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Selenabenzenes. I. Synthesis of 10-Selenaänthracene Derivatives[1]

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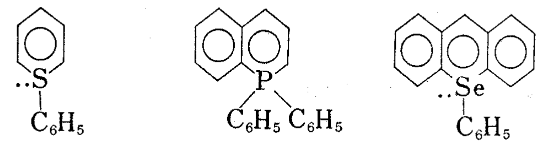
By the reaction of selenopyrylium salts with phenyllithium, two selenabenzene analogs, namely, 10-phenyl- and 9,10-diphenyl-10-selenaänthracenes have been prepared.

The selenaänthracene derivatives are very stable against light, heat, and oxygen.

The nuclear magnetic resonance and mass spectral data and the low dipole moment (1.08 D) strongly suggest a covalent aromatic structure for the selenaänthracene.

Recently much attention has been focussed on possible benzenoid conjugation in a novel heterocyclic ring system involving a sulfur or a phosphorus atom, which possesses vacant d-orbitals. So far, reports are being published on such novel aromatic heterocycles such as thiabenzene derivatives (I)[3] and 1,1-disubstituted phosphabenzene derivatives,[4] which are somewhat different from I in various properties. These compounds have been estimated to possess appreciable cyclic aromatic conjugation through the ylene-like structure, which contain the resonance by 2pπ-3pπ bonding in I and 2pπ-3dπ in II.

The authors will report below the preparations of the third novel aromatic heterocycles, so-called selenabenzenes, namely, 10-selenaänthracenes (III) and (XIII) which contain a decet selenium atom. The synthesis of 10-selenaänthracenes is achieved in ether by the reaction of corresponding selenoxanthylium salts with aryllithiums. The key point in the synthetic process was the safe handling of selenophenol, which is extreamly poisonous, and how to derive selenoxanthylium salts in a high yield from selenophenol, which is easily oxidized.



2pπ−3p(or 3d)π in $\rangle C=\ddot{S}\langle$ 2pπ−3dπ in $\rangle C=P\langle$ 2pπ−4p(or 4d)π in $\rangle C=\ddot{S}e\langle$

I II III

Chart 1

Selenoxanthylium Perchlorates

Lesser *et al.*, prepared *o*-phenylselenobenzoic acid (V) from sodium selenophenolate (IV) and *o*-carboxybenzenediazonium salt[5] and obtained selenoxanthone (VI)[5b] by the ring closure of V by sulfuric acid. However, the yield of VI was low. Therefore, the authors planned to synthesize selenoxanthylium perchlorate (VIII) through a route as shown in Chart 2. By the reaction of IV with potassium *o*-chlorobenzoate, V was obtained in a yield of 70%. By the ring closure reaction by polyphosphoric acid (PPA), VI was obtained in a yield of

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[1] 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; M. Hori, T. Kataoka, H. Shimizu, and C. Hsü, *Chem. Letts.*, **1973**, **391**.

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[3] *a*) G. Suld and C.C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); *b*) C.C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963); *c*) C.C. Price and H. Pirelahi, *J. Org. Chem.*, **37**, 1718 (1972); *d*) C.C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *ibid.*, **36**, 791 (1971); *e*) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1692 (1973).

[4] *a*) G. Märkl, *Angew. Chem.*, **75**, 168 (1963); *b*) H. Oehling and A. Schweig, *Tetrahedron Letters*, **1970**, 4941; *c*) M. Davies and N. Hughes, *J. Heterocyclic Chem.*, **9**, 1 (1972).

[5] *a*) R. Lesser and R. Weiss, *Chem. Ber.*, **47**, 2510 (1914); *b*) *Idem*, *ibid.*, **57**, 1077 (1924).

