material, m.p. 118–120°, which could not be dried *in vacuo* without decomposition.

*Anal.* Calcd. for $C_{16}H_{17}POS$: C, 65.19; H, 6.20; S, 11.60. Found: C, 65.11; H, 6.99; S, 11.25.

**Bis(2 - cyanoethyl) - 1 - hydroxy - 1 - methylethylphosphine Sulfide.**—Following the procedure above, 14.0 g. (0.1 mole) of bis(2-cyanoethyl)phosphine and 3.2 g. (0.1 g.-atom) of sulfur interacted in 60 cc. of acetone to produce 16.1 g. (70%) of crude product. Recovery of material melting at 113–115° from benzene was 40%.

*Anal.* Calcd. for $C_9H_{15}N_2OPS$: C, 46.94; H, 6.57; N, 12.17; P, 13.45; S, 13.93. Found: C, 46.92; H, 6.51; N, 12.27; P, 13.39; S, 13.88.

**Dibutyl-α-hydroxybenzylphosphine Sulfide.**—A mixture of 2.0 g. (0.11 mole) of Ia, 1.2 g. (0.11 mole) of benzaldehyde, and 5 drops of triethylamine was allowed to react exothermically before adding 2 cc. of benzene and heating at reflux 3 hr. Removal of solvent left 2.5 g. (83%) of product, melting at 54–55° on recrystallization from heptane. A similar uncatalyzed reaction produced 2.9 g. (95%) of product in 2 days.

*Anal.* Calcd. for $C_{15}H_{25}POS$: C, 63.35; H, 8.86; S, 11.27. Found: C, 63.56; H, 8.98; S, 11.49.

**Dibutyl-1-hydroxy-2,2,2-trichloroethylphosphine Sulfide (XI).**—A third method of preparation is illustrated by the dropwise addition of 8.0 g. (0.055 mole) of dibutylphosphine at 25–30° to a slurry of 2.0 g. (0.06 g.-atom) of sulfur and 10.5 g. (0.07 mole) of chloral in 90 cc. of benzene. The mixture was heated briefly to 40° after the exotherm subsided. Unchanged sulfur (0.2 g.) was filtered, and the filtrate was stripped under reduced pressure to 21 g. (85% solution, maximum) of yeasty-smelling liquid to be used in the rearrangement below.

**Rearrangement of XI. Method A. Base-Catalyzed.**—The crude residue above, containing a maximum of 17.9 g. (0.055 mole) of XI, was dissolved in 20 cc. of methanol containing a trace of hydroquinone. A solution of 3 g. (0.055 mole) of sodium hydroxide in 16% aqueous methanol was added dropwise at 10°. After overnight stirring, 1.2 g. of sodium chloride was filtered and the neutral filtrate was stripped to $^1/_3$ volume, diluted with 75 cc. of ice water, and extracted with 125 cc. of methylene chloride. After drying over sodium sulfate, the extract was distilled to obtain a main fraction, 4.1 g., b.p. 145–152°/1 mm., containing by infrared and elemental analysis approximately 80% *O*-1,1-dichlorovinyldibutylthiophosphinate and 20% *O*-chloroethynyl dibutylthiophosphinate.

*Anal.* Calcd. for $C_{10}H_{19}PSOCl_2$: C, 41.53; H, 6.62; Cl, 24.52; P, 10.71. Found: C, 42.66; H, 7.61; Cl, 22.14; P, 11.03.

Separation by vapor phase chromatography gave a major fraction of mass 260 (theory 289) with two chlorine atoms. (Infrared analysis indicated some decomposition during the chromatographic separation.) NMR proton analysis of the original distillate showed the presence of a singlet H, in addition to the butyl grouping. Use of 2 moles of base per mole of XI produced material of approximately the same composition.

**Method B. Thermal.**—Distillation of 3.3 g. of XI gave a fraction, 0.3 g. b.p. 145–150°/0.25 mm., richer in the chloroethynyl ester. NMR analysis did not detect any H singlet, but elemental analysis suggested about 16% of the dichlorovinyl ester was present.

*Anal.* Calcd. for $C_{10}H_{18}PSOCl$: C, 47.52; H, 7.18; Cl, 14.03; S, 12.69. Found: C, 46.73; H, 8.18; Cl, 15.49; S, 12.22.

