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Filip Gracias, Hana Dvořáková, Tomáš Martinů

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The Beckmann fragmentation of quadricyclanone oxime

Filip Gracias^a, Hana Dvořáková^b, Tomáš Martinů^{a,*}

^aDepartment of Organic Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

^bLaboratory of NMR Spectroscopy, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague, Czech Republic

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ABSTRACT

The attempted *O*-tosylation of tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-one (quadricyclanone) oxime with *p*-toluenesulfonyl chloride in dichloromethane in the presence of triethylamine/DMAP or pyridine resulted in the Beckmann fragmentation to give a mixture of 4-*exo*-/4-*endo*-tosyloxy- and 4-*exo*-/4-*endo*-chlorobicyclo[3.1.0]hex-2-ene-6-*endo*-carbonitriles in 90% overall yield. Solvolysis of all four products in 2,2,2-trifluoroethanol afforded the corresponding 4-*exo*-trifluoroethoxy derivative as the sole product. Quadricyclanone itself undergoes the fragmentation reaction with hydroxylamine-*O*-sulfonic acid, selectively affording the 4-*exo*-hydroxy-6-*endo*-nitrile in 90% isolated yield.

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* Corresponding author. Tel.: +420-220-444-173; fax: +420-220-444-288; e-mail: martinut@vscht.cz

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