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Oxidative cycloaddition and cross-coupling processes on unactivated benzene derivatives†

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Treatment of phenols or anilines containing a sulfonyl group in the presence of a hypervalent iodine reagent promotes a formal dearomatizing [2 + 3] cycloaddition reaction on unactivated benzene and naphthalene derivatives. This process occurs *via* an intramolecular nucleophilic addition to the Wheland species generated during the oxidative activation. Subsequent treatment under acidic conditions readily transforms the tricyclic system into a biaryl *via* a formal cross-coupling process.

Introduction

Cycloaddition[1] and cross-coupling[2] transformations are extensively used in organic synthesis. Cycloadditions are generally performed on alkenes and alkynes; however, a similar transformation involving dearomatization of the normally inert π-bonds of an aromatic core would provide a means of preparing key polyfunctional intermediates. Only a few examples of such cycloaddition methods have been reported in the literature.[3] Although the reported reactions have been exclusively intramolecular, a bimolecular approach would provide a greater variety of potential synthetic avenues. In particular, the remaining double bonds could be readily involved in further transformations to rapidly generate elaborate products from inexpensive aromatic derivatives. From a chemical standpoint, such a transformation has been regarded as difficult to achieve. However, biaryl syntheses involving cross-coupling of two unactivated aromatic systems have received attention due to the large number of natural targets incorporating these cores[4] and the potential for using axially chiral bi-aromatics as ligands in asymmetric reactions.[5] Previous methods of achieving this type of transformation have generally involved heavy metals, but a recent report in the literature suggested that similar cross-coupling methodologies may be accomplished under metal-free conditions using hypervalent iodine reagents[6] and thiophenes,[6a] polymethylbenzenes,[6b] or anisole derivatives[6f] as coupling partners. Other noteworthy cross-coupling processes involving hypervalent iodine reagents in combination with copper triflate have been efficiently developed by Gaunt and co-workers. In these reactions the copper salt remains crucial.[7] The few reported metal-free cycloaddition reactions involving phenols have been limited to electron-rich alkenes[8] and furan[9] and have not been successfully extended to include "dipolarophiles" similar to the aryl system **2**, Fig. 1.

In this paper, we present a versatile methodology facilitating [2 + 3] cycloaddition processes between benzene derivatives and phenols or anilines. Slightly modified conditions may be used to produce the cross-coupling adduct from these two unactivated aromatic subunits. The processes are reminiscent of Friedel–Crafts chemistry in their approach to the connection of two aromatic units under metal-free conditions.

Results and discussion

For the reactions to proceed, one of the systems must be converted into an electrophilic species for trapping by the remaining aryl acting as a nucleophile. This reversal of reactivity may be thought of as involving "aromatic ring umpolung".[10] An indication of how such selective aromatic activations may be accomplished is provided in the work of Kita,[11] who demonstrated the reactivity of electron-rich systems such as phenols in the presence of hypervalent iodine reagents,[12] for example (diacetoxyiodo)benzene (DIB) or phenyliodine bis(trifluoroacetate) (PIFA).[13] The activation is best performed in solvents such as trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP)[10f] and involves electron transfer to produce a phenoxonium ion **3**. This ion is readily trapped by an aryl partner **2**, leading to a Wheland species **4**. At this stage one of two pathways may occur, a classical elimination

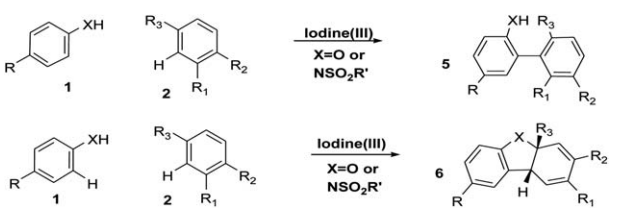

Fig. 1 Cross-coupling and aromatic cycloaddition.

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(*pathway a*) affording the biaryl core **5** or an intramolecular nucleophilic attack on arenium ion **4** (*pathway b*) leading to the polycycle **6**, Fig. 2.

A key aspect of this transformation is the relative stability of the electrophilic species generated. Indeed, the phenoxonium **3** and arenium **4** ions produced during the umpolung activation must be sufficiently stable to react with their respective nucleophile partners in order to avoid competitive elimination pathways such as benzylic hydrogen elimination from **3**, which generates an unstable polymerizable quinone methide (Fig. 3).

