Chemical synthesis: A simple technique for highly functionalized compounds

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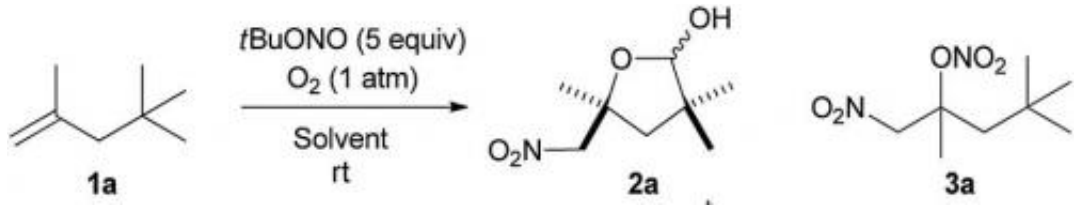

Oxidative nitration of alkene 1a to produce ɣ-lactol (2a) and nitrate ester (3a).

The addition of functional groups to certain unsaturated hydrocarbons, known as alkenes, is a crucial stage in the synthesis of various compounds, including many plastics. For these functionalization reactions to occur a carbon-hydrogen (C-H) bond must be activated, which is traditionally achieved using transition metal catalysts. However use of these catalysts has both economical and environmental drawbacks. Now researchers at Kanazawa University have demonstrated a technique that allows direct functionalization of alkenes without the need for metallic reagents, photolysis or extreme reaction conditions.

Tsuyoshi Taniguchi and colleagues at Kanazawa University developed work where they had reported a reaction of alkenes using tert-butyl nitrite and molecular oxygen. They monitored the reaction products—?-lactol and nitrate ester—using different solvents, and found that a high polarity aprotic (hydrogen-free) solvent gave the best yield, with ?-lactol as the major product.

They then experimented with different alkenes and observed how the products differed for branched and linear alkenes. Further reduction reactions demonstrated how the new synthesis technique could yield a range of useful derivatives, producing highly functionalized compounds from simple alkenes in only one or two steps.

The researchers were also able to propose a possible reaction mechanism. While the exact pathway remains uncertain, they suggest that the key step is the cleavage of an oxygen-oxygen bond to form a highly reactive alkoxy radical – a molecular component comprising an oxygen with single bonds either side to hydrocarbon chains.

The work demonstrates how substantial yields of highly functionalized compounds can be achieved from simple organic molecules in simple conditions with no metal catalyst. The authors conclude, "We believe that such 'simple and advanced reactions' are promising in the development of useful synthetic methods involving direct C–H functionalization."

More information: Taniguchi, T. et al. Multifunctionalization of alkenes via aerobic oxynitration and sp3 C–H oxidation, *Chem. Commun*, 49 (2013) 2198-2200.

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