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Received June 24, 1982

The chlorination of pyrrole with *N*-chloroacetanilide was catalyzed by acetic acid. Transfer of  $\text{Cl}^+$  occurred directly to the  $\alpha$  and  $\beta$  positions of pyrrole and a mixture of 2-chloro-, 3-chloro- and 2,5-dichloropyrrole was formed. The  $\alpha/\beta$  ratio was 10:1 under competitive conditions.

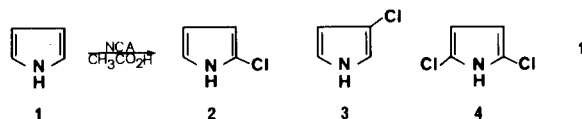
*J. Heterocyclic Chem.*, **19**, 1585 (1982).

Recently we reported that in the acid catalyzed intermolecular rearrangement of *N*-chloropyrrole, in methanol, to 2- and 3-chloropyrrole the most likely source of  $\text{Cl}^+$  was the conjugate acid of *N*-chloropyrrole (1). This suggested the possibility that *N*-chloro intermediates could be used to effect the chlorination(2) of pyrrole at the  $\alpha$  and  $\beta$  positions under acidic conditions. It was found that the *N*-chloro derivatives of diethylamine, pyrrolidine, piperidine and acetanilide can chlorinate pyrrole in carbon tetrachloride/methanol in the presence of acetic acid. The gc analysis indicated that a mixture of chloropyrroles was formed. The analytical procedure was identical to that previously reported in the study on *N*-Chloropyrrole (1).

The reaction of pyrrole with *N*-chloroacetanilide (NCA) was selected for detailed study. A solution of NCA (1 mole) in dichloromethane was added to a dichloromethane solution containing pyrrole and acetic acid in a molar ratio of 1:0.2. The NCA, at room temperature, was consumed on mixing the two solutions (< 5 sec.). No *N*-chloroacetanilide could be detected by iodometric analysis. Analysis of the reaction mixture by GC indicated the following products and yields (% area ratios): pyrrole (60%), 2-chloropyrrole (32%), 3-chloropyrrole (6%) and 2,5-dichloropyrrole (2%). Unidentified insoluble material was also formed under these conditions. Similar results were obtained in carbon tetrachloride and chlorobenzene. This reaction was completely stopped when 2,4,6-collidine (5 mole) was present instead of acetic acid. Essentially all of the NCA remained (98+ %) 30 min after mixing. This demonstrated that acid was necessary for chlorination to occur.

The most probable process was one in which the conjugate acid of NCA transferred  $\text{Cl}^+$  to pyrrole. This would be analogous to the carboxylic acid catalyzed halogenation of anisole by *para*-substituted *N*-chloro- and *N*-bromo acetanilides (3). Transfer of  $\text{Cl}^+$  could occur directly to the  $\alpha$  and  $\beta$  positions of pyrrole or to nitrogen. In the latter case the initially formed *N*-chloropyrrole would rearrange to the products. No reaction was observed after 15 minutes (iodometric analysis) when a solution of *N*-chloropyrrole (dichloromethane) was added to a dichloromethane solu-

tion of pyrrole and acetic acid. Clearly, the  $\alpha$  and  $\beta$  positions of pyrrole were chlorinated directly by NCA and acetic acid. The relative reactivities of the  $\alpha$  and  $\beta$  positions of pyrrole were determined by reacting a 10-fold excess of pyrrole with NCA-acetic acid. The  $\alpha/\beta$  ratio was 10:1. Similar values have been obtained for nitration (4), protodeuteration (5) and acetylation (6).



The results in this study can be compared to the chlorination of pyrrole with *N*-chlorosuccinimide where no 3-chloropyrrole was detected (7). The facile nature of this reaction prompted us to examine the reaction of pyrrole with *N*-bromoacetanilide. This reaction was equally fast and gc-ms indicated the formation of two monobromopyrroles. We are continuing the study of this interesting reaction and its extension to other heterocyclic compounds.

## REFERENCES AND NOTES

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