

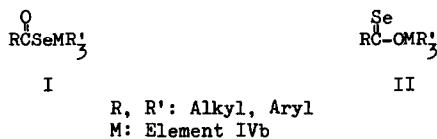
SELENOL AND SELENON ESTERS CONTAINING ORGANO GROUP IV METALS

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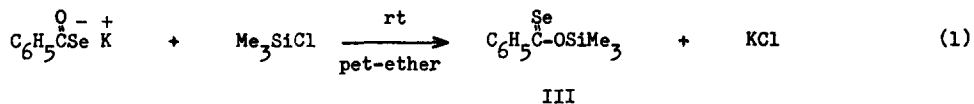
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Though the preparation of alkyl selenobenzoates has appeared in the literature,^{1,2)} organo group IV metal selenon or selenol esters such as I and II have no apparently been reported. This communication describes the preparation and some of the properties of this new type of compound.



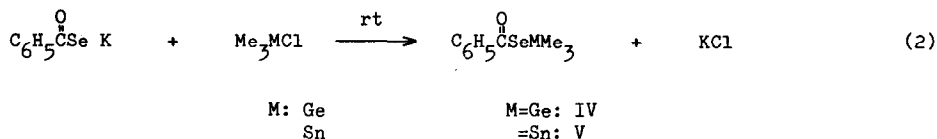
When an equimolar amount of chlorotrimethylsilane was added to a suspension of potassium selenobenzoate³⁾ in petroleum ether at room temperature, the color of the reaction mixture slowly



changed from slight green to reddish purple. Vacuum distillation of the reaction mixture gave

68% of reddish purple liquid (III) having a definite boiling point (100°C / 5 mmHg). The IR spectrum of III shows no absorption band in the range (1720 - 1600 cm⁻¹) expected for usual carbonyl compounds, and a new strong absorption band at 962 cm⁻¹ seemed due to ν C=Se. NMR peaks appeared at 9.45 (9H, s, SiCH₃), and 1.75 - 2.90 τ (5H, m, C₆H₅). The UV spectrum (cyclohexane) shows absorption maxima at 254 (ϵ 7000), 342 (ϵ 7700), and 539 m μ (ϵ 110). These results together with elemental analysis confirmed that the product is (selenobenzoyloxy) trimethylsilane (III).

Contrary to this result with chlorotrimethylsilane, reaction of selenobenzoate with chlorotrimethylgermane or -stannane under similar conditions gave the expected selenol esters (IV and V) as pale yellowish oils in 78 and 82% yield, respectively. The structures of IV and V could be

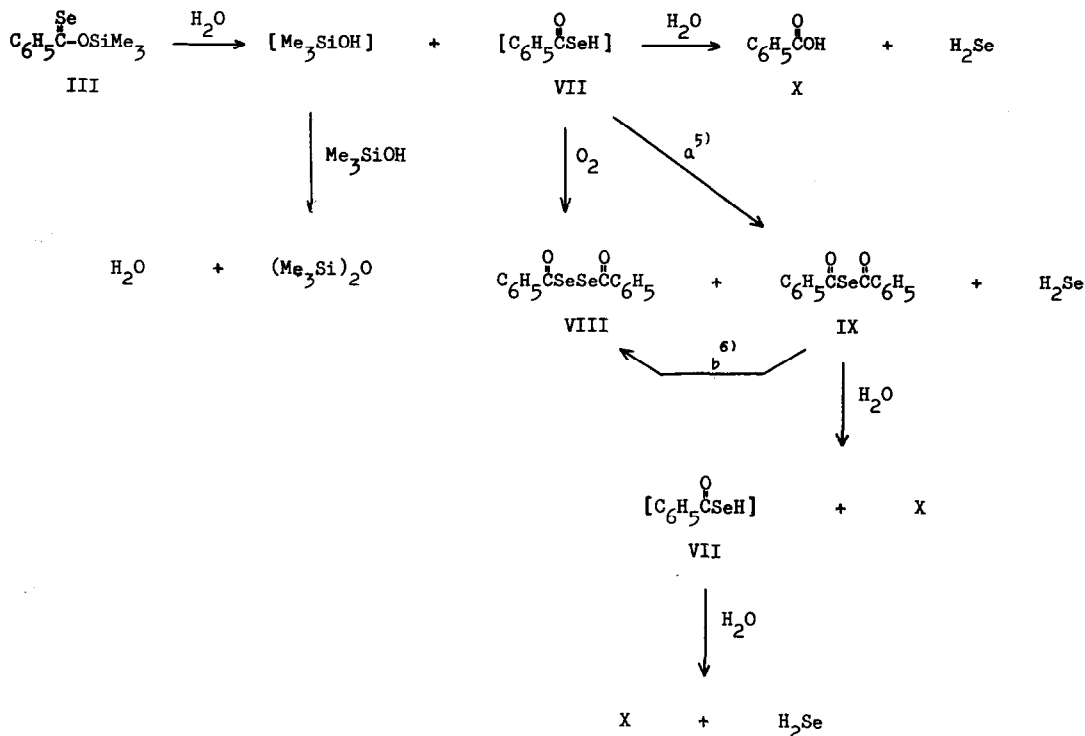


assigned from that elemental analysis and their spectroscopic data ; IV: IR (neat) 1673 and 1650 (ν C=O), 1235 (δ CH₃, scissoring) and 825 cm⁻¹ (δ CH₃, rocking) ; NMR (CCl₄) 9.30 (9H, s, CH₃) and 1.90 - 2.82 τ (5H, m, C₆H₅). V: IR (neat) 1640 (ν C=O), 1215 (δ CH₃, scissoring) and 780 cm⁻¹ (δ CH₃, rocking) ; NMR (CCl₄) 9.40 (9H, s, CH₃) and 1.90 - 2.90 τ (5H, m, C₆H₅), $J_{\text{Sn-C-H}}^{119}$ 58.0 and $J_{\text{Sn-C-H}}^{117}$ 54.5 cps.

The obtained selenon ester III readily hydrolyzed in the air to give hexamethyldisiloxane (VI), dibenzoyl diselenide (VIII), and a trace of benzoic acid (X) with evolution of hydrogen selenide. The products were identified by comparison of their IR spectra with those of the authentic samples. It may be considered that the diselenide and benzoic acid are formed via seleno-

5.6)

selenobenzoic acid (VII) or selenobenzoic anhydride (IX) (Scheme 1). During the hydrolysis, the color of the liquid first turned from reddish purple to red, indicating the formation of selenobenzoic acid (VII) [IR (neat) $2310\text{ cm}^{-1}(\text{SeH})$], finally becoming pale yellow.⁷⁾



Scheme 1

On the other hand, the selenol esters IV and V were relatively stable to moisture and were unchanged after leaving in the atmosphere for 1 hr.

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References

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- 6). Unpublished data : Selenobenzoic anhydride slowly changes in the atmosphere to dibenzoyl diselenide.
- 7). Unpublished data : During ethanolysis of selenobenzoic anhydride, a similar change of the color of the solution from colorless to reddish color was observed (eq 3).

