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LETTERS TO THE EDITOR

Reactions of 1,3-Dehydroadamantane with Some Aromatic Disulfides

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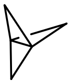
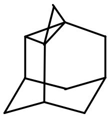
The reactions of some propellanes **I**–**IV** with disulfides are known [1–3]. For example, [1.1.1]propellane **I** reacts with diphenyl disulfide when heated [1] or by the photochemical initiation via a free-radical mechanism [2]. An asymmetric [4.4.1]propellane, 2,3-methano-2,4-didehydroadamantane **II**, reacts slowly, but selectively, in deuterated benzene with dimethyl disulfide to form 2,4-bis(methylthio)-2,4-methanoprotoadamantane [3]. No formation of other products was observed that would confirm the free-radical mechanism of this reaction.


I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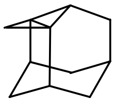
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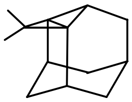
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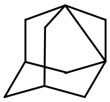
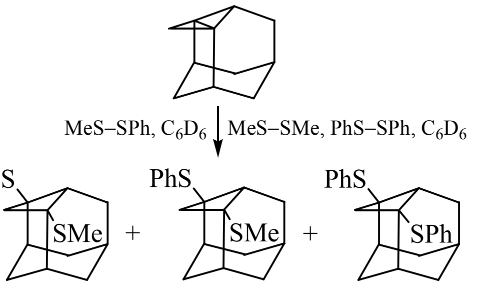

V

The structural analog of [3.1.1]propellane, 2,4-methano-2,4-didehydroadamantane **III**, reacts with the symmetrical disulfide (dimethyl and diphenyl) at room temperature in benzene-d_6 to open a propellane bond giving symmetric bisulfides: 2,4-bis(methylthio)-2,4-methanoadamantane and 2,4-bis(phenylthio)-2,4-methanoadamantane [4].



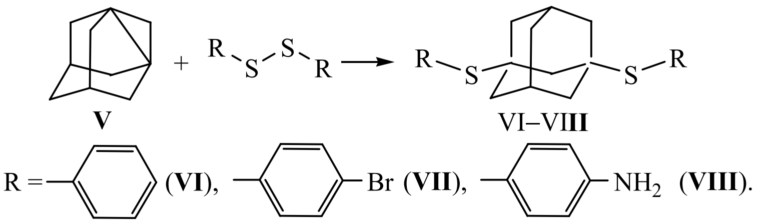
The reaction with an unsymmetrical methyl phenyl disulfide gives rise to a mixture of three products, symmetric bisulfides and unsymmetrical 2-(methylthio)-4-(phenylthio)-2,4-methanoadamantane (1:1:3). The formation of a bisulfides mixture was observed also in the reaction of symmetric dimethyl and diphenyl disulfides. The formation of a mixture of different bisulfides allows us a conclusion on the free-radical nature of the reactions of propellanes with disulfides. The generation of free radicals from [3.1.1]propellane was proved by the ESR in the reaction with CCl_4, as well as by the product of its reaction with *p*-benzoquinone [4].

The dimethyl analog of [3.1.1]propellane, 2,4-(dimethylmethano)-2,4-didehydroadamantane, also reacts readily with dimethyl sulfide at room temperature in benzene-d_6 to give bisulfide, 2,4-(methylthio)-2,4-(dimethylmethano)-2,4-didehydroadamantane [5].

1,3-Dehydroadamantane **V** is a promising reagent in organic synthesis, however, its reactions with the sulfur-containing compounds were poorly studied [6, 7]. In this work we investigated the reactions of adamantane **V** with various disulfides. The reactions are based on the previously unknown properties of adamantane **V** to cleave the S–S bond in disulfides at 80–110°C.

The reactions of compound **V** with disulfides proceed according to the scheme bellow.

In the case of disulfides **VI**–**VIII** there is 100% selectivity towards the formation of the product of insertion into the S–S bond. The yields of the target



products reach 50–52%. The formation of the target products was confirmed by the GC-MS method and thin layer chromatography.

