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PART III  THE ATTEMPTED PREPARATION OF BICYCLIC AMIDES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Charles Carey Walker, B.Sc., M.Sc.

The Ohio State University

1965

Approved by

[Signature]

Harold Shechter
Adviser
Department of Chemistry
Dedicated to my wife, Diane, whose patience and understanding helped make this possible.
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PART I

THE PREPARATION, PROPERTIES AND CHEMISTRY OF TRIIYENYLPHOSPHAZINES AND N-BENZAMIDOTRIIENYL-
PHOSPHINIMINE.
INTRODUCTION

Staudinger and Meyer (1) in attempts to prepare phosphoranes I


(Equation 1) by decomposition of diazo compounds in the presence of triphenylphosphine isolated instead simple adducts which were named phosphazines II (Equation 2).

\[
\begin{align*}
R^1_3P + R_2CN_2 & \rightarrow \overset{\#}{R^1_3P=CR_2+N_2} \\
& \rightarrow \overset{(I)}{R^1_3P-N-N=CR_2} \\
& \rightarrow \overset{(II)}{R^1_3P-N-N=CR_2}
\end{align*}
\]

This reaction of a diazo compound with triphenylphosphine subsequently was employed for synthesis of a variety of triphenylphosphazenes (2).


Reaction of hydrazones with triphenylphosphine dibromide and triethylamine (Equation 3), prior to the present study, was the only other
route to triphenylphosphazines (3).

(3) a. H. J. Bestmann and H. Fritzche, Ber., 94, 2477 (1961);

\[
\begin{align*}
R_2C = \text{NNH}_2 + \text{Br}_2\text{P} \rightarrow & \quad \frac{2\text{Et}_3\text{N}}{2\text{Et}_3\text{N-HBr}} \rightarrow R_2C = \text{N-N=P} \quad (3)
\end{align*}
\]

These methods are frequently limited in that synthesis of the required diazo compound or hydrazone may be inefficient or laborious. A portion of this work thus involved development of simple and effective methods for preparing triphenylphosphazines and study of their possible synthetic use.
Phosphazines react with dry hydrogen chloride to give salts which may be regenerated to the parent base (1,4) (Equation 4).

\[ \phi_3\text{P=N-N=CR}_2 + \text{HCl/CHCl}_3 \rightarrow [\phi_3\text{PNN=CR}_2]^+\text{Cl}^- \quad (4) \]

Such salts unlike the parent phosphazine are usually extremely stable towards moisture and are often recrystallizable from water (3b).

Methyl iodide reacts with phosphazines to give \([\alpha-N\text{-methyl-}\beta-N\text{-alkylidenehydrazino}]^-\text{phosphonium iodides (3b)}\) (Equation 5).

\[ \text{R}_2\text{C=N-N}=\phi_3 + \text{CH}_3\text{I} \rightarrow [\text{R}_2\text{C=N-}N^+\phi_3]^- \quad (5) \]

\(\alpha\)-Ketotriphenylphosphazines, unlike other phosphazines, do not always add methyl iodide normally; cleavage to the \(\alpha\)-diazo ketone and methyltriphenylphosphonium iodide may occur in high yield (2c,3b) (Equation 6).

\[ \text{R}_2\text{C}=\text{N-N}=\phi_3 + \text{CH}_3\text{I} \rightarrow \text{RCOOCR} + \phi_3\text{PCH}_3^+\text{I}^- \quad (6) \]
To account for the conversion of the \( \alpha \)-ketotriphenylphosphazines to \( \alpha \)-diazoketones it has been suggested that triphenylphosphazines are in equilibrium with their components (Equation 7). The equilibrium position is apparently influenced by alkyl substituents and determines

\[
RR'C=\overset{\equiv}{N}-\overset{\equiv}{P}=\overset{\equiv}{P}_3 \rightleftharpoons RR'CH_2=\overset{\equiv}{P}_3
\] (7)

the course of reaction of the phosphazine with methyl iodide. Electron withdrawing groups reduce the basicity of a phosphazine and the strength of the N-P bond. Strong electronegative groups which effect resonance stabilization, as does the acyl group in \( \alpha \)-ketotriphenylphosphazines, shift the equilibrium by weakening the N-P bond (2c, 3b). Cleavage of cyclopentadienone triphenylphosphazine by methyl iodide occurs readily because of similar reasons.

\[N,N\text{-Diaryltriphenylphosphazines have been reported to undergo reactions of the Wittig type (5) with aldehydes to give azines (3a)}\]


(Equation 8). In reaction of triphenylphosphazines with diphenyl

\[
Ar_2C=\overset{\equiv}{N}-\overset{\equiv}{P}=\overset{\equiv}{P}_3+RCHO \rightarrow Ar_2C=\overset{\equiv}{N}=\overset{\equiv}{CH}R+\overset{\equiv}{P}_3\text{PO}
\] (8)

ketene, \( \alpha \)-iminonitriles are formed instead of the anticipated ketene azine (3a) (Equation 9).
Phosphazines decompose with varying ease in the presence of moisture to produce hydrazones and phosphine oxides (1) (Equation 10).

\[ R_3'P=N-N=CR_2 + H_2O \rightarrow R_3'PO + R_2C=NNH_2 \] (10)

The stability of phosphazines to moisture are a function of the substituents attached to the phosphazine function. In general the more highly substituted is the function with aryl groups the greater is the hydrolytic stability of the phosphazine, i.e., \( \phi_3P=N-N=0\phi_2 > \phi_3P=N-N=CH\phi \) > \( \phi_3P=N-N=CH_2 > Et_3P=N-N=CH_2 \).

Recently \( \alpha \)-ketotriphenylphosphazines have found value for synthesis of \( \beta \)-ketoesters (6) (Equations 11, 12, and 13), and in a similar manner...
fashion hydrolysis of triphenylphosphazines to hydrazones permits the partial reduction of diazoketones to α-ketohydrazone and ultimately to methyl ketones (2c) (Equations 14 and 15).

\[
\begin{align*}
\text{RCCH=N-N=P} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{RCCH=NNH}_2 + \text{P}_3\text{PO} \\
\text{RCCH=NNH}_2 & \quad \xrightarrow{\text{KOH}} \quad \text{RCCH}_3 + \text{N}_2
\end{align*}
\]

Attempts have been previously made to effect loss of nitrogen from a phosphazine to give the corresponding phosphorane (1, 2b, and 4) (Equation 16). Such efforts, however, have almost universally met with failure; the only products isolated in most instances were azines and phosphines (Equation 17), or intractables. It has, however, been reported that thermolysis of benzophenone triphenylphosphazine yields diphenylmethylenetriphenylphosphorane along with benzophenone azine and triphenylphosphine (1).
Reactions of Hydrazinotriphenylphosphonium Bromide with Aldehydes and Ketones

Hydrazinotriphenylphosphonium bromide has been found to function as a hydrazine derivative in its reaction with aldehydes and ketones in that triphenylphosphazinium hydrobromides (Equation 18) are formed

\[
R_2C=O + \left[ \text{NH}_2\text{NHP}^+\text{Br}^- \right] \rightarrow \left[ R_2C=\text{NHP}^+\text{Br}^- \right] + \text{H}_2\text{O}
\]  (18)

in good yields. The reaction (Equation 18) occurs rapidly and efficiently in methanol with no particular precautions and the triphenylphosphazinium hydrobromides are isolated readily upon removal of methanol, trituration with ether, and recrystallization from isopropyl alcohol or isopropyl alcohol-ether. Triphenylphosphazinium hydrobromides have been synthesized previously by the reaction of triphenylphosphine dibromide with the appropriate hydrazone in the presence of triethylamine (Equation 19) (3c); this method has several disadvantages, i.e., the preparation of triphenylphosphine dibromide, although not laborious, is time-consuming.
consuring and must be carried out each time a synthesis is desired; also it requires preparation of the requisite hydrazone which in some cases may be inefficient, time consuming, and/or laborious.

Hydrazinotriphenylphosphonium bromide is a stable, storable reagent which lends itself favorably to large scale preparation. With this reagent the rapid, simple, and direct preparation of a large variety of triphenylphosphazinium hydrobromides is possible (Table 1). These compounds are stable solids and require no special handling techniques; they are valuable intermediates for synthesis of triphenylphosphazenes (see below). The one disadvantage in the present synthesis is formation of azines which either markedly reduces the yield (as for fluorenone triphenylphosphazinium hydrobromide) or in some cases (benzil monotriphenylphosphazinium hydrobromide and 2-methoxybenzaldehyde triphenylphosphazinium hydrobromide) renders the method valueless.

The formation of azines upon the reaction of hydrazinotriphenylphosphonium bromide with fluorenone (56%), 2-methoxybenzaldehyde (76%), benzil (52%), and 2-nitrobenzaldehyde (6%) suggests the intermediacy of triphenylphosphazenes which may give the azine according to the following equations:

\[
R_2C=O + [NH_2NHP\phi_3]^+Br^- \rightarrow [R_2C=N-NHP\phi_3]^+Br^- + H_2O
\]

\[
[R_2C=NNHP\phi_3]^+Br^- \xrightarrow{Base} HBr \xrightarrow{-HBr} R_2C=N-N=\phi_3
\]

\[
R_2C=N-N=\phi_3 + R_2CO \rightarrow R_2C=N-N=CR_2 + \phi_3PO
\]

\[
\phi_3PO + R_2C=NNH_2 \xrightarrow{R_2CO} R_2C=N-N=CR_2 + H_2O
\]
The behavior of 9,10-phenanthrenequinone to triphenylphosphazinium hydrobromide is of interest in that 10-diazo-9-phenanthrone is obtained. W. Ried and H. Appel (7) reported that 10-diazo-9-phenanthrone does not form a stable triphenylphosphazine; reaction of 10-diazo-9-phenanthrone and triphenylphosphine in dioxane in the presence of zinc chloride however gives a 1:1 adduct of the phosphazine and zinc chloride. These facts suggest that 10-triphenylphosphazino-9-phenanthrone is formed on reaction of hydrazinotriphenylphosphonium bromide with 9,10-phenanthrenequinone; however, the intermediate rapidly decomposes to 10-diazo-9-phenanthrone (Equation 20).

\[
\begin{align*}
    \text{HOP} & + \text{NH}_2\text{NHPP}_3^+\text{Br}^- \\
    \rightarrow \quad & \text{HOP}^+\text{NNHPP}_3\text{Br}^- \\
    & -\text{HBr} \quad \text{Base} (20)
\end{align*}
\]

The Reaction of Triphenylphosphazinium Hydrobromides with Base

A much superior synthesis of triphenylphosphazines has been developed based on reaction of triphenylphosphazinium hydrobromides with a base (Equation 21). This conversion when desired is effected
<table>
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</tbody>
</table>

a Based on phosphazinium hydrobromide. b p-Methoxybenzaldehyde azine was isolated in 76% yield. c p-Nitrobenzaldazine was obtained in 5% yield. d Only benzil azine was isolated in 52% yield. e Fluorenone azine was isolated in 56% yield. f 9-Diazo-10-phenanthrone is isolated in yields of 25 - 50%. g An overall yield of 50% based on fluorenone upon chromatography of the crude phosphazinium hydrobromide on alumina.
simply in chloroform by extraction with aqueous sodium hydroxide or by chromatography on basic alumina. The triphenylphosphazines derived from isobutyraldehyde (89%), benzaldehyde (76%), \( p \)-nitrobenzaldehyde (60%), acetone (98%), cyclohexanone (92%), acetophenone (96%), and fluorenone (50%) have been prepared by this method (Table 1).

Prolonged mixing with aqueous base or elution on basic alumina are to be avoided since cleavage of the phosphazine to triphenylphosphine oxide and the hydrazone can result (Equation 22).

\[
\begin{align*}
R_2C=\text{N-N-P} &\longrightarrow & \text{R}_2\text{C}=\text{N-N-P} \quad \text{OH}^\text{--} &\longrightarrow & \text{OH}^\text{--} \quad \text{H}_2\text{O} &\longrightarrow & \text{R}_2\text{C}=\text{N-H}_2 + \phi_3\text{PO} \\
& & & & & & (22)
\end{align*}
\]

Also prolonged standing of the chloroform extracts over drying agents is to be avoided since it was found that extensive cleavage of cyclohexanone triphenylphosphazine, presumably by hydrolysis, resulted under such conditions. After rapid preliminary drying the chloroform should be removed immediately in vacuo at room temperature to minimize the cleavage indicated.

This method is of distinct advantage over those previously described (Equations 2 and 3) in that the laborious and/or inefficient synthesis of diazo compounds or hydrazones is eliminated. It is of further advantage in that rapid synthesis of the triphenylphosphazine from its stable, storable phosphazinium hydrobromide salt is permitted, thus allowing preparation of large quantities of the triphenylphosphazine precursor and generation of the triphenylphosphazine as needed.
This procedure is limited only by the applicability of the reaction of hydrazinotriphenylphosphonium hydrobromide with aldehydes and ketones, and in spite of azine formation an effective route for the synthesis of a variety of triphenylphosphazines has been established (Table 1).

Reaction of N-Aminotriphenylphosphinimine with Carbonyl Compounds

N-Aminotriphenylphosphinimine has been prepared by reaction of n-butyllithium with hydrazinotriphenylphosphonium bromide in benzene (Equation 23); this method is superior to the previously described procedures (36, 8) (Equation 24) in that use of liquid ammonia is eliminated. N-Aminotriphenylphosphinimine is extremely sensitive to moisture and therefore was employed in situ.

\[
\left[\text{Ph}_{3}P\text{NHNH}_{2}\right]^{\cdot}\text{Br}^{-} + \text{CH}_{3}(\text{CH}_{2})_{2}\text{CH}_{2}\text{Li} \rightarrow \text{Ph}_{3}P=\text{NNH}_{2} + \text{CH}_{3}(\text{CH}_{2})_{2}\text{CH}_{3} + \text{LiBr} \quad (23)
\]

\[
\left[\text{Ph}_{3}P\text{NHNH}_{2}\right]^{\cdot}\text{Br}^{-} + \text{NaNH}_{2} \overset{(\text{NH}_{3})_{1}}{\rightarrow} \text{Ph}_{3}P=\text{NNH}_{2} + \text{NaBr} + \text{NH}_{3} \quad (24)
\]

N-Aminotriphenylphosphinimine was found to react with benzophenone, fluorenone, acetophenone and p-nitrobenzaldehyde as a hydrazine to give triphenylphosphazines (Equation 25) rather than as an ylide reagent effecting oxygen-hydrazine transfer to yield hydrazones (Equation 26). These results differ fundamentally with those of Appel and
Schöllhorn (8) (no experimental details are given in this work) who report that α-aminotriphenylphosphinimine functions as a ylide transfer reagent in reaction with ketones to give triphenylphosphine oxide and ketone hydrazones. Since water is one of the products of reaction (Equation 25), and triphenylphosphazines are very sensitive to moisture, it is believed that Appel and Schöllhorn's findings result simply from hydrolytic cleavage of the initially formed triphenylphosphazine to triphenylphosphine oxide and hydrazone (Equation 27). Removal of the water formed via molecular sieves prevents this hydrolytic cleavage. Fluorenone reacts with α-aminotriphenylphosphinimine to give fluorenone triphenylphosphazine without need of molecular sieves; the cleavage of fluorenone triphenylphosphazine is known to be quite slow (1). If α-aminotriphenylphosphinimine undergoes reaction with carbonyl compounds as suggested by Appel and Schöllhorn this should be especially evident with p-nitrobenzaldehyde, since this aldehyde undergoes a very rapid reaction with ylides (9). It was found, however, that p-nitrobenzaldehyde triphenyl-

\[
\phi_3 H = \text{PhH}_2 + O = \text{CR}_2 \rightarrow \phi_3 \text{H-} \text{H-} \text{H} = \text{PhH}_2 + \text{H}_2 \text{O}
\]  

(25) 

\[
\phi_3 \text{H-} \text{H-} \text{H} = \text{PhH}_2 + O = \text{CR}_2 \rightarrow \text{H}_3 \text{H-} \text{H-} \text{CR}_2 + \phi_3 \text{PO}
\]  

(26) 

\[
\phi_3 \text{H-} \text{H-} \text{H} = \text{PhH}_2 + O = \text{CR}_2 \rightarrow \text{H}_3 \text{H-} \text{H-} \text{CR}_2 + \phi_3 \text{PO}
\]  

(27) 


(\text{Table 2})
### Table 2

**Triphenylphosphazines from N-Aminotriphenylphosphinimine and Aldehydes or Ketones**

<table>
<thead>
<tr>
<th>Carbonyl compound</th>
<th>Phosphazine % Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Nitrobenzaldehyde</td>
<td>92</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>69</td>
</tr>
<tr>
<td>Fluorenone</td>
<td>44</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>39</td>
</tr>
</tbody>
</table>
Although this method yields triphenylphosphazines it offers no general advantage over that of triphenylphosphazinium hydrobromides with base, and is in fact experimentally less attractive since it requires use of n-butyllithium and rigorously dry conditions. The method is of specific advantage in preparation of benzophenone triphenylphosphazine since the phosphazinium hydrobromide is not formed readily from reaction of benzophenone with hydrazinotriphenylphosphonium bromide.

**Attempted Decomposition of Triphenylphosphazines**

A study has been made of possible synthesis of stabilized diazo compounds by reaction of phosphazines with methyl iodide (Equation 27). Although previous studies indicated that aryl phosphazines not bearing an α-keto group were methylated by methyl iodide (3b) (Equation 28) and

\[
R_2C=N-N=\Phi_3+CH_3I \xrightarrow{EtOAc} R_2CH_2 + [\Phi_3PCH_3]^+I^- \quad (27)
\]

\[
R_2C=N-N=\Phi_3+CH_3I \xrightarrow{EtOAc} [R_2C=N-NP\Phi_3]^-I^- \quad (28)
\]

thus were not convertible to the diazo compound, it was hoped that under varied and more vigorous conditions cleavage would occur and allow general synthesis of aryldiazo compounds.

Addition of methyl iodide to refluxing solutions of triphenylphosphazines of fluorenone, acetophenone and α-nitrobenzaldehyde in ethyl acetate failed to produce the desired diazo compound (Equation 27); instead the corresponding phosphonium iodides were isolated (Equation 28). The results observed for reactions of fluorenone triphenylphosphazine
and acetophenone triphenylphosphazine with methyl iodide to give phosphonium salts are in agreement with prior work (3b); while the present study was in progress it was reported that \( \alpha \)-nitrobenzaldehyde triphenylphosphazine is methylated by methyl iodide.

