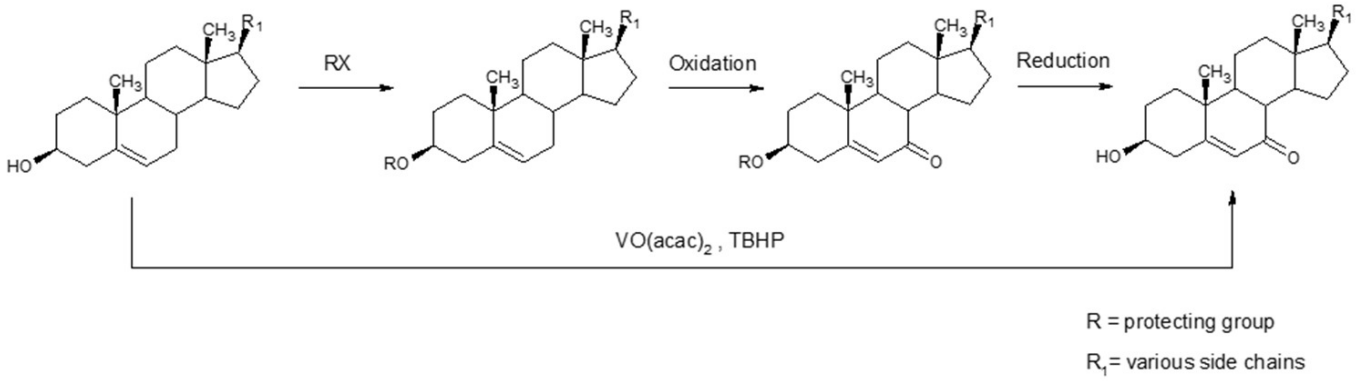
Allylic oxidation of steroidal olefins

The goal of steroid chemistry is to chemically modify naturally occurring steroids in a way that will alter their biological activity to the benefit of mankind, livestock, and plants. This process can be achieved by adding a new functional group to the four fused carbon rings that are characteristic of steroidal compounds. Our research, in particular, adds an oxygen atom to the ring system, forming what is called an alpha beta unsaturated ketone or enone. The enone has its own unique biological character apart from its parent steroid and can also be modified further.



Finding that a ketone could be formed at the allylic position of a steroidal compound is not in and of itself, novel. Nonetheless, this research is special for at least three reasons. First, our research has produced a tolerant and financially feasible method for steroidal oxidation that can be upsized. This method also does not require the steroidal substrate to have protection groups. In comparison to other methods used for steroidal oxidation, it is simply better. Second, our research has shown that vanadyl acetylacetonate, a poster child for epoxidation reactions, can be used for carbon-hydrogen activation at the laboratory scale. In addition, several vanadium species were tested and shown to work under our reaction's conditions. Third, we showed that ESI+ mass spectroscopy could be useful in qualitatively analyzing steroidal compounds without derivatization. Indeed, we submitted numerous spectra (including GCMS and NMR). In short, we expanded the boundaries of science by adding knowledge of a new steroid oxidation procedure, a new direction for a common reagent/catalyst, and a steroidal analytical method.

Publication

Allylic oxidation of steroidal olefins by vanadyl acetylacetonate and tert-butyl hydroperoxide.
Grainger WS, Parish EJ.
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