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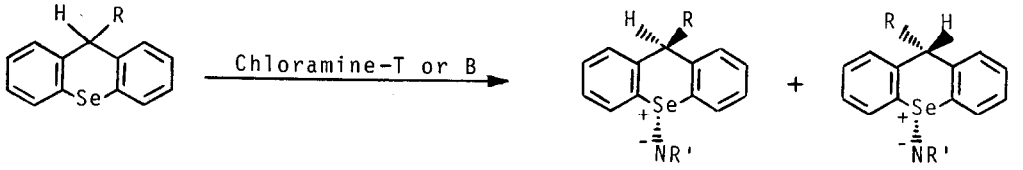
STEREOISOMERS OF SELENILIMINES: ISOLATION AND REACTIONS OF 9-PHENYLSELENOXANTHENE-N-ARYLSULFONYLSELENILIMINES

Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, and Kiminori Tomimatsu
Gifu College of Pharmacy, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan

Summary: The isolated cis- and trans-9-phenylselenoxanthene-N-arylsulfonylselenilimines were not interconverted thermally. cis-Isomers were converted to trans-isomers by chloramine-T or -B in a fashion of S_N2 type substitution. cis-Isomers did not rearrange but trans-isomers rearranged thermally to 9-arylsulfonamido-9-phenylselenoxanthenes, whereas both isomers underwent the base-catalyzed intermolecular rearrangement.

Despite current interest in organic synthesis using organoselenium compounds, little study has been reported with regard to their stereochemistry and their reactivity, particularly those of selenilimines. We wish to report here the first isolated stereoisomers of selenilimines and the difference of their stereochemical reactivity.

9-Phenylselenoxanthene-N-arylsulfonylselenilimines were prepared from 9-phenylselenoxanthene (1) and chloramine-T trihydrate or chloramine-B dihydrate in acetonitrile at room temperature for 3 hr.



1: R=Ph
R=C_6D_5

2a: R=Ph, R'=Ts 2b: R=Ph, R'=Ts
3a: R=Ph, R'=Bs 3b: R=Ph, R'=Bs
4a: R=C_6D_5, R'=Bs 4b: R=C_6D_5, R'=Bs

Ts=p-toluenesulfonyl, Bs=benzenesulfonyl

cis- and trans-Selenilimines[1] were separated by fractional recrystallization. trans-9-Phenylselenoxanthene-N-(p-toluenesulfonyl)selenilimine (2a) as colorless prisms (CH_2Cl_2-hexane), mp 173-176°(dec.), NMR ($CDCl_3$) δ 2.39 (3H, s, CH_3), 5.58 (1H, s, C_9-H), 6.60-6.90 (2H, m, $C_{2',6'}$-H), 7.00-7.70 (11H, m, ArH), 7.70-8.10 (4H, m, $C_{4,5}$-H and SO_2-). cis-9-Phenylselenoxanthene-N-(p-toluenesulfonyl)-

selenilimine (2b) as colorless prisms (CH_2Cl_2-hexane), mp 190-193°(dec.), NMR ($CDCl_3$) δ 2.38 (3H, s, CH_3), 5.13 (1H, s, C_9-H), 7.05-7.60 (13H, m, ArH), 7.65-8.10 (4H, m, $C_{4,5}$-H and SO_2- ). trans-9-Phenylselenoxanthene-N-(benzenesulfonyl)selenilimine (3a) as colorless prisms (CH_2Cl_2-hexane), mp 171-174°(dec.), NMR ($CDCl_3$) δ 5.59 (1H, s, C_9-H), 6.60-6.90 (2H, m, $C_{2',6'}$-H), 7.05-7.70 (12H, m, ArH), 7.70-8.20 (4H, m, $C_{4,5}$-H and SO_2- ). cis-9-Phenylselenoxanthene-N-(benzenesulfonyl)selenilimine (3b) as colorless prisms (CH_2Cl_2-hexane), mp 194-198°(dec.), NMR ($CDCl_3$) δ 5.12 (1H, s, C_9-H), 7.05-7.65 (14H, m, ArH), 7.70-8.15 (4H, m, $C_{4,5}$-H and SO_2- ).