In the previous experiments the phosphazine, methyl iodide, and ethyl acetate were mixed and then refluxed. An effort was made to effect thermolysis of the phosphazines in ethyl acetate to diazo compounds and scavenge the triphenylphosphine by addition of methyl iodide (Equation 29). Methylation of the phosphazine resulted, however, and

\[
R_2C=\text{N}=\text{N}=\text{P} \Phi_3 \xrightarrow{\text{reflux}} R_2C=\text{H}_2 + \Phi_3^+ + \Phi_3 \text{PCH}_3^+ + \text{I}^-
\]

there was no evidence for the equilibrium dissociation of the phosphazines under these conditions. Solution spectra (3b) of \( \alpha \)-ketomonotriphenylphosphazines and cyclopentadienone triphenylphosphazine exhibit diazo absorption in the infrared, thus establishing the existence of the equilibrium in (Equation 7) and further are cleaved by methyl iodide to the requisite diazo compound and methyltriphenylphosphonium iodide.

It is of note that solution spectra of the phosphazines of fluorenone, acetophenone, and \( \beta \)-nitrobenzaldehyde do not exhibit diazo absorption in the infrared further indicating the non-existence of the equilibrium in Equation (7) for these cases.

It has been recently reported (10) that triphenylphosphoranes are


produced upon decomposition of certain diazo compounds in the presence
of triphenylphosphine and cuprous chloride; diazoacetophenone thus gave the phosphorane under these conditions. The experimental conditions for reaction of diazoacetophenone and triphenylphosphine in the presence of cuprous chloride are favorable for formation of the phosphazine; consequently in principle two paths are possible for formation of the phosphorane: catalyzed decomposition of a triphenylphosphazene to a phosphorane (Equation 30) or of a diazo compound to a carbene which is captured by triphenylphosphine (Equation 31).

\[
\begin{align*}
\phi_3P + N_2CR_2 & \rightarrow \phi_3P=\text{N-N=CR}_2 \quad \text{CuCl} \quad \phi_3P=\text{CR}_2 \\
N_2CR_2 & \xrightarrow{\text{CuCl}} R_2C \xrightarrow{\phi_3P} \phi_3P=\text{CR}_2
\end{align*}
\]

(Equation 30)

(Equation 31)

The present study has shown acetophenone triphenylphosphazine to be thermally stable in boiling tetrahydrofuran with added cuprous chloride, conditions under which diazoacetophenone and triphenylphosphine yield the desired phosphorane. This makes it clear that the carbene is involved (Equation 31) in formation of phosphoranes by the Wittig and Schlosser method, and precludes the synthesis of Wittig reagents from triphenylphosphazines by this route. Ultraviolet irradiation of acetophenone triphenylphosphazene in tetrahydrofuran in the presence of cuprous chloride also failed to produce any of the desired phosphorane.

Formation of triphenylphosphoranes by thermolysis of phosphazines has generally been unsuccessful (Equation 32). Acetophenone triphenylphosphazene under thermolytic conditions in this work gave only triphenyl-
phosphine (25%), triphenylphosphine oxide (47%), acetophenone azine (34%), and nitrogen (50%). Methylbenzylidene triphenylphosphorane was not detected. Wittig and Schlosser contend this method for the preparation of phosphoranes is unsuitable since the thermal conditions required for the loss of nitrogen from the phosphazine exceeds the thermal limits of the phosphorane (10). Keeping this fact in mind it seems reasonable that a phosphorane which possesses considerable stability by virtue of resonance stabilization should be obtainable by thermolysis of its phosphazine. Fluorenone-9-triphenylphosphorane is one of the most stable phosphoranes known; however, vacuum pyrolysis of fluorenone triphenyl-

$$\phi_3 P-N-N=CR_2 \xrightarrow{\text{heat}} \phi_3 P=CR_2 + N_2$$

phosphazine at temperatures exceeding 200° failed to effect significant decomposition. It thus appears difficult to thermolyze triphenyl-phosphazines even to very stable phosphoranes.

The Preparation, Properties, and Chemistry of N-Benzamidotriphenylphosphinimine (11)

(11) While this manuscript was in preparation it was found that L. Horner and H. Oediger, Ann., 627, 147 (1959) prepared what they reported to be N-benzamidotriphenylphosphinimine, m.p. 177-180°, in an 18% yield from triphenylphosphine dibromide and benzhydrazide. The authors did not investigate the chemistry of N-benzamidotriphenylphosphinimine.

N-Benzamidotriphenylphosphiniminium bromide IV was prepared by two routes in good yield: from reaction of triphenylphosphine dibromide, benzhydrazide and one equivalent of triethylamine (Equation 33) or from
hydrazinotriphenylphosphonium bromide and benzoyl chloride in the presence of pyridine (Equation 34). N-Benzamidotriphenylphosphiniminium bromide upon reaction with base afforded isolation of either N-benzamido-
triphenylphosphinimine (sodium hydroxide-chloroform) (Equation 35) or its enolic isomer (triethylamine-tetrahydrofuran), α-hydroxybenzylidenetriphenylphosphazine (Equation 36).

\[
\begin{align*}
\Phi_3PBr_2 + \PhiCNHNH_2 & \quad \xrightarrow{\text{Et}_3N/HBr} \quad \Phi_3P\Phi_3^{+Br^-} \\
\text{IV (76%)} \\
\PhiCCl + [\Phi_3P\Phi_3]^{+Br^-} & \quad \xrightarrow{C_6H_5N/-C_6H_5N.HCl} \quad [\Phi_3PNHHNCPh]^{+Br^-} \\
\text{IV (64%)}
\end{align*}
\]

\[
\begin{align*}
\PhiCNHNHP\Phi_3^{+Br^-} & \quad \xrightarrow{\text{NaOH/CHCl}_3} \quad \PhiCNHN=\Phi_3 + H_2O + \text{NaBr} \\
\text{(29%)} \\
\PhiCNHNHP\Phi_3^{+Br^-} & \quad \xrightarrow{\text{Et}_3N/\text{THF}} \quad \PhiC=N-N=\Phi_3 + \text{Et}_3N.HBr \\
\text{(39%)}
\end{align*}
\]

α-Hydroxybenzylidenetriphenylphosphazine was also produced from triphenylphosphine dibromide and benzhydrazide in the presence of two equivalents of triethylamine (Equation 37).

\[
\begin{align*}
\Phi_3PBr_2 + \PhiCNHNH_2 & \quad \xrightarrow{2\text{Et}_3N/C_6H_5/\text{THF}} \quad \PhiC=N-N=\Phi_3 + 2\text{Et}_3N.HBr \\
\end{align*}
\]
The existence of these two tautomers is verified by: 1) their infrared spectra; the enol form shows no carbonyl absorption in the region 5.8-6.1 μ (Figures 11 and 13) whereas the amide does, 2) the production of an intense blue color upon reaction of the enol with ferric chloride and 3) both N-benzamidotriphenylphosphinimine and its stable enol form, α-hydroxybenzylidenetriphenylphosphazine react with m-nitrobenzaldehyde to give m-nitrobenzaldehyde benzoylhydrazone (Equation 38).

\[
\begin{align*}
\text{OH} & \quad \text{CHO} \\
\phi C = N - N = P \phi_3 & \quad \rightarrow \\
\phi C N H N = P \phi_3 & \quad + \phi_3 \text{PO}
\end{align*}
\]

(38)

α-Hydroxybenzylidenetriphenylphosphazine behaves as a typical enol on reaction with n-butyllithium to give the lithium salt (Equation 39), which is transparent in the carbonyl region of the infrared. This salt reacts rapidly with benzoyl chloride at room temperature to give 4,5-diphenyl-1,3,4-oxadiazole. This reaction must involve intramolecular reaction of α-benzoyloxybenzylidenetriphenylphosphazine V (Equation 40) to give the oxadiazole.

\[
\begin{align*}
\text{OH} & \quad \rightarrow \\
\phi C = N - N = P \phi_3 + CH_3(CH_2)_2CH_2L \rightarrow & \quad \phi C = N - N = P \phi_3 + CH_3(CH_2)_2CH_3 \\
\phi C = N - N = P \phi_3 + \phi C O C l & \quad \rightarrow \\
\phi C = N - N = P \phi_3 + & \quad \phi C - C \rightarrow \\
\phi C - C - O + LiCl & \quad \rightarrow \\
\phi C - C - O + & \quad \phi_3 \text{PO}
\end{align*}
\]

(39, 40)
1,3,4-Oxadiazoles were also prepared by reaction of α-hydroxybenzylidenetriphenylphosphazine with various substituted benzoyl chlorides in the presence of triethylamine at room temperature (Table 3). It is apparent that α-hydroxybenzylidenetriphenylphosphazine VI (Equation 41) reacts with benzoyl chlorides VII to give a common intermediate VIII which undergoes ring closure by a Wittig-like process.

\[
\begin{align*}
\text{(VI)} & \quad \text{OH} \quad \phi C=\text{NN}=\phi_3 \quad + \quad \begin{array}{c}
\text{COCl}
\end{array} \\
\text{(VII)} & \quad \begin{array}{c}
\text{Et}_3\text{N} \\
\text{-Et}_3\text{N}.\text{HCl}
\end{array} \\
\text{(VIII)} & \quad \begin{array}{c}
\phi C \quad \begin{array}{c}
\text{O}
\end{array} \\
\text{N} \quad \begin{array}{c}
\text{N}=\text{P}\phi_3
\end{array} \\
\cdots
\begin{array}{c}
\phi_3\text{PO}
\end{array}
\end{align*}
\]

1,3,4-Oxadiazoles previously have been obtained by: (1) dehydration of the appropriate N,N'-diacyl hydrazide at 250 - 300° (12).


(2) the use of dehydrating agents: phosphorous pentoxide, thionyl chloride, phosphorous oxychloride, zinc chloride, organic acid anhydrides, and phosphorous pentachloride (13) with N,N'-diacyl hydrazides IX (Equation 42) at lower temperature, (3) reaction of bis-α-chloro-
Table 3

1,3,4-Oxadiazoles Prepared by Reaction of VI with VII, Equation 41

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>1,3,4-Oxadiazole % Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>$H$</td>
<td>$H$</td>
<td>64</td>
</tr>
<tr>
<td>$H$</td>
<td>$p$-NO$_2$</td>
<td>$H$</td>
<td>94</td>
</tr>
<tr>
<td>$p$-NO$_2$</td>
<td>$H$</td>
<td>$p$-NO$_2$</td>
<td>79</td>
</tr>
</tbody>
</table>

\[
\text{RCONHNHCOR} \rightarrow \begin{bmatrix} \text{RC} = \text{N} - \text{N} = \text{CR} \\ \text{OH} & \text{OH} \end{bmatrix} - \text{H}_2\text{O} \rightarrow \text{N} = \text{N} \]

benzylidenehydrazines with hot water or silver nitrate (14) (Equation 43).

(14) E. Beckmann and E. Gunther, Ann., 252, 44 (1889).

\[
\text{RC} = \text{N} - \text{N} \overset{\text{H}_2\text{O or } \text{AgNO}_3}{\underset{\text{H}_2\text{O}}{\rightarrow}} \text{N} = \text{N} \]

(4) treatment of aromatic carboxylic acid hydrazides with excess ethyl orthoformate (15) (Equation 44), (5) oxidation of certain acylthiosemic-


\[
\text{ArCONHNH}_2 + \text{RC(OEt)}_3 \rightarrow \text{Ar-O} = \text{C-R} \]

+ EtOH
carbazides with lead or mercury oxides (16) (Equation 45), (6) treatment


\[
(C_6H_5)_2CHCONHNHCNSNH_2 \xrightarrow{Pb_3O_4} H_2N-C\_0\_C\_H(C_6H_5)_2
\]  

(45)

of tetrazoles with acyl chlorides in the presence of pyridine (17)


(Equation 46). Because of the great variety of synthetic routes

\[
\begin{align*}
\text{N} - \text{N}^\text{H} & \xrightarrow{R'\text{COCl}} \text{N} - \text{N}^\text{COR'} \\
\text{N} = \text{N} & \xrightarrow{C_6H_5\text{N}} \text{N} = \text{N} - \text{N}_2
\end{align*}
\]  

(46)

enumerated it seems apparent that extension of the new synthesis of 1,3,4-oxadiazoles will find only limited application.

The intramolecular reaction which occurs on benzylation of \(\alpha\)-hydroxybenzylidenetriphenylphosphazine is to be contrasted with the failure of the phosphinimine to undergo intramolecular or intermolecular reaction under more stringent conditions (Equations 47 and 48 respectively). This difference may be explained by the fact that reactions of N-benzamidotriphenylphosphinimine as indicated in 47 and 48 require nucleophilic attack of the nitrogen atom of the phosphorous-nitrogen ylide at a carbonyl carbon bearing an amido function. Such a reaction center is
less reactive than is an ester such as in Equation 41. It is also apparent that the final step in the 1,3,4-oxadiazole synthesis has a sterically-favored path in that a cyclic transition state is involved.

Internal Wittig reactions as encountered in preparation of 1,3,4-oxadiazoles may also find advantage in preparation of other heterocyclic compounds. For example additional entry into the 1,2,4-triazole area could result from the successful application of Equations 49 and 50. The sequence indicated is of interest in that a triphenylphosphinimine intermediate is involved which is analogous to that leading to 1,3,4-oxadiazoles. The value of such proposed syntheses remains to be demonstrated. Also extension of the present concept may lead to preparation

\[
\begin{align*}
\phi_C & \xrightarrow{P\phi_3} \phi_C = N + \phi_3PO \\
\text{HN} & \xrightarrow{N} \\
2\phi_C & \xrightarrow{CNH} \phi_C = CNH = P\phi_3 + \phi_3PO
\end{align*}
\]
of 1,3,4-isoaxadiazines \( X_a \), 1,3,4-isothiadiazines \( X_b \) and 5,6-dihydro-1,2,4-triazines \( X_c \) as shown in Equation 51. Preparation of the 4,5-dihydro derivatives of \( X_a \), \( X_b \), and \( X_c \), Equation 52, follows from logical extension of Equation 51. It is thus suggested that an internal Wittig reaction (Equations 53, 55 and 57) may be employed wherever dehydrative ring closure is involved (Equations 54, 56, and 58). The
routes suggested by Equations 53, 54 and 55 may be of advantage in particular cases.

\[
\begin{align*}
RC=N-N=PO_3 & \rightarrow RCO & \text{(53)} \\
RC=N & \rightarrow RCO & \text{(54)} \\
RCR=NH=PO_3 & \rightarrow RCO & \text{(55)} \\
RCR=NH & \rightarrow RCO & \text{(56)} \\
RCR=N=PO_3 & \rightarrow RCO & \text{(57)} \\
RCR=N & \rightarrow RCO & \text{(58)} \\
\end{align*}
\]

The chemistry of \( \alpha \)-hydroxybenzylidene triphenylphosphazine requires additional investigation. A new class of phosphazines: XII, XIII, XIV, and XV may result from successful application of Equations 59, 60, 61 and 62. The possible synthetic uses of this class of phosphazines are out-

\[
\begin{align*}
\text{OH} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{1)BuLi} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{OR} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{(60)} \\
\text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{2)RX} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{(XII)} \\
\text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{SOCl}_2,\text{PBr}_3 & \rightarrow \text{X} & \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{(XIII)} \\
\text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{NaX} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{(XV)} \\
\text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{CN} & \rightarrow \text{C}_6\text{H}_5\text{C}=\text{N-N}=PO_3 & \text{(XIV)} \\
\end{align*}
\]
lined by Equations 62, 63 and 64.

\[ \begin{align*}
  \text{Y} & \quad \text{C}_6\text{H}_5\text{C} = \text{N} = \text{N} - \text{P} \phi_3 & \quad \text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
  & \quad \phi_3\text{PO} & \quad \phi_3\text{PO} & \quad \phi_3\text{PO} \\
  \text{C}_6\text{H}_5\text{C} = \text{N} - \text{N} - \text{P} \phi_3 & \quad \rightarrow & \quad \text{C}_6\text{H}_5\text{C} = \text{N} - \text{N} - \text{P} \phi_3 & \quad + (\text{C}_6\text{H}_5\text{C} = \text{N})_2
\end{align*} \] (62)

\[ \begin{align*}
  \text{Y} & \quad \text{C}_6\text{H}_5\text{C} = \text{N} = \text{N} - \text{P} \phi_3 & \quad \rightarrow & \quad \text{C}_6\text{H}_5\text{C} = \text{N} - \text{N} - \text{P} \phi_3 & \quad + (\text{C}_6\text{H}_5\text{C} = \text{N})_2
\end{align*} \] (63)

\[ \begin{align*}
  \text{Y} & \quad \text{C}_6\text{H}_5\text{C} = \text{N} = \text{N} - \text{P} \phi_3 & \quad \rightarrow & \quad \text{C}_6\text{H}_5\text{C} = \text{N} - \text{N} - \text{P} \phi_3 & \quad + (\text{C}_6\text{H}_5\text{C} = \text{N})_2
\end{align*} \] (64)

Where Y = OR, X, CN.

The present results also raise the question as to the applicability of triphenylphosphine dibromide as a reagent for the synthesis of 1,3,4-oxadiazoles from appropriate N,N'-diacyl hydrazides (Equation 65). Such a synthetic route could be of advantage over those employing the dehydrative techniques previously mentioned (12).

\[ \begin{align*}
  \text{R} - \text{CNH} & \quad + \quad [\phi_3\text{PBr}]^+ \cdot \text{Br}^- & \quad \rightarrow & \quad \text{R} - \text{CNH} - \text{H} + \phi_3\text{PBr} \\
  \text{R} - \text{CNH} & \quad + \quad [\phi_3\text{PBr}]^+ \cdot \text{Br}^- & \quad \rightarrow & \quad \text{R} - \text{CNH} - \text{H} + \phi_3\text{PBr} \\
  \text{C}_6\text{H}_5\text{H} & \quad \rightarrow & \quad \text{C}_6\text{H}_5\text{H} & \quad + & \quad \text{C}_6\text{H}_5\text{H} \\
  \text{C}_6\text{H}_5\text{H} & \quad \rightarrow & \quad \text{C}_6\text{H}_5\text{H} & \quad + & \quad \text{C}_6\text{H}_5\text{H}
\end{align*} \] (65)
EXPERIMENTAL

General Information

Melting Points. All melting points were determined on a Fisher melting point block and are uncorrected.

Analyses. Analyses were carried out by Micro-Analyses Inc. of Wilmington, Del. and Galbraith of Knoxville, Tenn.

Chemicals and Solvents. All aldehydes and ketones were used as received from commercial sources; preliminary drying of these compounds, when required, was accomplished with molecular sieves. Benzene, reagent grade, was dried over sodium wire before use. Tetrahydrofuran was distilled from calcium hydride before use. Triethylamine was distilled from sodium hydroxide before use.

