

Short Communications

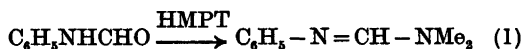
Phosphoramides. IV.* A New Synthesis of Biologically Important Formamidines

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N-Aryl-*N,N'*-dimethylformamidines represent a new class of pesticides.^{1,2} Especially interesting³ is the acaricide-insecticide *N*-(4-chloro-2-methylphenyl)-*N,N'*-dimethylformamide (chlordimeform). The active compounds are usually prepared by a Vilsmeier condensation of DMF and an aniline⁴ or by treatment of aryl isocyanates with DMF.⁵

In a previous investigation it was observed that *N,N*-dimethyl-*N'*-phenylformamide was formed by refluxing formamide in hexamethylphosphoric triamide (HMPT) (1).⁶ As formamide may be obtained by heating aniline and formic acid this opens up a new route.



Formamidines were now obtained by heating an aniline with formic acid to reflux tempera-

ture in HMPT. The yields of formamidines in this new synthesis are given in Table 1. Especially it should be noted that chlordimeform was obtained in a yield as high as 91 %.

Experimental. In all experiments commercial HMPT (Pierrefitte-Auby) was used.

General procedure. An aniline (0.1 mol), formic acid (0.13–0.17 mol, see Table 1), and HMPT (50 ml) were heated at reflux temperature in an oil bath (250 °C) for 3–8 h. The reaction mixture was allowed to cool to 100 °C and was then taken up in 400 ml of N NaOH and extracted four times with ether. The combined ether phases were washed with water and distilled. Correct spectroscopic data and satisfactory microanalyses were obtained for all new compounds.

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Table 1. Yields obtained in the reaction $\text{RC}_6\text{H}_4\text{NH}_2 \xrightarrow[\text{HMPT}]{\text{HCOOH}} \text{RC}_6\text{H}_4\text{N}=\text{CH}-\text{NMe}_2$.

R	HCOOH/mol	Reaction time/h	Yield/%	B.p./ (°C/mmHg)	n_D^{25}
H	0.13	3	35	68–70/0.08	1.5924
2-CH ₃	0.13	3	67	66–68/0.08	1.5762
4-CH ₃	0.13	3	54	77–79/0.08	1.5828
4-Bu	0.17	8	52	108–110/0.09	1.5973
4-OCH ₃	0.15	5	64	103–104/0.09	1.5883
4-Cl	0.13	3	76	90–92/0.09	1.6020
2-CH ₃ -4-Cl	0.17	6.5	91	96–99/0.08	1.5908