The ratio of stereoisomers changed greatly with the ratio of 1 and chloramine-T trihydrate or chloramine-B dihydrate as shown in the Table. This finding suggested that cis-isomers (2b, 3b) reacted with an excess of chloramine-T or -B to cause the S_N2 type substitution reaction on a selenium atom and were converted to the thermodynamically much more stable trans-isomers (2a, 3a).
Actually 3b reacted with chloramine-T trihydrate to form 2a in high yield with inversion of the configuration, but the reverse reaction did not take place.

Table. Reactions of 9-Phenylselenoxanthene (1) and Chloramine-T or Chloramine-B

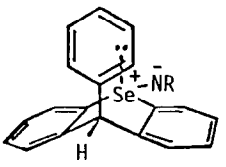
Mole Ratio of 1 and Chloramine-T or B	Ratio of Products[a]	Yield[b](%)
1 : 1	2a/2b = 1	78
1 : 2	2a/2b > 10	67
1 : 1	3a/3b = 1	80
1 : 2	3a/3b > 10	69

[a] The ratio of 2a-3a/2b-3b was determined in comparison with the C_9-H intensities of their NMR spectra.

[b] Isolated yield.

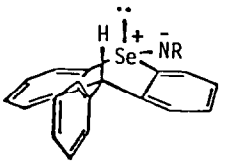
The conformations of the selenilimines were determined by the detailed investigation of their ^{1}H-NMR spectra. When the arylsulfonyl groups of sulfilimines are pseudoaxial (a'), the signals of aromatic protons appear at δ 7.05-7.90. Those of the isomers having pseudoequatorial (e') arylsulfonyl groups are shifted downfield by ca 0.3 ppm.[2] The selenilimines reported here showed the $C_{4,5}$-H signals shifted downfield by magnetic anisotropy of the Se^+-N^--R moiety. Therefore the arylsulfonamido group on a selenium atom should occupy e' position. On the other hand, conformation of C_9-phenyl groups was determined by

comparing the NMR spectra of cis- and trans-9-perdeuteriophenylselenoxanthene-N-(benzenesulfonyl)selenilimines (4a-b). Namely, the absorption assigned to $C_{2',6'}$-H was observed at δ 6.60-6.90 in 2a and 3a, which was not observed in 4a. Upfieldshifted absorption assigned to $C_{1,8}$-H was observed at δ 7.05-7.35 in 2b and 3b. Absorption of C_9-H of 2b and 3b were shifted upfield by ca 0.45 ppm compared with those of 2a and 3a. Therefore the phenyl groups of 2a and 3a must be situated in a' position and those of 2b and 3b are situated in e' position. C_9-H of 2b and 3b occupies a' position and those of 2a and 3a occupy e' position. On the basis of the above discussion, we determined that 2a and 3a were trans-isomers (A), and that 2b and 3b were cis-isomers (B).



