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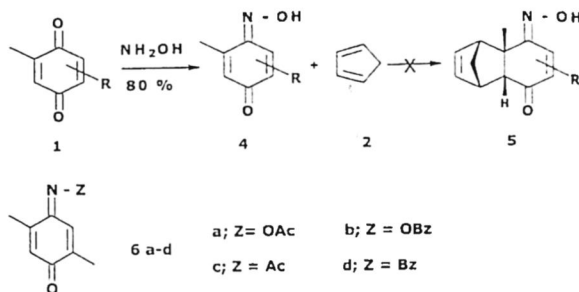
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Key words: Diels-Alder, quinone imines,

The Diels-Alder reactions of *para*-benzoquinones **1** and cyclopentadiene (**2**) are very well known, furnishing cycloadducts in excellent yields. On the other hand, the cycloadditions of the corresponding mono-oximes **4** with cyclopentadiene (**2**) are not effective, leading to recovery of the dienophile **4**. The proposed cycloadducts **5** should be useful intermediates in terpene and alkaloid synthesis.

We have investigated this complete reversal in reactivity by calculations on the energy differences of the cyclopentadiene HOMO orbital and the two series of dienophiles LUMO orbital. This study also allows us to predict nitrogen derivatives with potential reactivity as substitutes for the oximes, such as oxime acetate, **a**), oxime benzoate (**b**), *N*-acetyl quinone imine (**c**) and *N*-benzoyl quinone imine (**d**) of 2,5-dimethyl *para*-benzoquinone. The calculations may explain the total lack of reactivity of the quinone oximes **4** and suggest that success may be obtained with the quinone imine derivatives **6 c** and **d**.



FAPESP, CNPq and CAPES

Synthesis of the tetracyclic nucleus of *epi*-Sarcophytin, and evaluation of its phytotoxic activity

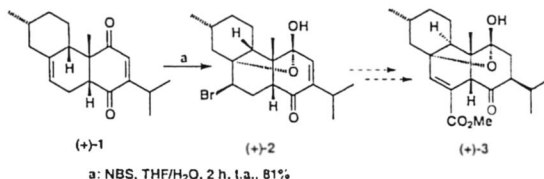
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Key words: Sarcophytin, Diels-Alder, Phytotoxic.

We have been investigating the synthesis of (+)-Sarcophytin (**3**) and correlated compounds, and also studying their possible phytotoxic activity. For the synthesis of the tetracyclic nucleus of the C-1-epimer of (+)-**3**, we chose the halocyclization reaction (NBS in THF/H₂O) of Diels-Alder cycloadduct (+)-**1**, producing compound (+)-**2** in 81% yield. Thus (+)-**2** can now be obtained in six steps from the cheap chiron (R)-(+)-pulegone in 24% overall yield. Compound (+)-**2** has 19 of the 20 carbon atoms, and five of the seven stereogenic centers of natural (+)-sarcophytin (**3**). The phytotoxic activity of (+)-**2** and other compounds synthesized here, was determined in Petri plates and greenhouse tests, using cucumber (*Cucumis sativus*), radish (*Raphanus sativus*) and sorghum (*Sorghum bicolor*) as test plants. The best results were obtained for (+)-**2**, with an inhibition of 70% on the aerial system and 76% on the root system of *S. bicolor* species (at 6µg.mL⁻¹ loading). The high inhibition values for analogues of (+)-**2** are related to the presence of the five-membered cyclic ether moiety. Computational chemistry calculations demonstrate that the cyclic ether strongly changes the three-dimensional structure of the molecules, thus resulting in increased electronegative potential.



a: NBS, THF/H₂O, 2 h, i.a., 81%

Acknowledgments: FAPESP, CNPq and CAPES.

The Regioselectivity of the Diels-Alder Reaction of 1-*t*-Butyldimethyl-Silyloxy-Pentadiene-1,3 with *para*-Benzoquinones

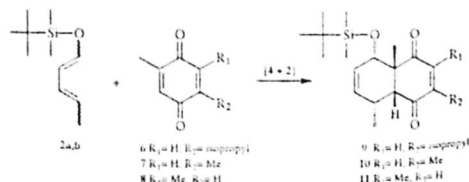
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Key words: Diels-Alder, *para*-Benzoquinones, 1-*t*-Butyldimethyl-Silyloxy-Pentadiene-1,3.

We have studied the Diels-Alder reaction between 1-*t*-butyldimethyl-silyloxy-pentadiene-1,3 (**2**) and the *para*-benzoquinones **6**, **7** and **8**, with regard to efficiency and regioselectivity. *Trans*-2-pentenal was converted into the diene **2**, as 2:1 mixture in 84% yield. The *para*-benzoquinones: **6**, **7** e **8** were obtained in excellent yields by oxidation of the respective phenols.



6 R₁ = H, R₂ = *tert*-butyl
7 R₁ = H, R₂ = Me
8 R₁ = Me, R₂ = H
9 R₁ = H, R₂ = *tert*-butyl
10 R₁ = H, R₂ = Me
11 R₁ = Me, R₂ = H

The cycloaddition reactions of the mixture of **2a** and **2b** with **6**, **7** and **8** under both catalytic (ZnCl₂) and thermal conditions furnished **9**, **10** and **11** as major products in very good yields, thus delineating the regioselectivity.

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