Study of Diels-Alder reactions of purpurogallin tetra-acetate with various dienophiles †

Salima Dib [1, 2], Bachir Mostefa-Kara [1], Didier Villemin [2, *] and Nathalie Bar [2]

[1]Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculte des Sciences, Universite de Tlemcen, BP 119,13000 Tlemcen, Algeria
[2]Normandie Université France, ENSICAEN, LCMT, UMR CNRS 6507, INC3 M, FR 3038, Labex EMC3, LabexSynOrg, 6 Bd Maréchal Juin 14050 Caen, France

*Correspondence: didier.villemin@ensicaen.fr

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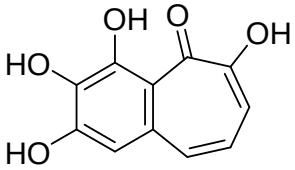
Study of Diels-Alder reactions of purpurogallin tetra-acetate with various dienophiles

The benzotropolones represent a class of natural products, which consists of a tropolone unit (hydroxycycloheptatrienone) fused to a benzene ring. The most popular is Purpurogallin (**1**) present in Quercus tree and displaying biological properties



Purpurogallin (**1**)

Figure 1. Structure of Purpurogallin

Purpurogallin (**1**) can yet be converted into purpurogallin tetra-acetate by peracetylation with acetic anhydride in the presence of DMAP as catalyst in a yield of 87 %.(Scheme1).

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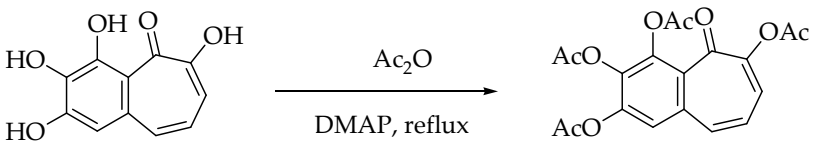
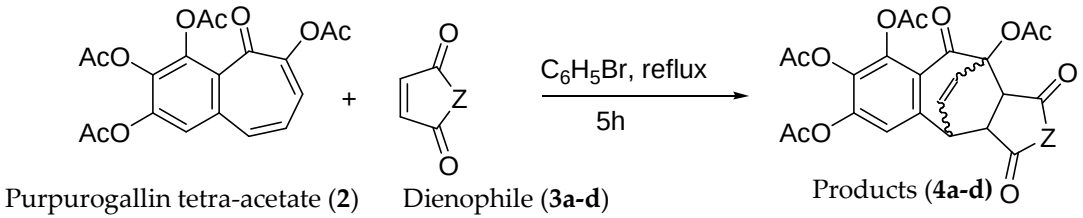


Purpurogallin (**1**) Purpurogallin tetra-acetate (**2**)

Scheme 1: acetylation of purpurogallin

Purpurogallin which possesses an antiaromatic tropolone nucleus is able to behave like a diene. So, we described herein the Diels–Alder reaction of Purpurogallin tetraacetate with different dienophiles in refluxing bromobenzene (154 ° C) according to the scheme 2.



Purpurogallin tetra-acetate (**2**) Dienophile (**3a-d**) Products (**4a-d**)

Z= NPh (**a**), NEt (**b**), O (**c**), CH=CH (**d**)

Scheme 2: Diels-Alder reactions between Purpurogallin tetraacetate and various dienophiles (3a-d).

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Entry	Dienophile	Product (3a-d)	Yield
a	N-phenylmaleimide	4a	39%
b	N-Ethylmaleimide	4b	36%
c	Maleic Anhydrid	4c	58%
d	Benzoquinone	4d	41%

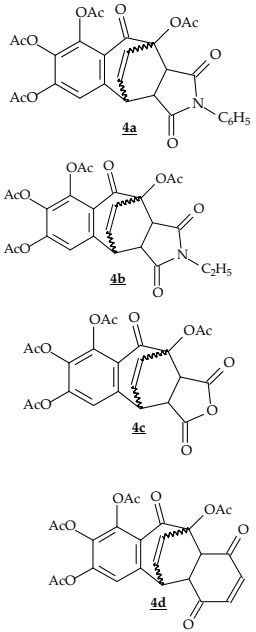

Table 1: Products of Diels-Alder reaction isolated

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Theoretical studies

The frontier orbitals of purpurogallin tetra-acetate **(2)** and dienophiles **(3a-d)** were calculated using the DFT-B3LYP with the 6-31G(d) basis set in vacuum and then in bromobenzene (dielectric constant ε = 5.4) using Continuum Solvation Models, SM8 and are reported in the **Table 2**.

Table 2: Frontier orbitales calculated

Product	HOMO (eV)	LUMO (eV)	μ debye
	In bromobenzene		
Purpurogallin (1)	-5.59	-1.86	3.36
Tetraacetylpurpurogallin	-6.10	-1.69	12.84
Tetramethylpurpurogallin	-5.65	-1.48	2.88
Maleic anhydride 3c	-7.99	-2.88	4.15
N-Phenyl maleimide 3a	-6.46	-2.50	1.31
N-Ethyl maleimide 3b	-7.27	-2.33	0.85
Benzoquinone 3d	-7.11	-3.22	0

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From the position of the frontier orbitals, i.e difference between $HOMO^d$ and $LUMO^a$ and difference between $HOMO^a$ and $LUMO^d$, the most probable Diels-Alder reaction appears as normal demand with a transfer of electrons from the purpurogallin tetraacetate or tetramethyl purpurogallin as donor to acceptor dienophile in the 4 cases studied. In the case of non-benzenoid aromatic compounds like purpurogallin or tetraacetate purpurogallin, the antiaromaticity leads to normal-electron-demand Diels-Alder reactions.

Conclusions:

- Tetraacetylpurpurogallin leads to reaction of Diels-Alder with cyclic dienophiles in moderate yield under thermal activation.
- The reactions of purpurogallin tetraacetate **2** with the different dienophiles **3a-d** correspond at a Normal Electron Demand (NED) Diels-alder reactions.