A

R=Ts or Bs

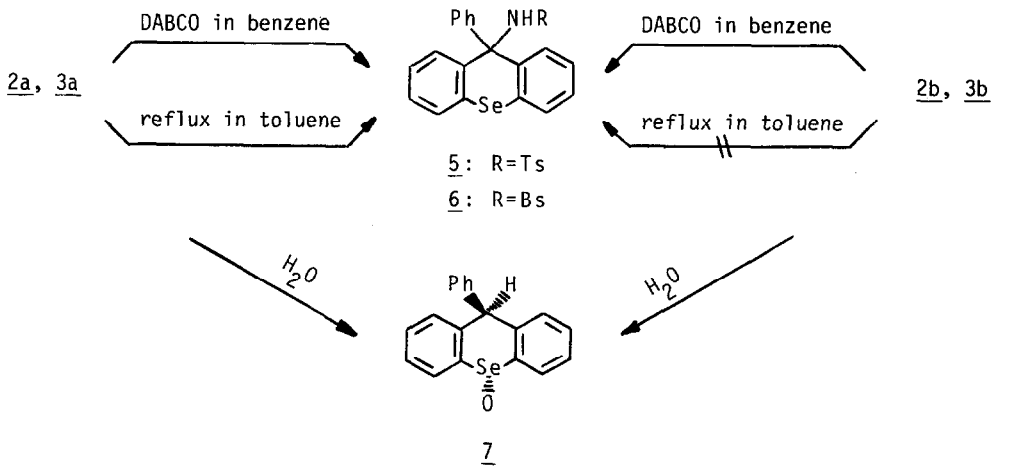


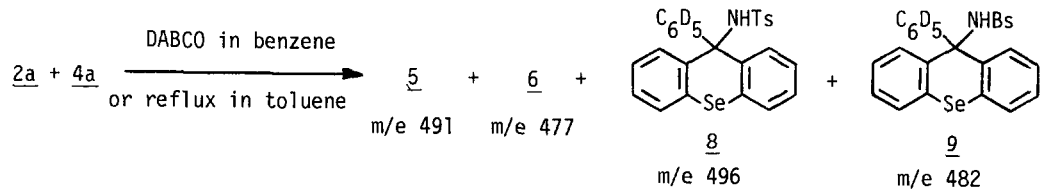
B

Treatment of both the stereoisomers (2a-b, 3a-b) with 1,4-diazabicyclo[2,2,2]octane (DABCO) in benzene at room temperature yielded qauntitatively 9-(p-toluenesulfonamido)- (5) and 9-benzenesulfonamido-9-phenylselenoxanthene (6), respectively.[1] Mechanism of the base-catalyzed rearrangement was elucidated by crossover experiment using 2a and 4a. Mass spectrum of the product showed four ion peaks at m/e 491, 477, 496 and 482 (as Se=80), which were attributed to the molecular ion peaks of 5, 6, 8 and 9, respectively. This reaction produced two crossover products 6 and 8; therefore this rearrangement proceeded intermolecularly.

Refluxing the trans-isomer 2a in toluene for 6 hr formed 5 in 96% yield, while the cis-isomer 2b did not rearrange to 5 under the same conditions. The thermal rearrangement of trans-selenilimine 2a was found to be an intermolecular reaction by crossover experiment. The marked difference of reactivity can be explained as follows: the conformation (A) is ring-inverted into another trans-conformation having a'-C_9-H and a'-N^--R. The amido anion can abstract the C_9-H intramolecularly and then the arylsulfonamido group is migrated to C_9 position.[4] However the amido anion cannot abstract the C_9-H because of their trans relationship in any of the cis-conformations.

Hydrolysis of the trans- and cis-selenilimines on silica gel TLC plates gave trans-9-phenylselenoxanthene 10-oxide (7),[3] colorless prisms, mp 160°





(dec.). NMR ($CDCl_3$) δ 5.58 (1H, s, C_9-H), 6.73-7.05 (2H, m, $C_{2',6'}$-H), 7.05-7.35 (3H, m, $C_{3',4',5'}$-H), 7.35-7.75 (6H, m, ArH), 7.85-8.20 (2H, m, $C_{4,5}$-H).[5] This fact can be explained by pyramidal inversion of the cis-selenoxides into much more stable trans-isomers or by hydration of the cis-selenoxides and dehydration of the hydrated intermediate to the trans isomers.[6]

REFERENCES AND FOOTNOTES

1. All new compounds provided satisfactory microanalytical data.
2. Y. Tamura, Y. Nishikawa, C. Mukai, K. Sumoto, and M. Ikeda, J. Org. Chem., 44, 1684 (1979); Y. Tamura, C. Mukai, Y. Nishikawa, and M. Ikeda, ibid., 44, 3296 (1979).
3. Oxidation of 1 with H_2O_2 or m-chloroperbenzoic acid gave only trans-selenoxide in good yields (M. Hori, T. Kataoka, H. Shimizu, C.-F. Hsu, Y. Asahi, and E. Mizuta, Chem. Pharm. Bull. (Tokyo), 22, 32 (1974)).
4. Intermolecular abstraction of C_9-H could not be excluded, but intramolecular abstraction might be preferred since the base-catalyzed rearrangement proceeded much more easily than the thermal rearrangement.
5. The NMR spectrum of 7 was very similar to that of the corresponding sulfoxide whose structure was well established (M. Hori, T. Kataoka, H. Shimizu, and S. Ohno, Heterocycles, 12, 1417 (1979)) and therefore 7 was determined to be trans-isomer.
6. M. Ōki and H. Iwamura, Tetrahedron Letters, 1966, 2917.

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