular transfer of oxygen from carbon to phosphorus.

[16] S. Litthauer, *Ber.*, **22**, 2144 (1889).

[17] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 109.

[18] W. Fossek, *Monatsh. Chem.*, **5**, 121 (1884); **7**, 20 (1886).

[19] H. J. Page, *J. Chem. Soc.*, 423 (1912).

[20] G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954).

[21] Melting points are uncorrected.

and phosphine was then generated and passed into the reactor over a 3-hour period along with fairly large quantities of dry HCl. A small rise in temperature was noted and Compound I began to separate after 1.5 hours. The mixture was allowed to stand for 3 days, then the product was collected and dried giving 35.0 g. (77%) of I, m.p. 270–272°. One recrystallization from acetic acid gave material of m.p. 273–274°. Compound I could be sublimed at atmospheric pressure without decomposition.

Anal. Calcd. for $C_9H_9O_6P$: C, 44.27; H, 3.72; mol. wt., 244.1. Found: C, 44.25; H, 3.71; mol. wt., 243.4 (ebullioscopic in acetone).

Bis-(1-carboxy-1-hydroxyethyl)-phosphinic Acid (IV). A. By the Oxidation of I with Nitric Acid.—A suspension of 0.75 g. (0.0031 mole) of I in 4 ml. of 35% nitric acid was prepared and warmed to 55° at which point a vigorous reaction took place, accompanied by dissolution. The solution was heated under reflux for 35 minutes and evaporated under reduced pressure. The residue which remained was recrystallized from acetic acid–petroleum ether to give 0.32 g. (43%) of IV, m.p. 144–145°. Further recrystallization from acetic acid raised the m.p. to 148–149°.

Anal. Calcd. for $C_6H_{11}O_8P$: P, 12.79; neut. equiv., 80.7. Found: P, 12.67; neut. equiv., 79.2.

The material readily forms a monohydrate upon exposure to air.

Anal. Calcd. for $C_6H_{11}O_8P \cdot H_2O$: C, 27.70; H, 5.04. Found: C, 27.71; H, 5.02.

B. From Pyruvic Acid and Hypophosphorous Acid.—A solution of 132 g. (1 mole) of 50% hypophosphorous acid and 176 g. (2 moles) of pyruvic acid was prepared and allowed to stand. The temperature rose gradually to a maximum of 62° in the course of 2 hours. After 7 days, the mixture had formed a semi-solid mass. The water was removed *in vacuo*, and the residue next recrystallized from acetic acid to give 121.6 g. (46%) of product. Further recrystallization gave material of m.p. 148–149° which was identical with that obtained by procedure A as shown by mixed melting point and a comparison of their infrared spectra.

1-Carbomethoxy-1-hydroxyethyltrimethylphosphonium Iodide (V).—A suspension of 3.0 g. (0.012 mole) of I in a solution of 15 ml. of methyl iodide and 60 ml. of anhydrous methanol was heated under reflux for 20 hours. The mixture became homogeneous after 2 hours. The solution was evaporated and the residue treated with 15 ml. of ethyl acetate. The solid was collected giving 3.1 g. (82%) of V, m.p. 118–119°. Recrystallization from 2-propanol gave the analytical sample, m.p. 120–121°.

Anal. Calcd. for $C_7H_{16}IO_3P$: C, 27.46; H, 5.27; P, 10.12. Found: C, 27.24; H, 5.28; P, 10.16.

This material showed hydroxyl (3325 cm.$^{-1}$) and ester (1750 cm.$^{-1}$) absorption in the infrared and gave a positive qualitative test for halogen. A foul odor characteristic of trimethylphosphine was noticed when V was dissolved in aqueous alkali.

Preparation of the Phosphine–Benzaldehyde Derivative (VIIb). A. Under Anhydrous Conditions.—A solution of 8.0 g. (0.075 mole) of benzaldehyde in 180 ml. of anhydrous ether was saturated with dry HCl and treated with phosphine in the apparatus described in method C. A gum was deposited which gave 1.2 g. (14%) of VIIb, m.p. 150–151°, when treated with ethanol. Recrystallization from ethanol gave the analytical sample, m.p. 152–153°.

Anal. Calcd. for $C_{21}H_{21}O_3P$: C, 71.58; H, 6.01; P, 8.79. Found: C, 71.57, 71.49; H, 6.24, 6.13; P, 8.79, 8.89.