Because of its polar and non-nucleophilic properties, HFIP is a valuable solvent that provides sufficient stabilization of electrophilic species **3** and **4** in the presence of fairly reactive and electron-rich partners such as enol ethers or furans.[8c] However, the reaction is inefficient with simple benzene derivatives such as iodo-aryls, naphthalene or benzene. To promote reactions with these important compounds other issues must be resolved. For instance, we have observed that a sulfonyl moiety on the lateral chain behaves similarly to HFIP, enabling nucleophilic attack even with poor electron systems such as iodobenzene. We assume that in an intramolecular pathway the poor nucleophilicity of the lone pairs on the sulfonyl oxygen atoms stabilize the transition state **10** by overlapping phenoxonium ion **3** (n–π* interaction) without producing a carbon–oxygen bond, Fig. 4.

Direct formation of compound **5** would be an interesting example of cross-coupling; however, the nascent relatively electron-rich system **5** would be reoxidized more quickly by the unreacted hypervalent iodine reagent than the remaining starting material **1**. It appears that formation of the cycloadduct **6** is essential during the process. In a sense, compound **6** serves as a protecting group for the phenol or aniline functionality and minimizes undesirable overoxidation of the latter. Moreover, further treatment of **6** in a second step under acidic conditions and in the absence of hypervalent iodine regenerates the arenium species **4** and displaces the equilibrium in favor of the irreversible pathway a, leading to biaryl **5**. For this reason, it is important to control the acidity of the medium during the reaction to avoid reopening the cycloadduct **6**, leading to compound **5** that could be subsequently overoxidized due to the presence of NH or OH bonds. Several conditions and hypervalent iodine reagents were investigated. Iodobenzene was the first "dipolarophile" tried because it is released during the process following reduction of the hypervalent iodine reagent. Bis(pivalate)iodobenzene (PIB, entry d) was the oxidizing agent

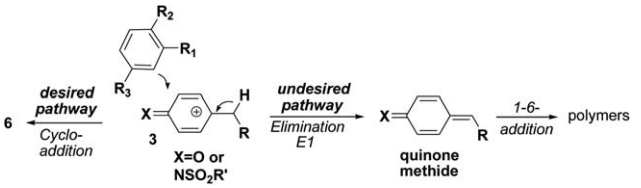


Fig. 3 Competitive transformations of phenoxonium species **3**.

of choice, and the reaction was optimized at −4 °C in a mixture of HFIP–DCM (2 : 1). Pivalic acid, a weak carboxylic acid, was released during the reaction. Similar results were observed using DIB combined with Na_2CO_3 to neutralize the acetic acid released, as the pH of the solution seems to be an important aspect of this transformation. As expected, compound **11** was not produced under harsher conditions employing PIFA. Since this process occurred in an intermolecular manner and due to the instability of species **3** (Fig. 3), ten equivalents of inexpensive iodobenzene were used to favor formation of compound **11** over the polymeric by-products. If desired, the excess aromatic partner could be chromatographically separated and reused. In no case was it necessary to add more than ten equivalents of iodobenzene (see Table 1, entries d, f and g). The nature of the sulfonyl group does not really influence the transformation, although a slight diminution of yield was observed in the presence of a withdrawing group (entry j). The reaction occurred in the presence of a Julia–Kocienski auxiliary[14] that could be useful for further elaboration of the lateral chain, Table 1.

With the optimized conditions in hand, we investigated the use of other aromatic systems as dipolarophiles. Iodo-aryl compounds were competent substrates for this transformation. The regioselectivity observed with *para*-substituted iodo-aryl compounds appears to be controlled by steric factors, and a protecting group was tolerated (entry e). In addition, the crucial sulfone moiety may be successfully incorporated in a six-membered-ring transition state with a lower overall yield as expected (entry f). We were pleased to observe that the new process even occurred using benzene and was efficient when naphthalene was used (72%), most probably due to the fact that one aromatic core remains intact during the formation of **12h**, Table 2.

In some cases when iodobenzene was not used as a dipolarophile, a small amount of compound **11** (~5%) was observed, originating from a competition with iodobenzene released during the umpolung activation. The successful extension of

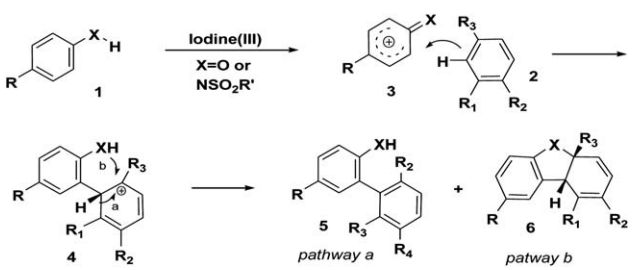


Fig. 2 Oxidative cross-coupling *vs.* cycloaddition.