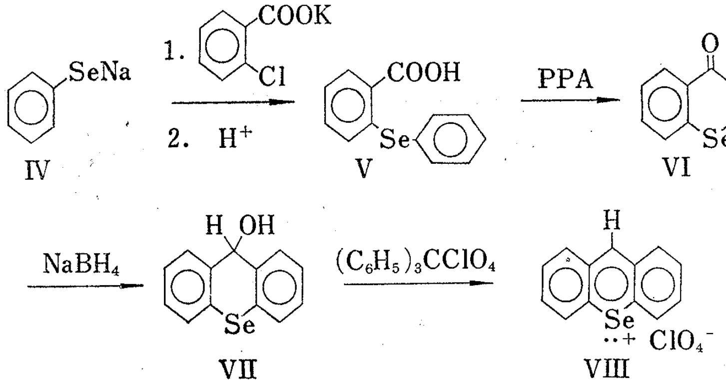

Chart 2

97%. The synthesis of selenoxanthenol (VII) has been reported by François⁶⁾ and that of VIII by Degani, *et al.*⁷⁾ The authors obtained selenoxanthenol (VII) by the reduction of VI with $NaBH_4$ in a yield of 89%. And also treatment of VII with trityl perchlorate, VIII was successfully synthesized in a yield of 92.8%.

Chart 3 shows the synthesis of 9-phenylselenoxanthylium perchlorate (XII). With a yield of 77%, *o*-phenylselenobenzophenone (IX) was obtained by the treatment of IV with *o*-chlorobenzophenone⁸⁾ in DMF. Then 9-phenylselenoxanthenol (X) was obtained in a good yield of 90% by the ring closure by PPA. This material was identified by the comparison with the authentic sample⁶⁾ synthesized from VI and phenylmagnesium bromide. By the reaction with $HClO_4$ or trityl perchlorate, X was easily derived to XII. On the synthesis of IX, Renson, *et al.*,⁹⁾ reported an interesting method using *o*-methylselenobenzoic acid as a starting material. However, they did not report on the yield.

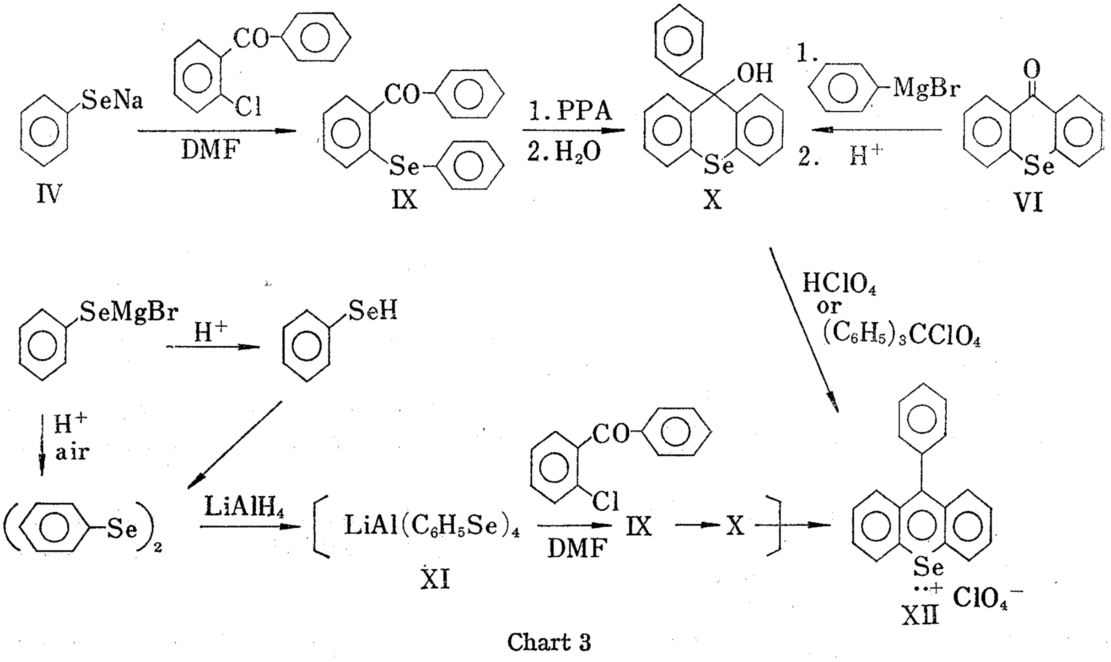

Chart 3

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6) M.F. François, *Compt. Rend.*, **190**, 192 (1930).

7) J. Degani, R. Fochi, and C. Vincenzi, *Bull. Sci. Fac. Chim. Ind. Bologna*, **23**, 21 (1965).

8) E. Berlinger, *J. Am. Chem. Soc.*, **66**, 533 (1944).

