[CONTRIBUTION NO. 192 FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO., INC.]

Elimination Reaction of Fluoroölefins with Organolithium Compounds

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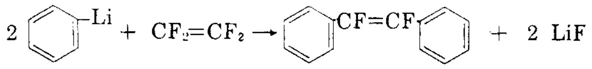
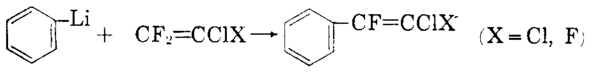
Fluoroölefins, $FCY{=}CX_1X_2$, where Y is F or fluoroalkyl and X_1X_2 are electronegative, react in inert media with organolithium compounds, RLi, to give new olefins, $RCY{=}CX_1X_2$ and lithium fluoride. Tetrafluoroethylene, at low temperatures, with phenyllithium gives trifluorostyrene and with excess phenyllithium gives difluorostilbene. At 25°, all fluorine atoms in tetrafluoroethylene may be replaced giving tetraphenylethylene. Examples are shown using tetrafluoroethylene, chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene, long chain fluoroölefins, and cyclic fluoroölefins with aryllithium, substituted aryllithium, alkyllithium, and heterocyclic lithium.

During a preliminary examination of the addition reactions of fluorine-containing olefins, carried out a few years ago in this Laboratory, it was observed that attempted addition of phenyllithium at −80° to tetrafluoroethylene resulted in the formation of lithium fluoride. The solid organic product obtained was shown, by oxidation to benzil and benzoic acid, to be the new compound difluorostilbene (I).

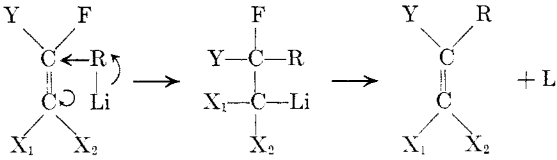
Chlorotrifluoroethylene was found to react in a similar fashion with phenyllithium to eliminate lithium fluoride, but gave a styrene (II) and not a stilbene derivative. An analogous result was obtained with 1,1-dichloro-2,2-difluoroethylene. In the case of these two olefins, therefore, only one mole of phenyllithium entered into reaction. Furthermore, it was observed that when an excess of alkyllithium (butyllithium) was substituted for phenyllithium in the reaction with tetrafluoroethylene only a 1:1 product (III) was obtained. Under similar low temperature conditions, there was either no reaction with vinylidene fluoride and 1,2-dichloro-1,2-difluoroethylene or very complex mixtures were produced.


I


II

$$C_4H_9Li + CF_2{=}CF_2 \longrightarrow C_4H_9CF{=}CF_2$$
III

From the compounds studied to date, the reaction appears to proceed best when the olefin has the structure (IV) where Y is F or fluoroalkyl and X_1, X_2 are both electronegative atoms or groups, though at higher temperatures, as is shown later, the reaction can sometimes be brought about even though all of these conditions are not fulfilled. The organic radical apparently attacks the positive carbon atom, *i.e.*, that one to which the greater number of fluorine atoms are attached. One postulate of the mechanism involved is that the intermediate so formed is unstable and spontaneously eliminates lithium fluoride to yield the new olefin (V). Such intermediates have been described.[1]


IV V

In studying the scope of this reaction, it was found that substituted, as well as unsubstituted, aromatic lithiums would react with fluoroölefins; thus *p*-dimethylaminophenyllithium with chlorotrifluoroethylene gave the chlorodifluorostyrene derivative which could readily be separated into its *cis-trans* isomers, a fact which amply demonstrates the β-location of the chlorine atom. The liquid isomer may be converted into the solid isomer by heating.

Nuclear magnetic resonance studies on several of the compounds prepared by this reaction confirm their structural assignments. For example, it is possible to predict accurately the F^{19} magnetic resonance patterns associated with the three possible forms of chlorodifluorostyrene (II, X = F). These, together with the experimentally determined pattern, are shown in Figure 1. The observed pattern represents a simple addition of the patterns predicted for the *cis* and *trans* isomers and there is a total absence of any contribution from α-chloro-β-difluorostyrene. The results obtained with chlorodifluoro-*n*-hexene-1 and trifluoromethyldifluorostyrene (VI, n = 1, X = F) are equally clear-cut.

