

The Reactions of 2-Aminopyrazine with Picryl Halides.
The Isolation of a Dimroth Intermediate (I)

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Received February 2, 1973

Sir:

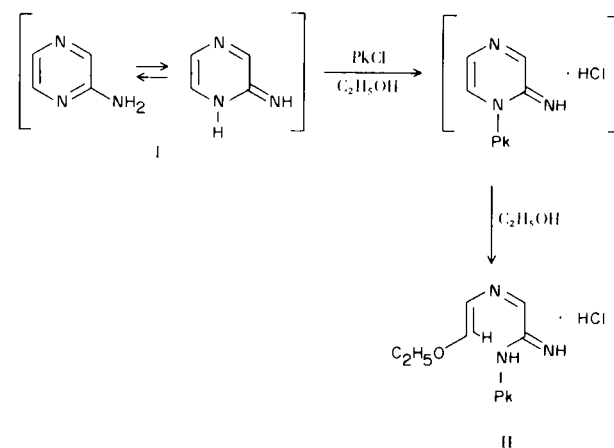
In a previous communication (3) we reported evidence indicating that the formation of 2-picrylamino-pyridine in the reaction of 2-aminopyridine with picryl halides may proceed through the intermediate formation and subsequent rearrangement of 2-imino-1-picryl-1,2-dihydropyridine. The possibility of a Dimroth rearrangement of the intermediate was suggested. Similar results were obtained from a study of the reactions of 2-aminopyrimidine with picryl halides (4).

We have recently found that 2-aminopyrazine (I), unlike 2-aminopyridine and 2-aminopyrimidine, failed to react with picryl chloride to give 2-picrylamino-pyrazine. When a molar excess of I or an equivalent amount of another base was employed as an acid scavenger in the reaction, intractable tar was the only product; however, when equimolar quantities of I and picryl chloride were dissolved in absolute ethanol at 25°, a yellow-orange solid crystallized from the solution within one hour. The product was collected by filtration, washed with a little cold ethanol, and air dried to give a 75% yield of the hydrochloride of the Dimroth intermediate, 1-ethoxy-5-imino-5-picrylamino-3-aza-1,3-pentadiene (II), m.p. 109°. Attempts to recrystallize the product resulted in decomposition; however, the analytical results obtained for the crude material indicate that it is reasonably pure.

Anal. Calcd. for $C_{12}H_{13}ClN_6O_7$: C, 37.08; H, 3.37; N, 21.62; Cl, 9.12. Found: C, 36.85; H, 2.92; N, 21.25; Cl, 8.73.

The nmr spectrum of II in DMSO- d_6 consists of a triplet at 1.10 δ (3H, $J = 7$ cps) and a quartet at 3.60 δ (2H, $J = 7$ cps), which are assigned to the protons of the ethyl group; a singlet at 5.73 δ (1H), which is assigned to the C-4 proton; two doublets at 6.20 δ (1H, $J = 6$ cps) and 6.35 δ (1H, $J = 6$ cps), which are assigned to the C-1 and C-2 protons; a singlet at 9.26 δ (2H), which is assigned to the picryl protons, and two broad singlets at 9.75 δ (1H) and 10.17 δ (1H), which are assigned to the amino and imino protons. The possibility of an ethanol solvate was eliminated when a drop of ethanol was added

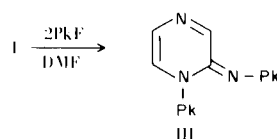
to the nmr sample. The hydroxyl proton of the ethanol appeared at 4.47 δ , and the chemical shifts of II were not altered.



Several attempts were made to convert II into 2-picrylamino-pyrazine by treating it with an equivalent amount of base; however, nothing but polymeric tar was obtained from these experiments.

Treatment of I with two molar equivalents of picryl fluoride in DMF produced 1-picryl-2-picrylimino-1,2-dihydropyrazine (III). The product, which precipitated when the DMF solution was diluted with water, was recrystallized from acetone-ethanol to give a 64% yield of pure III, m.p. 267° dec.

Anal. Calcd. for $C_{16}H_7N_9O_{12}$: C, 37.15; H, 1.36; N, 24.37. Found: C, 36.87; H, 1.51; N, 23.96.



The nmr spectrum of III in DMSO- d_6 contains two singlets, which are assigned to the 1-picryl protons (9.36 δ , 2H) and the picrylimino protons (9.00 δ , 2H); a doublet at 8.22 δ (1H, $J = 1$ cps), which is assigned to the C-3 proton; a quartet at 7.93 δ (1H, $J = 1$ cps and 5 cps), which is assigned to the C-5 proton; and a doublet at 7.71 δ (1H, $J = 5$ cps), which is assigned to the C-6 proton.

Acknowledgement.

The authors are grateful to Dr. L. C. Smith for helpful criticism of the manuscript.

REFERENCES

- (1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
- (2) To whom correspondence should be addressed.
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