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PHOSPHAZINES; REACTIONS OF CARBONYL COMPOUNDS WITH N-AMINOTRIPHENYLPHOSPHINIMINE AND WITH HYDRAZINOTRIPHENYLPHOSPHONIUM BROMIDE[1]

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Phosphazines (I) have been previously obtained by reactions of (1) diazo compounds with triphenylphosphine[2] (Equation 1) and (2) hydrazones with triphenylphosphine dibromide and triethylamine[3] (Equation 2). These methods are frequently limited in that synthesis of

$$\phi_3P: + R_2C{=}N_2 \longrightarrow \underset{\text{I}}{R_2C{=}N{-}N{=}P\phi_3} \qquad (1)$$

$$R_2C{=}N{-}NH_2 + Br_2P\phi_3 \xrightarrow[-2\,Et_3N\cdot HBr]{2\,Et_3N} \underset{\text{I}}{R_2C{=}N{-}N{=}P\phi_3} \qquad (2)$$

diazo compounds or hydrazones may be inefficient or laborious; the methods can be of real disadvantage in preparative work, particularly when a variety of aldehyde phosphazines is required. The present research thus involves development of simple and effective reactions and methods for preparing triphenylphosphazines (I). The varied chemistry of such phosphazines will be described in subsequent publications.

N-aminotriphenylphosphinimine (III) has been synthesized from triphenylphosphine dibromide and hydrazine in the presence of triethylamine[4] (Equation 3), and reaction of the resulting hydrazinotriphenylphosphonium bromide (II) with sodium amide in liquid ammonia[5,6] (Equation 4). In the

$$\Phi_3PBr_2 + H_2N\text{-}NH_2 \xrightarrow[-Et_3N\cdot HBr]{Et_3N} \underset{II}{[\Phi_3P\text{-}NH\text{-}NH_2]^+Br^-} + H_2N\text{-}NH_2\cdot HBr \qquad (3)$$

$$\underset{II}{[\Phi_3P\text{-}NH\text{-}NH_2]^+Br^-} + NaNH_2 \xrightarrow{NH_3} \underset{III}{\Phi_3P{=}N\text{-}NH_2} + NaBr + NH_3 \qquad (4)$$

present investigation a study of reactions of N-aminotriphenylphosphinimine (III) with aldehydes and ketones was initiated for possible advantageous synthesis of triphenylphosphazines (I,Equation 5). The behavior of N-aminotriphenylphosphinimine (III) with aldehydes and ketones was also of interest in determining whether III functions as an ylide reagent (III') for effecting oxygen-hydrazine transfer to give hydrazones (IV) and triphenylphosphine oxide (Equation 7).

$$\begin{array}{lcll}
\underset{III}{\Phi_3P{=}N\text{-}NH_2} + O{=}CR_2 & \longrightarrow & \underset{I}{\Phi_3P{=}N\text{-}N{=}CR_2} + H_2O & (5) \\
 & & \quad\downarrow & (6) \\
\underset{III'}{\Phi_3\overset{\oplus}{P}\text{-}\overset{\ominus}{N}\text{-}NH_2} + O{=}CR_2 & \longrightarrow & \underset{IV}{H_2N\text{-}N{=}CR_2} + \Phi_3P{=}O & (7)
\end{array}$$

It has been found that aromatic aldehydes and ketones react rapidly with N-aminotriphenylphosphinimine (III) in benzene and in the presence of molecular sieves (Linde pellets, 4A) as a desiccant to yield triphenylphosphazines (I) as principal products (Equation 5; Table 1)[7]. In the present study III was generated *in situ* from hydrazinotriphenylphosphonium bromide

TABLE 1

Triphenylphosphazines (I) from N-aminotriphenylphosphinimine (III) and Aldehydes or Ketones[7,8]

Carbonyl Compound	Phosphazine, % yield
p-Nitrobenzaldehyde	> 90
Acetophenone	69
Fluorenone	44
Benzophenone	39

(II) and equivalent quantities of n-butyllithium in hexane. These results differ fundamentally from that of Appel and Schöllhorn[6] who in a recent communication, in which experimental conditions were not given, report that III functions as an ylide transfer reagent in reaction with ketones to give triphenylphosphine oxide and ketone hydrazones (Equation 7). By the methods of the present research triphenylphosphazines (I) can indeed be adequately prepared. The triphenylphosphazines are sensitive however to moisture and to oxygen and may decompose on storage. Without proper desiccation or techniques of reaction and isolation, the triphenylphosphazines (I) may hydrolyze rapidly to hydrazones and triphenylphosphine oxide (Equation 6). Such processes in the presence of parent aldehydes or ketones (Equation 8) along with reaction of the phosphazines (I) with the aldehydes or ketones yield azines (Equation 9) in appreciable quantities.

