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$Bi(OTf)_3$-catalyzed allylation of quinones with allyltrimethylsilane

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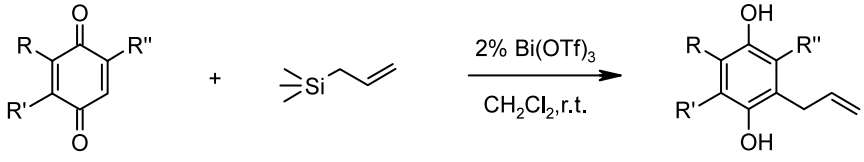
Abstract—*p*-Quinones react smoothly with allyltrimethylsilane in the presence of 2 mol% of $Bi(OTf)_3$ under mild reaction conditions to afford the corresponding allyl substituted benzene derivatives, *p*-allylquinols and allyl substituted 1,4-naphthoquinones in excellent yields with high regioselectivity. This method is very useful for the direct introduction of an allyl functionality onto a quinone moiety.

The allylation of quinones is an important reaction for the preparation of biologically active isoprenoid quinones such as vitamin E, vitamin K, coenzyme Q, and plastquinones, which play a vital role in biological processes including electron transport, blood clotting and oxidative phosphorylation.[1] Functionalized quinols are not only important in the biosynthesis and metabolism of natural phenols but are also useful as synthetic precursors to naturally occurring quinones and alkaloids.[2] The allylation of quinones is generally carried out with allylsilanes using acid catalysts such as titanium tetrachloride and lithium perchlorate in diethyl ether (LPDE).[3] These methods involve the use of a stoichiometric amount of catalysts and prolonged reaction times especially with LPDE to produce allylated quinones. Other methods involve the addition of allyl indium, allyl magnesium, allyl nickel complexes or allylstannane to the quinones.[4,5] A major side product in these procedures is the hydroquinone arising from simple reduction of *p*-benzoquinones. Furthermore, many of these procedures produce a mixture of products and also require a large excess of quinones to eliminate or at least minimize the formation of by-products. Therefore, the development of simple and novel reagents, which are more efficient and provide convenient procedures with improved yields, is needed. Recently, bismuth(III) triflate has attracted the interest of synthetic organic chemists because it is inexpensive and can be easily prepared even in multi-gram scale, in the laboratory from commercially available bismuth(III) oxide and triflic acid.[6] Owing to its unique catalytic properties, bismuth(III) triflate has been extensively used for a plethora of organic transformations.[7] However, there have been no reports on the allylation of quinones with allylsilane employing metal triflates as catalysts.

In this report, we wish to highlight our results on the allylation of quinones with allyltrimethylsilane using a catalytic amount of $Bi(OTf)_3$. The treatment of *p*-benzoquinone with allylsilane in the presence of 2 mol% $Bi(OTf)_3$ afforded the corresponding 2,5-diallylhydroquinone **2a** in 75% yield along with 2-allylhydroquinone **2a′** in 15% yield. However, substituted *p*-benzoquinones gave the corresponding mono-allylhydroquinones in high yields (Scheme 1).



Scheme 1.

Keywords: bismuth triflate; allylation; quinones; allyl benzenes.

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Similarly, various substituted *p*-quinones reacted smoothly with allylsilane at ambient temperature to produce the mono-allylhydroquinones in high yields. Quinones having methyl groups adjacent to unsaturated positions, i.e. 2-methylbenzoquinone and 2,3-dimethyl-, 2,5-dimethyl-, 2,6-dimethylbenzoquinones or 2,6-dimethoxybenzoquinone produced the corresponding allylhydroquinones resulting from allylation at the unsubstituted ring site (entries b–f). No attack at the methylated position was observed when both adjacent positions bear methyl groups (e.g. 2,3-dimethylbenzoquinone). However, 2,3,5,6-tetra-substituted *p*-benzoquinone (duroquinone) and anthroquinone afforded products of addition to one of the carbonyl groups in fairly good yields (entries g, l). Furthermore, the allylation of naphthoquinones with allyltrimethylsilane in the presence of $Bi(OTf)_3$ gave the corresponding allyl substituted naphthoquinones in high yields (entries i–k, Scheme 2).

