INDIRECT ELECTROOXIDATION OF tert-AMINES WITH RuO_4

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RuO_4 can be used as a versatile reagent for various oxidative transformations. Instead of usual methods using periodates or hypochlorites as co-oxidants, we developed electrochemical process for generation of RuO_4 from RuO_2 and attempted to oxidize cyclic and acyclic tert-amines 1 thereby. As shown in the schematic picture (Chart I), we found that RuO_4 generated *in situ* in aqueous NaCl can act as an efficient mediator in the electrolysis system for the conversion of 1 to amides 2.

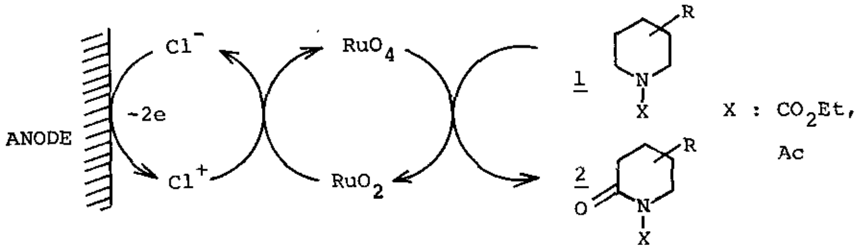

Chart I

Typically, electrooxidation of 1 (0.6 mmol) was carried out using $RuO_2 \cdot 2H_2O$ (0.02 mmol) in a acetone-saturated NaCl (2.5 ml-5.0 ml)-(Pt-Pt) system under a constant current of 10 mA/cm^2 (applied voltage: 2.0-.2.4 V; electricity: 7.0 F/mol), giving the desired 2 in 92% yield. It is interesting to note that only methylene group at the α-position are readily oxidized to carbonyl function and no reaction has been observed at the alkyl substituted α'-position of nitrogen. Cyclic amines are much more easily oxidized than linear ones.

The present oxidation procedure of amines can be used for selective functionalization of nitrogen containing compounds. For example, we demonstrate here transposition of α,β-enone 3 to reversed α,β- unsaturated amide 6. Thus, electrooxiation of 4 prepared by amination of 3 followed by reduction with $NaBH_4$ and protection of both amino and hydroxyl groups gave 5 in 77% yield whose dehydroacetoxylation with DBU afforded the desired 6, smoothly.