

SHORT
COMMUNICATIONSOxidation of Adamantane with Hypobromous Acid
Generated *in situ* from $\text{CH}_n\text{Br}_{4-n}$ and H_2O in the Presence
of Molybdenum ComplexesR. I. Khusnutdinov, N. A. Shchadneva, R. Yu. Burangulova,
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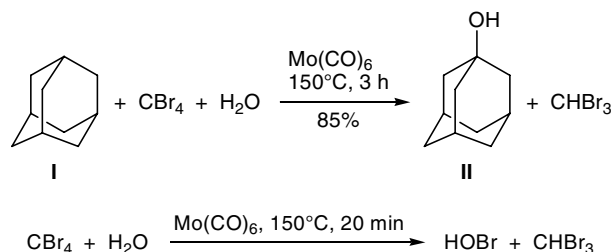
Oxidation of hydrocarbons of the adamantane (**I**) series underlie important preparative procedures for the synthesis of their oxygen-containing derivatives, in particular of adamantan-1-ol (**II**). Adamantan-1-ol is used as starting material for the preparation of such important drugs as Amantadine (Symmetrel), Remantadine, and Kemantan [1].

Adamantan-1-ol (**II**) can be synthesized by catalytic oxidation of adamantane (**I**) with such oxidants as oxygen, hydrogen peroxide, alkyl hydroperoxides, and iodosylbenzene in the presence of Co, Mn, Fe, and Ru complexes [1–12]. Catalytic oxidation of adamantane (**I**) generally gives mixtures of products. For example, the oxidation of **I** with atmospheric oxygen in pyridine–acetic acid in presence of an iron catalyst and zinc at 40°C afforded a mixture of adamantan-1-ol and adamantan-2-ol whose ratio ranged, depending on the conditions, from 10:1 to 24.8:1, the overall yield being 6–16% [8].

Porphyrin manganese complexes catalyze oxidation of adamantane (**I**) with such oxidants as NaClO_2 , magnesium monoperoxyphthalate, and potassium peroxosulfate; in these cases, the reaction occurred preferentially at the tertiary carbon atom [9]. Catalytic oxidation of adamantane (**I**) with formation of three oxygen-containing products, adamantan-1-ol (**II**, 68%), adamantane-1,3-diol (**III**, 25%), and adamantan-2-one (**IV**, 1%) was reported in [10]; here, 2,6-dichloropyridine *N*-oxide was used as oxidant in the presence of (tetraphenylporphyrinato)(carbonyl)ruthenium [Ru(TPP)(CO)] as catalyst. Ruthenium compounds

also catalyze oxidation of adamantane with sodium periodate at 40°C [11]. The reaction involves mainly the bridgehead carbon atom in molecule **I**. However, despite prolonged heating (26 h), the conversion did not exceed 81%, and the fraction of adamantan-1-ol (**II**) in the reaction mixture was 82%.

We performed selective oxidation of adamantane (**I**) to adamantan-1-ol (**II**) with the system $\text{CBr}_4\text{--H}_2\text{O--Mo(CO)}_6$. The reaction was complete in 3 h at 150°C, and the yield of **II** was about 85%, the conversion of **I** being 85%. The catalyst and reactant ratio $[\text{Mo(CO)}_6]:[\text{I}]:[\text{CBr}_4 \text{ or } \text{CHBr}_3]:[\text{H}_2\text{O}]$ was 1:100:100:(1000–2000). Apart from adamantan-1-ol (**II**), the reaction mixture contained bromoform (major product) and a small amount of CH_2Br_2 (according to the GLC and MS data), indicating that CBr_4 is involved in the oxidation process. No reaction occurred in the absence of CBr_4 . Iodometric titration of the reaction mixture revealed active bromine; this means that hypobromous acid (HOBr) is generated in the system. The concentration of HOBr was estimated at 0.9 mg/ml; therefore, we presumed that hypobromous acid is the true oxidant in this reaction.



The conversion of adamantane (**I**) attains 100% on prolonged reaction; however, the product mixture becomes more complex due to formation of 1-bromo-adamantane (**V**), 3-bromoadamantan-1-ol (**VI**), and adamantane-1,3-diol (**VII**), the molar ratio **II**:**V**:**VI**:**VII** being 5:1:4:2. Replacement of CBr_4 in the oxidizing system by CHBr_3 leads to reduced conversion of adamantane (**I**) (50%), and the reaction becomes less selective. After 1 h, the reaction mixture contained adamantan-1-ol (**II**), 3-bromoadamantan-1-ol (**VI**), and adamantane-1,3-diol (**VII**) at a ratio of 5:1:1.

The oxidation was carried out in a glass ampule or in a high-pressure stainless steel microreactor. The results of parallel runs differed insignificantly. A reactor (or an ampule) was charged at 90°C under argon with 0.1 mmol of $\text{Mo}(\text{CO})_6$, 10 mmol of adamantane (**I**), 10 mmol of CBr_4 (or CHBr_3), and 100–200 mmol of water. The reactor was hermetically capped (the ampule was sealed) and heated for 3 h at 150°C under stirring. When the reaction was complete, the reactor (ampule) was cooled to ~20°C and opened, the reaction mixture was extracted with methylene chloride (3×5 ml), the solvent was distilled off from the extract, and the residue was recrystallized from hexane.

Adamantan-1-ol (II) was isolated by column chromatography. The product sublimes at 92°C (10 mm), mp 282–283°C (subl.); published data [12]: mp 283–284°C (subl.). ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 67.90 (C^1), 45.32 (C^2 , C^8 , C^9), 30.85 (C^3 , C^5 , C^7), 36.15 (C^4 , C^6 , C^{10}).

1-Bromoadamantane (**V**), 3-bromoadamantan-1-ol (**VI**), and adamantane-1,3-diol (**VII**) were identified by comparing their properties with those of authentic samples and with reference data [1, 13, 14].

The products were analyzed by gas–liquid chromatography on Tsvet-102 and Chrom-5 instruments equipped with flame ionization detectors; 1.2-m×3-

mm column packed with 5% of SE-30 on Chromaton N-AW-HMDS (0.125–0.160 mm); carrier gas helium, flow rate 50 ml/min; oven temperature programming from 50 to 220°C. The ^{13}C NMR spectra were recorded on a JEOL FXQ instrument at 22.5 MHz using tetramethylsilane as internal reference.

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