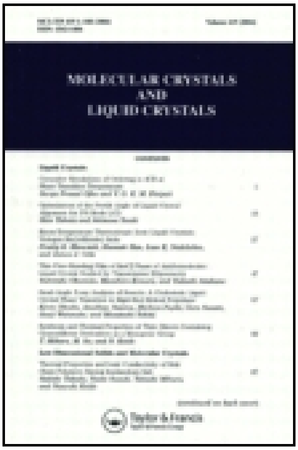

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Solid-State vs. Solution Stereospecificity in the Bromination of Fluorinated Olefins

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Solid-State vs. Solution Stereospecificity in the Bromination of Fluorinated Olefins

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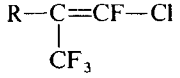
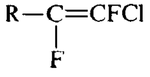
Previous work on the ionic addition of halogens to olefins in the solid-state has been published. For example, Paul and Curtin reported *trans*-stilbene adds chlorine *cis* in the solid-state.[1] Hadjoudis reported the *trans*-addition of bromine to crystalline olefins.[2] Solid fluorinated olefins react with bromine or chlorine vapor under radical conditions, and it has been shown that extensive melt formation does not occur when the olefin contains a carboxylic acid group.[3]

Previously developed synthetic techniques were used to prepare the following olefins (where $R = 3\text{- or }4\text{-}HO_2C{-}C_6H_4{-}$). These olefins are



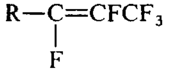
$\mathrm{R{-}}\underset{\substack{|\\ \mathrm{CF_3}}}{\mathrm{C}}\mathrm{{=}CF{-}Cl}$

1



$\mathrm{R{-}}\underset{\substack{|\\ \mathrm{F}}}{\mathrm{C}}\mathrm{{=}CFCl}$

2



$\mathrm{R{-}}\underset{\substack{|\\ \mathrm{F}}}{\mathrm{C}}\mathrm{{=}CFCF_3}$

3

isomerically pure and the reactions of each isomer with bromine in solution and the solid-state has been examined.

For the *cis* and *trans* isomers of **1**, addition of bromine to the double bond does not occur. Under conditions of radical bromination only isomerization is observed in solution. Starting from either the *cis* or the *trans* isomer an equilibrium mixture of 30% Z-isomer (CF_3 and Cl *cis*) and 70% *E*-isomer is formed. Attempts to react either isomer with bromine in a solid-gas reaction have resulted in no reaction.

The *cis* or *trans* isomers of **2** stereospecifically add bromine to form the *trans*-adduct in ionic reactions in either solution or the solid. With free radical conditions in solution the erythro diastereomer is stereoselectively formed from either the *cis* or the *trans* isomer. The solid-gas reactions show a mixture of ionic and radical pathways. Finally, the *cis* and *trans* isomers of **3** exhibit mainly non-stereospecific addition of bromine in solution for either an ionic or radical reaction. However, the gas-solid reactions lead preferentially to stereospecific formation of the *cis*-adducts.

The ionic brominations of **2** and **3** demonstrate differences in mechanism. A bromonium ion is involved for **2** because of the high degree of stereospecificity (*trans*-addition) observed in the reactions; while **3** is brominated *via* an open cation. Thus, the solution reactions of **3** are non-stereoselective, and the solid-gas reactions preferentially form the *cis*-adduct.

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