**Acknowledgment.**—For the analyses and interpretations thereof, the author is indebted to the following: infrared spectra, Mr. N. B. Colthup; mass spectra, Mr. A. H. Struck; NMR spectra, Dr. J. R. Lancaster; vapor phase chromatography, Dr. R. Feinland; and microanalyses, Dr. J. A. Kuck. For his constructive suggestions, we are also grateful to Dr. S. A. Buckler.

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# Reactions of Diethyl Phosphorochloridite with Alkali Salts of Nitroparaffins

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Reactions of alkali salts of primary nitroparaffins with diethyl phosphorochloridite gave nitriles and diethyl hydrogen phosphate as the main products. On the other hand, when the sodium salt of 2-nitropropane was treated with diethyl phosphorochloridite, diethyl isopropylideneaminophosphate was obtained. Further, benzanilide was formed by the Beckmann rearrangement of the product from the reaction of the potassium salt of diphenylnitromethane and diethyl phosphorochloridite.

It was confirmed that the trivalent phosphorus of the initially formed condensation product, nitronic ester, was readily converted into the pentavalent phosphorus of the iminophosphate.

The preceding papers have described intramolecular dehydrations of primary nitroparaffins into nitrile oxides by means of isocyanates,[1] carbodiimides, and acetylenic ethers.[2]

In the present study, dehydrations of primary nitroparaffins with diethyl phosphorochloridite were tried first on the assumption that such compounds, reacting violently with water, were effective dehydrating reagents. It was expected that nitrile oxides and diethyl phosphorate would be formed *via* condensation compounds of *aci*-nitroparaffins and diethyl phosphorochloridite.

Contrary to our expectation, dehydrated products could not be obtained when diethyl phosphorochloridite was treated with the potassium salt of phenylnitromethane in boiling ether. Instead,

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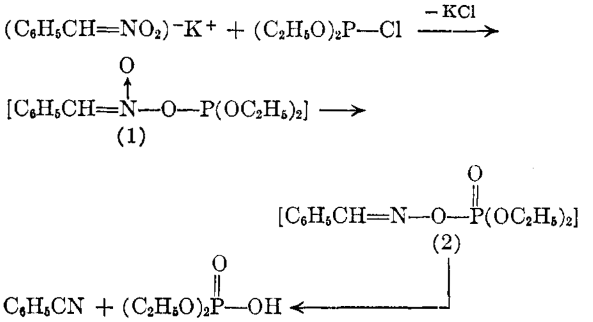
[1] T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, **82**, 5339 (1960).

[2] T. Mukaiyama and T. Hata, *Bull. Chem. Soc. Japan*, **33**, 1382 (1960).

after removal of potassium chloride, benzonitrile (49% yield) and phenylnitromethane (27% yield) were obtained by distillation and a tarry residue remained. Diethyl hydrogen phosphate (35% yield) was isolated as the lead salt from the tarry product.



$$(C_6H_5CH{=}NO_2)^-K^+ + (C_2H_5O)_2P{-}Cl \xrightarrow{-KCl} \underset{(1)}{[C_6H_5CH{=}\overset{O}{\overset{\uparrow}{N}}{-}O{-}P(OC_2H_5)_2]} \longrightarrow$$

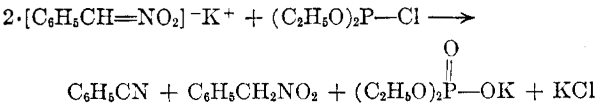
$$\underset{(2)}{[C_6H_5CH{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2]} \longrightarrow C_6H_5CN + (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}OH$$

The condensation product (1), nitronic ester, does not decompose into benzonitrile oxide and diethyl phosphirate, as expected. But it is preferentially converted into diethyl benzaldiminophosphate (2), which in turn decomposes into benzonitrile and diethyl hydrogen phosphate by a proton transfer.