B. Using Aqueous Hydrochloric Acid and Dioxane.—The apparatus used was much the same as that described for the preparation of I. The Morton flask was charged with a solution of 50 g. (0.48 mole) of benzaldehyde, 350 ml. of dioxane and 45 ml. of concentrated HCl. Phosphine was passed in for 2.5 hours and a rise in temperature to 40° was noted initially. The reaction mixture was evaporated *in vacuo* to give a viscous mass which was taken up in 80 ml. of hot ethanol. Upon cooling, 18.3 g. of VIIb was deposited, m.p. 152–153°. The filtrate was diluted with ether and allowed to stand for several days after which 15.3 g. of additional VIIb was collected (total yield 60%), m.p. 151–152°.

C. Using Aqueous Hydrochloric Acid.—This reaction was carried out in a standard Parr pressure reaction apparatus. A solution of 42.4 g. (0.4 mole) of benzaldehyde in 150 ml. of concentrated hydrochloric acid was prepared with cooling in a pressure bottle and the bottle was connected to the apparatus. The vessel was evacuated and filled with nitrogen a few times and finally filled with phosphine from the reservoir before shaking was started. The reaction was allowed to proceed under 2–3 atmospheres pressure until completed (55 minutes). A total of 0.13 mole of phosphine was taken up and a rise in temperature from 20 to 50° was noted in the course of the reaction. In removing the bottle from the apparatus, the evacuation and filling with nitrogen was repeated. The supernatant liquid was decanted from the gum which had deposited and the gum was washed with water and taken up in 100 ml. of boiling absolute alcohol. Upon cooling, 19.5 g. of VIIb was deposited, m.p. 152–153°. Water was added to the filtrate at 60° until a faint turbidity persisted. This solution deposited an additional 8.2 g. (total yield 59%) of VIIb, m.p. 150–152°.

Oxidation of VIIb with Nitric Acid.—A suspension of 3.0 g. (0.0085 mole) of VIIb in 16 ml. of 35% nitric acid was prepared and heated under reflux for 10 minutes. It was then cooled and diluted with 10 ml. of water giving an oil which crystallized on standing. The solid was collected and recrystallized from acetonitrile to give 0.93 g. (42%) of benzyl-α-hydroxybenzylphosphinic acid (IX), m.p. 180–182°. The analytical sample was prepared by recrystallization from acetic acid, m.p. 180–181°.

Anal. Calcd. for $C_{14}H_{15}O_3P$: C, 64.12; H, 5.77; P, 11.81; neut. equiv., 262.2. Found: C, 63.82; H, 5.74; P, 11.65; neut. equiv., 267.6.

Reaction of VIIb with Benzaldehyde.—A solution of 4 ml. of benzaldehyde, 15 ml. of dry benzene and a crystal of *p*-toluenesulfonic acid was prepared and 2.0 g. (0.0057 mole) of VIIb was added. This mixture was heated under reflux for 20 hours and the water formed was collected in a trap. The resulting solution was dried *in vacuo* and the residue taken up in ether. The solid present was collected giving 1.64 g. (66%) of 5-benzyl-2,4,6-triphenyl-1,3-dioxa-5-phosphacyclohexane-5-oxide (X), m.p. 176–195°, as a mixture of isomers. Two pure isomers were obtained by the following procedure: 1.40 g. of the mixture was treated with 50 ml. of boiling ethyl acetate and filtered. The residue (0.45 g.) was recrystallized twice from dioxane to give crystalline material of m.p. 220–222°.

Anal. Calcd. for $C_{28}H_{25}O_3P$: C, 76.35; H, 5.72; P, 7.03. Found: C, 76.32; H, 5.89; P, 7.15.

The ethyl acetate filtrate was cooled giving crystalline material of m.p. 172–182°. Further recrystallization from ethyl acetate or acetonitrile did not change the melting point; however, two recrystallizations from 2-propanol gave an isomer of X, m.p. 199.5–201°.

Anal. Found: C, 76.21; H, 5.61; P, 7.03.

Preparation of the Bis-(phenylurethan) of VIIb (XII).—A mixture of 7.04 g. (0.02 mole) of VIIb, 7.15 g. (0.06 mole) of phenyl isocyanate, 25 ml. of dry benzene and 2 drops of triethylamine was heated under reflux for 6.5 hours. The solid which deposited on cooling was collected and washed with benzene to give 7.1 g. (60%) of XII, m.p. 236–237° dec. Two recrystallizations from acetonitrile gave a product of m.p. 237–238° dec.

