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The Regioselective Addition Reaction of 1,2-Benzoquinones with Silyl Enol Ethers Catalyzed by Trityl Perchlorate

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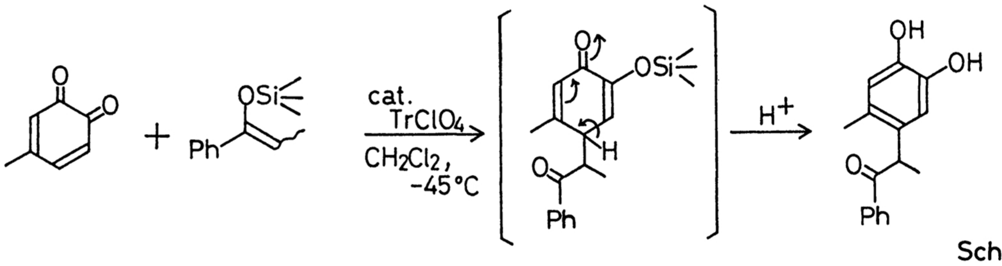
In the presence of a catalytic amount of trityl perchlorate, 1,2-benzoquinones react with silyl enol ethers to produce the corresponding adducts, homoacyl-pyrocatechol derivatives, regioselectively in good yields.

The addition reaction to 1,2-benzoquinone is one of the most efficient method for the synthesis of naturally occuring benzoquinones, naphthoquinones, and pyrocatechol derivatives, etc. However, compared with 1,4-benzoquinones, 1,2-benzoquinones are generally difficult to handle because of their lability; that is, decompositions, isomerizations, or polymerizations often occur under attemped reaction conditions. Further, a lack of control of regioselectivity still remains as a severe problem, especially in the case of synthetically valuable enolate components are employed as nucleophiles.[1)]

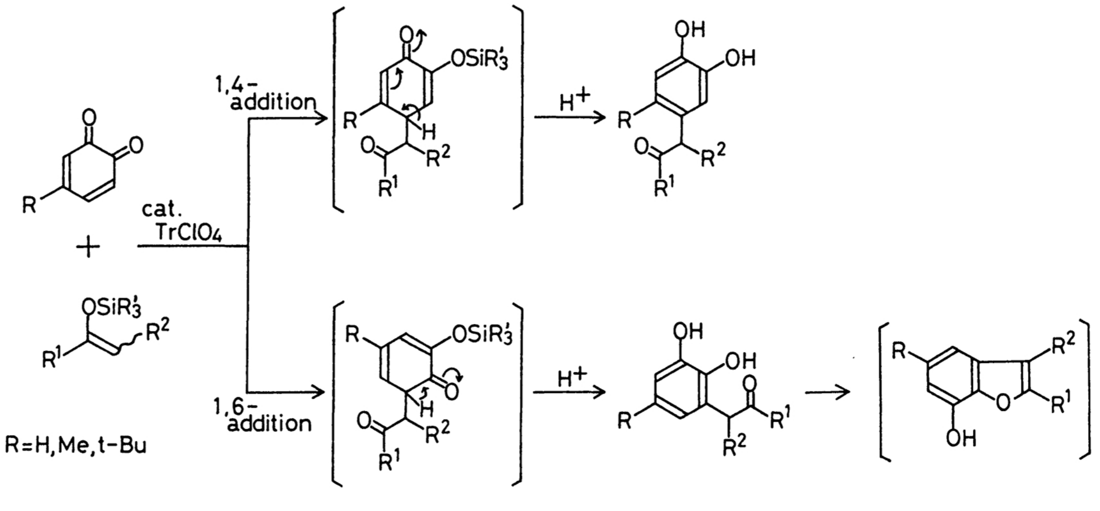
In the previous paper, we have shown that, in the presence of a catalytic amount of trityl perchlorate, 1,4-benzoquinones, quinone monoimides, or imidoquinones react with silyl enol ethers to produce the corresponding benzofuran or indole derivatives in high yields via the corresponding Michael adducts[2)]. As far as we know, this is the first general example of the Michael addition of enolate components to 1,4-benzoquinone derivatives. In this communication, we would like to describe the application of this methodology to the regioselective addition reaction of silyl enol ethers with labile 1,2-benzoquinones by the promotion of trityl perchlorate.

When the reaction of 4-methyl-1,2-benzoquinone[3)] with silyl enol ether of propiophenone was tried in the presence of a catalytic amount of trityl perchlorate, it was found that 4-(1-benzoyl-1-methyl)-5-methyl-pyrocatechol was obtained in 75% yield.[4] The reaction is considered to proceed via an initial regioselective 1,4-addition of the silyl enol ether to 1,2-benzoquinone, followed by aromatization as shown in Scheme 1.



