254. Organic Phosphorus Compounds. Part 64

Synthesis of 4,6-Dimethylamino-2-cyclohexyl-2*H*-1,3,5,2-P^V-thiadiazaphosphorin-2-thione[1])

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(27. VIII. 73)

Summary. In the reaction of cyclohexylmonothiophosphonic anhydride, $[C_6H_{11}P(S)O]_3$, with dimethylcyanamide not the expected 2*H*-1,3,5,2-P^V-thiadiazaphosphorin-2-oxide derivative is formed, but the corresponding thione derivative, the title compound, is obtained.

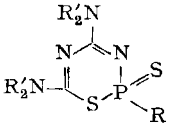
Recently we have reported a convenient method for the preparation of monothiophosphonic anhydrides (I) by the interaction of phosphonic dichlorides with H_2S in benzene solution in the presence of Et_3N [2]:

$$3\ RP(O)Cl_2 + 3\ H_2S \xrightarrow{6\ Et_3N} \underset{\text{I}}{[RP(S)O]_3} + 6\ Et_3N \cdot HCl$$

We also have described the reactions of I with alcohols, water, secondary amines, and PCl_5.

Now we report on the reaction of dialkylcyanamides with I. In analogy to the reaction of dimeric thionophosphine sulfides, $(RPS_2)_2$, with dialkylcyanamides which yield 2*H*-1,3,5,2-P^V-thiadiazaphosphorin-2-thione derivatives (II) [3]:

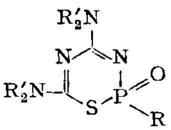
$$0.5\ [RPS_2]_2 + 2\ R'_2NC\equiv N \longrightarrow$$



(II)

we expected to obatin from I and dialkylcyanamides 4,6-dialkylamino-2*H*-1,3,5,2-P^V-thiadiazaphosphorin-2-oxides (III):

$$1/3\ [RP(S)O]_3 + 2\ R'_2NC\equiv N \longrightarrow$$



(III)

Interaction of $[RP(S)O]_3$, R = *cyclo*-C_6H_{11}, with dimethylcyanamide did, however, not yield III (R = C_6H_{11}, R' = CH_3); instead II (R = *cyclo*-C_6H_{11}, R' = CH_3) was obtained. One therefore has to assume that I either disproportionates with the formation of sulfur reach fragments which then react with cyanamides, or that first an addition

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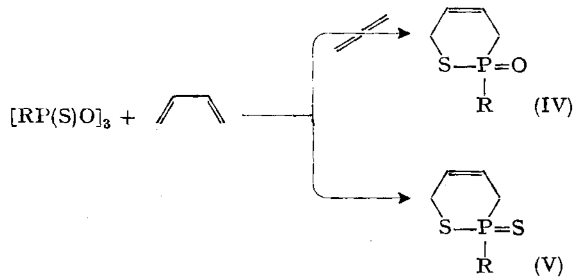
[1]) Part 63, see [1].

of cyanamide to the exocyclic P=S bond occurs and that this product interacts with excess I with exchange of S for O to give II.

A similar situation obtains in the reaction of I with dienes [4]. Here also not the expected tetrahydro-1,2-thiaphosphorin-2-oxides (IV) are formed, but tetrahydro-1,2-thiaphosphorin-2-thiones (V) are obtained [4].



Compound II is a white, high melting solid, m.p. 229–234° which shows in the ^{1}H-NMR. spectrum a broad signal for C_6H_{11} and a singlet for $(CH_3)_2N$. As expected it shows in the ^{31}P-NMR. spectrum only one signal at -73.5 ppm which is in line with the shift of similar compounds, *e.g.*, for II, $R=R' = C_2H_5$ a ^{31}P-chemical shift of -68.5 ppm has been reported [4].

The IR. spectrum shows bands for C=N at 1630 and 1560, C–N at 1105, and P–N at 773 [cm^{-1}], but no band for P=O.

The mass spectrum yields in addition to the molecular ion peak *m/e* = 318, a fragmentation pattern which indicates that first cyclohexene is lost to give a P–H bond; this intermediate then loses HS and then the ring fragments into the pieces PS_2, PS, $(CH_3)_2NCNH$, HCN etc. as indicated in the table below.

