

dride; however, no physical constants were given for the carbinol. In this laboratory I was distilled unchanged from both phosphoric oxide and aniline hydrobromine.

The carbinols were converted to the acetates by refluxing with acetyl chloride. The perfluoroalkyl group had a pronounced retarding effect on the formation of the acetates as the conversions were about 40–60% but the yields were high. The acetylation reactions were carried out on crude mixtures of the carbinols and the esters were obtained by distillation.

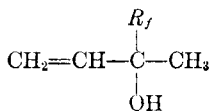
2-Trifluoromethyl- and 2-pentafluoroethyl-1,3-butadiene were obtained as essentially pure materials by distillation of the products from pyrolysis of the corresponding acetates at 500–550°. Gas chromatographic analysis of the product from the heptafluoropropyl compound indicated the presence of two other compounds with vapor pressures close to that of the desired diene. However, heptafluoropropylbutadiene was readily obtained in a pure state from the preparative scale chromatographic column.

EXPERIMENTAL⁵

Source of ketones. Trifluoroacetone was obtained from Peninsular ChemResearch, Inc. Pentafluoroethyl- and heptafluoropropyl methyl ketones were prepared from the corresponding acids by the method of Sykes, Tatlow, and Thomas.⁶

Preparation of the methylvinylperfluoroalkyl carbinol. The vinyl magnesium chloride was prepared in tetrahydrofuran solvent by the method of Ramsden, *et al.*³

Methyl perfluoroalkyl ketone was added dropwise to the stirred solution of vinyl magnesium chloride at such a rate that the temperature of the reaction mixture did not rise above 50°. The mixture was stirred 1 to 2 hr. and allowed to stand overnight. The Grignard intermediate was decomposed by the addition of water followed by 6*N* hydrochloric acid. The reaction mixture was steam distilled and the steam distillate was extracted with diethyl ether. The ethereal extracts were combined, dried, and distilled through a 25-cm. column packed with protruded nickel packing.

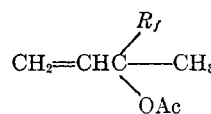


	$R_f=\text{CF}_3$	$R_f=\text{C}_2\text{F}_5$	$R_f=\text{C}_3\text{F}_7$
$\text{CH}_2=\text{CHCl}$	160 ml ^a	107 g	1.5 moles $\text{CH}_2=\text{CHMgCl}$
Tetrahydrofuran	1,200 ml	530 ml	
Mg	67 g	34 g	
$R_f\text{COCH}_3$	250 g	190 g	215 g.
Crude carbinol	300 g	134 g	191 g
Analytical sample ^b	1.3604	1.3510	1.3438 (25°)
n_D^{24}	(24°)	(24°)	
B.p.	97°	107°	121°
%C Calculated	42.85	37.89	35.00
%C Found	42.92	37.84	35.07
%H Calculated	5.00	3.68	2.92
%H Found	5.41	3.89	3.20

^a $\text{CH}_2=\text{CHBr}$ ^b Obtained by preparative scale v.p.c.

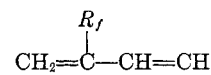
(5) Analyses by Galbraith Laboratories, Knoxville, Tenn.
(6) A. Sykes, J. C. Tatlow, and C. R. Thomas, *J. Chem. Soc.*, 835 (1956).

Acetylation of the methylvinylperfluoroalkylcarbinols. The crude carbinol was heated under gentle reflux with an equal weight of acetyl chloride for 4–5 hr. The reaction mixture was poured into iced water and the organic layer was separated, washed with dilute sodium bicarbonate solution and water, dried, and distilled through a 70-cm. column packed with protruded nickel packing.