Infrared Spectra. All spectra were taken on a Perkin-Elmer Infra­cord employing a potassium bromide pellet.


1. Reactions with acetaldehyde

Acetaldehyde (0.22 g., 5.0 x 10^{-3} mole) was added to a solution of hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 x 10^{-3} mole) in methanol (25 ml.) and the resulting mixture stirred overnight under nitrogen. Addition of ether to the oil which remained after removal of the solvent afforded 1.00 g (100%) of acetaldehyde triphenylphosphazinium hydrobromide, a stable white solid, m.p. 168-175°. This material could not be crystallized from the conventional solvents and thus it was not analyzed. Its identification was made on the basis of its infrared spectrum; absorption at 3.8, 7.0, and 9.0 μ were present. These peaks are characteristic of all the triphenylphosphazinium hydrobromides that have been prepared.

2. Reaction with butyraldehyde

A large excess of butyraldehyde (2 ml.) was added to a methanolic solution (25 ml.) of hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 x 10^{-3} mole) and the resulting solution stirred 10 hr. at room temperature. Removal of the excess methanol and aldehyde left behind a brown oil which on trituration with ether yielded 0.98 g. (92%) of butyraldehyde triphenylphosphazinium hydrobromide. An analytical
sample was prepared by recrystallization from isopropanol-ether, m.p. 150-151°. Butyraldehyde triphenylphosphazinium hydrobromide is a stable white solid requiring no special handling or storage techniques and shows principal absorption at 3.8 (s), 7.0 (s), 9.0 (s), 9.4 (m) and 13.7, 13.8 (s, poorly resolved doublet). See Figure 1 for the infrared spectrum (19).

(19) Due to unavoidable difficulties in reproduction of the spectra, often cited does not correspond to shown in the spectra.

Anal. Calcd. for C_{22}H_{24}BrN_{2}P: C, 61.85; H, 5.63; N, 6.56.

Found: C, 61.9%; H, 5.66; N, 6.55.

3. Reaction with isobutyraldehyde

The previous experiment was duplicated except that isobutyraldehyde was used. Recrystallization of the triturated solid, 0.98 g. (92%), from isopropanol-ether gave an analytical sample of isobutyraldehyde triphenylphosphazinium hydrobromide, a white stable crystalline solid, m.p. 165-166°. This solid requires no special handling or storage techniques. Isobutyraldehyde triphenylphosphazinium hydrobromide shows the following bands in the infrared: 3.8 (m), 7.0 (s), 9.0 (s, accompanied by a shoulder), 9.8 (s) and 13.7, 13.8 (s, poorly resolved doublet).

Anal. Calcd. for C_{22}H_{24}BrN_{2}P: C, 61.85; H, 5.63; N, 6.56.

Found: C, 61.62; H, 5.66; N, 6.62.
4. **Reaction with benzaldehyde**

A solution of hydrazinotriphenylphosphazinium bromide (0.93 g., 2.5 \times 10^{-3} \text{ mole}), absolute methanol and benzaldehyde (0.50 g., 4.6 \times 10^{-3} \text{ mole}) was refluxed under nitrogen for one hr. Trituration of the oil, which remained upon the removal of solvent, with ether gave 1.13 g. (98\%) of benzaldehyde triphenylphosphazinium hydrobromide. Isopropanol was employed for recrystallization of an analytical sample, m.p. 224-226\degree. Benzaldehyde triphenylphosphazinium hydrobromide is a white solid, stable at ambient conditions and shows the following bands in the infrared: 3.8 (m), 7.0 (s), 9.0 (s), 9.6 (m), 13.6 (s), and 14.5 (s)\mu. See Figure 2 for the infrared spectrum.\(^{19}\).

**Anal. Calcd. for C_{25}H_{22}BrN_{2}P:** C, 65.08; H, 4.79; N, 6.10.

**Found:** C, 65.09; H, 4.85; N, 6.32.

5. **Reaction with p-methoxybenzaldehyde**

A solution of p-methoxybenzaldehyde (0.63 g., 4.6 \times 10^{-3} \text{ mole}) and hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 \times 10^{-3} \text{ mole}) in methanol (50 ml.) was refluxed 30 min. Removal of the excess solvent gave a yellow oil which did not solidify upon trituration with ether; however, refluxing in benzene brought about solidification of 0.34 g. of a yellow-orange material. Recrystallization of this solid twice from isopropanol gave 0.20 g. of p-methoxybenzaldazine, a yellow solid (needles from isopropanol) stable to moisture and the atmosphere. Reduction in the volume of the benzene filtrate followed by cooling afforded an additional 0.23 g. of the azine. The two fractions of p-methoxybenzaldazine were combined and sublimed; 0.25 g. of a yellow
sublimate was obtained, m.p. 172-174° \cite{lit. m.p. 168° (20)}. The

(20) G. Knopfer, Montashft., 30, 32 (1909).

infrared spectrum of the sublimate, as well as those of the prior
fractions, were identical to that of authentic \( p \)-methoxybenzaldazine
(12); a mixed m.p. was undepressed. The infrared spectrum shows bands
at: 6.3 (s), 6.7 (s), 7.7 (s), 8.1 (s), 8.6 (s), 9.8 (s), and 12.0
(s) \( \mu \). Percentage yield of the azine, 76%.

6. Reaction with \( p \)-nitrobenzaldehyde

Methanol (20 ml.), \( p \)-nitrobenzaldehyde (0.71 g., \( 4.6 \times 10^{-3} \) mole)
and hydrazinotriphenylphosphonium bromide (0.93 g., \( 2.5 \times 10^{-3} \) mole)
were stirred at room temperature for 12 hr., and then heated for a
few minutes on a steam bath. Reduction in the volume of the solution
followed by filtration and washing of the separated solid with ethanol
afforded 0.04 g. (6%) of yellow \( p \)-nitrobenzaldazine, m.p. 320° with
prior decomposition \cite{lit. m.p. 305° (21)}. An infrared spectrum of


this material was identical to that of authentic azine (20).

Removal of the alcohol from the filtrate afforded 1.03 g. (82%)
of a yellow solid identified as \( p \)-nitrobenzaldehyde triphenylphosphazinium
hydrobromide; a stable, storable compound. An analytical sample was
prepared by recrystallization from isopropanol, m.p. 204-205°. The
infrared spectrum, Figure 3, showed absorption at: 3.7 (w), 6.6 (s),
7.0 (m), 7.5 (s), 9.0 (s), 9.6 (m), and 13.6 (s) M.

Anal. Calcd. for C_{25}H_{21}BrN_{3}O_{2}P: C, 59.29; H, 4.15; N, 8.29.
   Found:  C, 59.24; H, 4.31; N, 8.44.

7. Reaction with cinnamaldehyde

A solution of methanol (70 ml.), cinnamaldehyde (0.66 g., 5.0 x 10^{-3} mole) and hydrazinotriphenylphosphonium bromide (1.90 g., 5.1 x 10^{-3} mole) was warmed to 40-50° for 30 min. Removal of the solvent followed by trituration of the remaining oil with ether gave 2.15 g. (86%) of a white, stable solid, m.p. 174-177°. This solid was not recrystallizable from the common solvents, and showed considerable oiling out properties. Since it was not possible to obtain an analytical sample, the identification rests on the material's infrared spectrum; it shows absorption at: 3.8 (m), 7.0 (s), 9.0 (s), 9.7 (m, broad), 13.8 (s), and 14.5 (s) M. The spectrum is consistent with that of all previous triphenylphosphazinium hydrobromides. It is clear that Michael addition did not occur since there is no carbonyl absorption in the infrared.

8. Reaction with acetone

Acetone (0.29 g., 5.0 x 10^{-3} mole) was added to a solution of hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 x 10^{-3} mole) in absolute methanol (25 ml.); the resulting solution was stirred for 12 hr. at room temperature and then refluxed 10 min. Removal of the solvent left a clear oil, which on trituration with ether, gave 1.03 g. (100%) of acetone triphenylphosphazinium hydrobromide. Acetone triphenylphosphazinium hydrobromide is a white solid, stable to moisture.
and oxygen under ambient conditions, and thus requires no special handling or storage techniques. This material shows principal absorption at 3.7 (m), 7.0 (s), 9.0 (s), 10.4 (broad) and 13.2 (s) \( \mu \). An analytical sample was prepared by recrystallization from minimal acetone, m.p. 214-215°.

**Anal. Calcd. for C\textsubscript{21}H\textsubscript{22}BrN\textsubscript{2}P:** C, 61.00; H, 5.34; N, 6.80; P, 7.50.  
**Found:** C, 60.91; H, 5.26; N, 6.80; P, 7.31.

9. **Reaction with cyclohexanone**

A methanolic solution (25 ml.) of hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 \( \times \) \( 10^{-3} \) mole) and excess cyclohexanone (2 ml.) was stirred for 10 hr., and the excess methanol then removed by heating the open flask on a steam bath. On washing the solid residue with ether, 1.07 g. (96%) of cyclohexanone triphenylphosphazinium hydrobromide was obtained. Recrystallization from isopropanol-ether gave an analytical sample, m.p. 203-205° (turns pale green). Cyclohexanone triphenylphosphazinium hydrobromide is a stable, white solid showing absorption at: 3.7 (s), 7.0 (s), 9.0 (s), 10.4 (s), 13.8 (s, broad), and 14.5 (s) \( \mu \).

**Anal. Calcd. for C\textsubscript{24}H\textsubscript{26}N\textsubscript{2}P:** C, 63.57; H, 5.76; N, 6.20.  
**Found:** C, 63.48; H, 5.89; N, 6.31.

10. **Reaction with acetophenone**

Acetophenone triphenylphosphazinium hydrobromide was prepared by refluxing acetophenone (0.36 g., 3.0 \( \times \) \( 10^{-3} \) mole) and hydrazinotriphenylphosphonium bromide (0.93 g., 2.5 \( \times \) \( 10^{-3} \) mole) in methanol (25 ml.) for 3 hr. Removal of the solvent and trituration with ether gave 1.06 g. (89%) of acetophenone triphenylphosphazinium hydrobromide,
m.p. 200-205°. The infrared spectrum is given in Figure 4. The product is a stable white solid, and was identified by its near quantitative conversion to the known phosphazine (see The Reaction of Triphenylphosphazinium Hydrobromides with Base).

11. Reaction with mesityl oxide

Mesityl oxide did not react with hydrazinotriphenylphosphonium bromide in 4:1 isopropanol-ethanol at 40-50° for 30 min. A 74½% recovery of hydrazinotriphenylphosphonium bromide was achieved.

12. Reaction with benzophenone

After prolonged reflux of benzophenone and methanol, the only solid isolated after trituration with ether and three recrystallizations from isopropanol was hydrazinotriphenylphosphazinium bromide.

13. Reaction with benzil

A methanolic solution (50 ml.) of hydrazinotriphenylphosphazinium bromide (3.73 g., 0.01 mole) and benzil (2.10 g., 0.01 mole) was refluxed for 24 hr. The mixture was then cooled and the yellow solid which separated during reaction was filtered and sucked dry. The product, 1.08 g. (52%), was identified as benzil azine. Its infrared spectrum was identical to that of authentic azine (22).

14. Reaction with fluorenone

Fluorenone (0.45 g., $2.5 \times 10^{-3}$ mole) was dissolved in methanol (25 ml.) and hydrazinotriphenylphosphonium bromide (0.93 g., $2.5 \times 10^{-3}$ mole) was added; the resulting solution was stirred overnight at room temperature. The red solid, 0.15 g., which had separated during reaction was then removed by filtration and sucked dry. This solid was identified as fluorenone azine from its infrared spectrum and from its melting point; 207-272° [lit. m.p. 265° (23)].


Removal of the methanol from the filtrate in vacuo on a steam bath produced 0.80 g. of yellow solid contaminated with some red-brown material. The red-brown material was dissolved in hot xylene leaving behind 0.40 g. (36%) of fluorenone triphenylphosphazinium hydrobromide, a stable yellow solid, m.p. 202-206°. This material was identified from its infrared spectrum, Figure 5, which shows absorption in the characteristic triphenylphosphazinium hydrobromide regions: 4.0 (s), 7.0 (s), and 9.0 (s) M, as well as by its conversion to the known triphenylphosphazine (see The Reaction of Triphenylphosphazinium Hydrobromides with Base).

Concentration of the xylene filtrate until a red solid started to separate afforded another 0.10 g. of fluorenone azine. The total yield of azine is 0.25 g. (56%).
15. Reaction with 9,10-Phenanthrenequinone

(a) A solution of 9,10-phenanthrenequinone (1.04 g., 5.10 \times 10^{-3} mole), hydrazinotriphenylphosphonium bromide (1.86 g., 5.0 \times 10^{-3} mole) and methanol was refluxed overnight. Removal of the solvent in vacuo on a steam bath gave a near black residue which showed absorption in the infrared at 4.9 \mu (diazo) and 5.8 \mu (carbonyl). Dissolution of the residue in methylene chloride followed by chromatography on alumina and elution with methylene chloride yielded 0.72 g. (25\%) of 9-diazo-10-phenanthrone after recrystallization of the eluant residue from cyclohexane. The infrared spectrum of this material was identical to that of authentic diazo compound (24), and its m.p., 108-111\degree, agrees with the literature value 107-109\degree (23).

(b) A slurry of 9,10-phenanthrenequinone (1.86 g., 5.0 \times 10^{-3} mole), hydrazinotriphenylphosphonium bromide (1.86 g., 5.0 \times 10^{-3} mole) and acetonitrile (100 ml.) was stirred at room temperature for 3 hr. At this time nearly all of the solid material had dissolved. The solution was filtered and the acetonitrile removed with a nitrogen stream. Dissolution of the red tarry residue in chloroform followed by chromatography on alumina afforded 0.54 g. (50\%) of 9-diazo-10-phenanthrone in the first 150 ml. of chloroform eluant and 0.22 g. (15\%) of triphenylphosphine oxide in the second 100 ml. of chloroform eluant. There were no other solids isolated.

(c) A slurry of 9,10-phenanthrenequinone (2.08 g., 0.01 mole), hydrazinotriphenylphosphonium bromide (3.73 g., 0.01 mole) and tetrahydrofuran (200 ml.) was stirred 1.5 hr. at room temperature. Separation of the solid at the end of this time afforded 3.0 g. (81%) of hydrazinotriphenylphosphonium bromide.

(d) 9,10-Phenanthrenequinone (2.08 g., 0.01 mole) and hydrazinotriphenylphosphonium bromide (3.73 g., 0.01 mole) was dissolved in chloroform (150 ml.) and the resulting solution stirred 10 hr. at room temperature. Addition of ether (500 ml.) brought about the separation of 3.10 g. of a yellow solid, which on storing for 3 hr. decomposed. The solid was still contaminated with traces of chloroform and ether on storage. From experiments a and b it is not unreasonable to assume that this solid was crude 9-diazo-10-phenanthrone which when impure underwent facile decomposition.

(e) There is no reaction when 9,10-phenanthrenequinone (1.80 g., 8.4 x 10⁻⁴ mole), hydrazinotriphenylphosphonium bromide (3.10 g., 8.4 x 10⁻⁴ mole), and monoglyme (200 ml.) are stirred 4 hr. at room temperature. A 74% recovery of hydrazinotriphenylphosphonium bromide is obtained.

The Reaction of Triphenylphosphazinium Hydrobromides with Base. A New Synthesis of Triphenylphosphazines

1. Acetone triphenylphosphazinium hydrobromide

Acetone triphenylphosphazinium hydrobromide (0.50 g., 1.21 x 10⁻³ mole) was added to a rapidly stirring mixture of aqueous 20% potassium hydroxide (5 ml.) and chloroform (20 ml.). Immediately upon the addition
the organic layer took on a yellow color (25). After the mixture had
been stirred for 15 min. the chloroform layer was separated, washed
with water and dried 20 min. over sodium sulfate. Removal of the
chloroform in vacuo gave 0.39 g. (98%) of acetone triphenylphosphazine
m.p. 109-111° [lit. m.p. 111° (3a)]. The infrared spectrum of the
product exhibits the following bands: 7.1 (s), 8.0 (m), 8.5 (m, broad),
9.1 (v.s. broad), 10.1 (w), and 13.9 (s) μ and is consistent with the
phosphazine structure (26).

that the P=N band in (PCl₃)₃ appears at 8.2 μ; however, L. Horner and
H. Oediger, Ann., 627, 150 (1959) assign the region 8.50-8.61 μ to the
P=N bond in a variety of phosphinimines. Further assignments made by
Horner and Oediger are: P-phenyl, 6.95-7.10 and 10.0-10.1 μ; "Ligand

2. Benzaldehyde triphenylphosphazinium hydrobromide

Duplication of the preceding experiment, except for use of the
indicated phosphazinium salt (0.50 g., 1.09 x 10⁻³ mole), yielded
benzaldehyde triphenylphosphazine. This material on recrystallization
from minimal isopropanol gave 0.29 g. (76%) of satisfactory product
m.p. 65-68° [lit. 65° (3a)]. Its infrared spectrum showed the following
bands: 7.1 (s), 8.0 (m), 8.5 (v), 8.7 (v), 9.1 (v.s. broad poorly
resolved doublet), 10.1 (v), and 14.0 μ. These bands are consistent
with the phosphazine structure (26).
3. **Acetophenone triphenylphosphazinium hydrobromide**

A solution of acetophenone triphenylphosphazinium hydrobromide (0.48 g., 1.0 x 10^{-3} mole) in chloroform (20 ml.) was added to aqueous sodium hydroxide (15 ml., 0.1 N); the resulting mixture was shaken in a separatory funnel for 10 min. Upon addition of the two solutions the chloroform layer became yellow in color almost immediately. The aqueous portion was washed with water and dried for 20 min. over sodium sulfate. Removal of the chloroform in vacuo (prolonged pumping) gave 0.38 g. (96%) of acetophenone triphenylphosphazine, m.p. 134-136° [lit. 133-135° (3b)]. The infrared spectrum, Figure 6, is consistent with the phosphazine structure (26).

4. **Fluorenone triphenylphosphazinium hydrobromide**

Fluorenone (0.50 g., 5.0 x 10^{-3} mole), hydrazinotriphenylphosphonium bromide (1.86 g., 5.0 x 10^{-3} mole) and methanol (50 ml.) were refluxed 3 hr.; the fluorenone azine which formed (0.04 g.) was removed by filtration. Removal of the methanol from the filtrate gave a solid which was dissolved in chloroform; this solution was chromatographed on basic Fisher alumina using chloroform as an eluant. The first 200 ml. of eluant afforded a solid which was a mixture of the phosphazine and the azine. Minimal hot xylene was used to wash out the azine; 1.12 g. (50%) of fluorenone phosphazine, m.p. 215-218° [lit. 209-210° (1)] , was obtained. The infrared spectrum, Figure 7, is consistent with the phosphazine structure.

