Two original methodologies for the functionalization of exoglycals through radical pathways

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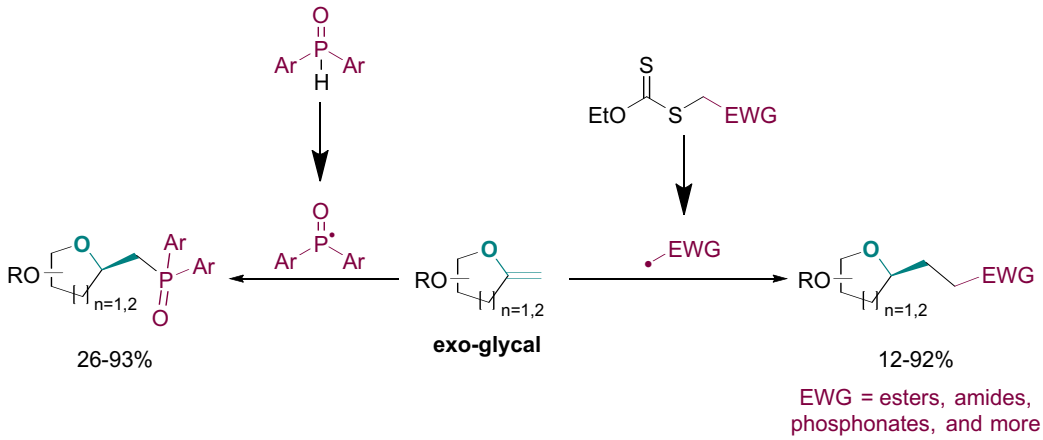
C-glycosides are a class of compounds constituted of a carbohydrate unit linked to an aglycon through a C-C linkage. They constitute powerful non-hydrolyzable mimics of *O*-glycosides and numerous examples of successful *C*-glycosides as therapeutic agents appeared, confirming the importance of their development. One efficient way to access *C*-glycosides is by reduction of a *C*-glycosylidene, often known as exoglycal and multiple methods were developed to functionalize glycals[1], some of them being by forming a radical glycosyl species[2].

We report two simple and original methods for the functionalization of exo-glycals as a way to synthesize *C*-glycosides. The first one is the hydrophosphorylation of exoglycals[3]: the reaction takes advantage of easily created P-centered radicals from secondary phosphine oxides *via* an EDA complex[4]. The second one is the hydroalkylation of exoglycals, allowed by an original initiating system using xanthates[5]. For both reactions, the radicals are added onto a range of glycals in moderate to excellent isolated yields. The methods present mild conditions, broad substrate scopes and good functional group tolerance. The mechanisms of the reactions were determined. Regiochemistry is completely controlled and stereochemistry is well to fully controlled in these reactions. Stereochemistry of the anomeric center was studied through NMR and XRD studies in both cases.



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