9) M. Renson and J.L. Piette, *Bull. Soc. Chim. Belges.*, **73**, 507 (1964) [*C.A.*, **61**, 10621f (1964)].

The synthesis of selenophenol by the reaction of phenylmagnesium bromide with selenium is accompanied by the evolution of extreamly poisonous H_2Se and is very dangerous.10) Therefore, diphenyl diselenide, which is safe to handle in a laboratory, was prepared by the air oxidation of selenophenol. Diphenyl diselenide11) was then treated with $LiAlH_4$ to give lithium aluminium tetraphenylselenide (XI). XI was then allowed to condence with *o*-chlorobenzophenone in DMF. Then XII was successfully synthesized in an over-all yield of 37.5% without isolating IX and X from each other.

Preparation and Properties of 10-Selenaänthracenes

Chart 4 shows the results of reactions of VIII and XII with phenyllithium together with the results of reactions of VIII and XII with Grignard reagents. When XII was allowed to react with excess phenyllithium in a nitrogen stream, the reaction took place at the selenium atom at 10-position and gave 9,10-diphenylselenaänthracene (XIII), mp 107—109° (decomp.). By the reaction between VIII and phenyllithium, a by-product, 9,9′-diselenoxanthenyl (XVI), mp>300°, was found to form in a yield of 13.0% besides 10-phenyl-10-selenaänthracene (III). mp 85—87°. The identification of XVI was performed by the comparison of infrared (IR) and nuclear magnetic resonance (NMR) spectra with those of the authentic sample synthesized independently by a photoreaction of selenoxanthene (XVIII), obtained by the reduction of VI with $LiAlH_4$ in benzene. It was also possible to obtain XVIII by treating VI with hydriodic acid and phosphorus.12)

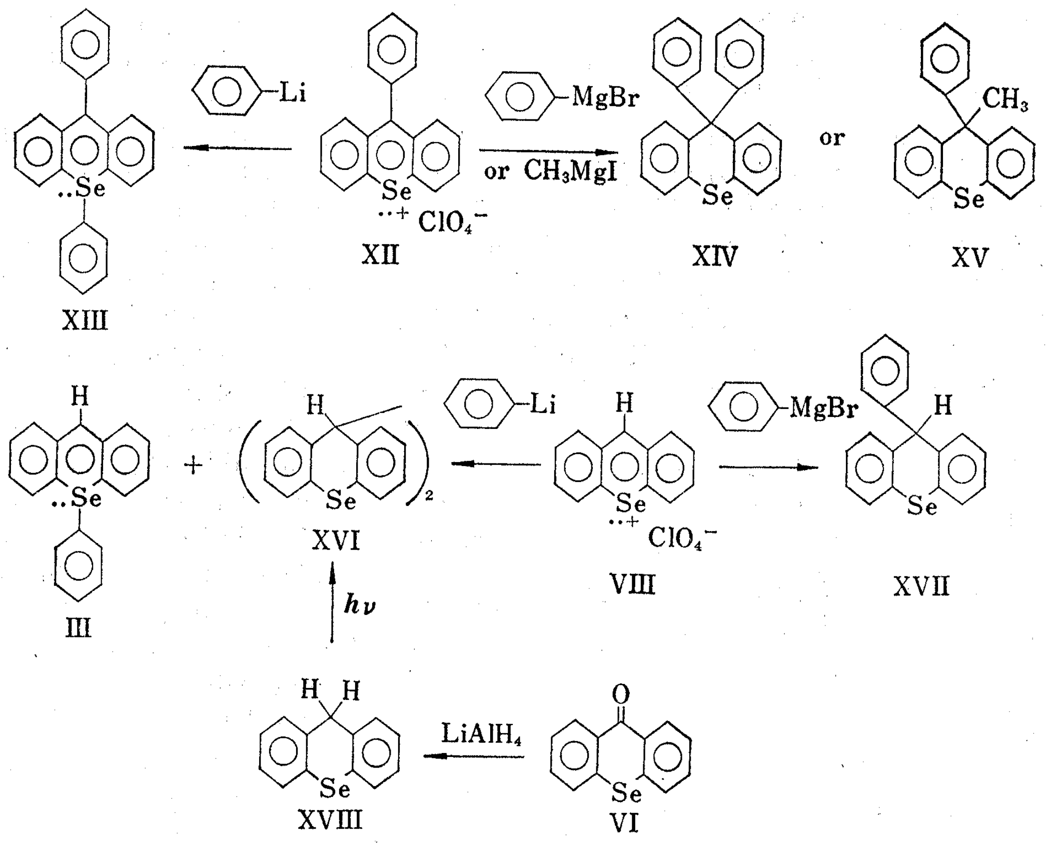

Chart 4

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10) D.G. Foster, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horning, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 771.

