Formal [2+3] Cycloaddition between Substituted Phenols and Allylsilane

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Abstract: Treatment of various substituted phenols in the presence of allyltrimethylsilane, iodobenzene diacetate, and perfluorinated alcohol promotes oxidative formal [2+3] cycloaddition in moderate to useful yields.

Key words: hypervalent iodine, allyltrimethylsilane, substituted phenols, [2+3] cycloaddition

The very usual ring system dihydrobenzofuran **1** has attracted the interest of many synthetic groups due to its occurrence in many natural products such as arthrographol (**2**),[1] a natural product isolated from *Aspergillus oryzae* or *Arthographis pinicola*, remirol (**3**),[2] isolated from *Remiria maritima* and other bioactive substances (Figure 1).[3]

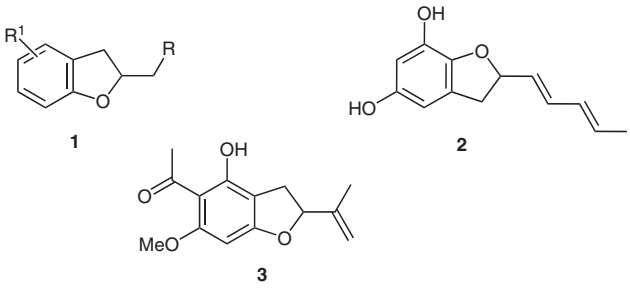
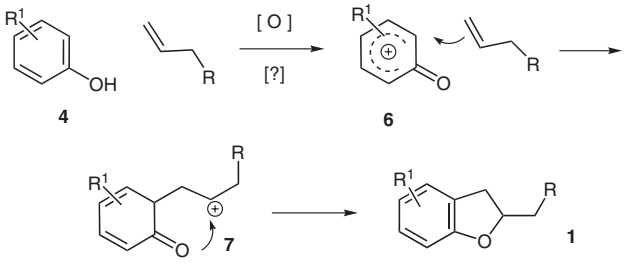


Figure 1

While a number of useful routes to substructure **1** are reported,[4] we have become interested in an approach that relies upon a hypothetical 'oxidative [2+3] cycloaddition' between phenols and alkenes, according to the format of Scheme 1.



Scheme 1

An important part of this reaction is the use of iodobenzene diacetate ('DIB') as oxidizing agent. Indeed, the potential of this environmentally benign reagent is now well known.[5] In particular, iodobenzene diacetate promotes noteworthy oxidative transformations of phenol[6] and aniline derivatives,[7] probably through cationic processes, in a manner consistent with the recent requirements for green chemical processes. As observed by Kita and co-workers,[8] iodobenzene diacetate reactions generally occur best in solvents such as trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP).[9] Under these conditions, oxidative attack of phenols in the presence of unhindered heteronucleophiles[10] tends to proceed through pathway b leading to the dienone compound **8** (Scheme 2). The protic perfluorinated solvent used in these conditions might explain the stabilization of cationic intermediate **6**.

Nevertheless, we have determined that carbon-based nucleophiles such as thiophene[11] attack the presumed intermediate **6** at a position adjacent to the carbonyl group (pathway a), resulting in formation of products **9**, albeit in low yield. Moreover, we have recently related an oxidative formal [2+3] cycloaddition between substituted phenols and furan to obtain dihydrofurobenzofuran core in only one step.[12]

In this letter, we enlarge the possibilities of this transformation to allyltrimethylsilane, a sufficiently reactive alkene capable to lead to dihyrobenzofuran skeleton **10** resulting from a formal oxidative [2+3] cycloaddition. This method enables the generation of dihydrofurans in one step and should find useful applications in medicinal chemistry. Thus, various substituted phenols are converted into **10** in 21–58% yields, presumably by the mechanism depicted in Scheme 3.

Similar transformations in aprotic solvents have already been described with *para*-methoxy-substituted phenols and with electron-rich styrene.[13] In addition, it has been shown by Quideau and co-workers,[14] that this reaction could lead to phenol oxidative allylation under specific conditions, e.g. in the presence of phenyliodine bistrifluoroacetoxy (PIFA) in aprotic solvent. Other pertinent works describing the scope of direct oxidation of arenol derivatives with different hypervalent iodine reagents in accord with this study deserve to be mentioned.[15]

The novel extension described in this letter between various substituted phenols and allyltrimethylsilane must be carried out in the presence of an excess of allyltrimethylsilane and also in solvents such as TFE or HFIP with sim-

