aid was combined with the main filtrate. The filtrate was distilled *in vacuo*, yielding 273 g. (84%) of a clear, colorless liquid (b.p. 102–106° at 7.0 mm.). The residue left in the distillation pot was a dark brown, low-melting resin which weighed 38.7 g. (11.8%).

The predominant products were isomers of octahydroacenaphthene and, on the basis of v.p.c. data, the product distribution was almost identical with that obtained when CDT was rearranged with catalytic amounts of polyphosphoric acid. The two major components, which were isolated by preparative v.p.c., were identical with the octahydroacenaphthene isomers from the preceding example. The comparison was made with v.p.c. retention times, infrared spectra, and mass spectral patterns.

Rearrangement of CDT with U.O.P. Catalyst in a Xylene Solvent System.—To 325 g. of (2 moles) CDT was added 110 g. of crushed Universal Oil Products polymerization catalyst and 250 ml. of xylene. The heterogeneous mixture was stirred vigorously and heated to 150°, at which temperature it was maintained 2 hr.[8] After the reaction was completed, the mixture was cooled to 90° and filtered through a layer of Hyflo Super-Cel. The filter cake was washed with xylene and the washings and the filtrate was combined and distilled *in vacuo*. About 281 g. (86.5%) of a clear, colorless liquid was distilled overhead, leaving a residue of 29 g. (9%) of brown, tarry polymeric bottoms. The product distribution was similar to that of the preceding examples where no solvent was used. The octahydroacenaphthene was isolated and identified as above.

Acknowledgment.—The authors wish to thank Dr. Paul Tschampel for his valuable assistance.

[8] In this case, there was no tendency for the reaction to become uncontrolled.

Fluoro Olefins. XII. The Reaction of Allylmagnesium Bromide with Fluoro Olefins[1,2]

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The reaction of fluoro olefins with allylic Grignard reagents generally gives good yields of allylfluoroethylenes. Crotonylmagnesium bromide gives exclusively the α-methallylethylene; a mechanism is offered to explain this behavior. Tetrafluoroethylene reacts abnormally with allylmagnesium bromide to give 1-bromo-1,2-difluoro-1,4-pentadiene as the chief product.

Although the reactions between fluoro olefins and organometallic alkyls, aryls, and acetylenes have been widely investigated,[3-7] there has been little mention of the reactions with olefinic organometallic compounds. The reactions between various fluoro olefins and trifluorovinyllithium were unsuccessful,[8,9] although the reaction between triethyltrifluorovinylsilane and vinyl- and allyllithium gave good yields of the substituted dienes $(C_2H_5)_3SiCF{=}CF{-}CH{=}CH_2$ and $(C_2H_5)_3SiCF{=}CFCH_2CH{=}CH_2$.[10] In order to prepare fluorine-containing dienes, *unsym*-dichlorodifluoroethylene was allowed to react with both vinylmagnesium chloride and vinyllithium under varying conditions; however, the Grignard reagent did not react, and the vinyllithium gave only a tar. The latter reaction might have given the diene $CH_2{=}CHCF{=}CCl_2$ which polymerized immediately. The isolation of $(C_2H_5)_3SiCF{=}CFCH{=}CH_2$ mentioned above would have been possible as the bulky silane grouping would prevent immediate polymerization.

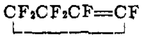
In a further effort to prepare a fluoro diolefin the reaction between allylmagnesium bromide and olefins containing the trifluorovinyl group was investigated. In general, a reasonable yield of the allyl-substituted fluoro olefin was formed.

$$CH_2{=}CHCH_2MgBr + CF_2{=}CFX \longrightarrow CH_2{=}CHCH_2CF{=}CFX$$

The products of these reactions are shown in Table I. The reactions were carried out using equimolar amounts of the fluoro olefin and the Grignard reagent in diethyl ether solution. The yield of the diolefin was not altered when an excess of the Grignard was used.

