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ADDITION-ELIMINATION REACTIONS BETWEEN PHENYL LITHIUM AND
SOME PERFLUOROVINYLETHER COMPOUNDS

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SUMMARY

Reactions between C_6H_5Li and $C_3F_7OCF=CF_2$ (I) yield phenyl substituted perfluorovinylethers. Stoichiometry and reaction temperature dictate the degree of substitution. With each replacement of F^\ominus by $C_6H_5^\ominus$ the subsequent substitutions require more forcing conditions. The F^\ominus is substituted easier than the $C_3F_7O^\ominus$ during the addition-elimination reactions.

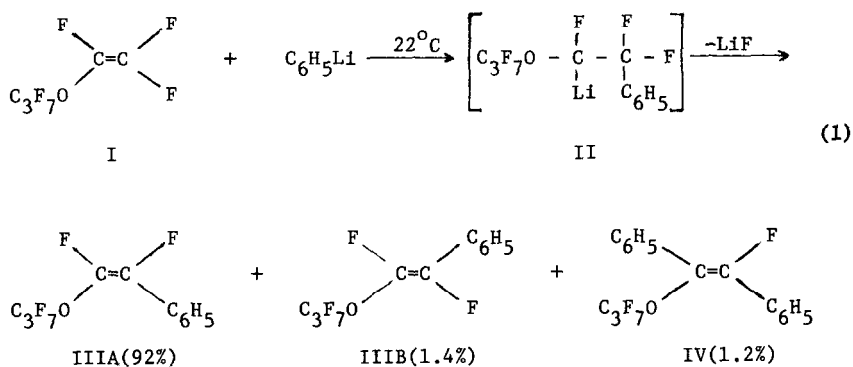
INTRODUCTION

McGrath and Levine [1] have reported earlier that $CF_2=CF_2$ reacts with C_6H_5Li by an addition-elimination process to yield $C_6H_5CF=CFC_6H_5$ and $(C_6H_5)_2C=CFC_6H_5$ as the principal reaction products. Subsequently Dixon [2] extended this type of reaction to a variety of organolithium compounds with $CF_2=CF_2$ and various chlorofluoroolefins to yield by the same addition-elimination process mono and polysubstituted fluoroolefins. Since perfluoroalkoxy substituted tetrafluoroethylene e.g., $C_3F_7OCF=CF_2$ has not been studied, it was of interest to us to examine this particular substituent's character in regard to its directive effects and its leaving ability during the addition-elimination reaction sequence.

DISCUSSION

$C_3F_7OCF=CF_2$ (I) [3] reacts with C_6H_5Li in diethyl ether solvent at $22^\circ C$ to yield the mono substituted olefin IIIA as the major reaction product. Gas chromatographic (G.C.) analysis of the reaction mixture indicated other minor components. The reaction products can be explained by considering the following (yield of products are expressed in G.C. area percent):

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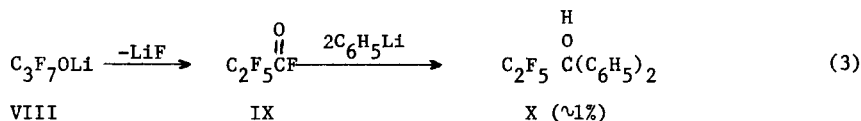
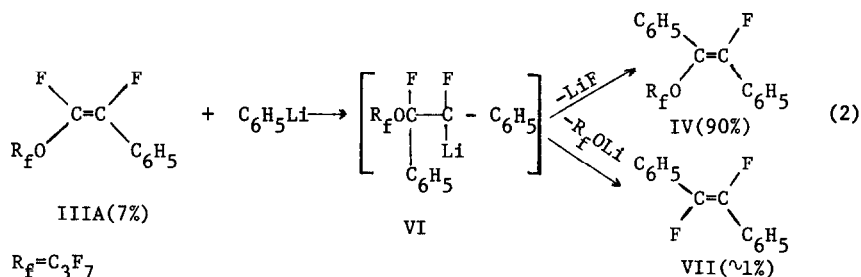


When the same reaction was repeated at -78°C and hydrolyzed at -78°C , the products of reaction were IIIA (97%) and the protonated product of II, $\text{C}_3\text{F}_7\text{OCFHCF}_2\text{C}_6\text{H}_5$ (V) (1%). By lowering the reaction temperature to -115°C , the yield of V was increased to 4% indicating a slightly although not significantly greater stability of the intermediate II. The unstable intermediate II, even at these low temperatures, eliminates LiF by a beta elimination process to form the compound IIIA as the major product. Under these conditions no products were produced which indicated a $\text{C}_3\text{F}_7\text{OLi}$ elimination.