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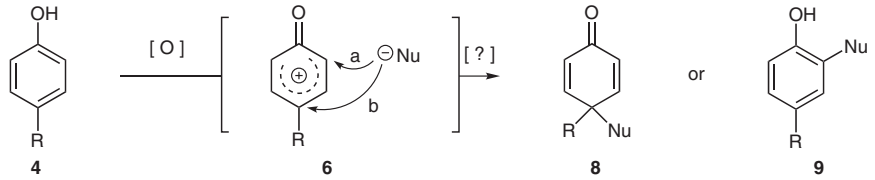
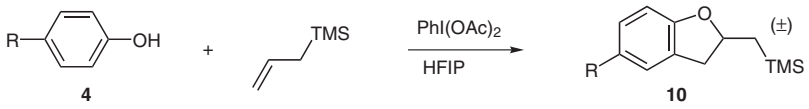


Scheme 2

Table 1 Representative Experiments with *para*-Substituted Phenols

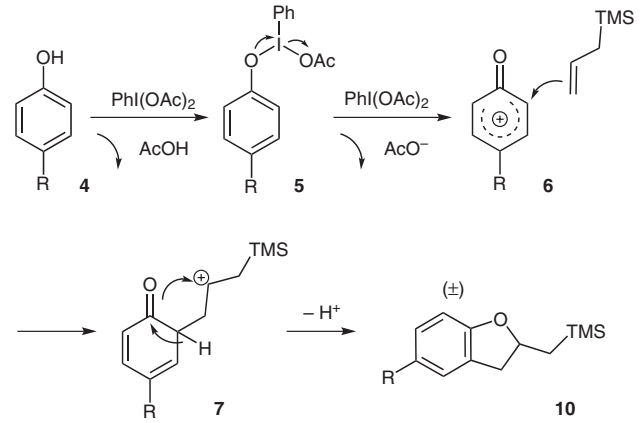


Entry	R	Yield
1	*t*-Bu	58
2	Cl	52
3	Br	53
4	I	41
5	OMe	43
6	CH_2CH_2OH	21
7	CH_2CH_2NHTs	35
8	TMS	53
9	OPh	40

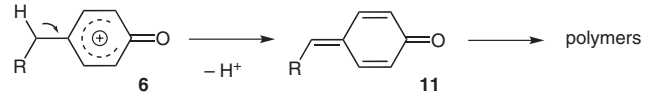
ilar yield.[16] A summary of representative experiments with *para*-substituted phenols appears in Table 1.[17]

It should be stressed that the reaction is not efficient when a benzylic hydrogen atom is in *para* position (cf. entries 6 and 7). Reaction with *para*-cresol occurs in low yield (21%). These latter results show some limit of our method and these unsatisfactory results could be explained by formation of the corresponding quinone methide **11** that leads to polymers, see Scheme 4. This problem could be overcome considering that the reaction with bromine **10c** or with iodine **10d** could allow introducing different R chains thanks to palladium chemistry.

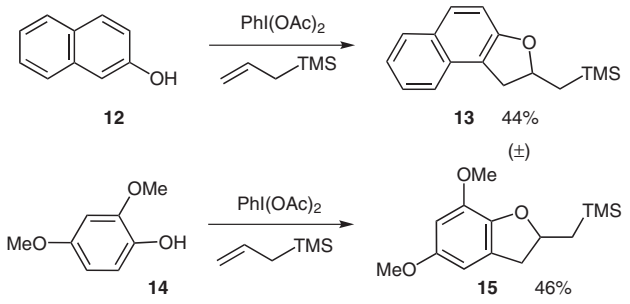
The reaction succeeds with polycyclic phenols such as β-naphthol (**12**, 44% of a single isomer) and with polysubstituted ones such as **14** with a similar yield, see Scheme 5.[18]