Decomposition of diethyl benzaldiminophosphate into benzonitrile and diethyl hydrogen phosphate was described in a preceding paper.[3]

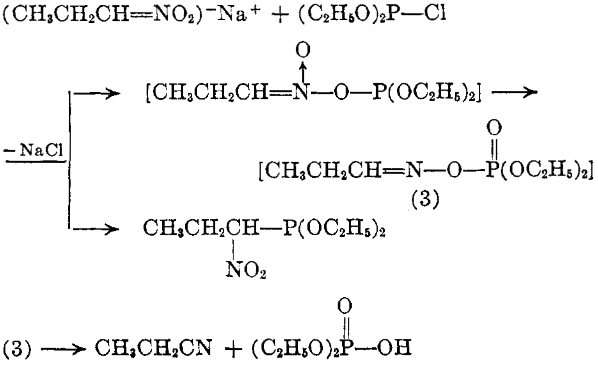
Of special interest in this reaction is the fact that the trivalent phosphorus of the nitronic ester is readily converted into the pentavalent phosphorus of the iminophosphate under such mild conditions.

The formation of phenylnitromethane can be explained by assuming that the potassium salt of phenylnitromethane is neutralized by the diethyl hydrogen phosphate previously formed. The following experiment was conducted to demonstrate this assumption; the use of two moles of the potassium salt of phenylnitromethane led to an 85% yield of benzonitrile.



$$2\cdot[C_6H_5CH{=}NO_2]^-K^+ + (C_2H_5O)_2P{-}Cl \longrightarrow C_6H_5CN + C_6H_5CH_2NO_2 + (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}OK + KCl$$

Similarly, when the sodium salt of 1-nitropropane was allowed to react with diethyl phosphorochloridite in dry ether at 0–5°, propionitrile (24% yield), diethyl (1-nitropropyl)phosphinite (13% yield), 1-nitropropane (19% yield), and diethyl hydrogen phosphate (13% yield) were obtained.



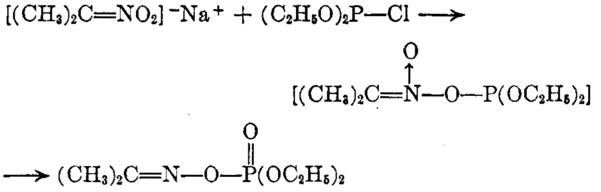
$$(CH_3CH_2CH{=}NO_2)^-Na^+ + (C_2H_5O)_2P{-}Cl \xrightarrow{-NaCl} [CH_3CH_2CH{=}\overset{O}{\overset{\uparrow}{N}}{-}O{-}P(OC_2H_5)_2] \longrightarrow \underset{(3)}{[CH_3CH_2CH{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2]}$$

$$\xrightarrow{-NaCl} CH_3CH_2\underset{NO_2}{\underset{|}{C}}H{-}P(OC_2H_5)_2$$

$$(3) \longrightarrow CH_3CH_2CN + (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}OH$$

Diethyl (1-nitropropyl)phosphinite obtained with propionitrile and diethyl hydrogen phosphate may have been formed by the combination of the carbon atom of an ambient nitronate anion with the phosphorus atom of diethyl phosphorochloridite.

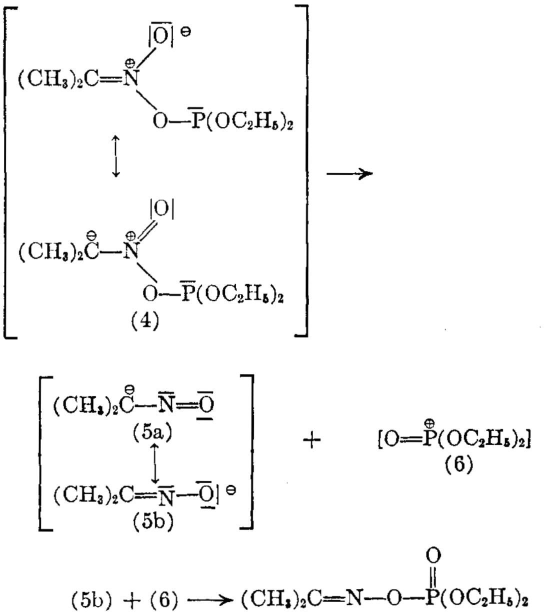
Further, when the sodium salt of 2-nitropropane was allowed to react with diethyl phosphorochloridite in dry ether at 0–5°, a 68% yield of diethyl isopropylideneaminophosphate was obtained.



