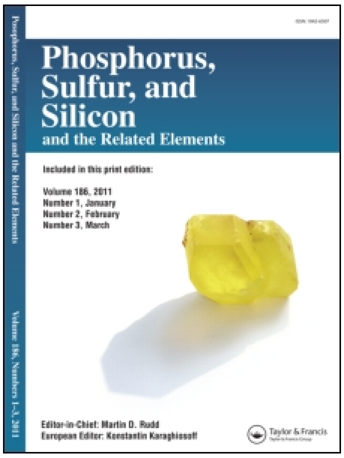

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New Phosphorus and Nitrogen Containing Bicyclic Compounds

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NEW PHOSPHORUS AND NITROGEN CONTAINING BICYCLIC COMPOUNDS

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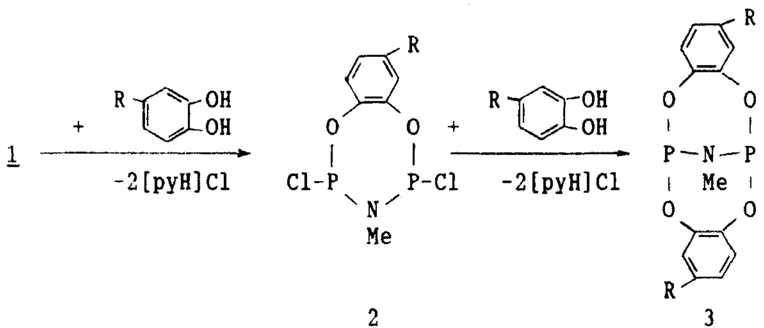
Abstract The reaction of bis(dichlorophosphino)methylamine (1) with bifunctional agents like catechols or N,N'-disubstituted ureas or thioureas in the molar ratio 1:1 leads to seven- or six-membered heterocyclic systems whereas in the molar ratio 1:2 the corresponding bicyclic, compounds are formed. Synthesis, properties and mass spectroscopic fragmentation behaviour of the title compounds are discussed.

The reaction of $MeN(PCl_2)_2$ (1)[1] and analogous compounds with nucleophiles like amines and alcohols has been studied very intensely (c.f. [2][3]). Thus, the reaction of bifunctional aliphatic compounds, e.g. of 1,2-ethane dithiol with 1 leads to (methylimino)bis(1,3,2-dithiaphospholane), $MeN(PSCH_2CH_2S)_2$.[4] In this case the nucleophilic attack of both functional groups takes place at the same phosphorus atom. Now we have found, that in the case of catechols or N,N'-disubstituted ureas and thioureas, respectively, the functional groups are probably more sterically fixed and therefore it will be possible that the reaction takes place simultaneously at both phosphorus atoms yielding bicyclic compounds. In this way 1 reacts with catechol or 4-methylcatechol, respectively, in anhydrous pyridine in the molar ratio of 1:1 forming partly the monocyclic compound 2 (c.f. equ. (1)). Obviously the reactivity of the Cl atoms at the two P atoms of the ring system is higher than that in 1, so formation of the bicyclic compound 3 in addition to unreacted 1 is observed.



(1)

2 3

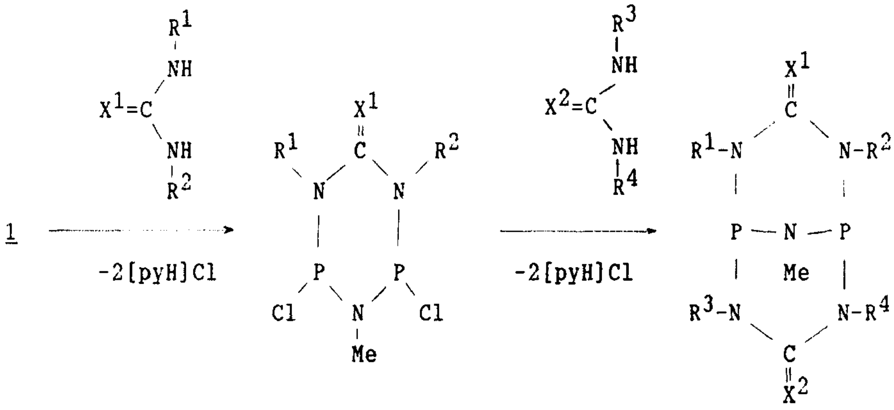
R = H, Me

Table 1 shows that the yields of monocyclic compounds 2 resulting from the reaction of the catechols with 1 in a molar ratio of 1:1 are only 17 and 30 %, respectively, whereas with a molar ratio of 2:1 the corresponding bicyclic compounds 3 are obtained in high yield.

