SOME REACTIONS OF α,β,β-TRIFLUOROSTYRENE

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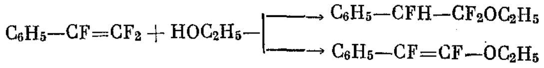
The reactions of fluoroolefins with electrophilic and nucleophilic reagents have been studied quite well. Here it was shown that due to the "electron depletion" of the π-bond, caused by the high electron-acceptor capacity of the fluorine atoms, the fluoroolefins are more inclined toward reactions with nucleophilic reagents, and less inclined toward reactions with radical and electrophilic reagents than are olefins. The reaction of tetrafluoroethylene and perfluoropropylene with alcohols is observed only at 100° in the presence of bases [1]. Perfluoroisobutylene reacts with methanol and ethanol at room temperature without a catalyst to give ethers [2]. The reaction of fluoroolefins with electrophilic and radical reagents has the reverse order. Tetrafluoroethylene reacts explosively with N_2O_4 in a closed system, and in order to run the process it is necessary to use an inert solvent or cooling. Perfluoropropylene reacts even at room temperature in 7 days, while heating to 170-180° is necessary for the reaction with perfluoroisobutylene [3, 4].

It seemed of interest to evaluate the reactivity of fluoroolefins, the multiple bond of which is conjugated with a phenyl radical. Such an olefin is α,β,β-trifluorostyrene (TFS). Its reactivity with radical and nucleophilic reagents has been studied inadequately. Only one communication exists on the reaction of TFS with ethanol in the presence of sodium alcoholate; it was shown there that the process proceeds in two directions [5]



$$C_6H_5{-}CF{=}CF_2 + HOC_2H_5 \rightarrow \begin{cases} C_6H_5{-}CFH{-}CF_2OC_2H_5 \\ C_6H_5{-}CF{=}CF{-}OC_2H_5 \end{cases}$$

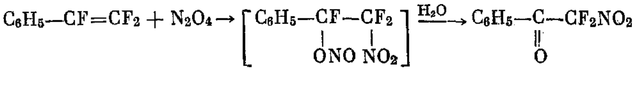
We made a study of the reactivity of TFS with diethylamine and ammonia, and also with N_2O_4 and tetrafluorohydrazine. It proved that reaction with diethylamine is observed only at 100°. Treatment of the reaction mass with water made it possible to isolate the diethylamide of α-fluorophenylacetic acid, which gave reason to interpret the reaction by the following scheme

$$C_6H_5{-}CF{=}CF_2 + HN(C_2H_5)_2 \rightarrow [C_6H_5{-}CFH{-}CF_2N(C_2H_5)_2] \xrightarrow{H_2O} C_6H_5{-}CFH{-}CO{-}N(C_2H_5)_2 .$$

The reaction of TFS with liquid ammonia in a sealed ampule, in ether, at room temperature, followed by treatment of the reaction mass with water, gave the nitrile of α-fluorophenylacetic acid in 70% yield. The reaction products of TFS with diethylamine and ammonia are analogous to the products that are formed in the case of aliphatic fluoroolefins. However, TFS reacts with the indicated nucleophilic reagents under somewhat more drastic conditions than does perfluoropropylene [2, 6]

$$C_6H_5{-}CF{=}CF_2 + NH_3 \rightarrow [C_6H_5{-}CFH{-}CF_2NH_2] \xrightarrow{H_2O} C_6H_5CFHCN$$

The reaction with reagents of a radical character proceeds with greater ease than in the case of the aliphatic fluoroolefins. Thus, TFS reacts very vigorously with N_2O_4, in which connection it is necessary to cool the reaction mass and use a solvent. The subsequent treatment of the reaction mass with 70% H_2SO_4 solution and water gave difluoronitromethyl phenyl ketone (difluoronitroacetophenone) in 90% yield



$$C_6H_5{-}CF{=}CF_2 + N_2O_4 \rightarrow \left[\begin{matrix} C_6H_5{-}\underset{\displaystyle ONO}{\underset{|}{C}F}{-}\underset{\displaystyle NO_2}{\underset{|}{C}F_2} \end{matrix}\right] \xrightarrow{H_2O} C_6H_5{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CF_2NO_2$$

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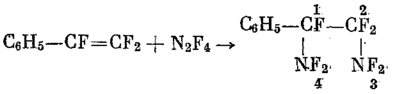
TABLE 1