TABLE I

ALLYLMAGNESIUM BROMIDE AND FLUORO OLEFINS

Olefin	Product	Yield, %
(1) $CF_2{=}CF_2$	I, $CH_2{=}CHCH_2CF{=}CFBr$	30
	II, $CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	10
(2) $CF_2{=}CF_2$[a]	III, $CH_2{=}CHCH_2CF{=}CFCl$	7
	II, $CH_2{=}CHCH_2CF{=}CFCH_2CH{=}CH_2$	15
$CF_2{=}CFCl$	III, $CH_2{=}CHCH_2CF{=}CFCl$	50
$CF_2{=}CFBr$	I, $CH_2{=}CHCH_2CF{=}CFBr$	30
$CF_2{=}CCl_2$	IV, $CH_2{=}CHCH_2CF{=}CCl_2$	40
$CF_2{=}CFCF_3$	V, $CH_2{=}CHCH_2CF{=}CFCF_3$	38
 $CF_2CF_2CF{=}CF$	[b]	
$CF_2{=}CFCH{=}CH_2$	VI, $CH_2{=}CHCH_2CF{=}CFCH{=}CH_2$[c]	30

[a] Reacted with allylmagnesium chloride. [b] Tar formed immediately at −78°. [c] Polymerizes on standing.

The reaction with tetrafluoroethylene gave none of the expected monoallyl derivative, although a low yield of the disubstituted compound II was formed: the main product was 1-bromo-1,2-difluoro-1,4-pentadiene (I).

$$CH_2{=}CHCH_2MgBr + CF_2{=}CF_2 \longrightarrow \underset{\text{I}}{CH_2{=}CHCH_2CF{=}CFBr} + \underset{\text{II}}{[CH_2{=}CHCH_2CF]_2{=}}$$

It is unlikely that the bromide ion as such attacks tetrafluoroethylene as the reaction of anhydrous magnesium bromide with neither tetrafluoroethylene nor 1,1,2-trifluoro-1,4-pentadiene, in diethyl ether, led to a bromine-containing product. It is more likely that the Grignard reagent itself brominated the fluoro olefin. No reaction took place between 1,1,2-trifluoro-1,4-pentadiene and allylmagnesium bromide. These re-

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[1] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[2] Part XI: P. Tarrant and D. E. O'Connor, *J. Org. Chem.*, **29**, 2012 (1964).

[3] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

[4] T. F. McGrath and R. Levine, *ibid.*, **77**, 4168 (1955).

[5] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[6] J. D. Park and R. Fontanelli, *ibid.*, **28**, 259 (1963).

[7] P. Tarrant, J. Savory, and E. S. Iglehart, *ibid.*, **29**, 2009 (1964).

[8] P. Tarrant, P. Johncock, and J. Savory, *ibid.*, **28**, 839 (1963).

[9] P. Tarrant and A. C. Wright, unpublished work.

[10] D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

sults suggest that the allylmagnesium bromide reacts first with tetrafluoroethylene to form bromotrifluoroethylene, which then reacts with another molecule of Grignard reagent to give 1-bromo-1,2-difluoropentadiene I.

The reaction of allylmagnesium chloride with tetrafluoroethylene gave more of the expected diallylfluoroethylene (II) than did the bromide; a small amount of allylchlorodifluoroethylene (III) was also observed.

The reaction of allylmagnesium bromide with 1,1,2-trifluorobutadiene gave 3,4-difluoro-1,3,6-heptatriene, which slowly polymerized on isolation. It was identified as the tetrabromide. The bromine saturated only the terminal double bonds, as indicated by infrared analysis.

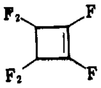
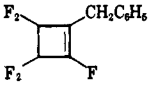
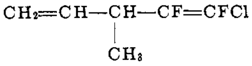
Allylmagnesium bromide was allowed to react with perfluorocyclobutene to form a tar even at −78°. Since half of the hexafluorocyclobutene was recovered, it seems probable that the initial product of the reaction was 1,2-diallyltetrafluorocyclobutene, which polymerized spontaneously. Perfluorocyclobutene has been found by workers in this laboratory to be by far the most reactive of the fluoro olefins toward attack by Grignard reagents.

