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Selenoxanthylium Salts. II. Chemical Reactivity of 9-Phenylselenoxanthylium Perchlorate[1]

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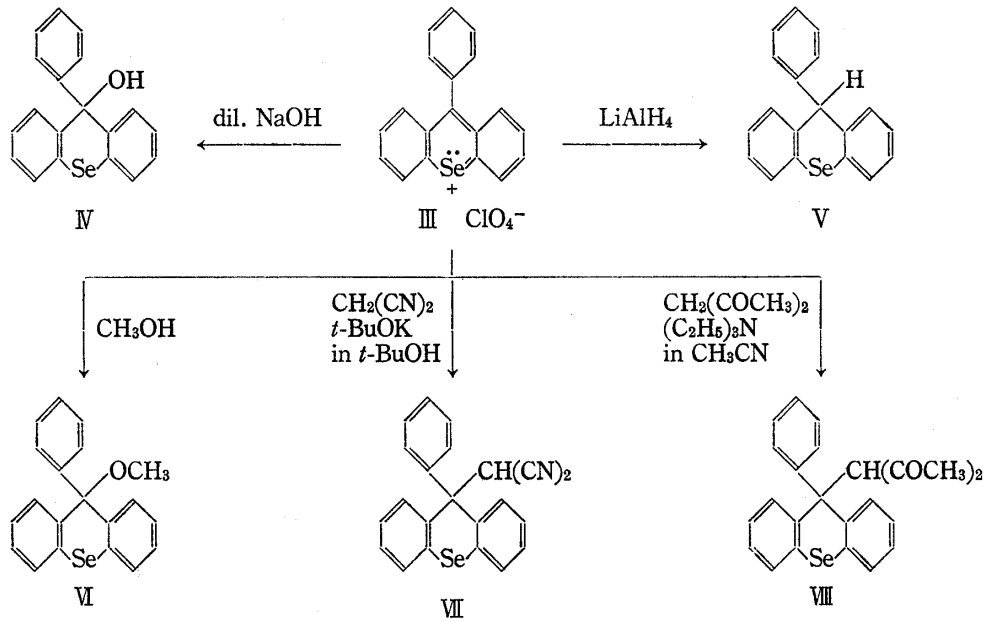
In order to investigate the reactivity of 9-phenylselenoxanthylium perchlorate (III), reaction of III and various nucleophiles have been examined. Theoretical consideration on the chemical reactivities of III in the electrophilic and nucleophilic reactions has been discussed, together with the reaction indices calculated from the ω-technique for 9-phenylxanthylium salt (I), 9-phenylthioxanthylium salt (II), and III.

In our previous studies,[1,3] striking difference was found among the reactivities of 9-phenylxanthylium (I), 9-phenylthioxanthylium (II), and 9-phenylselenoxanthylium perchlorate (III) in nitration. The reactions of I and II with active methylene compounds in the presence of a base have also been reported.[4] Thus, in order to investigate in detail the reactivity of III, it is of interest to examine the reactions of III with nucleophiles.

This paper is concerned with the reactions of III and various nucleophiles. The reactivities of III in the electrophilic and nucleophilic reactions are discussed, together with the reaction indices calculated from SCF-MO computation for I, II, and III.



IV III V VI VII VIII

Chart 1

1) Part I: M. Hori, T. Kataoka, and Chen-Fu Hsü, *Chem. Pharm. Bull.* (Tokyo), **22, 21 (1974)**; A part of this work was presented at International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, August, 1970, Abstracts of Papers, p. 35.
2) Location: *a) 492-36, Mitahora, Gifu; b) Juso-Nishino-cho, Higashiyodogawa-ku, Osaka.*
3) M. Hori T. Kataoka, K. Ohno, and T. Toyota, *Chem. Pharm. Bull.* (Tokyo), **21, 1272 (1973)**; M. Hori and T. Kataoka, *ibid.*, **21**, 1282 (1973).
4) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharu. Bull.* (Tokyo), **21, 1415 (1973)**.

