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STEREOCHEMICAL INTEGRITY IN POLYFLUORINATED LITHIATED PROPENES

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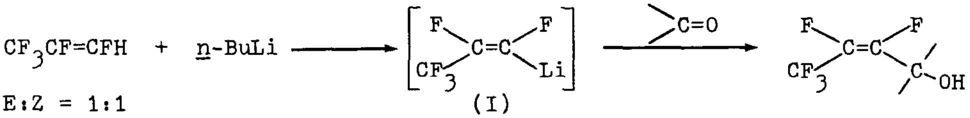
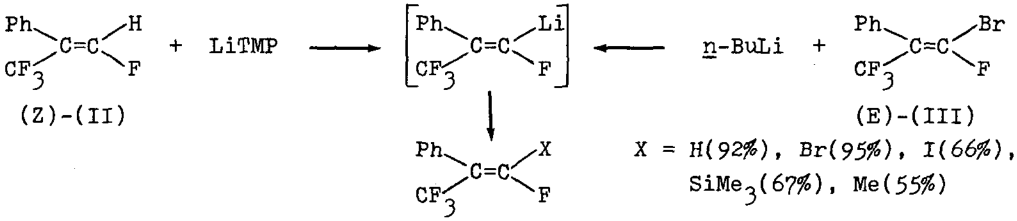
In contrast to the normal behavior of vinylic lithium compounds[1,2] in which the stereochemical integrity of the lithiated species is preserved, Tarrant and co-workers have recently reported that (Z)-pentafluoropropenyllithium (I) is exclusively formed from a 1:1 mixture of (Z)- and (E)-$CF_3CF=CFH$ and n-BuLi.[3] The high yields of (Z)-products with various trapping agents appear to preclude any selective decomposition of the intermediate (E)-lithiated species, and the rearrangement of pentafluoropropenyl lithium was suggested.[3] Recent reviews have misquoted[4] and questioned[5] these results.



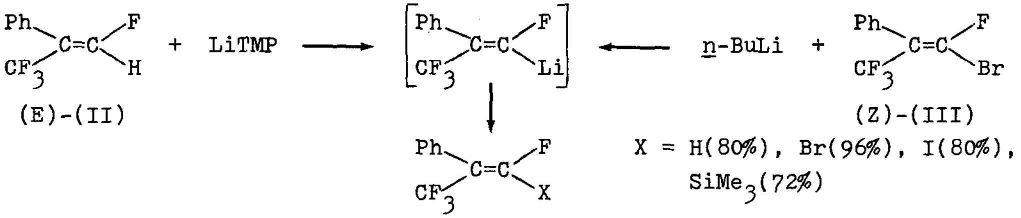
Our interest in lithium carbenoids has prompted us to ascertain whether fluorinated vinyl lithium compounds do indeed lose stereochemical integrity in contrast to their hydrocarbon analogues, since such information is of vital importance in the utility of fluorinated lithiated olefins in stereochemical synthetic sequences.

The (E)- and (Z)- isomers of 2-phenyltetrafluoropropene (II)[6] and 1-bromo-2-phenyltetrafluoropropene (III)[8] were converted to the respective lithiated compounds at -78°C in THF-hexane with either n-BuLi or lithium tetramethylpiperidide (LiTMP). Subsequent quenching of the lithiated olefins



(Z)-(II) (E)-(III)

X = H(92%), Br(95%), I(66%), SiMe$_3$(67%), Me(55%)

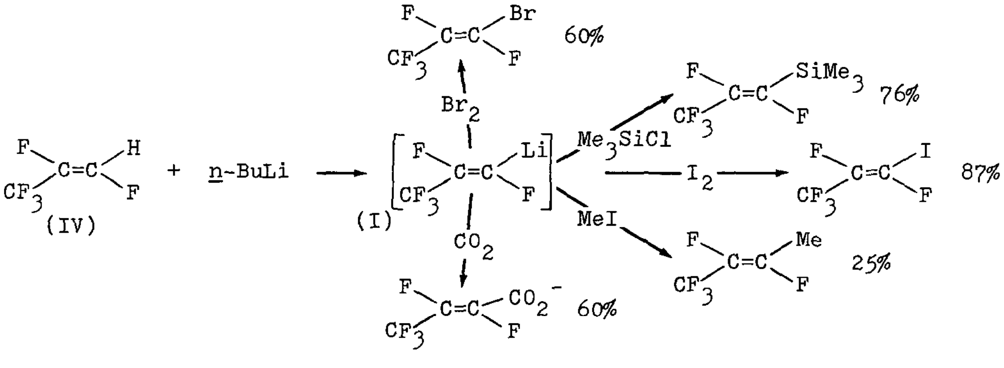


(E)-(II) (Z)-(III)

X = H(80%), Br(96%), I(80%), SiMe$_3$(72%)

with H_2O, Br_2, Me_3SiCl, I_2, or MeI results only in products in which stereochemical integrity is preserved. Stereochemical assignments are unambiguously made in both starting materials and products on the basis of the magnitude of $J_{CF_3,F}$.[10,11] Consequently, in the lithium derivatives of (II) and (III), stereochemical integrity is completely preserved.

The results of these experiments led us to reexamine (I). When pure (E)-pentafluoropropene (IV)[12] is lithiated at -78°C in THF-hexane with n-BuLi and subsequently reacted with Br_2, Me_3SiCl, I_2, MeI, or CO_2, the products



formed indicate stereochemical integrity is exclusively maintained.[11] No isomerization of the intermediate (I) is detected.

In a similar experiment, an 80:20 mixture of Z:E pentafluoropropenes was lithiated with n-BuLi at -78°C and subsequently quenched with Me_3SiCl to afford a 75:25 E:Z mixture of silanes. Again, within experimental error stereochemical integrity appears to be preserved.

Efforts to attain the results reported by Tarrant and co-workers have failed. These efforts included substitution of ether for THF and various reaction temperatures up to -23°C in the reactions with (E)-pentafluoropropene. In all cases yields were reduced but stereochemical integrity was maintained. The rearrangement reported by Tarrant, Whitfield, and Summerville remains unexplained.

We conclude that fluorinated vinylic lithium intermediates do not represent a special case, and their formation and reactions proceed with stereochemical integrity similar to non-halogenated lithium derivatives. Therefore, stereochemical reaction sequences using these organometallics as intermediates can be undertaken with confidence.

NOTES AND REFERENCES

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