Table 1: Reaction of Catecholes with 1 in Molar Ratios 1:1 and 2:1

	R	yield[%]	$\delta\ ^{31}P$[ppm]		yield[%]	$\delta\ ^{31}P$[ppm]
2a	H	17	171.6	3a	86	141.7
2b	Me	30	172.4	3b	93	142.0

On addition of a pyridine solution of N,N'-disubstituted ureas and thiourea, respectively, to a pyridinic solution of 1 in a molar ratio of 1:1 pyridinium hydrochloride and the corresponding 1,5-dialkyl (aryl)-2,4-dichloro-3-methyl-6-(thi)oxo-1,3,5-triaza-2,4-diphosphorinanes 4 are formed. The reaction in a molar ratio urea: 1 = 2:1 leads to bicyclic compounds 5 (2,4,6,8-tetraalkyl(aryl)-9-methyl-3,7-di(thi)oxo-2,4,6,8,9-pentaza-1,5-diphospha-bicyclo [3.3.1] nonanes).



(2)

4 5

R^1, R^2, R^3, R^4 = Me, Ph; X = O, S

In Table 2 the yields and chemical shifts of compounds 4 and 5 are given. Unlike the 1:1 reaction with the catechols, in this case the corresponding more stable monocyclic compounds 4 are formed so that the bicyclic compounds 5 are obtained only in smaller amounts. The compounds 5 which are obtained in relatively high yield from the reaction in a molar ratio of 2:1 (c.f. Table 2) can be purified by careful washing with cold water.

Table 2: Reaction of N,N'-disubstituted Ureas and Thioureas with 1 in Molar Ratios 1:1 and 2:1

Compound	R^1	R^2	R^3	R^4	X^1	X^2	yield[%]	$\delta\,^{31}P$ [ppm]
4 a	Me	Me			O		65	148.3
b	Ph	Ph			O		77	138.4
c	Me	Me			S		84	126.7
d	Me	Ph			S		88	124.8/120.8
5 a	Me	Me	Me	Me	O	O	56	105.6
b	Ph	Ph	Ph	Ph	O	O	84	94.9
c	Ph	Ph	Ph	Ph	O	O	65	101.9
d	Me	Me	Me	Me	O	S	64	89.6
e	Ph	Ph	Ph	Ph	O	S	82	77.9
f	Me	Me	Ph	Ph	O	S	54	86.2
g	Me	Me	Ph	Ph	S	O	69	85.1
h	Me	Me	Me	Me	S	S	71	70.6
i	Ph	Ph	Ph	Ph	S	S	62	62.3
j	Me	Me	Ph	Ph	S	S	71	70.3/68.2
k	Me	Ph	Me	Ph	S	S	45	68.0
l	Me	Ph	Ph	Me	S	S	45	67.6(d)/63.0(d)

The reaction of N-methyl-N'-phenyl thiourea with 1 in the molar ratio of 1:1 leads in nearly 90 % yield to 4d, which shows two signals in the ^{31}P NMR spectrum caused by the different electronic influence of the methyl and phenyl groups at the thiourea. Further addition of one mol N-methyl-N'-phenyl thiourea to the reaction mixture results in the formation of equimolar amounts of the symmetrical bicyclic compound 5k and the unsymmetrical 5l with two different phosphorus atoms (J_{P-P}=13 Hz, c.f. Table 2).

This result shows that the nucleophilic substitution at the initially formed monocyclic compound 4d occurs in a statistical manner.

In case of the reaction of 1 with N,N'-dimethylthiourea and N,N'-diphenylthiourea probably an equimolar mixture of two stereoisomeric bicyclic compounds (5j) is formed .

The mass spectroscopic fragmentation of the bicyclic compounds containing urea or thiourea groups leads in the first step to a monocyclic system by elimination of cyanate or thiocyanate.

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