48 hr in a stirring autoclave (pressure approximately 100 psi). Evaporation of the excess ammonia followed by acidification with acetic acid yielded a black oil and a white, insoluble solid. Warming caused the solid to dissolve and the solution was carefully separated from the oil (polymer?). The solution was cooled to about 0° and the white precipitate, the monoacetate of **17** (1.0 g) was filtered off. Its melting point was 119–120°; a mixture melting point with the monoacetate of **12** gave no depression.

Anal. Calcd for $C_{20}H_{42}N_2O_4$: C, 64.1; H, 11.3; N, 7.48. Found: C, 63.2; H, 11.0; N, 7.20.

Since the carbon analysis was slightly off, the monoacetate was divided into two portions for conversion to the dihydrochloride, mp 147–149° (identical with the dihydrochloride of **12**), and to the sulfate, mp 236–238° (identical with the sulfate of **12**).

Anal. Calcd for the dihydrochloride ($C_{18}H_{40}Cl_2N_2O_2$): C, 55.8; H, 10.4; Cl, 18.3; N, 7.23. Found: C, 55.6; H, 10.6; Cl, 18.2; N, 7.25.

Anal. Calcd for the sulfate ($C_{18}H_{40}N_2O_6S$): C, 52.4; H, 9.77; N, 6.79; S, 7.77. Found: C, 52.4; H, 9.39; N, 6.69; S, 7.96.

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Notes

Perfluoro Tertiary Alcohols

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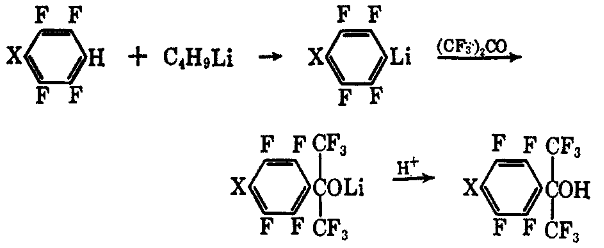
Attempts to prepare perfluoro tertiary alcohols through the reaction between a fluoro ester and a perfluoroorganolithium[1] or perfluoro Grignard[2] reagent thus far have been unsuccessful. In each case only perfluoroalkyl secondary alcohols $(R_F)_2CHOH$ were obtained. Recently, Graham and Weinmayr[3] have reported the reaction between perfluoro olefins, cesium fluoride, and certain perfluoro ketones to yield perfluoro tertiary alcohols. Two other nonorganometallic routes have been recently reported by Middleton and Lindsey[4] for the synthesis of specific perfluoro tertiary alcohols. Photoinitiated bimolecular reduction of hexafluoroacetone with isopropyl alcohol yielded the perfluoropinacol while hydration of tetrakis(trifluoromethyl)ethylene yielded the perfluoro(3H-2,3-dimethyl-2-butyl alcohol). Dyatkin, Mochalina, and Knunyants[5] have also reported the synthesis of perfluoro tertiary alcohols through the oxidation of *t*-nitrosoperfluoroisobutane and subsequent hydrolysis of the nitrite formed.

The physical and chemical properties of the hydroxyl group are strongly affected by the perfluoroalkyl substituents. The inductive effect of the perfluoroalkyl group increases the acidity of the alcohols. The ionization constants[4,5] of the perfluorinated alcohols indicates them to be strongly acidic. Perfluoro-*t*-butyl alcohol is a stronger acid ($pK_a = 3.9$) than acetic acid ($pK_a = 4.7$).[5] Other properties noted[4] in certain highly fluorinated alcohols were the strong hydrogen-bond formation, unusual solvent properties for certain polymers and formation of stable complexes.

The authors now wish to report on a general method for preparing perfluorinated arylalkyl tertiary mono- and dialcohols. Recently, the synthesis of a number of perfluoroaryllithium reagents[6] have been reported. These intermediates have now been treated with hexafluoroacetone to yield the perfluoro tertiary alcohols in good yields.


(1)

X = F (I), CF_3 (II), CH_3 (III), H (IV and V), *p*-HC_6H_4 (VI)

When X = H or *p*-C_6F_4, metalation can be controlled to yield predominantly the mono or dilithio intermediate. The dilithio intermediate will yield the biscarbinols.

The yields and properties of these alcohols are described in the Experimental Section. One attempt at preparing the carbinol I from the Grignard pentafluorophenylmagnesium bromide showed the advantage of the organolithium intermediate over the Grignard intermediate. The greater nucleophilic nature of the organolithium intermediate toward hexafluoroacetone resulted in much higher yields of the carbinol (79 *vs.* 33%).

None of the alcohols prepared in this study exhibited any tendency to form stable isolable complexes with tetrahydrofuran as was the case with the perfluoro secondary and tertiary alkyl alcohols.[4] However, infrared studies of tetrahydrofuran solutions of the arylalkyl alcohols synthesized in this study indicated hydrogen bonding between the alcohols and the sol-

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[1] E. T. McBee, C. W. Roberts, and S. G. Curtis, *J. Am. Chem. Soc.*, **77**, 6387 (1955).

[2] A. L. Henne and W. C. Francis, *ibid.*, **75**, 992 (1953).

[3] D. P. Graham and V. Weinmayr, *J. Org. Chem.*, **31**, 957 (1966).

[4] W. J. Middleton and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **86**, 4948 (1964).

[5] B. L. Dyatkin, E. P. Mochalina, and O. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965).

[6] C. Tamborski and E. J. Soloski, *J. Org. Chem.*, **31**, 743 (1966).

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.

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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 organometallic compound was described with no mention of other side products.

$$n\mathrm{C_6F_5MgBr} + \mathrm{M}^n\mathrm{Cl}_n \longrightarrow \mathrm{M}^n(\mathrm{C_6F_5})_n + n\mathrm{MgBrCl}$$

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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[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).