

Unusual Reaction of 3-(2-Hydroxyphenyl)enaminoketones with Phenolic Mannich Bases

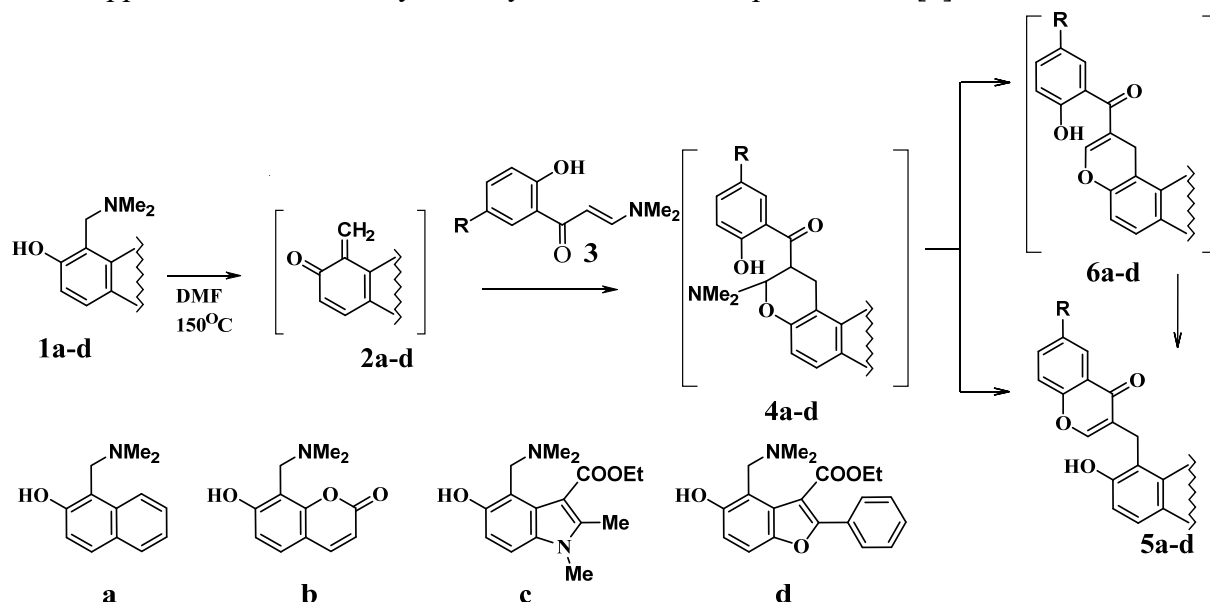
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Short-lived, highly reactive, *ortho*-quinone methide (*o*-QM) species are generated *in situ* by a large variety of synthetic methods. Such compounds are known to react with nucleophiles in 1,4-Michael-type fashion and with a range of electron-rich dienophiles to perform [4+2] cycloadditions. Inverse electron demand Diels-Alder reaction (iEDDA) represents an intriguing class of cycloaddition reaction which has attracted increasing attention for its applications in chemistry, total synthesis of natural products etc [1].



In our study, we suggest one-pot formation of chromone ring using [4+2] cycloaddition of 3-(2-hydroxyphenyl)enaminoketones **3** with *o*-QM thermally generated from 2-naphthol, 7-hydroxycoumarin, 5-hydroxybenzofuranes, and 5-hydroxyindoles. Thus, labile intermediate Diels-Alder adducts **4a-d** undergo deamination with formation of expected 9-(2-hydroxybenzoyl)-2H,9H-pyrano[2,3-f]chromen-2-ones **6a-d** and further intramolecular rearrangement to 8-(4-oxo-4H-chromen-3-yl)methyl phenols **5a-d**. However, intramolecular attack of phenolic group and further deamination in compounds **4a-d** could be alternative pathway for formation of compounds **5a-d**.

Structures of compounds **5a-d** were confirmed by HSQC and HMBC experiments and well as Michael addition of *o*-QM to chromones.

References

[1] Z. M. Png, H. Zeng, Q. Ye, J. Xu, *Chem. Asian. J.*, **2017**, *82*, 2142-2159.