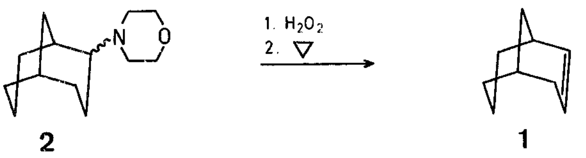
COMMUNICATIONS

A Facile Method of Preparation of Bicyclo[3.3.1]non-2-ene

Hirosi KATO and Mituyosi KAWANISI

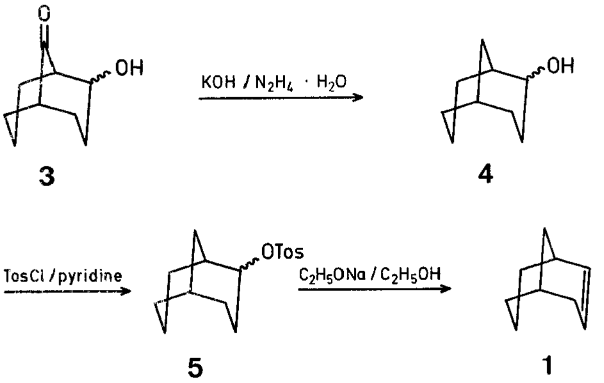
Department of Industrial Chemistry, Kyoto University, Kyoto, Japan

The heretofore most convenient method of preparation of bicyclo[3.3.1]non-2-ene[1] (**1**) involves the Cope elimination[2] on the intermediate amine (**2**) as a key step:



This procedure, however, requires the use of platinum black[3] to remove excess hydrogen peroxide, which considerably increases the period of reaction. According to our experience, insufficient removal of hydrogen peroxide can result in a violent explosion.

A more facile method is illustrated as follows:



An epimeric mixture of the keto-alcohols (**3**) is easily obtained using a procedure of Cope[4]. Wolff-Kischner-Huang Minlon reduction[5] of **3** gives **4** (*endo*:*exo* = 9:1) in 82% yield. Esterification of **4** with tosyl chloride in pyridine[6] gives **5** in 60% yield. Treatment of **5** with sodium ethoxide in ethanol affords the expected olefin (**1**) in 89% yield. The overall yield of **1** based on **3** is 43%.

These transformations are all familar reactions and do not involve any hazardous manipulations. A novel feature of the present method is the stereoselective elimination of the *endo*-tosyloxy group in **5** which gives exclusively **1**, whereas the *exo* group remains intact under the experimental conditions.

This result may reflect the chair conformation prevailing in the bicyclo[3.3.1]nonane system[7], which enables *trans* orientation of an *endo*-tosyloxy group and an adjacent methylene hydrogen in **5**, thus facilitating the base-catalyzed β-elimination[8].

Although the formation of **4** by means of lithium alanate reduction of 2-oxobicyclo[3.3.1]nonane derived from **2** has been claimed to be more stereoselective than the reaction **3**→**4** (*endo*:*exo* = 99:1)[9], this route from **2** leading to **1** seems less practical than the procedure reported here since more steps are involved.

2-Tosyloxybicyclo[3.3.1]nonane (5): A solution of tosyl chloride (9.1 g; 0.047 mol) in pyridine (15 ml) was added dropwise in the course of 5 min. to a solution of 2-hydroxybicyclo[3.3.1]nonene (4)[4] (5.2 g; 0.037 mol) in pyridine (20 ml) with cooling below −5°. After the slightly exothermic reaction had subsided, the mixture was allowed to stand overnight at room temperature, was extracted three times with benzene (3 x 30 ml), and the organic layer washed with water until pyridine was removed completely. Drying (Na_2SO_4) of the extract, followed by evaporation of the solvent, gave an epimeric mixture of **5** (6.9 g), which was subjected to the following reaction without further purification.

Bicyclo[3.3.1]nonene (1): To a suspension of **5** in absolute ethanol (10 ml), a solution of sodium ethoxide prepared from 0.50 g of sodium and 20 ml of absolute ethanol was added in the course of 5 min. and the mixture was heated under reflux overnight. After cooling to room temperature followed by neutralization with dilute acetic acid, the mixture was extracted with hexane (3 x 60 ml). The organic layer was washed several times with water and finally with a saturated sodium chloride solution, and dried (Na_2SO_4). Careful removal of the solvent gave a slightly yellow oil (2.1 g) which was purified by column chromatography on alumina. Elution with hexane gave **1**; yield: 180 g (89%); m.p. 94.5–96° (Lit.[9], m.p. 96.5–97°).

I.R. (®Nujol): 3040, 1650, 1000, 910, 880, 760, 700, and 670 cm^{-1}. N.M.R. ($CDCl_3$): $\delta = 5.85$–5.55 (m, 2 H, olefinic) and 2.3–1.0 (m, 12 H) ppm from TMS.

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