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. Especially interesting is the acaricide-insecticide N-(4-chloro-2-methylphenyl)-N',N'-dimethylformamidine (chlordimeform). The active compounds are usually prepared by a Vilsmeier condensation of DMF and an aniline or by treatment of aryl isocyanates with DMF.

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

\[
\text{HMPT} \xrightarrow{\text{C}_6\text{H}_5\text{NHCHO}} \text{C}_6\text{H}_5 - \text{N} = \text{CH} - \text{NMe}_2 \quad (1)
\]

Formamidines were now obtained by heating an aniline with formic acid to reflux temperature 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**

| R         | HCOOH/mol | Reaction time/h | Yield/% | B.p./(°C/mmHg) | n_D **

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| H | 0.13 | 3 | 35 | 68–70/0.08 | 1.5924 |
| 2-CH₃ | 0.13 | 3 | 67 | 66–68/0.08 | 1.5762 |
| 4-CH₃ | 0.13 | 3 | 54 | 77–79/0.08 | 1.5828 |
| 4-Bu | 0.17 | 8 | 52 | 108–110/0.09 | 1.5973 |
| 4-OCH₃ | 0.15 | 5 | 64 | 103–104/0.09 | 1.5883 |
| 4-Cl | 0.13 | 3 | 76 | 90–92/0.09 | 1.6020 |
| 2-CH₃-4-Cl | 0.17 | 6.5 | 91 | 96–99/0.08 | 1.5908 |