# Unsaturated Derivatives of Fluorinated Tertiary Alcohols

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A practical synthetic route for the production of 3,3'-fluoro-substituted isobutylenes by direct conversion from highly halogenated tertiary alcohols is described. Treatment of the alcohols with $PCl_5$ at reflux temperature proved to be the most effective method of all investigated. The mechanism of this reaction is presently unknown. Synthesis of other unsaturated fluorocarbon compounds is described. Yields of 59 to 75% were realized.

A number of highly fluorinated vinylidene-type monomers conforming to the general formula $CHR=C(CF_2X)_2$, where R = H or alkyl and X = halogen, have been previously reported in the literature. For example, Haszeldine[1] reported the formation of 2-trifluoromethyl-2-chlorodifluoromethylethylene and the hexafluoro analog from the treatment of 1,1-difluoroprop-1-ene with free radicals formed from trifluoromethyliodide, followed by various stages of dehydrohalogenation and halogenation.

With an interest in examining the chemistry and evaluating the reactivity of such compounds toward common monomers in free-radical polymerization systems, we investigated alternate preparative methods. The object of this research was to provide means of producing $CHR=C(CF_2X)_2$ on a practical scale.

The recent commercial availability of the highly halogenated acetones led us to examine these ketones as starting materials. The starting point for this investigation was the formation of tertiary alcohols from the ketones by means of the Grignard reaction (*cf.* Table I). Other reactions, developed by Gilbert and co-workers,[2] could have been used to form specific phenylpropanols. However, we used the Grignard reaction exclusively, as it was familiar and broadly versatile.

Ether was removed from alcohol–ether azeotropes with 20% oleum where necessary and yields of pure alcohol were in the range of 38 to 75%. When high-boiling ethers were used for the Grignard medium, the alcohols could often be separated by simple fractional distillation.

The high electron-withdrawing properties of the $CF_2X$ groups strengthen the tertiary carbon–oxygen bonds[3,4] to such an extent that cleavage by the more common techniques was difficult. Thus, the alcohols were extremely resistant to dehydration.

Attempts at halogenation of the alcohols by zinc chloride and hydrogen chloride, and thionyl chloride and sulfuryl chloride, were unsuccessful. A high-temperature sealed-tube reaction with phosphorus tribromide was also unsuccessful, resulting in a high recovery of starting alcohol.

Halogenation through tosylation of the alcohols was also attempted. Tosylates were easily formed at ambient temperature from reaction of the sodium fluoroalcoholates with toluenesulfonyl chloride in

tetrahydrofuran. Treatment of the tosylates with sodium iodide, lithium chloride, or potassium bromide in refluxing ethylene glycol, diethylene glycol ethers, or dimethylformamide was tried to obtain organohalide precursors of the desired olefins. The reactions either failed to go, or intractable mixtures of reaction products occurred. Infrared spectra of rough cuts indicated frequent ester interchange in these reactions when glycol-type solvents were employed. Similar reactions with perfluoro acid esters of the alcohols also failed to yield organohalide precursors. Only complex, intractable mixtures were obtained.

Formation of the acetate of the tertiary fluoro alcohol I by refluxing in acetyl chloride was accomplished in high yields. When pyrolyzed in a quartz tube[5] at about 500°, this acetate produced the desired fluoro olefin, but the compound was contaminated by small amounts of unidentified materials which could be removed only by tedious techniques. A clean method of olefin preparation therefore still remained to be found.

Swarts[6] observed that treatment of 2-trifluoromethylisopropyl alcohol with phosphorus pentabromide resulted in the formation of the desired bromide in about 29% yield. In addition, he obtained from the same reaction a 68% yield of 2-trifluoromethylpropene.