Fluoroölefins of more than two carbon atoms could be reacted at −80° with organolithium compounds; with phenyllithium both the 1:1 (VI) and 2:1 (VII) products were obtained. At higher temperatures (+25°), triphenyl derivatives were isolated.

Heterocyclic lithium compounds prepared from pyridine, thiophene and furan were reacted with chlorotrifluoroethylene to give the chlorodifluorovinyl heterocycles and with tetrafluoroethylene to give the 1,2-difluoro-1,2-diheteroethylenes, *e.g.*,

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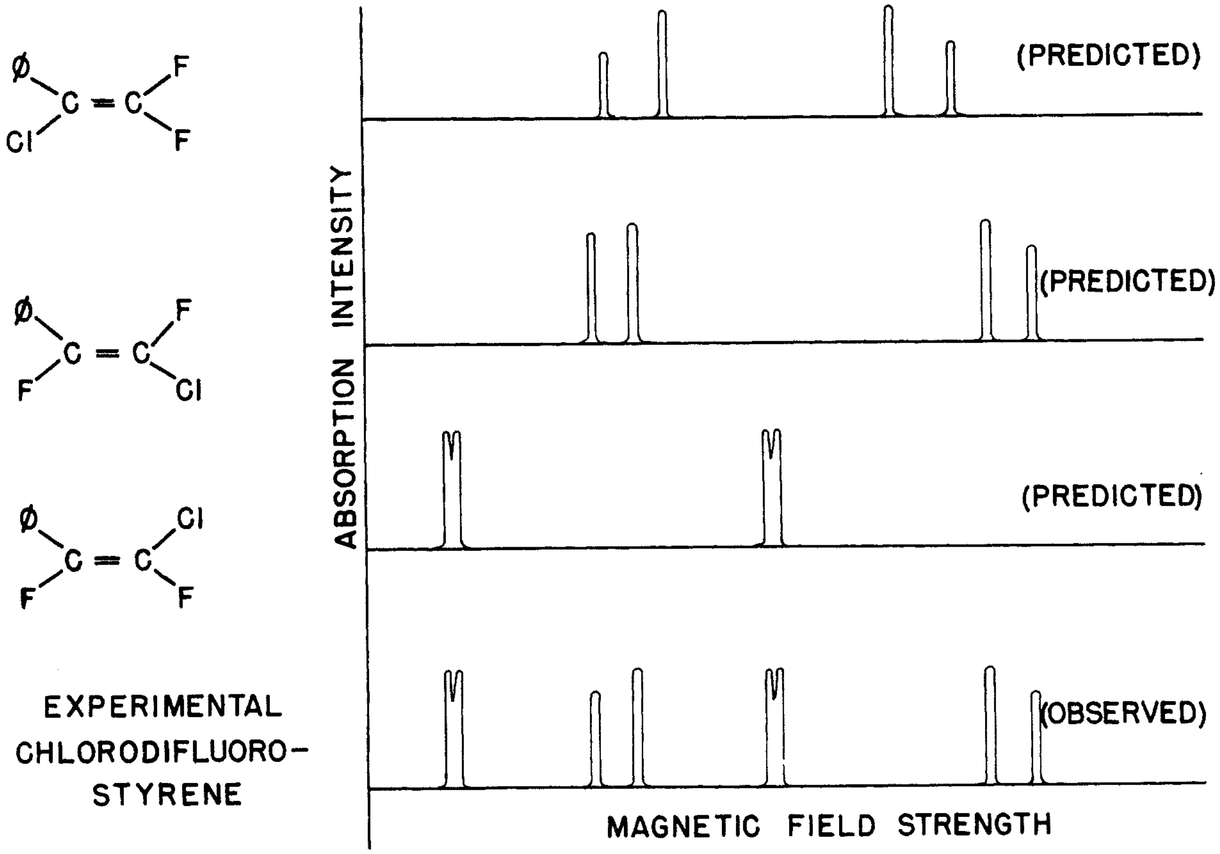
[1] Pierce, McBee, and Judd, *J. Am. Chem. Soc.*, **76**, 474 (1954).