$$[(CH_3)_2C{=}NO_2]^-Na^+ + (C_2H_5O)_2P{-}Cl \longrightarrow [(CH_3)_2C{=}\overset{O}{\overset{\uparrow}{N}}{-}O{-}P(OC_2H_5)_2] \longrightarrow (CH_3)_2C{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

The phosphate obtained was identified by infrared spectra compared with an authentic one prepared by the method of Allen.[4]

When diethyl phosphorochloridite was added quickly to the sodium salt of 2-nitropropane without cooling, an intense blue color was observed. It disappeared the moment the addition of diethyl phosphorochloridite was stopped. Under these conditions a small amount of acetoxime was obtained constantly. This may be caused by an unstable nitroso anion (5a) intermediate, formed by the nitrogen-oxygen bond fission of (4) as shown in the following equation:



$$(5b) + (6) \longrightarrow (CH_3)_2C{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

The anion of acetoxime (5b) may combine subsequently with the phosphate cation (6) to form diethyl isopropylideneaminophosphate.

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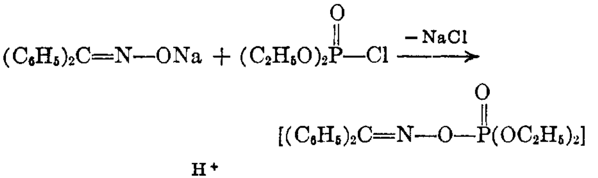
(3) T. Mukaiyama and T. Fujisawa, *Bull. Chem. Soc. Japan*, **34**, 812 (1961).

(4) J. F. Allen, *J. Am. Chem. Soc.*, **79**, 3071 (1957).

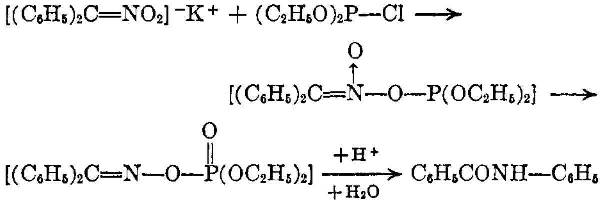
By this hypothetical mechanism, the potassium salt of diphenylnitromethane reacts with diethyl phosphorochloridite to form diethyl diphenylmethyleneaminophosphate, which however it is difficult to isolate. On the other hand, it was found that diethyl diphenylmethyleneaminophosphate prepared from the sodium salt of benzophenonoxime and diethyl phosphorochloridate readily underwent the Beckmann rearrangement to give benzanilide quantitatively in the presence of acid catalyst.



$$(C_6H_5)_2C{=}N{-}ONa + (C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}Cl \xrightarrow{-NaCl} [(C_6H_5)_2C{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2] \xrightarrow[+H_2O]{H^+} C_6H_5CONHC_6H_5$$

Therefore, the reaction product obtained in the reaction of the potassium salt of diphenylnitromethane and diethyl phosphorochloridite was confirmed as benzanilide formed by the Beckmann rearrangement.

When the mixture resulting from the reaction of the potassium salt of diphenylnitromethane with diethyl phosphorochloridite was boiled with acid catalysts such as dry hydrogen chloride, boron trifluoride, aluminum trichloride, and 100% phosphoric acid, in acetonitrile, a 50–70% yield of benzanilide was obtained. These results are shown in Table I.



$$[(C_6H_5)_2C{=}NO_2]^-K^+ + (C_2H_5O)_2P{-}Cl \longrightarrow [(C_6H_5)_2C{=}\overset{O}{\overset{\uparrow}{N}}{-}O{-}P(OC_2H_5)_2] \longrightarrow [(C_6H_5)_2C{=}N{-}O{-}\overset{O}{\overset{\|}{P}}(OC_2H_5)_2] \xrightarrow[+H_2O]{+H^+} C_6H_5CONH{-}C_6H_5$$

TABLE I[a]

| Catalyst | Amount | Reaction Time, Hr. | Benzanilide, % |
|---|---|---|---|
| Dry HCl | Saturated | 5 | 72 |
| 100% $H_3PO_4$ | 5 drops | 5 | 65 |
| $BF_3[(C_2H_5)_2O]$ | 10 drops | 6 | 51 |
| $AlCl_3$ | 0.1 g. | 4 | 67 |

[a] These results were obtained by the reaction of 0.015 mole of the potassium salt of diphenylnitromethane and 0.015 mole of diethyl phosphorochloridite.