The presence of the other structural isomer IIIB in the reaction mixture prior to G.C. analysis was not definitely established. The IIIA component could be partially converted to the IIIB structural isomer upon heating at an elevated temperature. When the original reaction mixture containing only IIIA, IIIB and IV (92:1.4:1.2 area %) was heated at 155°C for 24 h under vacuum the ratio of products changed to IIIA-55%, IIIB-35% and IV-1.2%. Since IIIA can be converted rather easily to IIIB simply on heating, it may be possible that the small percentage of IIIB (1.4%) in the original reaction mixture as indicated by G.C. analysis was actually formed through thermal isomerization in the injection port or on the column during the G.C. analysis.

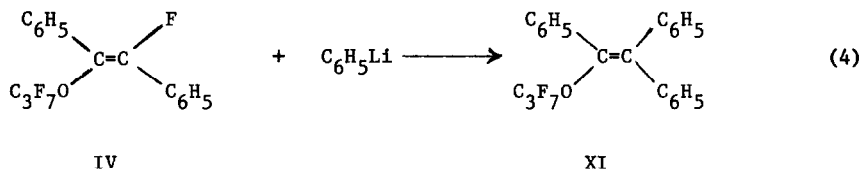
The reaction between $\text{C}_3\text{F}_7\text{OCF}=\text{CF}_2$ and two equivalence of $\text{C}_6\text{H}_5\text{Li}$ at -78°C produced (G.C. area %) the mono substituted products IIIA (91%), IIIB (2%) as the major components and the disubstituted compound IV in only 7% yield. At the low temperature, even though IIIA is present, it reacts very slowly with the second equivalent of $\text{C}_6\text{H}_5\text{Li}$. Upon allowing the reaction temperature to rise to 0°C , the rate of reaction increased significantly

whereby the disubstituted product IV was now the major reaction product. Analysis of the reaction mixture indicated other minor products whose formation can be rationalized by considering the following reactions:



In the 1:1 reaction as shown by equation 1, the intermediate II can only eliminate LiF by a beta elimination process to yield IIIA. In the 1:2 reaction as shown by equation 2, the intermediate VI can eliminate either LiF or $\text{C}_3\text{F}_7\text{OLi}$ by a beta elimination process. The reaction products IV and VII which were obtained in a 90:1 ratio clearly show the preference F^\ominus elimination over the $\text{C}_3\text{F}_7\text{O}^\ominus$ elimination. The formation of compounds VII and X does however substantiate the $\text{C}_3\text{F}_7\text{O}^\ominus$ elimination albeit to a very minor extent. ^{19}F NMR analysis of compounds IIIA and IV (see Table 1) which established the structural configuration, provided the suggested mode of $\text{C}_6\text{H}_5\text{Li}$ addition to olefins as shown by the intermediates II and VI.

As the F^\ominus in I are substituted by $\text{C}_6\text{H}_5^\ominus$ the rates of sequential addition of $\text{C}_6\text{H}_5\text{Li}$ to the olefins decreases. This can be seen by the last F^\ominus substitution on compound IV. In the reaction between $\text{C}_6\text{H}_5\text{Li}$ and IV a higher reaction temperature (22°C) and a longer reaction time were required to substitute the last F^\ominus . Analysis of the reaction mixture indicated unreacted IV (67%) and XI (23%).



Gas chromatography-mass spectral analysis of the reaction mixture indicated two other minor reaction products ($\sim 3\%$) whose identification was suggested by the mass spectral data as $(C_6H_5)_2C=C(C_6H_5)_2$ (XII) and compound X. The formation of these compounds probably occurred through subsequent reactions of XI and C_6H_5Li by addition to the olefin and C_3F_7OLi elimination.

