

BIS-(TETRAFLUOROPYRIDYL) MERCURIALS AND AN ATTEMPTED GENERATION OF TRIFLUOROPYRIDYNE

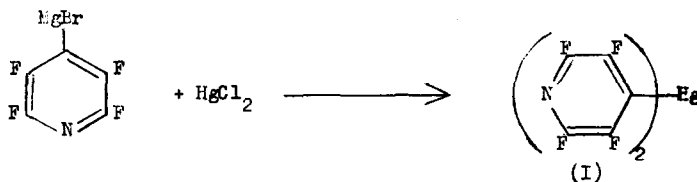
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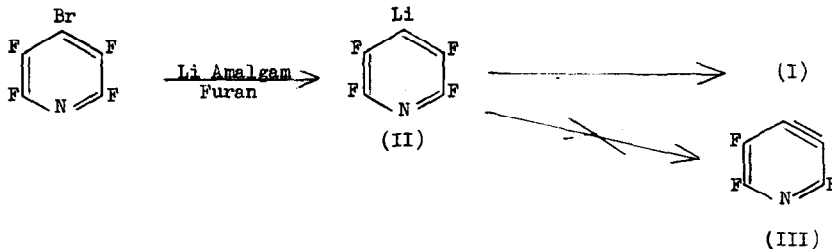
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In previous publications, we<sup>1</sup> and others<sup>2</sup> have described some of the chemistry of polyfluoropyridines including the formation of lithio-derivatives and Grignard reagents<sup>3,4</sup>. We wish now, to report the first isolable organometallic derivatives of polyfluoropyridines, the bis(tetrafluoropyridyl) mercurials. These organometallic derivatives are particularly interesting because of the extreme electronegativity of the organic group.

Tetrafluoropyridine-4-magnesium bromide reacted smoothly with mercuric chloride in diethyl ether giving 72% of bis-(2,3,5,6-tetrafluoropyridyl) mercury (I), m.p. 201-202°, a white hydrolytically stable solid which formed a stable co-ordination complex with 2,2'-bipyridyl, m.p. 181°. The complexes described in this publication and the complexes from bis(pentafluorophenyl)mercury<sup>5</sup> are the only stable co-ordination complexes of compounds containing mercury bonded to carbon, other than in cyanide.

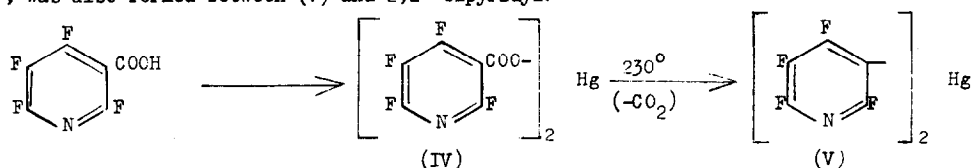


The mercurial (I), is also the principal product from the reaction between 4-bromotetrafluoropyridine and lithium amalgam in furan and, in contrast to reactions of pentafluorophenyl-lithium<sup>6</sup>, no evidence could be obtained from this and other attempted trapping experiments for the occurrence of trifluoropyridyne (III)



When the lithio derivative (II) was prepared by exchange of bromine in 4-bromotetrafluoropyridine with butyl-lithium, and allowed to decompose in the presence of furan, only polymeric material was produced, under conditions where an adduct of tetrafluorobenzene was obtained from pentafluorophenyl-lithium. It appears that the much increased susceptibility of the pyridine system to nucleophilic attack leads to self-condensation of (II) by nucleophilic displacement of fluoride ion rather than intramolecular fluoride elimination.

Bis-(2,4,5,6-tetrafluoropyridyl)mercury (V) m.p.  $200^{\circ}$  was obtained most conveniently by thermal decarboxylation of the corresponding mercury carboxylate (IV) prepared from tetrafluoronicotinic acid<sup>4</sup>. Pyrolysis of mercury carboxylates is a general route to mercurials with electron withdrawing organic groups<sup>7</sup>. A stable co-ordination complex, m.p.  $142^{\circ}$ , was also formed between (V) and 2,2'-bipyridyl.



Further work is proceeding to establish the properties of these and other organometallic derivatives of polyfluoropyridines and related polyfluoroheterocycles which constitute organic ligands of unprecedented electronegativity.

#### REFERENCES

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