vent. The same alcohols in a carbon tetrachloride solution, however, indicated unexpectedly two bands in the free OH stretching frequency region (3580–3620 cm^{-1}). Proton magnetic resonance spectrum of I at room temperature, however, indicates only one peak for the OH proton. To determine whether this anomaly is due to chemical exchange between magnetically nonequivalent protons, it is possible to slow down the exchange rate by cooling the sample. The spectrum of neat I was recorded at varying temperatures and, at −36°, the spectrum shows a doublet for the OH proton. More details on the infrared and nuclear magnetic resonance studies of these compounds will be published at a later date.

The availability of these tertiary alcohols as well as others which should be capable of synthesis by varying X in reaction 1 (for example, X = OH, SH, COOH, etc.) will provide opportunity to study the chemical and physical properties of perfluoro tertiary alcohols.

Experimental Section

1. **Perfluoro-α,α-dimethylbenzyl Alcohol (I) from Pentafluorophenyllithium.**—A solution (60 ml) containing 0.077 mole of *n*-butyllithium in hexane was cooled to −55° and treated with 12.9 g (0.077 mole) of pentafluorobenzene in 40 ml of diethyl ether. The addition required 30 min. The reaction was stirred for 2 hr. An excess of hexafluoroacetone was introduced above the surface of the stirred mixture. The temperature was maintained between −60 and −50° throughout the addition. After the product was warmed to 10° and hydrolyzed with 10% H_2SO_4, the organic layer and two 10-ml ether extracts of the aqueous portion were combined and dried over Na_2SO_4. Fractional distillation in two similar experiments gave an average yield of 79% of the alcohol boiling at 158–160°, $n^{26}D$ 1.3780. *Anal.* Calcd for $C_9HF_{11}O$: C, 32.35; H, 0.30; F, 62.56. Found: C, 32.62; H, 0.51; F, 62.31.

2. **Perfluoro-α,α,*p*-trimethylbenzyl Alcohol (II).**—To a stirred mixture of 20 ml of tetrahydrofuran and 15.8 ml of a hexane solution containing 0.025 mole of butyllithium, which was maintained at −60°, was added a solution of 5.2 g (0.024 mole) of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzene in 10 ml of tetrahydrofuran during 15 min. The mixture was stirred for 30 min. An excess of hexafluoroacetone was introduced above the surface of the liquid. After the product was warmed to room temperature, 40 ml of ice water containing 6.0 ml of H_2SO_4 was added, the organic layer was separated, the aqueous layer was extracted twice with ether, and the combined organic layer and extracts were dried over Na_2SO_4. Fractional distillation through a micro Claisen head gave 5.5 g (61%) of the alcohol boiling at 103–104°, $n^{28}D$ 1.3732. *Anal.* Calcd for $C_{10}HF_{13}O$: C, 31.27; H, 0.26; F, 64.30. Found: C, 31.39; H, 0.40; F, 64.19.

3. **4-Methylperfluoro-α,α-dimethylbenzyl Alcohol (III).**—Alcohol III was prepared in a similar manner to II except that 2,3,5,6-tetrafluorotoluene was used. The product III was obtained in 91% yield, $n^{23}D$ 1.3979, bp 193–194°. *Anal.* Calcd for $C_{10}H_4F_{10}O$: C, 36.38; H, 1.22; F, 57.55. Found: C, 36.53; H, 1.28; F, 57.90.

4. **Perfluoro-4-H-α,α-dimethylbenzyl Alcohol (IV).**—To a rapidly stirred solution of 21.9 g (0.146 mole) of 1,2,4,5-tetrafluorobenzene in 150 of tetrahydrofuran, which was maintained at −65°, was added during 45 min 92 ml of a hexane solution containing 0.146 mole of butyllithium. The reaction was stirred for 2 hr. An excess of hexafluoroacetone was introduced above the surface of the liquid. The mixture was warmed to room temperature and hydrolyzed with dilute sulfuric acid, and the organic phase was separated, combined with ether extracts of the aqueous phase, and dried over Na_2SO_4. Evaporation of the solvents and recrystallization of the residue from petroleum ether (bp 60–90°) gave 21.3 g (61% calculated on the basis of butyllithium) of perfluoro-1,4-phenylenebis(dimethylcarbinol) (V), mp 94–95°. *Anal.* Calcd for $C_{12}H_2F_{16}O_2$: C, 29.89; H, 0.42; F, 63.05. Found: C, 29.98; H, 0.62; F, 63.00.

Evaporation and distillation of the recrystallization liquors gave 4.9 g (11%) of the monosubstituted alcohol IV boiling at 161–163°. *Anal.* Calcd for $C_9H_2F_{10}O$: C, 34.19; H, 0.64; F, 60.11. Found: C, 34.01; H, 0.75; F, 60.00.

