

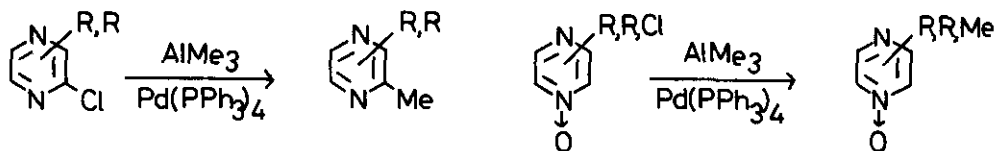
INTRODUCTION OF C-GROUPS INTO THE PYRAZINE RING
WITH ORGANOALUMINUM COMPOUNDS

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There are many alkylpyrazines, which have been noticed as the components contributing to the flavor of roasted or cooked foods. For example, 2,5-diethyl-3,6-dimethylpyrazine, 2,5-diethyl-3-methylpyrazine, and 2-isobutyl-3,6-dimethylpyrazine were isolated from coffee, peanuts, potato chips, and the other roasted foods. For the purpose of synthesizing these substances, the C-substitution of pyrazines with organoaluminum compounds was investigated.

1. Reaction of chloropyrazines with trimethylaluminum

Due to the coupling reaction of mono- and dichloropyrazines with trimethylaluminum in the presence of tetrakis(triphenylphosphine)palladium, the corresponding methylpyrazines were prepared in good yields. 2-Chloropyrazine 1- and 4-oxides were also submitted to this reaction under the same conditions as above. In this case, the N-oxide group was not affected, and the aimed compounds were satisfactorily obtained.



R = alkyl, phenyl

2. Reaction of chloropyrazines with triisobutylaluminum

In order to introduce the bigger alkyl groups into the pyrazine ring, the reaction of chloropyrazines with triisobutylaluminum was studied first under similar conditions as above. Besides the introduction of the isobutyl group, the dechlorination took place at the same time. Diisobutylaluminum hydride (DIBAL-H), which was generated by thermolysis of triisobutylaluminum, may take part in the dechlorination of chloropyrazines.