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Preliminary communication

REDUCTIVE HYDROSILYLATION OF QUINONES CATALYZED BY TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM(I)

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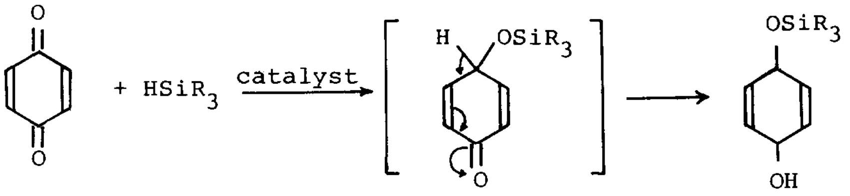
Summary

Tris(triphenylphosphine)chlororhodium(I) has been found to be an effective catalyst for the homogeneous reductive hydrosilylation of quinones. The reactions offer an easy procedure for protecting the highly reactive quinonic moiety of naturally-occurring and biologically-important macromolecules.

Reductive silylation of quinones has attracted much attention in the last few years [1–6] because it offers the possibility of protecting the reactive quinonic fragment in a wide range of naturally occurring and biologically important macromolecules [7]. The silylated products can be easily converted to their parent quinones [8,9] or readily hydrolysed to the hydroquinone derivatives [10]. However, of the silylation reactions studied only that proposed by Matsumoto et al. [1] seems to be a really effective one; all the others suffer from low yields of the silylated products, and from concurrent formation of by-products [2–6]. We describe in this communication a very efficient new method of silylation of quinones based on the rhodium(I) complex-catalysed homogeneous hydrosilylation.

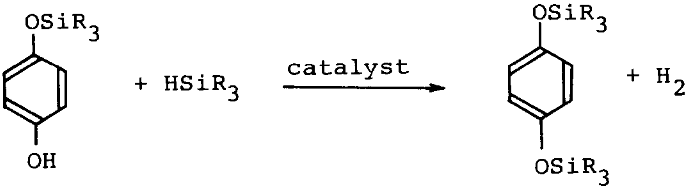
The rhodium(I) complex effectively catalysed the reductive silylation of 1,4-benzoquinone (**1**), 1,4-naphthalenedione (**2**) and 1,2-naphthalenedione (**3**) to give the bis-silyl ethers of the corresponding hydroquinone derivatives. In a typical procedure, tris(triphenylphosphine)chlororhodium (0.5 mol% relative to the quinone used) was added to a binary 1/5 mixture of quinone and hydrosilane in benzene solution and the mixture was refluxed under argon. After 3 h, GLC analysis showed that the bis-silyl ethers of the corresponding hydroquinone derivatives had been formed quantitatively. All the silylated products showed the expected IR, NMR and mass spectra for the structures assigned and there was good agreement with literature data [8,9].

We also carried out the hydrosilylation reactions of **1**, **2** and **3** using a binary 1/1 mixture of quinone and hydrosilane. Under these conditions the reactions proceeded slowly and gave in very low yields (10–20%) mixtures of the mono- and bis-silyl ethers of the corresponding hydroquinone derivatives, with the former predominating. These two sets of experiments clearly show that the reductive silylations of the quinones studied involve two steps. In the first step addition of the hydrosilane to the quinonic double bonds takes place in the presence of the rhodium(I) catalyst, affording the monosilyl ether of the hydroquinone derivative as shown in eq. 1.



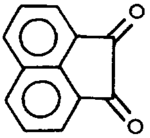
(1)

The second step involves the alcoholysis of the excess hydrosilane by the phenolic group of the mono-silyl ether, also with catalysis by the rhodium(I) catalyst [10], to give the bis-silyl ether, as in eq. 2.



(2)

The proposal of 1,2-addition of the hydrosilane to the quinonic double bond followed by the rearrangement in the first step of the reaction is further supported by the hydrosilylation of two more quinones, namely 9,10-anthracenedione (**4**) and acenephthenequinone (**5**). Under the same conditions **4** gave in very low yields (~ 20%) the bis-silyl ether, whereas in the presence of the equivalent quantity of the hydrosilane (1/1) the 1,2-addition product was also formed in very low yield. This is not surprising when account is taken of the fact that the electron rearrangement is more favourable for the 1,2-addition product from **4** than that from **1**, **2**, and **3**. Acenaphthenequinone (**5**) gave only the 1,2-addition product in the presence of one equivalent or an excess hydrosilane, with a quantitative yield in the last case. In this respect **5** shows a similar behaviour to that of the 2,3-butanedione [11], which is not surprising since the structure of **5** resembles that of the α,β-diketones more closely than that of 1,2-quinones.



(5)

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