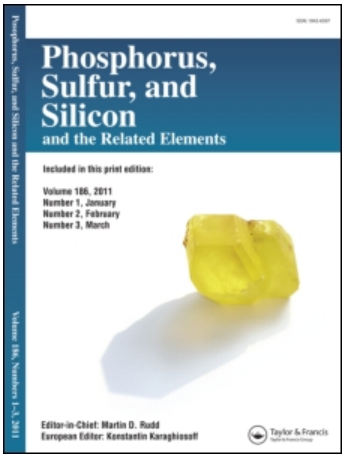

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

P-N COMPOUNDS *32.* PHOSPHAMINIMIDES 6. PHOTOISOMERIZATION TO 1H-1,2 DIAZEPINES[1]

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To cite this Article Cates, Lindley A. and Li, Ven-Shun(1990) 'P-N COMPOUNDS *32.* PHOSPHAMINIMIDES 6. PHOTOISOMERIZATION TO 1H-1,2 DIAZEPINES[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 54: 1, 203 — 204
To link to this Article: DOI: 10.1080/10426509008042138
URL: http://dx.doi.org/10.1080/10426509008042138

Phosphorus, Sulfur, and Silicon, 1990, Vol. 54, pp. 203–204
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P-N COMPOUNDS *32*. PHOSPHAMINIMIDES 6. PHOTOISOMERIZATION TO 1H-1,2 DIAZEPINES[1]

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(Received March 5, 1990; in final form April 18, 1990)

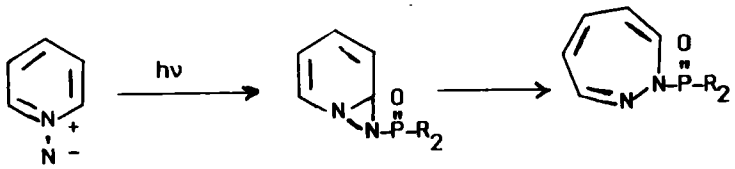
Photoinduced ring enlargement of diethoxy, diphenoxy and diphenyl pyridinophosphaminimides resulted in the formation of the corresponding 1-phosphinyl-1H-1,2-diazepines.

Key words: Ring enlargement, P-N compounds, phosphaminimides.

Chemistry involving phosphaminimides (phosphinylhydrazinium inner salts) has been shown in several instances to differ from that pertaining to their carbonyl analogs (herein designated carbaminimide). Examples of this are formation of hydrazinium iodide-hydrazinium inner salts[2] and of a novel monoethyoxyphosphinylhydrazinium salt,[3] inability of a bisdimethylaminophosphinyl hydrazinium bromide to undergo dehydrobromination[4] and formation of a hydrazonophosphonate isomer incapable of cyclization to a diazaphospholinium ylide.[5] Other possible anomalies existing between these closely related chemical types are investigated in this present study of the photoinduced ring enlargement of *N*-[(phosphinyl)-imino]pyridinium inner salts to 1-phosphinyl-substituted 1H-1,2-diazepines.

Streith, Sasaki and Balasubramanian independently reported the first synthesis of diazepine by the photochemically induced intramolecular 1,3-dipolar cycloaddition of 1-(ethoxycarbonyl)iminopyridinium inner salt.[6–8] Since then this reaction has been extensively investigated, including the effect of 3-position substituents on ring enlargement.[9,10]

Diethoxy (**1**), diphenoxy (**2**), and diphenyl (**3**) N-(phosphinylimino)pyridinium inner salts, obtained from 1-aminopyridinium iodides and diethyl or diphenyl phosphorochloridates or diphenylphosphinic chloride in the presence of potassium hydroxide,[4] were irradiated to yield phosphorylated 1H-1,2-diazepines (**4–6**), presumably via a diazabicycloheptadiene intermediate (Scheme 1). In this instance



1-3

1 and 4, R = OC_2H_5

2 and 5, R = OC_6H_5

3 and 6, R = C_6H_5

4-6

the reactions of the phosphaminimides leading to the formation of phosphorylated diazepines were comparable to those reported as occurring with carbaminimides. The nmr chemical shifts and coupling constants for **4–6** are nearly identical to those reported by Balasubramanian, McIntosh and Snieckus for H_3-H_6 in the 1-carbonyl analog of 4.[8] The proton at the 7-position in the phosphinyl compounds, of course, shows a different multiplicity due to splitting by the phosphorus atom.

