mol. wt., 1528. Found: C, 53.47; H, 2.50; N, 14.94; mol. wt., 1550 (in dioxane).

The remaining solid (X), with a melting point above 300° (turning brown around 230°), was insoluble in most organic solvents such as alcohol, ether, benzene, methylene chloride, dioxane, etc. The crude material gave the following elemental analysis.

Anal. Calcd. for $C_{26}H_{13}O_{11}N_7$: C, 52.08; H, 2.17; N, 16.36. Found: C, 51.48; H, 3.03; N, 16.14.

Upon cooling the forenamed aqueous solution, 0.5 g. (0.0025 mole, 5%) of an orange-red solid (IX) was isolated. It recrystallized from boiling water as shining red-orange needles, m.p. 249–250° dec. Infrared absorption from potassium bromide disk in cm.$^{-1}$ is: 650 w, 720 w, 732 w, 765 m, 775 m, 782 m, 813 m, 838 m, 845 m, 875 s, 930 s, 950 m, 990 w, 1050 w, 1095 m, 1115 m, 1172 s, 1205 m, 1265 m, 1290 s, 1310 s, 1400 s, 1455 w, 1495 w, 1570 s, 1615 s, 1633 m, 1670 m, 1692 s, 3060 m, 3300 s. The solid (IX) dissolved in 5% potassium hydroxide to give a red solution from which a red-orange solid was reprecipitated on acidification and was identified as IX by identical infrared absorption spectra.

Anal. Calcd. for $C_8H_6O_4N_2$: C, 49.47; H, 3.12; N, 14.43; mol. wt., 194. Found: C, 49.29; H, 3.10; N, 14.34; mol. wt., 197 (in water).

Concentration of the foregoing aqueous solution under vacuum to a small volume gave 2,6-pyridinedicarboxylic acid (XI) as a colorless solid, which recrystallized from water and was dried under vacuum at 100° for a few hours, m.p. 251–252° dec. (lit.[17] m.p. 252° dec.), 1.08 g. (12%), m.m.p. 251–252° dec.

Anal. Calcd. for $C_7H_5O_4N$: C, 50.21; H, 3.02; N, 8.38. Found: C, 50.10; H, 3.25; N, 8.35.

Dipicolinoylfuroxan (I) in Boiling Methanol and Hot Acetic Acid.—Dipicolinoylfuroxan (I) (0.3 g., 0.001 mole) in 50 ml. of boiling methanol gave a red solution from which red-black crystals separated, m.p. 195–196° dec. (pyridine odor). Formation of the product appears to take place more rapidly if the furoxan is initially moist. Infrared absorption of a sample in a potassium bromide disk gave no absorption near 1700 cm.$^{-1}$, the region characteristic of absorption for carbonyl groups. Purification of the product by thorough washing with methanol gave an analytical sample. Suitable solvents for recrystallization were not found; therefore, a molecular weight determination was not obtained.

Anal. Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found: C, 50.01; H, 3.10; N, 22.21.

The solid (0.2 g., 0.001 mole) from the previous experiment in 20 ml. of glacial acetic acid was heated to boiling. Upon cooling, a red-brown solid, m.p. 158–160° dec., was separated. Absorption from a potassium bromide disk of the product in the infrared at 1700 cm.$^{-1}$ confirmed the presence of a carbonyl group.

Anal. Calcd. for $C_8H_5O_3N_3$: C, 50.26; H, 2.64; N, 21.99. Found: C, 50.47; H, 3.03; N, 22.32.

Reaction of Dipicolinoylfuroxan (I) with Phenylhydrazine.—One gram (0.003 mole) of I was slowly added to 5 ml. of phenylhydrazine. The mixture was kept around 22° in order to prevent a violent reaction. After the addition was completed, the mixture was allowed to warm to 35° until evolution of gas had ceased. The reaction mixture was poured into a large volume of water. After decanting the water layer, the residue was recrystallized from ethanol in two fractions. One fraction of colorless needles, 0.3 g., m.p. 184–185°, was identified as 1-picolinoyl-2-phenylhydrazine (II) by mixture melting point with an authentic sample with no depression. Infrared absorption from a potassium bromide disk (in cm.$^{-1}$) is: 675 s, 695 s, 750 s, 820 m, 875 m, 920 s, 973 w, 1000 s, 1030 w, 1050 m, 1075 w, 1095 m, 1100 s, 1160 w, 1180 m, 1185 w, 1248 s, 1255 m, 1290 m, 1310 m, 1325 m, 1435 s, 1470 s, 1490 s, 1530 s, 1570 w, 1600 s, 1655 s, 1925 w, 3200 s.