EXPERIMENTAL

Unless otherwise noted, all materials were of reagent grade quality and were used without further purification. Diethyl ether was distilled from $LiAlH_4$ prior to use. The C_6H_5Li was prepared from C_6H_5Br and Li in diethyl ether. The $C_3F_7OCF=CF_2$ was synthesized by the method of Fritz and Selman [3]. All new compounds were characterized by NMR (^{19}F and 1H), infrared, mass spectral and combustion analyses. Infrared and NMR spectra were obtained by use of Perkin-Elmer 521 or 621 and XL-100 instruments respectively. Mass spectra were performed on a Du Pont Model 21-490 mass spectrometer using a chemical ionization mode. The physical measurements and analyses of the various reaction products are summarized in Table 1. The NMR results are reported in Table 2.

Synthesis of $C_3F_7OCF=CF(C_6H_5)$ (IIIA and IIIB)

To a diethyl ether (500ml) solution of $C_3F_7OCF=CF_2$ (I) (10.0 g; 37.6mmol) at $-78^\circ C$, was added C_6H_5Li (37.6ml of 1.00 M in diethyl ether, 37.6mmol) over 10 min during which the colorless solution turned cloudy and the reaction temperature rose to $-73^\circ C$. The reaction mixture was then allowed to warm to room temperature, and then stirred at room temperature for 1 h. The reaction mixture was hydrolyzed by 2N HCl (300ml), phase separated and aqueous layer further extracted with diethyl ether (3 x 100ml). The combined organic layers were dried with $MgSO_4$ and analyzed by G.C. The G.C. area % of the following products were indicated: $C_3F_7OCF=CF(C_6H_5)$ (IIIA) - 92%, (IIIB) - 2% and $C_3F_7O(C_6H_5)C=CF(C_6H_5)$ (IV) - 1%. The diethyl ether and low boiling liquids were removed with a rotary evaporator at $\sim 40^\circ C$. The crude product was distilled to give the pure olefin, III. The cis isomer, IIIA, was converted into the trans isomer, IIIB, by heating at 155° under vacuum for 24 h. The proposed structure of these two isomers were consistent with NMR (^{19}F and 1H) data (Table 2).

TABLE 1

Product	b. p. /mm (m. p.) ^a	IR(C ₆ F ₅ C) cm ⁻¹	M. S.	Combustion Data (Calc'd/Found)	
				C	H
C ₃ F ₇ OCF=CF(C ₆ H ₅) (III) (nc)	166°/760	1736 (cis) 1734 (trans)	324(M ⁺)	40.76 40.83	1.55 1.38
C ₂ F ₇ O(C ₆ H ₅)C=CF(C ₆ H ₅) (IV) (nc)	105°/0.08	1655 to 1687	382(M ⁺)	53.41 53.39	2.64 2.37
(C ₆ H ₅)CF=CF(C ₆ H ₅) (VII) ^b	(74°)	1750	216(M ⁺)	--	--
C ₂ F ₅ C(OH)(C ₆ H ₅) ₂ (X) ^c	(83°)	(3525) ^d	302(M ⁺)	59.61 59.42	3.67 3.36
C ₃ F ₇ O(C ₆ H ₅)C=C(C ₆ H ₅) ₂ (XI) (nc)	(96°)	1633	440(M ⁺)	62.73 62.62	3.43 3.37

^a Data in parentheses are melting point.

^b See Reference 1.

^c See Reference 4.

^d OH band.

TABLE 2

		19F NMR DATA					
COMPOUND		F _a	F _b	F _c	F _d	F _e	F _f
CF _a CF _b CF _c O		(I)	-129.9 (s)	-86.3 (7.2Hz, sx)	-135.9 (112.1Hz, d) (66.4Hz, d) (5.9Hz, t)	-122.5 (112.1Hz, d) (85.3Hz, d) (5.8Hz, t)	-114.7 (85.3Hz, d) (66.4Hz, d)
CF _a CF _b CF _c O		(IIIB)	-130.3 (s)	-85.6 (6.8Hz, sx)	-117.8 (116Hz, d) (5.9Hz, t)	-161.0 (116Hz, d) (7.0Hz, t)	---
CF _a CF _b CF _c O		(IIIA)	-130.2 (s)	-85.7 (7.6Hz, p)	-103.7 (24.4Hz, d) (8.4Hz, t)	---	-149.4 (24.4Hz, d)
CF _a CF _b CF _c O		(IV)	-130.0 (2.1Hz, t)	-83.5 (7.2Hz, q) (2.3Hz, t)	---	---	-122.3 (s)
F		(VII)	-157.3 (s)	-157.3 ; Analysis of carbon 13 satellites of F peak provided the F-F coupling of 120Hz indicative of trans configuration.			
CF _a CF _b C(OH)(C ₆ H ₅) ₂		(X)	-77.8 (s)	-117.3 (s)			

