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A NOVEL CLEAVAGE WITH NITRIC ACID OF POLYMETHYLATED DIBENZYL SELENIDES AND SELENOXIDES

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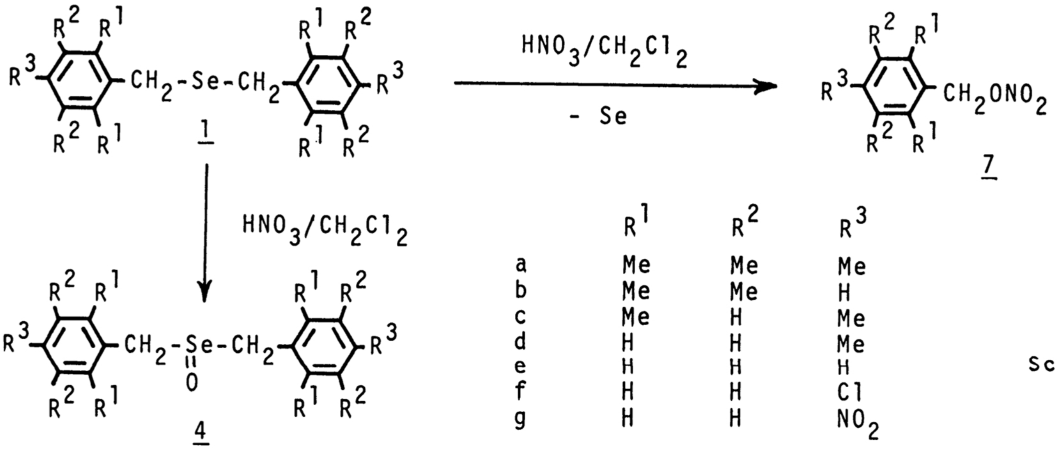
When treated with nitric acid at low temperature, the title selenides and selenoxides undergo a novel cleavage reaction to give the corresponding benzyl nitrates and elemental selenium.

Action of nitric acid upon organic selenides usually results in the oxidation of selenium atom, giving the corresponding selenoxides in good yields. Occasionally, carbon-selenium bond is severed and seleninic acids are formed.[1] By analogy to the nitric acid oxidation of sulfides to sulfoxides, the reaction is supposed to proceed through the attack of nitronium ion on selenium atom, followed by the nitro-nitrito rearrangement of a resulting Se-nitro onium intermediate.[2] In this letter, we wish to report a novel cleavage with nitric acid of polymethylated dibenzyl selenides and selenoxides, which leads to the formation of benzyl nitrates and elemental selenium.

Typically, nitric acid (d=1.5) was added dropwise to a stirred solution of bis(pentamethylbenzyl) selenide 1a in dichloromethane at -5 - 0 °C. The solution immediately turned deep red and free selenium precipitated as a red powder. After 1 h, the reaction mixture was diluted with water and the organic layer was separated, washed with water, dried over sodium sulfate, and evaporated *in vacuo* to leave a slightly yellowish oil, which gradually solidified and was identified as pentamethyl-



	R^1	R^2	R^3
a	Me	Me	Me
b	Me	Me	H
c	Me	H	Me
d	H	H	Me
e	H	H	H
f	H	H	Cl
g	H	H	NO_2

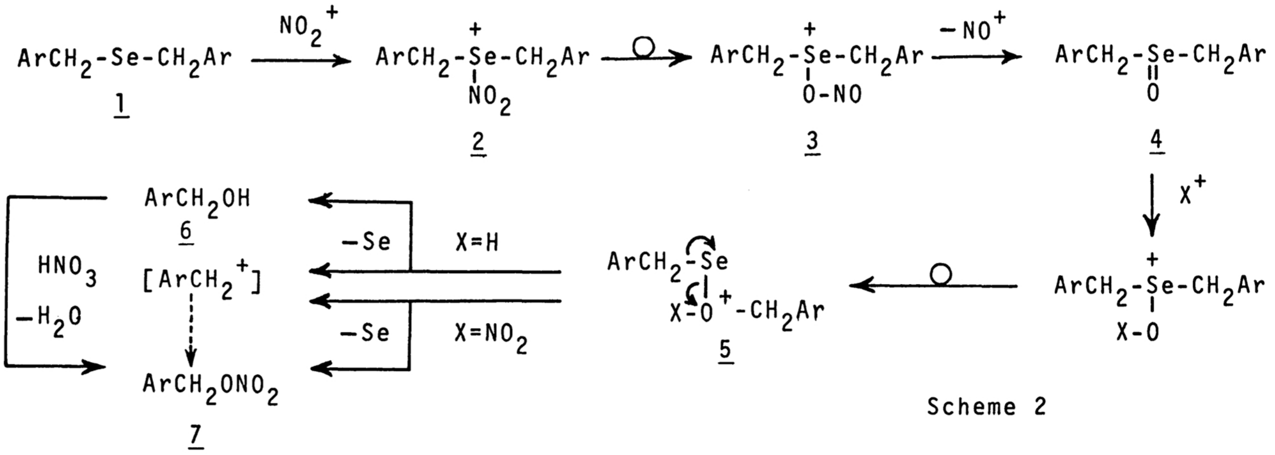
Scheme 1

benzyl nitrate 7a by direct comparison with authentic specimen. Yield, 93%.

Other polymethylated dibenzyl selenides 1b and 1c behaved similarly toward nitric acid; neither ring nitration product nor selenoxide could be detected in the product mixture. When the reaction was carried out in the presence of acetic acid or methanol, benzyl acetate and benzyl methyl ether were the respective important by-products. Interestingly, polymethylated dibenzyl selenoxides also reacted with nitric acid in a reductive way. Thus, 4a afforded 7a (98%) and elemental selenium. The reaction was considerably faster and cleaner than that of the corresponding selenide 1a. No Pummerer-type reaction was observed. In contrast, 4d reacted in an oxidative way to form 7d, p-tolualdehyde 8, and seleninous acid as minor products, in addition to the expected hydronitrates of 4d and p-methylbenzeneseleninic acid 9.

Treatment of unsubstituted dibenzyl selenide 1e with nitric acid yielded hydronitrate $(C_6H_5CH_2)_2SeO{\cdot}HNO_3$ as a white solid (75%), which decomposes at 104-105 °C. The same compound was obtained when 1e was treated with wet dinitrogen tetroxide in carbon tetrachloride at low temperature. Selenide 1d also formed hydronitrate of 4d which, however, decomposed easily to give 7d, 8, and 9. With cold nitric acid, 4,4'-dichloro- and 4,4'-dinitrodibenzyl selenides 1f and 1g were converted to the corresponding selenoxides 4f and 4g in 92-94% yields.

The mechanism of this novel cleavage of selenides and selenoxides is presently unclear. However, we would like to suggest a pathway shown in Scheme 2 as a working mechanism that is consistent with our findings so far obtained: the attachment of an electrophile to selenoxide 4 followed by a selenium-to-oxygen shift of benzyl group will produce 5,[3] which then cleaves by loss of selenium to yield benzyl nitrate 7.



Scheme 2

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