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Tetrahydronaphthalene-1,4-dione and its Chromiumtricarbonyl Complex

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§SCS Poster Prize Winner

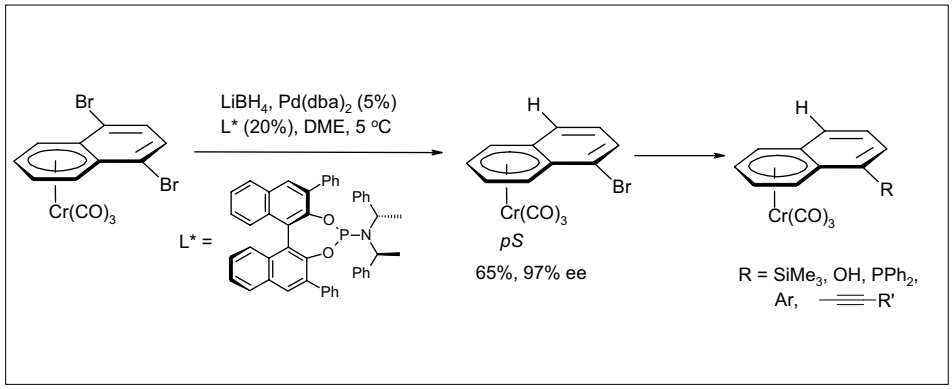
Abstract: The article gives a brief outline of the rediscovery of tetrahydronaphthalene-1,4-dione, a stable tautomer which has been known for over half a century but has not been applied in synthesis. Desymmetrization is readily achieved *via* enantioselective reduction. Synthetic potential apart, the dione and its chromiumtricarbonyl complex are of theoretical interest. Thus, whereas dihydroxynaphthalene requires quite harsh conditions and leads to a 1:1 mixture of the two tautomers, the chromiumtricarbonyl complex of dihydroxynaphthalene tautomerizes under very mild conditions to the tetrahydronaphthalene-1,4-dione complex. An earlier literature report showed that in trifluoroacetic acid, the dione tautomer is present exclusively. This has now been used to isolate multigram quantities of the compound.

Keywords: Arene complex · Asymmetric catalysis · Chromium · Ketone-enol tautomerism · Naphthoquinone

Arenes readily form π-complexes with a variety of transition metal complex fragments and the metal-coordinated arenes show a rich and varied chemistry.[1] The metal adds a third dimension to the planar aromatic compounds and the two faces of an arene with different *ortho*- or *meta*-substituents are enantiotopic. Coordination of a metal to an arene thus not only alters the reactivity of ring carbons and substituents, but in addition also gives access to highly stereoselective reactions. Of all arene complexes, those incorporating the electrophilic $Cr(CO)_3$ group have been most extensively studied, and their use in organic synthesis and as chiral ligands is well established.[1,2] In contrast, the analogous complexes of naphthalenes (or those of other extended aromatics) have received much less attention, primarily as a result of the lability of the metal–arene bond in this class of compounds.[3] This arises from a weaker but also far more labile metal arene bond. Easy haptotropic slippage of the naphthalene ligand (change from η^6 to η^4 or η^2-coordination) facilitates arene dissociation and results in a dramatic increase in sensitivity towards air and Lewis basic solvents or reagents.[4] The lability has been put to good use: [$Cr(CO)_3$(η^6-naphthalene)], in the presence of THF, is an efficient source of the $Cr(CO)_3$ fragment, either as a stoichiometric reagent in synthesis of more robust [$Cr(\eta^6$-arene)(CO_3)] complexes[5] or as a catalyst for diene hydrogenation.[6]

We recently initiated a project aimed at the synthesis of planar chiral naphthalene complexes for applications as chirons in synthesis, as chiral $Cr(CO)_3$ transfer agents, and, after further modification, as chiral ligands. The route that we chose is the desymmetrization of *meso*-naphthalene complexes. As a first successful example, Scheme 1 shows the enantioselective hydrogenolysis of [$Cr(CO)_3$(5,8-dibromonaphthalene] and its derivatization.[7]

In the context of these studies we also prepared the naphthoquinone complex **1** *via* hydrolysis/oxidation of the bis-trifluoroacetate naphthalene complex, which, in turn, was obtained using [$Cr(CO)_3(NH_3)_3$]/$BF_3.OEt_2$ as $Cr(CO)_3$ transfer agent.[8] The purple air-stable naphthoquinone complex



Scheme 1. Asymmetric catalytic hydrogenolysis to access highly enantiomerically enriched naphthalene complexes