11) F. Kraft and A. Kaschau, *Chem. Ber.*, 29, 431 (1896).

12) B.R. Muth, *Chem. Ber.*, 93, 283 (1960).

On the other hand, XII was allowed to react with phenylmagnesium bromide or methylmagnesium iodide under the same conditions as mentioned above. The reaction took place at the carbon atom of 9-position and gave 9,9-diphenylselenoxanthene (XIV), mp 212°, or 9-methyl-9-phenylselenoxanthene (XV), mp 186°, in a yield of 56.5% and 70%, respectively. Similarly, 9-phenylselenoxanthene (XVII), mp 115°, was obtained in a yield of 91% by the reaction between VIII and phenylmagnesium bromide.

10-Selenaänthracenes thus synthesized were much different from the isomeric selenoxanthenes in the appearance, solubility in various solvents, melting point, and NMR, IR, and ultraviolet (UV) spectral data. The former III and XIII was a brown powder, which is extreamly soluble in ether, benzene, and CCl_4 but was hardly soluble in ethanol and petroleum ether. Melting did not occur below the decomposition point. The NMR spectra of the former showed only an aromatic-type hydrogen, with absorption shifted downfield from that of tetramethylsilane to about 3.0 τ. On the other hand, all of the latter XIV, XV, and XVII consisted of colorless needles, which were easily recrystallized from ether. Hydrogen in isomeric selenoxanthenes, with cyclic conjugation interrupted by a carbon atom having sp^3-orbitals, is expected to show larger values of τ. In fact, the NMR spectrum of 9-phenylselenoxanthene corresponding to III had a singlet peak at 4.8 τ due to a proton of the carbon atom at 9-position.

The large ring currency of 10-selenaänthracenes is well estimated from the mass spectral data. The data of III and XIII showed of peak at m/e 245 (selenoxanthyl$^{+\cdot}$) as a base peak, besides 398 (M^+) and 322 (M^+). This kind of peak at m/e 245 was not noticed at all with XIV and XV. III and XVII do not agree with each other in the IR spectrum. The UV curves are also quite different from each other. Both are clearly discriminated from each other by the comparison of the UV curves of isomeric selenoxanthenes because 10-selenaänthracenes show a particular long tail curve like 10-thiaänthracenes.[3d)]

Thus covalent aromatic structure of 10-selenaänthracenes is strongly supported by the low dipole moment (μ=1.08 D) of XIII measured in benzene at 30° besides the NMR and mass spectral data. The large stability of selenaänthracenes is also attributable to its aromaticity. Consequently, as in the case of 10-thiaänthracenes,[3b)] it is estimated that the π-bond of $>C{=}\ddot{S}e<$, which can make through conjugation with the π-electrons of $>C{=}C<$ in the rings of 10-selenaänthracenes, is mainly $2p\pi$—$4p\pi$. It is reasonable to consider that the constellation of its decet selenium bonding utilizes sp^2-orbitals for σ-bonding, a $4p_z$-orbital for cyclic conjugation, and one (or more) 4d-orbital(s) for the unshared pair.

10-Selenaänthracenes are somewhat more stable than 10-thiaänthracenes against heat and light. This stability is explained as follows: the comparison of the stability of a six-membered aromatic compound containing a $>C{=}C<$ bonding with that of a six-membered aromatic compound containing a $>C{=}\ddot{S}<$ bonding indicates that, as is known from Fig. 1, the latter not only contains a hetero atom, which is not equivalent to $>C{=}C<$, but also partly contains an *anti*-bonding. However, $>C{=}\ddot{S}e<$ contained in 10-selenaänthracenes is somewhat less in the *anti*-bonding nature than $>C{=}\ddot{S}<$ in 10-thiaänthracenes.