## Experimental

**Reagent.**—Diethyl phosphorochloridite was prepared according to the procedure of Cook.[5]

**Preparations of Alkali Salts of Nitroparaffins. Method A.**—Alkali salts of 1-nitropropane, 2-nitropropane, and phenylnitromethane were prepared by the following procedure: Sodium metal (2.3 g., 0.1 g.-atom) was dissolved in 60 ml. of absolute ethanol and added to a solution of 1-nitropropane (8.9 g., 0.1 mole) in 100 ml. of dry ether. The sodium salt of 1-nitropropane was precipitated immediately. It was filtered and washed several times with dry ether and dried *in vacuo*.

**Method B.**—The potassium salt of diphenylnitromethane was prepared by the method of Konowaloff.[6]

The salt used in the following experiments has to be freshly prepared each time, since it decomposes by means of autoxidation.

**Reaction of Diethyl Phosphorochloridite with the Potassium Salt of Phenylnitromethane. Method A.**—A solution of diethyl phosphorochloridite (6.3 g., 0.04 mole) in 20 ml. of dry ether was added with stirring to a suspension of the potassium salt of phenylnitromethane (7.0 g., 0.04 mole) in 50 ml. of boiling ether over a period of 15 min. It was cooled and a solid material separated, weighing 3.52 g. and containing 2.24 g. (75%) of potassium chloride. After removal of ether, benzonitrile, 2.0 g. (49%), b.p. 74–75° (15 mm.), and phenylnitromethane, 1.5 g. (27%), b.p. 85–86° (4 mm.), were obtained by distillation. A tarry residue (about 4 g.) remained after distillation. From this residue, diethyl hydrogen phosphate was isolated in the following way; the residue was dissolved in 20 ml. of water and acidified with sulfuric acid. After the water was removed under reduced pressure, the residue was extracted with 20 ml. of ethanol. When 2 g. of lead acetate (10 ml. of water) was added to the solution, the lead salt of diethyl phosphate, 2.20 g. (35%), m.p. 178–179°, was obtained.

**Method B.**—In the same way, a suspension of the potassium salt of phenylnitromethane (14.1 g., 0.08 mole) in 70 ml. of dry ether was treated with a solution of diethyl phosphorochloridite (6.3 g., 0.04 mole) in 10 ml. of the same solvent. The reaction mixture was cooled and washed with 100 ml. of water to remove a water-soluble part. The ether layer was dried over anhydrous sodium sulfate. After removal of the ether, the residue was distilled and gave benzonitrile, 3.5 g. (86%), b.p. 79–81° (16 mm.) and phenylnitromethane, 2.3 g. (42%), b.p. 76–78° (1 mm.). The water layer was worked up in usual manner and gave the lead salt of diethyl phosphate, 1.94 g. (25%), m.p. 177–179°.

**Reaction of Diethyl Phosphorochloridite with the Sodium Salt of 1-Nitropropane.**—A solution of diethyl phosphorochloridite (7.85 g., 0.05 mole) in 10 ml. of dry ether was added with stirring to a suspension of the sodium salt of 1-nitropropane (5.55 g., 0.05 mole) in 60 ml. of the same solvent cooled with an ice–salt bath at 0–5° over a period of 20 min. The stirring was continued for an additional hour at 0–5° and then for 4 hr. at room temperature. A solid material (3.2 g., containing 2.56 g., 88%, of sodium chloride) separated. After the ether was removed under atmospheric pressure, the residue was fractionated into three major fractions. Fraction 1: 1.80 g., b.p.—45° (30 mm.): It was collected in a trap cooled by Dry Ice, and fractionated into two parts, b.p. 85–99° and b.p. 105–125°, respectively. Gas chromatography of these two parts showed that they consisted of propionitrile (0.66 g.) containing a small amount of 1-nitropropane (7:1) and 1-nitropropane (0.84 g.) containing a small amount of propionitrile (9:2).

Fraction 2: 1.04 g., b.p. 40–80° (0.5 mm.), contained about 17% of phosphorus by elementary analysis, but no compounds were isolated in pure state.