s=singlet; d=doublet; t=triplet; q=quartet; p=pentet; s=sextet

Reaction Between $C_3F_7OCF=CF_2$ (I) and C_6H_5Li (1:2 ratio)

To a diethyl ether (500ml) solution of $C_3F_7OCF=CF_2$ (I) (10.0 g; 37.6mmol) at $-78^\circ C$ was added C_6H_5Li (75.2ml of 1.00 M in diethyl ether, 75.2mmol) over 21 min. After 10 min at $-78^\circ C$, an aliquot sample was removed and analyzed by G.C. The reaction mixture was then allowed to warm to $0^\circ C$ and then stirred at $0^\circ C$ for 30 min, 1.4 h and 4 h during which, each time aliquot samples were removed and analyzed by G.C. The results of G.C. area % are given in Table 3.

TABLE 3

Temp./Time	IIIA	IIIB	IV	X	VII
$-78^\circ/10$ min	91%	2%	7%	--	--
$0^\circ/30$ min	21%	1%	76%	trace	trace
$0^\circ/1.4$ h	13%	1%	84%	1%	1%
$0^\circ/4$ h	7%	1%	90%	1%	1%

After 4 hr at $0^\circ C$, the reaction mixture was hydrolyzed with 2N HCl (300ml). The diethyl ether layer was phase separated and the aqueous layer was extracted with diethyl ether (3 x 100ml). The combined organic layers were dried with $MgSO_4$ and the diethyl ether and low boiling liquids were removed with a rotary evaporator at $\sim 40^\circ C$. The residue was distilled at reduced pressure to give crude products of $C_3F_7OCF=CF(C_6H_5)$ (III) ($50^\circ-82^\circ/0.08mm$), a mixture of $C_3F_7O(C_6H_5)C=CF(C_6H_5)$ (IV) and $C_2F_5C(OH)(C_6H_5)_2$ (X) ($82^\circ-105^\circ/0.08mm$) and $(C_6H_5)CF=CF(C_6H_5)$ (VII) ($105^\circ-110^\circ/0.08mm$). Pure IV and X were isolated by column chromatography (Al_2O_3) using hexane (for IV) and diethyl ether (for X) as eluting solvents.

Reaction of $C_3F_7O(C_6H_5)C=CF(C_6H_5)$ (IV) and C_6H_5Li

To a diethyl ether (70ml) solution of $C_3F_7O(C_6H_5)C=CF(C_6H_5)$ (IV) (0.96 g; 2.51mmol) was added C_6H_5Li (2.51ml of 1.00 M in diethyl ether, 2.51mmol) at $0^\circ C$. After 5 min, an aliquot sample was removed and analysis by G.C. indicated no new reaction products. The reaction mixture was then allowed to warm to room temperature. After 3 days at room temperature, an aliquot sample was removed and analyzed by GC/MS. The G.C. area % of the following compounds were indicated: $C_3F_7O(C_6H_5)C=CF(C_6H_5)$ (IV) - 67%, $C_3F_7O(C_6H_5)C=C(C_6H_5)_2$ (XI) - 23%, $(C_6H_5)_2C=C(C_6H_5)_2$ (XII) - 3% and $C_2F_5C(OH)(C_6H_5)_2$ (X) - $\sim 3\%$. The reaction mixture was hydrolyzed with 2N HCl (50ml). The organic layer was separated, dried with $MgSO_4$ and the

low boiling solvents were removed by aspiration. The residue on standing at room temperature for approximately one week, deposited white crystals which were separated and recrystallized from pentane (2x). The isolated yield of the product $(C_6H_5)_2C=C(C_6H_5)(OC_3F_7)$ (XI) was 0.22 g - 20%. (See Table 1)

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