C. R. Chimie 17 (2014) 1075–1079

Contents lists available at ScienceDirect

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Preliminary communication/Communication

ortho-Quinodimethane from anthracene epidioxide: Scope of the Diels–Alder reaction and mild preparation of naphthalene derivatives

ortho-*Quinodiméthane par thermolyse de l'épidioxyde d'anthracène : réaction de Diels–Alder et préparation douce de dérivés naphtaléniques*

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ARTICLE INFO

Article history:
Received 12 November 2013
Accepted after revision 28 January 2014
Available online 23 October 2014

Keywords:
ortho-Quinodimethane
Cycloaddition
Elimination

Mots clés :
ortho-Quinodiméthane
Cycloaddition
Élimination

ABSTRACT

The thermal isomerisation of anthracene epidioxide **3** has been known to give phenylenedioxy-*ortho*-quinodimethane **5** as a reactive transient. We presented herein the scope of the Diels–Alder reaction of this transient **5** with some dienophiles. In addition, a mild synthesis of naphthalene derivatives has been developed via base-induced cleavage of the obtained Diels–Alder adducts.

RÉSUMÉ

L'isomérisation thermique de l'épidioxyde de l'anthracène avait été décrite pour donner l'intermédiaire réactif **5** phénylènedioxy-*ortho*-quinodiméthane. Nous présentons les limitations de sa réaction de Diels–Alder avec quelques diénophiles. En complément, nous décrivons une synthèse simple de dérivés naphtaléniques par coupure basique des adduits obtenus.

1. Introduction

Ortho-quinodimethanes are reactive species that are not isolable, but have been suspected as transients in 1959 by Cava et al. [1]. They were originally obtained by the double elimination of α,α'-dibromo-*ortho*-xylenes [1] or by thermal opening of the corresponding benzocyclobutenes [2,3], and several reviews emphasised the importance of these transients as tools for the synthesis of cyclic organic compounds [4–9]. An interesting reaction was the direct formation of the naphthalene derivatives **2** by Diels–Alder reaction with dibromo-*ortho*-xylylene **1** (generated from tetrabromoxylene) with spontaneous loss of HBr [1,10,11] (Scheme 1).

An early study, presented in Scheme 2, showed that the thermal isomerisation of anthracene endoperoxide **3** led to *ortho*-quinodimethane **5** through diepoxide **4** and finally to two successive dimers of **5**, an original [8π+6π] one and the normal [8π+2π] one [12a]. Both isomeric transients **4** and **5** could be trapped with maleic anhydride (**6a**) or

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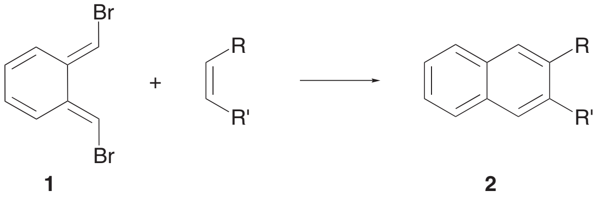
http://dx.doi.org/10.1016/j.crci.2014.01.024



Scheme 1.

N-methylmaleimide (**6b**) to give the isolated *endo* adducts **7b** and **8a,b**, respectively [12b]. From these latter adducts, a base-catalysed or thermal aromatisation into the corresponding naphthalene compounds **9a** and **9b** has been observed, with the release of catechol as a by-product [12b].

This synthesis of naphthalene compounds used only thermal and base-induced transformations and was also suitable to synthetize acid-sensitive compounds. The use of this *ortho*-quinodimethane **5** in organic synthesis has never been studied, although the latter was very easy to obtain from the cheap anthracene. The purpose of this work was to investigate the scope of this Diels–Alder reaction and the further formation of naphthalene derivatives.

2. Results and discussion

2.1. Case of reactive dienophiles

The addition of *N*-methylmaleimide **6a** or maleic anhydride **6b** has already been studied in the initial study of the thermal isomerisation of anthracene epidioxide **3** in refluxing benzene. The corresponding adducts **7b** (10%) and **8a,b** (70–76%) have been isolated along with minute amounts of anthraquinone [12b].