The carbon–oxygen bonds in our alcohols were expected to be more resistant to cleavage than 2-trifluoromethylisopropyl alcohol. For example, reaction between phosphorus pentachloride and the refluxing tertiary fluoro alcohols I, II, or V was very slow, and at the beginning we suspected that no reaction was occurring. However, small amounts of hydrogen chloride were observed after 10 min of refluxing of the higher boiling I with phosphorus pentachloride. More time was required for II and V. Refluxing, when continued for 5 days, resulted in direct conversion of I to 2,2-di(chlorodifluoromethyl)ethylene (VIII) in 75% yield. Unlike Swarts,[6] we obtained no identifiable quantities of high-boiling products, nor was any phosphorus trichloride observed. Several potential monomers were prepared in this fashion (*cf.* Table II). If the carbon $\alpha$ to the carbinol group contained hydrogen, no chloride substitution product was isolated. For example, treatment of the fluorinated tertiary alcohol III with phosphorus pentachloride yielded the fluorinated butene XI. A nuclear magnetic resonance (nmr) investigation revealed that XI was an approximately equal mixture of *cis* and *trans* isomers. This was found by comparing the heights of methyl and

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(2) E. E. Gilbert and co-workers, *J. Org. Chem.*, **30**, 998, 1001, 1003 (1965).
(3) I. L. Knunyants, Tsin-Yun Chen, and N. P. Gambaryan, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **5**, 112 (1960) (translated by Associated Technical Services, Inc., East Orange, N. J.); *Chem. Abstr.*, 20,872 (1960).
(4) I. L. Knunyants, N. P. Gambaryan, Ch'en Ch'ing-yun, and E. M. Rokhlin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **4**, 684 (1962).
(5) A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954).
(6) F. Swarts, *Bull. Chim. Belgrade*, **36**, 191 (1927).

## TABLE I

### PRODUCTS OF GRIGNARD REACTIONS WITH FLUORINATED KETONES

| Compound | No. | Formula | Bp, °C | $n^{25}D$ | Yield, % |
|---|---|---|---|---|---|
| 1,3-Dichloro-1,1,3,3-tetrafluoro-2-methyl-2-propanol | I | $C_4H_4F_4Cl_2O$ | 116.5–118 | 1.3821 | 75 |
| 1-Chloro-1,1,3,3,3-pentafluoro-2-methyl-2-propanol | II | $C_4H_4F_5ClO$ | 88.5 | 1.3405 | 55 |
| 1-Chloro-1,1,3,3,3-pentafluoro-2-ethyl-2-propanol | III | $C_5H_6F_5ClO$ | 107 | 1.3551 | 38 |
| 1-Chlorodifluoromethyl-1-trifluoromethyl-3-buten-1-ol | IV | $C_6H_6F_5ClO$ | 124–124.5 | 1.3700 | 35.6 |
| Hexafluoro-2-methyl-2-propanol | V | $C_4H_4F_6O$ | 60.5 | 1.2951[a] (extrpd) | 64 |
| 1-Chloro-1,1,3,3,3-pentafluoro-2-phenyl-2-propanol | VI | $C_9H_6F_5ClO$ | 186 | 1.4428 | 77 |
| 1-Chloro-1,1,3,3,3-pentafluoro-2-perfluorophenyl-2-propanol | VII | $C_9HF_{10}ClO$ | 187.5 | 1.4052 | 73 |

[a] Lit. $n^{20}D$ 1.3030: I. L. Knunyants, Tsin-Yun Chen, and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 686 (1960); *Chem. Abstr.*, 22,485 (1960).

## TABLE II

### REACTION PRODUCTS OF FLUORINATED TERTIARY ALCOHOLS WITH PHOSPHORUS PENTACHLORIDE[a]

| Compound | No. | Formula | Bp, °C | $n^{25}D$ | Yield, % |
|---|---|---|---|---|---|
| 2,2-Di(chlorodifluoromethyl)ethylene | VIII | $C_4H_2F_4Cl_2$ | 78.5–79 | 1.3613 | 71 |
| 3-Chloro-3,3-difluoro-2-trifluoromethylpropene | IX | $C_4H_2F_5Cl$ | 46[b] | 1.3132 | 59 |
| 1,1-Di(trifluoromethyl)ethylene | X | $C_4H_2F_6$ | 14.0–14.5[c] | ... | >69[d] |
| 1-Chloro-1,1-difluoro-2-trifluoromethylbutene-2 | XI | $C_5H_4F_5Cl$ | 84–85 | 1.3436 | 75 |
| 1,2-Dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane | XII | $C_9H_5F_5Cl_2$ | 186.0 | 1.4511 | 70 |
| 1,2-Dichloro-1,1,3,3,3-pentafluoro-2-(m-chlorophenyl)propane | XIII | $C_9H_4F_5Cl_3$ | 36 (0.1 mm) | 1.4707 | 45 |
| 1,2-Dichloro-1,1,3,3,3-pentafluoro-2-perfluorophenylpropane | XIV | $C_9F_{10}Cl_2$ | 188.5 | 1.4157 | 68 |
| Perfluoro-α-methylstyrene | XV | $C_9F_{10}$ | 126 | 1.3750 | 89 |
| α-Trifluoromethyl-β,β-difluorostyrene | XVI | $C_9H_5F_5$ | 128–128.5 | 1.4203 | 65 |