EXPERIMENTAL

The ^{1}H-nmr spectra were measured on a Nicolet NT-300 spectrometer using tetramethylsilane as the internal standard and deuterated chloroform as the solvent. Chemical shifts are reported in δ units and coupling constants in Hz. The ir (neat for **4** and **5**, KBr for **6**) spectra were obtained with a Perkin-Elmer 283 spectrophotometer and absorbances are reported in cm^{-1}. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Melting points were taken on a Thomas-Hoover apparatus and readings corrected to reference standards. A photochemical reaction assembly (Ace Glass, Inc.) with a 450 watt lamp (Canrad-Hanovia) was used for irradiation. Silica gel 60 (70–230 mesh) was employed for chromatography with neutral alumina TLC plates used to monitor the elutions.

1H-1,2-Diazepines (**4–6**). A solution of the appropriate phosphaminimide (**1–3**)[4] (0.5 g 1.5–2.2 mmoles) in acetone (250 mL) was irradiated under nitrogen for 11 h at 23–25°C. The light brown solution was evaporated under reduced pressure and the residue chromatographed using benzene and benzene-$CHCl_3$ (*4* and *5*) and $CHCl_3$ and MeOH-$CHCl_3$ (*6*) as the eluants.

For *4*: red oil ($C_9H_{15}N_2O_3P$, 51% yield); ir 1260 (P = O), 1030 (POEt); nmr 1.36 (t, 6H, $2CH_3$), 4.23 (m, 4H, $2CH_2O$), 5.71 (m, $J_{6,5}$ = 5.02, $J_{6,7}$ = 6.50, 1H, H_6), 6.01 (t, $J_{7,6}$ = 6.87, 1H, H_7), 6.22 (m, $J_{4,3}$ = 3.2, $J_{4,5}$ = 11.1, 1H, H_4), 6.49 (m, $J_{5,4}$ = 11.1, $J_{5,6}$ = 5.4, 1H, H_5), 7.37 (dd, $J_{3,4}$ = 3.3, $J_{3,5}$ = 1.29, 1H, H_3).

For *5*: red oil ($C_{17}H_{15}N_2O_3P$, 73% yield); ir 1170, 1190, 1220 (P = O); nmr 5.72 (m, $J_{6,5}$ = 5.36, $J_{6,7}$ = 6.2, 1H, H_6), 5.98 (t, $J_{7,6}$ = 6.67, 1H, H_7), 6.13 (m, $J_{4,3}$ = 3.25, $J_{4,5}$ = 1.07, 1H, H_4), 6.42 (m, $J_{5,4}$ = 11.12, $J_{5,6}$ = 5.39, 1H, H_5), 7.19 (dd, $J_{3,4}$ = 3.05, $J_{3,5}$ = 1.35, 1H, H_3), 7.33 (m, 6H, 2Ph), 7.44 (m, 4H, 2Ph).

For *6*: brown crystals (44% yield); mp 131–132°C; ir 1200, 1220 (P = O); nmr 5.70 (m, $J_{6,5}$ = 5.0, $J_{6,7}$ = 7.5, 1H, H_6), 6.04 (t, $J_{7,6}$ = 7.3, 1H, H_7), 6.27 (m, $J_{4,3}$ = 3.2, $J_{4,5}$ = 10.98, 1H, H_4), 6.56 (m, $J_{5,4}$ = 10.95, $J_{5,6}$ = 5.33, 1H, H_5), 7.27 (dd, $J_{3,4}$ = 2.92, $J_{3,5}$ = 1.36, 1H, H_3), 7.48 (m, 6H, 2Ph), 7,98 (m, 4H, 2Ph).
Anal. Calc. for $C_{17}H_{15}N_2OP$; C, 69.36; H, 5.14; N, 9.52. Found: C, 69.33; H, 5.17; N, 9.50.

ACKNOWLEDGEMENT

This research was supported by the Robert A. Welch Foundation, Houston, TX, Grant E-920.

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