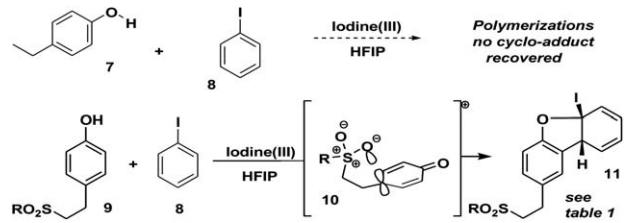
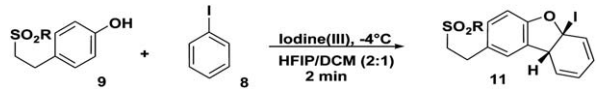


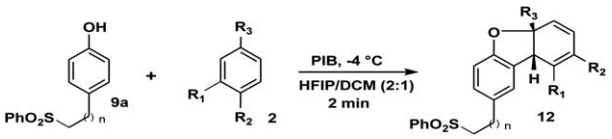
Fig. 4 Oxidative dearomatizing "2 + 3" cycloaddition.

Table 1 Cycloaddition optimization conditions



Entry	R	Iodine(III)	PhI equiv.	Yield (%)
a	Ph	PIFA	10	—
b	Ph	DIB	10	34
c	Ph	DIB + Na_2CO_3	10	47
d	**Ph**	**PIB**	**10**	**51**
e	Ph	PIB + Na_2CO_3	10	50
f	Ph	PIB	20	53
g	Ph	PIB	5	37
h	***n*-Propyl**	**PIB**	**10**	**55**
i	*p*-PhOMe	PIB	10	48
j	*p*-$PhNO_2$	PIB	10	41
k	**Benzothiazol**	**PIB**	**10**	**45**

Table 2 Cycloadditions with benzene derivatives



Entry	*n*	**2** (equiv.)	R_1	R_2	R_3	Yield (%)
a	1	10	H	H	I	51
b	1	10	H	Me	I	54
c	1	10	H	Et	I	47
d	1	10	H	*i*Pr	I	40
e	1	8	H	CH_2OTBS	I	35
f	2	10	H	H	I	31
g	**1**	**20**	**H**	**H**	**H**	**40**
h	**1**	**10**	**CH=CHCH=CH**		**H**	**72**

this process to systems other than iodobenzene provides support for the mechanism proposed in Fig. 2 and rules out an intramolecular process involving the hypervalent iodine reagent. This method could be employed in total syntheses of natural products containing hydrodibenzofuran cores such as linderol A,[15a] a potent inhibitor of melanin biosynthesis in cultured B-16 melanoma cells, or rubiyunnanin A[15b] (Fig. 5).

Other systems have been tested including anthracene, in which a formal "4 + 3" cycloaddition occurred to produce **13**. Compound **9i** reacted in the presence of furan to afford **14** in 95% yield. It should be stressed that in the presence of PIB and with a sulfone on the lateral chain, the overall yield observed was double that of the same transformation employing ethylphenol[9c] and furan, a fairly reactive and electron-rich partner (~45% yield), demonstrating the importance of the sulfonyl moiety as a stabilizing and anchimeric assisting group for the phenoxonium species generated in the reaction, Scheme 1.

Although the sulfone moiety present on the lateral chain could be further transformed using Julia–Kocienski chemistry (compound **11k**), it would be more convenient to introduce a removable auxiliary to enable the cycloaddition by stabilizing the electrophilic species **16**. In addition, the valence of the oxygen atom makes development of an asymmetric pathway difficult. Toward this goal a similar reaction involving a sulfonamide group has been envisaged; in this case the required stabilizing sulfonyl group is directly connected to the aniline and may stabilize the *ortho* positions of the electrophilic species **16** in a manner similar to **10**. This option could lead to a further asymmetric pathway through the introduction of a chiral sulfonamide. This alternative tolerated a variety of spectator functionalities and several sulfonamides. However, lower yields were observed with substituted sulfonamides (Table 3, entries **17c** and **17d**). Naphthalene underwent efficient reaction with sulfonamides **15**, most probably because the second aromatic ring stabilized the resulting areniun ion **4** (Table 3).

