

Para-benzoquinone *N*-tosylimines in Diels-Alder reactions with cyclopentadiene and 2,3-dimethyl-1,3-butadiene.

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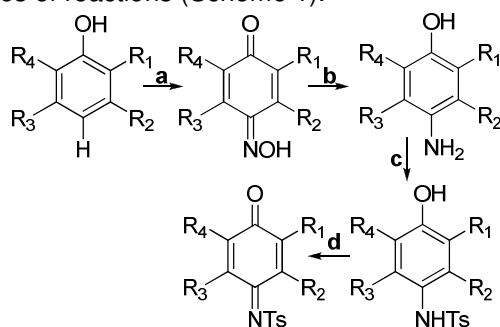
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INTRODUCTION

The Diels-Alder reaction ^{1,2} is of great utility for the synthesis of intermediates for bioactive natural products.³ We present recent results on the reactivity of *para*-benzoquinone *N*-tosylimines as dienophiles with two simple dienes.

RESULTS AND DISCUSSION

The *para*-benzoquinone *N*-tosylimines **1a-e** are obtained from the respective phenols by a simple series of reactions (Scheme 1).

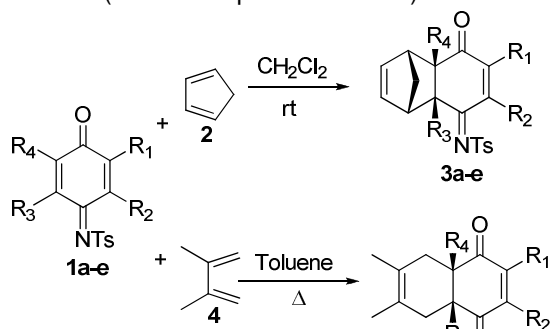


Condições:

a) NaNO₂, HCl, EtOH, 2h. b) SnCl₂, HCl, CH₂Cl₂, 16h.
c) TsCl, Py, 5h d) Ag₂O/AgO, CH₂Cl₂, 1h.

Scheme 1

The Diels-Alder reactions with cyclopentadiene (**2**) and 2,3-dimethyl-1,3-butadiene (**4**) furnish cycloadducts **3** and **5** respectively, as shown in Scheme 2. (ratio dienophile:diene 1:2).



1a R₁=Me R₂=H R₃=Me R₄=H
1b R₁=H R₂=Me R₃=Me R₄=H
1c R₁=*i*-Pr R₂=H R₃=Me R₄=H
1d R₁=Me R₂=H R₃=*i*-Pr R₄=H
1e R₁=Me R₂=H R₃=H R₄=Me

Scheme 2

Table 1. Diels-Alder reactions.

Dienophile	Diene	Condition	Yield (%)
1a	2	A	61
1b	2	A	56
1c	2	A	34
1d	2	A	44
1e	2	A	54
1a	2	B	67
1b	2	B	71
1c	2	B	40
1d	2	B	50
1e	2	B	62
1a	2	C	73
1b	2	C	74
1c	2	C	45
1d	2	C	60
1e	2	C	70
1a	4	D	15
1b	4	D	68
1c	4	D	-

A: rt, 24h; B: rt, 48h. C: rt 72h; D: reflux 21h.

As expected, cyclopentadiene reacts much more efficiently than diene **4**, which requires reflux in toluene. We are presently optimizing these reactions, and testing the use of microwave irradiation.

CONCLUSION

Cyclopentadiene reacts easily at room temperature with the *N*-tosylimines, whereas diene **4** requires reflux in toluene.

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