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1,3,2-DIAZAPHOSPHOLE DERIVATIVES FROM THE REACTION OF $PCl_n(NR_2)_{3-n}$ WITH DIAMINOMALEONITRILE

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Summary: Condensation of diaminomaleonitrile with PCl_3, Me_2NPCl_2, $(Me_2N)_2PCl$, $(Me_2N)_3P$ or $(Et_2N)_3P$ yields the 4,5-dicyano 1,3,2-diazaphosphole ring. In a slower reaction the two cyano groups by adding Me_2NH or Et_2NH form a second fivemembered ring to give 1,3,5,2-triazaphosphapentalenes.

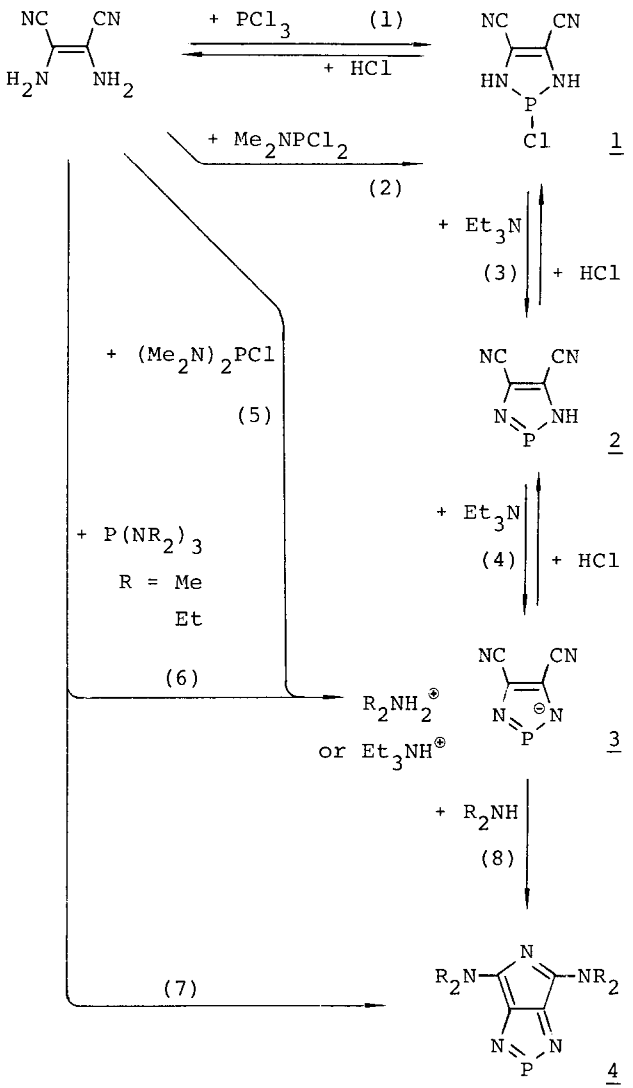
Diaminomaleonitrile (DAMN), a HCN tetramer, has been proposed to be an essential intermediate to purines in prebiotic origin of life[1] and has received much interest as a source of nitrogen heterocycles including 4,5-dicyano imidazoles[2,3] and 1,2,3-triazoles[3], 3,4-dicyano 1,2,5-thiadiazoles[4], 5,6-dicyano pyridines[5-9] and purines[10].

We find now that the reactions mentioned in the title and studied at first independently in the two laboratories[11-13] and which are summarized in Scheme 1 lead to new nitrogen heterocycles of dicoordinate phosphorus - 1,3,2-diazaphospholes - the specific products depending on conditions:

DAMN and dimethylamino dichlorophosphine after 5 h in CH_3CN at room temperature (2) give the 4,5-dicyano 2-chloro 1,3,2-diazaphospholine 1. It is also obtained by refluxing DAMN and PCl_3 in CH_3CN for 12 h (1). Triethylamine by deprotonation (3),(4) converts 1 to the triethylammonium salt of the diazaphosphole anion 3. ^{31}P-NMR spectra show a rapid proton exchange in solution between 1 and 3 in which the neutral diazaphosphole 2 participates too. The reaction sequence (1),(3),(4) can be reversed by addition of hydrogen chloride, finally leading to PCl_3.

The anion 3 is obtained directly as the main product from DAMN and bis(dimethylamino) chlorophosphine or tris(dimethylamino) or tris(diethylamino) phosphine in CH_3CN after 5 h at room temperature (5),(6). Reaction (6) R = Me has already been reported[12]. At higher temperatures and longer reaction times the yield of 3 decreases and the bicyclic diazaphospholes 4 are formed instead (7).