$$R_2C{=}N{-}NH_2 + O{=}CR_2 \longrightarrow R_2C{=}N{-}N{=}CR_2 + H_2O \qquad (8)$$

$$R_2C{=}N{-}N{=}P\phi_3 + O{=}CR_2 \longrightarrow R_2C{=}N{-}N{=}CR_2 + \phi_3PO \qquad (9)$$

A much superior general method for preparing triphenylphosphazines has been subsequently developed based on reaction of hydrazinotriphenylphosphonium bromide (II) with aldehydes and ketones to give triphenylphosphazinium bromides (V, Equation 10, Table 2) which are efficiently converted to their phosphazines (I) by bases[9] (Equation 11, Table 2).

$$\underset{\text{II}}{[\phi_3\text{P-NH-NH}_2]^+\text{Br}^-} + \text{O=CR}_2 \longrightarrow \underset{\text{V}}{[\phi_3\text{P-NH-N=CR}_2]^+\text{Br}^-} + \text{H}_2\text{O} \qquad (10)$$

$$\underset{\text{V}}{[\phi_3\text{P-NH-N=CR}_2]^+\text{Br}^-} + \text{KOH} \longrightarrow \underset{\text{I}}{\phi_3\text{P=N-N=CR}_2} + \text{H}_2\text{O} + \text{KBr} \qquad (11)$$

Hydrazinotriphenylphosphonium bromide (II), a storable reagent, is easily prepared in large quantity and in good yield[4] (Equation 3). Reaction of II with aldehydes and ketones occurs rapidly and efficiently in methanol with no particular precautions. The phosphazinium hydrobromides (V) are isolated readily upon removal of methanol, trituration with ether, and crystallization from isopropyl alcohol-ether. In general the phosphazinium hydrobromides (V) can be stored for long periods without significant deterioration. Conversion of the phosphazinium hydrobromides (V) to their phosphazines (I) when desired is effected simply in chloroform by extraction with aqueous alkali or by chromatography on basic alumina. Azines as derived from the phosphazinium hydrobromides and the aldehydes or ketones are usually minor consecutive products of the method. Benzil and hydrazinotriphenylphosphonium bromide (II) gave no detectable quantity of its monophosphazinium hydrobromide; benzil monoazine is formed. 9, 10-Phenanthrenequinone and hydrazinotriphenylphosphonium bromide (II) give 10-diazo-9-phenanthrone in 97% yield; under the experimental conditions neither its monophosphazinium hydrobromide nor its monophosphazine are stable.[11]

TABLE 2

Triphenylphosphazinium Salts (V) and Triphenylphosphazines (I) from Hydrazinotriphenylphosphonium Bromide (II) and Aldehydes or Ketones

Carbonyl Compounds	Phosphazinium Hydrobromide[10]	Phosphazine
	V, % yield	I, %yield[a]
Acetaldehyde	100	
Butyraldehyde	92	
Isobutyraldehyde	92	84
Benzaldehyde	98	76
p-Methoxybenzaldehyde	-[b]	-
p-Nitrobenzaldehyde	82[c]	80
Cinnamaldehyde	86	
Acetone	100	83
Cyclohexanone	96	92
Mesityl Oxide	0	
Acetophenone	89	96
Fluorenone	36[d,e]	60[e]
Benzophenone	0	

[a] Based on V. [b] p-Methoxybenzaldehyde azine was isolated in 76% yield. [c] p-Nitrobenzaldehyde azine was obtained in 10% yield. [d] Fluorenone azine was isolated in ~ 56% yield in this experiment. [e] An overall yield of 50%, based on fluorenone, was also obtained on chromatography of the crude phosphazinium hydrobromide (V) on alumina.

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7. Typical procedure.- To a stirred, cooled suspension of hydrazinotriphenylphosphonium bromide (II) and molecular sieves in benzene was added an equivalent of n-butyllithium. The appropriate aldehyde or ketone was introduced and the mixture then refluxed for several hours. The solid material was filtered from the benzene and washed with chloroform. Evaporation of the filtrate yielded the phosphazine.

8. All triphenylphosphazines (I) and phosphazinium hydrobromides (V) give proper analyses or correspond in melting points with literature values.

9. L. Horner and E. Lingnau, Ann., 591, 135 (1955) report that triphenylphosphazinium hydrochlorides in chloroform upon extraction with aqueous alkali yield the phosphazines.

10. Phosphazinium salts (V) are generally white and absorb strongly in the 3.8, 7.0 and 9.0μ regions. They hydrolyze in aqueous acid to aldehydes or ketones and in aqueous bases to hydrazones. The phosphazinium salt of p-nitrobenzaldehyde is yellow. The phosphazines show principal absorption at 7.0 and 9.0μ.

11. W. Ried and H. Appel, Ann., 646, 84 (1961) report that 10-diazo-9-phenanthrone does not form a stable triphenylphosphazine; reaction of 9-diazophenanthrone and triphenylphosphine in dioxan in the presence of zinc chloride however gives a 1:1 adduct of the phosphazine and zinc chloride.