Modified Synthesis of Nonsubstituted Quinoline Oligomers

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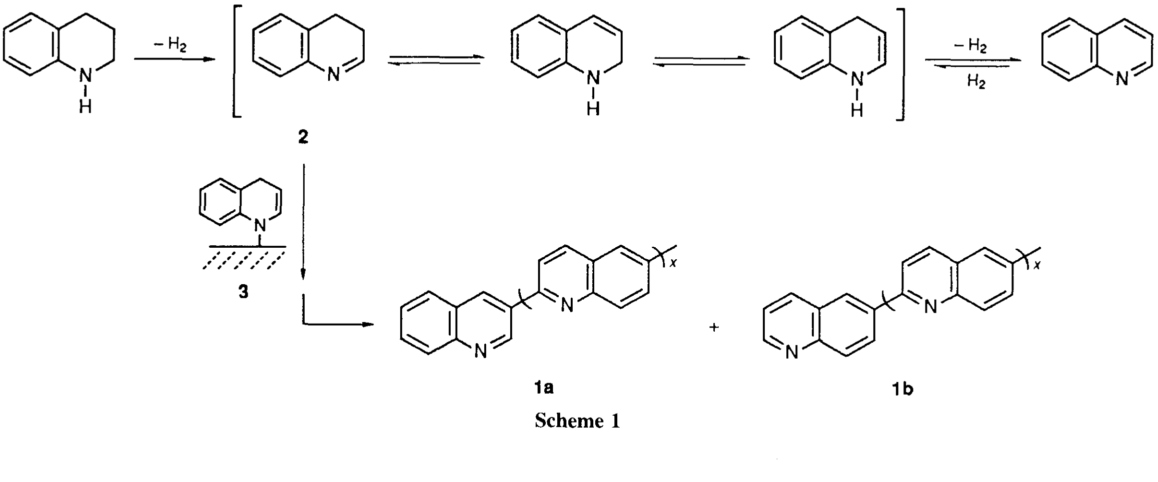
Quinoline oligomers have been synthesized by the catalytic dehydrogenative co-oligomerization of 1,2,3,4-tetrahydroquinoline (THQ) and quinoline, with a THQ/quinoline ratio >0.06, at 270 °C in a high yield using ruthenium sulphide as a catalyst.

Recently we reported the new process of catalytic dehydrogenative polycondensation (CDHP) for the synthesis of linear aromatic heterocyclic oligomers utilizing rhenium sulphides as catalysts[1–4] and the use of resulting products in the fabrication of highly conducting carbon thin films.[5,6] The reaction resulted in a catalytic conversion of 1,2,3,4-tetrahydroquinoline (THQ) directly to nonsubstituted quinoline oligomers **1a** and **1b**. A three-step reaction mechanism was proposed to account for this reaction involving dehydrogenation of THQ, oligomerization of 3,4-dihydroquinoline **2**, and aromatization of partially hydrogenated quinoline oligomers in sequence.[7] A simplified view of the CDHP surface reaction is depicted in Scheme 1. Owing to the high hydrogen donating capability of THQ at 270 °C under catalytic conditions on the rhenium sulphide surface, both the fast dehydrogenation of THQ early in the reaction and the quinoline–dihydroquinolines equilibrium favours quinoline. That allowed us to detect quinoline as an intermediate during a kinetic study of reaction. The slow consumption of quinoline later in the reaction can be correlated with a shift of equilibrium by the irreversible oligomerization of 3,4-dihydroquinoline, which is initiated by the surface-chemisorbed 1,4-dihydroquinoline **3**. Therefore, in principle, we can replace most of the THQ molecules by the commercially low cost quinoline in this reaction to produce quinoline oligomers without altering the efficiency of oligomerization. That prompted us to reinvestigate the CDHP reaction of THQ incorporating quinoline as a co-monomer.

It should be noted that quinoline itself cannot be polymerized in the presence of rhenium sulphide catalysts at 270 °C. An attempt to generate dihydroquinolines *in situ* from quinoline with the same catalysts under a hydrogen pressure of 50 psi followed by the polymerization of the resulting dihydroquinolines gave only a low yield of hydrogenated oligomeric materials with recovery of the unreacted quinoline. No significant amount of quinoline oligomers was obtained in



Scheme 1

Table 1 The catalytic dehydrogenative oligomerization reactivity of ruthenium sulphide using a 1,2,3,4-tetrahydroquinoline and quinoline mixture as co-monomers.