No reaction occurred between allylmagnesium bromide and trifluoroethylene, 1,1,2-trifluoro-4-bromo-1-butene, or 1,1,2-trifluoro-1,4-pentadiene. The inactivity of the former two olefins with organometallic compounds has been observed before[7]; it appears that an electron-withdrawing group should be attached to the trifluorovinyl group for the reaction to occur.

Further reactions of fluoro olefins with Grignard reagents containing the allylic system are shown in Table II.

TABLE II

FURTHER REACTIONS OF ALLYLIC GRIGNARD REAGENTS AND FLUORO OLEFINS

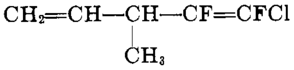
Grignard	Olefin	Product (%)
$C_6H_5CH_2MgBr$	$CF_2{=}CFCl$	No reaction
$C_6H_5CH_2MgBr$		 VII (40%)
$CH_3CH{=}CHCH_2MgBr$	$CF_2{=}CFCl$	$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}{-}CF{=}CFCl$ VIII (15%)

No reaction occurred between chlorotrifluoroethylene and benzylmagnesium bromide. This result is somewhat unexpected when compared with the good yield of the diolefin obtained from the reaction of chlorotrifluoroethylene and allylmagnesium bromide. However, the more reactive perfluorocyclobutene gave a reasonable yield of 1-benzylpentafluorocyclobutene VII when allowed to react with benzylmagnesium bromide.

The reaction of chlorotrifluoroethylene and crotonylmagnesium bromide would be expected to give 1-chloro-1,2-difluoro-1,4-hexadiene (IX); however, the nuclear magnetic resonance spectrum of the product showed only the presence of 1-chloro-1,2-difluoro-3-methyl-1,4-pentadiene (VIII).

$CH_3CH{=}CHCH_2CF{=}CFCl$

IX

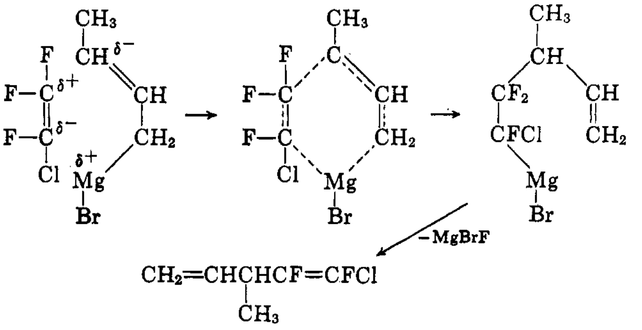


$CH_2{=}CH{-}\underset{\displaystyle CH_3}{\underset{\vert}{CH}}{-}CF{=}CFCl$

VIII

There has been some discussion in the literature concerning the structure of crotonylmagnesium bromide as to whether it exists in the crotonyl form or the α-methylallyl form.[11] Recent work using nuclear magnetic resonance and infrared spectroscopy, however, indicates that it exists exclusively as the crotonyl form.[12-14]

It would appear that the normal mechanism associated with this reaction, *i.e.*, the attack of the electronegative α-carbon atom of the Grignard reagent in the crotonyl form with the electropositive carbon atom of the fluoro olefin, is not taking place. It is more likely that the reaction is occurring by a mechanism similar to that suggested by Young and Roberts[15] for the addition of allylic Grignard reagents to carbonyl compounds.



The allylic system is able to transfer the negative charge induced on the α-carbon atom by the electropositive magnesium atom to the γ-carbon atom, which can then combine with the polarized fluoro olefin to give the transient six-membered ring. The newly formed addition product will then lose magnesium halide to give the fluoro diolefin.

Three reasons can be offered to support this mechanism for the reaction of allylic Grignard reagents with fluoro olefins. First, the reaction of crotonylmagnesium bromide gives only the methylpentadiene, as explained above. Second, the yields of the products using allylmagnesium bromide are much better than those from other aliphatic Grignard reagents such as vinylmagnesium chloride and methyl- or ethylmagnesium bromide; the latter reactants would be unable to form this six-membered ring system. Third, no reaction occurred with benzylmagnesium bromide and chlorotrifluoroethylene; this suggests that the reaction does not occur at the α-carbon atom, for it would otherwise be difficult to explain how the two structurally similar compounds, benzylmagnesium bromide and allylmagnesium bromide, behave so differently. A logical explanation for the lack of reaction at the allylic carbon atom in benzylmagnesium bromide is that the aromatic resonance energy would have to be overcome in forming this reaction site.

