New reagents for the iodobromination of alkenes

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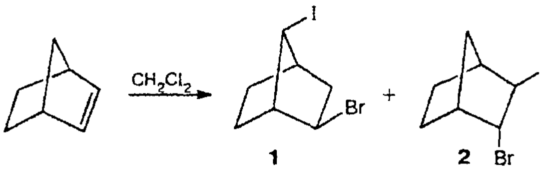
Despite a great number of studies dealing with mixed halogenation of unsaturated compounds, only few examples of the interaction of IBr with olefins resulting in mixtures of iodobromides, dibromides, and diiodides are known.[1]

Earlier,[2] we found effective iodochlorinating reagents based on $KICl_2$. In continuation of these studies, we discovered the perfect iodobrominating properties of $KIBr_2$ and of the KI—PBr_5 system.

Thus, $KIBr_2$ reacts with norbornene at −30 °C to give a mixture of bromoiodonorbornanes **1** and **2** in high yield. In the case of the KI—PBr_5 system, the reaction proceeds analogously even at −70 °C, which suggests its stronger electrophilic properties. When comparing the ratio of the rearranged adduct (**1**) to the non-rearranged one (**2**), one can conclude that the reagents have an approximately equal effective electrophilicity.[3]



	1	**2**
KI—PBr_5	24%	25%
$KIBr_2$	39%	33%

Thus, we found two new reagents for iodobromination of olefins. It was demonstrated that use of $KIBr_2$ results in a high yield of iodobromination products and is convenient for carrying out the reaction. The KI—PBr_5 system has a high reactivity, but gives a lower yield of the main products due to side processes.

^1H and ^{13}C NMR spectra were obtained on a VXR-400 Varian instrument (^1H, 400 and ^{13}C, 100 MHz). The chemical shifts are given in the δ scale with tetramethylsilane as the internal standard.

Procedure of iodobromination. ***A.*** **$KIBr_2$.** $KIBr_2$ (1.63 g, 0.005 mol) was added to a solution of norbornene (0.47 g, 0.005 mol) in 15 mL of CH_2Cl_2 cooled to −30 °C and stirred at this temperature for 0.5 h. The solvent was removed *in vacuo*, and the residue was chromatographed on silica gel «Silpearl» with hexane as the eluent. 2-*exo*-Bromo-7-*syn*-iodobicyclo[2.2.1]heptane (**1**) (0.58 g, 39%) was obtained, ^1H NMR ($CDCl_3$), δ: 1.25—1.40 (m, 2 H, *endo*-H-5, *endo*-H-6); 1.60—1.79 (m, 2 H, *exo*-H-5, *exo*-H-6); 2.21 (ddd, 1 H, *endo*-H-3, J_1 = 14 Hz, J_2 = 8.2 Hz, J_3 = 1.1 Hz); 2.44 (t, 1 H, H-4, J = 4 Hz); 2.65 (m, 1 H, *exo*-H-3); 22.70 (d, 1 H, H-1, J = 4 Hz); 3.81 (br.s, 1 H, H-7); 3.92 (ddd, 1 H, H-2, J_1 = 8 Hz, J_2 = 5 Hz, J_3 = 1 Hz), ^{13}C NMR ($CDCl_3$), δ: 24.1; 26.3; 29.0; 43.1; 46.0; 48.5; 50.8; 2-*endo*-Bromo-3-*exo*-iodobicyclo[2.2.1]heptane (**2**) (0.50 g, 33%) was obtained, ^1H NMR ($CDCl_3$), δ, J: 1.33—1.40 (m, 1 H, *endo*-H-6); 1.47 (m, 1 H, *anti*-H-7); 1.60—1.68 (m, 2 H, *exo*-H-5, *exo*-H-6); 1.80—1.87 (m, 1 H, *endo*-H-5); 2.09 (m, 1 H, *syn*-H-7); 2.38 (br.s, 1 H, H-1); 2.49 (br.s, 1 H, H-4); 3.93 (dd, 1 H, H-3, J_1 = 3.9 Hz, J_2 = 2.8 Hz); 4.52 (dd, 1 H, H-2, J_1 = 4.1 Hz, J_2 = 4.3 Hz), ^{13}C NMR ($CDCl_3$), δ: 27.8; 29.0; 34.6; 38.1; 41.6; 46.7; 48.6. For the mixture of **1** and **2**, found (%): C, 43.15; H, 3.60. C_8H_8BrCl. Calculated (%): C, 43.74; H, 3.64.

B. **The KI—PBr_5 system.** KI (0.83 g, 0.005 mol) was added to a solution of PBr_5 (2.16 g, 0.005 mol) in 10 mL of CH_2Cl_2 cooled to −70 °C and stirred for 5 min. Then, a solution of norbornene (0.47 g, 0.005 mol) in 5 mL of CH_2Cl_2 was added. The reaction mixture was stirred at this temperature for 0.5 h. The isolation of products was performed by analogy with procedure *A*. Compound **1** (0.36 g, 24%) and compound **2** (0.37 g, 25%) were obtained.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33250).

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Received April 25, 1997

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1557—1558, August, 1997.