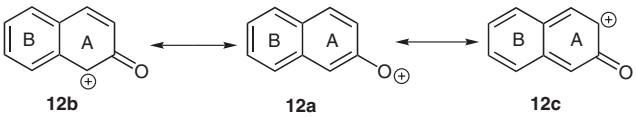
Scheme 3



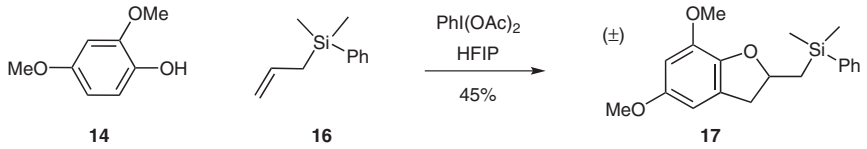
Scheme 4



Scheme 5

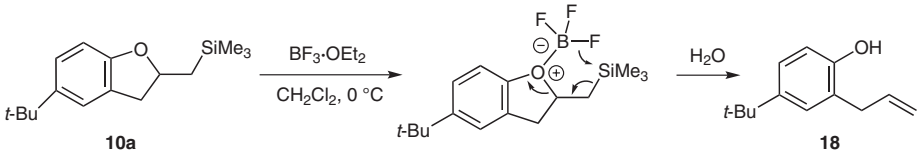


Scheme 6



14 16 17

Scheme 7



10a 18

Scheme 8

The selectivity observed on compound **13** might be explained by the fact that the electronegative oxygen in **12a** would delocalized the presumed cationic charge into the ring A, the aromatic ring B in **12b** renders this mesomer a stronger contributor to the overall delocalized system in comparison with **12c** (Scheme 6).

Similar result has been obtained with dimethylphenylallylsilane **16** to conduce to the compound **17**, a potential precursor of arthrographol (Scheme 7).[19]

A treatment of compound **10a** in the presence of a Lewis acid such as boron trifluoride diethyl etherate leads to the allylic phenol **18** quantitatively (Scheme 8).

Regardless, the various examples provided herein suggest that the reaction is certainly synthetically useful to obtain dihydrobenzofuran skeleton such as **10** quickly. Despite the moderate yield of this reaction, generally few byproducts are present, mainly polymers. In addition, only little amounts (5–10%) of compounds such as **8** and **18** have been detected sometimes.

In conclusion, a practical method to induce a formal 'oxidative [2+3] cycloaddition' between substituted phenols and the allyltrimethylsilane is now available. The transformation provides new strategic opportunities in the chemical synthesis of oxygenated substances, and results in ongoing investigations in this domain will be disclosed in due course.

Experimental Procedure

A solution of $PhI(OAc)_2$ ('DIB', 98 mg, 0.3 mmol, 1.5 equiv) in $(CF_3)_2CHOH$ ('HFIP', 0.35 mL) was added dropwise on 30 s to a vigorously stirred solution of phenol (0.2 mmol, 1 equiv) in allyltrimethylsilane (230 mg, 2 mmol, 10 equiv) and HFIP (0.6 mL). The mixture was then stirred for 30 s, concentrated under vacuum and the residue was purified by silica gel chromatography with a mixture of EtOAc–hexane (5:95).

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(9) TFE (p*K*a ca. 12.4, nucleophilicity ca. –2.8); HFIP (p*K*a ca. 9.3, nucleophilicity ca. –4.2).

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(16) Reaction effected with HFIP as solvent is easier to purify by chromatography than with TFE as solvent.

(17) **NMR Data (Table 1)**

Entry **1**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, 1 H, *J* = 1.7 Hz), 7.27 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.76 (d, 1 H, *J* = 8.2 Hz), 4.92 (m, 1 H), 3.29 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.81 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.34 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.11 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.24 (s, 9 H), 0.11 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 130.8, 128.7, 128.6, 126.4, 122.5, 122.5, 118.5, 112.1, 82.9, 36.9, 25.6, –0.7.

Entry **2**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, 1 H, *J* = 1.7 Hz), 7.08 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.66 (d, 1 H, *J* = 8.2 Hz), 4.90 (m, 1 H), 3.26 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.82 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.26 (m + s, 4 H), 1.05 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.09 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 129.4, 127.6, 124.8, 118.4, 110.0, 82.9, 38.1, 25.1, –0.8.

Entry **3**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (d, 1 H, *J* = 1.7 Hz), 7.18 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.60 (d, 1 H, *J* = 8.2 Hz), 4.93 (m, 1 H), 3.27 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.79 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.30 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.09 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.09 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0, 129.4, 127.6, 124.8, 118.4, 110.0, 82.9, 38.1, 25.1, –0.8.

Entry **4**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (d, 1 H, *J* = 1.7 Hz), 7.36 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.51 (d, 1 H, *J* = 8.2 Hz), 4.92 (m, 1 H), 3.26 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.77 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.29 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.07 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.08 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.3, 136.6, 133.5, 130.4, 111.5, 82.8, 37.8, 25.1, –0.9.

Entry **5**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.71 (s, 1 H), 6.62 (d, 1 H, *J* = 8.2 Hz), 6.58 (d, 1 H, *J* = 8.2 Hz), 4.85 (m, 1 H), 3.71 (s, 3 H), 3.21 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.74 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.28 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.07 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.07 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.7, 128.3, 113.1, 112.5, 111.3, 108.9, 82.3, 56.0, 38.6, 25.1, –0.8.