Anal. Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.80; H, 5.11; N, 19.62.

A second fraction was isolated as a red solid, 0.1 g., m.p. 188–189° dec., and was identified as 3-(β-phenylhydrazino)-4-nitroso-5-α-pyridylisoxazole (III). Infrared absorption from a potassium bromide disk in cm.$^{-1}$ is: 640 m, 680 m, 750 s, 786 s, 880 m, 983 s, 1030 w, 1075 m, 1100 w, 1148 s, 1185 w, 1235 s, 1285 m, 1337 w, 1400 s, 1350 w, 1505 s, 1530 w, 1565 w, 1600 s, 3400 m.

Anal. Calcd. for $C_{14}H_{11}O_2N_5$: C, 59.78; H, 3.94; N, 24.90. Found: C, 59.87; H, 3.63; N, 24.41.

Dipicolinoylfuroxan picrate was obtained from picric acid in methanol. It recrystallized from methanol as yellow needles, m.p. 140–141°.

Anal. Calcd. for $C_{14}H_8O_4N_4 \cdot 2C_6H_3O_7N_3$: C, 41.39; H, 1.87; N, 18.57. Found: C, 40.79; H, 1.87; N, 18.88.

Reaction of Di(6-acetylpicolinoyl)furoxan (V) with Phenylhydrazine.—One gram of the furoxan was suspended in 5 ml. of phenylhydrazine in a small flask and shaken until an exothermic reaction began. This was noted by the evolution of gas. The flask was allowed to cool slowly to room temperature. The reaction mixture was then poured into a large volume of water. After decanting the water layer, the residue was fractionally crystallized from ethanol to yield two fractions, 0.40 g. (0.00096 mole, 37%) which melted at 200–201° dec., and 0.1 g. (0.00028 mole, 11%) which melted at 180–181°.

The red material, melting at 200–201° dec., appears to be 2-[3-(β-phenylhydrazino)-4-nitroso-5-isoxazolyl]-6-acetylpyridine phenylhydrazone (VII), which would be analogous to the product obtained by Quist[9] from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{22}H_{19}O_2N_7$: C, 63.92; H, 4.60; N, 23.72. Found: C, 64.19; H, 4.84; N, 23.42.

The yellow material, melting at 180–181°, appears to be 2-(2-phenylhydrazino-formyl)-6-acetylpyridinephenylhydrazone (VI), which would be analogous to a second product Quist[9] isolated from the reaction of dibenzoylfuroxan with phenylhydrazine.

Anal. Calcd. for $C_{20}H_{19}ON_5$: C, 69.54; H, 5.55; N, 20.28. Found: C, 69.62; H, 5.74; N, 20.63.

Reaction of IX with Phenylhydrazine.—Applying the preceding procedure for the combination of phenylhydrazine with IX with the exception that heating was applied in order to start the reaction, a red solid was obtained which recrystallized from ethanol, m.p. 240–242° (sublimation around 200°).

Anal. Calcd. for $C_{14}H_{11}O_3N_3 \cdot H_2O$: C, 58.33; H, 4.52; N, 14.63. Found: C, 58.46; H, 4.84; N, 14.79.

Reaction of VIII with Phenylhydrazine.—In the same manner as the reaction with IX, the exception that VIII was added slowly to phenylhydrazine, a mixture of solids was obtained. One pure red solid was isolated and identified as 2-[3-(β-phenylhydrazino)-4-nitro-5-isoxazolyl]-6-acetylpyridine phenylhydrazone (VII) by its identical infrared absorption with a product from V and phenylhydrazine.

Reaction of Di(6-acetylpicolinoyl)furoxan (V) with 2,4-Dinitrophenylhydrazine.—A solution of 0.1 g. (0.00026 mole) of V in 25 ml. of methanol was heated to boiling while a solution of 0.25 g. (0.00126 mole) of 2,4-dinitrophenylhydrazine in 25 ml. of methanol was added. Upon addition of a few drops of concentrated hydrochloride, the yellow bis-2,4-dinitrophenylhydrazone derivative precipitated immediately. The solid was separated and recrystallized from nitromethane, m.p. 231–232° dec., 0.15 g. (76%). Infrared absorption from potassium bromide disk (in cm.$^{-1}$) is: 650 w, 725 s, 745 m, 760 m, 835 m, 920 m, 945 m, 995 m, 1055 w, 1100 w, 1135 w, 1160 w, 1220 w, 1240 w, 1265 m, 1310 m, 1335 m, 1378 m, 1460 s, 1500 m, 1570 w, 1590 w, 1610 m, 1695 s, 2895 s.

