CHEMISTRY LETTERS, pp. 965 - 968, 1984.

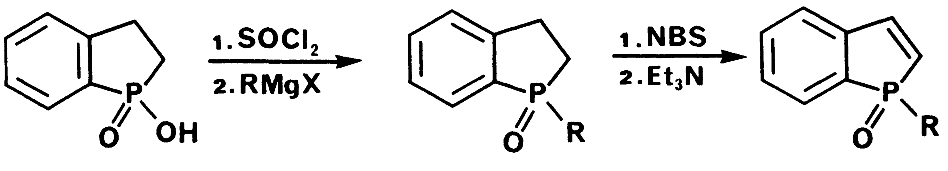
# PRELIMINARY RESULTS IN CYCLOADDITION OF DIPHENYLNITRILIMINE TO PHOSPHINDOLE OXIDES

Ahmed SEDQUI, Joël VEBREL, and Bernard LAUDE*
Laboratoire de Chimie Organique, Université de Franche-Comté,
Route de Gray, 25030 BESANCON Cedex, France

Diphenylnitrilimine cycloaddition reactions to two phosphindoles oxides are regiospecific and stereospecific. The approach of the dipole occurs from the less hindered diastereotopic side of the dipolarophile.

$\alpha,\beta$-Unsaturated organophosphorus compounds are good substrates for the cycloaddition of 1,3-dipolar systems.[1,2] It appears interesting to study the reactivity of phosphindole oxides towards diphenylnitrilimine in order to compare with this of N-methylindole and benzofuran which are moderate dipolarophiles.[3]

Phosphindole oxides 1 are unusual molecules[4]; however a useful precursor of these species, phosphinic acid 2 can be synthesized very easily.[5] Conversion of 2 into its acid chloride and condensation with a Grignard reagent gives the phosphindoline oxides 3 which can be converted into 1 by NBS bromination followed by HBr elimination according to Mathey et al.[6]

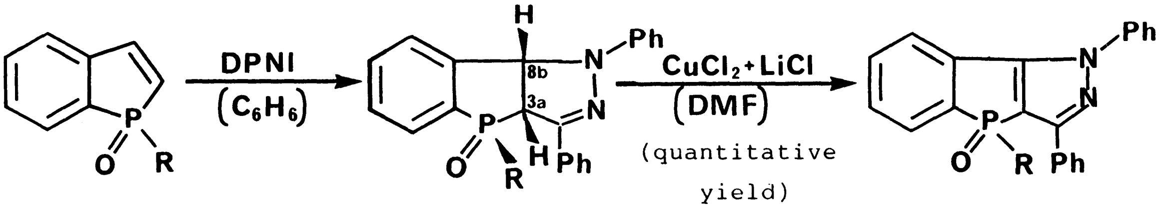


1a, R=$CH_3$
Yield = 70% from 3
1b, R=Ph
Yield = 65% from 3

2 3 1

Product 1a was unknown, and compound 1b was obtained with better yield than that given in literature.[7]

The five-membered benzo-annelated phosphoryl heterocycles are excellent dipolarophile-partners towards diphenylnitrilimine (DPNI) prepared in situ according to Huisgen et al.[8)]



1 6 7

6a, R=$CH_3$ ; Yield = 90% ; mp 265 °C

6b, R=Ph ; Yield = 95% ; mp 243 °C

7a, mp 232 °C

7b, mp 223 °C

The crude reaction products were subjected to TLC and $^{1}H$ NMR in order to detect any minor regio- and/or stereo-isomers.

Cycloaddition reaction is regiospecific with the two dipolarophiles 1a and 1b, and a treatment of every crude cycloaddition product 6 with cupric chloride and lithium chloride according to Halton and Morrison yields quantitatively only one oxidation compound 7.[9)]

The regiochemistry of the reaction is based on the interpretation of the $^{13}C$ NMR spectra of cycloadducts. Thus in the case of 6a, coupling constants $J_{P-C}3a$ = 103,5 Hz and $^{2}J_{P-C}8b$ = 18 Hz are in good agreement with literature data.[10)] This is not unreasonable considering that the weakest coupled $C^{8b}$ ($\delta$ = 62 ppm) more deshielded than $C^{3a}$ ($\delta$ = 44 ppm) is bounded to a nitrogen atom in the cycloadduct.[11)]

It is interesting to point out that the regiospecificity observed here is the reverse of that proposed by Kolokol'tseva et al.[12)] in cycloaddition of DPNI with vinylphosphorus compounds $R_2P(O)CH=CH_2$ which give 5-phosphinyl 2-pyrazolines.