Entry **6**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, 1 H, *J* = 1.7 Hz), 6.94 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.67 (d, 1 H, *J* = 8.2 Hz), 4.91 (m, 1 H), 3.81 (t, 2 H, *J* = 6.4 Hz), 3.26 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.79 (m, 3 H), 1.33 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.09 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.10 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.1, 129.7, 128.3, 127.8, 125.4, 109.0, 82.3, 63.9, 38.5, 38.2, 25.2, –0.8.

Entry **7**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, 2 H, *J* = 8.2 Hz), 7.29 (d, 2 H, *J* = 8.2 Hz), 6.85 (d, 1 H, *J* = 1.7 Hz), 6.76 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.60 (d, 1 H, *J* = 8.2 Hz), 4.89 (m, 1 H), 4.40 (t, 1 H, *J* = 6.6 Hz), 3.21 (dd, 1 H, *J* = 15.4, 8.2 Hz), 3.15 (q, 2 H, *J* = 6.6 Hz), 2.74 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.66 (t, 2 H, *J* = 6.6 Hz), 2.42 (s, 3 H), 1.31 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.09 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.09 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.3, 143.3, 136.8, 129.6, 128.8, 128.0, 127.9, 127.0, 125.1, 109.1, 82.4, 44.5, 38.1, 35.0, 25.2, 21.5, –0.9.

Entry **8**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, 1 H, *J* = 1.7 Hz), 7.27 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.76 (d, 1 H, *J* = 8.2 Hz), 4.92 (m, 1 H), 3.29 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.81 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.34 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.11 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.24 (s, 9 H), 0.11 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2, 133.3, 130.5, 129.7, 127.0, 108.9, 82.2, 38.0, 25.3, –0.7.

Entry **9**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (t, 2 H, *J* = 8.2 Hz), 7.02 (t, 1 H, *J* = 8.2 Hz), 6.94 (d, 2 H, *J* = 8.2 Hz), 6.85 (d, 1 H, *J* = 1.7 Hz), 6.79 (dd, 1 H, *J* = 8.2, 1.7 Hz), 6.68 (d, 1 H, *J* = 8.2 Hz), 4.93 (m, 1 H), 3.26 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.79 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.34 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.13 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.10 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.8, 155.7, 149.6, 129.4, 128.7, 122.0, 119.3, 117.3, 117.0, 109.3, 82.7, 38.4, 25.2, –0.8.

(18) **NMR Data**

Compound **13**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, 1 H, *J* = 8.2 Hz), 7.63 (d, 1 H, *J* = 8.2 Hz), 7.54 (d, 1 H, *J* = 8.2 Hz), 7.43 (t, 1 H, *J* = 8.2 Hz), 7.27 (d, 1 H, *J* = 8.2 Hz), 7.05 (d, 1 H, *J* = 8.2 Hz), 5.10 (m, 1 H), 3.56 (dd, 1 H, *J* = 14.8, 8.8 Hz), 3.03 (dd, 1 H, *J* = 14.8, 8.2 Hz), 1.37 (dd, 1 H, *J* = 13.7, 6.6 Hz), 1.18 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.11 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 130.8, 128.9, 128.7, 128.6, 126.4, 122.5, 122.5, 118.5, 112.1, 82.9, 36.9, 25.6, –0.7.

Compound **15**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.35 (s, 2 H), 4.92 (m, 1 H), 3.84 (s, 3 H), 3.77 (s, 3 H), 3.22 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.79 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.42 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.19 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.10 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 144.3, 141.9, 128.3, 101.4, 99.1, 82.9, 56.0, 38.9, 30.9, 25.0, –0.9.

(19) **NMR Data of Compound 17**
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (m, 2 H), 7.36 (m, 3 H), 6.33 (s, 1 H), 6.29 (s, 1 H), 4.89 (m, 1 H), 3.83 (s, 3 H), 3.73 (s, 3 H), 3.06 (dd, 1 H, *J* = 15.4, 8.2 Hz), 2.69 (dd, 1 H, *J* = 15.4, 8.2 Hz), 1.69 (dd, 1 H, *J* = 14.3, 6.6 Hz), 1.39 (dd, 1 H, *J* = 14.3, 8.8 Hz), 0.38 (s, 3 H) 0.37 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.4, 144.3, 141.8, 138.2, 133.5, 129.1, 128.2, 127.8, 101.3, 99.1, 82.6, 55.9, 38.7, 24.3, –2.2, –2.4.