Two equivalents of malononitrile was allowed to react with III in *t*-BuOH containing *t*-BuOK as a base to give 9-dicyanomethyl-9-phenylselenoxanthene (VII), mp 214°, with a yield of 84.1%. The structure of VII was determined by the following instrumental data; IR ν_{max}^{KBr} cm^{-1}: 1275 (CN). NMR ($CDCl_3$)τ: 1.80—3.30 (13H, m, aromatic H) and 4.68 (1H, s, CH).

The reaction of III with two equivalents of acetylacetone in acetonitrile in the presence of triethylamine gave 9-diacetylmethyl-9-phenylselenoxanthene (VIII), which is not a deacetylation product, with a yield of 50%, mp 145°. IR ν_{max}^{KBr} cm^{-1}: 1725, 1690 (CO). NMR ($CDCl_3$)τ: 2.30—3.28 (13H, m, aromatic H), 4.50 (1H, s, CH) and 8.30 (6H, s, $COCH_3$).

The reduction of III with lithium aluminium hydride in ether gave 9-phenylselenoxanthene (V), with a yield of 78.2%, mp 115°. NMR ($CDCl_3$)τ: 2.3—3.2 (13H, m, aromatic H) and 4.61 (1H, s, C_9–H). Mass Spectrum *m/e*: 322 (M^+). Treatment of III with sodium methoxide in methanol also proceeded to form 9-methoxy-9-phenylselenoxanthene (VI) with a yield of 88%, mp 125—126°. NMR ($CDCl_3$)τ: 2.30—3.10 (13H, m, aromatic H) and 6.90 (3H, s, OCH_3). All the reaction products were those formed by the attack of carbon at 9-position by the nucleophiles.

Theoretical Consideration on the Chemical Reactivities of I, II, and III in Electrophilic and Nucleophilic Reactions

The authors reported in the previous paper that II is much more reactive than I and that II is dinitrated under the condition, which mononitrates I.[3] The nitration of I mainly occurrs at *m*-position of the phenyl group at 9-position whereas the nitrations of II give more *p*(or 4')-substituents than *m*(or 3')-substituents. It was also found that the order of the relative reactivity of I, II, and III in the electrophilic reaction is not correspond to the order of atomic number of the elements of the VI-B group in the periodic table, but is:

the reactivity of II (–$\ddot{S}^+$=)>the reactivity of III (–$\ddot{S}e^+$=)>the reactivity of I (–$\ddot{O}^+$=).

It was further found in the present study that III forms reaction products as a result of the attack of the nucleophiles against a carbon at 9-position as in the case of I and II.[4] Chart 2 summarizes the results.

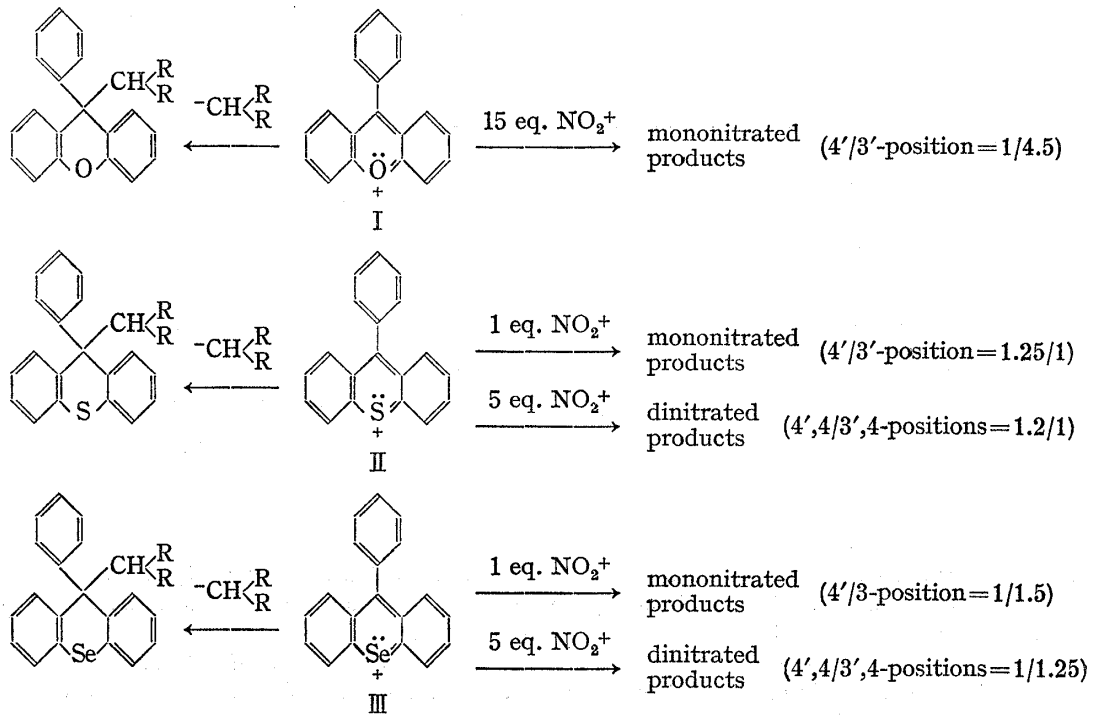
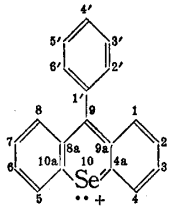