[a] Products XV and XVI were formed by dehalogenation of XIV and XII, respectively. However, XV was also formed in low yield when XII was formed from VII *via* phosphorus pentachloride. [b] Lit.[1] bp 52–55°. [c] Lit.[1] bp 11–13°. [d] Loss from apparatus leak.

trifluoromethyl nmr signals of the two isomers. Signal widths of the two isomers were identical.

In an attempt to prepare butadiene derivatives, an allyl Grignard was treated with chloropentafluoroacetone. The alcohol IV on treatment with phosphorus pentachloride furnished a dense liquid, bp 88° (14 mm). The infrared spectrum indicated hydroxyl function but no unsaturation. Elemental analysis conformed to 1-chlorodifluoro-2-trifluoromethyl-4,5-dichloropentanol-2. However, nmr and vapor phase chromatography (vpc) indicated two compounds, possibly stereoisomers, present in a ratio of approximately 3 to 1.

If no hydrogen is available on the α carbon, the phosphorus pentachloride reaction takes the more usual route of direct chlorination of the hydroxyl group, unless the reaction temperature is too high. For example, treatment of the alcohol VI resulting from the reaction of phenyl Grignard with chloropentafluoroacetone with phosphorus pentachloride resulted in carbon–oxygen cleavage and the desired chloro derivative, which was stable. When this same reaction was carried out at higher temperatures by removal of phosphorus oxychloride as it formed, m-chloro substitution of the benzene ring occurred to give the 2-chloro-2-chlorophenylfluoropropane (XIII). Dehalogenation occurred smoothly with zinc in glacial acetic acid resulting in a high yield of α-trifluoromethyl-β,β-difluorostyrene (XVI). Compound XVI has also been formed *via* a novel reaction by Burton and Herkes.[7]

Unexpectedly, perfluoro-α-methylstyrene (XV) in low yield resulted from treatment of the alcohol VII with phosphorus pentachloride along with a 68% yield of the expected chloro derivative XIV. Dehalogena-

(7) D. Burton and F. Herkes, *Tetrahedron Letters*, **No. 23**, 1883 (1965).

tion of XIV with zinc in glacial acetic acid occurred smoothly furnishing XV in 89% yield.

### Experimental Section[8]

**Preparation of 1,3-Dichloro-1,1,3,3-tetrafluoro-2-methyl-2-propanol (I).**—To a suspension of 60.8 g (2.5 g-atoms) of dry magnesium turnings in 550 ml of dry ether at 0–5° was added, in a nitrogen atmosphere with stirring, 238 g (2.5 moles) of gaseous methyl bromide over a period of 2.5 hr. The resulting Grignard solution was added dropwise with stirring to 435.5 g (2.28 moles) of 1,3-dichlorotetrafluoroacetone in 750 ml of dry ether at 0–5° over a period of 2.5 hr. The mixture was warmed to 20°. After 30 min, the mixture was cooled to 0–5° and hydrolyzed with 25% sulfuric acid. Water was added to dissolve the precipitate. The ether layer was washed with several portions of water, 2% sodium hydroxide, and water until neutral. The washings were neutralized, saturated with sodium chloride, and extracted with ether. The combined ether extracts were thoroughly dried, and distillation yielded 369.3 g (75%) of the alcohol: bp 116.5–118.5; infrared bands at 3500–3700 (OH), 1230–1060 (CF), and 3000–2950 cm$^{-1}$ (CH).

*Anal.* Calcd for I ($C_4H_4Cl_2F_4O$): C, 22.37; H, 1.88; Cl, 33.00; F, 35.37. Found: C, 22.57; H, 2.00; Cl, 33.05; F, 35.50.