Anal. Calcd. for $C_{30}H_{20}O_{12}N_{12}$: C, 48.65; H, 2.72; N, 22.70. Found: C, 48.45; H, 3.20; N, 22.41.

Acknowledgment.—The author wishes to thank Drs. J. H. Boyer and F. E. Brinckman for helpful discussion and reading of the manuscript.

Reaction of Lithium Diphenylphosphide and Carbonyl Compounds

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Although alkali metal organophosphides are known to react with aldehydes and ketones, in no case has the

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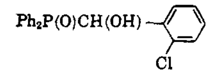
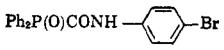
(17) I. Heilbron, ref. 12, Vol. II, p. 436.

TABLE I[a]

	Product	Carbonyl reactant	Yield, %	M.p., °C.	Formula	% C Calcd. (found)	% H Calcd. (found)	% P Calcd. (found)	% N Calcd. (found)	% X Calcd. (found)
I	$Ph_2P(O)CH(OH)Ph$[b]	Benzaldehyde	50	177–178	$C_{19}H_{17}PO_2$	74.03 (74.13)	5.52 (5.51)			
II	$Ph_2P(O)C(OH)Ph_2$	Benzophenone	50	173–174	$C_{25}H_{21}PO_2$	78.10 (78.56)	5.46 (5.52)	8.06 (7.98)		
III	$Ph_2P(O)C(OH)(CH_2)_5$	Cyclohexanone	65	165–166	$C_{18}H_{21}PO_2$	72.0 (72.29)	7.00 (7.06)	10.35 (10.44)		
IV		o-Chlorobenz-aldehyde	65	196–198	$C_{19}H_{16}PO_2Cl$	66.60 (66.30)	4.67 (4.63)	9.05 (8.85)		10.35 (Cl) (10.28)
V	$Ph_2P(O)CONHPh$[c]	Phenyl isocyanate	60	163–164	$C_{19}H_{16}PO_2N$	1.00 (71.05)	4.99 (5.09)	9.68 (10.67)	4.36 (4.38)	
VI	$Ph_2P(O)CONHBu$[c]	Butyl isocyanate	65	107-108	$C_{17}H_{20}PO_2N$	67.80 (68.07)	6.65 (6.77)	10.3 (10.10)	4.65 (4.73)	
VII		p-Bromophenyl isocyanate	55	191–192	$C_{19}H_{15}PO_2NBr$	57.00 (57.05)	3.75 (3.77)	7.75 (7.86)	3.50 (3.52)	19.90 (Br) (19.89)
VIII	$Ph_2P(O)CONHC_2H_5$	Ethyl isocyanate	65	162.5–163	$C_{15}H_{16}PO_2N$	66.00 (65.74)	5.86 (5.48)	11.35 (11.75)	5.14 (5.37)	

[a] The yields are based on triphenylphosphine used in the formation of the phosphide. [b] This compound was characterized by melting point, mixture melting point, and infrared spectral comparison with known material (R. C. Miller, C. D. Miller, W. Rogers, Jr., and L. A. Hamilton, *J. Am. Chem. Soc.*, **79**, 424 (1957). [c] See ref. 5.

isolation of an (α-hydroxy)-*t*-phosphine oxide been reported.[3] The establishment of an equilibrium between a metal ketyl and adduct has been postulated.[4] Furthermore, the structure of the adduct has been concluded not to be that of the salt of an α-hydroxy-*t*-phosphine.[4]

We now report the isolation of (α-hydroxy)-*t*-phosphine oxides from the reaction of a tetrahydrofuran solution of lithium diphenylphosphide and lithium chloride with aldehydes and ketones followed by treatment with dilute hydrogen peroxide.

$$Ph_2PLi + RCOR' \longrightarrow [Ph_2PC(O)RR']Li \xrightarrow[H_2O_2]{H_2O} Ph_2P(O)C(OH)RR'$$

We also have found that lithium diphenylphosphide reacts with alkyl and aryl isocyanates under the same conditions to afford N-substituted diphenylcarbamoylphosphine oxides.[5]

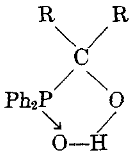
$$Ph_2PLi + RNCO \longrightarrow (Ph_2PC(O)NR)Li \xrightarrow[H_2O_2]{H_2O} Ph_2P(O)C(O)NHR$$

These results are summarized in Table I.

