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REACTIONS OF PERFLUORO-2-METHYLPENTENE-2 WITH AROMATIC NUCLEOPHILES

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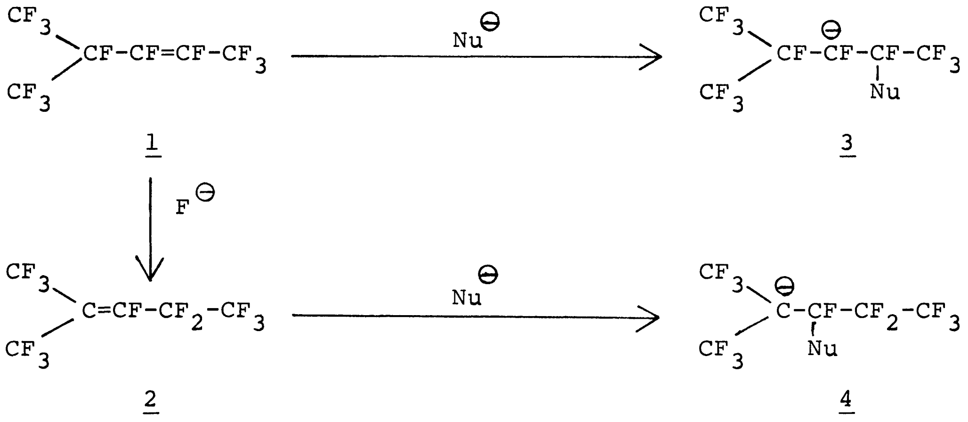
While one mole of phenol reacted with perfluoro-2-methylpentene-2 [2] to give usual phenoxy substituted compound [5], two or four moles of aniline reacted with 2 affording quinoline derivatives.

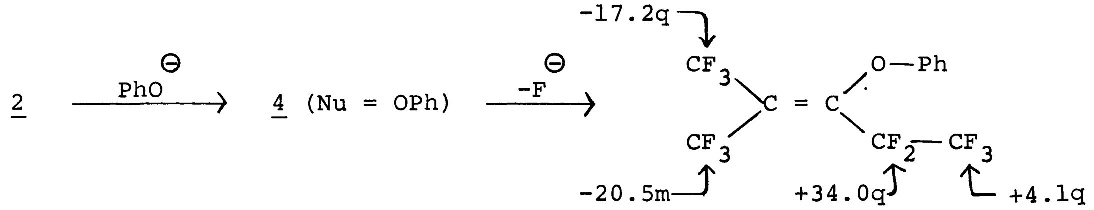
Hexafluoropropene is known to oligomerize readily in the presence of fluoride ion, giving a mixture of dimer and trimer.1,2) The dimer is composed of perfluoro-4-methylpentene-2 [1] and perfluoro-2-methylpentene-2 [2], of which the former is predominant.2) Owing to the negative hyperconjugation and the electron-withdrawing inductive effect of the trifluoromethyl groups adjacent to the double bond, 2 seems to be more stable thermodynamically, and more susceptible to the reaction with the nucleophiles than 1 because it will give more stable anionic intermediate [4]. Since 1 reacted with strong nucleophiles as dialkyl amines via carbanion 3,3) 2 was expected to be more reactive and more useful as synthetic intermediate, so that a convenient method for the isomerization of 1 to 2, and several reactions of 2 with aromatic nucleophiles were studied.



While 1 did not react with phenol or aromatic amines easily, we found 2 reacted with these nucleophiles in the presence of a base, even at room temperature. Phenol gave a usual substituted phenoxy compound, but aromatic primary amines gave quinoline derivatives. The formation of quinoline derivatives from 2 and aromatic or heterocyclic amines was disclosed very recently by Haszeldine et al.,4) but not in detail. We now wish to report our results on the above reactions.

Preparation of 2 : Although a few procedures for the conversion of 1 to 2 had been reported,2,5) it was most conveniently carried out by heating in sulfolane with potassium fluoride. For example, a mixture of 1 (80 g), KF (8 g) and dried sulfolane (40 ml) was heated in an autoclave at 130°C for 25 hr with stirring. The mixture was thrown into water and the oily layer was separated and distilled to give pure 2, b.p. 51°C, in a yield of 81%. When a small amount of HF-adduct of 2 was contained, which was detectable by the ^{19}F NMR, the reaction mixture was treated with 10% aqueous potassium hydroxide solution for 10 hr at room temperature, prior to the distillation.