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(11) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y. 1954, pp. 1154–1157, and references cited therein.

(12) M. Gaudemar, *Bull. soc. chim. France*, 1475 (1958).

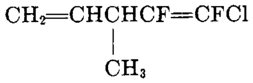
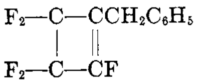
(13) J. E. Nordlander, W. C. Young, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 494 (1961).

(14) G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962).

(15) W. C. Young and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 649 (1946).

Table III

New Fluoro Olefins[a]

Compound	No.	B.p., °C.	$n^{22}D$	d^{22}	% carbon Calcd.	% carbon Found	% hydrogen Calcd.	% hydrogen Found	% fluorine Calcd.	% fluorine Found
$CH_2{=}CHCH_2CF{=}CFBr$	I	98	1.4315	1.463	32.79	32.94	2.73	2.90	20.76	20.61
$CH_2{=}CHCH_2CF{=}CFCl$	III	78.5	1.3986	1.141	43.32	43.60	3.61	3.88	27.44	27.22
$CH_2{=}CHCH_2CF{=}CFCF_3$	V	63	1.3346	1.197	41.86	42.04	2.91	3.08	55.23	55.29
$CH_2{=}CHCH_2CF{=}CFCH{=}CH_2$[b]	VI	...	1.4349	0.960			Polymer contains 23.13% F			
$[CH_2{=}CHCH_2CF]_2{=}$	II	114.5	1.4146	0.965	66.67	66.56	6.94	7.18	26.39	26.14
$CH_2{=}CHCH_2CF{=}CCl_2$	IV	119	1.4472	1.205	38.72	38.50	3.23	3.41	12.26	12.50
 $CH_2{=}CH\underset{CH_3}{\underset{\vert}{C}H}CF{=}CFCl$	VIII	94	1.4067	1.065	47.22	47.53	4.59	4.78	24.92	25.25
 $\begin{array}{l} F_2{-}C{-}CCH_2C_6H_5 \\ F_2{-}C{-}CF \end{array}$	VII	180	1.4434	1.300	56.41	56.20	2.99	3.10	40.60	40.28

[a] Analyses were by Galbraith Laboratories, Knoxville, Tenn. [b] Polymerizes on standing.

The physical properties and results of analyses of the new fluoro olefins are shown in Table III.

Experimental

Allylmagnesium Bromide and Fluoro Olefins. 1. Reaction with Chlorotrifluoroethylene, Bromotrifluoroethylene, Hexafluoropropene, 1,1,2-Trifluorobutadiene,[16] and *unsym*-Dichlorodifluoroethylene.—Allylmagnesium bromide in diethyl ether (150 ml., 0.25 mole) was placed in a three-necked flask with a stirrer and an acetone–Dry Ice condenser. The fluoro olefin (0.25 mole) was added to the cooled solution (−78°) over 0.5 hr. The solution was stirred at this temperature for 0.5 hr. and then allowed to warm to room temperature; stirring was continued for a further hour. The solution was hydrolyzed with sulfuric acid (100 ml. of *ca.* 6 *N*) and the ether layer was separated, dried (Drierite), and distilled to obtain the new fluoro diolefin. The distillates were checked for purity by analytical vapor phase chromatography using a silicone elastomer column at 100°.

2. **Reaction with Hexafluorocyclobutene.**—A reaction similar to the above gave 19 g. of the recovered butene (0.124 mole) and 15 g. of a brittle, black residue (36.89% fluorine) which was recovered from the reaction mixture by steam distillation.

3. **Reaction with 1,1,2-Trifluoro-4-bromo-1-butene.**[17]—Run at half scale (0.125 mole), the reaction was stirred for 70 hr. at room temperature. A similar reaction in tetrahydrofuran was refluxed for 5 hr. before hydrolysis.