The lithium diphenylphosphide solution was prepared by the cleavage of triphenylphosphine with lithium followed by addition of *t*-butyl chloride to remove the phenyllithium.[6]

These reactions are essentially additions of lithium diphenylphosphide across a carbonyl group followed by protonation of the alkoxide or amide ion and oxidation of the phosphine. The presence of lithium chloride may help affect the addition by coordination with the carbonyl oxygen and stabilization of the addition compound. However, no substantial difference in yield of product was found between normal and inverse addition in the case of cyclohexanone. In the isolation of product, oxidation converts the apparently unstable (α-hydroxy)-*t*-phosphine to the more stable oxide.[7] Further work is being carried on to elucidate the mechanism of these additions.

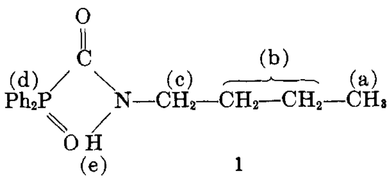
The infrared spectra of the products obtained from the aldehydes and ketones showed peaks at 2.8 and 3.0 (broad) μ (assigned to "free" and hydrogen-bonded hydroxyl groups). These peaks did not seem to change much upon dilution of the sample indicating some intramolecular hydrogen bonding.



No peaks between 5.5 and 6.1 μ (region of carbonyl absorption) could be detected in these compounds. A peak at 7.0 μ (indicative of a phenyl to phosphorus bond) and peaks in the regions of 8.5 (phosphoryl group) and 9.0 μ indicated the presence of the diphenylphosphine oxide moiety.

All of the isocyanate reaction products gave infrared spectra displaying strong, sharp bands in the 6.0–6.1-μ region indicative of a carbonyl conjugated with a strongly electron-donating group.[5] The sharp peak at 3.0 μ was assigned to the NH group, while the bands at 7.0 μ and in the 8.5 and 9.0-μ regions indicated the presence of the diphenylphosphine oxide moiety.

Proton n.m.r. spectra were obtained for the carbamoyl compounds on a Varian A60 instrument at 60 Mc. Solutions of the compounds in deuteriochloro-



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(2) National Science Foundation Undergraduate Research Participant.

(3) K. Issleib, *Z. Chem.*, **2**, 1963 (1962).

(4) K. Issleib and A. Tzschach, *Ber.*, **92**, 1397 (1959).

(5) R. C. Schulz and H. Hartmann, *Monatsh.*, **93**, 905-910 (1962).

(6) A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, **27**, 1001 (1962).

(7) H. Hoffmann, *Angew. Chem.*, **72**, 77 (1960).

Table II

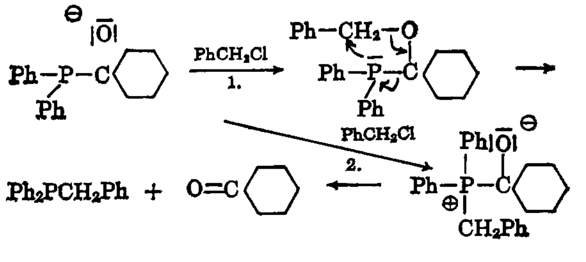
Multiplet centers, p.p.m.		Assignment, cf. 1	Relative area
0.85	Multiplet	a	3
1.4	Multiplet	b	4
3.2			
3.32		c	2
3.42			
3.55			
7.45	Multiplet	d	10
7.85	Multiplet		
8.64		e	1

form and an internal standard of tetramethylsilane were employed. The spectrum for the butyl derivative VI with peak assignments and relative integrated areas are summarized in Table II. The quartet in the region centering at 3.37 p.p.m. is indicative of the NH and CH_2 groups adjacent to this methylene.

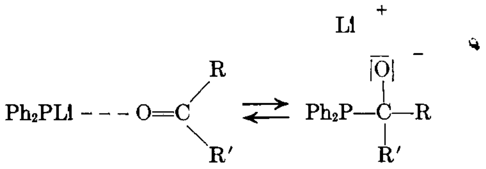
Essentially similar results were obtained with the ethyl derivative VIII. Spectra of the phenyl V and p-bromophenyl VII compounds showed signals only in the area assigned to phenyl protons. In the latter compounds the NH proton resonance appeared further downfield than in the aliphatic derivates, falling at 10.3 p.p.m. and 10.9 p.p.m., respectively. This is in agreement with the decrease in shielding expected on replacement of aliphatic by aromatic substituents and substitution in the ring by elctronegative atoms.

