Formation of dehydrogenated derivatives upon the oxidative dehydrogenation of adamantanes

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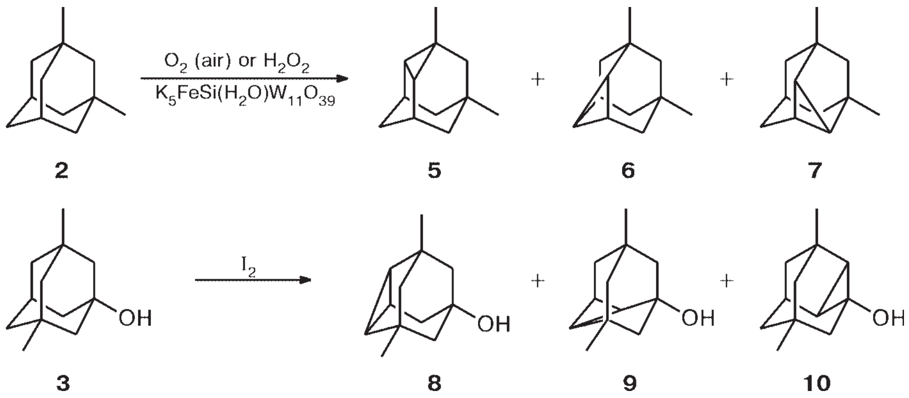
Dehydroadamantanes whose framework includes a three-membered cyclic fragment are usually obtained from the corresponding dihalides.[1] We demonstrated for the first time with adamantane (**1**), 1,3-dimethyladamantane (**2**), and 3,5-dimethyladamantan-1-ol (**3**) as examples that three-membered rings can close upon direct oxidative dehydrogenation of these compounds on polyoxometallates (POMs) or under the action of iodine. The presence of strained three-membered rings makes dehydroadamantanes convenient starting reagents for the preparation of difficultly accessible adamantane derivatives.[2—4]

Compounds **1** and **2** were dehydrogenated in the presence of the POMs $K_5FeSi(H_2O)W_{11}O_{39}$ and $Na_6MnSi(H_2O)W_{11}O_{39}$ applied to Al_2O_3 at 150—250 °C in the pulse regime in a flow of helium (with H_2O_2 as an oxidant or without any oxidant) or air. Actually, the dehydrogenation occurs only with the iron-containing POM. Starting from adamantane (**1**), we obtained (250 °C, air, contact time 6 s) two compounds with $[M]^+$ 134 in the ratio 3 : 1 (yield 0.8%). Apparently, these are 2,4-dehydroadamantane[5] and 1,3-dehydroadamantane (**4**), respectively. When oxidized with H_2O_2 (150—250 °C, contact time 2 to 6 s), hydrocarbon **2** gave 1,3-dimethyl-4,8- (**5**), -4,6- (**6**), and -4,9- (**7**) -dehydroadamantanes (1.6 : 1 : 1.6) in 2.0—2.6% yield (Scheme 1). With atmospheric oxygen as an oxidant, compounds **5** and **6** were formed in the ratio 1 : 2.3 (yield 0.1—3.0%). In a flow of helium, without any oxidant except for the oxygen contained in POM, the sole product was dehydroadamantane **6** (250 °C, contact time 6 s, yield 0.2%). No oxygen-containing products were detected.

Under the action of iodine, adamantane (**1**) (250 °C, the molar ratio 2 : 1, 2 h) decomposes into HI and a number of destruction products (yield 84%). The reaction of 1,3-dimethyladamantane (**2**) with I_2 (200 °C, 1 : 1, 2 h) yields compound **6** only in trace amounts (<0.1%). The presence of the OH group significantly increases the reactivity of the H atoms of the adamantane framework. Dehydrogenation of alcohol **3** with iodine (200 °C, 1 : 1, 2 h) gives only dehydrogenated products, namely, 3,5-dimethyl-6,8- (**8**), -6,10- (**9**), and -2,10- (**10**) -dehydroadamantan-1-ols (2 : 7 : 1, yield 40%, see Scheme 1).

The reaction products were analyzed by GLC-MS using a Finnigan MAT 95 XL instrument (ionizing voltage 70 eV, cathodic current 1 mA, mass range 20—800, resolution 1000, source temperature 200 °C, scan rate 1 s per mass decade) and an HP 6890+ chromatograph (capillary column, SE-30, helium as

Scheme 1



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a carrier gas (0.7 mL min^{-1}); temperature elevation was programmed from 30 to 120 °C at a rate of 5 °C min^{-1} and from 120 to 270 °C at a rate of 10 °C min^{-1}, with keeping at 270 °C for 10 min). The structures of isomers **5**—**7** and **8**—**10** were assigned on the assumption that a lower yield of isomeric dehydrogenated products from the reaction with atmospheric oxygen and iodine is due to more considerable steric hindrances to their formation.

MS, *m/z* (I_{rel} (%)): (**3**) 180 $[M]^+$ (27.3), 123 $[M - Me - C_3H_6]^+$ (100); (**4**) 134 $[M]^+$ (100); (**5**) 162 $[M]^+$ (100); (**6**) 162 $[M]^+$ (100); (**7**) 162 $[M]^+$ (97.5), 106 $[M - Me - All]^+$ (100); (**8**) 178 $[M]^+$ (79.5), 93 $[M - Me - C_5H_{10}]^+$ (100); (**9**) 178 $[M]^+$ (73.9), 107 $[M - Me - C_4H_8]^+$ (100); (**10**) 178 $[M]^+$ (89.6), 107 $[M - Me - C_4H_8]^+$ (100).

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References

1. E. I. Bagrii, *Adamantany. Poluchenie, svoistva, primenenie* [*Adamantanes: Synthesis, Properties, and Application*], Nauka, Moscow, 1989, 218 pp. (in Russian).
2. B. I. No, G. M. Butov, and S. M. Ledenev, *Zh. Org. Khim.*, 1992, **28**, 606 [*Russ. J. Org. Chem.*, 1992, **28** (Engl. Transl.)].
3. B. I. No, G. M. Butov, V. M. Mokhov, and S. A. Safonov, *Zh. Org. Khim.*, 1998, **34**, 942; 1570 [*Russ. J. Org. Chem.*, 1998, **34** (Engl. Transl.)].
4. B. I. No, G. M. Butov, and S. M. Ledenev, *Zh. Org. Khim.*, 1999, **35**, 154 [*Russ. J. Org. Chem.*, 1999, **35** (Engl. Transl.)].
5. J. Mitera, P. Zachar, J. Burkhard, and L. Vodicka, *Sbornik Vysoke Skoly Chemicko-technologicke v Praze*, 1976, **32**, 103.

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