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NOVEL BICYCLIC SELENURANES: SYNTHESES AND PROPERTIES OF 10-CHLORO-10,9-EPOXYETHANOSELENOXANTHENES AND THEIR RELATED COMPOUNDS

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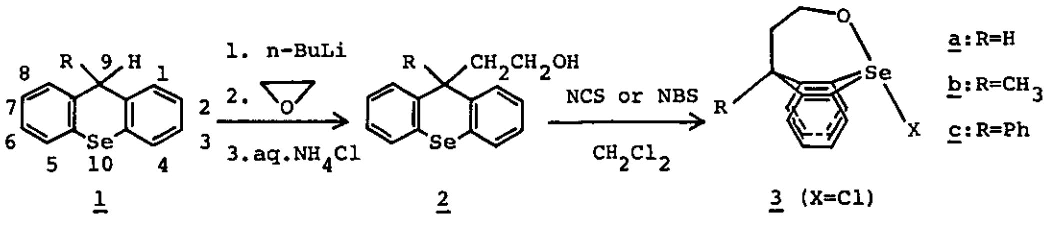
Abstract ——— The novel stable bicyclic selenuranes, 10-chloro(or bromo)-10,9-epoxyethano(or epoxymethano)selenoxanthenes and 10-chloro(or bromo)-9,10-epoxy-9-phenylselenoxanthene were synthesized. Some properties of these selenuranes are also described.

Chemistry of stable σ-sulfuranes[1] has currently occupied one field in organosulfur chemistry. Organoselenium compounds generate hypervalent species more easily than organosulfur compounds. However no report has been published concerning the stable bicyclic alkoxyhaloselenuranes. We previously reported the isolation and reactions of stereoisomers of π-selenuranes (selenilimines and selenium ylides) having a selenoxanthene ring.[2] We wish to report here the syntheses and properties of novel stable bicyclic σ-selenuranes having a selenoxanthene ring. These compounds have a bridged structure between C(9) and Se(10) positions of selenoxanthenes by an epoxy or epoxyalkano group.

Selenide-alcohols (2a-c) were prepared from selenoxanthenes (1a-c) by deprotonation with n-butyllithium followed by the reaction with ethylene oxide in 63.8 - 94.2% yields. Treatment of 2a-c with 1 eq. of N-chlorosuccinimide (NCS) or N-bromosuccinimide (NBS) in CH_2Cl_2 at room temperature for 30 minutes gave stable selenuranes (3a-c, 4a).[3]

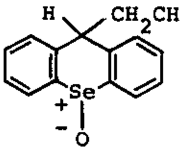


3 (X=Cl)

4 (X=Br)

10-Chloro-10,9-epoxyethanoselenoxanthene (3a) as colorless prisms (82.2%): mp 137 - 139.5°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 2.03 - 2.20 (2H, m, $\underline{CH_2}CH_2O$), 3.80 - 3.95 (2H, m, $CH_2\underline{CH_2}O$), 4.54 (1H, t, J=4.5 Hz, C_9-H), 7.45 - 7.75 (6H, m, ArH), 8.27 - 8.43 (2H, m, $C_{4,5}$-H). 10-Chloro-10,9-epoxyethano-9-methylselenoxanthene (3b) as colorless prisms (81.2%): mp 191 - 192°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 1.85 - 2.00 (2H, m, $\underline{CH_2}CH_2O$), 2.07 (3H, s, CH_3), 3.84 - 4.00 (2H, m, $CH_2\underline{CH_2}O$), 7.45 - 7.85 (6H, m, ArH), 8.37 (2H, dd, J=7.3, 1.7 Hz, $C_{4,5}$-H). 10-Chloro-10,9-epoxyethano-9-phenylselenoxanthene (3c) as colorless prisms (87.5%): mp 182.5 - 183.5°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 2.40 - 2.60 (2H, m, $\underline{CH_2}CH_2O$), 3.72 - 3.93 (2H, m, $CH_2\underline{CH_2}O$), 6.73 - 6.95 (2H, m, ArH), 7.30 - 7.85 (9H, m, ArH), 8.34 (2H, dd, J=7.1, 1.0 Hz, $C_{4,5}$-H). 10-Bromo-10,9-epoxyethanoselenoxanthene (4a) as yellow prisms (88.9%): mp 115.5 - 117°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 2.05 - 2.20 (2H, m, $\underline{CH_2}CH_2O$), 3.80 - 3.95 (2H, m, $CH_2\underline{CH_2}O$), 4.54 (1H, t, J=4.0 Hz, C_9-H), 7.40 - 7.70 (6H, m, ArH), 8.43 (2H, d, J=7.1 Hz, $C_{4,5}$-H). It is well-known that the five-membered alkoxychlorosulfuranes are easily prepared from the corresponding sulfoxide-alcohols with HCl.[4,5] Reaction of selenoxide-alcohol (5)[3,6] with excess amount of HCl afforded no 3a but dichloroselenurane (6).[3,7] This reaction might proceed via 3a, because treatment of 3a with HCl gave 6.

