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Rapid Synthesis of Etherimides via Catalytic Arylation of Silylated Phenols

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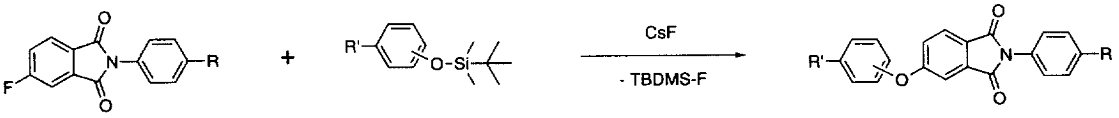
Abstract: We report here a rapid and efficient method for the synthesis of aromatic etherimides from silylated phenols and 4-fluorophthalimides catalyzed by CsF. Reaction times are a few minutes and products are easily purified requiring no column chromatography. © 1999 Elsevier Science Ltd. All rights reserved.

Aromatic polyetherimides are very important commercial high temperature polymers that exhibit excellent thermooxidative stability, chemical resistance, and mechanical properties making them useful for many specialty applications.[1-3] There are many synthetic methods known for their synthesis, but the most common methods involve either the condensation of diamines and dianhydrides followed by imidization [4] or aromatic nucleophilic substitution reactions involving phenolate salts and 4-nitrophthalimides.[5] We have been investigating new methods for the synthesis of polyetherimides with the specific goal of inventing chemistry which is amenable to the synthesis of hyperbranched structures.[6] In the course of our studies, we have discovered an extremely rapid catalytic method for the synthesis of aromatic etherimides from aromatic 4-fluorophthalimide derivatives and aromatic silyl-protected phenols (Scheme 1).



Scheme 1

Nucleophilic aromatic substitution reactions of 4-nitrophthalimide derivatives with phenolate salts have been studied extensively at G.E.[7-13] While the chemistry is well investigated and

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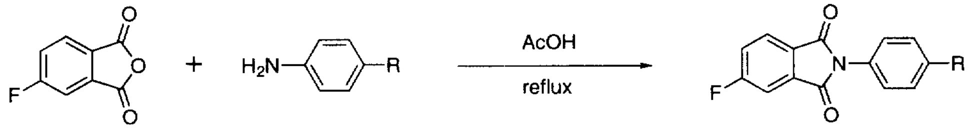
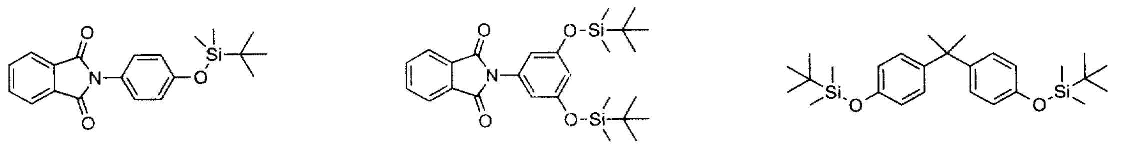
developed, there are inherent disadvantages to this method. The nature of this chemistry requires strict adherence to anhydrous conditions in order to achieve high yields and requires the synthesis of sensitive phenolate salts. The formation of product is accompanied by a nitrite salt byproduct that must be removed. The nitrite ion has been shown under certain conditions to be reactive leading to unwanted side products.[8] The method is also limited in that reactions and polymerizations using benzenediol salts give poor yields due to electron transfer between the nitrophthalimide and the benzenediol dianion.[10] Krickeldorf *et al.* have published a series of reports on the synthesis of polyetherketones and polyethersulphones. Their arylation method involved the use of trimethylsilyl (TMS) protected diphenols, activated diaryl fluorides, and a catalytic amount of CsF.[14-19] Here we show that this method is easily extended to the synthesis of etherimides from fluorophthalimide derivatives and eliminates the disadvantages of the aforementioned chemistry.



