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Fluorination with Xenon Difluoride. Reactions with 1,1-Diphenylethylenes

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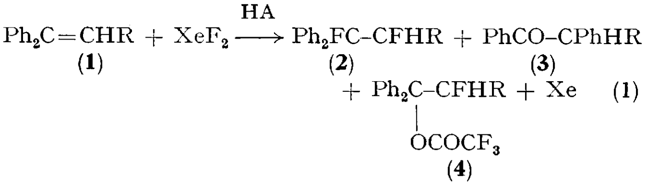
Summary Xenon difluoride reacts with 1,1-diphenylethylenes in the presence of hydrogen fluoride or trifluoroacetic acid as catalyst to form the corresponding 1,2-difluoro-1,1-diphenylethanes in nearly quantitative yields.

Although the fluorination of aromatic compounds with xenon difluoride, in both the liquid[1] and vapour[2] phase, has been investigated, there has been, up to now, only one report of fluorine addition to olefins[3] with this reagent. In the course of our efforts to elucidate the reactions of xenon difluoride with olefins, we found it reasonable to fluorinate some 1,1-diphenylethylenes. The fluorination of 1,1-diphenylethylene has been achieved with a variety of reagents, such as lead tetra-acetate–hydrogen fluoride,[4] aryliododifluorides,[5] and molecular fluorine[6] at low temperature. The processes with lead tetra-acetate–hydrogen fluoride and aryliododifluorides led to rearranged products, *e.g.* phenyl migration to yield 1,1-difluoro-1,2-diphenylethane[4,5] and fluorination with molecular fluorine[6] gave both addition and substitution products.

We now report that xenon difluoride readily adds fluorine to 1,1-diphenylethylenes (**1**) in the presence of HF or CF_3CO_2H as catalyst[7] to give the corresponding 1,2-difluoro-1,1-diphenylethanes (**2**) in 65 to 95% yield [equation (1)]. In addition to (**2**) small amounts of deoxybenzoins (**3**) or trifluoroacetate (**4**) were observed. In a typical experiment, (**1a**) (10 mmol) was dissolved in methylene chloride (40 ml) at room temperature, anhydrous HF or CF_3CO_2H (1 to 25 mmol) was introduced in the reaction mixture and under stirring pure xenon difluoride (10 mmol) was added. After few seconds the colourless solution turned dark green and xenon gas was evolved. After 30 min, gas evolution had ceased and the reaction appeared to be complete. As a routine work up procedure, ^1H and ^{19}F n.m.r., and mass spectra were taken on crude reaction mixtures and then the products (**2**)—(**4**) were separated by g.l.c. or t.l.c.



$$\underset{(\mathbf{1})}{\mathrm{Ph_2C{=}CHR}} + \mathrm{XeF_2} \xrightarrow{\mathrm{HA}} \underset{(\mathbf{2})}{\mathrm{Ph_2FC\text{-}CFHR}} + \underset{(\mathbf{3})}{\mathrm{PhCO\text{-}CPhHR}} + \underset{(\mathbf{4})}{\underset{\mathrm{OCOCF_3}}{\underset{|}{\mathrm{Ph_2C\text{-}CFHR}}}} + \mathrm{Xe} \qquad (1)$$

a; R = H
b; R = Me
c; R = F
HA = HF or CF_3CO_2H

The structures of previously known (**2a**),[6] (**2c**),[6] (**3a**), and (**3b**) were identified and those of unknown (**2b**) and (**4c**) assigned by their i.r., ^1H and ^{19}F n.m.r., and mass spectra.

In the absence of HF or CF_3CO_2H fluorine addition is very slow. Several interesting features are apparent. Deoxybenzoins (**3**), the only rearranged products, are formed in HF catalysed reactions with olefins (**1a**) and (**1b**), but not with (**1c**). However, when CF_3CO_2H was used as catalyst, the competitive trifluoroacetate (**4c**), was obtained in the reaction with (**1c**) only. We found neither evidence for the formation of rearranged fluorine products nor presence of 1,1-diphenyl-2-fluoroethylenes which might arise *via* a substitution fluorination[6] or from an HF elimination of adducts (**2**).†

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† The adducts (**2a**) and (**2b**) readily eliminate HF and could be quantitatively transformed into the corresponding 2-fluoro-1,1-diphenylethylenes at 165 °C. These transformations were also observed in attempted g.l.c. separations of these adducts.

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