Only five equivalents of naphthalene were required when a sulfonamide was used as the polarophile. This process represents an expeditious route to indoline cores, an important functionality present in a large number of bioactive products. The synthesis of scaffolds such as **12** or **17** has not been documented in the literature, and only a few examples of isomers having modified connectivity have been prepared from benzofuran, oxabicycle and styrene derivatives.[16] Most of these methods have involved transition metals. Reactions have been attempted using other aromatic partners in combination with sulfonamide **15**, including a substituted naphthalene, to generate tetracycle **18**. Highly electron-rich methoxynaphthalene derivatives were unsatisfactory substrates for the cycloaddition pathway and led to several cross-coupling adducts. However, when using a moderate electron-donor group such as a mesylate, cycloadduct **18** was obtained as well as the C–N cross-coupling compound **19** resulting from direct attack of the naphthalene derivative on the nascent electrophilic nitrogen generated during the umpolung activation. A

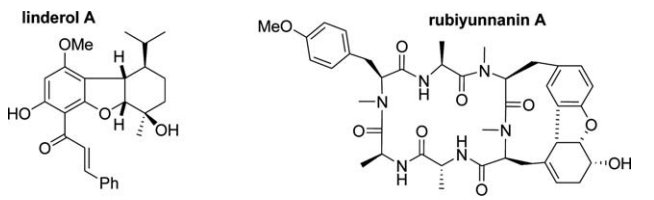
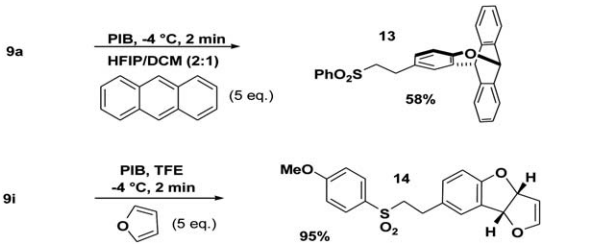
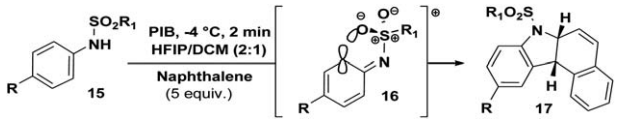


Fig. 5 Natural products containing hydrodibenzofuran cores.



Scheme 1 Anthracene and furan cycloadditions.

Table 3 Cycloaddition with sulfonamides

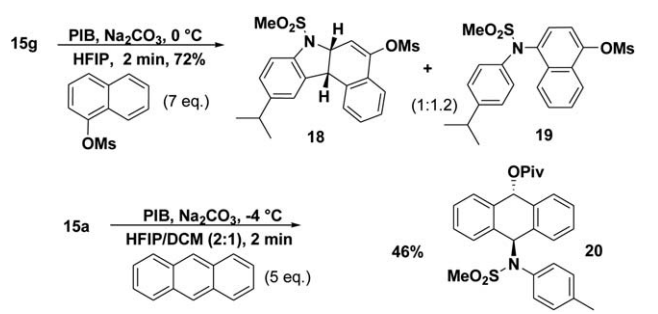


Entry	R_1	R	Yield (%)
a	**Me**	**Me**	**61**
b	**Et**	**Me**	**59**
c	Tol	Me	32
d	*i*Pr	Me	38
e	Bn	Me	45
f	Me	Cl	51
g	Me	*i*Pr	52
h	Me	*n*Pr	51
i	Me	$CH_2CH_2SO_2Ph$	54
j	Me	CH_2OH	53
k	**Me**	**CH_2CH_2OH**	**62**
l	Me	CH_2CH_2OTBS	52
m	Me	TMS	43

similar transformation was observed in the presence of anthracene, and we assumed that the quite stable dibenzylic arenium ion **4** generated from the anthracene attack was trapped by pivalic acid released in the medium, leading to compound **20** in 46% yield, Scheme 2.

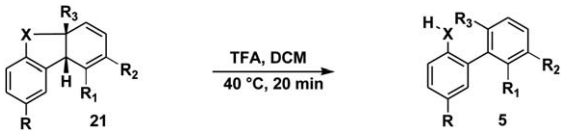
Interestingly, in a second step under acidic conditions mediated by trifluoroacetic acid, the conversion of cycloadduct **21** to biaryl **5** was quantitatively observed, probably *via* regeneration of species **4** and displacement of the equilibrium in favor of pathway a as discussed in Fig. 2. This suggests that further acid treatment of compounds **12** or **17** leads to a formal cross-coupling process involving unactivated aromatic subunits as a route to C–H activation, Table 4.

