

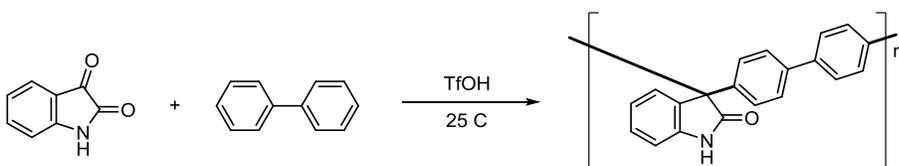
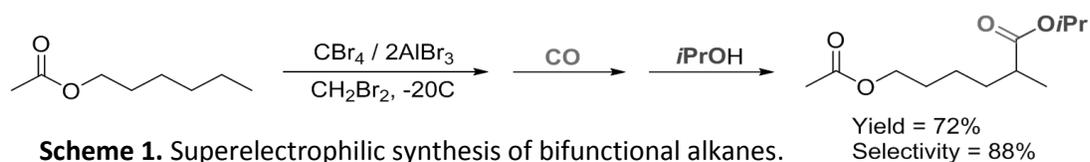
## REACTIONS OF SUPERELECTROPHILES

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### Introduction and Background

In polar chemical reactions, electrophiles and nucleophiles of opposite strengths are paired so that reaction rates can be controlled. For example, Friedel crafts alkylations employ weak nucleophiles (arenes) and strong electrophiles (in situ generated carbocations).<sup>1</sup> Even more polarized nucleophile / electrophile combinations are possible. Superelectrophiles are densely-charged cations that are activated by superacids and can react with very weak nucleophiles. For example, trihalomethyl cations ( $CX_3^+$ ) are aprotic superelectrophiles that undergo reactions with C-H bonds. Recently, this reactivity has been harnessed for the selective carbonylation of monofunctional alkanes to produce bifunctional alkanes with good site selectivity<sup>2</sup> (Scheme 1). Superelectrophiles can also be generated by reaching high protonation states in Brønsted superacids, which has recently been applied to the synthesis of linear<sup>3</sup> (Scheme 2) and hyperbranched<sup>4</sup> polymers.



The reactivity of most nucleophiles and electrophiles can be quantified using kinetic measurements<sup>1</sup>, but these experimental approaches have not been applied to superelectrophiles. However, computational studies of superelectrophiles have shown that at high protonation states, molecules will possess low energy LUMOs and high reactivities<sup>5</sup>. Because high protonation states are unfavorable, superacids are required for superelectrophilic activation. For small cations, even partial protonation can generate superelectrophiles capable of hydride abstraction<sup>6</sup>. Recently, IR spectroscopy has been used to directly observe hydrogen bonding between an oxonium ion (oxatriquinane) and carborane acid.<sup>7</sup>

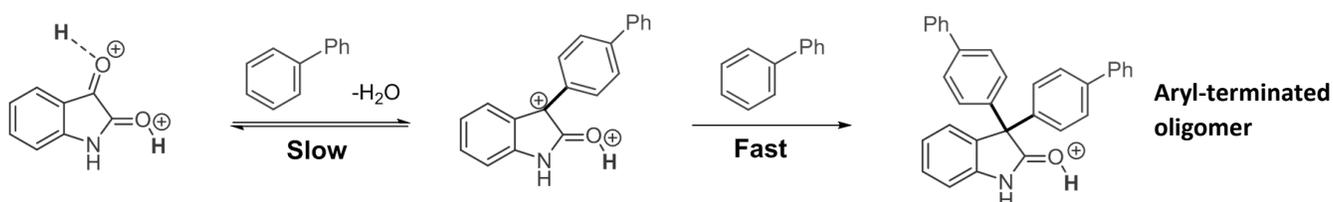
### Charge Repulsion and Superelectrophilic C-H Functionalization

In molecules containing multiple positive charges, reactivity can be dictated by charge repulsion. For example, rearrangements of dicationic species can occur spontaneously<sup>8</sup>, and migration of positive charge

across phenyl rings has been observed by comparing NMR spectra of different polycations<sup>9</sup>. The phenomenon of charge repulsion can also be harnessed to control site-selectivity. For example, C(sp<sup>3</sup>)-H functionalization of alkyl acetates by trihalomethyl superelectrophiles (Scheme 1) occurs primarily at the most distant secondary carbon. Because binding of a CBr<sub>3</sub><sup>+</sup> cation to the carbonyl oxygen creates a positive charge center, C-H bonds near the ester functional group are deactivated to cationic attack. In a similar way, the favorability of chain-contracting isomerization depends on the length of the tether between the two positive charge centers.<sup>2</sup> Although superelectrophilic C-H functionalization has limitations (functional group intolerance and a dependence on alkyl tether length), this new method offers a unique strategy for remote functionalization that merits further exploration.<sup>2</sup>

### Polymerizations in Superelectrophilic Conditions

Hydroxyalkylation of 1,2-diketones with arenes has recently been applied to polymer synthesis in superelectrophilic conditions (Scheme 2).<sup>3</sup> The reaction rate of the second arene condensation is much faster than the first, so there is an excess of aryl-terminated oligomers in the polymerization reaction (Scheme 3). Consequently, linear polymers synthesized in these conditions are less likely to macrocyclize and can reach very high molecular weights (MW > 10<sup>6</sup> Daltons). Furthermore, longer oligomers are less



**Scheme 3.** Difference in reaction rates in hydroxyalkylation leads to aryl-terminated oligomers.

nucleophilic because they possess a higher amount of positive charge due to protonation in the superacid medium. This results in a step-selective growth mechanism with low polydispersities (PDI < 1.2).<sup>3</sup> Hyperbranched polymers have also been synthesized in superelectrophilic conditions using AB<sub>2</sub> monomers. Because of a difference in reaction rates (Scheme 3), virtually 100% branching can occur even in a one-pot reaction.<sup>4</sup> In the future, a step-selective polymer growth mechanism based on differences in oligomer nucleophilicity might also be applied to hyperbranched polymers.

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