**1-Chloro-1,1,3,3,3-pentafluoro-2-phenyl-2-propanol (VI)** was prepared in a similar manner. The yield was 77%.

*Anal.* Calcd for VI ($C_9H_6ClF_5O$): C, 41.48; H, 2.32; Cl, 13.61; F, 36.45. Found: C, 41.72; H, 2.31; Cl, 13.61; F, 36.19.

**1-Chloro-1,1,3,3,3-pentafluoro-2-methyl-2-propanol (II).**—When II was prepared in the same manner as I, an ether azeotrope resulted. The azeotrope was resolved by destruction of the ether in 20% oleum. The desired product was obtained by vacuum distillation in 65% yield. Preparation of II in dry n-butyl ether resulted in a yield of 55%: bp 88.5°; infrared bands at 3580 (OH), 1250–1160 (CF), and 3000 (CH) cm$^{-1}$.

*Anal.* Calcd for II ($C_4H_4F_5ClO$): C, 24.20; H, 2.03; Cl, 17.86; F, 47.85. Found: C, 24.40; H, 2.19; Cl, 18.04; F, 47.51.

(8) Chloro and fluoro analogs with preparations similar to those compounds listed are cited immediately after each respective preparation.

**1-Chloro-1,1,3,3,3-pentafluoro-2-ethyl-2-propanol (III)** and **hexafluoro-2-methyl-2-propanol (V)** were prepared in a similar manner, using 20% oleum to resolve the azeotropes formed in both cases. Yields were 38 and 64%, respectively.

*Anal.* Calcd for III ($C_5H_6F_5ClO$): C, 28.25; H, 2.84; Cl, 16.68; F, 44.69. Found: C, 27.96; H, 2.55; Cl, 16.64; F, 44.50.

*Anal.* Calcd for V ($C_4H_4F_6O$): C, 26.38; H, 2.21; F, 62.61. Found: C, 26.27; H, 2.36; F, 62.57.

**1,3-Dichloro-1,1,3,3-tetrafluoro-*t*-butyl Acetate.**—A solution of 150 g (0.70 mole) of the tertiary fluoro alcohol I and 82.3 g (1.05 moles) of acetyl chloride was refluxed for 45 hr during which time the pot temperature rose from 65 to 105°. After thorough washing, neutralizing with 3% NaOH, and drying, distillation yielded 160 g (89.5%) of the acetate: bp 148–149°, infrared bands at 1250–1160 (CF) and 1800–1750 (C=O) cm$^{-1}$.

*Anal.* Calcd for $C_6H_6Cl_2F_4O_2$: C, 28.03; H, 2.35; Cl, 27.61; F, 29.59. Found: C, 28.07; H, 2.28; Cl, 27.27; F, 29.80.

**Tosylate of 1-Chloro-1,1,3,3,3-pentafluoro-*t*-butyl Alcohol.**—To a concentrated solution of 5.4 g (0.1 mole) of sodium methoxide in dry methanol at 23° was added, all at once, 19.8% (0.1 mole) of the tertiary fluoro alcohol II. After all volatiles had been removed by rotary evaporation, the salt was dissolved in 100 ml of dry tetrahydrofuran. To the tetrahydrofuran solution at 23° was added, all at once, a solution of 17.1 g (0.09 mole) of toluenesulfonyl chloride in 50 ml of dry tetrahydrofuran. After 24 hr, the reaction solution was separated from the precipitated salt, dried over anhydrous magnesium sulfate, and then distilled to yield 26.4 g of tosylate (85%): bp 81–82° (0.5 mm), $n^{25}$D 1.4610.

*Anal.* Calcd for $C_{11}H_{10}ClF_5O_3S$: C, 37.45; H, 2.85; Cl, 10.05; F, 26.93. Found: C, 37.61; H, 3.01; Cl, 10.11; F, 26.70.

**1-Chloro-1,1,3,3,3-pentafluoro-2-perfluorophenyl-2-propanol (VII).**—To a suspension of 36 g (1.5 g-atoms) of dry magnesium turnings in 1500 ml of dry ether at 0–10° was added, in a nitrogen atmosphere with stirring, 370.5 g (1.5 moles) of freshly distilled (78° at 98 mm) pentafluorobromobenzene over a period of 22 hr. Stirring was continued at 23° for 19 hr. The black Grignard solution was cooled to 0–10° and 15% excess of monochloropentafluoroacetone was added over a 12-hr period. There was very little precipitation. After stirring at room temperature for 16 hr, the solution was hydrolyzed with 25% sulfuric acid, washed, dried and distilled. Compound VII (383 g, 73% yield), bp 187.5°, was obtained: infrared bands at 3060 (OH) and 1250–1100 (CF) cm$^{-1}$.

