Syntheses and Thermal Behaviour of 9-Substituted 9-Thia-10-azaphenanthenes.

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Synthetic approaches to a variety of 9-thia-10-azaphenanthenes having various kinds of substituent at the 9-position were investigated. Their thermal stabilities were found to depend upon the nature of the substituent of the sulfur atom. Several 9-alkyl and 9-phenyl derivatives are quite stable at room temperature. 9-Benzyl, 9-(4-substituted benzyl), 9-fluoren-9-yl and 9-cyanomethyl derivatives underwent, even below room temperature, 1,2-rearrangement of 9-substituent to afford the corresponding 6-substituted 6H-dibenzo[c,e] [1,2]thiazines.

A Novel Example of Thermal Oxygenation of Aromatic Hydrocarbons
with a Heterocyclic N-Oxide: Unusual Reactivity of Pyrimido[5,4-g]-
pteridinetetrone 10-Oxide.

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Aromatic hydrocarbons, i.e., benzene, naphthalene, phenanthrene, toluene, p-xylene, mesitylene, and durene, were oxygenated by a member of a novel class of heterocyclic N-oxides, 1,3,6,8-tetraethylpyrimido[5,4-g]-pteridin-2,4,5,7(1H,3H,6H,8H)-tetrone 10-oxide, under certain thermal conditions to give the corresponding products oxygenated in either the benzene ring or the methyl group, presumably via a single-electron transfer process. The present results provide the first example demonstrating that a heterocyclic N-oxide can behave as an electron acceptor and subsequently as an oxygen-atom donor under thermal conditions.

Facile Conversion of $N^6$-Benzoyladenosines into 5'-Chloro-5'-deoxy-
8-hydroxyadenosines by a Reaction with Cupric Chloride: A Prominent
Substituent Effect of the $N^6$-Benzoyl Group.

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Treatment of $N^6$-benzoyl-2,3'-O-isopropylidenedenosine (1) with cupric chloride in refluxing acetonitrile resulted in the facile conversion of (1) into $N^6$-benzoyl-5'-chloro-5'-deoxy-8-hydroxy-2,3'-O-isopropylidenedenosine via an intermediary formation of $N^6$-benzoyl-5'-O,8-cyclo-2,3'-O-isopropylidenedenosine. This reflects the prominent substituent effect of the $N^6$-benzoyl group on the chemical reactivity of adenosines and provides a new method for the chemical modification of adenosines.