Tetrahedron Letters No. 26, pp 2313 - 2316, 1978. 0040-4039/78/0622-2313$02.00/0
©Pergamon Press Ltd. Printed in Great Britain.

SYNTHESIS OF 1H-1,2,3-DIAZAPHOSPHOLE DERIVATIVES. A NEW DIAZAPHOSPHOLENE HETEROCYCLIC SYSTEM.

Graziano Baccolini* and Paolo E. Todesco
Istituto di Chimica Organica, Viale Risorgimento n. 4 - 40136 Bologna (Italy)

(Received in UK 20 April 1978; accepted for publication 4 May 1978)

In the course of our studies(1) on phosphorus heterocycles, we have discovered examples of the diazaphosphole system, namely the 2,3-dihydro-3-methoxy-1-methyl-2,4,5-triphenyl-1H-1,2,3-diazaphosphole-3-oxide (2a) and the corresponding 5-benzyl derivative (2b). Treatment of the azoalkenes (1; R=Ph, $PhCH_2$) with $P(OCH_3)_3$ afforded the unexpected compounds 2 which we believe represent the first derivatives of the unknown 1H-1,2,3-diazaphosphole.

Small amounts of 3I were also observed. The reaction was carried out in dry hexane at reflux temperature for five days, with rigorous exclusion of moisture. After evaporation of the solvent the resulting mixture, chromatographed over SiO_2 (benzene:ether = 9:1 as eluent), afforded pure 2 (60% yield) and pure 3I (10% yield). The products have been characterized, by ^1H-NMR, ir and mass spectroscopy.

The mass spectrum of 2a showed the parent ion at m/e=376 $(C_{22}H_{21}O_2N_2P)^+$ as the base peak and the predominant fragments m/e=361 (M^+-CH_3) and m/e=118 $(Ph-C\equiv\overset{+}{N}-CH_3)$. Analogous fragmentation pattern was observed in the mass spectrum of 2b.

The ^1H-NMR data are reported in the Table. It is interesting to note that isomer 3I does not interconvert into 3II in several solvents ($CDCl_3$, C_6H_6, hexane), even after many days under neutral conditions; on the contrary interconversion of isomer 3I into 3II occurs slowly under acidic conditions. In isomers 3 the differences in the chemical shifts between the NH as well as the methinic protons resonance suggest(1cd,2) that isomers 3I have the syn-configuration defined as that in which the anilino and phosphonic groups are on the same side of the C=N bond.

The NH of 3I is strongly intramolecularly bonded as indicated by its low-resonance value; this is due to a mutual interaction of the NH and PO groups in which must therefore lie on the same side of the C=N bond. On the other hand the NH of the other form 3II, cannot give hydrogen bonding and this resonates at higher magnetic field.

It should be noted that when $P(OEt)_3$ was used in this reaction formation of compounds with the N-Ethyl group was not oberved even after longer reaction times. The overall results, including the mechanism for the product formation, are shown in the Scheme.

TABLE - ^{1}H-NMR Data^a (CDCl$_3$) of 2 and 3.

Comp.(Rf.)	m.p(°C)	δNCH$_3$(J.Hz)	δPOCH$_3$ (J.Hz)		δPCH(J.Hz)	δArom.	δNH
2a(0,15)	103-105	2,61(d,1,5)	3,15(d,13)			6,50-7,35(m)	
2b(0,18)	135-137	2,87(d,1,5)	3,45(d,13)			6,90-7,85(m)	
3aI(0,35)	145-148		3,46(d,11)	3,54(d,11)	4,76(d,31)	6,30-7,65(m)	9,90
3aII(0,05)	oil		3,42(d,11)	3,52(d,11)	4,15(d,23)	6,20-7,65(m)	b
3bI(0,35)	oil		3,60(d,12)	3,65(d,12)	4,60(d,28)	6,85-7,90(m)	9,95
3bII(0,05)	166-168		3,70(d,11)	3,80(d,11)	4,35(d,24)	6,90-7,95(m)	b

^{a}Concentrations of 3 to 5 mol % phenylhydrazone were used; Chemical shifts in parts per million from MeSi$_4$; ^{b}Masked by aromatic protons.

