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A NEW REDUCTIVE SILYLATION OF p-QUINONES WITH HEXAMETHYLDISILANE CATALYZED BY IODINE

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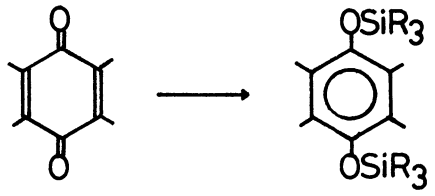
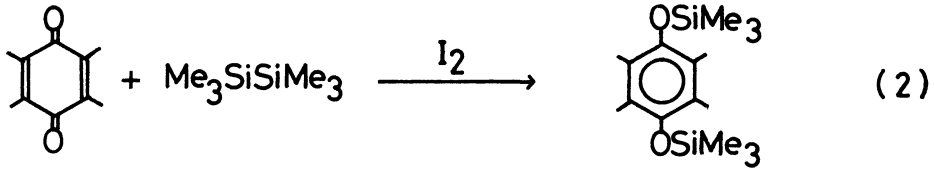
In the presence of a catalytic amount of iodine, hexamethyldisilane can reductively silylate p-quinones under mild conditions to afford 1,4-bis(trimethylsiloxy)arenes in high yields.

Reductive silylation of type 1 may be an attracting method for protecting the quinone fragment which is widely found in natural products, since the resulting bis(silyl)arenes can be readily converted to their parent quinones.[1] Nevertheless, only scattered reports have appeared concerning the silylation of quinones. Thus, Bouas-Laurent and coworkers reported the silylation of several p-quinones with Me_3SiCl/Mg to give the corresponding 1,4-bis(trimethylsiloxy)arenes in 30-94% yields.[2] Also, Tsutsumi and coworkers treated p-benzoquinone with Me_3SiCl/K to obtain the silylated product in 28% yield.[3] These conventional silylations are generally accompanied by the concurrent formation of a large amount of inorganic salts. Further, bis(trimethylsilyl)mercury has been reported by Eaborn and coworkers[4] and Neumann and Neumann[5] to be an effective reagent for the silylation of p-quinones (44-63%). Moreover, Kumada and coworkers have reported that 1,2-difluorotetramethyldisilane reacted at 100°C in the presence of a palladium catalyst with p-benzoquinone to afford the bis(silyl)benzene in 41% yield.[6] The utility of reaction 1 has led us to explore the reductive silylation of a newer type. We now report our finding that, in the presence of a catalytic amount of iodine, hexamethyldisilane silylates effectively p-quinones (eqn. 2).



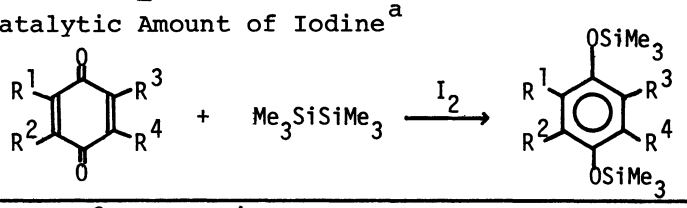
(1)



(2)

The reductive silylation can be simply performed by heating a benzene solution of a binary mixture of quinone (1 equiv) and hexamethyldisilane (1.5 equiv) in the presence of iodine (0.02 equiv). Results are summarized in Table 1, and it will be seen from the Table that the reductive silylation proceeds very smoothly at temperatures of 60-80°C to afford 1,4-bis(trimethylsiloxy)arenes in over 85% yield.

Table 1. Reductive Silylation of p-Quinones with Hexamethyldisilane in the Presence of a Catalytic Amount of Iodine[a]



Run	R^1	R^2	R^3	R^4	Conditions	Yield,%[b,c]
1	H	H	H	H	60°C, 3 h	99
2	Me	H	H	H	60°C, 3 h	91
3	Me	H	H	Me	60°C, 7 h	100
4	Me	Me	Me	Me	60°C, 12 h	86
5	Cl	H	H	Cl	80°C, 7 h	85
6	CH=CHCH=CH		H	H	60°C, 3 h	96
7	CH=CHCH=CH		H	Me	60°C, 5 h	95

[a] [Quinone]/[disilane]/[I_2] = 1/1.5/0.02. Solvent = benzene. [b] Determined by GLC. [c] All the silylated products showed the expected IR, NMR, and Mass spectra for the structures assigned.

A typical procedure is as follows: a mixture of 1.39 g (10.1 mmol) of 2,5-dimethyl-p-benzoquinone, 2.18 g (14.8 mmol) of hexamethyldisilane, 0.059 g (0.23 mmol) of iodine, and 10 ml of benzene was stirred at 60°C under nitrogen. After 7 h, GLC analysis showed that the reaction had produced 1,4-bis(trimethylsiloxy)-2,5-dimethylbenzene in quantitative yield. The IR and NMR spectra of the product were in good agreement with literature.[1)]

The present silylation has advantages of simplicity of the reaction procedure, high yield of the products, and ready availability of the silylating agent. Work is in progress to extend the synthetic scope and to study on the mechanistic aspect.

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