FIGURE I

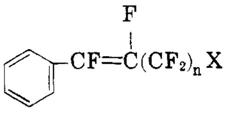
F^{19} MAGNETIC RESONANCE PATTERNS



(Courtesy W. D. Phillips)

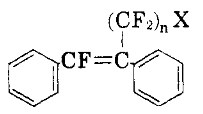
from thiophene were obtained chlorodifluorovinyl thiophene (VIII) and 1,2-difluoro-1,2-dithienylethylene (IX).

Cyclic fluoroölefins could be used in the reaction. For example, with perfluorocyclobutene, diarylperfluorocyclobutenes (X) were produced using aryllithium and both the monoalkyl (XI) and dialkyl (XII) perfluorocyclobutenes could be isolated using alkyllithium.

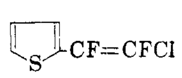


VI

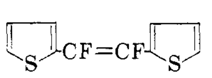
X = F, H



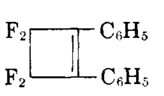
VII



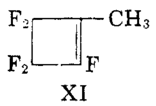
VIII



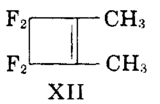
IX



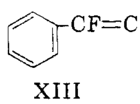
X



XI



XII



XIII

The reaction between phenyllithium and tetrafluoroethylene was studied more closely and it was found possible, by employing an excess of the olefin, to obtain α,β,β-trifluorostyrene (XIII). At higher temperatures and in the presence of excess phenyllithium, it was possible to replace successively every one of the fluorine atoms and so ultimately to obtain tetraphenylethylene.

It has been observed both by us and by others[2] that Grignard reagents sometimes give similar products in these reactions, though often in poorer yield. This is particularly true in the case of alkyl Grignard reagents.[2] The majority of organosodium compounds lack solubility in the inert media in which the reactions are conducted and in consequence their participation is difficult to bring about.

EXPERIMENTAL

Preparation of organolithium compounds. All organolithium compounds were prepared in ether solution by standard techniques. Specific references are as follows:

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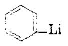
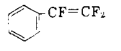
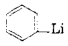
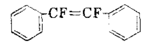
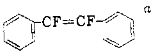
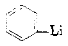
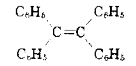
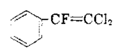
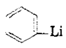
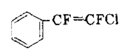
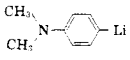
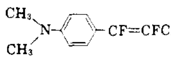
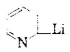
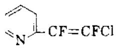
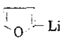
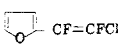
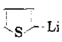
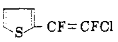
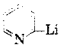
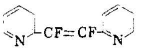
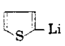
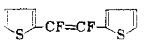
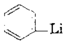
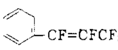
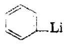
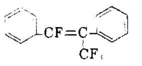
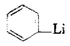
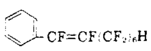
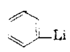
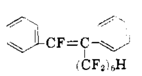
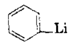
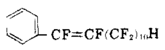
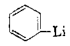
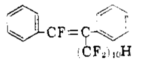
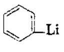
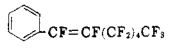
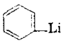
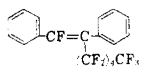
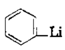
(2) Tarrant and Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