	$R_f=\text{CF}_3$	$R_f=\text{C}_2\text{F}_5$	$R_f=\text{C}_3\text{F}_7$
Crude carbinol	300 g	134 g	190 g
Ester + carbinol	125 g	59.8 g	121 g.
Pure ester	135 g	69.9 g	45 g
B.p. Pure ester	119°	132°	148°
n_D^{24}	1.3685 (24°)	1.3590 (23°)	1.3528 (24°)
%C Calculated	46.15	41.37	38.29
%C Found	46.26	41.19	38.41
%H Calculated	4.95	3.88	3.19
%H Found	5.31	3.68	3.39

Pyrolysis of the acetates of the methylvinylperfluoroalkylcarbinols. The pyrolyses were carried out in an atmosphere of dry nitrogen in a vertical pyrex glass tube (16 in. × 1 in. dia.) packed with Pyrex glass rods (each 0.6 ± 0.2 cm. × 0.3 cm. dia.) at 500–550°. The rate of ester addition was ca. 30 g./hr. and the products were continuously swept from the hot tube into a trap cooled in Dry Ice–acetone by a nitrogen sweep. The volatile dienes were isolated by distillation. Preparative scale vapor phase chromatography was employed to obtain a pure sample of 2-heptafluoropropyl butadiene.



	$R_f=\text{CF}_3$	$R_f=\text{C}_2\text{F}_5$	$R_f=\text{C}_3\text{F}_7$
Carbinol ester	135 g	67 g.	75 g
Substituted butadiene	37 g	15.4 g	21.5 g ^a
Analytical sample n_D^{24}	1.3448 (23°)	1.3328 (24°)	1.3260 (21°)
B.p.	41–42°	54°	68°
%C Calculated	49.18	41.86	37.83
%C Found	48.91	42.2	37.87
%H Calculated	4.10	2.91	2.25
%H Found	4.36	3.15	2.23

^a v.p.c. showed 70% purity.

Impurities isolated by v.p.c. but not identified:

	x	y
B.p.	81–82°	88–89°
n_D^{24}	1.3388 (22°)	1.3490 (21°)
%C Found	38.08	37.39
%H Found	2.68	2.67

Preparative scale chromatography. A column accepting 6–8 ml. of liquid sample was used to obtain pure material for physical constants other than boiling points. The column was made of glass tubing 25 mm. in diameter and was 20 ft. in length. The packing was Johns-Manville Chromosorb and the liquid phase was dinonyl phthalate. Nitrogen was used as the carrier gas.

The desired material was collected in cold traps immersed in either liquid air or Dry Ice.

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On the Continuous Preparation of Vinyl Grignard Reagents

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In 1934 H. Normant² showed that vinylmagnesium bromide could be prepared in good yields using tetrahydrofuran as a solvent. In many subsequent publications Normant and co-workers demonstrated the syntheses of several vinyl derivatives.³ Recently, Ramsden, *et al.*,⁴ have shown the generality of Normant's method by extending it to vinyl chloride. Since then, vinylmagnesium halides have been used extensively in the syntheses of olefinic derivatives.

Recent investigations in this laboratory have been concerned with the syntheses of new vinyl compounds. During the course of this work considerable quantities of vinylmagnesium halides, primarily vinylmagnesium chloride, had to be prepared. In order to avoid large batch operations and still maintain an economical procedure, a continuous process has been developed and employed. This not only afforded a convenient method of preparing the vinyl Grignard reagents, but also circumvented possible side reactions by maintaining a permanent excess of magnesium and removing the changed vinyl chloride essentially quantitatively.

The process may best be described by referring to Fig. 1 which shows the design and construction of the apparatus for operations on a laboratory scale.

EXPERIMENTAL

Vinyl chloride was fed into the apparatus of Fig. 1 at *y* having the stopcock *b* adjusted in such a way that the gas passed through vessel *E*. *E* served as a bubble counter. The end of the feed tube was immersed in a few milliliters

(1) Present address: Allied Chemical, National Aniline Division, Hopewell, Va.

