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 quinaldaldehyde (**3**) in good yields. The reaction with **A** in hot acetic acid (condition-c) affords quinaldaldehyde (**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-methylcarbostyril 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.