Reaction with Phenol : The reaction between 2 and phenol readily occurred in the presence of triethylamine in diethyl ether. Thus into an ice cooled solution of 2 (6.0 g) in ether (15 ml), a solution of phenol (1.88 g) and triethylamine (2.23 g) in ether (15 ml) was added dropwise. The mixture was stirred for 2 hr at room temperature and the precipitated triethylamine hydrofluoride was removed by filtration. After washing the filtrate with dilute hydrochloric acid and water, and drying over magnesium sulfate, 2-trifluoromethyl-3-phenoxy-1,1,1,4,4,5,5,5-octafluoropentene-2 [5] (4.0 g, 54%, b.p. 86-88°C/50 mmHg) was obtained by distillation. Found: F, 56.7%. Calcd for $C_{12}H_5OF_{11}$: F, 55.9%. IR: 1647 (C=C), 1100-1400 (C-F) cm^{-1}. ^{19}F NMR (neat): Chemical shifts are shown below.*



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Reaction with Primary Aromatic Amines : The reaction between 2 and aromatic amines proceeded with more complexity. With two moles of arylamine, 2-pentafluoroethyl-3-trifluoromethyl-4-arylaminoquinoline [7] was obtained, presumably through formation of ketenimine [6] and subsequent cyclization, as was reported by Haszeldine et al.[4] However, one mole of 2 could react even with four moles of aniline, and a condensed product was obtained in a rather good yield. The structure of this compound was estimated to be 2-pentafluoroethyl-3-(N,N'-diphenylamidino)-4-anilinoquinoline [8] from its spectral data. Since no reaction was observed between 7 and aniline under the same conditions, it was evident that the formation of 8 resulted from direct attack of two moles of aniline on 6, but not via 7. This means that, when aniline is in excess, another nucleophilic attack of aniline on the ketenimine [6] forming an amidine took place in preference to the cyclization to 7, and subsequent dehydrofluorination followed by further attack with aniline should have occurred to give another ketenimine, which finally cyclized to 8.

Typical procedures are as follows.

Into a solution of 2 (3.0 g, 0.01 mol) in dimethylformamide (15 ml), aniline (2.23 g, 0.022 mol) in dimethylformamide (5 ml) was added and stirred at 70°C for 2.5 hr in a sealed tube. The reaction mixture was thrown into water and the precipitate was collected to give a crude product (3.31 g, 81%). Recrystallization from hexane gave pure 2-pentafluoroethyl-3-trifluoromethyl-4-anilinoquinoline, m.p.

