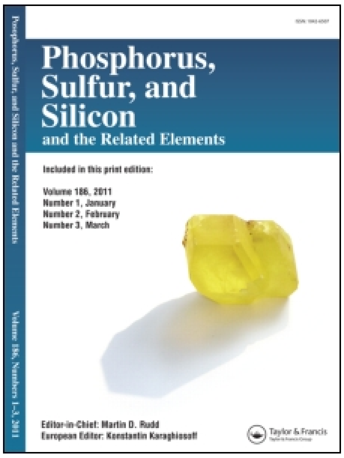


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of 1,3,4-Diazaphospholidinones by Mannich-Type Reaction

Ru-Yu Chen[a]; Ke-Sheng Feng[a]
[a] Research Institute of Elemento-Urganic Chemistry, Nankai University, Tianjin, China

To cite this Article Chen, Ru-Yu and Feng, Ke-Sheng(1993) 'Synthesis of 1,3,4-Diazaphospholidinones by Mannich-Type Reaction', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 123 — 126

To link to this Article: DOI: 10.1080/10426509308037380

URL: http://dx.doi.org/10.1080/10426509308037380

Phosphorus, Sulfur, and Silicon, 1993, Vol. 75, pp. 123–126
Reprints available directly from the publisher
Photocopying permitted by license only

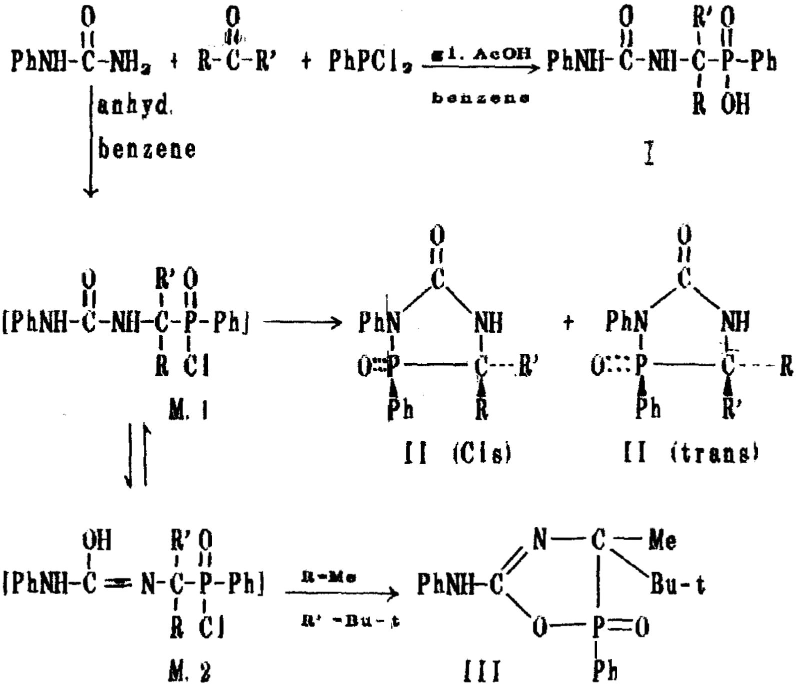
SYNTHESIS OF 1, 3, 4-DIAZAPHOSPHOLIDINONES BY MANNICH-TYPE REACTION

RU-YU CHEN KE-SHENG FENG
Research Institute of Elemento-Organic Chemistry,
Nankai University, Tianjin 300071, China

Abstract A number of 1, 3, 4-Diazaphospholidinones and their corresponding thiones were synthesized by Mannich-type reaction starting with phenyl urea or phenyl thiourea, phenyl dichloro phosphine and various aldehydes or ketones. The results were discussed.

INTRODUCTION

Birum[1] prepared 1, 3, 4-diazaphospholidinones by the reaction of 1, 3-dimethylurea with phosphites and aldehydes. However, when he used urea or phenyl urea instead of 1, 3-dimethyl urea, only straight chain compounds were obtained. In order to investigate the Mannich-type reaction further with an attempt to look for a new herbicide, we used phenyl urea to react with phenyl dichloro phosphine and various aldehydes or ketones. It was found that different products were formed depending on the property of the solvents and the structure of ketones employed.