Fragmentation of II in the mass spectrum at 12 and 70 eV

Z	*m/e*	intensity	Z	*m/e*	intensity
M^+	318	23	$[PS_2]^+$	95	12.6
$[M—C_6H_{10}]^+$	236	36.8	$[PS]^+$	63	17.2
$[M—C_6H_{11}]^+$	235	3.6	$[(CH_3)_2NCNH]^+$	71	35.6
$[M—C_6H_{11}—S]^+$	203	100	$[(CH_3)_2NCH]^+$	55	20.7
$[M—C_6H_{11}—(CH_3)_2NCN]^+$	165	41.4	$[HCN_2]^+$	41	20.7
$[M—C_6H_{11}—S—(CH_3)_2NCN]^+$	133	23	$[HCN]^+$	27	6.9
			$[CH_3]^+$	15	1.1

Experimental Part[2])

(with Miss *H. Benz*)

*4,6-Dimethylamino-2-cyclohexyl-2*H*-1,3,5,2-P^V-thiadiazaphosphorin-2-thione* (II, $R = C_6H_{11}$, $R' = CH_3$).

A mixture of 4.86 g (0.01 mol) of $[C_6H_{11}P(S)O]_3$ and 4.2 g (0.06 mol) of dimethylcyanamide was heated for 20 min to 110–130°. A yellowbrown colored solution was formed. On cooling the reaction mixture crystallized. The crystals were dissolved in 50 ml benzene under reflux and then

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[2]) Microanalyses were carried out by *W. Manser*/ETH Zürich. ^{31}P- and ^{1}H-NMR. spectra were run on an HA 60 IL *Varian* spectrometer using H_3PO_4 or TMS as reference.

the solution cooled to 10°. A yellow powder precipitated (1.2 g) which was suspended in hot ethanol and filtered when cold to give 0.9 g of II, a white powder, m.p. 229–234°.

^{1}H-NMR. (in $CDCl_3$): C_6H_{11} at 0.9–2.35 ppm (*m*, 11.1 H), CH_3 at 3.11 (*s*, 11.9 H); ^{31}P-73.5 ppm (in $CHCl_3$).

IR. (in KBr) bands for: CH_3CH_2 at 2800, 2970; C=N at 1630, 1560; C–N at 1105; P–N at 773 [cm^{-1}].

$C_{12}H_{23}N_4PS_2$ (318.4)	Calc.	C 45.26	H 7.28	N 17.59	P 9.72	S 20.13%
	Found	C 45.31	H 7.21	N 17.46	P 9.60	S 20.04%

Mol. weight: 318 (mass spectroscopically)

REFERENCES

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[4] *A. Ecker & U. Schmidt*, Mh. Chem. *103*, 736 (1972).

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255. Controlled Allylic Transformations *via* the *Meisenheimer* Rearrangement

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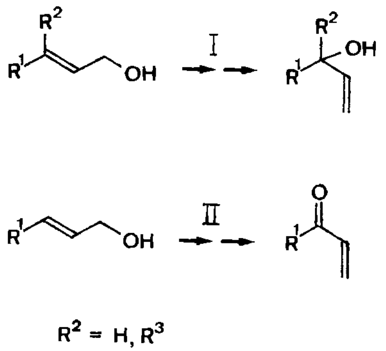
(31. VIII. 73)

Summary. Described are synthetic sequences which effect allylic transformations I and II. Sequence I involves (1) conversion of a primary allyl alcohol into the corresponding N, N-dimethylamine oxide, (2) [2,3]-rearrangement to give an N, N-dimethylhydroxylamine and (3a) reduction to give the 'rearranged' secondary or tertiary allyl alcohol [*e.g.* **36** → **35** → **37** → **40**]. Sequence II involves the same steps (1) and (2), followed by (3b) N-methylation of a secondary N, N-dimethylhydroxylamine and (4) *Hofmann* elimination to give a vinyl ketone [*e.g.* **11** → **12** → **13** → **14** → **15**].

Introduction. – In one approach to the problem of converting the ionones into the isomeric damascones[1]), we have found synthetic sequences which are based on the *Meisenheimer* rearrangement and which effect allylic transformations of the general



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[1]) For a discussion of this problem, see ref. [1] [2].