4. **Reaction with Tetrafluoroethylene and Trifluoroethylene and the Reaction of Allylmagnesium Chloride with Tetrafluoroethylene.**—The olefin (0.125 mole) was vacuum condensed into a Porter–Fisher compatibility tube containing the Grignard reagent in diethyl ether (75 ml., 0.125 mole). The tube was sealed and shaken under the following conditions (temperature, time): (1) $CF_2{=}CF_2 + CH_2{=}CHCH_2MgBr$, room temperature, 17 hr.; (2) $CF_2{=}CFH + CH_2CHCH_2MgBr$, room temperature, 3 hr., 100°, 2 hr.; (3) $CF_2{=}CF_2 + CH_2{=}CHCH_2MgCl$, room temperature, 65 hr. The solutions were cooled and any unreacted gas condensed and identified by vapor phase chromatography. In the second reaction, 9.0 g. of trifluoroethylene (0.11 mole) was recovered. The solutions were then hydrolyzed with sulfuric acid (50 ml. of *ca.* 6 *N*) and the ether layers were worked up as previously indicated.

Bromination of 3,4-Difluoro-1,3,6-heptatriene.—The olefin (1.0 g.) was dissolved in carbon tetrachloride (5 ml.) and treated slowly with bromine until a slight excess was present. After washing with dilute sodium hydroxide and water, drying, and evaporating the solvent, the product was identified as 1,2,6,7-tetrabromo-3,4-difluoro-3-heptene. Absorption peaks in the infrared spectrum at 5.77 and 5.90 μ were associated with the *cis* and *trans* —CF=CF— group.

Anal. Calcd. for $C_7H_8Br_4F_2$: C, 18.66; H, 1.78; Br, 71.11; F, 8.45. Found: C, 18.73; H, 1.75; Br, 71.47; F, 8.73.

Benzylmagnesium Bromide and Fluoro Olefins.—(1) Benzylmagnesium bromide in diethyl ether (200 ml., 0.25 mole) was treated with chlorotrifluoroethylene (29.1 g., 0.25 mole) at room temperature for 36 hr. Chlorotrifluoroethylene (19.8 g. 0.17 mole) was recovered. After hydrolysis (100 ml. of 6 *N* H_2SO_4), vapor phase chromatographic analysis showed the only product to be toluene.

(2) Benzylmagnesium bromide in diethyl ether (125 ml., 0.125 mole) was allowed to react with hexafluorocyclobutene (20.2 g., 0.125 mole). After stirring for 3 hr. at room temperature, the solution was refluxed for 5 hr. and worked up as indicated above.

Crotonylmagnesium Bromide and Chlorotrifluoroethylene.—Crotonylmagnesium bromide in diethyl ether (200 ml., 0.25 mole) was refluxed with chlorotrifluoroethylene (29.1 g., 0.25 mole) for 36 hr. The solution was processed as described above.

Anhydrous Magnesium Bromide and Fluoro Olefins.—Anhydrous magnesium bromide (7.5 g.), prepared by heating an equimolecular amount of $MgBr_2 \cdot 6H_2O$ and ammonium bromide, was placed in a Carius tube with diethyl ether (50 ml.). Tetrafluoroethylene (12 g.) was vacuum transferred and the tube sealed. No reaction occurred after shaking at 70° for 72 hr. A similar experiment using 1,1,2-trifluoro-1,4-pentadiene (6.1 g.)[17] and magnesium bromide (9.2 g.) was also unsuccessful.

Acknowledgment.—We are grateful to the U. S. Army Natick Laboratories, Natick, Massachusetts, for the financial support of this project. Dr. Malcolm. Henry acted as the project leader.

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(16) Prepared by the dehalogenation of 4-bromo-3-chloro-3,4,4-trifluoro-1-butene with zinc dust in ethanol. See P. Tarrant and M. R. Lilyquist, *J. Am. Chem. Soc.*, **77**, 3640 (1955), for experimental details and properties of the diene.

(17) Prepared as by P. Tarrant and E. G. Gillman, *ibid.*, **76**, 5423 (1954).