I:	a	b	c	d	e
R	H	H	H	H	CH_3
R'	CH_3	CH_2CH_3	$CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_3$	CH_3

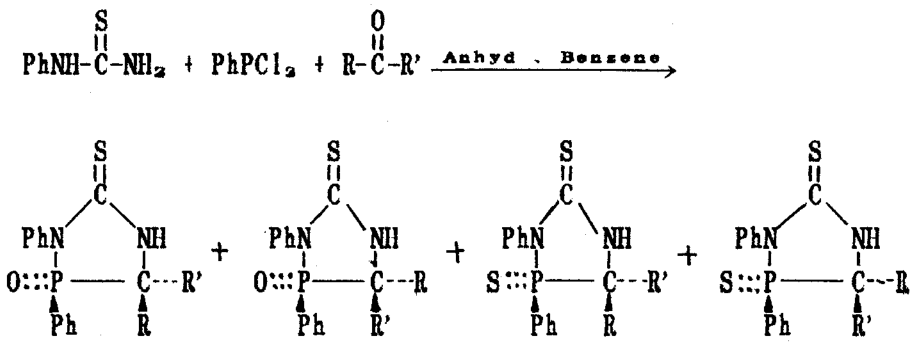
II:	a	b	c	d	e	f
R	H	H	H	H	H	CH_3
R'	CH_3	CH_2CH_3	$CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_3$	$CH(CH_3)_2$	CH_3

II:	g	h	i	j
R	CH_3	CH_3	CH_3	CH_2CH_3
R'	CH_2CH_3	$CH_2CH_2CH_3$	$CH(CH_3)_2$	CH_2CH_3

RESULTS AND DISCUSIONS

Compounds I were synthesized by carrying out the reaction of phenylurea with aldehydes(ketones)and phenyl dichlorophosphine in a mixture of benzene and glacial acetic acid . However, when anhydrous benzene was used as the solvent, cyclic compounds such as II or III were obtained instead. Theoretically the tautomeric intermediate compounds M. 1 and M. 2 could undergo intramolecular nucleophilic attack resulting in compounds II and III respectively, but actually only compound III was obtained when R and R' were methyl and t-butyl groups respectively. It was probably due to the fact that M. 1 was comparatively more stable than M. 2. The bulky group , t-butyl, at the carbon atom would eventually block the large phenylamino group to attack the phosphoryl chloride, while the small hydroxyl group attacked the latter readily to form compound III in spite of the presence of t-butyl group at the carbon atom . The cis and trans isomers for each of the compounds II had been confirmed by ^{1}HNMR and ^{31}PNMR spectra.

Besides, when phenyl urea was replaced by phenyl thiourea in the same reaction with dry benzene as the solvent, the colorless product was dissolved in chloroform and chromatographed with silica gel column. Two components were collected with R_f values of 0. 6 and 0. 8 respectively. They were confirmed by elemental analysis, ^{1}HNMR, ^{31}PNMR, MS and IR as compound IV(R_f 0. 6) and compound V(R_f 0. 8). Each of them possesses cis and trans forms with different R and R' groups.



$$\text{PhNH-}\overset{S}{\overset{\|}{C}}\text{-NH}_2 + \text{PhPCl}_2 + \text{R-}\overset{O}{\overset{\|}{C}}\text{-R}' \xrightarrow{\text{Anhyd . Benzene}}$$

IV (Cis) IV (trans) V (Cis) V (trans)

19-57. 6% 6-16. 1%

	a	b	c	d	e	f
R	H	H	H	H	CH_3	CH_3
R'	CH_2CH_3	$CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_3$	$CH(CH_3)_2$	CH_3	CH_2CH_3

	g	h	i
R	CH_3	CH_3	CH_2CH_3
R'	$CH_2CH_2CH_3$	$CH(CH_3)_2$	CH_2CH_3

By X-ray crystallography study, it was found that the molecular structures of compounds II, VI and V showed that unlike the envelop-type structures of normal five-membered phosphorus heterocycles, the five atoms, P, N, C, N and C were coplanar. The bond lengths of P-N in II, IV and V were respectively 1.687 Å, 1.682 and 1.71 Å each of which was shorter than that of the single bond of P-N(1.76 Å), indicating the double bond character between P and N. The sum of angles around the N was equal to about 360° The x-ray diffraction of the single crystal of compound V_g gave the molecular structure indicating that the planarity of its five-membered heterocycle was not as good as that of compounds II, or IV_f

The preliminary biological screening tests for all the compounds synthesized showed that compounds II possess significant herbicidal activity.

REFERENCES

1. G.H. Birum, US 3,965,127(1976); US 3,980,618(1976); US 3,989,727(1976).