*Anal.* Calcd for VII ($C_9HClF_{10}O$): Cl, 10.11; F, 54.19. Found: Cl, 10.17; F, 54.36.

**1-Chlorodifluoromethyl-1-trifluoromethyl-3-buten-1-ol (IV).**—To a suspension of 36.3 g (1.5 g-atoms) of dry magnesium turnings in 125 ml of dry ether at 5° was added, in a nitrogen atmosphere with stirring, a solution of 122.2 g (1.0 mole) of allyl bromide in 135 ml of dry ether over a period of 90 min. The resulting solution was separated from 14.8 g (0.61 mole) of unreacted magnesium, and treated at 0° in a nitrogen atmosphere with gaseous monochloropentafluoroacetone at a rate of approximately 1 mole/hr for 1 hr. A flow meter measured delivery of the fluoro ketone. The product was worked up in the usual manner. Distillation yielded 39.7 g of the ether azeotrope, bp 102–103°, followed by 71.1 g (35.6% based on Mg consumed) of the desired alcohol: bp 124–124.5°; infrared bands at 3750 (OH), 3100–3000 ($H_2C$=), 1250–1160 (CF), and 1630 (C=C) cm$^{-1}$.

*Anal.* Calcd for IV ($C_6H_6ClF_5O$): C, 32.09; H, 2.69; Cl, 15.79; F, 42.30. Found: C, 32.18; H, 2.78; Cl, 15.87; F, 42.05.

**2,2-Di(chlorodifluoromethyl)ethylene (VIII).**—A mixture of 318.5 g (1.48 moles) of the tertiary fluoro alcohol I and 323.9 g (1.55 moles) of phosphorus pentachloride was refluxed in a round-bottom flask over a period of 5 days. The reflux condenser exit led to a Dry Ice trap. During reflux, the temperature fell from 110 to 102°. The reaction products were distilled from phosphorus oxychloride, combined with material in the trap, and hydrolyzed with cracked ice. The organic layer was separated and thoroughly washed with water, 2% sodium hydroxide, and water until neutral. The washings were neutralized, saturated with sodium chloride, and extracted with ether. The combined organic layers were dried over anhydrous magnesium sulfate and distilled, yielding 42.6 g of I and 180.9 g of VIII: bp 78–79° (71% based on I consumed); infrared bands at 1640 ($H_2C$=C), 3150–3000 ($CH_2$=), and 1200–1060 (CF)

cm$^{-1}$. An acetone solution of VIII rapidly decolorized 2% aqueous permanganate.

*Anal.* Calcd for VIII ($C_4H_2Cl_2F_4$): C, 24.40; H, 1.02; Cl, 36.04; F, 38.60. Found: C, 24.33; H, 1.13; Cl, 35.86; F, 38.47.

**3-Chloro-3,3-difluoro-2-trifluoromethylpropene (IX)** and **1-chloro-1,1-difluoro-2-trifluoromethylbutene-2 (XI)** were prepared similarly. Yields were 59 and 75%, respectively.

*Anal.* Calcd for IX ($C_4H_2ClF_5$): C, 26.61; H, 1.12; Cl, 19.64; F, 52.63. Found: C, 26.76; H, 1.28; Cl, 19.51; F, 52.52.

*Anal.* Calcd for XI ($C_5H_4ClF_5$): C, 30.87; H, 2.07; Cl, 18.23; F, 48.83. Found: C, 31.00; H, 2.22; Cl, 18.04; F, 49.08.