Fraction 3: 1.61 g., b.p. 82–87° (0.5 mm.), was distilled to yield diethyl (1-nitropropyl)phosphinite, 1.29 g. (13%), b.p. 85–87° (0.5 mm.). Infrared spectra of this product showed intensive absorption at 1385 cm.$^{-1}$ and 1560 cm.$^{-1}$ attributed to the nitro groups.

*Anal.* Calcd. for $C_7H_{16}NO_4P$: C, 40.19; H, 7.65; N, 6.69; P, 14.83. Found: C, 40.17; H, 7.52; N, 6.55; P, 15.0.

The lead salt of diethyl phosphate, 1.02 g. (13%), m.p. 176–178°, was isolated from a tarry residue.

**Reaction of Diethyl Phosphorochloridite with the Sodium**

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[5] H. G. Cook, J. D. Ilett, B. C. Sainder, G. J. Stacey, H. G. Watson, I. G. E. Wilding, and S. J. Woodcock, *J. Chem. Soc.*, 2921 (1949).

[6] M. Konowaloff, *Chem. Zentr.* (**2**), 33 (1894).

**Salt of 2-Nitropropane. Method A.**—A solution of diethyl phosphorochloridite (7.83 g., 0.05 mole) in 10 ml. of dry ether was added with stirring to a suspension of the sodium salt of 2-nitropropane (5.55 g., 0.05 mole) cooled with an ice bath at 0–5° over a period of 20 min. The stirring was continued for an additional hour at 0–5° and then for 4 hr. at room temperature. After a solid material (containing 2.23 g., 70%, of sodium chloride) was separated, the ether was removed. The residue was distilled to yield diethyl isopropylideneaminophosphate, 4.8 g. (68%), b.p. 93–96° (0.18 mm.). This compound showed the same infrared spectra as the authentic sample prepared by the procedure of Allen.[4]

*Anal.* Calcd. for $C_7H_{16}NO_4P$: N, 6.69; P, 14.83. Found: N, 6.59; P, 15.1.

**Method B.**—A solution of diethyl phosphorochloridite (0.05 mole) in 10 ml. of dry ether was added with stirring to a suspension of the sodium salt of 2-nitropropane (0.05 mole) in 50 ml. of the same solvent at room temperature over a period of 2 min. During this period, a blue color was observed which disappeared a few seconds after the addition was completed, and the ether solution turned pale yellow. After stirring for an additional 2 hr., the mixture was worked up in the usual manner: sodium chloride, 2.43 g. (83%), acetoxime 0.04 g. (1%), m.p. 60°, and diethyl isopropylideneaminophosphate 2.03 g. (23%), b.p. 95–97° (0.2 mm.), were obtained. Acetoxime showed no depression in mixing melting point with an authentic sample.

**Benzanilide from the Reaction of Diethyl Phosphorochloridite with the Potassium Salt of Diphenylnitromethane.**—A solution of diethyl phosphorochloridite (2.35 g., 0.015 mole) in 5 ml. of anhydrous acetonitrile was added with stirring to an ice-cooled suspension of the potassium salt of diphenylnitromethane (3.76 g. 0.015 mole) in 20 ml. of the same solvent over a period of 10 min. The stirring was continued for 0.5 hr. with an ice bath and then for 2 hr. at room temperature. After a solid separated, the solution was refluxed for 5 hr. with 10 drops of boron trifluoride (40% ether solution). It was cooled and acetonitrile was removed *in vacuo*. The residue, when poured with vigorous shaking into 20 ml. of water solidified to give crude benzanilide. It was recrystallized from ethanol, giving 1.5 g. (51%) of benzanilide, m.p. 159–160°, mixed m.p. 159–160°.

**Benzanilide from the Reaction of Diethyl Phosphorochloridate with the Sodium Salt of Benzophenone Oxime.**—A solution of diethyl phosphorochloridate (0.015 mole) in 5 ml. of anhydrous acetonitrile was added with stirring to a suspension of the sodium salt of benzophenone oxime (0.015 mole) in 15 ml. of the same solvent at room temperature. After removal of sodium chloride, the acetonitrile solution was refluxed for 6 hr. with 10 drops of boron trifluoride (40% ether solution). After evaporation of the acetonitrile under reduced pressure, the residue was treated with 15 ml. of water to give benzanilide (95%), m.p. 160°, mixed m.p. 160°.

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