Rhodium-Catalyzed Reactions of 1,4-Benzoquinones with Electrophiles

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Substituted benzoquinones play key roles in diverse biological processes.1,2 Benzoquinones are also cytotoxic by virtue of their ability to stimulate oxidative stress or effect alkylation of cellular nucleophiles.3,4 Unsurprisingly, there has been significant recent interest in the development of methodologies for the C-H functionalization of benzoquinones, especially as such approaches might allow analogue synthesis by late stage derivatization.5 The lack of general methods to promote reaction of benzoquinone C-H bonds with electrophiles prompted us to explore the possibility of effecting related Rh-catalyzed processes on this substrate class.

Under Rh-catalyzed conditions, typically electrophilic 1,4-benzoquinones exhibit nucleophilic reactivity, such that exposure to appropriate electrophiles generates products of C-H iodination, bromination and selenylation. This provides a mild and general method for direct halofunctionalization, and the first method that can achieve direct C-H selenylation of this compound class. The scope and limitations of the new protocols were studied and representative derivatizations highlighted.

References