Chart 2

In order to quantitatively examine on the experimental results shown in Chart 2, the electron density (Qr) and reaction indices,[5] such as the superdelocalizabilities ($Sr^{(E)}$) for the electrophilic reaction and the frontier electron densities ($fr^{(N)}$) for the nucleophilic reactions of III, were calculated by ω-technique.[6] The results are shown in Table I.

TABLE I. Reaction Indices of 9-Phenylselenoxanthylium Salt (III) by ω-Technique



Position	Qr		$Sr^{(E)}$		$fr^{(N)a)}$	
1, 8	0.9364		0.7869		0.1774	
2, 7	0.9873		0.8116		0.0046	
3, 6	0.9273		0.6993		0.1776	
4, 5	0.9942	0.9823(O^+)[b] 0.9947(S^+)	0.8570	0.8109(O^+)[b] 0.8635(S^+)	0.0064	
4a, 10a	0.9343		0.6788		0.1782	
8a, 9a	0.9763		0.6547		0.0034	
9	0.7277	0.6997(O^+)[b] 0.7327(S^+)	0.4554	0.3989(O^+)[b] 0.4735(S^+)	0.7119	0.7325(O^+)[b] 0.7117(S^+)
10	1.7840		1.5444		0.1454	
1'	0.9982		0.8180		0.0000	
2', 6'	0.9937		0.8267		0.0160	
3', 5'	0.9988	0.9975(O^+)[b] 0.9995(S^+)	0.8297	0.8262(O^+)[b] 0.8318(S^+)	0.0000	
4'	0.9935	0.9869(O^+)[b] 0.9972(S^+)	0.8244	0.8098(O^+)[b] 0.8296(S^+)	0.0160	

Parameters: $\alpha_{Se}=\alpha+\beta$, $\alpha_{adj}=\alpha+0.1\beta$, $\beta_{Se-C}=0.5\beta$;
$\omega_r=0.55$ in $\alpha_{r'}=\alpha_r+\omega_r(P_r-Q_r)$.
Twist angle θ of $C_9-C_{1'}$, positions of III was estimated as *ca.* 72° from the relation $\beta_{9-1'}=\beta\cos\theta$.
a) energy of the lowest vacant orbital: $\varepsilon=\alpha+0.016\beta$
b) compare with values of I (O^+) and II (S^+)

Table I explains that the electrophilic reaction usually takes place at the positions where the Qr and $Sr^{(E)}$ values are large in I, II, and III, namely, at 3'(5'), 4' and 4(5)-positions. Experimental results also show that mononitration does not take place at 2'(6') and 4(5)-positions through these positions show large $Sr^{(E)}$ values.[7] This contradiction is attributable to the steric or electrostatic effects at these positions. The product ratio of the two isomers obtained by the mononitration of II or III, was almost the same with that by the dinitration. From these results, it is concluded that the reactivity of I, II, and III is given by the ratio of 9-*para* (or 4')/9-*meta* (or 3')-nitrophenyl derivatives. Therefore, in the mononitration, the order of relative reactivity of I, II, and III is:

II: $Sr^{(E)}=\begin{cases}0.8296 & (4'\text{-position})\\ 0.8318 & (3'\text{-position})\end{cases}$ > III: $Sr^{(E)}=\begin{cases}0.8244 & (4'\text{-position})\\ 0.8297 & (3'\text{-position})\end{cases}$ > I: $Sr^{(E)}=\begin{cases}0.8098 & (4'\text{-position})\\ 0.8262 & (3'\text{-position})\end{cases}$ as noticed in Table I. This order is also the same as that of the extend of the resonance forbidding between 9-phenyl group at 9-position and heterocyclic ring. The

5) K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).
6) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).
7) However, the ratio of formation of the isomers obtained by mononitration and dinitration of II and III, do not agree with the values of $Sr^{(E)}$ of the corresponding positions of II and III. More exact MO calculation, which takes the 3d-orbital of sulfur and the 4d-orbital of selenium into consideration, will be made in the future.

extent is supported by the order of the twist angle θ between the 1′- and 9-positions, namely, II (*ca.* 78°)>III (*ca.* 72°) I>(*ca.* 66°).

The order of the relative reactivity in the electrophilic reactions of I, II, and III thus obtained suggests that the order of the electronegativity of the elements of the VI-B group is not the same as that of the atomic number in the periodic table, but is O>Se>S. It is very interesting that this order agrees with that of the electronegativity of the elements of the VI-B group, which calculated from stability ratio values by Sanderson,[8] as shown below.

O (3.46)>Se (2.76)>S (2.66)

One possible factor that explains the difference in the reactivity among I, II, and III is the difference in the state of π-bonding of O–C, S–C, and Se–C bondings. $-\overset{+}{\underset{\cdot\cdot}{S}}=C<$ and $-\overset{+}{\underset{\cdot\cdot}{Se}}=C<$ bondings, which contain an anti-bonding,[9] are weaker than $-\overset{+}{\underset{\cdot\cdot}{O}}=C<$ bonding, and stabilization of the former by the I-effect is less than that of the latter. And further, $-\overset{+}{\underset{\cdot\cdot}{Se}}=C<$ bonding contained in III is somewhat less in the anti-bonding nature than $-\overset{+}{\underset{\cdot\cdot}{S}}=C<$ bonding in II as shown in Fig. 1. Therefore, it is concluded that II and III are more reactive in the electrophilic reaction than I.

On the other hand, the nucleophilic reaction is expected to occur at the 9-position which shows large $f_r^{(N)}$ values and small Qr values in I, II, and III. The experimental results well agreed with those of the theoretical calculation. The results of theoretical calculation indicates that the reactivity of I in nucleophilic reaction is larger than those of II and III, but it is difficult to experimentally confirm this difference.

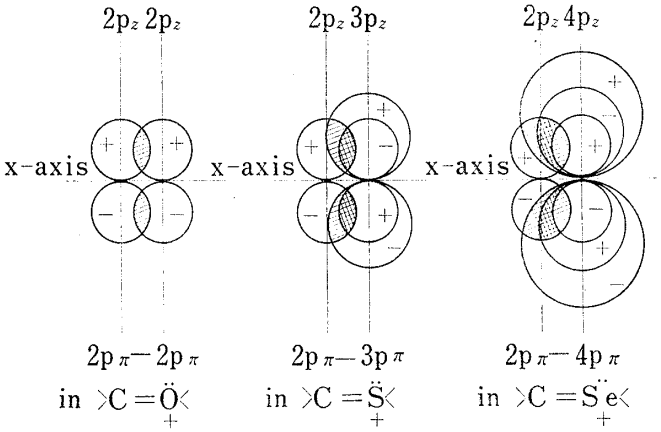


Fig. 1. Features of π–π Overlappings

Now the authors are investigating on the reactions of I, II, and III with various ambi-functional nucleophiles, such as aromatic amines and phenols, to experimentally prove the difference of reactivity in the nucleophilic reaction, which is theoretically expected.

Experimental[10]

9-Phenylselenoxanthenol (IV)——To a solution of III[11] (0.5 g) in CH_2Cl_2 (10 ml), 5% NaOH (10 ml) was gradually added. After stirring for 30 min, the CH_2Cl_2 layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The extract was dried (K_2CO_3) and evaporated. Recrystallization of the residue from *n*-hexane gave colorless prisms (0.3 g), mp 105°, which was identified by the comparison of the infrared spectrum with that of an authentic sample.