TABLE I

PRODUCTS OBTAINED FROM FLUOROÖLEFIN ELIMINATION REACTION

Fluoroölefin	Organometallic	Product	M.P. (°C.)	B.P. (°C.)	Yield[c] (%)	Analyses Calc'd. C	Calc'd. H	Calc'd. Other	Found C	Found H	Found Other
$CF_2{=}CF_2$			—	68°/75 mm.	30	Known Compound					
$CF_2{=}CF_3$			74	—	50	77.7	4.6	F: 17.6	77.7	4.5	F: 17.6
 [a]			223	—	72	Known Compound					
$CF_2{=}CCl_2$			—	101°/12 mm.	50	50.2	2.6	Cl: 37.2	50.3	2.8	Cl: 37.5
$CF_2{=}CFCl$			—	174	60	55.0	2.9		55.4	2.8	
$CF_2{=}CFCl$			—	87°/2 mm. [b]	50	55.2	4.6	Cl: 16.3	55.1	4.6	Cl: 16.3
			54	92°/2 mm.		55.2	4.6	Cl: 16.3	54.9	4.7	Cl: 17.0
$CF_2{=}CF_2$	CH_3Li	$CH_3CF{=}CF_2$	—	−18	20	14.1	1.2[d]		14.0	1.2[d]	
$CF_2{=}CF_2$	C_2H_5Li	$C_2H_5CF{=}CF_2$	—	+13	20	17.8	1.9[d]		17.8	1.9[d]	
$CF_2{=}CF_2$	C_4H_9Li	$C_4H_9CF{=}CF_2$	—	70	80	52.0	6.5		51.5	6.7	
$CF_2{=}CF_2$	$C_{12}H_{25}Li$	$C_{12}H_{25}CF{=}CF_2$	—	71°/1 mm.	51	67.2	10.0	F: 22.8	67.4	9.9	F: 22.6
$CF_2{=}CFCl$	C_4H_9Li	$C_4H_9CF{=}CFCl$	—	109	60	46.6	5.8	Cl: 23.0	47.3	5.9	Cl: 22.8
$CF_2{=}CFCl$			—	115°/16 mm.	40	48.0	2.3	N: 8.0	48.8	2.5	N: 8.3
$CF_2{=}CFCl$			—	135	50	43.8	1.8	Cl: 21.6	43.6	1.9	Cl: 21.7
$CF_2{=}CFCl$			—	90°/14 mm.	55	39.9	1.7	Cl: 19.7	40.0	1.7	Cl: 19.6
$CF_2{=}CF_2$			91	—	10	66.7	2.8	F: 17.6	66.6	3.6	F: 17.5
$CF_2{=}CF_2$			98	—	30	52.6	2.6	F: 16.7	52.7	2.8	F: 16.6
$CF_2{=}CFCF_3$			—	148	50	51.9	2.4		51.5	2.6	
$CF_2{=}CFCF_3$			38	133°/12 mm.	20	67.7	3.8		68.0	3.8	
$CF_2{=}CF(CF_2)_6H$			—	72°/2 mm.	40	38.2	1.5		37.6	1.5	
$CF_2{=}CF(CF_2)_6H$			69	138°/2 mm.	25	48.2	2.2		48.4	2.3	
$CF_2{=}CF(CF_2)_{10}H$			49	105°/2 mm.	20	33.7	0.94		33.3	0.96	
$CF_2{=}CF(CF_2)_{10}H$			69	155°/2 mm.	25	41.3	1.58		41.9	1.57	
$CF_2{=}CF(CF_2)_4CF_3$			—	76°/6 mm.	60	38.3	1.2		38.8	1.2	
$CF_2{=}CF(CF_2)_4CF_3$			73	106°/2 mm.	20	48.9	2.1		48.8	2.3	
$CF_2{=}CF(CF_2)_4CF_3$[a]		$C_{25}H_{15}F_{11}$	97	—	30	57.3	2.9		57.0	3.1	

Alkyllithium compounds	(3)
Phenyllithium	(4)
p-Dimethylaminophenyllithium	(5,6)
2-Furyllithium	(7)
2-Thienyllithium	(8)
2-Pyridyllithium	(9)

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(3) Wittig, *Neuere Methoden der präparativen organischen Chemie*, I, p. 575.

(4) Wittig, *Neuere Methoden der präparativen organischen Chemie*, I, p. 576.

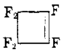
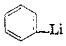
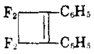
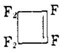
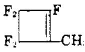
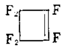
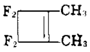
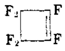
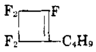
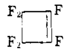
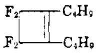
(5) Gilman and Banner, *J. Am. Chem. Soc.*, **62**, 344 (1940).

