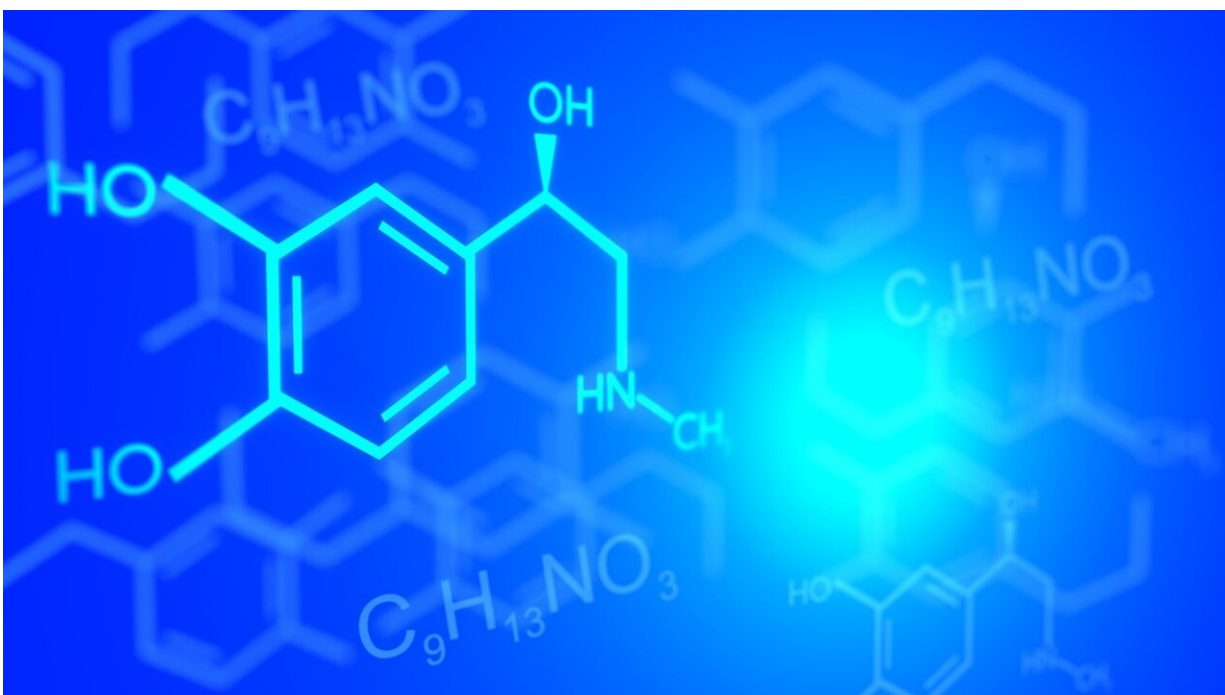


Breaking the C–H bonds in hydrocarbons to synthesize complex organic molecules

July 19 2021



Credit: Pixabay/CC0 Public Domain

The carbon–hydrogen bonds in alkanes—particularly those at the ends of the molecules, where each carbon has three hydrogen atoms bound to it—are very hard to "crack" if you want to replace the hydrogen atoms with other atoms. Methane (CH₄) and ethane (CH₃CH₃) are made up, exclusively, of such tightly bound hydrogen atoms. In the journal *Angewandte Chemie*, a team of researchers has now described how they

break these bonds while forming new carbon–nitrogen bonds (amidation).

If it were possible to easily break the C–H bonds in hydrocarbons, it would be possible to synthesize [complex organic molecules](#), such as pharmaceuticals, much more conveniently and directly from petroleum. This strategy could also provide more pathways for recycling plastic waste. The formation of carbon–nitrogen bonds is of particular interest because these play an important role in [natural products](#). For example, amide bonds link individual amino acids into proteins.

Although there has been some success in the functionalization of heavy hydrocarbons, even at the end positions, the particularly strong C–H bonds of light alkanes, especially methane, can hardly be split at all. The use of these primary components of natural gas as synthetic building blocks is especially desirable, as it would allow for the use of this often wasted side-product of oil extraction.

A team led by Ana Caballero and Pedro J. Pérez (Universidad de Huelva, Spain), as well as John F. Hartwig (University of California, Berkeley, U.S.) has now successfully coupled amides (nitrogen-containing organic compounds) to light alkanes with loss of a hydrogen atom. The products of these dehydrogenative amidations are known as N-alkyl amides.

The starting point for this approach was the amidation of C–H bonds in heavy alkanes with a copper-based catalyst and di-tert-butyl peroxide as an oxidizing agent, as developed several years ago by the Hartwig group. Variation of the catalyst led to success. If the copper has phenanthroline-type ligands (an aromatic, nitrogen-containing system of three six-membered rings), it is possible to produce [high yields](#) in the reaction of ethane with benzamide—as well as a number of other amides—using benzene as a solvent. The reaction also worked when supercritical carbon

dioxide—a more environmentally friendly option—was used as a solvent. The reaction with ethane is an unusual C–N bond formation with a non-activated primary C–H [bond](#).

Propane, n-butane, and iso-butane gave similar results. In the light alkanes, reactivity correlates significantly more strongly with the dissociation energy of the C–H bonds than in higher alkanes.

And methane? Even the toughest candidate—amidation of methane has never previously been observed—could be coupled to the amide. Isotopic experiments were used to prove that methane reacts to form N-methylbenzamide.

More information: M. Ángeles Fuentes et al, Copper-Catalyzed Dehydrogenative Amidation of Light Alkanes, *Angewandte Chemie International Edition* (2021). [DOI: 10.1002/anie.202104737](https://doi.org/10.1002/anie.202104737)

Provided by Wiley

Citation: Breaking the C–H bonds in hydrocarbons to synthesize complex organic molecules (2021, July 19) retrieved 23 June 2024 from <https://phys.org/news/2021-07-ch-bonds-hydrocarbons-complex-molecules.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.