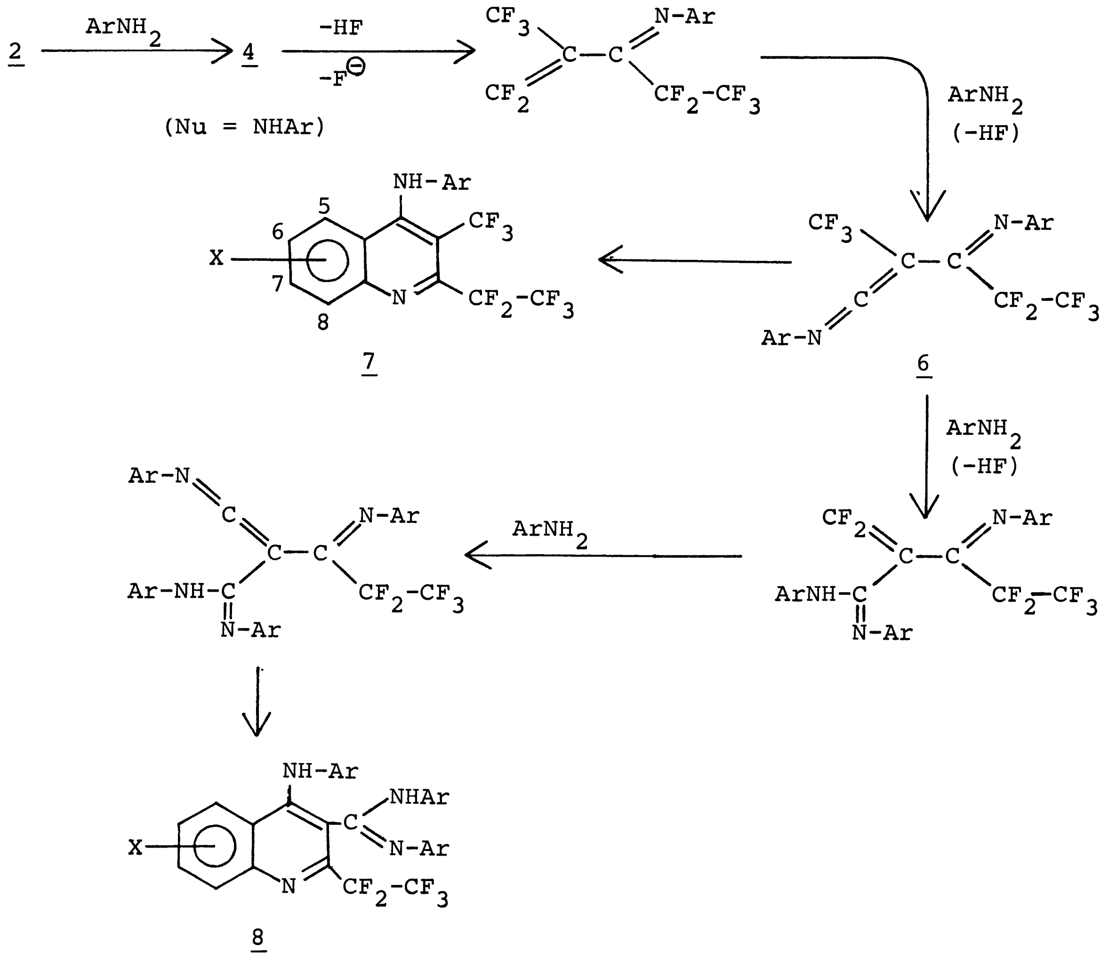

Table 1 Preparation of 7

Compd.		Yield	M.P.	F Anal (%)		IR (cm^{-1})		^{19}F NMR (δ ppm)*		
Ar	X	(%)	(^{o}C)	Found	Calcd	C-F	N-H	CF$_3$	CF$_2$CF$_3$	
C$_6$H$_5$	H	81	99.5-100	37.8	37.4	1100-1240	3450	-24.3	+29.0	+0.3
o-Me-C$_6$H$_4$	8-Me	77	99.5-100	34.9	35.0	1050-1250	3420	-23.8	+28.7	+0.6
p-Me-C$_6$H$_4$	6-Me	63	94.5-95	34.7	35.0	1100-1250	3400	-24.1	+29.6	+0.4
o-Cl-C$_6$H$_4$	8-Cl	8	124-125	31.1	32.0	1100-1240	3420	-23.4	+28.7	+1.0
m-Cl-C$_6$H$_4$	7(or 5)-Cl	8	103-104	31.9	32.0	1100-1240	3450	-23.7	+29.8	+1.2
p-Cl-C$_6$H$_4$	6-Cl	37	120-121	32.0	32.0	1100-1250	3455	-23.2	+29.7	+1.2

99-100°C. Found: C, 53.51; H, 2.48; N, 7.03; F, 37.8%. Calcd for $C_{18}H_{10}N_2F_8$: C, 53.20; H, 2.46; N, 6.90; F, 37.4%. MS: M^+ 406.

Other arylamines such as o- and p-toluidines and o-, m-, and p-chloroanilines gave the similar quinoline derivatives (Table 1).

Into a mixture of aniline (8.2 g, 0.088 mol), triethylamine (14.2 g, 0.154 mol) and diethyl ether (30 ml), a solution of 2 (6.0 g, 0.02 mol) in ether (15 ml) was added at room temperature. After stirring for 1 hr, the mixture was washed with dilute hydrochloric acid then with water to remove excess amines. Concentrating the solvent yellow crystals came out, which were collected to give crude product (7.05 g, 67%). Recrystallization from hexane gave pure 2-pentafluoroethyl-3-(N,N'-diphenylamidino)-4-anilinoquinoline [8 (Ar = Ph, X = H)], m.p. 135.5 -136°C. Found: C, 67.62; H, 3.87; N, 10.55; F, 17.7%. Calcd for $C_{30}H_{21}N_4F_5$: C, 67.66; H, 3.97; N, 10.52; F, 17.8%. MS: M^+ 532. IR (KBr): 1660, 1485 (C(=N)NH), 1060-1260 (C-F). ^{19}F NMR ($CHCl_3$): +2.3 (CF_3), +31.2 (CF_2).

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* The chemical shifts for ^{19}F NMR spectra through this article are given in δ ppm from ext. CF_3CO_2H.

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