The xylene filtrate, on reduction in volume, yielded 0.30 g. of fluorenone azine; the total yield of azine was 38%.
5. **p-Nitrobenzaldehyde triphenylphosphazinium hydrobromide**

   The phosphazinium hydrobromide (2.04 g., 5.0 x 10^-3 mole) was almost entirely dissolved in chloroform (40 ml.) and the resulting yellow solution was shaken with aqueous 1 N sodium hydroxide (10 ml.) for 5 min. Addition of the base brought about an immediate red color to the organic layer. The organic layer was washed once with water and dried for a short time over sodium sulfate. Removal of the chloroform at steam bath temperature *in vacuo* (prolonged pumping) gave 1.68 g. of a red-orange solid which after one recrystallization from isopropanol yielded 1.29 g. (80%) of red *p*-nitrobenzaldehyde triphenylphosphazine, m.p. 165-166° [lit. 162° (3c)]. This compound shows appropriate bands in the infrared, Figure 8, which are attributed to the phosphazine structure (26): 7.0 (s), 8.5 (w), 9.0 (shoulder), 9.1 (s, very broad), 10.0 (w), and 14.0 (w) M.

6. **Isobutyraldehyde triphenylphosphazinium hydrobromide**

   Sodium hydroxide (0.42 g., 1.03 x 10^-2 mole) in water (200 ml.) was added to a solution of isobutyraldehyde triphenylphosphazinium hydrobromide (4.72 g., 1.00 x 10^-2 mole) in methylene chloride (50 ml.) and the resulting mixture was shaken in a separatory funnel for 10 min. Immediately upon the addition of base the organic layer became yellow in color. The methylene chloride layer was then separated, washed once with water and dried for a short time over sodium sulfate. Removal of the methylene chloride at room temperature *in vacuo* (prolonged pumping) gave 3.30 g. (89%) of crude isobutyraldehyde triphenyl-
phosphazine, a yellow solid, m.p. 92-98°. Attempts to improve the melting point of the product resulted in its cleavage to triphenylphosphine oxide. The infrared spectrum is consistent with the phosphazine structure (26); absorption occurs at: 7.0 (s), 8.4 (s), 8.6 (w), 9.0 (v.s. broad), 10.0 (m), and 14.0 (s).

7. Cyclohexanone triphenylphosphazine hydrobromide

Chromatography of the phosphazinium hydrobromide (2.00 g., $4.5 \times 10^{-3}$ mole) on basic alumina, employing chloroform as the eluant, afforded 1.55 g. (92%) of a yellow solid. This solid, m.p. 130-133°, was obtained only after prolonged pumping on the chloroform solution. It was extremely sensitive to moisture and could not be stored in vacuo over sodium hydroxide, over a period of several weeks, without undergoing cleavage to triphenylphosphine oxide. Infrared evidence indicates that this solid is cyclohexanone triphenylphosphazine; absorption occurs at: 7.0 (s), 8.3 (m), 8.5 (m), 9.0 (v.s. broad), 10.1 (m), and 14.0 (s).

Reaction of N-Aminotriphenylphosphinimine with Carbonyl Compounds

All equipment was baked at 110° and flame dried before use, also precautions were always taken to prevent the introduction of moisture into the reaction before and during the addition of n-butyllithium.

1. Reaction with p-nitrobenzaldehyde

A flask equipped as in Experiment 1 was charged with dry benzene (75 ml.), hydrazinotriphenylphosphonium bromide (3.73 g., 0.01 mole) and
Linde 4-A molecular sieves (10 g.). The flask was purged with dry nitrogen and cooled to 7-10°. n-Butyllithium (0.01 mole) was then added to the stirred mixture at a rate such that the temperature did not exceed 10°. The reaction mixture took on a red-brown color when the base was added; upon completion of the addition the reaction was stirred an additional 0.5 hr. at 7-10° and 0.5 hr. at room temperature. p-Nitrobenzaldehyde (1.51 g., 0.01 mole) was added all at once to this stirred mixture at room temperature. The addition was accompanied by a near immediate color change from red-brown to yellow; after stirring for one hour at room temperature the solution turned deep red. The molecular sieves were separated by filtration and washed with chloroform. Removal of the solvent from the combined filtrate and wash (in vacuo) gave 3.9 g. (92%) of a red glass-like material identified as crude phosphazine from its infrared spectrum. Grinding this glass with ether gave 2.4 g. (56%) of a red-brown powder whose infrared spectrum is identical to that in Figure 8.

2. Reaction with acetophenone

A 100 ml. reaction flask equipped with a TrueBore stirrer, serum cap, thermometer, and condenser with a drying tube was charged with hydrazinotriphenylphosphonium bromide (1.86 g., 5.0 x 10⁻³ mole), dry benzene and Linde 4-A molecular sieves (10 g.). The system was flushed with dry nitrogen and then n-butyllithium (5.0 x 10⁻³ mole, in hexane) was added dropwise with stirring over a 15 min. period. The temperature was maintained at 7-10° during the addition. Immediately upon the addition of n-butyllithium the reaction mixture turned red-brown; after
completion of the addition the solution was brought to room temperature and stirred an additional hour. Acetophenone (0.60 g., 5.0 x 10^-3 mole) was added to the rapidly stirring mixture at room temperature, bringing about the separation of a jelly-like solid; after refluxing for one hour, the mixture was cooled to room temperature and stirred overnight. The reaction mixture was filtered under nitrogen and the solid was washed with dry benzene. Removal of the benzene from the filtrate (in vacuo) left a yellow oil which resisted solidification. Only after prolonged pumping did solidification occur and 1.35 g. (69%) of yellow acetophenone triphenylphosphazine was obtained. Attempts to crystallize this material resulted in considerable oiling out (perhaps due to trace acetophenone present) and because of its moderate sensitivity to moisture at ambient conditions further attempts at purification were not pursued. Except for a trace of acetophenone present the infrared spectrum of this material is identical to that of authentic acetophenone triphenylphosphazine described on page 35.

3. Reaction with benzophenone

N-Aminotriphenylphosphinimine (0.01 mole) was prepared in situ as above. The intense red-brown color was again noted on the addition of n-butyllithium. Benzophenone (1.82 g., 0.01 mole) was added all at once with stirring to the benzene solution of the phosphinimine at room temperature. A jelly-like material was also observed in this reaction. Stirring of the mixture was continued for 30 hr. after the addition; the reaction mixture was filtered and the solid residue washed with chloroform. Removal of the organic solvents (in vacuo) gave a red-brown oil which on prolonged stirring with ether gave a
finely divided yellow powder along with a red-brown semi-solid; the latter material adhered so strongly to the walls of the flask and stirrer that the fine yellow powder could be poured from the flask suspended in the ether without contamination by the semi-solid. The yellow solid, 1.47 g., was identified as benzophenone triphenylphosphazene, m.p. 173-175° dec. [lit. m.p. 173° dec. (3a)]; the infrared spectrum, Figure 9, is consistent with the phosphazene structure (26). Continued stirring of the remaining red-brown semi-solid in ether afforded an additional 0.30 g. of the phosphazene. The total yield of the phosphazene is 1.72 g. (39%).

4. Reaction with fluorenone

N-Aminotriphenylphosphinimine (5.0 x 10^{-3} mole) was prepared in situ as previously described except that the molecular sieves were not employed in this reaction; also the mixture was stirred 2 hr. after the addition of butyllithium and then refluxed 10 min. under nitrogen. The red-brown color noted previously upon the addition of base was also observed here. Fluorenone (0.92 g., 5.1 x 10^{-3} mole), dissolved in benzene, was then added to the stirred mixture at room temperature; stirring was continued for 7 hr. at room temperature and the mixture was refluxed 0.5 hr. Removal of the solvent with a stream of nitrogen deposited a yellow solid in the flask; the product was washed out of the flask with ethanol and dried. Fluorenone triphenylphosphazene, 1.0 g. (44%), as isolated in this manner melted at 212°-213° [lit. m.p. 209-210° (1)]. Its infrared spectrum is identical to that of Figure 7.
Attempted Decomposition of Triphenylphosphazines

1. Acetophenone triphenylphosphazine with methyl iodide.

Acetophenone triphenylphosphazine (1.00 g., 2.5 x 10^{-4} mole) was dissolved in ethyl acetate (30 ml.) and the resulting solution brought to reflux. Excess methyl iodide (1.0 ml.) was introduced through a serum cap into the refluxing solution and the mixture refluxed for 4 hr. A white crystalline solid was then filtered and washed with ether giving 1.0 g. (82%) of \( \text{[\( \alpha \)-N-methyl-\( \alpha \)-N-methylbenzylidenehydrazino]} \) -triphenylphosphonium iodide, m.p. 180-182° [lit. m.p. 180-182° (3b)].

2. Fluorenone triphenylphosphazine with methyl iodide. The above experiment was duplicated except that fluorenone triphenylphosphazine was employed and the reflux time increased to 14 hr. A 73% yield of yellow \( \text{[\( \alpha \)-N-methyl-\( \alpha \)-N-fluorenlylidenehydrazino]} \) -triphenylphosphonium iodide was isolated, m.p. 168-171° [lit. m.p. 175-178° (3b)].

3. p-Nitrobenzaldehyde triphenylphosphazine with methyl iodide.

p-Nitrobenzaldehyde upon treatment with methyl iodide as above gave only the yellow \( \text{[\( \alpha \)-N-methyl-\( \alpha \)-N-p-nitrobenzylidenehydrazino]} \) -triphenylphosphonium iodide (71%), m.p. 218-221° [lit. m.p. 223° (3c)].

4. Thermolysis of acetophenone triphenylphosphazine in tetrahydrofuran. Acetophenone triphenylphosphazine was dissolved in dry tetrahydrofuran (30 ml.) and cuprous chloride (0.10 g.) was added to this solution. The flask was flushed with nitrogen and the solution refluxed 4 hr. There was no color change of the mixture. Additional cuprous chloride (0.10 g.) was added and the solution refluxed an
additional 12 hr. Removal of the solvent in vacuo gave 3.42 g. (86%) of the starting phosphazine.

5. Neat pyrolysis of acetophenone triphenylphosphazine. A flask equipped with an exhaust port leading to a gas measuring device was charged with acetophenone triphenylphosphazine (7.70 g., 1.96 x 10⁻² mole). The system was flushed with nitrogen and heated between 160-170° for 3 hr. Nitrogen (1.03 x 10⁻³ mole, 50%) was evolved. A red-brown oil remained which did not solidify at room temperature. Trituration of this product with ether gave 1.31 g. of triphenylphosphine oxide. The ether solution on concentration gave an additional 1.24 g. of triphenylphosphine oxide (total triphenylphosphine oxide, 47%). Removal of the ether from the filtrate which afforded the second crop of triphenylphosphine oxide resulted in an oil containing crystals of acetophenone azine (0.78 g., 34%). Vacuum filtration of this oil followed by an ethanol wash effected separation of the azine. Reduction in the volume of this ethanol wash gave 1.33 g. (25%) of triphenylphosphine. Final evaporation of the ethanol wash gave 2.60 g. of an oil composed of triphenylphosphine and triphenylphosphine oxide (from the infrared spectrum).

6. Irradiation of acetophenone triphenylphosphazine. A quartz reaction flask equipped with an internal magnetic stirrer and cooled externally with running water was charged with acetophenone triphenylphosphazine (3.95 g., 0.01 mole), tetrahydrofuran (300 ml.) and cuprous chloride (0.20 g.). The solution was then irradiated for 20 hr. with a Hanovia 500 watt ultraviolet lamp. At the end of this time a 98% recovery of the initial phosphazine was realized as the phosphonium
iodide upon heating the solution with added methyl iodide followed by reduction in volume of the solvent.

7. Vacuum pyrolysis of fluorenone triphenylphosphazaine.

Fluorenone triphenylphosphazaine (1.48 g., $3.3 \times 10^{-3}$ mole) was placed in a vacuum sublimator and the apparatus (evacuated to 5 mm. Hg.) immersed in an oil bath at 180° for 30 min.; during this time a red oil deposited on the cold finger. The temperature was then raised to 205° over a 20 min. period; during this time additional red material collected on the cold finger. At 205° the solid in the bottom of the sublimator melted with apparent decomposition. Upon completion of the melting, the sublimator was removed from the oil bath whereupon the red oil solidified on the cold finger. The infrared spectra of the discolored residue, 0.91 g. (61%), quite surprisingly, was identical to that of the initial phosphazaine. Dissolution of the sublimate in minimal chloroform followed by ether afforded 0.12 g. (8.1%) of fluorenone triphenylphosphazaine. Removal of the solvent from the ether-chloroform filtrate gave 0.20 g. of a semi-solid which was a mixture of triphenylphosphine and fluorenone azine.

The Preparation, Properties and Reactions of N-Benzamidotriphenylphosphinimine

The preparation of N-benzamidotriphenylphosphiniminium bromide

(A) Hydrazinotriphenylphosphonium bromide (9.34 g., $2.5 \times 10^{-2}$ mole) was added to a solution of benzene (60 ml.), pyridine (2.6 g., $3.3 \times 10^{-3}$ mole), and benzoyl chloride (3.6 g., $2.6 \times 10^{-2}$ mole). The resulting mixture was refluxed 2 hr.; at this time a white solid was
separated which was washed with ether and water and dried in vacuo, 7.65 g. (64%); it was identified as N-benzamidotriphenylphosphiniminium bromide, m.p. 180° (turns red). Its infrared exhibits bands at 3.6 (s), 5.9 (s), 6.9 (s), 7.7 (m), 9.0 (s, broad), 11.0 (m), and 13.6, 13.7 (s, poorly resolved doublet). It is stable to moisture and the atmosphere at normal conditions. An analytical sample was prepared by recrystallization from isopropanol.

Anal. Calcd. for C_{22}H_{22}N_{2}OPBr: C, 62.90; H, 4.65; N, 5.87; P, 6.49

Found: C, 63.62; H, 4.93; N, 6.28; P, 6.31

Found: C, 64.86; H, 4.92; N, 6.17; P, 6.43.

(E) Triethylamine (12.12 g., 0.12 mole) was added to a suspension of triphenylphosphine dibromide (4.22 g., 0.10 mole) (18); benzhydrazide (13.6 g., 0.10 mole) was added to the resulting suspension over a 2 hr. period. The mixture was stirred 18 hr. after the addition was completed; at this time the solid was separated and washed with benzene, ether, and finally water. A stable white solid, 36.29 g. (76%) identified as N-benzamidotriphenylphosphiniminium bromide was isolated, m.p. 179-183° (turns red). The infrared spectrum of this stable white solid is identical to that of the solid isolated in the experiment previously described.

The preparation of N-benzamidotriphenylphosphiniminium

(C) N-Benzamidotriphenylphosphiniminium bromide (10.0 g., 0.027 mole) was added to chloroform (200 ml.) in a separatory funnel and shaken until near dissolution of all the solid was achieved. Sodium hydroxide (50 ml., 1.0 N) was added and the resulting mixture shaken 5 min. The
chloroform layer was separated and the aqueous layer extracted with chloroform; the combined chloroform extracts were washed once with water and dried over sodium sulfate. Removal of the chloroform (in vacuo) gave a red brown oil which upon trituration with ethyl acetate gave a cream-colored solid, N-benzamidotriphenylphosphinimine, 3.1 g. (29%), m.p. 194-200°. An analytical sample was prepared by recrystallization from ethyl acetate, m.p. 202-203°. The infrared spectrum, Figure 10, shows absorption at: 5.8 (s), 7.0 (m), 7.4 (s), 8.1 (s), 8.5 (w) 9.0 (m), 10.0 (v), 13.8 (m), and 14.3, 14.4 (s, doublet) M, and is consistent with the proposed structure. Further proof of structure of N-benzamidotriphenylphosphinimine is also supplied by its reactions.

**Anal. Calcd. for C$_{25}$H$_{21}$N$_2$O$_7$: N, 7.07**

**Found: N, 6.58.**

(D) The reaction of N-benzamidotriphenylphosphinimine with p-nitrobenzaldehyde. p-Nitrobenzaldehyde (0.378 g., 2.5 x 10$^{-3}$ mole) and N-benzamidotriphenylphosphinimine (1.00 g., 2.5 x 10$^{-3}$ mole) were added to dry benzene (60 ml.), and the resulting mixture stirred 15 hr. Complete dissolution of the reactants occurred a few minutes after stirring had been initiated; at this point a yellow solid separated from solution. This solid, 0.55 g. (82%), was identified as p-nitrobenzaldehyde benzoylhydrazone, m.p. 241-244° [lit. m.p. 243° (27)].

Its infrared spectra is identical to authentic p-nitrobenzaldehyde benzoylhydrazone.

(E) Reaction of \( N \)-benzamidotriphenylphosphinimine with \( m \)-nitrobenzaldehyde. \( m \)-Nitrobenzaldehyde (0.23 g., 1.5 \( \times \) 10\(^{-3} \) mole) and \( N \)-benzamidotriphenylphosphinimine (0.60 g., 1.5 \( \times \) 10\(^{-3} \) mole) were added to dry benzene and the resulting mixture shaken 10 min., then refluxed 30 min. The solvent was removed by blowing nitrogen over the mixture. The solid deposited was washed successively with benzene, methanol, and ether. The pale yellow product, 0.32 g. (79%), was identified as \( m \)-nitrobenzaldehyde benzoylhydrazone, m.p. 197-199\(^\circ\) [lit. m.p. 197\(^\circ\) (27)]. Its infrared spectrum was identical to that of the authentic benzoylhydrazone (27).

(F) Attempted thermolysis of \( N \)-benzamidotriphenylphosphinimine. \( N \)-Benzamidotriphenylphosphinimine was recovered unchanged (79% recovery) after refluxing 62 hr. in dry benzene. There was no triphenylphosphine oxide detected.

The preparation of \( \alpha \)-hydroxybenzylidene-triphenylphosphazine

(G) \( N \)-Benzamidotriphenylphosphinimium bromide (21.88 g., 0.046 mole) was stirred with triethylamine (5.0 g., 0.05 mole) in tetrahydrofuran (300 ml.) for 30 hr. The solid material was filtered; on removing the solvent from the reddish filtrate a pink solid remained. This product was washed with water, dried in vacuo, and then washed with ethyl acetate. A white solid, 7.00 g. (39%), was obtained whose infrared spectrum, Figure 11, showed an extremely weak carbonyl absorption, m.p. 185-189\(^\circ\). On the basis of the spectral evidence and the
product of reaction with m-nitrobenzaldehyde this solid is a stable enolic form of N-benzamidotriphenylphosphinimine and is named α-hydroxybenzylidenetriphenylphosphazine.