	Yield (%)		
THQ/Quinoline	QO[a]	HQO	Quinoline
1.0	92.0 (57.0)[a]	6.0	<0.5
0.25	94.0 (48.5)	6.0	<0.5
0.12	90.0 (53.0)	9.5	<0.5
0.06	87.0 (45.5)	11.0	1.0
0.03	7.0 (1.5)	1.0	89.5
0.015	5.5 (1.0)	0.0	94.0

[a] In parentheses, proportion (%) of $CHCl_3$-insoluble product in QO product

this reaction. Apparently, a reductive transformation of the catalyst itself from a high oxidation state of the metal to a lower one by reaction with THQ is necessary to activate the catalyst surface for polymerization. During the transformation a proportional amount of THQ was oxidized to quinoline. The activated transition metal sulphide is capable of hydrogenating quinoline to dihydroquinoline intermediates if a sufficient quantity of hydrogen is present. Thus to provide the hydrogen source and to facilitate the catalyst activation simultaneously, the presence of THQ molecules is critical for the initiation of quinoline oligomerization. Mechanistically, at the beginning of reaction, THQ molecules activate the catalyst, initiate the oligomerization and generate hydrogen on the catalyst surface. The hydrogen is then utilized for the hydrogenation of quinoline to dihydroquinolines ready for oligomerization. Meanwhile, the aromatization of oligomeric intermediates to products of quinoline oligomers regenerates hydrogen back to surface. The cycle of hydrogenation–dehydrogenation continues until the completion of reaction. This chemistry was substantiated by the study of the copolymerization of THQ and quinoline in a variable ratio and the results are summarized in Table 1.

The catalyst precursor used in the present study was synthesized by the reaction of ammonium hexachlororuthenate, $(NH_4)_2RuCl_6$ with 3.5 equiv. of lithium sulphide in ethanol at ambient temperature to afford black ruthenium sulphides in a chemical composition close to $(NH_4)_{1.5}Li_{0.5}RuS_{1.6}Cl_{1.8}$ in a nearly quantitative yield. The thermal chemistry involved in the conversion of this precursor to the active ruthenium sulphides resembles that described for rhenium sulphides.[3,4] To minimize the amount of THQ required for co-oligomerization as well as to prevent the substantial discharge of hydrogen from the surface and the reaction vessel during the reaction, a pressure-adjustable reaction system was used. The oligomerization was carried out with a mixture of THQ and quinoline in an appropriate ratio and a finely divided ruthenium sulphide catalyst precursor (3% by wt.) at 210 °C for 4 h then at 270 °C for 24 h under N_2. Under these conditions the chemical composition of active ruthenium sulphides was found to consist of a sulphur to ruthenium ratio of close to 1 : 1. The oligomer products in all cases were separated into fractions, differing in solubility, of QO and HQO, where QO represents quinoline oligomers **1a** and **1b** and HQO represents partially hydrogenated quinoline oligomers. Based on GPC analysis of the molecular weight distribution, the chloroform-soluble fraction and the chloroform-insoluble fraction of quinoline oligomers have an estimated repeating quinoline unit of 2–12 and 11–25, molecules, respectively. As shown in Table 1, the efficiency of the CDHP reaction maintained remarkably steady as the THQ to quinoline ratio decreased from 1.0 to 0.06 : 1, with the yield of quinoline oligomers and HQO in the ranges 87–94 and 6–11%, respectively. When the THQ to quinoline ratio decreased further to 0.03 : 1, a sharp decline in the yield of quinoline oligomers was observed with nearly 90% recovery of unreacted quinoline. Below a ratio of 0.03 : 1, the oligomerization activity of ruthenium sulphide was extremely low.

In conclusion, we describe an efficient modified synthesis of nonsubstituted quinoline oligomers by the catalytic dehydrogenative co-oligomerization of 1,2,3,4-tetrahydroquinoline and quinoline at 270 °C in a high yield using ruthenium sulphide as a catalyst, which functions best with a THQ to quinoline ratio > 0.06 : 1. The new procedure should provide a flexible route for the synthesis of functionalized quinoline copolymers, since functionalized quinolines are readily available whereas functionalized 1,2,3,4-tetrahydroquinolines need to be synthesized.

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