Clearly our results involve a group transfer reaction presumably in pentacoordinated phosphorus intermediates(3).

The mechanism we propose for this reaction involves the formation of a trigonal bipyramidal phosphorane such as 4 with its tautomeric form 5 and (or) the ylide form 7. The formation of 7 may be favoured by its possible "aromatic character"(4).

A nucleophilic attack of 5 (or 4) on the activated(5) equatorial methoxy carbon of 4 gives the N$_1$-Me phosphorane 6 and the ring-opening compound 3I. A further nucleophilic attack of 5 (or 4) on the equatorial methoxy carbon of 6 gives 2 with reformation of 6. In this case the exclusive ring-retention is rationalized both on the basis of the expected(6) apicophilicities of the =N-N-Ph (A) and the -NMe-N- (B) groups compared to the methoxy group and on the basis of the relative anionic stability of the leaving group(7).

In 4, A is more apicophilic and a better leaving group than the methoxy group(1c); on the contrary the B group in compound 6 is a poorer apicophile and has a smaller leaving ability than the methoxy group.

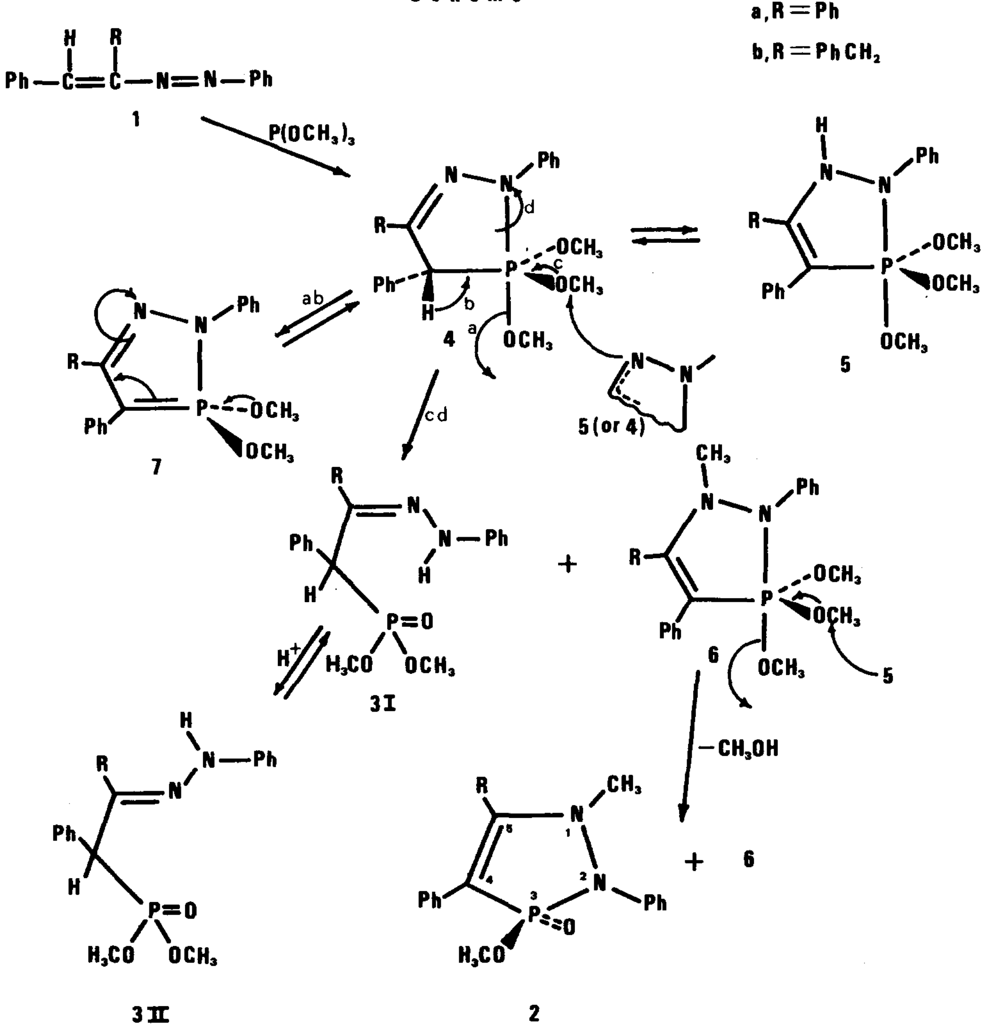
This is to be expected in view of the fact that the A group has a greater π-acceptor character than the B group(6a).

