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THE SOLID-GAS CHLORINATION AND BROMINATION OF A FLUORINATED OLEFIN

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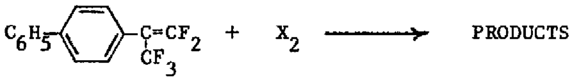
The solid-gas reactions of bromine or chlorine with crystalline olefins have been reported only occasionally until the last few years[1]. Recent work has been directed at understanding the influence of the crystal lattice upon the course of these reactions[2-4]. Some systems have showed relatively high solid phase reactivity, even in the dark[3].

Because of this increased reactivity it was of interest to determine if crystalline polyfluorinated olefins would also exhibit high solid-state reactivity toward chlorine and bromine. The usual solution reaction conditions for the chlorination or bromination of fluorinated olefins favor a radical reaction[5]. Thus, the solid-gas reaction of 2-(4-biphenylyl)-F-propene, **1**, with chlorine and bromine was studied to determine its reactivity relative to solution reactions.

The results of the reaction of **1** with chlorine and bromine are given in the Table. The solution reactions demonstrate that halogenation of the olefin double bond occurs under radical conditions (i.e., exposure to light and in either an ionizing or non-ionizing solvent). Aromatic substitution by halogen occurs under ionic conditions (i.e., in the dark and only in an ionizing solvent-HOAc).

Powdered **1** reacts very slowly with chlorine gas in the dark. Less than 1/2% total product yield is formed after eight days; aromatic substitution and addition across the olefin bond occur to approximately the same extent. During its exposure to chlorine, microscopic examination of single crystals of **1** did not reveal visible changes, although the rate of sublimation of the sample was retarded. The difference in the o/p ratio in **2** for HOAc (DARK) and the solid-gas reaction appears to be a medium effect and not a result of the crystal structure of **1**.[6]

In room light solid **1** reacts more rapidly with chlorine gas. The initial re-



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	Reaction Conditions	Per-Cent Conversion[a]	Product Ratios $XC_6H_4C_6H_4\overset{CF_3}{C}{=}CF_2$ ortho 2	para	$C_6H_5C_6H_4\overset{CF_3}{C}XCF_2X$ 3	$XC_6H_4C_6H_4\overset{CF_3}{C}XCF_2X$ ortho 4	para
X = Cl	HOAc (solvent) DARK-2 days	90%	43	57	trace	-	-
	HOAc (solvent) hν-1 day	100%	trace	trace	20	30	50
	113[b] (solvent) DARK-6 days	trace	-	-	100	-	-
	113 (solvent) hν-1 day	98%	-	-	99	trace	trace
	Solid-gas	ca. 1/2%	17	34	49	trace	trace
	DARK-8 days						
	Solid-Gas hν-2 days	ca. 95%[c]	-	-	40	1.9	2.0
X = Br	HOAc (solvent) DARK-5 days	7%	trace	100	-	-	-
	HOAc (solvent) hν-16 hrs	75%	-	-	100	-	-
	113 (solvent) DARK-5 days	trace	-	-	100	-	-
	113 (solvent) hν-1 day	95%	-	-	100	-	-
	Solid-Gas DARK-6 hours	100%	2	92	6	-	< 1
	Solid-Gas hν-3 days	100%	< 1	35	-	-	64

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a. G. C. yields based on 1. Product structures were confirmed by either independent synthesis or by mass spectrometry and ^{19}F and ^{13}C nmr analysis.

b. Fluorocarbon 113, $CF_2ClCFCl_2$

c. ca. 56 parts of the product was a complex mixture of hexachlorocyclohexane compounds, 5, $C_{15}H_9Cl_8F_5$ and $C_{15}H_8Cl_9F_5$, as determined by mass spectral analysis. The individual products were not separated from the reaction mixture.

action is formation of **3** followed by either formation of **4** (a minor process) or by chlorine addition to the aromatic rings and formation of hexachlorocyclohexane derivatives, **5**. The chloro olefins, **2**, were not detected during the reaction. Complete consumption of **1** did not occur, because the rate of reaction of **1** was slower toward the end of the reaction. This was presumably due to the tacky coating of **4** and **5** formed on the surface of **1** which prevented the chlorine from reaching unreacted **1**. A similar result had been noted in the solid-gas chlorination of *trans*-stilbene[4].

This solid-gas reaction has two competing reactions after chlorination of the alkene occurs; aromatic substitution and aromatic addition. The relative rates of these two paths were studied by examination of the solid-gas reaction of powdered **3** and chlorine.

$$\mathbf{3}(X = Cl) + Cl_2 \xrightarrow[\text{6 days}]{\text{Solid-Gas}} \underline{\text{ortho}}\text{-}\mathbf{4} + \underline{\text{para}}\text{-}\mathbf{4} + \mathbf{5}$$

Dark: 6% 11% 5%

hν: *ca.*2% *ca.*3% 42%

Formation of **5** was suppressed in the dark, as would be expected[7]. In both reactions the sample of **3** became tacky and wet-looking as reaction proceeded. The increased solid-gas reactivity of **3** in the dark relative to **1** is probably a result of formation of liquid products (**4** and **5**) on the surface of the solid. This provides a medium for further reaction and accelerates the rate of reaction. The solid-gas reaction of **1** in the dark forms products which are solids (**2** and **3**); thus, no liquid coating is formed on the surface of the solid and the rate of chlorination is not accelerated[8]. A similar result is obtained in the solid-gas chlorination of biphenyl. The sample turns to liquid after a few hours and complete consumption of the biphenyl occurs in *ca.* 1 day.

The reaction of crystalline **1** with bromine gas is a moderately fast reaction. In the dark the major process is aromatic bromination with *para*-**2** being formed almost exclusively. A minor amount of addition occurs. In room light aromatic bromination occurs first followed by addition to the olefin bond and formation of a substantial amount of **4**. For both reactions the process in actually a liquid phase reaction as bromine quickly condenses on the surface of 1 and a solution results[8].

Other solid-state reactions of this and related fluoroolefins are being examined with a variety of reagents.

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