Recrystallization of 0.50 g. of the solid isolated from ethyl acetate resulted in the isolation of 0.28 g. (56%) of a white solid, m.p. 194-196°. The infrared spectrum, Figure 12, of this material (after prolonged heating in vacuo) is identical to N-benzamidotriphenylphosphinimine. A mixed m.p. is not depressed.

m-Nitrobenzaldehyde (0.46 g., 3.0 x 10^{-3} mole) was refluxed with α-hydroxybenzylidenetriphenylphosphazine (1.20 g., 3.3 x 10^{-3} mole), isolated in the above reaction, in dry benzene (20 ml.) for 1.5 hr. Initially upon heating the reactants dissolved; however, after a few minutes crystals began to deposit on the walls of the flask. After cooling the solid was separated and washed in turn with benzene and ether. A pale yellow solid, 0.55 g. (67%) identified as m-nitrobenzaldehyde benzoylhydrazone, m.p. 194-195° [lit. m.p. 197° (27)], was obtained. Its infrared spectrum was identical to that of the authentic benzoylhydrazone (27).

(H) Triethylamine (20.2 g., 0.20 mole) was added to a stirred suspension of triphenylphosphine dibromide (4.22 g, 0.10 mole) (18) in benzene. Benzhydrazide (13.6 g., 0.10 mole) in tetrahydrofuran was added dropwise to this cooled suspension (7-10°) over a 2 hr. period. The reaction was stirred 14 hr. after completion of the addition and then refluxed 15 min.; at this time a white solid, 32.5 g. (89%), identified as triethylamine hydrobromide was separated by filtration.
Removal of the benzene-tetrahydrofuran from the filtrate yielded a reddish semi-solid which upon trituration with ethyl acetate gave a micro-fine red solid. Washing this solid with ethyl acetate removed the red color leaving behind 11.14 g. (34%) of white micro-fine crystals, m.p. 183-186°. The infrared spectrum of this material, Figure 13, shows no carbonyl absorption and is nearly identical to that obtained in Experiment G, Figure 11. The chemistry of this material, which is described in the following experiments, in conjunction with its infrared spectra suggest that it is the enol form of N-benzamidotriphenylphosphinimine, i.e., α-hydroxybenzylidenetriphenylphosphazine, encountered previously in Experiment G. It was found to be relatively stable at ambient conditions and required no special handling techniques. It is recommended that the phosphazine be stored in a desiccator if it is to be kept for great lengths of time.

The red contaminant was isolated and identified as 3,6-diphenyl-1,2,4,5-tetrazine, 0.60 g. (5.0%, analytically pure), m.p. 199-200° [lit. m.p. 195° (28)]. Its infrared spectrum is identical to that of authentic tetrazine (28).


(I) When the α-hydroxybenzylidenetriphenylphosphazine isolated in G (1.20 g., 3.3 x 10⁻³ mole) was added to m-nitrobenzaldehyde in benzene an exothermic reaction took place which subsided after 10 min. The solution was refluxed 1.5 hr., whereupon a crystalline solid began to deposit on the walls of the flask. After standing overnight this
pale yellow solid was separated and identified as \( m \)-nitrobenzaldehyde benzoylhydrazone, 0.67 g. (87\%), m.p. 194-197° [lit. m.p. 197° (27)].

Its infrared spectrum was identical to that of authentic benzoylhydrazone.

\( (J) \) Reaction of benzoyl chloride with \( \alpha \)-hydroxybenzylidenetriphenylphosphazine. \( \alpha \)-Hydroxybenzylidenetriphenylphosphazine (0.40 g., \( 1.0 \times 10^{-3} \) mole) was dissolved in dry benzene (30 ml.); then triethylamine (0.20 g., \( 2.0 \times 10^{-3} \) mole) was added, with stirring, to the benzene solution and the resulting pale yellow solution stirred 0.5 hr. Benzoyl chloride (0.14 g., \( 1.0 \times 10^{-3} \) mole) was added and the mixture was stirred at room temperature for 24 hr. Removal of the benzene (in vacuo) gave a crude white solid which was washed with water and then recrystallized from ethanol to give 0.12 g. of a fluffy white solid, m.p. 136-138°. The infrared spectrum of this solid shows no carbonyl absorption and is identical to that of 2,5-diphenyl-1,3,4-oxadiazole (29), [lit. m.p. 138° (30)]. Treatment of an ethanolic

\( (29) \) E. Muller and W. Rundel, Ber., 88, 917 (1955).

solution of the oxadiazole with ethanolic silver nitrate gave the silver salt, m.p. 271-275° dec. [lit. m.p. 275° dec. (30)]. Concentration


of the ethanolic mother liquor gave an additional 0.02 g. of the oxadiazole. The yield of the oxadiazole was 64\%. Evaporation of the ethanolic mother liquor to dryness yielded 0.25 g. (90\%) of crude triphenylphosphine oxide.
(K) Preparation of the lithium salt of $\alpha$-hydroxybenzylidenetriphenylphosphazine. $\alpha$-Hydroxybenzylidenetriphenylphosphazine (0.80 g., $2.0 \times 10^{-3}$ mole) was dissolved in dry benzene; the flask was flushed with nitrogen and n-butyllithium ($2.0 \times 10^{-3}$ mole, in hexane) was added at a rate such that the temperature was maintained at $35-40^\circ$. Upon completion of the addition of base the mixture was green-yellow. After the mixture had been stirred at room temperature for 16 hr., a yellow solid had precipitated from the reaction, it was filtered, washed in turn with benzene and ether, and dried, m.p. 205° (dec.). This material 0.20 g. (87%) was not hygroscopic or sensitive to atmospheric conditions on short exposure; it is only sparingly soluble in water, but treatment of its aqueous suspension with excess aqueous hydrobromic acid (40%) caused the discharge of yellow color giving N-benzamidotriphenylphosphiniminium bromide. An infrared spectrum, identical to authentic N-benzamidotriphenylphosphiniminium bromide, showed absorption at: 7.0 (s), 9.0 (s, accompanied by a shoulder), 10.1 (v), and 13.7 (m, poorly resolved doublet) $\mu$. This information in conjunction with the reaction of this material with benzoyl chloride (see below) indicates that it is the lithium salt of $\alpha$-hydroxybenzylidenetriphenylphosphazine.

(L) Reaction of the lithium salt of $\alpha$-hydroxybenzylidenetriphenylphosphazine with benzoyl chloride. The lithium salt (0.80 g., $2.0 \times 10^{-3}$ mole) of $\alpha$-hydroxybenzylidenetriphenylphosphazene was suspended in dry benzene (30 ml.) and benzoyl chloride (0.28 g., $2.0 \times 10^{-3}$ mole) then added. The mixture lost its yellow color immediately and was stirred 48 hr. at room temperature. The solvent was removed (in vacuo)
and the white solid residue was washed with water and then cold ethanol. A solid, 0.35 g. (80%), identified as 2,5-diphenyl-1,3,4-oxadiazole was isolated, m.p. 130-133° [lit. m.p. 138° (30)]. Its infrared spectrum is identical to that of authentic material (29).

(II) Reaction of α-hydroxybenzylidenetriphenylphosphazine with p-nitrobenzoyl chloride. α-Hydroxybenzylidenetriphenylphosphazine (0.40 g., 1.0 x 10^{-3} mole) was dissolved in dry benzene (30 ml.); then triethylamine (0.20 g., 2.0 x 10^{-3} mole) was added, with stirring, to the benzene solution and the resulting pale yellow solution was stirred 0.5 hr. p-Nitrobenzoyl chloride (0.19 g., 1.0 x 10^{-3} mole) was added and the reaction was stirred at room temperature for 24 hr. Removal of the benzene (in vacuo) at steam bath temperature gave a crude pale yellow solid. This solid was washed with water and then minimal ethanol giving 0.25 g. (94%) of 2-phenyl-5-p-nitrophenyl-1,3,4-oxadiazole, a pale yellow solid, m.p. 210-211°, sublimes, prior to melting [lit. m.p. 209° (31)].


(II) Reaction of α-hydroxybenzylidenetriphenylphosphazine with 3,5-dinitrobenzoyl chloride. Repetition of the above experiment, except for use of the indicated acid chloride, gave 0.24 g. (74%) of 2-phenyl-5,3,5-dinitrophenyl-1,3,4-Oxadiazole, a cream-colored solid, m.p. 226-228° [lit. m.p. 228° (31)].
Figure 4

\[ \text{CH}_3 \]

\[ [\text{C}_6\text{H}_5 - \text{C} = \text{N} - \text{NH} - \text{P(C}_6\text{H}_5)_3]^{+}\text{Br}^- \]

Figure 5

\[ \text{N} - \text{N} - \text{P(C}_6\text{H}_5)_3]^+ \text{Br}^- \]

Figure 6

\[ \text{CH}_3 \]

\[ \text{C} = \text{N} - \text{N} - \text{P(C}_6\text{H}_5)_3 \]
PART II

THE REACTION OF GLYOXAL WITH p-TOUENESULFONYL HYDRAZIDE AND 9-NAPHTHALENESULFONYL HYDRAZIDE; THE BASE CATALYZED DECOMPOSITION OF VICINAL-BIS-TOSYLHYDRAZONES AND 1-p-
TOUEN SULFONAMIDO-1,2,3-TRIAZoles
INTRODUCTION

In 1952 Bamford and Stevens (1) reported that base-catalyzed decomposition of \( p \)-tosylhydrazones of aldehydes and ketones in ethylene glycol yields diazo compounds or products resulting from their decomposition. A specific example is given below (Equation 1). This work subsequently led to new insights into the chemistry of carbenic and cationic intermediates and the disciplines involved in their decomposition (2). Decomposition of salts of \( p \)-tosylhydrazones subsequently became a useful synthetic route for preparation of certain aliphatic diazo compounds (3). A fundamental conclusion that can be drawn from

\[
\text{N-NH-SO}_2\text{C}_7\text{H}_7 \quad + \text{NaOCH}_2\text{CH}_2\text{OH}^-\text{H}_2 \quad \rightarrow \quad \text{N-O}_2\text{SC}_7\text{H}_7 \quad + \quad (\text{CH}_2\text{OH})_2
\]  

(1)


base-catalyzed decompositions of \( \alpha \)-tosylhydrazones is that the diazo specie is formed from decomposition of the conjugate anion of the parent \( \alpha \)-tosylhydrazone and its fate depends on its structure and its environment.

\( \alpha \)-Diazocarbonyl compounds play important roles in synthetic and physical-organic chemistry: the interest and depth of study of \( \alpha \)-diazocarbonyl compounds is well documented by the large number of publications in this area. Some of the synthetic routes to \( \alpha \)-diazocarbonyl compounds, specifically \( \alpha \)-diazoketones are: reactions of diazomethane with carboxylic acid chlorides (Equation 2) (4), oxidation of the appropriate vicinal dicarbonyl monohydrazone (Equation 3) (5),

\[
\text{RCOCl} + 2\text{CH}_2\text{N}_2 \rightarrow \text{RCOCHN}_2 + \text{CH}_2\text{Cl} + \text{N}_2
\] (2)

and base-catalyzed decomposition of the appropriate mono-\( \alpha \)-tosylhydrazone (Equation 4) (6).


(5) L. Smith and H. Hoehn, Org. Syn., Coll. Vol. 3, 356 (1955), give a procedure for the preparation of azibenzil which is generally applicable to other \( \alpha \)-diazoketone preparations.

The synthesis and chemistry of α-diazoacetaldehyde I, the parent compound, have received little attention. Diazoacetaldehyde would be of value for the direct preparation of cyclopropanecarboxaldehyde, (Equation 5) from olefins. Of interest also would be its possible 1,3-dipolar addition to multiple bonds (Equation 6), or its laboratory utility upon controllable decomposition to ketene (Equation 7).

\[
\begin{align*}
R_2C=CR_2 + N_2CHCHO & \rightarrow CHCHO + N_2 \\
(5) \\
RC≡CR + N_2CHCHO & \rightarrow C≡C-H + N_2 \\
(6) \\
N_2CHCHO & \rightarrow H_2C=O \\
(7)
\end{align*}
\]

A possible satisfactory entry into this area would be preparation of glyoxal monotosylhydrazone II (Equation 8), followed by its base catalyzed decomposition (Equation 9). A variety of attempts to prepare glyoxal monotosylhydrazone, however, were not successful and only glyoxal
bis-π-tosyldiazirine could be isolated (Equation 11). The ready obtention

\[
\text{OHCH} + \text{TosNH₂} \rightarrow \text{OHCH} \text{H₂} + \text{Tos}^-
\]  

(10)

of glyoxal bis-π-tosyldiazirine prompted a reinvestigation of base
catalyzed decompositions of vicinal-bis-π-tosyldiazirines (11). This

(11) W. Bamford and T. Stevens (1) found that in ethylene glycol
the course of this decomposition was a function of the groups attached to
the carbon bearing the tosylhydrazone (see Historical).

decomposition in principle can lead to a vicinal-bis-diso intermediate
XII which may ultimately yield an acetylene (Equation 12). In general,

\[
\text{Tos-\text{H}-H-\text{H}Tos} \ \ 
\begin{array}{c}
\text{RC-OR} \\
\text{Base} \\
\text{-2H₂}
\end{array} \rightarrow \text{2Tos}^- + \text{RC-OR} \\
\begin{array}{c}
\text{RC} \\
\text{RC}
\end{array}
\]  

(12)

the literature preparations of acetylenes suffer from low yield and/or
tedious workup; it was hoped, therefore, by alteration of conditions
and/or solvent that Equation 12 would provide an improved route to
acetylenes.
Diarylacetylenes such as diphenylacetylene, o,o'-dimethoxydiphenylacetylene and p,p'-dimethoxydiphenylacetylene have been prepared by oxidation of the requisite vicinal-bis-hydrazone with mercuric oxide (Equation 13) (12). Cycloalkynes of medium sized rings such as cyclo-

\[
\text{ArC=CAr + 2H}_2\text{O} \xrightarrow{\text{2HgO}} \text{2ArC=CAr + 2N}_2
\]

 yields respectively by reaction of the appropriate bis-vicinal-hydrazone with mercuric oxide and potassium hydroxide (Equation 14) (13). Cycloheptyne and cyclohexyne were prepared in 26 and 7% yields

\[
(\text{CH}_2)_n \xrightarrow{\text{KOH}} (\text{CH}_2)_n + 2\text{H}_2
\]

respectively upon employing this method (14).
Triazoles are also formed in oxidation of bis-vicinal-hydrazones. 2,2'-Dimethoxybiphenyl-bis-hydrazone when boiled with mercuric oxide gave chiefly the requisite aminotriazole and little 2,2'-dimethoxytolane (Equation 15) (12a). Triazoles also were produced in 25 and 33% yields respectively, from oxidation of 1,2-cycloheptanedione and 1,2-cyclohexanedione bis-hydrazones (Equation 16) (14). There is no mention of triazoles being formed in oxidation of medium-ring 1,2-cycloalkanedione bis-hydrazones (13).

Oxidation of vicinal-bis-hydrazones is limited in that triazole formation reduces the yield of acetylene; also mercuric oxide is expen-
sive and cumbersome to use and it may oxidize other groups in the molecule. A rapid non-oxidative procedure would therefore have advantage.

Diphenylacetylene is produced in 73% yield by base-catalyzed decomposition of benzil-bis-p-tosylhydrazone employing sodium in ethylene glycol at unspecified temperature (Equation 17) (1). However 2,3-butanedione, 4,5-octanedione and methylphenylglyoxal bis-p-tosylhydra-

\[
\begin{align*}
\phi-C=\text{NNHTos} & \xrightarrow{2\text{Na}/(\text{CH}_2\text{OH})_2} \phi-\text{C}=\phi + 2\text{H}_2 + 2\text{NaTos}^- \\
\phi-C=\text{NNHTos} & \xrightarrow{(\text{NaOCH}_2\text{CH}_2\text{OH})} \phi-\text{C}=\phi + 2\text{H}_2 + 2\text{NaTos}^- 
\end{align*}
\]  

zones upon reaction with potassium hydroxide in ethylene glycol, at unspecified temperatures, afforded only the p-tosylanido-triazoles in 79, 81, and 72% yields respectively (Equation 18); there were no hydrocarbons detected in these experiments (1).

\[
\begin{align*}
\text{R}_1\text{C}=\text{NNHTos} & \xrightarrow{\text{KOI}/(\text{HOCH}_2)_2} \text{R}_2(\text{R}_1)\text{C}=\text{N}^+ \text{N}^-\text{Tos}^- \\
\text{R}_2\text{C}=\text{NNHTos} & \xrightarrow{\Delta} \text{R}_2(\text{R}_1)\text{C}=\text{N}^+ \text{N}^-\text{Tos}^- 
\end{align*}
\]  

Triazoles have been observed to be in equilibrium with their corresponding unrearranged diazo compounds when dissolved in ethanol at 25° (Equation 19) (15). The value of the equilibrium constant in

(15) O. Dimroth, Ann., 373, 349 (1910).

Equation 19 varies from 3 when \( R \) is H and \( R^1 \) is CONH\(_2\) to 555 when \( R \) is
2-NO₂C₆H₄ and R¹ is CO₂CH₃. Such ring-chain tautomerization has also been postulated to account for the mobile equilibrium, in the melt, between 1-substituted 1,2,3-triazoles IV and the corresponding 5-substituted isomers V (Equations 20, 21 and 22) (16). Since 1-benzoyle-


4,5-diphenyl-1,2,3-triazole loses nitrogen to give 2,4,5-triphenyloxazole in 29% yield (Equation 23) (17), it appears that a diazo intermediate is

involved.
A study has been made of reaction of glyoxal and p-toluenesulfonyl hydrazide under various conditions in an effort to prepare glyoxal monotosylhydrazone. Glyoxal and p-toluenesulfonyl hydrazide, in a 1:1 mole ratio, gave 68-69% yields of glyoxal bis-tosylhydrazone in methanol at 40°. Lowering the reaction temperature to -5° and 25°, maintaining a 1:1 mole ratio, still resulted in formation of the bis-tosylhydrazone in 53 and 70% yields respectively; methanol was used as a solvent (18). The use of diethyl ether-methanol as a solvent, and varying the mole ratio of tosylhydrazide to glyoxal from 1:1 to 1:10, gave only glyoxal bis-tosylhydrazone in 66 and 55% yields respectively.