Both classes of compounds exhibit pyrolytic decomposition and facile hydrolytic cleavage in hot aqueous base. Diphenylphosphinic acid is obtained by either path from both types of compound. The thermal behavior of the p-bromophenylcarbamoyl compound indicates a stepwise path proceeding through a higher melting solid.

In the reaction of cyclohexanone and o-chlorobenzaldehyde an attempt at "capturing" the suspected intermediate (lithium salt of an α-hydroxy-t-phosphine) by reaction with benzyl chloride or bromide to form the benzyl ether of an α-hydroxy-t-phosphine resulted in the isolation of sizable amounts of benzyldiphenylphosphine oxide. This compound may have arisen through reaction of the benzyl halide with the type of adduct postulated by Issleib[4] or by reaction with the α-hydroxy-t-phosphine salt followed by decomposition or rearrangement.



Since the temperature was never allowed above 40° in the reaction of the benzyl bromide with the adduct of lithium diphenylphosphide and o-chlorobenzaldehyde, it seems unlikely that an ether formed by path 1 (see above) should rearrange. Perhaps a mobile equilibrium exists between the "normal" adduct and a coordination complex of lithium diphenylphosphide with the carbonyl compound.



Experimental

Preparation of Lithium Diphenylphosphide.—A suspension of 26.2 g. (0.1 mole) of triphenylphosphine, 200 ml. of dry tetrahydrofuran, and 1.4 g. (0.2 g.-atom) of lithium metal strips was stirred rapidly at room temperature under nitrogen for 3 hr., during which time most of the lithium dissolved exothermically producing a deep red solution. The phenyllithium was destroyed by the addition of 9.3 g. (0.01 mole) of t-butyl chloride at reflux followed by a 15-min. reflux period. After cooling to ambient temperature, the reaction mass was transferred under a nitrogen atmosphere to a dropping funnel.

Reaction of Carbonyl Compounds with Lithium Diphenylphosphide.[8] **Method A (Normal Addition).**—The solution of lithium diphenylphosphide was added rapidly to a flask under nitrogen, leaving the unchanged lithium in the dropping funnel, and a solution of the carbonyl compound in THF was added dropwise to the refluxing lithium diphenylphosphide solution.

Method B (Inverse Addition).—The solution of lithium diphenylphosphide was added dropwise to a refluxing solution of the carbonyl compound in THF.

Method C (Normal Addition at 20°).—The procedure described under method A was followed, but the lithium diphenylphosphide solution was kept at 20° during the addition.[9]

The color of the phosphide solution was always discharged giving way either to colorless suspension or to a variety of colors depending on the reactant and time after addition. Notable was the final deep blue color obtained in the benzophenone case showing the presence of metal ketyl. After refluxing for 2–3 hr. (except in the case of o-chlorobenzaldehyde), the reaction mass was allowed to return to room temperature under nitrogen and then added to 2 l. of water containing 300 ml. of 3% hydrogen peroxide solution.[10] After standing for 12 hr. in some cases a white solid was obtained, while in other cases an oil settled out of the emulsion. After separation from the supernatant aqueous layer, the oil usually yielded the solid product by trituration with ether. Acidification of the basic supernatant aqueous layer led to the precipitation and isolation of diphenylphosphic acid.

Acknowledgment.—We are grateful to Research Corporation and National Science Foundation for their generous support of this work. We wish to thank the Esso Research Center, Linden, New Jersey, for the n.m.r. work on the carbamoyl compounds.

[8] Method A was used in all cases except that of o-chlorobenzaldehyde. Method B was used only in the reaction of cyclohexanone. Method C was used only in the reaction of o-chlorobenzaldehyde.

[9] Aryl halides have been found to react with lithium diphenylphosphide: A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, **28**, 2091 (1963).

[10] Addition of the reaction mass to an acidic aqueous peroxide solution did not seem to increase the yield of product.

Pyrolysis Studies. IX.[1] Rates and Mechanism of Thermal Decomposition of Phenyl and Benzyl Ethyl Carbonates

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Carbonates containing at least one β-hydrogen atom are known to decompose at elevated temperatures to