Aluminium Acetal in Radical Chemistry: The Ueno-Stork chemistry revisited

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γ-Lactones and butenolides represent important classes of compounds that are present in the skeleton of a large number of natural compounds. We have developed an efficient route to γ-lactols and methylene γ-lactols based upon an original Ueno-Stork-type radical cyclisation1 using thermally labile α-bromoaluminium acetics as the radical precursors.2 The resulting cyclic aluminium acetics proved to be suitable substrates for an oxidation reaction in the presence of aldehydes to give the corresponding γ-lactones3 or butenolides.4 This methodology was successfully applied to the synthesis of several natural compounds such as cognac lactone and maculalactone.5

A mechanistic study gave us insights into the mechanism of this cyclisation involving aluminium acetics, the structure of which was determined by low temperature NMR experiments, with the help of computational methods.5 Very recently we discovered that the diastereoselectivity of this original radical cyclisation involving α-bromo aluminium acetics could be controlled and, surprisingly, reversed, allowing us to prepare in a stereoselective manner polysubstituted tetrahydrofuran derivatives with up to 5 contiguous stereogenic centres. Our recent results in this field will be discussed here.

References

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