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FLUORINATION WITH XENON DIFLUORIDE. STEREOCHEMISTRY OF THE FLUORINE ADDITION TO STILBENE

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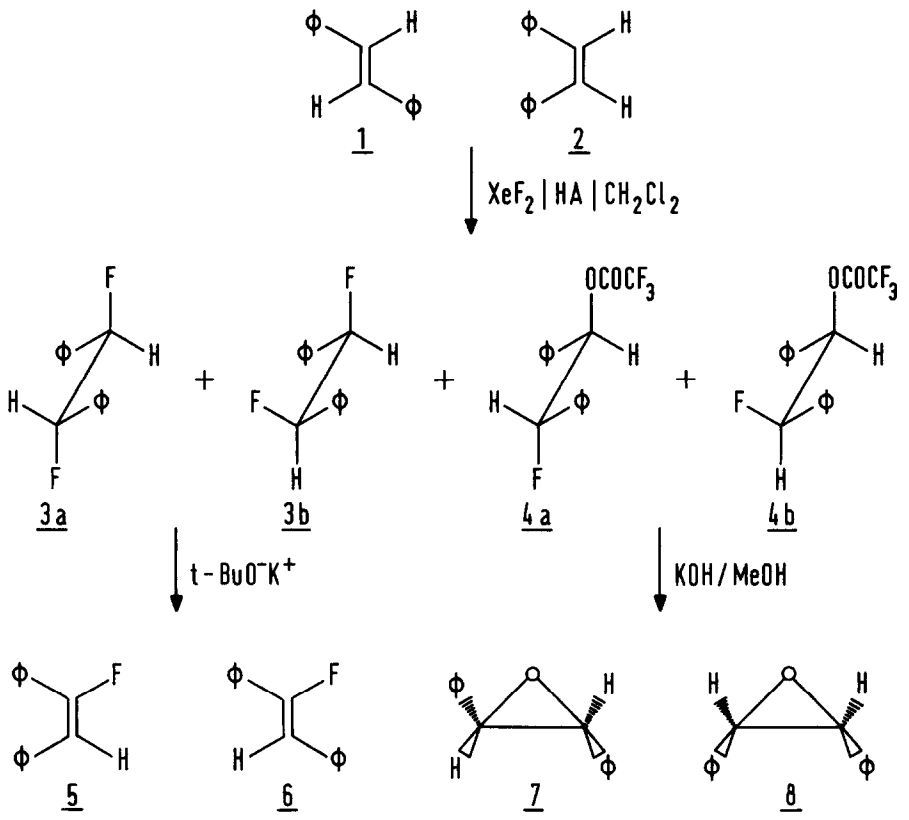
Recently, we have found that xenon difluoride reacts with 1,1-diphenylethylenes in the presence of hydrogen fluoride or trifluoroacetic acid as catalyst to form corresponding 1,2-difluoro-1,1-diphenylethanes in nearly quantitative yield[2]. We report now the results of similar fluorine addition to cis- and trans-stilbene with this reagent. The attempted fluorination of trans-stilbene with aryliododifluorides[3] has failed. On the other hand, cis isomer has been successfully fluorinated with molecular fluorine in a low temperature process yielding a 5:1 mixture of meso- and d,l-1,2-difluoro-1,2-diphenylethanes[4].

Being interested in learning whether each number of a cis and trans isomeric olefin pair would exhibit the same stereochemistry of the fluorine addition with xenon difluoride, we chose trans- (1) and cis-stilbene (2) for this study. In a typical experiment, 1 (1 mmol) was dissolved in methylene chloride (10 ml) at 20°C, anhydrous HF (1 mmol) or CF_3CO_2H (1 ml 1,0 M in CH_2Cl_2) was introduced in the reaction mixture and under stirring pure XeF_2 (1 mmol) was added. 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 standard procedure, ^1H and ^{19}F n.m.r. spectra were taken on crude reaction mixtures and the products (3a), (3b), (4a) and (4b) were separated by g.l.c. or t.l.c. The conversions of 1 and 2 into products were of the order of 90%, as determined by n.m.r. or g.l.c.

