HETEROCYCLES, Vol 21, No 2, 1984

NOVEL BICYCLIC σ-SELENURANES : SYNTHESES AND REACTIONS OF 9-ALKYL-(OR ARYL)-10-CHLORO-10,9-EPOXYETHANOSELENOXANTHENES AND THEIR RELATED COMPOUNDS

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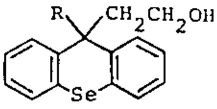
Previously we reported the isolation of the stereoisomers of π-selenuranes containing a selenoxanthene ring and their stereospecific reactions1). We wish to report here the syntheses and reactivities of stable σ-selenuranes containing a selenoxanthene ring.

Alkoxychloroselenuranes 4 easily obtained from selenide-alkohols 1 and N-chlorosuccinimide were fairly stable at room temperature. Reaction of selenoxide-alkohols 2 with HCl did not give alkoxychloroselenuranes 4 but dichloroselenuranes 3, which were also prepared from alkoxychloroselenuranes 4 and HCl. In the ^{1}H-NMR spectra $C_{4,5}$-H absorptions of 4 were largely downfield-shifted to δ ca.8.3. This shift suggests that 4 is the σ-selenuranes. On the treatment with 10% NaOH 4 and alkoxyselenonium perchlorates 5 gave selenoxide-alkohols 2.

Thermolysis of 4a at 150° for 10min gave 1a and 6. Refluxing 4a in ethanol gave 1a and 7. However 5a was stable under the same conditions.

The syntheses and reactions of other bicyclic σ-selenuranes, 10-chloro-9,10-epoxy-9-phenylselenoxanthene(8) and 10-chloro-10,9-epoxymethanoselenoxanthene(9) will be presented.



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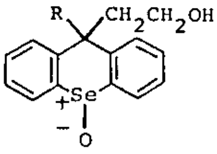

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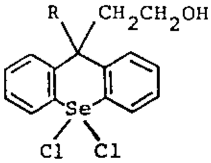

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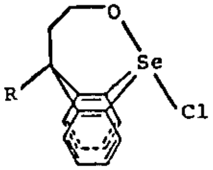

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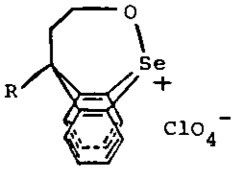

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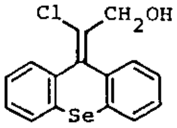

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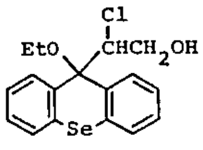

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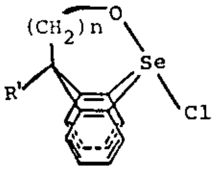

8:n=0,R'=Ph
9:n=1,R'=H

a:R=H, b:R=CH_3, c:R=Ph

1) M.Hori et al., Tetrahedron Lett., 23, 901(1982); 24, 75(1983).