In the present work (Scheme 3), the thermal isomerisation of epidioxide **3** was performed at higher temperature in order to favour the reaction with *ortho*-quinodimethane **5**, i.e. in refluxing chlorobenzene (ca. 132 °C) for 1 h in the presence of a dienophile in slight excess (ca 1.2 equiv.).

Using 1,4-benzoquinone **10a**, 1,4-naphthoquinone **10b** or *trans*-dibenzoylethylene **11** as dienophiles, adducts **14a**, **14b** or **15**, respectively, were isolated in good yields (60–70%).

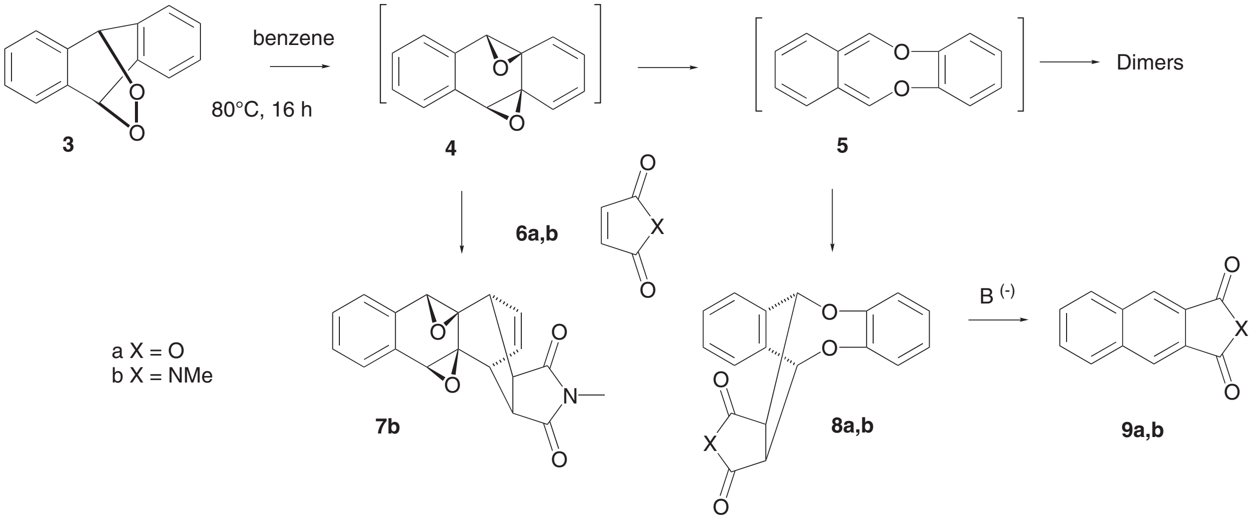
In the particular case of benzoquinone **10a**, a double addition was observed when epidioxide **3** was used in two-fold excess. However, the adduct could not be isolated as a pure compound and was treated directly with a base (see below).

2.2. Case of less reactive dienophiles

Cyclohex-2-en-1-one, cyclohexene, and coumarin were unreactive and dimers of **5** were only observed. In the case of the cyclopentenone **12**, the adduct **16** was isolated in poor yield (20–30%) and required to heat under refluxing benzene for 16 h with an 8-fold excess of the dienophile (Scheme 3). An inactivated double bond or a double bond activated by only one carbonyl function was also too less reactive for this Diels–Alder reaction to compete with dimerization. The more reactive 5-membered ring **12** gave only poorly the desired adduct.

2.3. Structure of the adducts

In all cases, we obtained a single adduct. Adduct **15** possessed the benzoyl groups in *trans* relation, as indicated by the important coupling between the protons in α-position to the carbonyl functions ($J = 8$ Hz). We assumed that adducts **14a,b** and **16** possessed an *endo*-configuration (see Scheme 3) as it has already been demonstrated for **8b** [12b]. This was confirmed in ^{1}H NMR spectra of **14a** and **14b** by the clear deshielding of the protons H-α in α-position to the carbonyl groups (δ 4.40 and 4.05 ppm, respectively) in comparison to the corresponding protons



Scheme 2.