Intramolecular attack with formation of 3 is also possible and in pentacoordinated forms 4 and 5 this attack may be favoured by their intramolecular overcrowding.

The absence of N-Et compounds when P(OEt)$_3$ is used confirms this SN2 reaction at the carbon atom. The absence of attack at the ethoxy methylene carbon is most likely due to the lower reactivity of the ethyl with respect to the methyl in the SN2 reactions.

This effect is seen, for example, in the average 30-fold greater reactivity of methyl as compared to ethyl in SN2 reaction(8). It might be also noted that the C-O cleavage has been observed in phospholanium salts(9) and in oxaphosphoranes(10).

Scheme



The observed good configurational stability of 3I excludes any possibility of rapid isomerization of this compound in reaction conditions and confirms that even the formation of 3I implies a cyclic intermediate such as 4.

In conclusion, we believe that our findings clearly indicate that OMe groups attached to a pentacoordinated phosphorus are activated to undergo a SN2 reaction at carbon, and this result may probably lead a further insight into biochemical reactions involving phosphorus compounds.

Acknowledgements. We wish to thank the Italian C.N.R. for financial support and Mr. Mario Faggiano who carried out some of the experiments.

REFERENCES AND NOTES

1 a) G. Baccolini and P.E. Todesco, J.Org.Chem., 39, 2650 (1974).
b) G. Baccolini and P.E. Todesco, J.Org.Chem., 40, 2318 (1975).
c) G. Baccolini and P.E. Todesco, Tetrahedron Lett., 1891 (1976).
d) G. Baccolini and P.E. Todesco, J.Org.Chem., 43, 216 (1978).

2 G.J. Karabatsos and R.A. Taller, J.Am.Chem.Soc., 85, 3624 (1963).

3 For a recent review on phosphorane intermediated see R. Luckenbach "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements" - Verlag, Stuttgart, 1973.

4 For a review with many references about new "nonclassical" heteroaromatic systems see P. Jutzi, Angew.Chem.Int.Ed.Engl., 14, 232 (1975).

5 Since in the equatorial position the back-bonding is more efficient than in the apical position (6), the equatorial methoxy carbon is activated to undergo a nucleophilic attack.

6 a) R. Hoffman, J.M. Howell and E.L. Muetterties, J.Am.Chem.Soc., 94, 3097 (1972).
b) F. Ramirez and I. Ugi, Bull.Soc.Chem., 453 (1974).

7 a) L. Horner and H. Hoffmann, Ber., 91, 52 (1958).
b) M. Zanger, C.A. Vander Werf and W.E. McEwen, J.Am.Chem.Soc., 81, 3806 (1959).

8 A. Streitweser, Jr. "Solvolitic Displacements Reactions" Mc. Graw-Hill, New York, N.Y. 1962 p. 73.

9 K.L. Marsi, J.Org.Chem., 40, 1779 (1975).

10 W.G. Voncken, A.M.C.F. Castelijns, S.H.J. de Leeuw and H.M. Buck, Tetrahedron Lett., 729 (1977).