**1,1-Di(trifluoromethyl)ethylene (X).**—Compound X was prepared in a manner similar to VIII, except that its low boiling point required the use of Dry Ice traps to trap out the product as it formed. A scrubbing train (water) was used to remove HCl and other impurities from the low-boiling olefin, which was then passed through a desiccant to remove water and stored in a stainless steel flask. A 69% yield of olefin was obtained: bp 14.0–14.5°; infrared bands at 3000–3120 ($H_2C$=), 1670 ($H_2C$=C), and 1250–1100 (CF) cm$^{-1}$. Its structure was confirmed by nmr: proton spectra at 60 Mcps—single peak at 376 cps with tetramethylsilane as internal reference; fluorine spectra at 56.4 Mcps—peak at 3760 cps with fluorotrichloromethane as internal reference.

**1,2-Dichloro-1,1,3,3,3-pentafluoro-2-phenylpropane (XII).**—A mixture of 104.2 g (0.4 mole) of the tertiary fluoro alcohol VI and 91.6 g (0.44 mole) of phosphorus pentachloride was refluxed for 5 days. The temperature fell from 157 to 135°. The reaction mixture was distilled to remove excess PCl$_5$ and the distillate was hydrolyzed over cracked ice. After washing and drying, the organic layer on distillation yielded 78.1 g of a mixture containing 90% XII and 10% of unreacted VI (vpc). The yield of XII was 70%: bp 186.0°; infrared bands at 2000–1600 (phenyl), 1500 (phenyl), and 1200–1060 (CF) cm$^{-1}$. The mixture was found to be suitable for preparation of the styrene derivative (XVI).

*Anal.* Calcd for XII ($C_9H_5Cl_2F_5$): C, 38.73; H, 1.81; Cl, 25.41; F, 34.04. Found: C, 38.75; H, 1.78; Cl, 25.63; F, 33.92.

**1,2-Dichloro-1,1,3,3,3-pentafluoro-2-perfluorophenylpropane (XIV)** was prepared similarly. The yield was 68%. Perfluoro-α-methylstyrene (XV) was derived from this compound.

**1,2-Dichloro-1,1,3,3,3-pentafluoro-2-(*m*-chlorophenyl)propane-(XIII).**—The reaction conditions for the preparation of XII were altered by removing phosphorus oxychloride as it formed. A mixture containing approximately 55% XII and 45% XIII (*meta* substitution by nmr) resulted.

*Anal.* Calcd for XIII ($C_9H_4Cl_3F_5$): C, 34.47; H, 1.28; Cl, 33.94; F, 30.30. Found: C, 34.54; H, 1.26; Cl, 33.93; F, 30.61.

**Perfluoro-α-methylstyrene (XV).**—A mixture of 76.6 g (0.22 mole) of the tertiary fluoro alcohol VII and 48 g (0.23 mole) of phosphorus pentachloride was heated for 30 hr in a round-bottom flask on an oil bath set at 125°. The condenser exit led to a funnel dipping about 0.25 in. into a sodium hydroxide solution (0.44 mole of NaOH). Ninety per cent of the required quantity of hydrogen chloride was trapped during 24 hr. After distillation, water washing, neutralizing, and drying, fractionation furnished 6.6 g (11%) of XV, bp 127°, and 50.1 g (68%) of XIV, bp 188.5°. Treatment of XIV with zinc and glacial acetic acid in the usual fashion furnished XV in 89% yield. Identification was made by nmr and elemental analysis. The infrared spectrum showed a band at 1750 ($F_2C$=C) cm$^{-1}$.

*Anal.* Calcd for XV ($C_9F_{10}$): C, 36.26; F, 63.74. Found: C, 35.61; F, 63.89.

**α-Trifluoromethyl-β,β-difluorostyrene (XVI).**—To a stirred mixture of 9.81 g (0.135 g-atom) of 90% zinc dust in 50 ml of glacial acetic acid was slowly (exothermic) added 27.9 g (0.1 mole) of the fluorinated tertiary chloride XII (90% XII, 10% VI). After refluxing with stirring for 22 hr, the mixture was cooled and filtered. The filtrate was washed with water, 5% sodium carbonate, and water. The neutralized washings were saturated with sodium chloride and extracted with ether. The combined organic liquids which were thoroughly dried and distilled furnished 12.16 g of product (65% yield, based on XII

consumed): bp 128–128.5°; $n^{25}$D 1.4203 (vpc bp 125.5°); infrared bands at 1750 ($F_2C=C$), 3100, 200–1600, 1500, 1450 (phenyl), and 1270–1100 (CF) cm$^{-1}$.