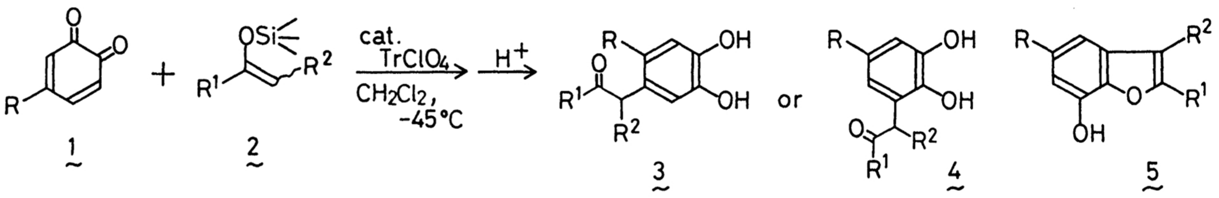
Scheme 1.

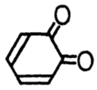
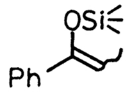
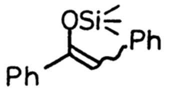
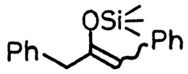
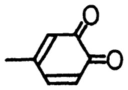
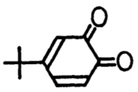
Several examples of the reaction of 1,2-benzoquinones with silyl enol ethers are demonstrated in Table 1. In the cases of the reaction of 1,2-benzoquinone[5] and 4-methyl-1,2-benzoquinone, 1,4-addition products, 4-homoacyl-pyrocatechol derivatives, are obtained regioselectively in good yields. On the other hand, 1,6-addition products, 3-homoacyl-pyrocatechol or benzofuran derivatives, are produced in good yields with high regioselectivities when 4-t-butyl-1,2-benzoquinone[6] was employed. In these cases, the bulky t-butyl group at 4-position of the 1,2-benzoquinone caused the preferential 1,6-addition rather than 1,4-addition, and benzofuran derivatives are yielded by 1,6-addition of silyl enol ethers, followed by aromatization and cyclization (Scheme 2).



Scheme 2.

Table 1. The reaction of 1,2-benzoquinones with silyl enol ethers a)



1,2-Benzoquinone(1)	Silyl enol ether(2)	Product	Yield/%
 (1a)	 (2a)	3 (R=H,R^1=Ph,R^2=Me)	55
(1a)	 (2b)	3 (R=H,R^1=R^2=Ph)	68
(1a)	 (2c)	3 (R=H,R^1=CH_2Ph,R^2=Ph)	59
 (1b)	(2a)	3 (R=Me,R^1=Ph,R^2=Me)	75
(1b)	(2b)	3 (R=Me,R^1=R^2=Ph)	83
(1b)	(2c)	3+5 (R=Me,R^1=CH_2Ph,R^2=Ph)	74 b)
 (1c)	(2a)	4 (R=t-Bu,R^1=Ph,R^2=Me)	60
(1c)	(2b)	3+5 (R=t-Bu,R^1=R^2=Ph)	79 c)
(1c)	(2c)	5 (R=t-Bu,R^1=CH_2Ph,R^2=Ph)	63

a) All the products gave satisfactory NMR and IR spectral data.

b) 3/5 = 82/18.

c) 3/5 = 26/74.

A typical procedure is described for the reaction of a 1,2-benzoquinone with a silyl enol ether; the mixture of a quinone (0.4 mmol), a silyl enol ether (0.44 mmol), and trityl perchlorate (5-10 mol%) in dichloromethane (3 ml) was stirred at -45 °C for an appropriate time (2-3 h). After completion of the reaction, water was added and the aqueous layer was extracted with dichloromethane. The combined organic layer was evaporated and then the residue was treated with the solution of THF and 1 mol/dm^3 HCl(5:1) at room temperature. After usual work-up, the crude product was purified by thin layer chromatography on silica gel.

It is noted that the present reaction realizes the regioselective addition reaction of labile 1,2-benzoquinones with enolate components derived from ketones under mild conditions, and also provides a ficile synthetic method for the preparation of pyrocatechol derivatives. Further progress concerning the utilization of this reaction leading to naturally occuring quinones is now in progress.

References

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3) E. Alder and R. Magnusson, Acta Chem. Scand., 13, 505 (1959); R. Magnusson, ibid., 14, 1643 (1960).

4) Other trityl salts are also effective in this reaction,$^{7)}$ however there observed a little different regioselectivity when a new catalyst system, combined use of trityl chloride and tin(II) chloride,$^{8)}$ was used. These detailed results will be reported in due course.

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