It was possible that continued formation of the bis-tosylhydrazone was related to the expected solubility of the monotosylhydrazone in methanol, thus permitting the mono-derivative to react with additional tosylhydrazide (also soluble in methanol). In an effort to prepare a monosulfonylhydrazone of glyoxal which might separate or precipitate rapidly, a study was made of reaction of glyoxal and p-naphthalenesulfonyl hydrazide. Glyoxal bis-p-naphthalenesulfonylhydrazone was formed in high yield however, instead of the desired monohydrazone; in these
reactions the mole ratio of hydrazide to glyoxal was varied from 1:1 to 1:5.

Commercial aqueous glyoxal has a pH of approximately two. Since strong acids accelerate decomposition of tosylhydrazones (19) and in


the present case might catalyze disproportionation of the glyoxal monotosylhydrazone to glyoxal and glyoxal bis-tosylhydrazone (20), a study

(20) L. Jones, C. K. Hancock, and R. B. Seligman, J. Org. Chem., 26, 228 (1961) report that only the bis-2,4-dinitrophenylhydrazone was isolated from reaction of glyoxal and 2,4-dinitrophenylhydrazine under acidic conditions. Formation of the bis-hydrazone was attributed to rapid disproportionation of the mono-derivative.

was then made of reactions of neutralized solutions of glyoxal and p-toluenesulfonyl hydrazide. Neutralized glyoxal under heterogeneous conditions gave a 64% yield of glyoxal bis-tosylhydrazone; the mole ratio of glyoxal to tosylhydrazide was 10:1. Buffered solutions of glyoxal also afforded only the bis-derivative when either p-toluene-

sulfonyl hydrazide (mole ratio of glyoxal to hydrazide, 1:1) or p-
naphthalenesulfonyl hydrazide (mole ratio of glyoxal to hydrazide, 5:1) was used.

Additional experiments with basic glyoxal yielded only polymeric material; glyoxal is known to polymerize in alkaline solution (21).

(21) H. Raudnitz, Chem. and Ind., 27, 366 (1944).
When glyoxal sulfate was employed as the source of glyoxal (Equation 23) a solid was isolated which exhibited characteristics of

\[
\text{SO}_2\overset{0}{\text{O}}\overset{0}{\text{CH}_2} \overset{0}{\text{O}}\text{SO}_3 \xrightarrow{\text{H}_2\text{O}} \text{OHCCHO} + \text{Na}_2\text{SO}_4
\]

anticipated glyoxal monotosylhydrazone; i.e., it decomposed in base turning yellow then red and finally gave off gas. Since glyoxal sulfate is prepared by a rather tedious and independent route from 30% oleum and sym-tetrachloroethane, it is not a suitable source for rapid and direct preparation of glyoxal monotosylhydrazone.

The most striking feature of base-catalysed decomposition of vicinal-bis-p-tosylhydrazones is the different path taken by diaryl as compared to alkylaryl and dialkyl derivatives (Equations 25 and 26). In the former system formation of acetylenes is very facile; every experiment involving a diaryl vicinal-bis-p-tosylhydrazone resulted in evolution of two equivalents of nitrogen. The volume of nitrogen evolved is indicative of acetylene formation, although in several cases it was not possible to isolate the acetylenic product quantitatively. The yields of acetylene isolated and the percentages of nitrogen evolved for
base-catalyzed decomposition of various vicinal-bis-p-tosylhydrazones are summarized as follows:

TABLE 1
ACETYLENES FORMED ACCORDING TO EQUATION 25

<table>
<thead>
<tr>
<th>Ar</th>
<th>% Yield of Acetylene</th>
<th>% Nitrogen Evolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_6H_5(22)</td>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>p-NO_2-C_6H_4</td>
<td>22-41</td>
<td>100</td>
</tr>
<tr>
<td>p-NC_O-C_6H_4</td>
<td>42-50</td>
<td>100</td>
</tr>
</tbody>
</table>

(22) W. Bamford and T. Stevens, (1), report a 73% yield of diphenylacetylene for decomposition of benzil di-p-tosylhydrazones under different conditions.

For non-diaryl substituted vicinal-bis-p-tosylhydrazones there was no significant formation of nitrogen or hydrocarbons and triazoles were isolated in the indicated yield:

TABLE 2
TRIAZOLE FORMED ACCORDING TO EQUATION 26

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>% Yield of Triazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>42-54</td>
</tr>
<tr>
<td>CH_3</td>
<td>CH_3(23)</td>
<td>70-75</td>
</tr>
<tr>
<td>CH_3</td>
<td>H</td>
<td>26-64</td>
</tr>
</tbody>
</table>
It was hoped that by employing suitable solvents and/or conditions that the \( N \)-tosylanidotriazoles formed could be converted to their salts and decomposed to acetylenes with loss of nitrogen and tosylamido salts (Equation 27).

\[
\begin{align*}
RC-N &= RC-N + M^+ \quad \text{heat} \\
RC-H^+ &= RC-H + M^+ \\
-2N &= RC=CR
\end{align*}
\]

Photolysis of alkali metal salts of \( p \)-tosylhydrazones results in formation of diazo compounds (2c). Photolysis of the present system was attempted in an effort to prepare acetylenes. Irradiation of biacetyl \( \text{bis-}p \)-tosylhydrazone in \( N \)-methylpyrrolidone or diethyl Carbitol containing an excess of two equivalents of sodium methoxide yielded only \( 4,5 \)-dimethyl-\( 1-p \)-toluenesulfonamido-1,2,3-triazole (75\%) when the mixture was allowed to warm; the initial \( \text{bis-}p \)-tosylhydrazone was unaffected when irradiated cold.

Use of an \( \alpha \)-diketone possessing a phenyl group adjacent to one of the hydrazone functions and a better leaving group in the arylhydrazone moiety still afforded a triazole. Decomposition of methylphenylglyoxal \( \text{vicinal-bis-}p \)-nitrobenzenesulfonfylhydrazone under conditions more vigorous than those of Bamford and Stevens (1) resulted in no evolution of nitrogen and formation of the requisite \( 1-p \)-nitrobenzenesulfonamido-1,2,3-triazole.
To account for the varying courses of reaction it is necessary to explain why the energy of activation for acetylene formation in the diaryl series is lower relative to that for the alkylaryl and dialkyl series. The reason for this may be (1) opening of the triazole ring (Equation 26) is facilitated by stabilization of the diazo function in the ring opened aryl-substituted intermediate VI which decomposes to acetylene or (2) the aryl functions stabilize developing carbenic or diazo centers in the intermediates leading to acetylenes in the event initial triazole formation does not occur (Equation 29).

\[
\begin{align*}
\text{Ar}-\text{C}-\text{N} & \quad \text{+HTos} \\
\text{Ar}-\text{C}-\text{N} & \quad \rightleftharpoons \\
\text{Ar}-\text{C}-\text{N} & \quad \text{Ar}-\text{C}=\text{N}_2 \\
\text{Ar}-\text{C}=\text{N}_2 & \quad \text{Ar}-\text{C}=\text{N}_2 \quad \text{Ar}=\text{C}=\text{Ar} \\
\text{Tos}^- & \quad \text{Tos}^- \\
\text{Base} & \quad \text{Base} \\
\text{Ar}=\text{C}=\text{NNHTos} & \\
\text{Ar}=\text{C}=\text{NNHTos} & \\
\end{align*}
\]
EXPERIMENTAL

General Information

Melting Points. All melting points were determined on a Fisher melting point block and are uncorrected.

Analyses. Analyses were carried out by Micro-Analyses Inc. of Wilmington, Del. and Galbraith of Knoxville, Tenn.

Infrared Spectra. All spectra were taken on a Perkin-Elmer Infracord employing a potassium bromide pellet.

Ultraviolet Spectra. Ultraviolet spectra were obtained with a Perkin-Elmer No. 202 recording spectrophotometer. The solvent used was 95% ethanol.

The Attempted Preparation of Glyoxal Mono-p-toluenesulfonylhydrazone and Glyoxal Mono-μ-naphthalene-sulfonylhydrazone

(A) A solution of 100 ml. of 30% aqueous glyoxal (24) (3.0 g.,

(24) Commercial glyoxal—supplied by Union Carbide Corp. is a 30% aqueous solution.

0.05 mole) in methanol (220 ml.) was warmed to 40°; then with stirring tosylhydrazide (25) (10.0 g., 0.053 mole) was added all at once.

Almost immediately a solid began to separate from the solution. The reaction mixture was stored at room temperature 4 hr., and then the solid material was filtered, washed with cold methanol and sucked dry. The white solid, 7.0 g. (68%) showed no carbonyl absorption in the infrared and was identified as the bis-tosylhydrazone of glyoxal, m.p. 142-144°.

Anal. Calcd. for C_{16}H_{10}N_{2}O_{4}: C, 48.73; H, 4.56; N, 14.02.

Found: C, 48.77; H, 4.03; N, 14.00.

(b) Tosylhydrazide (19.50 g., 0.105 mole) was added all at once with stirring to a solution of 18.4 ml. of aqueous glyoxal (5.5 g., 0.095 mole) in methanol at 40°. The solid isolated, 13.13 g. (69%), was the bis-tosylhydrazone of glyoxal.

(c) To a solution of 73.6 ml. of aqueous glyoxal (22.0 g., 0.38 mole) in methanol (350 ml.) at room temperature was added tosylhydrazide (78.0 g., 0.42 mole) with stirring. The mixture was stirred at room temperature until all of the tosylhydrazide dissolved. It was then placed in an ice-bath for one hr., and then finally into an ice-chest at 10° for 13 hr. The solid, 58.0 g. (70%), was identified as the bis-tosylhydrazone of glyoxal.

(d) Tosylhydrazide (9.30 g., 0.05 mole) was completely dissolved in methanol (200 ml.), and the resulting solution was added dropwise to 10 ml. of aqueous glyoxal (3.0 g., 0.05 mole) in methanol (100 ml.) at -5°. The addition time was 40 min.; a solid, 5.2 g. (53%) identified as the bis-tosylhydrazone of glyoxal was isolated.

(e) Tosylhydrazide (1.86 g., 0.01 mole) was added to a solution of diethyl ether (35 ml.) and ethanol (5 ml.) to make a slurry. Aqueous
glyoxal (20.0 ml., 6.0 g., 0.10 mole) was added to this slurry with stirring. Complete dissolution of the solid material was not entirely achieved. The reaction mixture was refrigerated overnight. A solid was isolated, 1.30 g. (66%), identified as the bis-tosylhydrazone of glyoxal.

(f) Tosylhydrazide (9.3 g., 0.05 mole) was placed in a solution of diethyl ether (240 ml.) and methanol (10 ml.). To this slurry at room temperature 10 ml. of aqueous glyoxal (3.0 g., 0.05 mole) was added dropwise with stirring and the reaction was stirred for 3 hr. A solid, 5.4 g. (52%), identified as the bis-tosylhydrazone of glyoxal was isolated.

(f) A slurry consisting of 4-naphthalenesulfonylhydrazide (26)


(2.22 g., 0.01 mole), ethanol (25 ml.), and diethyl ether (25 ml.) was prepared. To this slurry at room temperature 10 ml. of aqueous glyoxal (3.0 g., 0.05 mole) in ethanol (20 ml.) was rapidly added. Upon complete addition the undissolved hydrazide went immediately into solution; at this point the reaction was quenched by addition of ice. Evaporation of the organic solvents brought the separation of 1.72 g. of a cream solid which was insoluble in hot and cold chloroform, carbon tetrachloride, water, 50% acetic acid, ether and low boiling petroleum ether. Its infrared spectra showed no carbonyl absorption. From this information it was obvious that the desired product was not obtained, and the product was in fact probably the bis-4-naphthalenesulfonylhydrazone of glyoxal (73%), m.p. 142-143° from ethanol-water.
(H) Aqueous glyoxal (5.0 ml., 1.5 g., 0.025 mole) was added all at once to a stirred slurry of \( \beta \)-naphthalenesulfonylhydrazide (5.66 g., 0.026 mole) and 50\% acetic acid (20 ml.). The resulting mixture was stirred for 2 hr.; at the end of this time a solid, 5.1 g., was separated. All the properties of this material were the same as those of the solid obtained in G. This compound is therefore also assumed to be the bis derivative. Per cent yield: 85\%.

\[
\text{Anal. Calcd. for } C_{22}H_{18}O_2N_4: \text{ N, } 12.02
\]

\[
\text{Found: N, 12.07}
\]

(I) Aqueous glyoxal (100 ml., 30 g., 0.50 mole) was neutralized with sodium bicarbonate; to the resulting solution was added tosylhydrazide (9.30 g., 0.05 mole) all at once. The resulting heterogeneous reaction mixture was stirred at room temperature for 2 hr., and then refrigerated 4 hr. A crude yellow solid, 6.28 g., was separated. The infrared spectrum of this product showed no carbonyl bond, and was nearly identical to that of bis-tosylhydrazone of glyoxal. Per cent yield: 64\%.

(j) Aqueous glyoxal (20 ml., 6.0 g., 0.10 mole) was neutralized with sodium bicarbonate; the resulting solution was weakly basic, pH = 8. This solution was cooled to 0° and then tosylhydrazide (3.76 g., 0.02 mole) dissolved in tetrahydrofuran (25 ml.) was added with stirring in 40 min.; at the end of this time there was no solid evident in the reaction. The tetrahydrofuran was removed from the solution (in vacuo) bringing about the separation of a very small amount of taffylike material. At this point the mixture was chilled in a refrigerator overnight; there was no additional solid separation. The taffylike material was separated...
and resisted all attempts at solidification. Dilution of the aqueous filtrate with water followed by neutralization with aqueous hydrochloric acid did not bring about the formation of additional solid.

(k) Aqueous glyoxal (20 ml., 6.0 g., 0.10 mole) was neutralized with sodium bicarbonate and the resulting slightly basic solution was added all at once at room temperature with stirring to tosylhydrazide (1.06 g., 0.01 mole) in ethanol (10 ml.). The mixture was then stirred at room temperature for 2 hr. Water (10 ml.) was added to the resulting clear solution. Chilling of the resulting solution did not bring about the separation of a solid. Addition of more water (15 ml.) brought about the separation of a solid which in spite of overnight refrigeration became fluffy and could not be solidified.

(l) Twenty ml. of aqueous glyoxal (6.0 g., 0.10 mole) was neutralized with sodium bicarbonate so that the resulting solution had a pH of approximately 6; this solution was then added to distilled water (1.0 lit.) containing sodium acetate (100 g.). The resulting solution was then added to tosylhydrazide (13.6 g., 0.10 mole) in 50% acetic acid (60 ml.). Only the bis-tosylhydrazone of glyoxal and tosylhydrazide were isolated in low yield.

(m) The pH of 10 ml. of aqueous glyoxal (3.0 g., 0.05 mole) was adjusted to approximately 6 with sodium acetate; then an additional 30 g. of sodium acetate in water (125 ml.) was added. 5-Naphthalenesulfonylhydrazide (2.22 g., 0.01 mole) dissolved in glacial acetic acid (25 ml.) was added to the resulting stirred solution over a period of 2 hr. A cream colored solid, 0.97 g. (42%), precipitated from the reaction. From the infrared spectra it is clear that this is the same solid isolated in
(G) and (H); that is the bis-8-naphthalenesulfonylhydrazone of glyoxal.

(H) A solution of sodium acetate (18.0 g., 0.22 mole), glyoxal bis-sodium bisulfite (2.66 g., 0.01 mole) and water (120 ml.) was added to a slurry of tosylhydrazide (1.86 g., 0.01 mole) and acetic acid. The reaction was allowed to run for 40 min. with stirring at ice bath temperature. Only tosylhydrazide was isolated.

(J) Sufficient sodium hydroxide (45 ml. of a 20% solution), (9.0 g., 0.23 mole) was added to glyoxal bis-sodium bisulfite (27.0 g., 0.10 mole) to regenerate the glyoxal. This solution was stirred overnight and then filtered. The filtrate was then neutralized with 20% hydrochloric acid; then sodium acetate was added to the neutralized filtrate. Tosylhydrazide (1.86 g., 0.01 mole) in 50% acetic acid (6 ml.) was then added, with stirring, all at once to the neutralized filtrate at 7-10°. After 40 min. only a very small amount of a crude solid was isolated. This solid showed no carbonyl absorption in the infrared and was not investigated further.

(P) Several experiments were attempted employing pure monomeric glyoxal (27). The amount of polymerization encountered was such that

(27) Prepared according to the U.S. Patent issued to Union Carbide and Carbon Corp., #2,339,346 (1944).

work up was futile. Even in those cases where polymerization was reduced to a tolerable level the only product isolated was the bis-derivative in poor yield.

(Q) Glyoxal sulfate (28) (3.0 g., 0.014 mole) was added to warm

(28) Prepared according to the method of M. Perkins, U.S. patent #1,999,995 (1935).
water (120 ml.) containing sodium acetate (18.0 g., 0.22 mole) and the resulting mixture stirred until complete dissolution occurred. After cooling, this solution was added with stirring to tosylhydrazide (1.57 g., 0.086 mole) in 50% acetic acid (6 ml., 0.05 mole). After the addition the reaction mixture was cooled in an ice bath and the reaction was allowed to proceed at this temperature 20 min. (29). Almost immediately

(29) This experiment is identical to the one employed by H. Fischer, Ber., 59, 856 (1926) for the preparation of the monophenyl-hydrazone of glyoxal.

upon mixing, a solid separated; there was no color change during reaction. A crude solid, 1.37 g., was isolated by filtration. When this solid was added to conc. sodium hydroxide, it turned yellow, then red and then appeared to give off gas. Dissolution of this solid in dimethylformamide followed by precipitation with water gave a solid, 1.0 g. (60%), identified as glyoxal bistosylhydrazone.

The Base Catalyzed Decomposition of Vicinal-bis-p-tosylhydrazones and 1-p-Toluenesulfonamide-1,2,3-triazoles

Glyoxal bistosylhydrazone

(A) A round bottom flask equipped with an internal magnetic stirrer and a condenser possessing a gas take-off leading to a Dry Ice trap and a gas measuring device was charged with glyoxal bistosylhydrazone (11.3 g., 0.029 mole), diethyl Carbitol (75 ml.) and 72% sodium methoxide (3.90 g.; total OH⁻ and OMe⁻: 0.075 mole) was heated and stirred for 15 hr. at 115°. A crude cream solid (10.50 g.) was filtered from the diethyl
Carbitol and washed with ether. Upon solution of the solid in water and acidification, a white crystalline material was obtained. Recrystallization once from water gave 3.7 g. (54%) of 1-p-toluenesulfonamido-1,2,3-triazole, a stable white solid, m.p. 151-153. The ultraviolet spectrum show at 215, 230, 246, 255, 261, and 275. The molecular weight, (calcd.) 238, (found) 239, was determined by titration in ethanol with aqueous sodium hydroxide employing bromothymol blue as indicator.