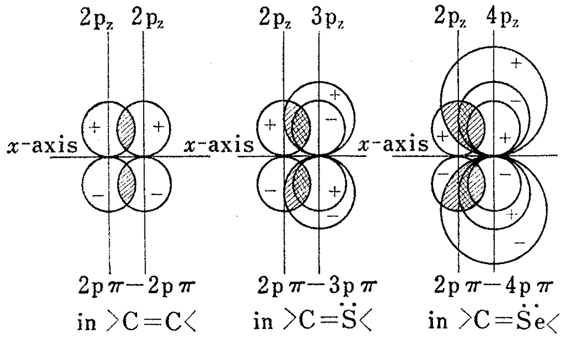

Fig. 1. Features of π—π Overlappings

Thus, it is possible to explain the difference in stability. The mechanism of the reaction between selenoxanthylium salts and organometallic reagents will be reported in the following paper.

Experimental[13]

***o*-Phenylselenobenzoic Acid (V)**——Potassium *o*-chlorobenzoate was prepared from *o*-chlorobenzoic acid (1.6 g) and KOH (0.6 g). The mixture of potassium *o*-chlorobenzoate, sodium selenophenolate (1.8 g), and Cu powder (0.5 g) was molten for 1 hr at 200°. At the end of the reaction, water was added, and the reaction mixture was filtered. The filtrate was extracted with ether and then was acidified with dil. HCl. The resulting colorless precipitate was collected by filtration and dried. Recrystallization from EtOH gave colorless plates (2.0 g, 70%), mp 190° (reported[5a] 190°).

Selenoxanthone (VI)——V (2 g) was cyclized for 3 hr at 100° with polyphosphoric acid (PPA), which was prepared from 85% H_3PO_4 (5 ml) and P_2O_5 (8 g). The cooled reaction mixture was decomposed with crushed ice and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with dil. Na_2CO_3, dried (K_2CO_3), and evaporated. Purification by sublimation afforded pale yellow needles (1.8 g, 97%), mp 191° (reported[5b] 192°). IR ν_{max}^{KBr} cm^{-1}: 1665 (CO).

Selenoxanthenol (VII)——To a suspension of VI (1.0 g) in MeOH (50 ml), $NaBH_4$ (0.8 g) was gradually added. At the end of the reaction the reaction mixture was warmed for 30 min on a water bath. The cooled mixture was poured into water with filtration. After standing overnight the precipitate was collected by filtration and dried. Recrystallization from *n*-hexane gave colorless needles (0.8 g, 89.5%), mp 115° (reported[6] 115°). IR ν_{max}^{KBr} cm^{-1}: 3385 (OH).

Selenoxanthylium Perchlorate (VIII)——To a solution of VII (0.8 g) in AcOH (20 ml), trityl perchlorate (1.3 g) was added with stirring. After standing for 1 hr anhydrous ether (20 ml) was added to the reaction mixture. The resulting precipitate was collected by filtration and rinsed with anhydrous ether. Recrystallization from CH_3CN–ether gave purple plates (1.0 g, 92.5%), mp 142—143° (decomp.) (reported[7] 143° (decomp.)).

***o*-Phenylselenobenzophenone (IX)**——The method previously described for the oxygen analog was used.[14] To a boiling solution of IV (3.6 g) in DMF (70 ml) a solution of *o*-chlorobenzophenone[8] (4.2 g) in DMF (15 ml) was gradually added. After refluxing for 3 hr, the reaction mixture was evaporated under diminished pressure. Vacuum distillation gave colorless oil (5.0 g), bp 230—232° (0.5 mmHg) (reported[9] bp 230° (0.5 mmHg)). IR ν_{max}^{neat} cm^{-1}: 1665 (CO).

9-Phenylselenoxanthenol (X)——IX (2 g) was added to PPA prepared from 85% H_3PO_4 (5 ml) and P_2O_5 (8 g). The mixture was stirred for 4 hr at 100° and then cooled. After decomposition of the mixture with crushed ice the resulting solid was taken up in benzene. The benzene layer was washed with dil. Na_2CO_3, dried (K_2CO_3), and evaporated. After purification of the residual oil by column chromatography, the pale yellow solid was recrystallized from ether–pet. ether to give colorless prisms (1.6 g, 80%), mp 105° (reported[6] 105°). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH). Cyclization of IX with the cold conc. H_2SO_4 did not give X.