5. **Perfluoro-1,4-phenylenebis(dimethylcarbinol) (V).**—A stirred mixture of 100 ml of tetrahydrofuran and 93 ml of a hexane solution containing 0.148 mole of butyllithium was treated with a solution of 21.7 g (0.071 mole) of dibromo-2,3,5,6-tetrafluorobenzene in 45 ml of tetrahydrofuran at −60°. The addition required 20 min. After an excess of hexafluoroacetone was introduced above the surface of the mixture, the product was hydrolyzed with dilute H_2SO_4; the organic layer was separated, combined with ether extracts of the aqueous layer, and dried over Na_2SO_4. Evaporation of the solvents and two recrystallizations from petroleum ether gave 24.0 g (71%) of the diol V, mp 94–95°.

6. **Perfluoro-4,4′-biphenylenebis(dimethylcarbinol) (VI).**—A solution of 2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl in 145 ml of tetrahydrofuran was added over 30 min to a stirred mixture of 100 ml of tetrahydrofuran and 90 ml of a hexane solution containing 0.144 mole of butyllithium at −60°. After 1 hr an excess of hexafluoroacetone was introduced above the liquid surface. The product was hydrolyzed with dilute sulfuric acid and the organic layer was separated and dried over Na_2SO_4. Evaporation of the solvents and recrystallization from chloroform gave 32.4 g (74%) of the diol VI, which melted at 192–193°. *Anal.* Calcd for $C_{18}H_2F_{20}O_2$: C, 35.20; H, 0.33; F, 61.87. Found: C, 34.83; H, 0.44; F, 62.00.

Acknowledgment.—The authors wish to thank Miss Mary Ryan and Mr. Neil McDevitt of Air Force Materials Laboratory Analytical Department for their determination and interpretation of the infrared and nmr spectra.

Decomposition Products from Pentafluorophenylmagnesium Bromide

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Pentafluorophenylmagnesium bromide has been used as the intermediate for the synthesis of other organometallic compounds containing a pentafluorophenyl group.[1] In most cases, only the desired organometal-

$$nC_6F_5MgBr + M^nCl_n \longrightarrow M^n(C_6F_5)_n + nMgBrCl$$

lic compound was described with no mention of other side products. In a few instances,[2] however, a reaction between the pentafluorophenylmagnesium bromide or its decomposition product and the solvent (toluene, benzene) were reported to yield side products.

Recently, the authors have reported[1] on the reaction of pentafluorophenylmagnesium bromide with group IV metallic halides in tetrahydrofuran according to the above equation. In the reaction between the Grignard and silicon tetrachloride, germanium tetrachloride, and tin tetrachloride, side products were obtained in all instances. Only the side products from the silicon tetrachloride were examined in detail, although the others were of similar nature as indicated

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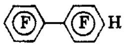
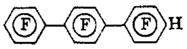
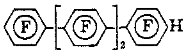
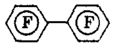
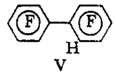
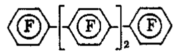
(1) See references cited in C. Tamborski, E. J. Soloski, and S. M. Dec. *J. Organometal. Chem.* (Amsterdam), **4**, 446 (1965).

(2) (a) J. L. W. Pohlman and F. E. Brinckman, *Z. Naturforsch.*, **20b**, 5 (1965); (b) N. N. Vorozhtsov, V. A. Barkhasch, N. G. Ivanova, and A. K. Petrov, *Tetrahedron Letters*, 3575 (1964); (c) J. P. N. Brewer and H. Heaney, *ibid.*, 4709 (1965).

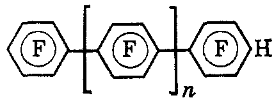
TABLE I

	Mp, °C (uncor)	Calcd, % C	Calcd, % H	Calcd, % F	Found, % C	Found, % H	Found, % F	Mol wt Calcd	Mol wt Found
 I	81–82[a]	45.59	0.32	54.09	45.80	0.67	54.27	316	305
 II	176–177	46.56	0.23	53.20	46.22	0.16	53.87	464	450
 III	210–211	47.07	0.18	52.75	46.76	0.03	52.72	612	596
 IV	70[b]								
 V	42–43[c]								
 VI	193–194[d]								
 VII	233–234[d]								

[a] Prepared by an alternate method, mp 82–83°. C. Tamborski, E. J. Soloski, and J. P. Ward, unpublished studies. [b] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 166 (1959). [c] D. E. Fenton, A. J. Park, D. Shaw, and A. G. Massey, *J. Organometal Chem.* (Amsterdam), **2**, 437 (1964). [d] J. Thrower and M. A. White, private communication.

by vapor phase chromatographic analysis. The authors now wish to report on the separation and characterization of some of the side products.

