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REACTIONS OF 1,1-DIFLUORO-1-OLEFINS WITH ELECTROPHILIC REAGENTS

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1,1-Difluoro-1-olefins react smoothly with electrophilic reagents such as bromine and acid chloride-Lewis acid at room temperature producing the addition products.

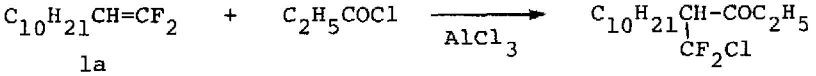
Fluoroolefins are well known to exhibit high reactivity toward nucleophilic reagents, and a large number of reactions of polyfluorinated olefins with various kinds of nucleophiles have been reported. This marked reactivity is attributed to the strong inductive effect of fluorine atoms. For this reason, reactivity of fluoroolefins toward electrophilic reagents has been believed to be quite low, and actually has been examined only scarcely. Addition of halogen and some other electrophilic reagents to polyfluorinated ethylenes and propylenes has been reported1), and only vinylidene fluoride and trifluoroethylene have been acylated by acid chloride(fluoride) in the presence of a Lewis acid2). We wish to report here that 1,1-difluoro-1-olefins 1 react with electrophilic reagents such as bromine and acid chloride-Lewis acid under mild reaction conditions producing the addition products in fair yields.

When 1,1-difluoro-1-olefins 1a($R=C_{10}H_{21}$) and 1b($R=p\text{-}ClC_6H_4$) were treated with bromine in dichloromethane at room temperature, the color of bromine disappeared almost completely within 10 min, and expected dibromides 2a,b were obtained in 90 and 87% yields, respectively.

$$\underset{\mathbf{1}}{RCH{=}CF_2} \quad + \quad Br_2 \longrightarrow \underset{\mathbf{2}}{RCHBr\text{-}CF_2Br}$$

	R
a;	$C_{10}H_{21}$
b;	$p\text{-}ClC_6H_4$

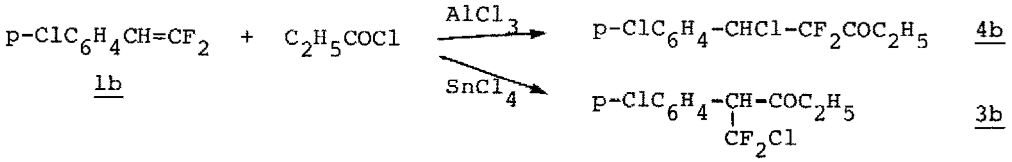
Similarly, acylation occurred smoothly at room temperature. When a mixture of 1a, propionyl chloride and aluminium chloride in dichloromethane was stirred at room temperature, addition product 3a was isolated in 54% yield.



$$\underset{\mathbf{1a}}{C_{10}H_{21}CH{=}CF_2} \quad + \quad C_2H_5COCl \xrightarrow[AlCl_3]{} C_{10}H_{21}\underset{\displaystyle CF_2Cl}{\underset{|}{C}}H\text{-}COC_2H_5$$

3a

When 1b was treated with propionyl chloride and aluminium chloride, only 4b was obtained in 41% yield. Isomeric adduct 3b was not detected at all (by glc analysis). While, when stannic chloride was used in place of aluminium chloride in the above reaction, only 3b was formed in 63% yield. Again, 4b was not present in the crude reaction product[3].

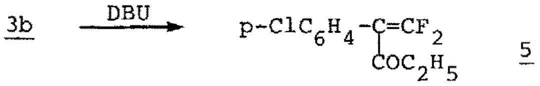


$$\underset{\textbf{1b}}{p\text{-}ClC_6H_4CH{=}CF_2} + C_2H_5COCl \; \xrightarrow{AlCl_3} \; p\text{-}ClC_6H_4\text{-}CHCl\text{-}CF_2COC_2H_5 \quad \textbf{4b}$$

$$\xrightarrow{SnCl_4} \; p\text{-}ClC_6H_4\text{-}\underset{\displaystyle CF_2Cl}{\underset{|}{C}H}\text{-}COC_2H_5 \quad \textbf{3b}$$

The structures of addition products 3 and 4 were determined by their spectroscopic properties. Especially, ^{19}F-NMR spectroscopy was helpful to distinguish 3 and 4. In ^{19}F-NMR spectra, 3a and 3b exhibit absorptions at δ[4] (vs CF_3COOH) 26.4 and 15.7, respectively, which are in the vicinity of those of 2a(δ 24.0 and 32.6) and 2b(δ 26.7 and 33.0). While, 4b has an AB quartet at δ -28.1 and -38.2.

Chemically, 3b was dehydrochlorinated smoothly by DBU and corresponding β,β-difluoro-α,β-unsaturated ketone 5 was obtained. While, 4b was completely inert to DBU under the same reaction conditions.



$$\textbf{3b} \xrightarrow{DBU} p\text{-}ClC_6H_4\text{-}\underset{\displaystyle COC_2H_5}{\underset{|}{C}}{=}CF_2 \quad \textbf{5}$$

We have shown that 1,1-fluoro-1-olefins are more reactive toward electrophilic reagents than have been expected. Also, the effect of fluorine substitution on the stabilty of carbonium ions was found to be quite marked (as indicated by the formation of 3a,b). Further studies are under way.

REFERENCES AND NOTE

1) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, "Fluorine Chemistry Reviews", Marcel Dekker, 1969, Vol. 3, p45.
2) I. L. Knunyants, R. N. Sterlin, L. N. Pinkina, and B. L. Dyatkin, Izv. Akad. Nauk. SSSR Ser. Khim., 1958, 296. G. G. Belen'kii and L. S. German, ibid, 1974, 942. See also ref. 1).
3) Among other Lewis acids examined, boron trifluoride(added as its etherate) and titanium tetrachloride were ineffective, and ferric chloride gave a complex mixture containing both 3b and 4b, the latter being the major product. Propionic anhydride serves as the acylating agent, although the yield was low.
4) (+); lower field.

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