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PII: S0040-4039(17)30032-1
DOI: http://dx.doi.org/10.1016/j.tetlet.2017.01.020
Reference: TETL 48523

To appear in: *Tetrahedron Letters*

Received Date: 21 October 2016
Revised Date: 22 December 2016
Accepted Date: 6 January 2017

Please cite this article as: Gracias, F., Dvoř áková, H., Martinů, T., The Beckmann fragmentation of quadricyclanone oxime, *Tetrahedron Letters* (2017), doi: http://dx.doi.org/10.1016/j.tetlet.2017.01.020

Tetrahedron Letters
journal homepage: www.elsevier.com

The Beckmann fragmentation of quadricyclanone oxime

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Beckmann fragmentation
Cage molecules
Small molecules
Ring-opening reactions
Reactive intermediates

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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