9-Phenylselenoxanthylium Perchlorate (XII)——a) To an ethereal solution of X (2 g) containing a small amount of AcOH, 70% $HClO_4$ was added until the purple precipitate ceased to appear. The precipitate was collected by filtration and rinsed thoroughly with anhydrous ether. Recrystallization from AcOH or $CHCl_3$–ether gave purple plates (2.0 g, 80%), mp 172—173° (decomp.). *Anal.* Calcd. for $C_{19}H_{13}O_4ClSe$: C, 54.37; H, 3.12. Found: C, 54.17; H, 3.33. IR ν_{max}^{KBr} cm^{-1}: 1090 (ClO_4^-). b) The reaction of X (2.0 g) with trityl perchlorate (2.0 g)[15] in AcOH (30 ml) was continued with reflux for 10 min. Addition of anhydrous ether to a cooled mixture gave the purple crystals (2.3 g), which was identified by the comparison of the IR spectrum with that of the sample prepared by method a).

XII from Diphenyl Diselenide——i) Diphenyl Diselenide: An ethereal solution of selenophenol was prepared from phenylmagnesium bromide (bromobenzene (78.5 g) and Mg (12 g)) and Se (38 g) by a literature procedure.[10] Air was passed through the solution of selenophenol for 2 hr. After removal of the solvent, the resulting solid was recrystallized from EtOH to give yellow needles (38.5 g), mp 61° (reported[11] 62.5°).

ii) 9-Phenylselenoxanthylium Perchlorate (XII): A solution of diphenyl diselenide (15.6 g) in ether (50 ml) was added to a suspension of $LiAlH_4$ (1.2 g) in ether (50 ml). After the reaction mixture was refluxed for 3 hr, the solvent was removed. To a solution of the residual solid in DMF (100 ml), a solution of *o*-chlorobenzophenone (30 g) in DMF (50 ml) was gradually added with reflux. The reaction mixture was refluxed for 6 hr and then the solvent was removed. Water was added to the residual oil and the mixture was extracted with benzene. The extract was dried (K_2CO_3) and evaporated. IX thus prepared was treated in the same way as mentioned above to give XII as purple plates (15.7 g, 37.5%), mp 172—173° (decomp.).

Reaction of XII with Phenyllithium——To an ethereal solution of excess C_6H_5Li XII (1.5 g) was gradually added under an N_2 stream. After 2 hr at room temperature the reaction mixture was decomposed with

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[13] All melting and boiling points are uncorrected.

[14] M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.* (Tokyo), **21**, 1318 (1973).

[15] W. Bonthrone and D.H. Reid, *J. Chem. Soc.*, **1959**, 2774.

a cold NH_4Cl solution and extracted with ether. The ether extract was dried (K_2CO_3) and evaporated at reduced pressure. The residual oil was treated with pet. ether. The resulting solid was dissolved in a small amount of ether and then the ethereal solution was poured into pet. ether with stirring. The precipitate was collected. After this treatment was repeated for several times, the resulting solid was purified by column chromatography on alumina. The pure product was obtained as brown powders (0.4 g, 28%), mp 107—108° (decomp.). *Anal.* Calcd. for $C_{25}H_{18}Se$: C, 75.56; H, 4.57. Found: C, 75.80; H, 4.93. UV $\lambda_{\max}^{\text{EtOH}}$ (log ε) mμ: 211 (4.79), 260 (sh) (4.05), 274 (sh) (3.88), 286 (sh) (3.84). NMR ($CDCl_3$) τ: 2.30—3.00 (multiplet, aromatic H). Mass Spectrum *m/e*: 398 (M^+), 321 (M^+-C_6H_5), 245 (base peak, selenoxanthyl), 165 (fluorene). Dipole moment $\mu = 1.08$ D.