After the desired tetra(pentafluorophenyl)silane was separated by filtration (see Experimental Section) the solvent-soluble material was analyzed by vapor phase chromatography and shown to be a mixture of many components. Although it was a complex mixture, there were three major components which accounted for approximately 90% of the material. The per cent area concentration of the three components decreased as the molecular weight of the component increased (I > II > III). These major components could be separated on an alumina column using petroleum ether (bp 60–90°) as the eluent. Characterization of these major components indicated a series of oligomers of the structure shown.

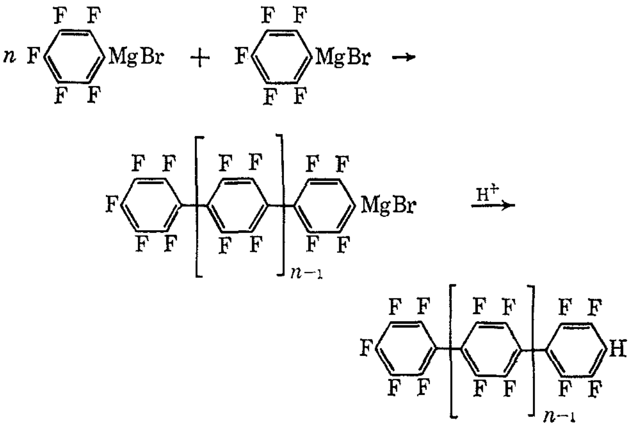


$n = 0, 1, 2$

When the reaction was repeated under similar conditions except in the absence of the silicon tetrachloride, there were no indications of any side products. Pentafluorophenylmagnesium bromide in tetrahydrofuran (THF) is quite stable at 0°. Only after 55 hr was there any sign of initial decomposition (as determined by vapor phase chromatography) of the Grignard.

It appears, therefore, that the greater quantity of side products obtained from the Grignard and metallic halide reaction may be due to an increased rate of Grignard decomposition in the reaction mixture.

It is quite possible that the Grignard decomposes by several mechanisms. As an example,[2c,3] the Grignard may form a tetrafluorobenzyne (C_6F_4) intermediate which then can react with a number of different species in the reaction media. It is more likely, in our case, however, that the Grignard reacts with the *p*-fluorine of another Grignard molecule. This repeating process would then account for the oligomeric products isolated.



The physical properties and characterization of the products are shown in Table I. For comparison reasons, there are also included a few related structures.

Experimental Section

Pentafluorophenylmagnesium bromide was prepared by adding pentafluorobromobenzene (0.60 mole, 148.2 g) in 50 ml of dry THF to magnesium turnings (0.60 mole, 14.6 g) suspended in 620 ml of dry THF at 0°. The addition required 30 min. Two hours after the addition, a 10-ml sample was removed, hydrolyzed, dried, and analyzed by vapor phase chromatography. Other than unreacted pentafluorobromobenzene and pentafluorobenzene, no side products were observed. Analysis of the Grignard by titration indicated a 90% yield. A solution of silicon tetrachloride (0.135 mole, 22.94 g) in 50 ml of THF

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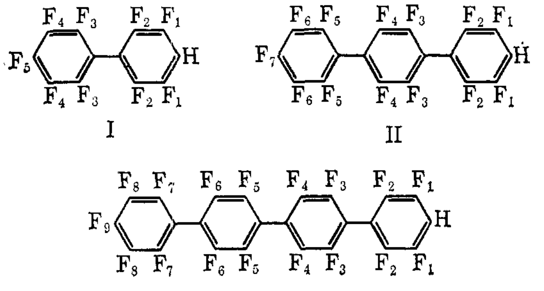
[3] E. J. P. Flear, J. Thrower, and M. A. White, 19th International Congress of Pure and Applied Chemistry, London, July 1963.

was added over 1.75 hr at 0°. After the addition was complete, the reaction mixture was slowly allowed to come to room temperature. The precipitate which consisted of the product tetra-(pentafluorophenyl)silane (69% yield) and inorganic salts was filtered. The filtrate was hydrolyzed with dilute hydrochloric acid and extracted three times with diethyl ether. The diethyl ether extracts were dried and distilled to leave 25 g of a solid which consisted of the side products of the reaction. The material was dissolved in petroleum ether (bp 60-90°) and separated by passing through an alumina (Woelm, neutral grade) column. Petroleum ether (bp 60-90°) was used as the eluent. Compounds I-III (Chart I) were recrystallized from petroleum ether (bp 30-90°).

CHART I



I II III

The F^{19} spectra were recorded on a Varian Associates V-4300B spectrometer at 40 Mc/sec with trifluoroacetic acid as an external standard (see Table II).