Anal. Calcd. for $C_{35}H_{31}N_2O_5P$: C, 71.17; H, 5.29; N, 4.74; P, 5.25. Found: C, 70.95; H, 5.28; N, 4.86; P, 5.34.

Preparation of the Diacetate Derivative of VIIb (XI).—A mixture of 2.0 g. (0.0057 mole) of VIIb, 0.5 g. of fused sodium acetate and 15 ml. of acetic anhydride was heated under reflux for 17.5 hours. The solution became dark red. It was poured on ice and stirred occasionally for 2 hours. The tan solid was filtered, washed with water and recrystallized from ethanol to give 1.96 g. (79%) of XI, m.p. 174–176°. The analytical sample, m.p. 177–178°, was prepared by repeated recrystallization from ethanol.

Anal. Calcd. for $C_{25}H_{25}O_5P$: C, 68.80; H, 5.77; P, 7.10. Found: C, 68.85; H, 6.19; P, 6.92.

Treatment of VIIb with Hot Alkali.—A solution of VIIb and potassium hydroxide in alcohol was refluxed for 1 hour. The solution was swept slowly with nitrogen and the gas was passed into a trap containing iodic acid solution. No iodine was liberated, indicating the absence of phosphine.

An acidic and a neutral fraction were recovered from this solution. Infrared examination indicated the former to be a mixture of organophosphorus acids and benzoic acid. The neutral fraction contained benzaldehyde and possibly benzyl alcohol. A 2,4-dinitrophenylhydrazone derivative of the aldehyde component had m.p. 235–236° alone and mixed with an authentic specimen of this derivative of benzaldehyde.

Reaction of Phosphine with *p*-Tolualdehyde.—This reaction was conducted as described for the preparation of VIIb, method C. A solution of 48 g. (0.4 mole) of *p*-tolualdehyde, 100 ml. of concentrated hydrochloric acid and 50 ml. of tetrahydrofuran was allowed to react with an excess of phosphine. The reaction was completed after 45 minutes. A temperature rise from 25 to 53° was observed and 0.14 mole of phosphine was taken up. Water (150 ml.) was added to the mixture and, after cooling to 0°, the supernatant liquid was decanted. The residual gum was thoroughly washed with water and triturated with 100 ml. of ethanol. The solid which formed was collected to give 24.6 g. of *p*-methylbenzylbis-(*p*-methyl-α-hydroxybenzyl)-phosphine oxide (XIII), m.p. 165–166°. An additional 4.5 g. was obtained from the aqueous and ethanolic filtrates (total yield 55%). The analytical sample was prepared by recrystallization from ethanol, m.p. 167–168°.

Anal. Calcd. for $C_{24}H_{27}O_3P$: C, 73.08; H, 6.90; P, 7.85. Found: C, 72.82; H, 6.94; P, 8.01.

Reaction of Phosphine with *p*-Chlorobenzaldehyde.—This reaction also was carried out by method C. A solution of 42 g. (0.3 mole) of *p*-chlorobenzaldehyde, 150 ml. of tetrahydrofuran and 40 ml. of concentrated hydrochloric acid was treated with phosphine. The reaction was completed in 50 minutes and a rise in temperature from 25 to 32° was noted. The resulting solution was concentrated *in vacuo* and the residue was washed thoroughly with water and recrystallized from ethanol to give 19.5 g. of (XIV) *p*-chlorobenzyl-bis-(*p*-chloro-α-hydroxybenzyl)-phosphine oxide, m.p. 163–165°. An additional 9.5 g. m.p. 162–164°, was obtained from the filtrates (total yield 64%). The analytical sample prepared by further recrystallization from ethanol had m.p. 165–166°.

Anal. Calcd. for $C_{21}H_{18}Cl_3O_2P$: Cl, 23.34; P, 6.80. Found: Cl, 23.06; P, 6.92.