1 R = H 89%
2 R = t-Bu 90%

Scheme 2

Following a previously reported method, the 4-fluorophthalimides shown in Scheme 2 were easily obtained in high yields.[10] We found the TMS protected phenols difficult to isolate with purities greater then 96% due to the lability of the TMS group. We therefore chose to use the more stable *tert*-butyldimethylsilyl (TBDMS) group. The catalytic arylation reaction is sensitive to chloride ion impurities [15] and it was therefore necessary to use conditions for installing the TBDMS group in which all chloride ions are removed in the workup. Compounds **3-5** in Scheme 3 were obtained in good yields from reaction of the corresponding phenols with *tert*-butyldimethylsilylchloride and imidizole as the base in methylene chloride. These conditions allowed for facile removal of the imidizole hydrochloride salt by filtration. The absence of chloride ions was confirmed with $AgNO_3$ solution.

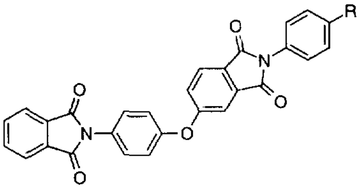
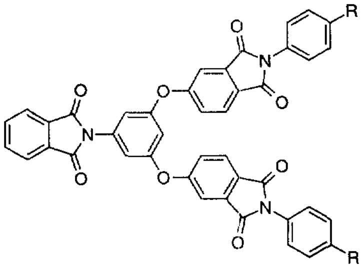
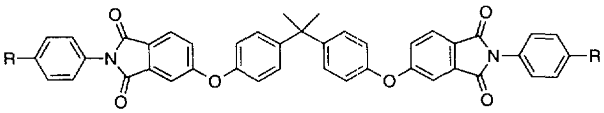


3 **4** **5**

Scheme 3

Table I shows the results for the catalytic arylation reactions of 4-fluorophthalimides **1** and **2** with TBDMS-protected phenols **3-5**. All of the arylation reactions were run under similar conditions. The diphenylsulfone solvent (DPS) and reagents are preheated to 240 °C yielding a slightly yellow molten solution. The catalyst was added and allowed to dissolve. Within seconds, the reaction mixture started to bubble vigorously and the evolution of *tert*-butyldimethylsilyl fluoride was observed. The mixture was allowed to stir until the bubbling ceased (less than five minutes for all reactions we have performed to date). The reaction was removed from heat and allowed to cool. Before solidification, ethanol was added to the reaction mixture. The hot mixture was slurried to dissolve the solvent DPS and the pure product was isolated by filtration.

Table 1: Results of catalytic arylation reactions between 4-fluorophthalimides **1** and **2** and silyl-protected phenols **3-5**.

Entry	Reactants	Products^a	R group	Yield^b
1	3 + 1		R = H	86 %
2	3 + 2		R = t-Bu	81 %
3	4 + 1		R = H	56 %
4	4 + 2		R = t-Bu	85 %
5	5 + 1		R = H	65 %

(a) All products structures have been confirmed by NMR (^{1}H and ^{13}C), Mass Spectrometry, and elemental analysis. (b) All yields are unoptimized.

This catalytic arylation method has several advantages over the method developed at G.E. The starting materials are easily synthesized and can be stored for long periods of time with no special precautions. The conditions appear to be insensitive to moisture. The byproduct of the reaction is tert-butyldimethylsilyl fluoride which at 240 °C boils off and drives the reaction forward. The removal of TBDMS fluoride also eliminates its possible role b vcin sideproduct formation. As shown in entries 3 and 4 in Table 1, this catalytic method also allows for the synthesis of diaryletherimides from benzenediol based substrates.

Etherimides can be efficiently synthesized in multigram quantities using fluorophthalimides and TBDMS-protected phenols. The examples shown in Table 1 represent model reactions for AB and A_2B_2 linear polymerizations and AB_2 hyperbranched polymerizations. We are currently pursuing these avenues and will report on them in due course.

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