In all cases, the reactions proceeded rapidly at room temperature with high regioselectivity. Unlike other reported methods, this method does not require the use of additives or ligands to suppress reduction of quinones thereby increasing overall yields. This procedure avoids the disadvantages of polyalkylation, chromanol formation or side-chain cyclization. This method is also effective for the allylation of hindered 1,4-benzoquinones such as duroquinone while most existing methods fail to produce *p*-allylquinols from duroquinone. Among various metal triflates such as $Bi(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$ and $Ce(OTf)_3$ studied for this transformation, bismuth(III) triflate was found to be the most effective in terms of conversion and reaction rates. However, similar yields and selectivity were also obtained when using (5 mol%) scandium(III) triflate under these reaction conditions. As solvent, dichloromethane appears to give the best results. The products were characterized by ^1H NMR, IR and mass spectroscopic data and also by comparison with authentic samples. Other allylating agents such as allyltributylstannane and tetraallyltin also reacted smoothly with *p*-quinones in the presence of 2 mol% $Bi(OTf)_3$ in dichloromethane to produce allyl benzoquinones in excellent yields. The probable pathway seems to be addition of the allyl group at the less hindered carbonyl group followed by a [3,3]sigmatropic rearrangement resulting in the formation of allyl-substituted hydroquinones (Scheme 3) or their oxidation products (entries i–k).

The scope and generality of this process is illustrated with respect to various quinones and allylsilane and the results are presented in Table 1.[8]

In summary, this paper describes an efficient protocol for the allylation of quinones with allyltrimethylsilane using bismuth(III) triflate as the catalyst. This method offers several advantages including mild reaction conditions, enhanced rates, cleaner reactions with improved yields, no production of by-products such as polyalkylated or cyclized products, ready availability of starting materials, small quantity of catalyst, high regioselectivity, operational and experimental simplicity which makes this method a useful and attractive strategy for the synthesis of allyl substituted quinones and hydroquinones.

Acknowledgements

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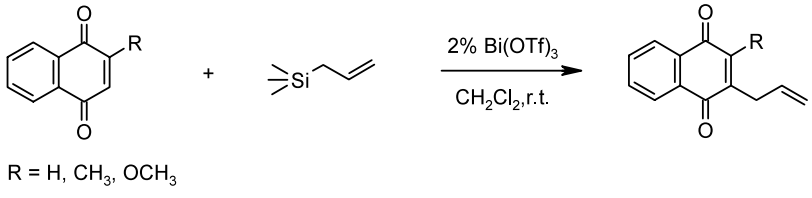
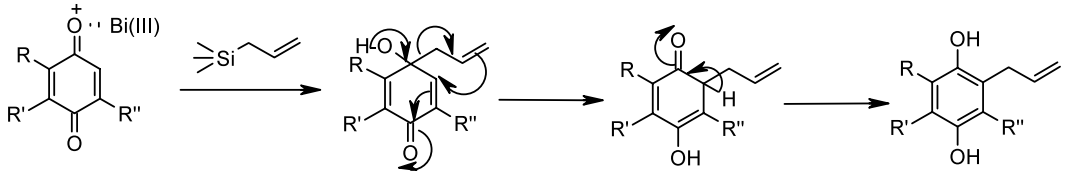
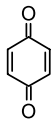
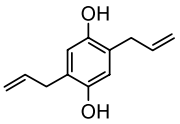
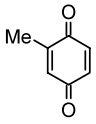
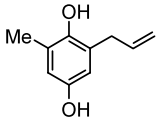
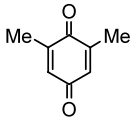
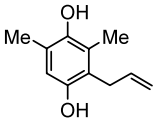
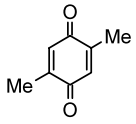
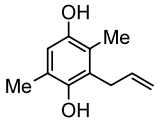
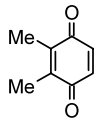
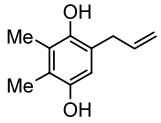
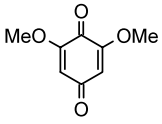
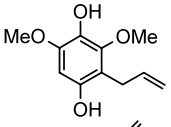
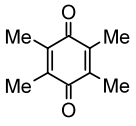
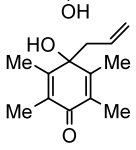
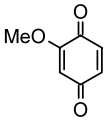
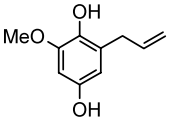
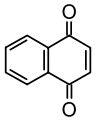
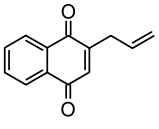
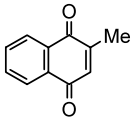
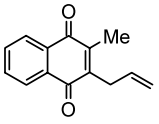
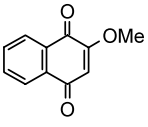
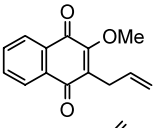
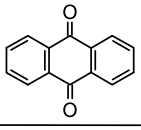
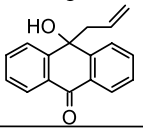


Scheme 2.



