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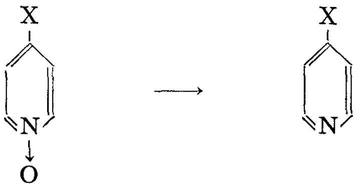
A New Deoxygenation Reaction of an Aromatic Heterocyclic N-Oxides

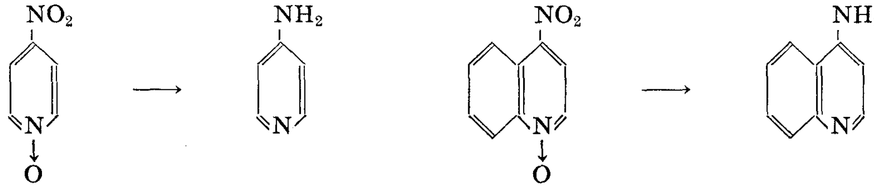
The best known method for the selective reduction of N-oxide group has been the reaction employing phosphorus trichloride reported by Hamana.[1] However, this process is somewhat unsatisfactory in the way of yield and purification when a group containing active hydrogen, such as amino and hydroxyl, is present in a position conjugated to the N-oxide group. Hertog and others[2] recommended the use of iron and acetic acid in the reduction of 4-nitropyridine 1-oxides and 4-nitroquinoline 1-oxides to the corresponding 4-amino derivatives but this is rather complicated in experimental procedures.

It has recently been found that deoxygenation of N-oxide group in various aromatic heterocyclic compounds could be effected smoothly by catalytic reduction in neutral, methanol solution, employing Raney nickel[3] as a catalyst, at ordinary temperature and pressure. Application of this reductive method has established laboratory process for the manufacture of 4-substituted pyridines and quinolines through their N-oxides.



$X = -OCH_2Rh, -Cl, -OH, -NH_2$

This process is characterized by the fact that the redution of the N-oxide group takes place preferentially over other easily reducible groups as shown. In the case of 4-nitro-pyridine and -quinoline 1-oxides, however, reduction of the nitro group occurs in parallel with that of the N-oxide group, affording the corresponding 4-amino derivatives, and 4-nitro-pyridine and -quinoline cannot be isolated as intermediates. It has also been found that the acidification of this reaction with acetic acid has effected a tremendously increased velocity of the reduction.



This reaction has many advantages such as (i) rapid absorption of hydrogen and consequently termination of the reaction in a short time; (ii) simple after-treatment and production of pure samples; (iii) reduction of various forms of N-oxide groups which had heretofore been considered difficult to reduce; and (iv) a very good yield (80～100%) in every case. It is considered that this reaction leaves no room for improvement as a means of deoxygenation of N-oxide group in a laboratory.

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[1] M. Hamana : Yakugaku Zasshi, **75**, 123(1950),*et seq.*

[2] H.J. den Hertog, J. Overhoff : Rec. trav. chim., **69**, 468(1950)(C.A., **44**, 6418(1950)).

[3] Prepared according to Formula W-1 (cf. L.W. Covert, H. Adkins : J. Am. Chem. Soc., **54**, 4116 (1932)).