HETEROCYCLES, Vol. 9, No. 1, 1978

OXYGENATION OF 2,3-DIPHENYLINDOLES

Tohru Hino, Masako Nakagawa, Noriko Ohyoshi, Shiro Kato,
Mutsumi Takano, and Akiko Hirose

Faculty of Pharmaceutical Sciences, Chiba University, Chiba-shi, 280

2,3-Diphenylindole(1) is known to be stable towards oxygen in neutral conditions, though many 2,3-dialkylindoles having a hydrogen at 1-position are susceptible to air to form the corresponding 3-hydroperoxyindolenines and their rearranged products. We now examined base-catalyzed O_2-oxygenation and dye-sensitized oxygenation of 1 and its derivatives. When oxygen was bubbled into a DMSO solution of 1 for 48 hr in the presence of KOH at room temperature, o-benzoylbenzanilide(2, 68%) and 2,2-diphenylindoxyl (3, 14%) were obtained. Irradiation of 1 in MeOH under O_2 atmosphere in the presence of rose bengal for 4.5 hr gave 2 and 3-hydroxy-2,3-diphenylindolenine(4) as main products. At low temperature(-70°) the reaction slowed down and 4 was obtained in 80% yield after reduction with Me_2S. At about 0° the reaction gave 4(58%) and 2(37%), while 2 became a major product at about 20°. The reaction at 0° in the presence of Ph_2S gave 4 in 80% yield, indicating the presence of the hydroperoxide as an intermediate.

Dye-sensitized oxygenation of N-methyl-2,3-diphenylindole(5) in MeOH, on the other hand, gave N-methyl-o-benzoylbenzanilide(6, 60%) and 2-hydroxy(or methoxy)-3-methoxy(or hydroxy)-2,3-diphenyl-1,4-benzoxiazine(15%) as major products. In the presence of thiourea or 2-mercaptopyridine the reaction gave a small amount of 1-methyl-2,2-diphenylindoxyl besides 6, indicating the presence of zwitter ionic peroxyindolenine or perepoxide. Irradiation of 5 in benzene in the presence of benzil under O_2 also gave 6 as a major product.

Dye-sensitized oxygenation of N-acetyl-2,3-diphenylindole in MeOH proceeded slowly and gave N-acetyl-2,3-dihydroxy-2,3-diphenylindole(54%) and 2(2%).

Substituents at the nitrogen and reaction conditions were found to give a remarkable influence on the products.