The cycloaddition reactions of DPNI with 1a and 1b are stereospecific and the stereochemistry of the single cycloadducts 6a and 6b is specified by high field $^{1}H$ NMR - BRUKER 400 MHz. It is now well-established[4)] that for phosphoryl heterocycles, the coupling constant $^{2}J_{P-H}$ between P atom and every α-proton is different and larger for the proton cis to oxygen atom of P=O group.

It is the case for all phosphoryl heterocycles known up to this day ($^2J_{P-Hcis} \geqslant 15$ Hz) where the proximity with oxygen is associated with extra coupling.[4)] For cycloadducts 6a and 6b $^2J_{P-H^{3a}} = 6$ Hz, and $H^{3a}$ atom is trans to oxygen and cis to R. Consequently, the approach of the dipole occurs only by the face of the dipolarophile involving the oxygen atom of P=O group.

Table 1 . $^1$H NMR data of cycloadducts 6

| Compound | R | $H^{3a}$ | $H^{8b}$ | Aromatic H |
|---|---|---|---|---|
| 6a | $\delta$ = 1,9 ppm (d)<br>$^2J_{P-CH_3}$ = 13 Hz | $\delta$ = 4,35 ppm (dd)<br>$^2J_{P-H^{3a}}$ = 6 Hz<br>$^3J_{H^{3a}-H^{8b}}$ = 11 Hz | $\delta$ = 5,9 ppm (dd)<br>$^3J_{P-H^{8b}}$ = 16 Hz<br>$^3J_{H^{8b}-H^{3a}}$ = 11 Hz | 6,8 to 7,85 ppm<br>14 H |
| 6b | | $\delta$ = 4,35 ppm (dd)<br>$^2J_{P-H^{3a}}$ = 6 Hz<br>$^3J_{H^{3a}-H^{8b}}$ = 11 Hz | $\delta$ = 6 ppm (dd)<br>$^3J_{P-H^{8b}}$ = 17 Hz<br>$^3J_{H^{8b}-H^{3a}}$ = 11 Hz | 6,9 to 7,9 ppm<br>19 H |

Stereoelectronic effects on regio and stereoselectivities of the reaction are now in study and this work will be extended to the cases of others dipoles, six-membered benzo-annelated phosphorus heterocycles as dipolarophiles and also to the study of chemical properties of cycloadducts.

## References

1) N.G. Khusainova and A.N. Pudovik, Russ. Chem. Rev., 47, 803 (1978).

2) S.D. Venkataramu, G.D. Macdonell, W.R. Purdum, M. El-Deek, and K.D. Berlin, Chem. Rev., 77 , 121 (1977).

3) M. Soufiaoui, B. Laude, and J. Arriau, J. Heterocycl. Chem., 14, 1183 (1977).

4) L.D. Quin, The Heterocyclic Chemistry of Phosphorus, J. Wiley, New-York (1981), pp. 83, 330.

5) D.J. Collins, L.E. Rawley, and J.M. Swan, Aust. J. Chem.,27, 831 (1974); L.E. Rawley and J.M. Swan, ibid.,27, 801 (1974).

6) F. Nief, C. Charrier, F. Mathey, and M. Simalty, Nouveau Journal de Chimie, 5, 187 (1981).

7) T.H. Chan and L.T.L. Wong, Can. J. Chem., 49, 530 (1971).

8) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, Tetrahedron, 17, 3 (1962).

9) D.D. Halton and G.A. Morrison, J. Chem. Res., 1979, (S) 4, (M) 301.

10) T.M. Balthazor, J. Org. Chem., 45, 2519 (1980).

11) R.S. Jain, H.F. Lawson, and L.D. Quin, J. Org. Chem., 43, 108 (1978); L.D. Quin, C. Symmes Jr., E.D. Middlemas, and H.F. Lawson, ibid., 45, 4688 (1980).

12) I.G. Kolokol'tseva, V.N. Chistokletov, B.I. Ionin, and A.A. Petrov, J. Gen. Chem. USSR, 38, 1248 (1968).

(Received March 8, 1984)