Compound	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	*MR*		Found, %				Calculated, %			
				found	calc.	C	H	F	N	C	H	F	N
$C_6H_5CFHCON(C_2H_5)_2$	137 (4)	1,0841	1,5280	59,20	58,53	69,01	7,91	10,34	7,55	68,88	7,65	9,09	6,70
C_6H_5CFHCN	80 (9)	1,1214	0,4964	35,20	35,65	71,19	4,69	14,28	10,35	71,11	4,45	14,13	10,37
$C_6H_5COCF_2NO_2$*	83 (4)	1,4048	1,4880	41,22	41,74	47,71	2,51	19,48	7,60	47,70	2,50	18,91	6,96
$C_6H_5CF(NF_2)CF_2(NF_2)$	65 (30)	1,4380	1,4131	45,40	44,60	37,1	2,1	50,5	11,5	36,6	1,9	50,7	10,7

*Dinitrophenylhydrazone, mp 146°. Found : F 9.71; N 18.35%. $C_{14}H_9O_6N_5F_2$. Calculated : F 9.75; N 18.05%.

The reaction of TFS with another reagent that has a well-defined radical character, namely tetrafluorohydrazine, also proceeds quite vigorously at 60° in ethyl acetate; α,β-(difluoroamino)-α,β,β-trifluoroethylbenzene is formed in 60% yield



$$C_6H_5{-}CF{=}CF_2 + N_2F_4 \rightarrow C_6H_5{-}\underset{\underset{4}{NF_2}}{\overset{1}{C}F}{-}\underset{\underset{3}{NF_2}}{\overset{2}{C}F_2} \qquad (1)$$

EXPERIMENTAL

The ^{19}F NMR spectra were taken on a Hitachi–Perkin–Elmer R-20 spectrometer, with a field strength of 14,092 gauss at a frequency of 56.456 MHz. The chemical shifts (δ) were measured in parts per million, and CF_3COOH was used as the external standard. The IR spectra were taken on a UR-20 instrument in CCl_4.

Diethylamide of α-Fluorophenylacetic Acid. To 10.5 g of α,β,β-trifluorostyrene at ~20° was added 13.7 g of diethylamine in drops. The reaction mixture was heated at 100° for 6 h, cooled (the formation of crystals was observed), treated with water, and the oil was separated, dried over $MgSO_4$, and fractionally distilled. We obtained 9.0 g (65%) of the diethylamide of α-fluorophenylacetic acid.

Nitrile of α-Fluorophenylacetic Acid. To a glass ampule, cooled to –40°, were added 4.0 g of α,β,β-trifluorostyrene and 1.2 ml of ammonia, dissolved in 5 ml of absolute ether. The ampule was sealed and kept at ~20° for a day. Then the reaction mass was treated with water, and the ether layer was separated, dried, and fractionally distilled to give 2.4 g of the nitrile of α-fluorophenylacetic acid.

Difluoronitromethyl Phenyl Ketone (Difluoronitroacetophenone). To a stirred solution of 5.0 g of α,β,β-trifluorostyrene in 10 ml of dry CCl_4 at –10° was added 4.5 g of N_2O_4 in drops. The mixture heated up to 0°. The mixture was allowed to stand overnight at ~20°. Then the solvent was distilled off, the residue was treated with 70% H_2SO_4 solution, and the oil was separated, washed twice with water, dried over $MgSO_4$, and fractionally distilled. We obtained 5.7 g (90%) of difluoronitromethyl phenyl ketone. Infrared spectrum (ν, cm^{-1}): 1720 (C=O), 1609 (asymm. NO_2), 1290 (symm. NO_2), 121 (CF_2), 3090 (CH).

α,β-Bis(difluoroamino)-α,β,β-trifluoroethylbenzene. Through a solution of 6.0 g of α,β,β-trifluorostyrene in 70 ml of anhydrous ethyl acetate, placed in a bubbling column, at 60°, was passed 2.5 liters of tetrafluorohydrazine for 2.5 h. Then the solution was cooled, blown with nitrogen, followed by fractional distillation to give 6.0 g (60%) of α,β-bis(difluoroamino)-α,β,β-trifluoroethylbenzene. ^{19}F NMR spectrum [see Eq. (1)]: $\delta_1 = +90$, $\delta_2 = +36$, $\delta_3 = -104$, $\delta_4 = -96$, $J_{1\,2} = 12$.

The physicochemical characteristics of the synthesized compounds are given in Table 1.

CONCLUSIONS

α,β,β-Trifluorostyrene reacts vigorously with reagents of the radical type (nitrogen tetraoxide, tetrafluorohydrazine), and reacts quite sluggishly with nucleophilic reagents (ammonia, diethylamine).

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