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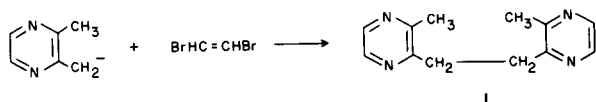
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The reaction of alkylpyrazine anions with *trans*-1,2-dichloroethylene produces pyrrolo[1,2-*a*]pyrazines in low yields.

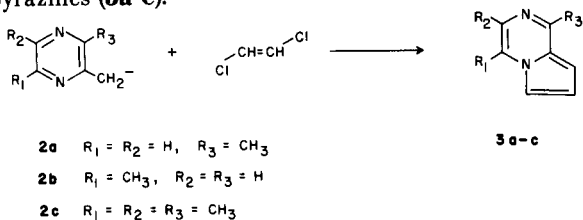
J. Heterocyclic Chem., **18**, 445 (1981).

Sir:

In a previous paper (1) we reported that 2,3-dimethylpyrazine anion reacts with 1,2-dibromoethylene to form 1,2-bis(3-methyl-2-pyrazyl)ethane (**1**) in 55% yield. This rather unusual dimerization led us to explore the reactions of alkylpyrazine anions with other dihaloethylenes. This communication describes the reaction of these anions with *trans*-1,2-dichloroethylene.



Alkylpyrazines were easily converted into their anions by reaction with lithium diisopropylamide. Treatment of a suspension of each of these anions, in ether at 0°, with one equivalent of *trans*-1,2-dichloroethylene resulted in the unexpected formation of the corresponding pyrrolo[1,2-*a*]pyrazines (**3a-c**).



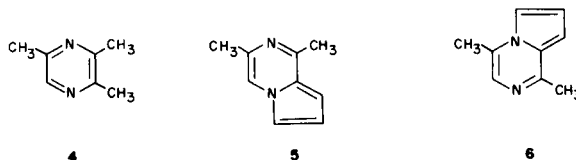
In all cases studied the reaction proceeded smoothly with only the product, unreacted alkylpyrazine, and a small amount of tar detected in the reaction mixture. The yields obtained from the various alkylpyrazines are summarized in the Table. In the case of 2,3,5-trimethylpyrazine (**4**) only two isomers of the corresponding pyrrolo[1,2-*a*]pyrazine, **5** and **6**, were formed (2).

Table

Yields of Pyrrolo[1,2-*a*]pyrazine from the Reaction of Alkylpyrazine Anions with *trans*-1,2-Dichloroethylene

Alkylpyrazine	Yield (%)	Recovered Alkylpyrazine (%) ^(a)
2a	29	56
2b	15	65
4	8(b)	72
2c	<1	>95

(a) By distillation. (b) A mixture of **5** and **6** in a 2:1 ratio.



In each of the above reactions the anion reacted completely as was indicated by the disappearance of its characteristic red color after the addition of *trans*-1,2-dichloroethylene. The dichloride could not be detected in the crude reaction mixture indicating that it also reacted completely. These results, as well as the observed high recoveries of the alkylpyrazines (see Table), indicate that the low yields of the pyrrolo[1,2-*a*]pyrazines are due mainly to competing reactions taking place between the anion and the dichloride. Organolithium reagents are known to react with 1,2-dichloroethylenes by proton abstraction, followed by chloride anion elimination (3). Indeed we found that more than 30% of the chlorine in the dichloride was converted into lithium chloride. Moreover, treatment of the crude reaction mixture with carbon dioxide resulted in the formation of both 2,3-dichloroacrylic acid and chloroacetylene carboxylic acid.

The data in the Table show that the yields decrease significantly with increasing methyl substitution on the pyrazine ring. This, in part, may be due to steric effects (compare for example **2a** and **2b**). However, the large difference between **2b** and **2c** suggests that electronic effects are also involved in determining the relative rates of the various competing reactions.

There has been renewed interest in the chemistry of pyrrolo[1,2-*a*]pyrazines as a result of their recent detection as new components of roasted meat aroma (4). A few synthetic methods for their preparation have been developed (4), giving in general better yields than those shown in the Table. Our method however, may serve as an alternative due to its simplicity [a one step reaction, the ease of separation of the product and the high recovery of starting material (5)].

The results obtained for 1,2-dichloroethylene are completely different from those obtained for 1,2-dibromoethylene. While the 1,2-dibromoethylene mediated coupl-

ing reaction of alkylpyrazine anions can be easily explained (1), the formation of pyrrolo[1,2-*a*]pyrazines in the reaction of these anions with the 1,2-dichloroethylene is not, at present, well understood. Being a novel ring closure reaction it opens the field for considerable mechanistic studies. We are now exploring the mechanism as well as the generality of this reaction. In particular we are examining the possibility that the pyrrolo[1,2-*a*]pyrazines are formed *via* a [1,3]anionic cycloaddition mechanism. The synthetic potential, as reflected by optimizing yields as well as applying the reaction to other substrates is also being investigated.

REFERENCES AND NOTES

- (1) Y. Houminer and E. B. Sanders, *J. Heterocyclic Chem.*, **17**, 647 (1980).
- (2) A similar observation was made in the alkylation of the anion of **4**; G. P. Rizzi, *J. Org. Chem.*, **33**, 1333 (1968).
- (3) G. Kobrich and K. Flory, *Chem. Ber.*, **99**, 1773 (1966).
- (4) I. Flament, P. Sonnay and G. Ohloff, *Helv. Chim. Acta*, **60**, 1872 (1977).
- (5) Compounds **3a-b**, **5** and **6** were purified by distillation. All were found to be identical with authentic samples prepared according to reference (4). Compound **3c** was purified by tlc; nmr (deuteriochloroform): δ 2.48 (6H, s, 2CH₃), 2.64 (3H, s, CH₃), 6.68-6.91 (2H, m, pyrrole ring), 7.22-7.31 (1H, m, pyrrole ring).