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Pyrimidines. 65. Synthesis of 6-Substituted Thieno[2,3-d]pyrimidine-2,4(1H,3H)-diones.

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Several 6-substituted thieno (2,3-d) pyrimidine-2,4 (1H,3H)-dione derivatives were synthesized. 6-Ethoxycarbonylthieno (2,3-d) primidine derivatives were prepared by the treatment of 6-chloro-5-formyluracil and 6-chloro-5-cyanouracil with ethyl 2-mercaptoacetate in the presence of a base. Electrophilic substitution reactions (Vilsmeier-Haack reaction, bromination, and nitration) of 5,6-unsubstituted thieno (2,3-d) pyrimidine, prepared by condensation of 6-mercaptouracil with chloro-acetaldehyde, afforded the corresponding 6-formyl, 6-bromo-, and 6-nitrothieno (2,3-d) pyrimidines, respectively.

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Synthesis of Ethynyl(phenyl)iodonium Tetrafluoroborate. A New Reagent for Ethynylation of 1,3-Dicarbonyl Compounds.

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Hydrogen fluoride-induced protodetrimethylsilylation of trimetylsilylethynyl (phenyl) iodonium tetrafluoroborate, prepared from bis(trimethylsilyl)acetylene, affords hitherto unknown ethynyl-(phenyl)iodonium tetrafluoroborate, which undergoes  $\alpha$ -ethynylation of  $\beta$ -dicarbonyl compounds under mild conditions. While Pinhey ethynylation involves the attack of nucleophiles to an  $\alpha$ -acetylenic carbon of ethynyllead triacetate, our reaction probably proceeds via 1,2-hydrogen migration of alkylidenecarbenes, produced by the attack of nucleophiles to a  $\beta$ -acetylenic carbon of the ethynyl(phenyl)-iodonium salt.

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Synthesis of Chiral Hypervalent Organoiodinanes, Iodo (III) binaphthyls, and Evidence for Pseudorotation on Iodine.

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Reported here for the first time is evidence for pseudorotation on trivalent iodine. Hypervalent organoiodinanes bearing chiral carbon ligands, acetoxyiodo(III)binaphthyls, were synthesized from (R)-2,2'-diamino-1,1'-binaphthyl. Acetoxyiodo(III)binaphthyls undergo degenerate isomerization of the acetoxy ligands about iodine(III). Dynamic NMR studies of racemic and optically active iodo(III) binaphthyls suggest that pseudorotation pathways on the iodine are responsible for the degenerate isomerization.