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[Lab. of Pharm. Chemistry]

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

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Synthetic approaches to a variety of 9-thia-10-azaphenanthrenes having various kind 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 6*H*-dibenzo[*c,e*] [1,2]thiazines.

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[Lab. of Medicinal Chemistry]

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-tetrabutylpyrimido [5,4-*g*] pteridine-2,4,5,7(1*H*,3*H*,6*H*,8*H*)-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.

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[Lab. of Medicinal Chemistry]

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*-isopropylideneadenosine (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*-isopropylideneadenosine *via* an intermediary formation of *N*⁶-benzoyl-5'-*O*, 8-cyclo-2',3'-*O*-isopropylideneadenosine. 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.