G. LAUDADIO, Y. DENG, K. VAN DER WAL, D. RAVELLI, M. NUÑO, M. FAGNONI, D. GUTHRIE, Y. SUN, T. NOËL* (EINDHOVEN UNIVERSITY OF TECHNOLOGY, THE NETHERLANDS)

C(sp³)-H Functionalizations of Light Hydrocarbons using Decatungstate Photocatalysis in Flow Science 2020, 369, 92-96.

C-H Activation of Gaseous Alkanes

R¹-H + R³ TBADT (1.0-5.0 mol%)

R1 - H (4.1-20 equiv) R³ 365 nm LED, r.t. acetonitrile-H₂O (7:1), r.t., 4-8 h

R¹ = Me, Et, Pr,
$$\dot{F}$$
Bu continuous flow 38 examples 93

 R^2 , R^3 = nitrile, ester, amide, ketone R4 = H, arene, Alk...

continuous flow 38 examples, 93% yield

Proposed mechanism:

Selected examples:

Significance: Noël and co-workers describe a photocatalytic C-H activation of gaseous alkanes and subsequent trapping with various Michael acceptors in continuous flow. The corresponding alkylated products were obtained in moderate to excellent yields.

Comment: Mechanistically, the authors propose an initial activation of the photocatalyst TBADT, which relaxes to its active form wO. A hydrogen abstraction forms a carbon-centered radical, which undergoes a 1,4-addition to a Michael acceptor. Hydrogen back-donation affords the alkylated product and regenerates the catalyst.

SYNFACTS Contributors: Paul Knochel, Ferdinand H. Lutter DOI: 10.1055/s-0040-1705827; Reg-No.: F02220SF

Flow Chemistry

Key words

photocatalysis C-H functionalization hydrocarbons

