OXIDATION OF INDOLES WITH MOLYBDENUMPEROXO COMPLEX, MoO_5·HMPA

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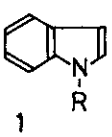
The oxidation of indoles with peracids proceeds via the formation of the 2,3-epoxy intermediates, which undergoes the nucleophilic ring opening by peracids. This observation prompted us to investigate the oxidation of indoles with the presumably non-nucleophilic epoxidizing agent, (hexamethylphosphoramide)oxodiperoxomolybdenum (VI), MoO_5·HMPA. We wish to describe the oxidation of indoles with MoO_5·HMPA to give 2-hydroxyindoxyl, isatogen, and 2,3-dihydroxyindoline derivatives.

Oxidation of 1-acetylindoles, 1a and 2, with MoO_5·HMPA in CH_2Cl_2 gave the corresponding 2-hydroxyindoxyls 3. 3a was also derived from indoxyl 4a by the treatment with MoO_5·HMPA.

Oxidation of 2-phenylindole (5) with MoO_5·HMPA afforded a dimeric product 6, while treatment of 5 with 3 mole equiv. of MoO_5·HMPA gave isatogen 7.

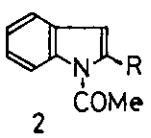
In methanol, oxidation of 1 with MoO_5·HMPA gave 3-hydroxy-2-methoxyindolines 8, which were treated with $SnCl_4$ to give 1-acylindoxyls 4.

The oxidation of other indoles with MoO_5·HMPA is also described, and the mechanism for these oxidation is discussed.



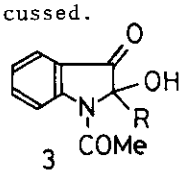
1

a) R=-COMe
b) R=-COPh
c) R=-CO_2Me
d) R=-$SO_2C_6H_4$Me



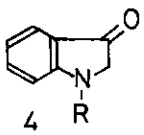
2

a) R=Me
b) R=Ph



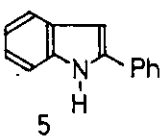
3

a) R=H
b) R=Me
c) R=Ph



4

a) R=-COMe
b) R=-COPh
c) R=-CO_2Me



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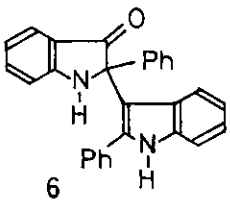

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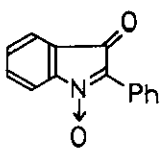

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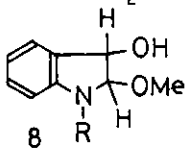

8

a) R=-COMe
b) R=-COPh
c) R=-CO_2Me
d) R=-$SO_2C_6H_4$Me