Syntheses of and photochemical studies of 2,3-disubstituted 1,4-epoxy-1,4-dihydronaphthalenes

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A method for synthesis of 3-methyl-1,4-epoxy-1,4-dihydronaphthalene-2-carboxylic acid and 3-methyl-1,4-epoxy-1,4-dihydronaphthalene-2-carbonitrile was developed starting from 1,4-epoxy-1,4-dihydronaphthalene; direct photolysis of 3-methyl-1,4-epoxy-1,4-dihydronaphthalene-2-carbonitrile and methyl 3-methyl-1,4-epoxy-1,4-dihydronaphthalene-2-carboxylate in benzene gave indene derivatives.

Keywords: 2,3-disubstituted 1,4-epoxy-1,4-dihydronaphthalenes, naphthol derivative, indene derivatives, photolysis

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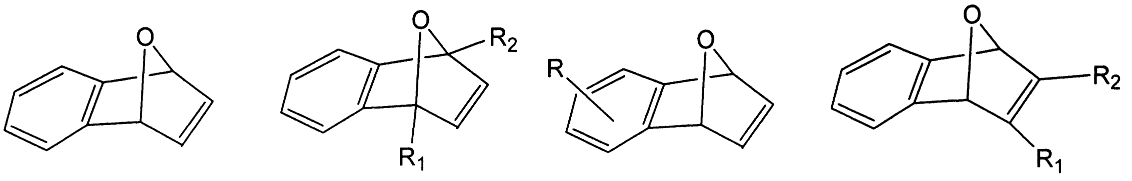
1,4-epoxy-1,4-dihydronaphthalene **1** is of great synthetic interest because of its ready conversion into other types of compounds. For example 1,4-epoxy-1,4-dihydronaphthalene **1** and its derivatives have been used as starting materials to generate enantiomerically enriched hydronaphthalene products[4a,b] and to synthesise benzocoumarins[4c] biaryls[4d] and precursors of isobenzofuran.[4e] Lautens and Rovis[5] achieved a concise stereoselective synthesis of an important antidepressant sertraline using 1,4-epoxy-1,4-dihydronaphthalene as a starting material. Wolthuis[6] and coworkers investigated the reactions of different derivatives of 1,4-epoxy-1,4-dihydronaphthalene with HCl in MeOH, and showed the formation of naphthol derivatives. Franck and Yanagi[7] described the synthesis of 1,4-di-*t*-butylnaphthalene derivatives by a similar method. Zeigler showed the conversion of 1,4-epoxy-1,4-dihydronaphthalenes into benz[*f*]oxepines by direct photolysis.[3c]

It is well established that the preparation of 1,4-epoxy or aryl substituted 1,4-epoxy-1,4-dihydronaphthalene derivatives, **2** and **3**, requires a few steps whereas 2,3-disubstituted ones **4** do not as is evident from their retro analyses.

Herein we report an efficient and convenient preparation of compounds **4** with a benzofuran skeleton. We also discuss the photolysis of derivatives of **4**.

Our synthetic approach includes the use of 1,4-epoxy-1,4-dihydronaphthalene **1** as a starting material. Balci[8a] *et al.* recently reported that high-temperature bromination of **1** followed by elimination gave **4a** and that repetition of the procedure afforded 2,3-dibromo-1,4-epoxy-1,4-dihydronaphthalene (**4b**) (Scheme 1).

We prepared the disubstituted 3-methyl-2-carboxylic acid **4d** and 3-methyl-2-carbonitrile **4e** derivatives of 1,4-epoxy-1,4-dihydronaphthalene from the dibromide **4b**. For this, we prepared the dibromide **4b**[8a] as described in the literature from 1,4-epoxy-1,4-dihydronaphthalene and then disubstituted derivatives following the literature procedure.[8b] At first we set out to determine if **4b** could be mono metalated. Treatment of the dibromide **4b** with slightly more than a molar equivalent of *t*-butyllithium at –78°C followed by methyl iodide addition produced the bromo-methyl derivative **4c**. By a similar sequence the other bromide was substituted to give methyl-