In the ^{1}H-NMR spectra of the five-membered bicyclic alkoxychlorosulfuranes the covalency of S-Cl bond is characterized by a large downfield shift of the ortho protons in the fused rings as compared with the corresponding alkoxysulfonium salts. The ortho protons of the bicyclic alkoxychlorosulfuranes are fixed on the S-Cl bond and the anisotropic deshielding effects of the S-Cl bond causes this large downfield shift. However, such downfield shifts of $C_{4,5}$-H were not observed in the ^{1}H-NMR spectra of 3a-c and 4a. Since an examination of Dreiding models of 3a-c and 4a reveals that the $C_{4,5}$-H bonds are not parallel to the Se-X bond, the Se-X bond would exert not so much deshielding effect on the $C_{4,5}$-H as the S-Cl bond of the bicyclic alkoxychlorosulfuranes. The bridged methylene signals of the selenonium salts (7a-c) appeared in the lower field than those of 3a-c and 4a.[8] This difference is attributable to that of the nature of an Se-X bond, namely, covalent Se-X bonds for 3a-c and 4a and an ionic $Se^+ \ ClO_4^-$ bond for 7a-c, because the counter ions in the ionic sulfonium species cause negligible change in the ^{1}H-NMR spectra.[4] Furthermore, 3a-c and 4a showed molecular ion peaks in the field desorption mass spectra, which are important data indicating the covalent Se-X bonds. Measurement of ^{13}C- and ^{77}Se-NMR and the X-ray crystal structure analysis of 3a are now in progress in order to obtain further information regarding the structure and covalent nature of the selenuranes (3a-c, 4a).



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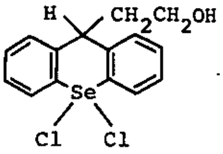

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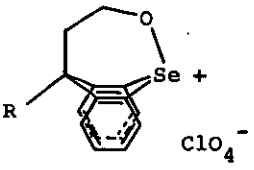
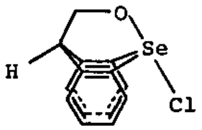


a:R=H
7 b:R=CH_3
c:R=Ph

Six- and five-membered selenuranes were also synthesized by the similar methods. 10-Chloro-10,9-epoxymethanoselenoxanthene (8)[3] as colorless columns: mp 112 - 113°C (dec.); ^{1}H-NMR ($CDCl_3$)[9] δ 3.93 (2H, d, J=1.8Hz, CH_2), 4.66 (1H, t, J=1.8 Hz, C_9-H), 7.30 - 7.65 (6H, m, ArH), 8.23 - 8.53 (2H, m, $C_{4,5}$-H). 10-Chloro-9,10-epoxy-9-phenylselenoxanthene (9)[3,10] as colorless needles: mp 239 - 243°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 7.25 - 7.47 (4H, m, ArH), 7.47 - 7.80 (5H, m, ArH), 8.40 - 8.60 (2H, m, $C_{4,5}$-H). 10-Bromo-9,10-epoxy-9-phenylselenoxanthene (10)[3,10] as colorless needles: mp 210.5 - 215°C (dec.); ^{1}H-NMR ($CDCl_3$) δ 7.25 - 7.45 (4H, m, ArH), 7.45 - 7.70 (5H, m, ArH), 7.78 - 7.90 (2H, m, ArH), 8.53 - 8.64 (2H, $C_{4,5}$-H).



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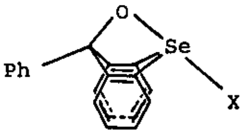

9 (X=Cl)
10 (X=Br)

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2. M. Hori, T. Kataoka, H. Shimizu, and K. Tomimatsu, *Tetrahedron Lett.*, 1982, **23**, 901; K. Tomimatsu, T. Kataoka, H. Shimizu, and M. Hori, *Phosphorus and Sulfur*, 1983, **16**, 97; T. Kataoka, K. Tomimatsu, H. Shimizu, and M. Hori, *Tetrahedron Lett.*, 1983, **24**, 75.
3. Compounds (3 - 10) provided satisfactory microanalytical data.
4. J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, 1977, **99**, 152.
5. A similar synthetic method for the selenuranes was examined: J. E. Trend, Ph. D. Thesis, Wisconsin Univ., 1976.
6. Selenoxide-alcohol [5, mp 212.5 - 214°C (dec.)] was obtained from 2a and 1.1 eq. of m-chloroperbenzoic acid at ice bath temperature for 10 minutes in 79.7% yield.
7. Dichloroselenurane (6) as pale yellow prisms: mp 130 - 131.5°C.
8. Bridged methylene signals of 7a-c in $\mathrm{CDCl_3}$ appeared at δ 2.25 - 2.42 (m, $\underline{\mathrm{CH_2}}\mathrm{CH_2O}$) and 4.13 - 4.27 (m, $\mathrm{CH_2}\underline{\mathrm{CH_2}}\mathrm{O}$) for 7a; 2.13 - 2.30 (m, $\underline{\mathrm{CH_2}}\mathrm{CH_2O}$) and 4.18 - 4.30 (m, $\mathrm{CH_2}\underline{\mathrm{CH_2}}\mathrm{O}$) for 7b; 2.60 - 2.73 (m, $\underline{\mathrm{CH_2}}\mathrm{CH_2O}$) and 4.05 - 4.20 (m, $\mathrm{CH_2}\underline{\mathrm{CH_2}}\mathrm{O}$) for 7c.
9. The ^{1}H-NMR spectrum was measured on a Hitachi R-20B spectrometer (60 MHz) and others were recorded on a JEOL FX-200 spectrometer (200 MHz).
10. In the case of 9 and 10, long reaction time was needed in comparison with other selenuranes (30 minutes for 3a-c, 4a, 8).

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