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SHORT COMMUNICATIONS

Reaction of [3.3.1]Propellanes with Diaryl Diselenides

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Selenium-containing compounds play an important role in both synthetic chemistry and biological processes [1]. However, published data on the synthesis of selenium-containing adamantane derivatives remain so far few in number. An example is the reaction of adamantylideneadamantane with benzeneselenenyl chloride [2].

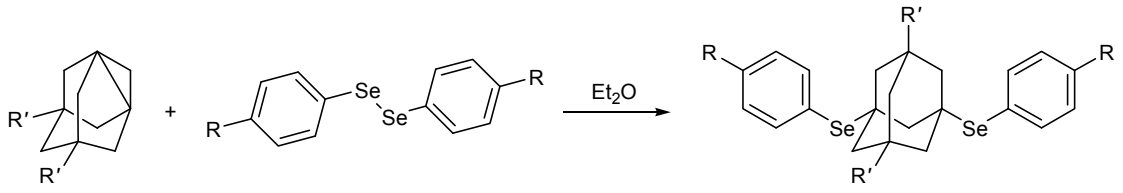
While searching for methods of synthesis of new selenium-containing adamantane derivatives, we used as initial compounds two representatives of [3.3.1]propellanes, 1,3-dehydroadamantane (**Ia**) and 5,7-dimethyl-1,3-dehydroadamantane (**Ib**), which are known to be highly reactive in radical processes. Reactions of diaryl diselenides with propellanes were studied previously only with [1.1.1]propellane as an example [3].

We found that 1,3-dehydroadamantane (**Ia**) and 5,7-dimethyl-1,3-dehydroadamantane (**Ib**) react with diphenyl diselenide (**IIa**) and bis(4-chlorophenyl) diselenide (**IIb**) on heating in boiling diethyl ether to give the corresponding 1,3-bis(arylselanyl)adamantanes **IIIa**–**IIId** in high yields (81–86%).

The complete conversion of [3.3.1]propellanes **Ia** and **Ib** was attained in 0.5–1 h; higher reaction temperature and the use of higher boiling solvents is undesirable, for the reaction rate is fairly high. A necessary condition ensuring sufficient purity of the resulting 1,3-bis(arylselanyl)adamantanes is stoichiometric ratio of compounds **I** and **II**. Excess dehydroadamantane favors formation of a considerable amount of side polymerization products, whereas excess diaryl diselenide contaminates the target product.

General procedure for the synthesis of 1,3-bis(arylselanyl)adamantanes. A solution of freshly sublimed 1,3-dehydroadamantane (**Ia**) or 5,7-dimethyl-1,3-dehydroadamantane (**Ib**) in anhydrous diethyl ether was added at room temperature under dry nitrogen to a solution of an equimolar amount of diaryl diselenide **IIa** or **IIb** in anhydrous diethyl ether. A weak exothermic effect was observed during the addition. The mixture was then heated for 0.5–1 h under reflux, the solvent was distilled off, and the residue was kept for 2 h under reduced pressure (water-jet pump) at 60–80°C. The structure of the products was confirmed by the ^{1}H NMR and GC–MS data.

1,3-Bis(phenylselanyl)adamantane (IIIa) was synthesized from 1 g (3.2 mmol) of diphenyl diselenide (**IIa**) and 0.43 g (3.2 mmol) of 1,3-dehydroadamantane (**Ia**). Yield 1.23 g (86%). ^{1}H NMR spectrum, δ, ppm: 1.42–2.10 m (14H, CH_2, CH), 7.14–7.43 m (10H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 448 (7) $[M]^+$, 291 (100), 235 (6), 157 (50), 133 (78).



Ia, **Ib** **IIa**, **IIb** **IIIa–IIId**

I, R′ = H (**a**), Me (**b**); **II**, R = H (**a**), Cl (**b**); **III**, R = R′ = H (**a**); R = Cl, R′ = H (**b**); R = H, R′ = Me (**c**); R = Cl, R′ = Me (**d**).

1,3-Bis(4-chlorophenylselanyl)adamantane (IIIb) was synthesized from 1 g (2.62 mmol) of bis(4-chlorophenyl) diselenide (**IIb**) and 0.35 g (2.62 mmol) of 1,3-dehydroadamantane (**Ia**). Yield 1.12 g (83%), mp 117–118°C. ^{1}H NMR spectrum, δ, ppm: 1.53–2.14 m (14H, CH_2, CH), 7.18 d (4H, H_{arom}), 7.34 m (4H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 516 (3) $[M]^+$, 325 (20), 191 (100), 133 (25).

5,7-Dimethyl-1,3-bis(phenylselanyl)adamantane (IIIc) was synthesized from 1 g (3.2 mmol) of diphenyl diselenide (**IIa**) and 0.525 g (3.2 mmol) of 5,7-dimethyl-1,3-dehydroadamantane (**Ib**). Yield 1.31 g (86%), mp 102–103°C. ^{1}H NMR spectrum, δ, ppm: 0.74 s (6H, CH_3), 1.00–2.02 m (12H, CH_2), 7.14–7.27 m (6H, H_{arom}), 7.40–7.42 m (4H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 476 (3) $[M]^+$, 319 (65), 263 (5), 161 (100). Found, %: C 61.09; H 5.97. $C_{24}H_{28}Se_2$. Calculated, %: C 60.76; H 5.91.

1,3-Bis(4-chlorophenylselanyl)-5,7-dimethyladamantane (IIId) was synthesized from 1 g (2.62 mmol) of bis(4-chlorophenyl) diselenide (**IIb**) and 0.43 g (3.2 mmol) of 5,7-dimethyl-1,3-dehydroadamantane (**Ib**). Yield 1.15 g (81%), mp 145–147°C. ^{1}H NMR spectrum, δ, ppm: 0.76 s (6H, CH_3), 1.03–1.75 m (12H, CH_2), 7.17 d (4H, H_{arom}), 7.34 d (4H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %): 544 (2) $[M]^+$, 353 (81), 191 (29), 161 (100). Found, %: C 53.70; H 5.01. $C_{24}H_{26}Cl_2Se_2$. Calculated, %: C 53.04; H 4.79.

The ^{1}H NMR spectra were recorded on a Varian Mercury-300 spectrometer (300 MHz) at 28°C from solutions in carbon tetrachloride. The chemical shifts were determined relative to tetramethylsilane as internal reference. The mass spectra were obtained on a Hewlett–Packard HP 5972 mass-selective detector (electron impact, 70 eV) coupled with an HP 5890 Series II gas chromatograph.

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REFERENCES

1. Nogueira, C.W., Zeni, G., and Rocha, J.B.T., *Chem. Rev*., 2004, vol. 104, p. 6255.
2. Garratt, D.G., *Tetrahedron Lett*., 1978, vol. 19, p. 1915.
3. Wiberg, K.B. and Waddell, S.T., *J. Am. Chem. Soc*., 1990, vol. 112, p. 2194.