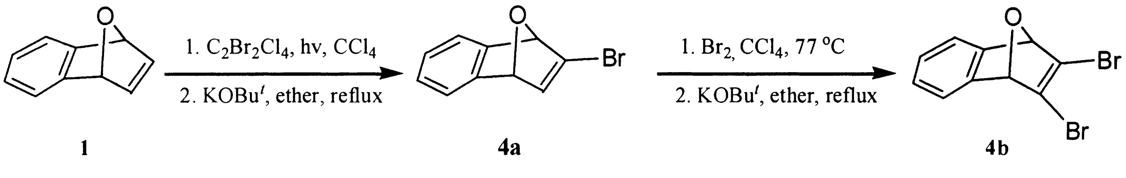


1 **2** **3** **4**

4a; R_1= H, R_2= Br, **4b**; R_1= R_2= Br; **4c**, R_1= CH_3, R_2= Br

4d; R_1= CH_3, R_2= COOH, **4e**; R_1= CH_3, R_2= CN, **4f**; R_1= CH_3, R_2= COOMe

Fig.1



Scheme 1

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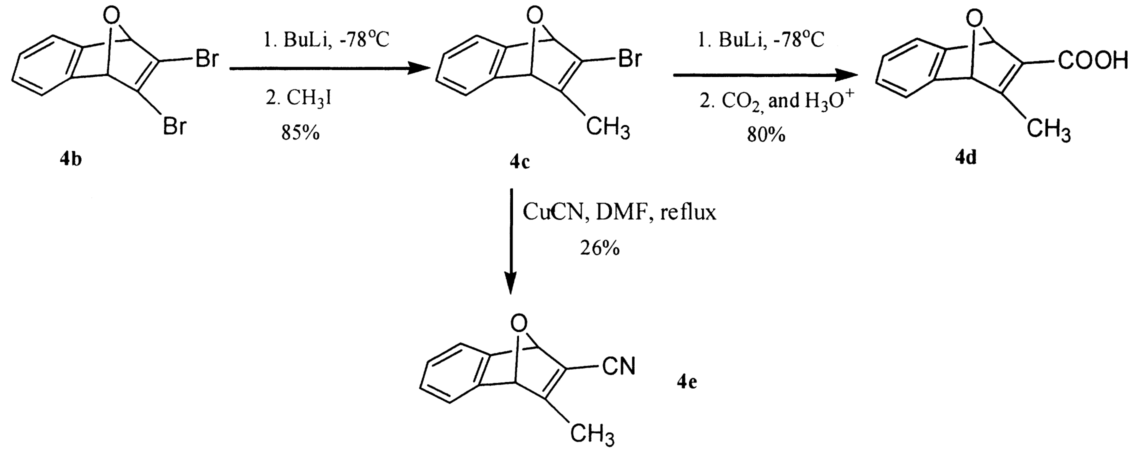
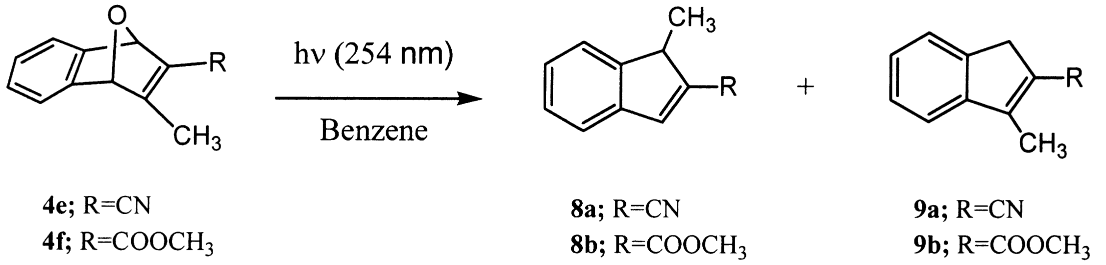


Scheme 2



Scheme 5

carboxylic acid **4d**. On the other hand, allowing **4c** to react with cuprous cyanide in DMF at reflux temperature for 72 h gave substitution product **4e** (Scheme 2). The structures of **4d** and **4e** were determined on the basis of ^{1}H- and ^{13}C-NMR data, which were straightforward.

Ziegler[3c] reported the photorearrangement of 1-mono or 1,4-disubstituted-1,4-epoxy-1,4-dihydronaphthalenes to benz[*f*]oxepins by direct photolysis at 254 nm. Again, Prinzbach[10] *et al.* showed that 7-azabenzonorbornadienes might isomerise to 3-benzazepines upon direct photoexcitation at 240 nm. In our previous studies, we investigated the photochemistry of bicyclic systems involving heteroatoms which showed no surprising results[11]. Expecting the formation of benz[*f*]oxepin derivatives and following the literature we carried out direct photolysis of **4e** and **4f** at 254 nm. Repeated experiments surprisingly showed the formation of indene derivatives **8** and **9** instead of benz[*f*]oxepins probably by decarbonylation (Scheme 5).

We identified the mixture of **8b**[12a,b] and **9b**[12a,c] by comparison of ^{1}H-NMR spectra with the literature data.

In conclusion, in this paper we have presented an easy way to prepare 2,3-disubstituted 1,4-epoxy-1,4-dihydronaphthalene derivatives. We showed that 3-methyl-1,4-epoxy-1,4-dihydronaphthalene-2-carboxylic acid (**4d**) is very sensitive to acidic reaction conditions and gives a naphthol and 1,4-addition products. Direct photolysis of these disubstituted derivatives surprisingly results in the formation of disubstituted indenes.

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Techniques used: 1H and 13C-NMR, IR, Mass Spectrometry

References: 12

Schemes: 5

Table: 1

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