

[Spectrosc. Lett., 27, 787-799(1994)]

[Lab. of Instrumental Center]

**Structure of 3-Phenyl-2-thiopyruvic Acid as Studied by FT-IR,
FT-Raman, and NMR Spectroscopies.**

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FT-IR, FT-Raman, and high-resolution NMR spectra of 3-phenyl-2-thiopyruvic acid (PTPA) were measured in solution and in the solid state. The spectral assignments were made by referring to the data of PTPA derivatives including *para*-substituted PTPA's, PTPA-*d*₅ and PTPA disulfide. The spectral evidence indicates that PTPA exists exclusively as the ene-thiol form both in solution and in the solid state.

[J. Chem. Soc., Perkin Trans. 1, 1709-1717 (1994)]

[Lab. of Inst. of Manufacturing Pharmacy]

**Reactions of 9-Substituted 9-Thia-10-azaphenanthrenes with
Electrophiles.**

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Reactions of 9-substituted 9-thia-10-azaphenanthrenes with several electrophiles have been investigated. Reaction of 9-alkyl-9-thia-10-azaphenanthrenes with dimethyl acetylenedicarboxylate afforded dibenzothiazonine derivatives, dibenzothiazocine derivatives, 2-alkylsulfinyl-2'-vinylaminobiphenyls, and bis(biphenylylimino)ethane derivatives. The product distribution was markedly influenced by the substituent on the sulfur atom. 9-Methyl and 9-isopropyl derivatives afforded predominantly dibenzothiazonine derivatives, while 9-ethyl, 9-propyl and 9-cyclohexyl derivatives gave predominantly dibenzothiazocine derivatives and alkylsulfinyl vinylaminobiphenyls.

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**Polar Cycloaddition of 2-Benzothiopyrylium Salts with
Conjugated Dienes.**

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2-Benzothiopyrylium salts underwent polar cycloaddition with conjugated dienes to afford benzo-fused bicyclic sulfonium salts having sulfur at a bridgehead position in good yields. The structures of the cycloadducts have been established by X-ray crystallography, indicating a *cis*-fused configuration. The cycloadducts underwent retro-addition to generate 2-benzothiopyrylium ion, which was easily trapped with other dienes or active methyl compounds to give the corresponding adducts or 1-alkylated 1*H*-2-benzothiopyrans, respectively. Reactions of the cycloadducts with a variety of nucleophiles caused ring opening to afford 1-allyl- and 1-homoallyl-substituted 1*H*-2-benzothiopyrans in good yields.