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SHORT COMMUNICATIONS

Oxidation of Adamantane with Hypobromous Acid Generated *in situ* from CH_nBr_{4-n} and H_2O in the Presence of Molybdenum Complexes

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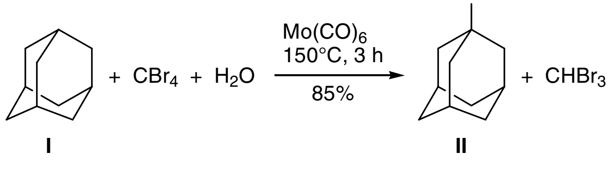
Oxidation of hydrocarbons of the adamantane (**I**) series underlie important preparative procedures for the synthesis of their oxygen-containing derivatives, in particular of adamantan-1-ol (**II**). Adamantan-1-ol is used as starting material for the preparation of such important drugs as Amantadine (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 CBr_4–H_2O–$Mo(CO)_6$. 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 $[Mo(CO)_6]$: [**I**] : [CBr_4 or $CHBr_3$] : [H_2O] 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.



I **II**

$$CBr_4 + H_2O \xrightarrow{Mo(CO)_6,\ 150°C,\ 20\ min} HOBr + CHBr_3$$

The conversion of adamantane (**I**) attains 100% on prolonged reaction; however, the product mixture becomes more complex due to formation of 1-bromoadamantane (**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 $Mo(CO)_6$, 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.

REFERENCES

1. Bagrii, E.I., *Adamantany* (Adamantanes), Moscow: Nauka, 1989.
2. Landa, S., Vais, J., and Burkhard, J., *Z. Chem.*, 1967, vol. 7, p. 223.
3. Janku, J. and Landa, S., *Collect. Czech. Chem. Commun.*, 1970, vol. 35, p. 375.
4. Kovalev, V.V., Fedorova, O.A., and Shokova, E.A., *Zh. Org. Khim.*, 1987, vol. 23, p. 451.
5. Shul'pin, G.B., Lederer, P., and Matsova, E., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, p. 2638.
6. Baciocchi, E., Del-Gacco, T., and Sebastiani, G.V., *Tetrahedron Lett.*, 1987, vol. 28, p. 1941.
7. Olah, G.A. and Lucas, J., *J. Am. Chem. Soc.*, 1968, vol. 90, p. 933.
8. Barton, D.H.R., Boivin, J., Ozbalik, N., and Schwartzentuber, K.M., *Tetrahedron Lett.*, 1984, vol. 25, p. 4219.
9. Bagrii, E.I. and Nekhaev, A.I., *Neftekhimiya*, 1996, vol. 36, p. 483.
10. Ohtake, H., Higuchi, T., and Hirobe, M., *J. Am. Chem. Soc.*, 1992, vol. 114, p. 10660.
11. Bakke, J.M. and Lundquist, M., *Acta Chem. Scand., Ser. B*, 1986, vol. 40, p. 430.
12. Lerman, B.M., Aref'eva, Z.Ya., Tolstikov, G.A., Galin, F.Z., and Kuzyev, A.R., *Khimiya i fizicheskaya khimiya monomerov* (Chemistry and Physical Chemistry of Monomers), Ufa, 1975, p. 121.
13. Fort, R.C., *Adamantane: The Chemistry of Diamond Molecules*, New York: Marcel Dekker, 1976.
14. *Catalog Handbook of Fine Chemicals*, Aldrich, 2003–2004.