Scheme 3.

Table 1. Bismuth(III) triflate catalyzed allylation of *p*-quinones, naphthoquinones and anthroquinone with allyltrimethylsilane

Entry	Quinone **1**	Product[a] **2**	Reaction time (min)	Yield (%)[b]
a.			10	75[c]
b.			15	91
c.			12	89
d.			10	87
e.			15	90
f.			10	85
g.			20	82
h.			10	87
i.			15	90
j.			18	88
k.			15	85
l.			25	75

a: All products were characterized by ^{1}H NMR, IR and mass spectroscopy.
b: Isolated and unoptimized yields.
c: 2-allylbenzene-1,4-diol **2a'** was also obtained in 15% yield.

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8. ***General procedure***: A mixture of *p*-quinone (2 mmol) and $Bi(OTf)_3$ (0.05 mmol) and allyltrimethylsilane (4 mmol) in dichloromethane (10 mL) was stirred at room temperature for the specified time (see Table 1). After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (15 mL) and extracted with dichloromethane (2×10 mL). Evaporation of the solvent followed by purification on silica gel (Merck, 100–200 mesh, ethyl acetate-hexane, 0.5–9.5) afforded the pure allyl derivative.

Spectral data for selected products: **2,5-Diallyl benzene-1,4-diol, 2a** (see Table 1): solid, mp 195–197°C, ^{1}H NMR ($CDCl_3$) δ: 3.32 (d, 4H, $J=6.5$ Hz), 4.35 (brs, 1H), 4.40 (brs, 1H), 5.15 (dd, 4H, $J=1.7$, 17.3 Hz), 5.90-6.0 (ddt, 2H, $J=6.5$, 10.2, 17.3 Hz), 6.55 (s, 2H). δ IR (KBr): ν 3461, 2935, 2861, 1610, 1219, 772 cm^{-1}. EIMS: m/z (%): 190 M$^+$ (100), 149 (15), 71 (8), 57 (10).

2-Allyl benzene-1,4-diol, **2a′** (see Table 1): solid, mp 90–91°C, ^{1}H NMR ($CDCl_3$) δ: 3.30 (d, 2H, $J=6.5$ Hz), 4.35 (brs, 1H), 4.40 (brs, 1H), 5.09 (dd, 2H, $J=1.7$, 17.3 Hz), 5.95–6.0 (ddt, 1H, $J=6.5$, 10.2, 17.3 Hz), 6.57–6.75 (m, 3H). IR (KBr): ν 3461, 2935, 2861, 1610, 1219, 772 cm^{-1}. EIMS: m/z (%): 150 M$^+$ (20), 121 (100), 71 (35), 57 (75).

2-Allylnaphthalene-1,4-dione, 2i: solid, 138–140°C: ^{1}H NMR ($CDCl_3$) δ: 3.38 (d, 2H, $J=6.5$ Hz), 5.20 (dd, 2H, $J=1.8$, 17.3 Hz), 5.95-6.0 (ddt, 1H, $J=6.5$, 10.3, 17.3 Hz), 6.80 (s, 1H), 7.60–7.80 (m, 2H), 8.05–8.15 (m, 2H). EIMS: m/z (%): 198 M$^+$ (100), 181 (20), 169 (15), 141 (60), 115 (18), 104 (16), 176 (50), 65 (5), 50 (12). IR (KBr) ν: 2930, 1720, 1664, 1595, 1497, 1301, 1221, 1071, 757 cm^{-1}.

2-Allyl-3-methyl-naphthalene-1,4-dione, 2j: ^{1}H NMR ($CDCl_3$) δ: 2.50 (s, 3H), 3.50 (d, 2H, $J=6.5$ Hz), 5.05–5.10 (dd, 2H, $J=1.7$, 17.3 Hz), 5.75–5.85 (ddt, 1H, $J=6.5$, 10.3, 17.3 Hz), 7.30 (d, 1H, $J=8.0$ Hz), 7.65–7.70 (m, 1H), 8.05–8.15 (m, 2H). EIMS: m/z (%): 212 M$^+$ (100), 198 (25), 170 (20), 142 (55), 105 (15), 104 (40), 76 (10), 50 (25). IR (KBr) ν: 2925, 1720, 1659, 1521, 1460, 1294, 1219, 1078, 772 cm^{-1}.