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SYNTHESIS OF p-THIOCYANOARYLDIOXOPHOSPHAZANES

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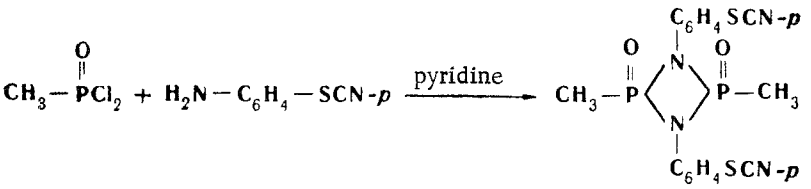
p-Thiocyanophenyldioxophosphazanes are synthesized by reacting alkylphosphonic dichlorides with p-thiocyanoanilines at room temperature.

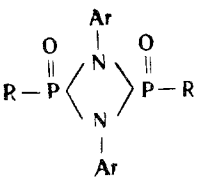
Phosphonic dichlorides react with anilines and other aromatic amines to give the corresponding phosphodianilides [1]. When the latter are heated under drastic conditions, they can split off amine, and undergo conversion to polyamides or heterocyclic compounds containing 4-membered rings, aryldioxophosphazanes [2]. The literature also describes indirect preparation of these 4-membered ring compounds by reacting phosphonic dichlorides with amines, with prolonged heating of the reaction mixture to 100°-120° C [3].

During an investigation of the phosphorylation of substituted p-thiocyanoanilines, we studied the reaction of 4-thiocyanoaniline, 3-chloro-4-thiocyanoaniline, and 3-methyl-4-thiocyanoaniline with methyl- and phenylphosphonic dichlorides, and showed that the reaction is peculiar, the corresponding heterocyclic compounds being formed even at room temperature:



The structures of the compounds obtained follows from the elementary data, molecular weight, and IR spectra. Formation of cyclic compounds containing phosphorus, and not of phosphonic dianilides is shown by the IR spectrum not containing bands characteristic of the NH fragment. It should be mentioned that the thiocyano group is unaffected by the reaction, as the IR spectrum has a band at 2160 cm^{-1} [4].

p-Thiocyanoaryldioxophosphazanes



No.	R	Ar	Mp °C	Formula	Found, % Cl	Found, % N	Found, % S	Calculated, % Cl	Calculated, % N	Calculated, % S	Yield, %
1	CH_3	C_6H_4SCN-*p*	140—141	$C_{16}H_{14}N_4O_2P_2S_2$		13.08 12.90	14.90 14.85		13.35	15.25	10
2	CH_3	$C_6H_3(Cl)SCN$-3,4	147—148	$C_{16}H_{12}Cl_2N_4O_2P_2S_2$	14.15 14.55	11.35 11.03	12.96 13.02	14.55	11.45	13.1	12
3	CH_3	$C_6H_3(CH_3)SCN$-3,4	151—152	$C_{18}H_{18}N_4O_2P_2S_2$		12.43 12.35	13.88 13.63		12.5	14.3	7
4	C_6H_5	C_6H_4SCN-*p*	123—124	$C_{26}H_{18}N_4O_2P_2S_2$		10.12 10.41	11.53 11.55		10.3	11.75	13
5	C_6H_5	$C_6H_3(Cl)SCN$-3,4	154—155	$C_{26}H_{16}Cl_2N_4O_2P_2S_2$	11.05 11.05	8.93 9.01	9.9 9.9	11.6	9.15	10.04	15
6	C_6H_5	$C_6H_3(CH_3)SCN$-3,4	160—161	$C_{28}H_{22}N_4O_2P_2S_2$		9.72 10.03	11.32 11.52		9.8	11.18	15

Experimental

1,3-Dimethyl-3,4-di-p-thiocyanophenyldioxophosphazane (I). 1.3 g (0.1 mole) methylphosphonic dichlorides in 10 ml dichloroethane was added dropwise, at 20° C, to 1.5 g (0.1 mole) p-thiocyanoaniline in 50 ml dry dichloroethane and 2.1 ml dry pyridine. The reaction mixture was left overnight, the precipitated pyridine hydrochloride filtered off, the reaction products washed a few times with cold water, the solvent vacuum-distilled off, and the residue, a viscous oil, treated with EtOH, when crystals separated, mp 140°–141° C, yield 10%. Found: N 13.08, 12.90; S 14.90, 14.85%; M 472, (isothermal distillation method). Calculated for $C_{16}H_{14}N_4O_2P_2S_2$: N 13.35; S 15.25%; M 489.

The other compounds for which data are given in the table were prepared similarly.

REFERENCES

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3. H. Binder and R. Heinle, West German Republic patent no. 1 083 818; C. A., 55, 17543, 1961.
4. L. J. Bellamy, The Infra-Red Spectra of Complex Molecules [Russian translation], IL, Moscow, 1957.

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