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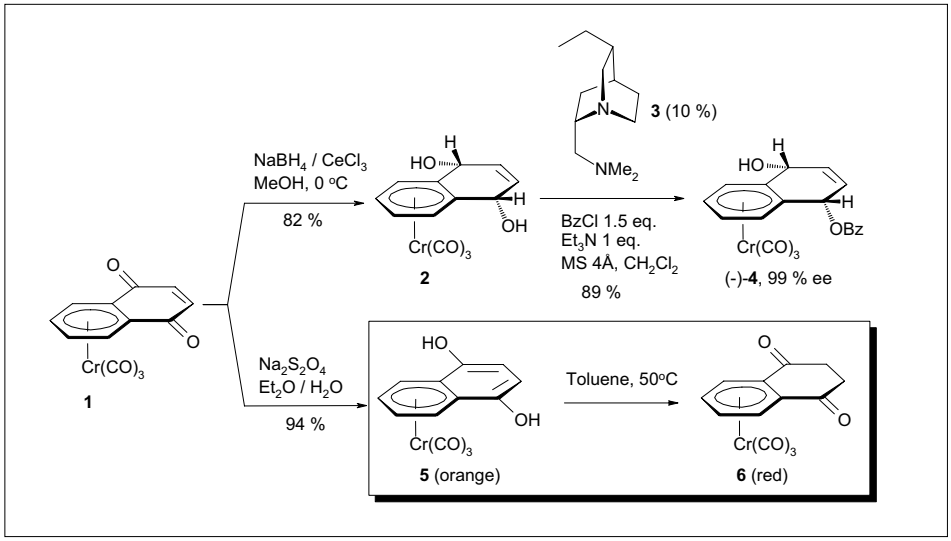


Scheme 2. Synthetic potential of naphthoquinone complex **1**

1 could be reduced under Luche conditions to the *cis*-diol **2** (Scheme 2). Desymmetrization of **2** was achieved *via* acetyl transfer using new readily available cinchona alkaloid-derived chiral diamine catalysts such as **3**[8c]. This afforded the mono-benzoate **4** in excellent yield and enantioselectivity. Reduction of **1** with sodium dithionite yielded cleanly the dihydroxynaphthalene complex **5**. The synthetic potential of the naphthoquinone complex, of the chiral complex **4** and the scope and limitations of the new diamine acyl transfer catalyst are presently under study.

Complex **5** is only slightly soluble in toluene. To our surprise, upon heating to 50 °C, the solution changed color from orange to deep red. This could not be due to the well-established arene exchange of naphthalene complexes because the expected product, $[Cr(CO)_3(toluene)]$, is yellow. The color turned out to be that of the tautomer **6**.[9]

A literature search revealed that this is not an exclusivity of the $Cr(CO)_3$ complex. Tetrahydronaphthalene-1,4-dione (**8**) has been computed to be 10.2 kcal/mol less stable than its tautomer 1,4-dihydroxynaphthalene (**7**).[10] However preliminary results of calculations taking into account solvent effects show that the tautomeric equilibrium is strongly influenced by the polarity of the solvent.[11] Tetralindione **8** has been known in the literature for many years. Thomson isolated **8** in 10.5% yield from a mixture with **7** following fusion,[12] and Pearson *et al.* showed that melting **7** under vacuum generates a 2:1 equilibrium (1 h, 200 °C) with its tautomer **8**.[13] The conversion of **1** into **2** can also be effected in neat CF_3COOH.[14] The dione **8** has also been obtained by hydrogenation of naphthoquinone with Wilkinson's catalyst[15] and very recently by benzylic oxidation of tetrahydronaphthalene-I-one catalyzed by $Rh_2(cap)_4$.[16]

The dione is kinetically stable at RT but rapidly converts to the phenolic form in the presence of base. The keto-form is implicated in the acid-catalyzed monoalkylation of **7**[14] but, surprisingly, to our knowledge, no chemistry of isolated **8** has ever been reported.

Tautomerization of **7** to **8** in trifluoroacetic acid as reported by Laatsch,[14] followed by addition of toluene, rapid solvent removal and crystallization from diisopropylether gave **8** in 72% yield.[9e] This can be carried out conveniently on a 10 g scale.

Dihydroxynaphthalene tautomerizes slowly in solution. A *ca.* 1:1 equilibrium is reached after more than 20 days upon heating a sample in benzene at 120 °C in a sealed NMR tube. This compares to the 90% conversion of complex **5** to **6** upon heating at 50 °C for 20 h (Scheme 3 and Fig.). Kinetic and computational studies are underway to rationalize these observations.

Dione **8** is an attractive starting material for synthesis as shown by the series of transformations in Scheme 4. This chemistry is currently being extended and applied in our laboratory.