Reaction of XII with Phenylmagnesium Bromide——To an ethereal solution of C_6H_5MgBr prepared from bromobenzene (2.8 g) and Mg (0.5 g) XII (1.5 g) was added under an N_2 stream. The reaction was continued for 1 hr at room temperature and then for another 3 hr under reflux. The cooled solution was decomposed with dil. NH_4Cl solution and extracted with ether. The extract was dried (K_2CO_3) and evaporated. The residue was recrystallized from benzene–EtOH or ether to give 9,9-diphenylselenoxanthene (XIV) as colorless prisms (0.8 g, 56.5%), mp 212°. *Anal.* Calcd. for $C_{25}H_{18}Se$: C, 75.56; H, 4.57. Found: C, 75.71; H, 4.81. UV $\lambda_{\max}^{\text{EtOH}}$ (log ε) mμ: 211 (4.60), 258 (3.70), 286 (3.99). NMR ($CDCl_3$) τ: 2.25—3.35 (multiplet, aromatic H).

Reaction of XII with Methylmagnesium Iodide——To an ethereal solution (10 ml) of 0.5N CH_3MgI, XII (0.84 g) was added under an N_2 stream. After refluxing for 3 hr, the reaction mixture was taken up in the usual way. The resulting solid was recrystallized from ether to give 9-methyl-9-phenylselenoxanthene (XV) as colorless needles (0.5 g, 70%), mp 185—186°. *Anal.* Calcd. for $C_{20}H_{16}Se$: C, 71.64; H, 4.81. Found: C, 71.43; H, 4.72. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 218 (4.15), 257 (3.58), 280 (3.60). NMR ($CDCl_3$) τ: 2.30—3.45 (13H, multiplet, aromatic H), 7.90 (3H, singlet, CH_3).

Reaction of VIII with Phenyllithium——VIII (1.0 g) was added to an ethereal solution of excess C_6H_5Li under an N_2 stream. The reaction mixture was decomposed with a cold NH_4Cl solution and an insoluble material was filtered. The filtrate was extracted with ether. The extracts were dried (K_2CO_3) and evaporated. The same treatment as for XIII gave 10-phenyl-10-selenaänthracene (III) as brown powders (0.2 g, 21.4%), mp 85—87° (decomp.). *Anal.* Calcd. for $C_{19}H_{14}Se$: C, 71.02; H, 4.39. Found: C, 71.30; H, 4.50. UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 211 (4.25), 258 (sh) (3.83), 278 (sh) (3.59). NMR ($CDCl_3$) τ: 2.20—3.20 (multiplet, aromatic H). Mass Spectrum *m/e*: 322 (M^+), 245 (base peak, selenoxanthyl, M^+-C_6H_5), 165 (fluorene). The insoluble material was dried and recrystallized from xylene to give 9,9′-diselenoxanthenyl (XVI) as colorless needles (0.1 g, 13%), mp>300°, XVI was identified by the comparison of the IR spectrum with that of an authentic sample.

Reaction of VIII with Phenylmagnesium Bromide——To an ethereal solution (12.5 ml) of 0.4N C_6H_5MgBr, VIII (0.68 g) was added with stirring. The reaction mixture was treated in the usual manner. The resulting solid was recrystallized from pet. ether to give 9-phenylselenoxanthene (XVII) as colorless plates (0.58 g, 91%), mp 115°. *Anal.* Calcd. for $C_{19}H_{14}Se$: C, 71.05; H, 4.40. Found: C, 70.81; H, 4.56. UV $\lambda_{\max}^{\text{EtOH}}$ 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).

Selenoxanthene (XVIII)——VI (1.5 g) was added to a suspension of $LiAlH_4$ (1 g) in an ether–benzene mixture. After the reaction mixture was decomposed with a cold NH_4Cl solution, the organic layer was separated and the aqueous layer was extracted with benzene. The extract was dried (K_2CO_3) and evaporated. The resulting solid was recrystallized from EtOH–$CHCl_3$ to give colorless needles (1.1 g, 80%), mp 145° (reported[12] 145°).

9,9′-Diselenoxanthenyl (XVI)——A benzene solution of XVIII (1 g) was exposed to sunlight for 15 days, and then the solvent was removed under reduced pressure. The resulting solid was recrystallized from xylene to give colorless needles (0.5 g, 50%), mp>300°. *Anal.* Calcd. for $C_{26}H_{18}Se$: C, 63.94; H, 3.72. Found: C, 64.08; H, 3.87.

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