(2) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(3) (a) H. Normant, *Compt. rend.*, **239**, 1811 (1954); **240**, 314, 440, 631, 1111, 1435 (1955). (b) H. Normant and C. Crisan, *Compt. rend.*, **240**, 1946 (1955). (c) H. Normant and P. Maitte, *Bull. soc. chim. France*, 951, 1439 (1956). (d) H. Normant and J. Ficini, *Bull. soc. chim. France*, 1441 (1956). (e) J. Ficini, *Bull. soc. chim. France*, 119 (1956). (f) V. Levy and H. Normant, *Compt. rend.*, **242**, 202 (1957). (g) H. Normant and G. Martin, *Bull. soc. chim. France*, 429, 728 (1957).

(4) Hugh E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

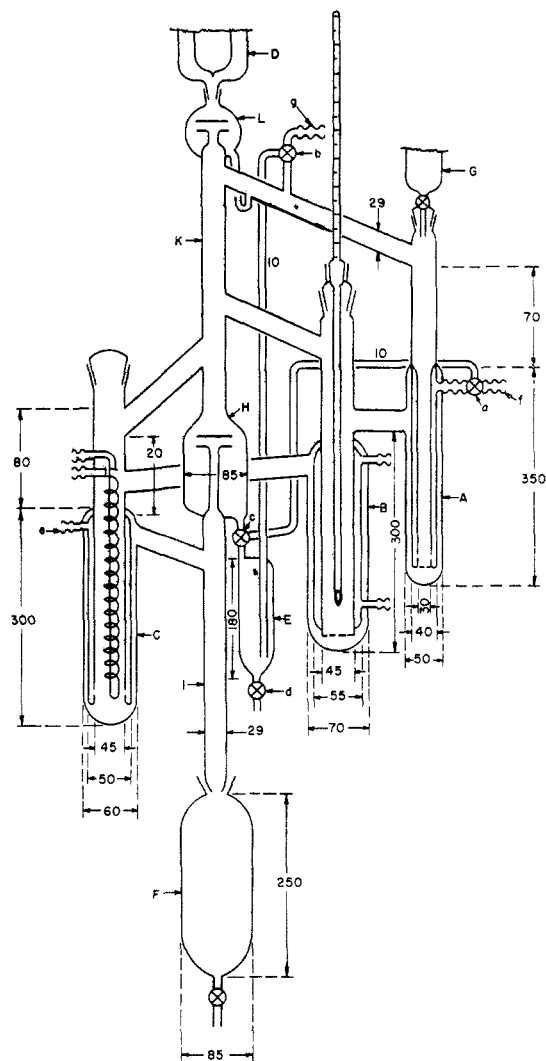


Fig. 1. Apparatus for the continuous preparation of vinyl Grignard reagents. Units are millimeters

of tetrahydrofuran, saturated with vinyl chloride. Having the stopcocks *c* and *a* appropriately adjusted, the gas was allowed to pass through the second of the three concentric tubes, which were the principal parts of the absorption column *A*. The gas left this tube from the bottom and then entered the inner tube which was packed with 6-mm. Raschig rings. In this tube the gas was absorbed by tetrahydrofuran, addition of which was maintained at a constant rate from the supply container *G*. The vinyl chloride-tetrahydrofuran solution rose in the outer tube of *A* which ran over into the inner tube of the reaction apparatus *B* which was also composed of three concentric tubes. This inner tube of *B* was filled with magnesium turnings. The reaction occurred while flowing through this tube. To keep the system at the required temperature and to carry off the exothermic heat, water, thermostatically controlled at 50–52°, was pumped through the second tube.

The reaction solution rose in the outer tube and passed into the inner tube of *C*. *C* again consisted of three concentric tubes. Nitrogen was introduced at *e*, left the middle tube at the bottom, and entered the inner tube. Passing through the reaction mixture, the nitrogen removed the unchanged vinyl chloride and a part of the tetrahydrofuran. Both the vinyl chloride and the tetrahydrofuran were then condensed from the gas in the condenser *D*, which was charged with a carbon dioxide-acetone mixture. Due to