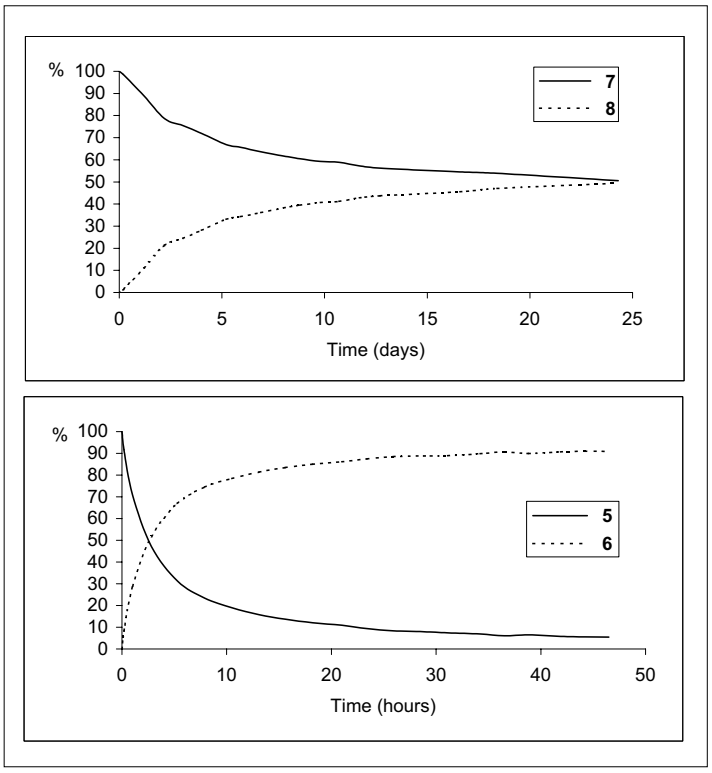
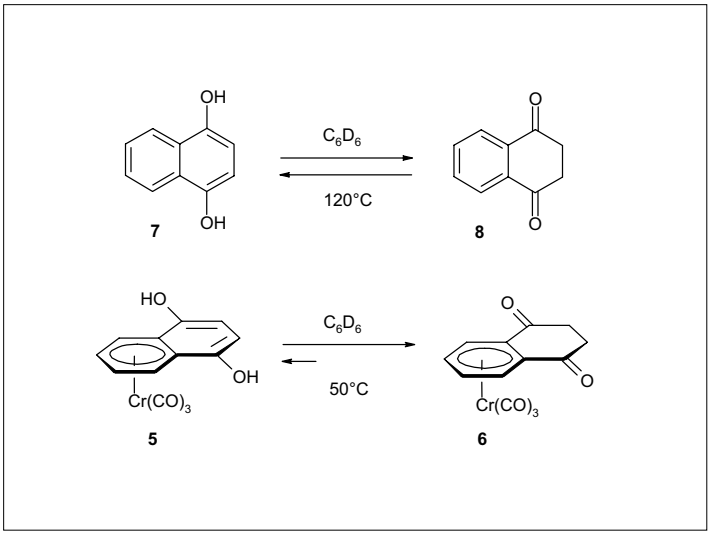
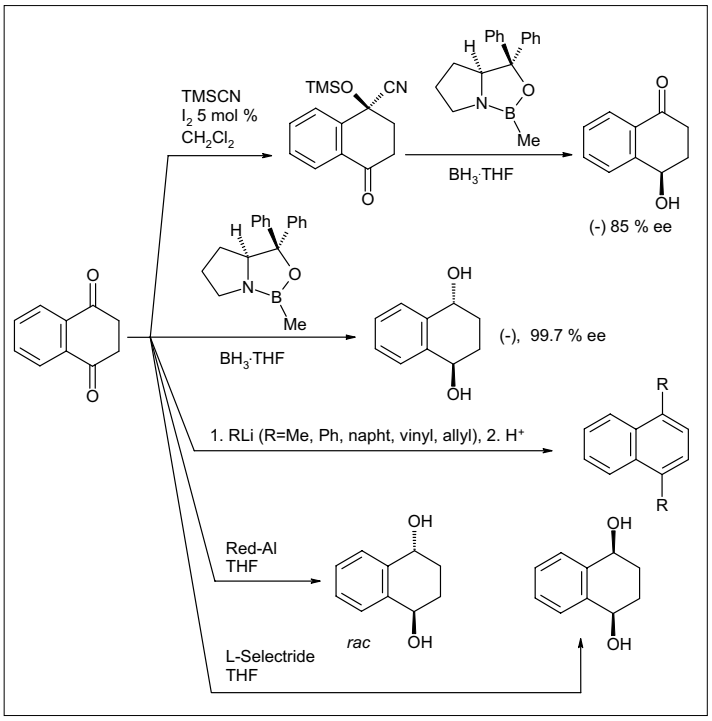


Fig. Rate and equilibria in the tautomerization of **5** (at 50 °C) and **7** (at 120 °C) (NMR ratios)



Scheme 3. Influence of the chromium fragment on the tautomerization of **7** and **8**



Scheme 4. Some transformations of dione **8**

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