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Generation and Thermal Reactions of 2-Methyl-4-oxo-2-selenoniochroman-3-ide.

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The thermal reaction of 2-methyl-4-oxo-2-selenoniochroman-3-ide in aprotic solvents afforded (E)-bis-(2-((methylseleno)methyl)benzoyl)ethylene and trans-1,2,3-tris(2-((methylseleno)methyl)benzoyl)-cyclopropane via a carbene intermediate. Ethanol reacted thermally with the ylide to open the chroman ring, giving ethyl 2-((methylseleno)methyl)benzoate and ethyl 2-(ethoxymethyl)benzoate, whereas reaction with methanol yielded only methyl 2-((methylseleno)methyl)benzoate. Hydrolysis of the ylide eliminated dimethyl selenide, giving phthalide and 2-(hydroxymethyl)benzoic acid.

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Synthesis of New Cyclic Sulfur Ylides 9-Alkyl-10-cyano-9-thiaphenanthrenes and Their Novel Addition Reactions with Acetylenic Electrophiles.

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Novel cyclic sulfur ylides 9-alkyl-10-cyano-9-thiaphenanthrenes were synthesized in good yield by proton abstraction from the corresponding 10H-9-thiaphenanthrenium salts with triethylamine in ethanol. 10-Cyano-9-methyl-9-thiaphenanthrene was treated with dimethyl or diethyl acetylenedicar-boxylate in benzene to afford three 1:1 adducts, novel spiro compounds, dibenzothiocin derivatives and dibenzothiocinium ylide derivatives. On the contrary, treatment of 9-ethylthiaphenanthrene derivative with above acetylenes afforded dibenzothiepin derivatives as major products together with dibenzothiocinium ylide derivatives.

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Energetics of Sequential Electroreduction and Electrooxidation Steps of Benzenoid Hydrocarbons(BAH).

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The First and second reduction $(E_{1/2.1}^{\rm red}, E_{1/2.2}^{\rm red})$ and oxidation $(E_{1/2.1}^{\rm oxd}, E_{1/2.2}^{\rm oxd})$ potentials of BAH were determined by means of cyclic voltammetry in nonaqueous solvents. The equations pertinent to these potentials and their mutual relations were formulated from viewpoints of Born-Haber type thermodynamic energy cycle and SCFMO calculation. The MO paring property found in neutral BAH and also between the anion and the cation of BAH was very successful in the discussion of the given equations. Using the MO pairing property, we can derive the relation of $(E_{1/2.1}^{\rm oxd} + E_{1/2.1}^{\rm red}) = (E_{1/2.2}^{\rm oxd} + E_{1/2.2}^{\rm red})$, which was experimentally satisfied. Examination of the solvation energies has shown that these values would be interpreted by the Born type equation.