**Anal.** Calcd. for C\textsubscript{12}H\textsubscript{16}N\textsubscript{2}S\textsubscript{2}O\textsubscript{4}: C, 45.49; H, 4.20; N, 23.52; S, 13.50

**Found:** C, 45.29; H, 4.21; N, 23.77; S, 13.59.

The loss of water in the gas measuring device in this experiment is 74% of the theoretical amount; in view of the yield of the triazole it is clear that apparatus was leaking. The trap contained only diethyl Carbitol. There were no additional products isolated.

(3) A stirred slurry consisting of glyoxal bis-p-tosylhydrazone (22.6 g., 0.058 mole), 72% sodium methoxide (7.8 g., 0.10 mole OH\textsuperscript{-} and 0.06 mole OH\textsuperscript{2-}), and cyclohexene (125 ml.) was refluxed for 24 hr. The mixture was poured into water and the organic layer was separated. Extraction of the aqueous layer with ether followed and the combined organic extracts were dried over sodium sulfate; removal of the organic solvents left behind a small amount (approximately 05 ml.) of brown tar which was not investigated.

Acidification of the aqueous extract resulted in separation of 5.8 g. (42%) of 1-p-toluenesulfonamido-1,2,3-triazole.
(c) The bis-p-tosylhydrazone of glyoxal (11.3 g., 0.03 mole) was added to cyclohexene (75 ml.) followed by 72% sodium methoxide (3.9 g., total OH⁻ and OMe⁻ 0.075 mole). The resulting stirred slurry was refluxed for 15 hr. A crude solid (11.0 g.) which separated from the reaction mixture was dissolved in water and the aqueous solution was acidified with dil. hydrochloric acid. Upon acidification a solid separated from solution. This solid was filtered and after one recrystallization from water gave 2.8 g. (42%) of 1-p-toluenesulfonamido-1,2,3-triazole. No other products were isolated. As noted previously the apparatus leaked and it was not possible to determine the extent of gas evolution.

Biacetyl bis-p-tosylhydrazone (30)

(A) A mixture of 0.03 g. of 72% sodium methoxide (0.02 g., 0.004 mole) and diethyl Carbitol (30 ml.) was placed in the apparatus subsequently described, stirred and heated to 100°. Biacetyl bis-p-tosylhydrazone (0.844 g., 0.002 mole) was added by means of the boat in the apparatus. After 30 min. at 100° there had been no gas evolved, and there was still considerable solid suspended in the diethyl Carbitol. The solid was filtered, washed with water and air-dried; it was identified as the starting hydrazone, 0.66 g. (79%) m.p. 200-204°.

(30) Prepared according to the method of W. Bamford and T. Stevens, (1).

Description of the apparatus in A. This apparatus permits introduction of reagents simply by inversion of a self contained boat without opening the flask and thus loss of gases is eliminated. This apparatus did not suffer from the disadvantage of leakage as previously mentioned.
Hereafter, when used in describing an experiment, it will be simply designated as "the apparatus."

(B) Diacetyl bis-p-tosylhydrazone (2.00 g., 0.05 mole) was added to N-methylpyrrolidone (25 ml.) in "the apparatus" which was then immersed in an oil bath at 140-150°. After the mixture had reached this temperature sodium methoxide (0.270 g., 0.005 mole) was added from the boat with internal stirring; heating at the specified temperature was continued for 30 min. At the end of this time only 10 ml. of water was displaced from the graduate cylinder, and there was no material evident in the Dry Ice traps. Final acidification of the mixture via the boat, followed by slight warming, also afforded no visible appearance of material in the Dry Ice traps or solid in the reaction vessel.

Although there was no material visibly present in the traps, the trap contents were checked for the presence of hydrocarbon gases by vapor phase chromatography (v.p.c.). A 5' column using Dow Corning silicone oil 550 (5%) on Fluoropack was employed for this purpose. The chromatograms showed that hydrocarbons were not present.

The acidified N-methylpyrrolidone solution was poured over ice water (300 ml.); a solid did not separate. Dilution with an additional 2 lit. of water and refrigeration of the solution and reduction of its volume to 40 ml. failed to give a solid.

(C) A slurry consisting of diacetyl bis-p-tosylhydrazone (2.00 g., 0.005 mole) 72° sodium methoxide (1.00 g., 0.013 mole) and diethyl Carbitol (25 ml.) was placed in "the apparatus." The entire apparatus, with internal stirring, was then immersed in an oil bath at 155-160° for 45 min. Approximately 30 ml. of water was displaced from the graduate
cylinder; however, the Dry Ice-acetone traps were visibly empty. The
trap gases showed no hydrocarbons present by v.p.c. even after acidifi-
cation of the reaction mixture and warming.

Dilution of the acidified reaction solution afforded no solid;
however after standing 2 weeks, 1,5-dimethyl-1-n-toluenesulfonylido-
1,2,3-triazole (0.88 g., 70%), m.p. 135-137° [lit. m.p. 139° (1)],
separated. The ultraviolet spectrum of the triazole exhibited λ max at
212, 230, 248, 255, 262, and 272 nm.

(b) A quartz reaction flask, equipped with an internal magnetic
stirrer and a gas take-off leading to Dry Ice traps and an inverted
graduate cylinder to measure gas evolution, was charged with the hydra-
zone (2.00 g., 0.005 mole), N-methylpyrrolidone (25 ml.) and sodium
methoxide (0.72 g., 0.013 mole). Upon addition of the base the reaction
mixture became red-brown and very thick. The reaction mixture was then
irradiated for 3 hr. with a Hanovia 500 watt U.V. lamp; external cooling
was achieved by running water over the outside of the flask. The stir-
ring became inefficient (10 min.) as the reaction mixture thickened. No
gas was evolved during the irradiation. Separation of the solid from
N-methylpyrrolidone was accomplished by filtration; dissolution of the
solid in water followed by acidification of the resulting solution af-
forded a 90% recovery of initial biacetyl bis-2-tosylhydrazones.

(e) The preceding reaction was duplicated except that Pyrex
glassware was employed, the water circulation was decreased to allow the
reaction mixture to warm, and a True-Bore stirrer was employed. Irradia-
tion time was 2 hr., and stirring was effective throughout the entire time.
Gas evolution was negligible during the irradiation. Water (200 ml.) was
added to the clear red-brown solution which was then acidified with 20% hydrochloric acid. Solid separation failed to occur; however, upon standing in an ice-box for 2 weeks the solution upon seeding yielded 4,5-dimethyl-1-p-toluenesulfonamido-1,2,3-triazole (0.85 g., 75%).

(F) Experiment E was duplicated except that efficient cooling was maintained. The only solid isolated, in 50% recovery was the starting biacetyl bis-p-tosylhydrazone.

(G) A slurry consisting of biacetyl bis-p-tosylhydrazone (2.00 g., 0.005 mole), diethyl Carbitol (35 ml.) and 1.00 g. of 72% sodium methoxide (0.72 g., 0.013 mole) was irradiated for 3 hr. with a 500 watt U.V. source. The slurry was contained in a Pyrex flask equipped with a mechanical stirrer and a gas measuring device; the reaction was allowed to warm during the irradiation by keeping the external cooling minimal. Gas evolution was not observed during the experiment. The reaction mixture was poured over ice-water and acidified with 20% aqueous hydrochloric acid. Almost immediately a solid (0.11 g., 5.0%) separated from solution which was identified as the starting biacetyl bis-p-tosylhydrazone. The resulting filtrate on long standing in a refrigerator at 10° gave white crystals identified as 4,5-dimethyl-1-p-toluenesulfonamido-1,2,3-triazole (0.94 g., 75%).

Pyruvic aldehyde bis-p-tosylhydrazone (31)

(31) Pyruvic aldehyde bis-p-tosylhydrazone was prepared from a 43% aqueous solution of pyruvic aldehyde (Union Carbide Corp.) and tosylhydrazide in a 1:2 mole ratio. Methanol was used to dissolve the hydrazone. The solid isolated had no carbonyl absorption in the infrared, m.p. 125-126°.
(a) Pyruvic aldehyde bis-p-tosylhydrazone was added to N-methylpyrrolidone (25 ml.) in "the apparatus" and the resulting slurry was immersed in an oil bath at 120°. Sodium methoxide (0.72 g., 0.013 mole) was then added all at once, with internal stirring through the boat. After 20 min., 80 ml. of water was displaced from the graduate cylinder; however, no material was visible in the traps. Acidification of the reaction mixture followed by warming produced no visible material in the traps. Water (300 ml.) was then added to the acidified reaction mixture; clouding occurred, but no solid separated. After 2 days, a white crystalline solid (0.76 g., 64%) separated which was recrystallized twice from water, m.p. 156.0-156.5°. It is either 5-methyl-1-p-toluenesulfonamido-1,2,3-triazole or 4-methyl-1-p-toluenesulfonamido-1,2,3-triazole; from the sharp melting point it evidently is not a mixture of both. The ultraviolet spectrum is nearly identical to those of the two triazoles previously described.

Anal. Calcd. for C_{10}H_{12}N_{4}O_{2}: C, 47.52; H, 4.75; N, 22.07

Found: C, 47.61; H, 4.91; N, 22.21.

(b) The apparatus was charged with pyruvic aldehyde bis-p-tosylhydrazone (2.00 g., 0.005 mole) and N-methylpyrrolidone (25 ml.). Sodium methoxide (0.72 g., 0.013 mole) was then added after the apparatus had been immersed in an oil bath at 180-190°. After 20 min., with internal stirring, the apparatus was removed from the oil bath. Visual observation of the traps revealed that they were apparently empty. The reaction mixture was then acidified and warmed slightly; material was not condensed in the traps.
Analysis of the trap contents by vapor phase chromatography, employing the column described in Experiment B of biacetyl bis-p-tosylhydrazone, showed no hydrocarbons present.

Workup of the acidified reaction mixture was extremely difficult in that the coating of magnetic stirrer underwent apparent decomposition giving a black mixture. It was possible to isolate 0.20 g. (26%) of the triazole obtained in Experiment A.

Benzil bis-p-tosylhydrazone (32)

(32) Prepared according to the method of W. Bamford and T. Stevens, (1).

(a) A stirred slurry consisting of 0.11 g. of 72% sodium methoxide (0.08 g., 0.014 mole) and diethyl malonitrate (10 ml.) contained in "the apparatus" was immersed in an oil bath at 120°, and benzil bis-p-tosylhydrazone (0.27 g., 5.0 x 10^-4 mole) was added all at once. Immediate evolution of gas ensued upon the addition; 15 min. after the addition the reaction was allowed to cool to room temperature.

Diphenylacetylene was produced in 82% yield by v.p.c. analysis and the evolution of nitrogen was theoretical.

4,4'-Dinitrobenzil bis-p-tosylhydrazone was prepared by refluxing 4,4'-dinitrobenzil (33) dissolved in 1% ethanolic hydrochloric acid with tosylhydrazide for 1.25 hr. The bis-p-tosylhydrazone melts at 225-231°; decomposition starts at 210°.

(A) Sodium methoxide, 0.22 g. of 72.2% assay (0.16 g., 0.003 mole) was added to diethyl Carbitol (25 ml.) in "the apparatus." This slurry was stirred and heated to 120°. 4,4'-dinitrobenzil bis-p-tosylhydrazone was then added. Upon addition of the hydrazone there was immediate evolution of gas. After 40 min. the apparatus was removed from the oil bath and allowed to cool. Very fine yellow needle-like crystals were observed suspended in the diethyl Carbitol along with some black solid. Workup was accomplished by pouring the reaction mixture into water and extracting with ether. The extraction was made very difficult due to emulsion formation; removal of the ether gave a brown oil which could not be crystallized. Theoretical nitrogen was evolved.

(B) The apparatus was charged with 0.11 g. of 72.2% sodium methoxide (0.08 g., 2.0 x 10^-3 mole) and N-methylpyrrolidone (25 ml.) and then immered in an oil bath at 120°. Upon addition of 4,4'-dinitrobenzil bis-p-tosylhydrazone (0.32 g., 5.0 x 10^-4 mole), accompanied with internal stirring, the mixture became light red, then blood red, and finally black. After 15 min. the apparatus was removed from the heat. The evolution of nitrogen was theoretical.

The reaction mixture was poured into water and the aqueous solution was extracted continuously. Removal of the ether from the washed and dried extract gave a brown oil which failed to solidify. It was investigated no further.

(C) The above experiment was duplicated exactly except that diethylene glycol dimethyl ether was employed as a solvent, but the solid isolated failed to crystallize from glacial acetic acid, the solvent which is reportedly successful in the recrystallization of 4,4'-dinitrotolaln (34).
(D) A mixture of \(4,4\-'\)-dinitrobenzil bis-\(p\-)tosylhydrazone (0.32 g., 5.0 \(\times\) \(10^{-4}\) mole), benzene (25 ml.) and sodium methoxide (0.10 g., \(1.8 \times 10^{-3}\) mole) was refluxed for 4 hr. At the end of this time a black solid was suspended in the benzene; upon cooling the mixture a red brown solid separated. The reaction mixture was then reheated to boiling, and the hot solution was filtered from the black solid; on cooling the filtrate gave a solid which was crystallized once from ethanol, and then from acetic acid with no improvement in melting point. Sublimation afforded \(4,4\-'\)-dinitrotolan (0.03 g., 22\%\), m.p. 214-215° [lit. m.p. 202-203° (34)]. The black solid offered no \(4,4\-'\)-dinitrotolan after sublimation for 4 days at 200-210° 4 mm.

(E) A slurry of 0.22 g. of 72\% assay sodium methoxide (0.16 g., 0.03 mole) and ethylene glycol (15 ml.) was placed in "the apparatus" and then immersed in an oil bath at 120°; \(4,4\-'\)-dinitrobenzil, bis-\(p\-)tosylhydrazone (0.64 g., 0.001 mole) was then added. The addition brought about immediate development of an intense red color accompanied by theoretical evolution of nitrogen. After 20 min. the mixture was cooled to room temperature depositing 0.11 g. (41\%) of \(4,4\-'\)-dinitrotolan. There was no additional solid isolated from the glycol filtrate.

\(4,4\-'\)-Dimethoxybenzil bis-\(p\-)tosylhydrazone

A mixture of benzene (20 ml.), ethanol (25 ml.), \(4,4\-'\)-dimethoxybenzil (2.70 g., 0.010 mole), and \(p\-)tosylhydrazone (3.82 g., 0.02 mole) was refluxed for 3 hr. The solvent was then removed in vacuo on a steam
bath. The yellow oily residue was dissolved in a hot solution of carbon tetrachloride (50 ml.) and ethanol (5 ml.). Cooling the solution overnight yielded 3.72 g. (62%) of \(4,4'\)-dimethoxybenzil, bis-p-tosylhydrazone as white needle-like crystals. This material starts to decompose at 144° and melts at 166-169°; the infrared shows no carbonyl absorption.

**Anal. Calcd.** For \(C_{30}H_{30}N_4S_2O_6\): N 9.24

**Found:** N 9.21

(A) The apparatus was charged with sodium methoxide (0.78 g., 0.014 mole) and diethyl Carbitol (20 ml.). This slurry was then heated to 120°; then \(4,4'\)-dimethoxybenzil bis-p-tosylhydrazone (0.61 g., 0.001 mole) was added. Upon the addition, moderate evolution gas was observed; however, the evolution was not as vigorous as that in decomposition of \(4,4'\)-dinitrobenzil bis-p-tosylhydrazone. After 7 min. at 120° theoretical nitrogen had been evolved, and the mixture had turned brown; at this point 0.11 g. of 72% sodium methoxide was added; no additional gas was evolved. A brown solid separated from the diethyl Carbitol which was filtered and washed with ether.

Water (100 ml.) was then added to the diethyl Carbitol-ether filtrate. The aqueous portion was extracted with ether until it was colorless. Evaporation of the ether from the extracts gave a yellow solution (25 ml.) smelling heavily of diethyl Carbitol. Addition of water (100 ml.) brought about the separation of an oil which on long standing gave a semi-solid. Recrystallization from ethanol gave \(4,4'\)-dimethoxytolan, (0.07 g.) m.p. 142-145° lit. m.p. 142° (35). Concentration of the mother

(35) H. Wiechell, Ann., 272, 338 (1894).
liquor gave additional \(4,4'\)-dimethoxytolan (0.05 g.). The total yield of \(4,4'\)-dimethoxytolan is 50%.

(B) Addition of \(4,4'\)-dimethoxybenzil bis-p-tosylhydrazone to a stirred slurry of 0.11 g. of 72% sodium methoxide (0.08 g., 0.014 mole) and ethylene glycol (15 ml.) at 140°, in the previously described manner, brought about effervescence but no significant color change except for a slight yellow tint. Upon cooling to room temperature a white solid crystallized from the glycol. This solid was separated by filtration, washed with water, and air dried to give \(4,4'\)-dimethoxytolan (0.10 g., 42%). A theoretical amount of nitrogen was evolved in this reaction.

**Methylphenylglyoxal bis-p-nitrobenzenesulfonylhydrazone**

A mixture of methylphenylglyoxal (1.48 g., 0.01 mole), p-nitrobenzenesulfonyl hydrazide (36) (4.34 g., 0.02 mole) and ethanol (75 ml.) was stirred at room temperature for 48 hr. and then refluxed 40 min. On cooling methylphenylglyoxal bis-p-nitrobenzenesulfonylhydrazone, a white solid, m.p. 176-177°, was isolated. Its infrared spectrum showed no carbonyl absorption.

*Anal. Calcd. for C\(_{21}\)H\(_{18}\)N\(_6\)O\(_8\)S\(_2\):  N 15.49*

*Found :  N 15.59*

(A) A slurry of methylphenylglyoxal bis-p-nitrobenzenesulfonylhydrazone (0.55 g., 0.001 mole), ethylene glycol (15 ml.) and 0.18 g. of 72% sodium methoxide (0.13 g., \(2.4 \times 10^{-3}\) mole) was placed in "the
apparatus," stirred and heated to 140° for 1.25 hr. No gas was evolved during the experiment. It was noted that upon the addition of the base to the mixture an intense red color developed which ultimately became yellow.

Acidification of the reaction mixture with dil. hydrochloric acid followed by dilution with water gave 0.22 g. of a yellow powder. After two recrystallizations from ethanol-water a light yellow-colored solid (0.13 g., 36%), m.p. 219-220°, was obtained. This solid showed the characteristic \( \lambda_{\text{max}} (\text{EtOH}) \) of all 1,2,3-triazoles; i.e., 211 nm (37) and was

(37) L. Hartzel and F. Benson, J. Am. Chem. Soc., 76, 667 (1954) report that all 1,2,3-triazoles show a characteristic (EtOH) at 210-216 nm.

not investigated further. This solid is 4-methyl-1-\( p \)-nitrobenzenesulfonamido-5-phenyl-1,2,3-triazole or 5-methyl-1-\( p \)-nitrobenzenesulfonamido-4-phenyl-1,2,3-triazole or a mixture of both.