Reaction of Dibutylphosphine with Benzaldehyde.—Dibutylphosphine (14.6 g., 0.1 mole) was added in a nitrogen atmosphere to a solution of 21.2 g. (0.2 mole) of benzaldehyde, 11 ml. of concentrated hydrochloric acid and 40 ml. of tetrahydrofuran in the course of 20 minutes. The solution then was heated under reflux for 1.5 hours. Most of the tetrahydrofuran now was distilled, and the residual liquid was added to a mixture of 100 ml. of water and 150 ml. of ether in a separatory funnel. A three-phase system resulted. The middle phase was separated and solidified when dried *in vacuo*. After washing with ether, 18.2 g. (46%) of dibutylbis-(α-hydroxybenzyl)-phosphonium chloride was obtained, m.p. 88–91°. Repeated recrystallization from ethyl acetate gave a sample of m.p. 96–98°.

Anal. Calcd. for $C_{22}H_{32}ClO_2P$: C, 66.90; H, 8.17; Cl, 8.98; P, 7.84. Found: C, 66.66; H, 8.29; Cl, 8.81; P, 7.99.

Acid-catalyzed Reaction of Dibenzylphosphine Oxide with Benzaldehyde.—A solution of 4.6 g. (0.02 mole) of dibenzylphosphine oxide (prepared by the method of Miller, Bradley and Hamilton[22]), 2.1 g. (0.02 mole) of benzaldehyde, 25 ml. of tetrahydrofuran and 5 drops of concentrated hydrochloric acid was allowed to stand at room temperature for 16 hours. The solution then was evaporated to dryness and the residue washed with ether and filtered to give 6.6 g. (98%) of dibenzyl-α-hydroxybenzylphosphine oxide (VIII), m.p. 161–163°. There was no depression of this melting point upon admixture with a specimen prepared by the base-catalyzed procedure[11] (reported yield, 85%).

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(22) R. C. Miller, J. S. Bradley and L. A. Hamilton, THIS JOURNAL, **78**, 5299 (1956).

STAMFORD, CONN.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY, SCHENECTADY, N. Y.]

Reactions of Active Nitrogen with Silane and Methylsilanes

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The reactions of silane and the methylsilanes with active nitrogen have been investigated at 28 and 250°. Hydrogen was the only volatile product obtained from silane, while the methylsilanes yielded hydrogen cyanide and ammonia, in addition to hydrogen. At 250° one mole of hydrogen cyanide was produced for each carbon atom in the silane consumed, but at 28° only approximately one-half the carbon was recovered as hydrogen cyanide. The ratio of ammonia to hydrogen cyanide was independent of temperature but increased with increasing methyl substitution. The results of this study indicate that the imine (NH) radical is not an important intermediate in ammonia formation. It is suggested that ammonia is formed directly by some sort of molecular process or that the amine (NH_2) radical is the intermediate.

The chemical reactions of active nitrogen with hydrocarbons and their derivatives have been studied extensively by a number of workers.[1,2] At the time this work was initiated, the only published work on silicon-containing molecules was a spectroscopic study of the reaction flame with $SiCl_4$.[3] In a recent note the results of a survey study of the reactions of active nitrogen with tetramethylsilane and some hydrocarbons were presented.[4] In all cases it was found that significant amounts of ammonia were formed.

The failure of other workers to observe ammonia has been cited as evidence that nitrogen atoms, alone of the electronegative atoms, do not attack hydrocarbons by hydrogen atom abstraction.[2] The fact that ammonia *is* formed raises the question of the importance of hydrogen abstraction by nitrogen atoms. In this connection it was of interest to examine the reactions of active nitrogen with compounds containing the Si–H bond since the low dissociation energy of this bond compared with the C–H bond should favor hydrogen atom abstraction. Accordingly, the reactions of active nitrogen with silane, SiH_4, and the methylsilanes CH_3SiH_3, $(CH_3)_2SiH_2$, $(CH_3)_3SiH$ and $(CH_3)_4Si$ have been investigated.

Experimental

The apparatus and procedure used in carrying out the reactions was similar to that described by Gartaganis and Winkler,[5] except that the discharge tube and reaction bulb

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(1) H. G. V. Evans, G. R. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

(2) K. R. Jennings and J. W. Linnett, *Quart. Rev.*, **12**, 116 (1958).

(3) S. C. Jevons, *Proc. Royal Soc. (London)*, **A89**, 187 (1914).

(4) H. A. Dewhurst, *J. Phys. Chem.*, **63**, 1976 (1959).

(5) P. A. Gartaganis and C. A. Winkler, *Can. J. Chem.*, **34**, 1457 (1956).