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COPPER COUPLING OF ARYL AND VINYL IODIDES

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Copper coupling of 1,2-diiodoperfluorocycloalkenes has led to the synthesis of unusual and highly strained benzene and cyclooctatetraene derivatives. Recently discovered properties of the planer molecule, tetrakis (tetrafluorocyclobuta)cyclooctatetraene indicate that it is an unusually powerful oxidizing agent and reacts with ferrocene and mercury to form colored complexes.

Yields in excess of 90 percent have been achieved in the coupling of various perfluoroalkyl iodides to 1,3-bis(2-hydroxyhexafluoroisopropyl)-5-iodobenzene. The improved synthesis of these important polymer intermediates will be presented.

$$HO \stackrel{CF_3}{\sim} \stackrel{CF_3}{\sim} OH$$
 $F_3C \stackrel{C}{\sim} CF_3 + R_fI \stackrel{Cu}{\longrightarrow} DMSO$
 $HO \stackrel{CF_3}{\sim} \stackrel{CF_3}{\sim} OH$
 $F_3C \stackrel{C}{\sim} CF_3 + CuI$

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KINETICS AND MECHANISM OF ELIMINATION OF HYDROGEN FLUORIDE FROM FLUORINATED SUCCINIC ACIDS

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About a decade ago the author described a rather surprising base-promoted elimination of hydrogen fluoride in preference to hydrogen bromide from methyl and ethyl esters of α -bromo- α '-fluorosuccinic acids (J. Fluorine Chem. 1972, $\underline{2}$, 1). In order to gain a deeper insight into this rare and quite unique reaction rates of base-promoted elimination of hydrogen fluoride from erythro- and threo- α -bromo- α '-fluorosuccinic acids were measured using proton NMR technique. The rates were compared with the rates of elimination of hydrogen fluoride from fluorinated succinic acids. The ease of elimination of hydrogen fluoride increases in the series: DL-α,α'-difluorosuccinic acid, meso-α,α'-difluorosuccinic acid, fluorosuccinic acid, and α, α' -difluorosuccinic acid. Surprisingly, meso- $-\alpha, \alpha'$ -difluorosuccinic acid undergoes dehydrohalogenation more rapidly than its DL-diastereomer. This finding contrasts with dehydrobromination of meso- and DL-dibromosuccinic acids where the meso-isomer reacts less rapidly than the DL-form. Both diastereomeric bromofluorosuccinic acids undergo dehydrofluorination preferentially to dehydrobromination. The rates of dehydrofluorination of both erythro- and threo-a-bromo-a-fluorosuccinic acids are comparable and much higher than those of any fluorinated succinic acid. An explanation of the reactions will be offered and a possible mechanism will be proposed based on the role of hydrogen bonds in the conformations of transition states and on the stereochemical outcome of the dehydrofluorinations.