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-d5, and PTPA dithiol. The spectral evidence indicates that PTPA exists exclusively as the ene-thiol form both in solution and in the solid state.

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 dibenzoithiazoline derivatives, dibenzothiazoline derivatives, 2-alkylsulffinyl-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 dibenzothiazoline derivatives, while 9-ethyl, 9-propyl and 9-cyclohexyl derivatives gave predominantly dibenzothiazoline derivatives and alkylsulfanyl vinylaminobiphenyls.

Polar Cycloaddition of 2-Benzothiopyrylum Salts with Conjugated Dienes.

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2-Benzothiopyrylum 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-benzothiopyrrolyl ion, which was easily trapped with other dienes or active methyl compounds to give the corresponding adducts or 1-alkylated 1H-2-benzo-thiopyrans, respectively. Reactions of the cycloadducts with a variety of nucleophiles caused ring opening to afford 1-allyl- and 1-homoallyl-substituted 1H-2-benzo-thiopyrans in good yields.