

SHORT
COMMUNICATIONSFirst Example of Ionic Hydrogenation
in the Bicyclo[1.1.0]butane SeriesV. A. Vasin^a, S. G. Kostryukov^a, S. Yu. Vovod^a, P. S. Petrov^a, and V. V. Razin^b^a Ogarev Mordovian State University, Saransk, Russia^b St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
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Received March 14, 2007

DOI: 10.1134/S1070428007090266

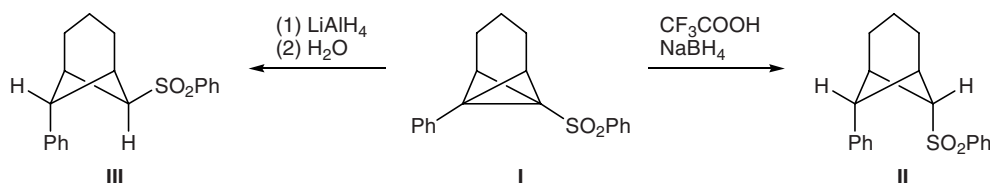
Bicyclo[1.1.0]butanes having an electron-withdrawing sulfonyl group at the bridgehead position (“activated bicyclobutanes”) are known [1] to undergo reduction to cyclobutyl sulfones by the action of LiAlH_4 as hydride ion carrier in a way similar to the reduction of activated alkenes (α,β -unsaturated sulfones) to alkyl sulfones with the same reducing agent [2]. Taking into account the olefin-like character of the central bicyclobutane C–C bond [3], it might be expected that bicyclobutanes having an electron-donor group at the bridgehead position, like nucleophilic alkenes (e.g., 2-methylpropene or styrene), will undergo ionic hydrogenation [4, 5] by the action of strong acids in the presence of a hydride ion source (Et_3SiH , NaBH_4 , etc.). However, we have found no published data on such version of hydrogenation of bicyclobutane derivatives. In the present communication we report on the first example of successful ionic hydrogenation in the bicyclobutane series.

As initial compound we selected a bridged bicyclobutane derivative, 1-phenyl-7-phenylsulfonyltricyclo[4.1.0.0^{2,7}]heptane (**I**) [6]. Treatment of **I** with trifluoroacetic acid and NaBH_4 at -10°C under dry argon (i.e., under the conditions of ionic hydrogenation reported in [5]) gave norpinane **II** in 41% yield. Despite moderate yield, the product can be readily isolated from the reaction mixture by crystallization. Its structure and steric configuration were reliably determined on the basis of the ^1H and ^{13}C NMR data.

As expected, compound **I** was also reduced with LiAlH_4 in THF at 0°C , but the product was compound **III** (yield 91%) which is epimeric to norpinane **II** at C^7 . By special experiment we showed that sterically hindered norpinane **II** is converted almost completely into more stable diastereoisomer **III** in 5 h on heating with potassium *tert*-butoxide in boiling THF. We also found that even trace amounts of norpinane **III** were not formed in the ionic hydrogenation of tricycloheptane **I** with LiAlH_4 .

6-*exo*-Phenyl-7-*anti*-phenylsulfonylbicyclo[3.1.1]-heptane (II). mp $134\text{--}135^\circ\text{C}$ (from hexane–ethyl acetate). ^1H NMR spectrum, δ , ppm: 1.80–2.04 m (2H, 3-H); 2.05–2.22 m and 2.23–2.40 m (2H each, 2-H, 4-H); 3.06 d (1H, 6-H, $J = 3.1$ Hz); 3.23 d (1H, 7-H, $J = 3.1$ Hz); 3.30 br.s (2H, 1-H, 5-H); 7.22–7.32 m (3H), 7.32–7.43 m (2H), 7.44–7.53 m (2H), 7.56–7.66 m (1H), and 7.71 d (2H, $J = 7.6$ Hz) (H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 14.8 (C^3); 33.0 (C^2 , C^4); 40.0 (C^1 , C^5); 47.5 (C^6); 70.2 (C^7); 125.7, 126.9 (3C), 127.7 (2C), 127.9 (2C), 128.9 (2C), 133.0, 140.5 (C_{arom}). Found, %: C 72.87; H 6.37. $\text{C}_{19}\text{H}_{20}\text{SO}_2$. Calculated, %: C 73.04; H 6.45.

6-*exo*-Phenyl-7-*syn*-phenylsulfonylbicyclo[3.1.1]-heptane (III). mp $127\text{--}128^\circ\text{C}$ (from chloroform–hexane, 2:1). ^1H NMR spectrum, δ , ppm: 1.89–2.09 m (1H, *endo*-3-H); 2.09–2.21 m (3H, *exo*-3-H, *endo*-2-H, *endo*-4-H); 2.73–2.87 m (2H, *exo*-2-H, *exo*-4-H);



3.00 br.d (2H, 1-H, 5-H); 3.22 s (1H, 6-H); 3.58 t (1H, 7-H, $J = 5.8$ Hz); 7.19–7.27 m (2H), 7.27–7.38 m (3H), 7.50–7.69 m (3H), and 7.84 d (2H, $J = 7.6$ Hz) (H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 14.6 (C^3); 24.6 (C^2, C^4); 43.1 (C^1, C^5); 44.8 (C^6); 60.0 (C^7); 126.4, 127.0 (2C), 127.4 (3C), 128.6 (2C), 129.2 (2C), 133.3, 140.4 (C_{arom}). Found, %: C 72.99; H 6.41. $\text{C}_{19}\text{H}_{20}\text{SO}_2$. Calculated, %: C 73.04; H 6.45.

The ^1H and ^{13}C NMR spectra were recorded from solutions in CDCl_3 on a Bruker DPX-300 spectrometer at 300.130 and 75.468 MHz, respectively.

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