1,3-Bis(phenylthio)adamantane (VI). To a solution of 1.33 g (0.0061 mol) of diphenyldisulfide in 10 ml of anhydrous diethyl ether was added a solution of 0.74 g (0.0055 mol) of the freshly sublimated 1,3-dehydroadamantane (diphenyl disulfide:1,3-dehydroadamantane = 1.1:1) in 10 ml of anhydrous diethyl ether in a nitrogen atmosphere at room temperature. The ether was removed, and the reaction was carried out for 2 h at 100–110°C in the disulfide melt. The reaction mixture was recrystallized from benzene. Yield 0.37 g (50%), yellow-brown crystals, resinification point 315° C. Mass spectrum, *m*/*z* (*I*, %): 352 (11%) $[M]^{+\bullet}$, 243 (100%) $[M - PhS]^+$, 187 (33%) $[M - PhSC_4H_8]^+$, 133 (44%) $[C_{10}H_{13}]^+$, 109 (66%) $[PhS]^+$, 91 (53%) $[C_7H_7]^+$, 77 (26%) $[C_6H_5]^+$. Found, %: C 75.82; H 7.76. $C_{22}H_{24}S_2$. Calculated, %: C 75.00; H 6.82.

1,3-Bis(*p*-bromophenylthio)adamantane (VII). To a solution of 0.6 g (0.0016 mol) of *p*,*p*'-bis(bromophenyl) disulfide in 5 ml of THF was added a solution of 0.19 g (0.00145 mol) of the freshly sublimated 1,3-dehydroadamantane [*p*,*p*'-bis(bromophenyl) disulfide: 1,3-dehydroadamantane = 1.1:1] in 5 ml of THF in a nitrogen atmosphere at room temperature. The solvent was distilled off, and the reaction was performed for 2 h at 100–110°C in the disulfide melt. Then the reaction mixture was boiled at 35°C for 2 h and recrystallized from benzene. Yield 0.37 g (50%), yellow-brown crystals, resinification point 235°C. Mass spectrum, *m*/*z* (*I*, %): 510 (6%) $[M]^{+\bullet}$, 323 (87%) $[M - BrC_6H_4S]^+$, 187 (49%) $[BrC_6H_4S]^+$, 133 (82%) $[C_{10}H_{13}]^+$, 109 (73%) $[PhS]^+$, 91 (100%) $[C_7H_7]^+$. Found, %: C 52.62; H 4.76. $C_{22}H_{22}S_2Br_2$. Calculated, %: C 51.77; H 4.31.

1,3-Bis(*p*-aminopheniltio) adamantane (VIII). To a solution of 0.1 g (0.0004 mol) of *p*,*p*'-bis(aminophenyl) disulfide in 10 ml of benzene was added a solution of 0.049 g (0.00037 mol) of the freshly sublimated 1,3-dehydroadamantane [*p*,*p*'-bis(aminophenyl) disulfide: 1,3-dehydroadamantane = 1.1:1] in 10 ml of benzene in a nitrogen atmosphere at room temperature. The reaction mixture was heated at 80°C for 9 h, and then benzene was removed. The residue was recrystallized from benzene. Yield 0.08 g (52%), white crystals, mp 215°C. Mass spectrum, *m*/*z* (*I*, %): 382 (10%) $[M]^{+\bullet}$, 258 (40%) $[M - NH_2C_6H_4S]^+$, 135 (4%) $[C_{10}H_{15}]^+$, 124 (100%) $[NH_2C_6H_4S]^+$. Found, %: C 70.32; H 7.36. $C_{22}H_{26}N_2S_2$. Calculated, %: C 69.11; H 6.81.

The mass spectra were recorded on a Hewlett Packard GC 5890 Series II/MSD 5972 Series GC mass spectrometer. The thin layer chromatography was performed on a Silufol UV 254 plates, eluent – benzene.

REFERENCES

1. Wiberg, K.B., Waddell, S.T., and Laidig, K., *Tetrahedron Lett.*, 1986, vol. 27, no. 14, p. 1553.
2. McGarry, P.F., Johnston, L.J., and Scaiano, J.C., *J. Org. Chem.*, 1989, vol. 54, p. 6133.
3. Majerski, Z. and Zuanic, M., *J. Am. Chem. Soc.*, 1987, vol. 109, p. 3496.
4. Majerski, K.M., Majerski, Z., Rakvin, B., and Veksli, Z., *J. Org. Chem.*, 1989, vol. 54, p. 545.
5. Majerski, K.M., Cvitas, D.C., and Veljkovib, J., *J. Org. Chem.*, 1994, vol. 59, p. 2374.
6. No, B.I., Butov, G.M., and Mokhov, V.M., *Zh. Org. Khim.,* 1999, vol. 35, no. 1, p. 154.
7. Butov, G.M., Ivankina, O.M., Mokhov, V.M., and Ivanov, V.A., *Uspekhi sovremennogo estestvoznaniya* (The Successes of Modern Natural Science), 2011, no. 9, p. 97.