Found: C, 50.93; H, 4.02.
PART III

THE ATTEMPTED PREPARATION
OF BRIDGED AMIDES
INTRODUCTION

This study involves possible preparation of bicyclic amides containing nitrogen at the bridgehead such as I and V and 4,5-diphenyl-2H-imidazol-2-one III a nitrogen analog of 4,5-diphenylcyclopentadienone, which may dimerize to V. Experimentally these syntheses were attempted by: (1) alkylation of 4,5-diphenyl-4-imidazolin-2-one with 1,3-dibromopropane (Equation 1) and (2) dimerization of 4,5-diphenyl-2H-imidazol-2-one III (Equation 3) generated by:

\[
\begin{align*}
\phi C-\text{NH} &\xrightarrow{1) \text{2KOH}} \phi C-NH_2 \xrightarrow{2) \text{Br(CH}_2)_3\text{Br}} \phi C-NCH_2CH_2 \\
\phi C-\text{NH} &\xrightarrow{1) \text{2KOH}} \phi C-NH_2 \xrightarrow{2) \text{Br(CH}_2)_3\text{Br}} \phi C-NCH_2CH_2
\end{align*}
\]  

(1)

loss of \( p \)-toluenesulfonic acid from 4,5-diphenyl-1-\( p \)-toluenesulfonyl-4-imidazolin-2-one (II, Equation 2) or by dealcoholation of 4,5-diethoxy-4,5-diphenyl-2-imidazolidone (IV, Equation 4).

\[
\begin{align*}
\phi C-\text{NH} &\xrightarrow{1) \text{Base}} \phi C = \phi C = \phi C = 0 \xrightarrow{2) \text{Tos}} \phi C = \phi C = \phi C = 0 \\
\phi C-\text{NH} &\xrightarrow{1) \text{Base}} \phi C = \phi C = \phi C = 0 \xrightarrow{2) \text{Tos}} \phi C = \phi C = \phi C = 0
\end{align*}
\]  

(II)  

(III)  

(IV)
HISTORICAL

It is predicted that bicyclic amides containing nitrogen at the bridge-head will be unstable due to restriction of normal amide resonance (Equation 5); such resonance would involve violation of Bredt's rule (1). Attempts, however, have been made to prepare such compounds because of their theoretical significance. Synthesis of VII by lactamization of VI has been unsuccessful; such a ring closure fails even when the carbonyl-containing bridge contains two or three carbon atoms (Equations 6 and 7) (2). Synthesis of 2,2-dimethyl-6-quinuclidone


\[
\begin{align*}
\text{CO}_2\text{H} & \quad \longrightarrow \quad \text{O} \\
(\text{VI}) & \\
(\text{VII})
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2\text{H} & \quad \longrightarrow \quad \text{O} \\
(\text{VIII}) & \quad (\text{VIII}) \ R = \text{H}, n = 2 \text{ or } 3 \\
(\text{VIIIa}) & \quad R = \text{CH}_3, n = 1
\end{align*}
\]
VIIIa by a sixteen step sequence involving a final intramolecular alkylation has been claimed (3). In 1958 preparation of 1,4-diaza-


bicyclo-[2:2:1]-heptan-7-one was attempted from piperazine and phosgene (Equation 8); the only product isolated was the carbamoyl chloride hydrochloride shown in Equation 8 (4).


\[
\begin{align*}
\text{CH}_2 \text{NHCH}_2 \text{CH}_2 + \text{COCl}_2 \rightarrow \\
\text{CH}_2 \text{NHCH}_2 \text{CH}_2 + \text{COCl}_2 \rightarrow \\
\text{Cl} + \text{H}_2 \text{N} \text{CH}_2 \text{CH}_2 \text{NCOCl}
\end{align*}
\]

(8)

4,5-Diphenyl-4-imidazol-2-one has been mono and dimethylated (5a) (Equation 9 and 10). It also may be mono and dibenzoylated by benzoyl chloride in pyridine (Equations 11 and 12) (5b).

(5) a. H. Biltz, Ann., 368, 156 (1909); b. H. Biltz, ibid., 332, 263 (1905).
Pyrolysis of 4,5-dihydroxy-4,5-diphenyl-2-imidazolidone IX to benzonitrile may be imagined to involve 4,5-diphenyl-2H-imidazole-2-one (X, Equation 13) (5a). Also 4-ethoxy-4,5-diphenyl-5-imidazolidin-2-one XII is produced on pyrolysis of 4,5-diethoxy-4,5-diphenyl-2-imidazolidone XI (Equation 14) (5a).
DISCUSSION

Formation of benzonitrile upon pyrolysis of 4,5-diethyl-4,5-diphenyl-2-imidazolidine (Equation 15) indicates that isolation of

\[
\begin{align*}
\text{OEt} & \quad \phi C - N - \phi C = 0 \\
\Delta & \rightarrow \quad \text{ETOH} \\
(15) & \quad \phi C = N - \phi C = 0
\end{align*}
\]

4,5-diphenyl-2H-imidazolone XIII or its dimers XIV may not be possible since 4,5-diphenyl-2H-imidazolone may undergo facile loss of carbon monoxide.

Preparation of 1,5-diazabicyclo-[3:2:1]-6,7-diphenyl-6-octen-8-one XV was attempted by treating 4,5-diphenyl-4-imidazolin-2-one with two equivalents of potassium hydroxide followed by addition of 1,3-dibromopropane (Equation 16). Biltz(5a) found that it was possible to N,N'-dimethylate 4,5-diphenyl-4-imidazolin-2-one and the sequence outlined in 16 therefore was anticipated. The only product isolated (100% yield), however, was 6,7-dihydro-2,3-diphenyl-5H-imidazo-[2,1-b] [1,3] oxazine XVI, a stable white solid. Its N.M.R. spectrum showed the presence of three adjacent methylene groups with the termini in
different environments; its analysis and molecular weight support the assigned structure. The formation of XVI may proceed according to the sequence outlined in 17. The final step, intramolecular O-alkylation completes the reaction. Alternately, initial O-alkylation followed by N-alkylation may also occur.

Attempts were made to effect the synthesis of 1-\(\mu\)-toluenesulfonyl-4,5-diphenyl-4-imidazolin-2-one from \(\mu\)-toluenesulfonyl chloride and aqueous sodium hydroxide (Equation 18). This procedure failed and resulted only in near quantitative recovery of 4,5-diphenyl-4-imidazolin-2-one. N-Tosylation of a number of ureas under these conditions has
also failed for unexplained reasons (6); the only material isolated in


these efforts was the initial urea.

Additional attempts to prepare 1-p-toluenesulfonyl-4,5-diphenyl-
\( \text{imidazolin-2-one} \) using pyridine or dimethylformamide as solvents also
resulted in high recovery of 4,5-diphenyl-4-imidazolin-2-one (7).

(7) F. Kurzer, J. Chem. Soc., 1035 (1949) reports that N-arylure-
reas react with arylsulfonyl chlorides to give arylsulfonylcyranamides
rather than arylsulfonylureas via O-tosylation. This explains the dif­
ficulty encountered in the attempts to N-tosylate 4,5-diphenyl-4-
imidazolin-2-one.

Failure of 4,5-diphenyl-4-imidazol-2-one to undergo N-tosylation and its
recovery, therefore, may be explained by formation of a O-sulfonyl
intermediate which is cleaved to initial imidazol-2-one on work up
(Equation 19). The isolation of P-toluenesulfonic acid (experiment I)

\[
\begin{align*}
\text{C-N} & \quad \text{C-O} \quad \text{Tos} \\
\text{H} & \quad \text{H} \\
\Downarrow & \\
\text{C-N} & \quad \text{C-OH} + \text{TosOH} \\
\text{H} & \\
\Downarrow & \\
\text{C-NH} & \quad \text{C}=\text{O} \\
\text{H} & \\
\Downarrow & \\
\text{C-NH} & \\
\text{H} & \\
\end{align*}
\]

(19)

also indicates that an O-sulfonyl intermediate is formed.

Plausible reasons for the failure of 4,5-diphenyl-4-imidazolin-
2-one to N-sulfonylate have been suggested; however, the scope of the
work was not originally intended to determine the reasons for the suc-
cess desired or the failure which in fact was encountered. The persistent failure to obtain the desired N-sulfonyl derivative of the requisite imidazoline has been established under a variety of experimental conditions.
EXPERIMENTAL

Pyrolysis of 4,5-Diethoxy-4,5-diphenyl-2-imidazolidine

4,5-Diethoxy-4,5-diphenyl-2-imidazolidine (5.00 g., 0.15 mole) (5) was mixed with an equivalent amount of sand. A flask equipped with a gas exit leading to a Dry-Ice trap was charged with this mixture and then pyrolyzed at 220° for 15 min. The Dry-Ice trap contained ethanol (1.20 g., 100%) and small amounts of benzonitrile at the end of the pyrolysis. The pyrolytic residue, a black solid, smelled strongly of benzonitrile; attempts to purify this residue by chromatography and recrystallization failed.

Attempted Preparation of 1,5-Diazabicyclo-3.2.1-6,7-diphenyl-6-octen-3-one; The Formation of 6,7-Dihydro-2,3-diphenyl-5H-imidazo[2,1-b][1,3]oxazine

A flask equipped with an addition funnel, mechanical stirrer and condenser was charged with 4,5-diphenyl-5-imidazolin-2-one (23.6 g., 0.10 mole), 41.0 ml. of 30% potassium hydroxide (0.22 mole), methanol (80 ml.) and water (30 ml.). This slurry was heated on a steam bath for one hr., and then allowed to stand overnight. The resulting yellow solution was brought to reflux, and 1,3-dibromopropane (13.9 g., 0.07 mole) was added dropwise with stirring over a 9/2 hour period. Upon completion of the addition stirring was continued an additional one-half hour. The methanol was then removed by distillation. After
cooling to room temperature the reaction was stirred overnight.

A solid, 13.48g., was isolated by filtration of the reaction mixture. This solid (5.00g.) was then taken up in sufficient hot methanol to bring about complete dissolution (175ml.). Cooling failed to produce any solid; however, reduction in volume to 25 ml. afforded 1.65g. of the initial imidazol-2-one. Water was added to the hot methanolic filtrate until the cloud point was reached, and on cooling 3.13g. of a lustrous white solid separated, m.p. 165-240°. This solid was then dissolved in excess hot chloroform (150 ml.) and the volume reduced to 50 ml.; cooling this solution gave 0.60g. of the initial imidazolin-2-one.

Reduction in the volume of the chloroform solution which yielded 0.60 g. of the imidazolin-2-one failed to produce any additional solid; however, addition of low boiling petroleum ether to the hot filtrate until the cloud point was reached gave 1.66g. (18%, based on 13.48g. of initially isolated solid) of white, well defined, cube-like crystals, m.p. 172-182°.

The product (1.00g.) was dissolved in chloroform and eluted on a Super-Cell (75%) - Norite (25%) column. Addition of low boiling petroleum ether to the hot chloroform eluant, until the cloud point was reached, gave 0.93g. of weak leaflets, m.p. 181-182°.

The N.M.R. spectrum of the product (20% in chloroform), in addition to aromatic protons, showed one triplet at 5.69 Υ, another at 6.39 Υ, and a perturbed pentuplet at 7.69 Υ. This spectrum is indicative of three adjacent methylene groups with the termini in different environments.
A potassium bromide pellet of the solid showed no carbonyl absorption; however, a moderately strong peak at 6.4 μ was noted which may be attributed to C=N. A peak of lower intensity at 6.7 μ was also observed and may be attributed to the methylene group.

This spectral evidence indicates that the product following structure is 6,7-dihydro-2,3-diphenyl-5H-imidazo [2,1-b] [1,3] oxazine. XVII

\[
\begin{array}{c}
\text{N} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]

**XVII**

**Anal.** Calcd. for XVII: C, 78.63; H, 5.83; N, 10.14

**Found:** C, 79.14; H, 6.48; N, 9.47

Molecular Weight: Calcd.: 276

**Found:** 258

The Attempted Preparation of 4,5-Diphenyl-1-p-toluenesulfonyl-4-imidazolin-2-one

(A) to a stirred cooled solution (-5°) of 4,5-diphenyl-4-imidazolin-2-one (0.59 g., 2.5 x 10⁻³ mole) in pyridine (80 ml.) was added dropwise in 2 hr. tosyl chloride (0.47 g., 2.5 x 10⁻³ mole) in pyridine. The mixture was then allowed to warm to room temperature and kept for 2 hr. Acification with dil. hydrochloric acid resulted in recovery of 0.51 g. (96%) of the initial imidazolin-2-one.

(B) Repetition of the above reaction and workup except that the addition was conducted at room temperature, resulted in 98% recovery of initial imidazolin-2-one.
(c) A solution of the imidazolin-2-one (1.20 g., $5.1 \times 10^{-2}$ mole), pyridine (50 ml.) and tosyl chloride (1.00 g., $5.3 \times 10^{-3}$ mole) was refluxed for 4 hr. Work up after acidification with dil. hydrochloric acid brought about the isolation of 0.77 g. (64%) of the original imidazolin-2-one.

(d) A mixture of the imidazolin-2-one (1.20 g., $5.0 \times 10^{-3}$ mole), tosyl chloride (1.00 g., $5.3 \times 10^{-3}$ mole) and 35 ml. of 50% sodium hydroxide was refluxed for 4 hr. At the end of this time the solid 1.20 g. (100%) which remained was separated and identified as the initial imidazolin-2-one.

(e) Sodium hydroxide (25 ml. of a 1 N solution, 0.025 mole) was added to a stirred solution of the imidazolin-2-one (11.8 g., 0.05 mole) in dimethyl sulfoxide (250 ml.). Addition of the base caused the initially blue-phosphorescent solution to become pale-clear yellow. This solution was then refluxed and tosyl chloride (9.55 g., 0.05 mole), in sufficient dimethyl sulfoxide for solution, was then added dropwise with stirring over a 30 min. period. Reflux was continued for 30 min. after the addition was complete. After standing overnight the reaction was poured over 500 g. of crushed ice and acidified with dil. hydrochloric acid. A yellow oil separated which partly solidified on long standing.

The aqueous filtrate was then extracted with ethyl acetate, and this extract was combined with the ethyl acetate solution of the solidified yellow solid. The resulting solid was washed with water and then dried over sodium sulfate. Removal of the ethyl acetate to a final volume of 50 ml. followed by ether addition afforded 6.52 g. of starting imidazolin-2-one. The mother liquor on evaporation yielded an additional
1.71 g. of imidazolin-2-one. The total recovery of starting material is 8.23 g. (70%).

(F) A solution of sodium hydroxide (0.20 g., 5.0 x 10^{-3} mole) in water (30 ml.) was slowly added with stirring to the imidazolin-2-one (0.60 g., 2.5 x 10^{-3} mole) in tetrahydrofuran (80 ml.). At the end of the addition nearly all of the imidazolin-2-one had dissolved; tosyl chloride (0.47 g., 2.5 x 10^{-3} mole) in tetrahydrofuran was then slowly added to the basic solution in one hour. Upon completion of the addition the reaction was stirred for 2 hr. and then poured into water giving 0.43 g. (72%) of initial imidazolin-2-one.

(G) Tosyl chloride (19.5 g., 0.11 mole) in dimethyl formamide (35 ml.) was added dropwise to a cooled (0°) stirred solution of the imidazolin-2-one (11.6 g., 0.05 mole) in triethylamine (20.2 g., 0.20 mole) and dimethyl formamide (80 ml.). The mixture was warmed to room temperature and stirred for 9 hr. The solid left in the reaction flask was filtered, washed with dimethyl formamide and finally water; after drying 5.33 g. of the initial imidazolin-2-one was isolated.

Dilution of the filtrate with water (1500 ml.) followed by acidification with dil. hydrochloric acid afforded an additional 5.41 g. of the initial imidazolin-2-one. The total recovery of the imidazolin-2-one was 10.74 g. (91%).

(H) A reaction flask (500 ml.) equipped with a mechanical stirrer, serum cap, and drying tube was charged with the imidazolin-2-one (1.18 g., 5.0 x 10^{-3} mole) and pure, dry dimethylformamide (200 ml.). To the resulting stirred solution sodium hydride (0.125 g., 5.2 x 10^{-3} mole) in mineral oil suspension was added dropwise through the serum cap. The
initially blue-phosphorescent solution became clear yellow upon addition of sodium hydride. Stirring was continued for 0.5 hr. after the addition was completed. Tosyl chloride (0.91 g., $5.0 \times 10^{-3}$ mole) in dimethyl formamide was then added dropwise with vigorous stirring; 20 min. after the addition was complete the reaction solution was clear yellow, and upon stirring overnight it became turbid and no solid separated. When the mixture was poured onto acidified ice-water a white solid separated, which when recrystallized from acetone gave 0.83 (77%) of the initial imidazolin-2-one.

(I) A flask equipped with a serum cap, thermometer, internal magnetic stirrer and reflux condenser fitted with a drying tube was charged with the imidazolin-2-one (2.36 g., 0.01 mole) and dry ethylene glycol-dimethyl ether (100 ml.). The flask was then cooled to 7-10° and flushed with nitrogen; n-butyllithium (0.01 mole in hexane) was then added at a rate such that the temperature did not exceed 10°. After the addition was completed the mixture was warmed to room temperature and stirred for 4 hr.; at the end of this time the reaction had become clear-yellow in color. Dry tosyl chloride (1.90 g., 0.01 mole) was then added all at once; there was no observable color change upon this addition. After stirring at room temperature for 4 hr., there was considerable lightening of color, and a fine white solid appeared to be separating from solution. The mixture was then refluxed 14 hr. and cooled to room temperature; 3.2 g. of a white solid was then separated from the ethylene glycol dimethyl ether by filtration. The infrared spectrum of the solid revealed that it contained initial imidazol-2-one along with additional material exhibiting
bands at 8.2, 8.5, 8.9 and 10.0 \textmu m; further the spectrum revealed there are no bands present which are attributable to Ar-SO$_2$-N or ArSO$_2$Cl (7.0-7.5 \textmu m and 8.3-8.5 \textmu m) groups. Treatment of the crude solid (1.00 g.) with water (5 ml.) containing a trace of dil. hydrochloric acid at room temperature afforded 0.60 g. (77\%) of the pure imidazolin-2-one. The acidified filtrate upon treatment with p-toluidine gave 0.38 g. of the p-toluidine salt of p-toluene sulfonic acid, m.p. 189-192° [lit. m.p. 197° (8)]. The infrared spectrum of the salt was identical to the authentic material (8).