In refluxing acetonitrile or benzene after 2 d 3 and 4 are obtained in comparable amounts. 4 apparently is a secondary product of 3 and the dialkylamine from reaction (6). In fact 4 is formed as the only final product when 3 is reacted with R_2NH in benzene at room temperature for 20 d (8). Being a sequence of (6) and (8), reaction (7), especially with R = Me, ordinarily will stay incomplete, as (8) is relatively slow and the dialkylamine from (6) is partly lost meanwhile; the yield of 4 can be increased by continued addition of R_2NH.



c'less crystals[14,15]
decompose 190°C
$\delta\ ^{31}P(CH_3CN) = 136$

$\delta\ ^{31}P(CH_3CN) = 255$
$J_{PNH} = 10$ Hz

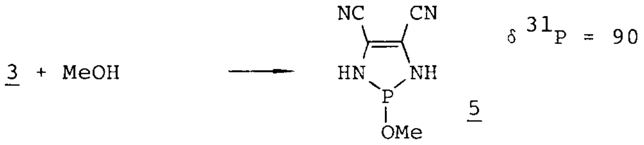
R = Me[12]
c'less crystals
mp 123 - 125°C
$\delta\ ^{31}P(CH_3CN) = 262$

R = Me[14,16]
red crystals
mp 250°C
$\delta\ ^{31}P(CHCl_3) = 300$
R = Et[14,17]

Scheme 1

The structure of 4 is suggested by analysis and spectra R = Me[15], Et[16]. A characteristic feature of the ^1H- and ^{13}C-NMR spectra is the pairwise non-equivalence of the alkyl groups R. It is obviously due to hindered rotation of the R_2N-C bond and is maintained up to 110°C. The proposed structure is confirmed by a single crystal X-ray determination[18].

The diazaphosphole 2 (formed in situ from its anion 3) easily adds alcohol to the P=N bond, as is known for the triazaphospholes[19]. With methanol the 2-methoxy-1,3,2-diazaphospholine 5 is obtained, with pinacol (in CH_3CN, 20°C) the spirophosphorane 6 is formed, which equilibrates slowly with the monocyclic aminophosphite 7.



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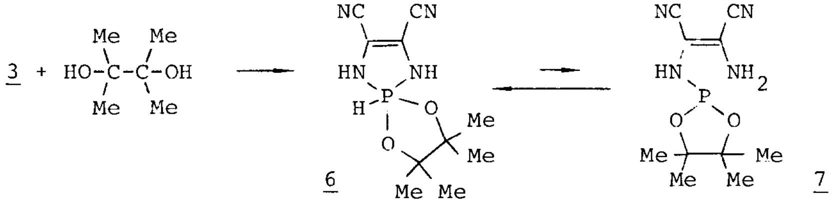
$\delta\ ^{31}P = 90$



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7

$\delta\ ^{31}P = -57.5$

$^1J_{PH} = 778$ Hz

$\delta\ ^{31}P = 140$

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12) A. Schmidpeter and K. Karaghiosoff, Z. Naturforsch. 36b, 1273 (1981).

13) The reaction of PCl_5 with DAMN is being investigated by E. Fluck, Frankfurt (personal communication).

14) The compound gave a correct elemental analysis and mass spectrum.

15) IR (KBr pellets): 2240(s,CN); 2205(S,CN), 1635, 1590, 1560, 1530, 1500, 1380, 1350, 1240.
^{13}C-NMR (CH_3CN): δ = 110.8 (d, $^3J_{PC}$ = 12.8 Hz), 110.1 (d, $^2J_{PC}$ = 1.7 Hz).

16) IR (KBr pellets): 2925, 1668(m), 1600(s), 1465(m), 1410, 1385(s), 1325(w), 1308(w), 1252(s), 1161, 1046.
^1H-NMR ($CDCl_3$): δ 3.67, 3.17.
^{13}C-NMR ($CDCl_3$): δ 166.3 (d sept, $^3J_{PC}$ = 7.7 Hz, $^3J_{HC}$ = 4 Hz); 154.4 (d, $^2J_{PC}$ = 4.3 Hz); 39.6 (qq, $^{1,3}J_{HC}$ = 140.1, 3.1 Hz) 38.4 (qq, $^{1,3}J_{HC}$ = 141.0, 3.5 Hz).

17) ^1H-NMR ($CDCl_3$): δ = 4.66 (q), 4.06 (q), 1.83 (t), 1.90 (t).

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