(6) Austin, *J. Am. Chem. Soc.*, **54**, 3726 (1932).

(7) Gilman and Bebb, *J. Am. Chem. Soc.*, **61**, 109 (1939).

(8) Gilman and Shirley, *J. Am. Chem. Soc.*, **71**, 1870 (1949).

(9) Adamson and Billinghurst, *J. Chem. Soc.*, 1039 (1950).

			58	—	20	69.1	3.6	F: 27.3	68.9	3.6	F: 27.3
	CH$_3$Li		—	50	30			Not Available			
	CH$_3$Li		—	104	35	46.7	3.9		46.7	3.9	
	C$_4$H$_9$Li		—	112	20	48.0	4.5		47.3	4.5	
	C$_4$H$_9$Li		—	110°/20 mm.	40	60.5	7.6		60.5	7.6	
CF$_2$=CFCl	CH$_3$ONa	CH$_3$OCF=CFCl	—	59	58	28.0		F: 29.5	27.9		F: 29.8
CF$_2$=CFCl	C$_2$H$_5$ONa	C$_2$H$_5$OCF=CFCl	—	83	80	33.7	3.5		33.8	3.4	
CF$_2$=CFCl	C$_3$H$_7$ONa	C$_3$H$_7$OCF=CFCl	—	107	75	38.3	4.5	F: 24.3	38.1	4.4	F: 24.0
CF$_2$=CFCl	H(CF$_2$)$_2$CH$_2$ONa	H(CF$_2$)$_2$CH$_2$OCF=CFCl	—	109	72	26.3	1.3		25.3	1.6	
CF$_2$=CFCl	H(CF$_2$)$_8$CH$_2$ONa	H(CF$_2$)$_8$CH$_2$OCF=CFCl	—	95°/10 mm.	60			Cl: 6.72			Cl: 6.78
CF$_2$=CF$_2$	C$_3$H$_7$ONa	C$_3$H$_7$OCF=CF$_2$	—	63	10	42.9	5.0		43.0	5.1	

[a] Reaction at +25°. [b] *Cis-trans* isomers. [c] Not considered optimum. [d] Dibromide.

General procedure for the reaction between organolithium and fluoroölefin. A solution of organolithium (1 mole) in ether (1000–1500 cc.) is cooled to −80° and a mixture of the fluoroölefin (1.2 mole) and nitrogen slowly is passed in. The mixture then is allowed to warm to room temperature and is treated with sufficient dilute hydrochloric acid to yield a clear mixture. The phases are separated, the aqueous phase is extracted further with ether, and the combined ether layers are washed and dried. The dried extract is evaporated and the residue is distilled in the case of a gas or liquid and recrystallized in the case of a solid.

In cases where a 1:1 and a 2:1 product can be obtained, the relative amounts of each product may be controlled by adjusting the ratio of olefin to organolithium and by reversing the order of addition; *e.g.*, if trifluorostyrene is the desired product, phenyllithium is added to an excess of tetrafluoroethylene in ether solution. If difluorostilbene is the desired product, tetrafluoroethylene is added to an excess of phenyllithium in ether solution.

In some cases, the above reaction was conducted at room temperature (+25°) to yield 3:1 and 4:1 products. The procedure was entirely analogous.

Proof of structure of difluorodiphenylethylene obtained from phenyllithium and tetrafluoroethylene. The difluorodiphenylethylene (2 g.) was dissolved in 75% sulfuric acid. To the vigorously stirred solution was added finely powdered potassium dichromate (2.5 g.) over a period of 30 minutes. Stirring was continued for 10 hours after which time the mass was poured onto ice. The resultant precipitate was recrystallized from alcohol-water to give pale yellow needles, m.p. 93°, alone or in admixture with an authentic specimen of benzil. Yield: 1.8 g., 92%. The material was also converted to a known derivative of benzil with *o*-phenylenediamine. A later crystal crop (0.15 g.) was shown to be benzoic acid.

There is little doubt, therefore, that the structure of the starting material is 1,2-difluoro-1,2-diphenylethylene.

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