The structures of the vicinal difluorides were assigned from the products formed when the pure isomers were treated with base under conditions for anti elimination. The products, α-fluoro-cis- (5) and α-fluoro-trans-stilbene[5] (6), were identified on the basis of differences in their n.m.r. spectra (5 J_{HF} 22 cps, 6 J_{HF} 40 cps). One difluoride reacts more rapidly then the other yielding 6 as the product. The anti stereospecifity of elimination requires that this difluoride be assigned structure 3b [(100 and



TABLE

The Product Distribution of the Fluorine Addition to Stilbene with Xenon Difluoride

Olefin	Catalyst	Relative Yields (%)[a] 3a	3b	4a	4b
trans-Stilbene	HF	62	38		
	CF_3CO_2H	30	18	35	17
cis-Stilbene	HF	53	47		
	CF_3CO_2H	26	24	26	24

[a]Determined by ^{19}F n.m.r. spectroscopy

94,1 MHz, CCl_4) ∂ 5,37 (m 2H) ∂ -203,3 (m 2F)]. The slower reacting difluoride which eliminates to give olefin 5 is assigned structure 3a [(100 and 94,1 MHz, CCl_4) ∂ 5,46 (m 2H) ∂ -206,3 (m 2F)]. The structures of the competitive fluoro trifluoroacetates were assigned on the basis of the following chemical transformation. When mixtures containing both isomers in ratio 1,5:1, in one case, and 1,22:1, in another, were treated with ethanolic potassium hydroxide, trans- (7) and cis-stilbene oxide[6,7] (8) were formed in ratio 1,5:1 and 1,2:1, respectively. This shows that fluoro trifluoroacetates react stereospecifically with base and indicates that the isomer present in higher concentration is d,l-erythro-1-fluoro-2-trifluoroacetoxy-1,2-diphenylethane (4a) [(94,1 MHz, CCl_4) ∂ -206,5 (dd 1F) ∂ -83,8 (s 3F) J_{FH_1} 46,5 cps J_{FH_2} 15,0 cps], and in lower concentration present one is d,l-treo-fluoro trifluoroacetate 4b [(94,1 MHz, CCl_4) ∂ -200,1 (dd 1F) ∂ -83,8 (s 3F) J_{FH_1} 48,0 cps J_{FH_2} 13,5 cps].

Isomerisation of the reactant olefin was evaluated in separate experiments stopped prior to completion. The unreacted olefin was analysed by g.l.c. Isomerisation of 1 during the course of reaction is negligible, but that of 2 is of the order of 10% and 21 % in HF and CF_3CO_2H catalysed reactions, respectively. We found neither evidence for the secondary isomerisation of reaction products nor presence of α-fluorostilbenes 5 or 6 which might arise via a substitution fluorination or from HF elimination of adducts 3a-b.

The product distribution of the fluorine addition to cis- and trans-stilbene with XeF_2 is presented in the Table. Although vicinal difluorides are the only products in HF catalysed reactions, the amount of competitive trifluoroacetates is close to 50% in CF_3CO_2H catalysed reactions. The results show that the fluorine addition to stilbene system with XeF_2 is clearly a nonstereospecific process. Correcting for olefin isomerisation, the data of the Table indicate that there exists some preference for anti addition of fluorine to trans-stilbene and a similar tendency for the mixed adduct formation. Contrary, the addition to cis olefin is practically nonstereoselective.

The observed stereochemical results seem us of interest in particular with comparison with molecular fluorine addition to stilbene[4], 1-phenyl-propene[5], indene[8], and acenaphthylene[8], where a general preference for syn addition was observed. We are therefore currently investigating the stereochemistry and mechanism of the fluorine addition to these double bond systems with xenon difluoride.

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