A direct cross-coupling process may also be undertaken from the sulfamide derivative **22**. In this case biaryl systems were directly obtained and only a small amount of cycloadduct product was occasionally detected. This compound was rapidly transformed into the biaryl **23** in the presence of slightly acidified $CDCl_3$. This result may be rationalized if we consider that the new cycloadduct derivative is rapidly transformed into **23** due to the presence of the additional basic pyrrolidine moiety. The sulfamide segment appears to be a direct C–H



Scheme 2 *O*-Mesylnaphthol and anthracene.

Table 4 Formal cross-coupling process



Entry	X	R	R_1	R_2	R_3	Yield (%)
a	O	$CH_2CH_2SO_2Ph$	H	H	I	97
b	O	$CH_2CH_2SO_2Ph$	H	Me	I	91
c	O	$CH_2CH_2SO_2Ph$	H	Et	I	98
d	O	$CH_2CH_2SO_2Ph$	H	*i*Pr	I	90
e	O	$CH_2CH_2SO_2Ph$	H	H	H	97
f	O	$CH_2CH_2SO_2C_6H_4OMe$	H	H	I	87
g	O	$CH_2CH_2SO_2Ph$	$-C_4H_4-$[a]		H	98
h	NSO_2Et	Me	$-C_4H_4-$		H	97
i	NSO_2Me	*n*Pr	$-C_4H_4-$		H	83
j	NSO_2Me	*i*Pr	$-C_4H_4-$		H	97
k	NSO_2Me	CH_2CH_2OH	$-C_4H_4-$		H	76
l	NSO_2Me	CH_2CH_2OTBS	$-C_4H_4-$		H	79[b]
m	NSO_2Me	$CH_2CH_2SO_2Ph$	$-C_4H_4-$		H	94

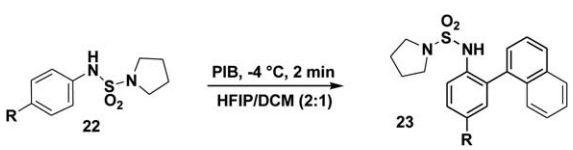
[a] $-C_4H_4-$ = $-CH{=}CHCH{=}CH-$. [b] The trifluoro ester derivative is isolated.

inductor, enabling cross-coupling with naphthalene derivatives, Table 5.

Guziec and Wang have described reductive removal of the sulfonamido group[17] in the presence of NH_2Cl and NaH to produce biaryls **25** from compound **24** through an overall sequence that neatly complements established methods, Fig. 6.

An interesting aspect of this transformation is its ability to dearomatize a benzene derivative into a functionalized system ready for further transformations. As an illustration of some possibilities provided by this method, several conventional reactions enabling quick transformation of the key cycloaddition product into further functionalized cores are presented in Scheme 3. For example, Diels–Alder reaction of **12a** led to compound **26** in 59% yield. Hydrogenation of **17a** provided the tetracyclic indoline **27** in 66% yield, and treatment of **17a** with OsO_4 and NMO produced diol **28** in 60% yield.

Table 5 Direct cross-coupling process



Entry	R	Yield (%)
a	Me	55
b	Et	64
c	*i*Pr	54
d	Cl	81
e	CH_2CO_2Me	36
f	TMS	52

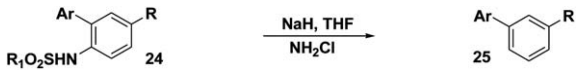
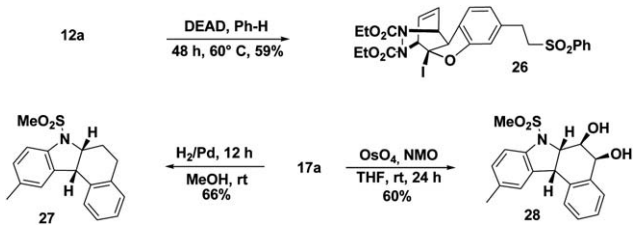


Fig. 6 Guziec and Wang desulfonamidation.



Scheme 3 Functionalization of cycloadducts **12** and **17**.

Conclusions

In summary, a new oxidative dearomatizing cycloaddition process between phenols or anilines and aromatic derivatives has been developed. This process is made possible by the introduction of a key sulfonyl group to stabilize the electrophilic species generated during the hypervalent iodine-mediated umpolung activation. Slightly modified conditions may be used to obtain a cross-coupling adduct from these two unactivated aromatic subunits as an alternative C–H activation transformation. Ongoing investigations of these processes, including an asymmetric version with a chiral sulfonamide moiety, and potential applications will be disclosed in due course.

Acknowledgements

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