

REACTION OF PICOLINE AND METHYLQUINOLINE N-OXIDES
WITH THALLIUM TRIACETATE

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Quinaldine N-oxide (1) reacts readily at room temperatures with thallium triacetate (A) and acetic anhydride in acetic acid (condition-a), giving 2-acetoxymethylquinoline N-oxide (2) in good yields. When 1 is treated with A and acetic anhydride without acetic acid (condition-b), the reaction proceeds to further step, forming diacetate of quinaldinaldehyde (3) in good yields. The reaction with A in hot acetic acid (condition-c) affords quinaldinaldehyde (4) and its N-oxide (5).

The reaction of 1 using lead tetraacetate (B) instead of A progresses in similar manners, but its selectivity is somewhat lower. However, the reaction under the condition-b is an excellent method for preparing 3.

The reaction is apparently initiated by oxidation of 1 to 2, which subsequently undergoes rearrangement to 3 (or 4) by means of acetic anhydride or is further oxidized to 5.

The reactivity of lepidine N-oxide (6) is appreciably lower and the selectivity of the reaction is also decreased. Thus, the reaction under the condition-a requires warming at 30-50° and the use of the excess acetic anhydride, giving 4-acetoxymethylquinoline N-oxide (7), 4-quinolinemethanol N-oxide (8), quinoline-4-carboxyaldehyde (9), its diacetate (10) and quinoline-4-carboxyaldehyde N-oxide (11) in various yields depending upon the reaction conditions. The stronger conditions increase the amount of oxidation-rearrangement products, 9 and 10; those of 7 and 8 are decreased. The reaction under the condition-b is promoted also by warming, and 4-acetoxymethylquinoline and 3-acetoxylepidine resulting only from rearrangement of 6 are isolated besides 7, 9, 10 and 11. It is interest that N-hydroxy-4-methylcarbostyrl is formed when 6 is treated with B in acetonitrile independently in the presence of acetic anhydride.

The reactivity of α -picoline N-oxide is found to be further lower, but the products of the same type are obtained from reactions with A and acetic anhydride.