9-Phenylselenoxanthene (V)——To a suspension of $LiAlH_4$ (0.5 g) in ether (50 ml), III (0.5 g) was gradually added with stirring, and the reaction was continued for 3 hr. The reaction mixture was decomposed with a cold solution of NH_4Cl and extracted with ether. The extract was dried (K_2CO_3) and evaporated. Recrystallization of the residue from MeOH gave colorless needles (0.3 g, 78.2%), mp 115°. *Anal.* Calcd. for $C_{19}H_{14}Se$: C, 71.05; H, 4.40. Found: C, 70.89; H, 4.67. UV λ_{max}^{EtOH} mμ (log ε): 211 (4.15), 256 (3.80), 277 (2.50). NMR ($CDCl_3$) τ: 2.30—3.20 (13H, multiplet, aromatic H), 4.61 (1H, singlet, C_9-H).

9-Methoxy-9-phenylselenoxanthene (VI)——III (1.0 g) was added to a 10% CH_3ONa solution in MeOH under an N_2 stream. After 2 hr the reaction mixture was poured into ice-water and extracted with ether.

8) R.T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, 1960, pp. 32—34.
9) C.C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N.Y., 1962, pp. 9—19.
10) All melting points are uncorrected.
11) M. Hori, T. Kataoka, and Chen-Fu Hsu, *Chem. Pharm. Bull.* (Tokyo), 22, 15 (1974).

The ether extracts were washed with water and dried ($MgSO_4$), and evaporated. The resulting residue was purified by column chromatography and then recrystallized from pet. ether to give colorless plates (0.78 g, 88%), mp 125—126°. *Anal.* Calcd. for $C_{20}H_{16}OSe$: C, 68.37; H, 4.59. Found: C, 68.59; H, 4.84. NMR (CCl_4) τ: 2.30—3.10 (13H, multiplet, aromatic H), 6.90 (3H, singlet, OCH_3).

9-Dicyanomethyl-9-phenylselenoxanthene (VII)——Malononitrile (0.67 g) was added to a solution of *t*-BuOK[12] (1.86 g) in *t*-BuOH (45 ml) under an N_2 stream at 50°. After 30 min III (2.1 g) was gradually added to the mixture thus prepared. The reaction was continued for 3.5 hr, and then the precipitate was filtered off. The filtrate was evaporated under reduced pressure. The resulting solid was purified by chromatography and then recrystallized from benzene–pet. ether to give colorless prisms (1.62 g, 84.1%), mp 214°. *Anal.* Calcd. for $C_{22}H_{14}N_2Se$: C, 68.57; H, 3.67; N, 7.27. Found: C, 68.70; H, 3.89; N, 7.15. NMR ($CDCl_3$) τ: 1.80—3.30 (13H, multiplet, aromatic H), 4.68 (1H, singlet, CH). IR ν_{max}^{KBr} cm^{-1}: 2270 (CN).

9-Diacetylmethyl-9-phenylselenoxanthene (VIII)——To a mixture of acetylacetone (1.0 g) and triethylamine (1.1 g) in CH_3CN (10 ml), III (2.0 g) was gradually added. After 2 hr the solvent was removed and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was washed with water, dried ($MgSO_4$), and evaporated. After purification by chromatography, the product was recrystallized from benzene–*n*-hexane (1: 1) to give colorless prisms (1.0 g, 50%), mp 144—145°. *Anal.* Calcd. for $C_{24}H_{20}O_2Se$: C, 68.73; H, 4.81. Found: C, 68.80; H, 4.91. IR ν_{max}^{KBr} cm^{-1}: 1725, 1690 (CO). NMR ($CDCl_3$) τ: 2.30—3.28 (13H, multiplet, aromatic H), 4.50 (1H, singlet, C_9-H), 8.30 (6H, singlet, CH_3).

12) A.J. Speziale and K.W. Ratts, *J. Am. Chem. Soc.*, **84**, 854 (1962).