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Study on the Total Synthesis of Hainanolide (V)—Oxidation of the Tricyclic Alkenes with Singlet Oxygen

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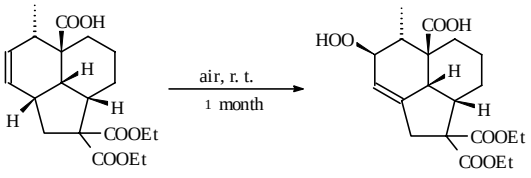
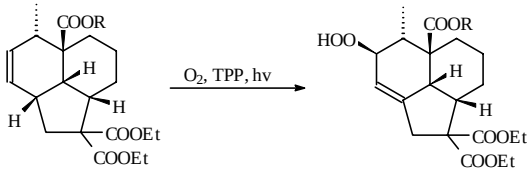
Abstract: Six tricyclic compounds containing C_3, C_4 double bonds were oxidized with singlet oxygen. Different regio-selectivity was found with regard to steric hinderence.

Keywords: Hainanolide, singlet oxygen.

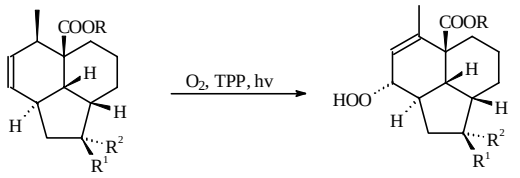
In the previous papers[1] we reported that from the mother liquid of recrystalizing exocycloadditive **1** from intramolecular Diels-Alder reaction (IMDA)[2] on exposure to air for a long period, a hydroperoxide **2** was isolated. This was explained as to be resulted from oxidation of the alkene by $^1O_2$ with subsequent rearrangement. Perceiving the hydroperoxide might serve as a valuable intermediate in the total synthesis of hainanolide, photochemical singlet oxygen oxidation, using *meso*-tetraphenylporphyrin (TPP) as sensitizing agent[3], of six unsaturated tricyclic compounds **1**, **3**, **5**, **7**, **9** and **11** were studied to support the above proposed mechanism.



1 **2**



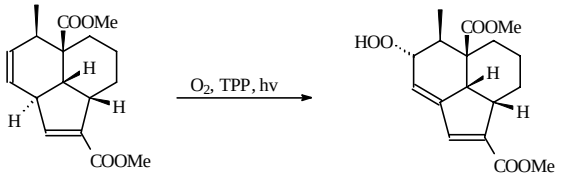
1 R = H **2** R = H (65%)
3 R = Me **4** R = Me (57%)



5 R = H, $R^1 = R^2$ = COOEt **6** R = H, $R^1 = R^2$ = COOEt (51%)

7 R = Me, $R^1 = R^2$ = COOEt **8** R = Me, $R^1 = R^2$ = COOEt (81%)

9 R = Me, R^1 = COOMe, R^2 = H **10** R = Me, R^1 = COOMe, R^2 = H (91%)



11 **12**

* The numerical value in the bracket is the yield obtained

The results obtained revealed that the singlet oxygen oxidation proceeds in an ene-like mood with the yield of 60-90%, following strict regio selectivity controlled by steric effect. The structures of products were determined by ^{1}HNMR.

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