H. ZHANG, E. B. HAY, S. J. GEIB, D. P. CURRAN* (UNIVERSITY OF PITTSBURGH, USA) Radical Cyclications of Cyclic Ene Sulfonamides Occur with β -Elimination of Sulfonyl Radicals to Form Polycyclic Imines

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Polycyclic Imines via Radical Cyclization of Ene Sulfonamides

$$X = 1, Br$$

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$$X = 1 55\% \text{ yield}$$

$$X = 1 48\% \text{ yield}$$

Significance: Reported is a radical cyclization of cyclic ene sulfonamides to give stable bicyclic and tricyclic imines in good yields. Mechanistically, an α -sulfonamidoyl radical, which is generated after the initial radical cyclization, undergoes β-elimination to form the imine product and a phenylsulfonyl radical. In a related method, 3,4-dihydroquinolines can also be synthesized by radical translocation (1,5-hydrogen transfer) reactions of N-(2-halophenylsulfonyl)tetrahydroisoquinolines. In both cases, the very stable sulfonamides are cleaved under mild reductive conditions.

Comment: Imines are highly versatile synthetic intermediates, which are commonly made by condensing the corresponding aldehydes and ketones with amines. The radical cyclization methodology described in this paper provides alternative bond construction and reaction conditions. It is also synthetically useful due to the facile cleavage of the strong N–SO₂Ar bond; these are hard to remove otherwise, for example, by hydrolysis or reduction.

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Synthesis of Heterocycles

Key words

polycyclic imines radical cyclization β-sulfonyl radical elimination