TABLE II

Compd	F atom	Ppm[a]	Multiplicity[b]	Integrated peak area
I	$F_1F_2F_3$	+60.3	m	6
	F_4	+83.6	m	2
	F_5	+72.9	t ($J_{F_4F_5}$ = ~20 cps)	1
II	$F_1F_2F_3F_4F_5$	+62.3	m	10
	F_6	+86.4	m	2
	F_7	+75.5	t ($J_{F_6F_7}$ = ~20 cps)	1
III	$F_1F_2F_3F_4F_5F_6F_7$	+62.8	m	c
	F_8	+83.2	m	...
	F_9	+74.0	t ($J_{F_8F_9}$ = ~20 cps)	...

[a] Trifluoroacetic acid as external standard. [b] m = multiplet; t = triplet. [c] Concentration was too low to obtain a good integration.

The H^1 spectra were recorded on a Varian A60 spectrometer. The spectra of I and II exhibited a first-order triplet of triplets centered at 7.6 ± 0.1 ppm with characteristic *o*- and *m*-fluorine-hydrogen coupling constants[4,5] (J_{F_1H} = 10.1 ± 0.1 cps, J_{F_2H} = 7.8 ± 0.1 cps). This observed pattern confirms the *para* orientation of the protons. Tetramethylsilane was used as the internal standard for I. The spectrum of II was obtained by using a dimethylacetamide solution (20% by weight) at 100°. The protons of the $CH_3\overset{|}{C}{=}O$ of the solvent were used as a reference point.

Acknowledgments.—The authors wish to thank J. V. Pustinger, Jr., and J. Strobel, Monsanto Research Corporation, and R. De Pasquale, Air Force Materials Laboratory, for the determination and interpretation of the nmr spectra reported in this work.

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(4) H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

(5) J. Burdon, W. B. Hollyhead, and J. C. Tatlow, *J. Chem. Soc.*, 6336 (1965).

Organic Fluoronitrogens.[1a] V. Bis(difluoramino)difluoromethane

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The synthesis of bis(difluoramino)difluoromethane, $F_2NCF_2NF_2$, by the direct fluorination of cyanuric chloride was recently reported.[2] The identification of the compound was based primarily on molecular weight, elemental analyses, and infrared spectral analysis.[3] During our investigations of direct fluorination, bis(difluoramino)difluoromethane was prepared by the fluorination of aminoiminomethanesulfinic acid. We wish to report the details of this synthesis as well as the properties of bis(difluoramino)difluoromethane which unequivocally establish its structure.

The direct fluorination of a mixture of aminoiminomethanesulfinic acid and sodium fluoride was carried out under mild conditions at 0° with 10% by volume of fluorine in nitrogen. In addition to the formation of a large amount of sulfuryl fluoride, the fluorination yielded bis(difluoramino)difluoromethane, difluoramidosulfuryl fluoride[4] (F_2NSO_2F), thionyl fluoride, difluoraminoperfluoromethane, nitrogen trifluoride, and other cleavage products.

Bis(difluoramino)difluoromethane is apparently formed from aminoiminomethanesulfinic acid by the replacement of hydrogen, addition to the imino bond, and carbon-sulfur cleavage. The formation of difluoramidosulfuryl fluoride is presumed to occur by the combination of difluoramino and sulfuryl fluoride radicals.

$$H_2N\overset{\overset{\displaystyle NH}{\|}}{C}SO_2H + 6F_2 \longrightarrow F_2NCF_2NF_2 + SO_2F_2 + 4HF$$

Bis(difluoramino)difluoromethane (8-10% yield) was isolated by gas chromatography and identified by infrared, nuclear magnetic resonance, and mass spectroscopy as well as molecular weight and elemental analyses. Difluoramidosulfuryl fluoride was identified by comparison of its infrared spectrum with the published spectrum.[4]

The vapor pressure of bis(difluoramino)difluoromethane, measured from −123 to −46°, can be expressed by the Clausius-Clapeyron equation. The

$$\log P_{\text{mm}} = 7.653 - \frac{1149}{T}$$

boiling point, obtained by extrapolation of the vapor pressure curve, is −32 ± 1°. The compound has a

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(1) (a) Preceding paper in this series: R. A. Mitsch, E. W. Neuvar, R. J. Koshar, and D. H. Dybvig, *J. Heterocyclic Chem.*, **2**, 371 (1965). (b) Deceased, Aug 5, 1965.

(2) M. A. Englin, S. P. Makarov, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **35**, 1416 (1965).

(3) The disclosures relating to the infrared spectrum were insufficient to enable a comparison with the spectrum of bis(difluoramino)difluoromethane obtained by the method described in this present communication.

(4) M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).