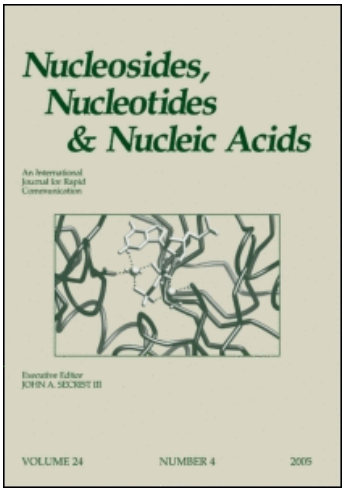

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Raffaele Saladino[a]; Paola Carlucci[a]; Claudia Crestini[a]; Pietro Tagliatesta[b]; Donato Monti[b]; Tristano Boschi[b]
[a] Dipartimento A. B. A. C., Università degli Studi della Tuscia, Viterbo, Italy [b] Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Roma, Italy

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MANGANESE TETRAPHENYLPORPHYRINS CATALYZED SELECTIVE OXIDATION OF PURINE DERIVATIVES

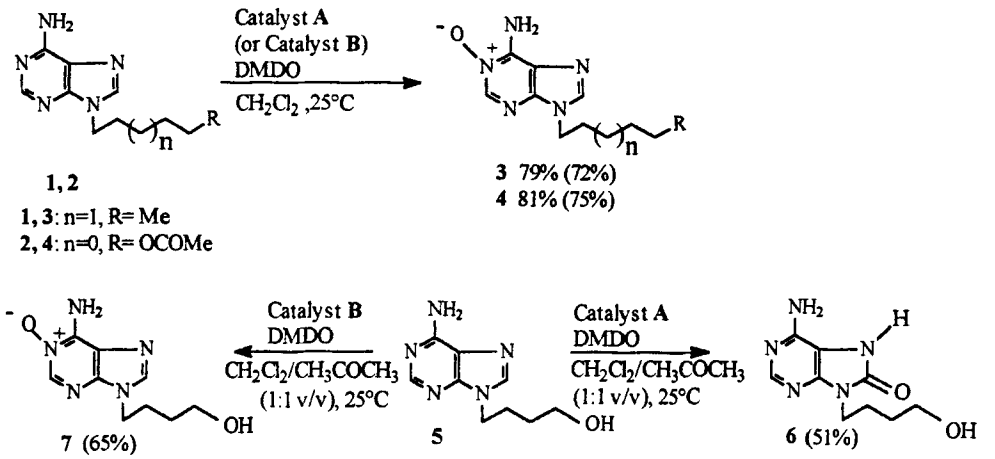
Raffaele Saladino*[1], Paola Carlucci[1], Claudia Crestini[1], Pietro Tagliatesta*[2], Donato Monti[2], Tristano Boschi[2].[1] Dipartimento A.B.A.C., Università degli Studi della Tuscia, Via S.Camillo de Lellis, 01100 Viterbo, Italy.[2] Dipartimento di Scienze e Tecnologie Chimiche, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133, Roma, Italy.

ABSTRACT: The oxidation of purine derivatives using porphyrins as catalysts and dimethyldioxirane (DMDO) as oxygen atom donor is reported. The regioselectivity of the oxidation was found to be dependent on the presence of a free OH moiety on the N(9)-side chain of the substrate and on the structure of the catalyst.

A number of synthetic metalloporphyrins have been studied as catalysts for the oxidation of organic substrates.[1] The most well studied of such compounds have been *meso*-tetraphenylporphyrins containing electron withdrawing groups as substituents either on the four phenyl rings or on the β-pyrrole positions of the macrocycle, or on both.[2] Several papers appeared on the interaction between DNA and metalloporphyrins, focusing on the attention of molecular recognition. In this context, weak interactions between porphyrins and several nucleosides were attributed to the presence of hydrogen bond interactions involving the nitrogen atoms present on the heterocyclic ring.[3] Recentely, we have reported the first described synthesis of uracil epoxides based on the use of porphyrins as catalysts.[4] As a continuation of these studies, we report here the manganese tetraphenylporphyrins catalyzed selective oxidation of purine derivatives. The catalysts used in the transformations were Mn[(Cl_{16})TDMPP] (catalyst **A**) and Mn[(Cl_8)TDCPP] (catalyst **B**) porphyrins, where (Cl_{16})TDMPP, and (Cl_8)TDCPP, are the dianions of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(3,5-dichloro-2,6-dimethoxyphenyl) and (2,6-dichlorophenyl)porphyrin, respectively. The reaction of

N(9)-[(n-hexan-1'-yl)]adenine **1** and N(9)-[(4-acetoxy-n-butan-1'-yl)]adenine **2** performed with DMDO in CH_2Cl_2 at 25°C in the presence of catalytic amounts of catalyst **A** or **B** gave the corresponding N-1 oxide derivatives **3** and **4** in 79% (72%) and 81% (79%) yields, respectively (FIG.1). Noteworthy, the reaction of N(9)-[4'-hydroxy-butan-1'-yl]adenine **5**, with DMDO in the presence of catalyst **A** afforded the C-8 oxo-derivative **6** in 51% yield as the only recovered product (FIG.1). The different regioselectivity observed in the oxidation of **5**, with respect to **1** and **2**, may be attributed to the presence of hydrogen bond interactions involving the polar groups present on the porphyrin ring of catalyst **A** (–OMe group) and the free OH group on the N-9 side chain of **5**. This hypothesis is further confirmed by the oxidation of **5** in the presence of catalyst **B**, which doesn't present polar groups for hydrogen bond interactions. In this case, only the N-1 oxide derivative **7** was obtained in 65% yield (FIG.1). This procedure may be a useful tool for the selective N-1 versus C-8 oxidation of purine derivatives.

FIG.1



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