*Anal.* Calcd for $C_9H_5F_5$: C, 51.93; H, 2.42; F, 45.64. Found: C, 51.58; H, 2.40; F, 45.22.

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# Friedel–Crafts Reactions of Amino Tertiary Alcohols[1a]

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ω-Arylalkylamines are prepared in generally good yield by the Friedel–Crafts reactions of amino tertiary alcohols with *o*-xylene, naphthalene, veratrole, thiophene, and benzo[*b*]thiophene. In every case one isomer predominates to the extent of 95% or greater. Dimethylamino-2-methyl-2-propanol gives Friedel–Crafts products as well with toluene, 1- and 2-chloronaphthalene, and 1,5- and 2,3-dimethylnaphthalene, but not with veratrole, thiophene, or benzothiophene.

The Friedel–Crafts reactions of amino tertiary alcohols provide a satisfactory and fairly general method for preparing ω-arylalkylamines. The aluminum chloride promoted condensation of various amino *t*-butyl alcohols (1,2-amino alcohols) with benzene was first reported by Suter and Ruddy in 1943;[2] we have found that 1,3-, 1,4-, and 1,5-amino tertiary alcohols as well can, under rather specific conditions, be induced to condense with a variety of aromatic compounds in generally excellent yield.

The amino alcohols used have all been described previously: dimethylamino-2-methyl-2-propanol (1),[3] 4-dimethylamino-2-methyl-2-butanol (2),[3] 4-amino-2-methyl-2-pentanol (3),[4] 5-dimethylamino-2-methyl-2-pentanol (4),[3] 6-dimethylamino-2-methyl-2-hexanol (5),[3] and 6-amino-2-methyl-2-heptanol (6). Aromatic substrates were *o*-xylene, naphthalene, veratrole, thiophene, and benzo[*b*]thiophene, and in each product one isomer predominated to the extent of 95% or greater. The 1,2-amino alcohol 1 gave Friedel–Crafts products as well with toluene, 1- and 2-chloronaphthalene, and 1,5- and 2,3-dimethylnaphthalene, but not with veratrole, thiophene, or benzothiophene.
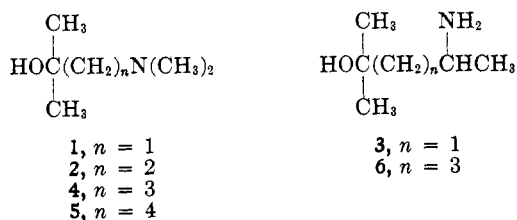


Reactions with *o*-xylene were carried out in nitrobenzene using a 2.5:1 mole ratio of aluminum chloride to amino alcohol. The product was in each instance almost exclusively the 4 isomer 8–10. Structures were established by means of the strong, low-frequency infrared bands (725, 820, and 880 cm$^{-1}$) characteristic of 1,2,4 substitution and present in the spectrum of 3,4-

dimethyl-*t*-butylbenzene.[5] With *o*-xylene as solvent the 1,2-amino alcohol 1 also gave the 4 isomer 7, and with toluene the product was the *para* isomer 11 ($\nu_{max}$ 810 cm$^{-1}$).
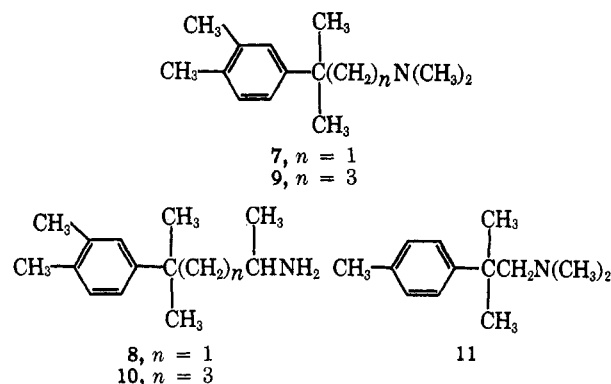


The reaction with naphthalene also utilized aluminum chloride in nitrobenzene (cyclohexane for the 1,2-amino alcohol), yielding in each case the β isomer 12–15. The low-frequency infrared pattern for each (750, 820, 855, and 890 cm$^{-1}$) was nearly identical with that of β-*t*-butylnaphthalene.[6]
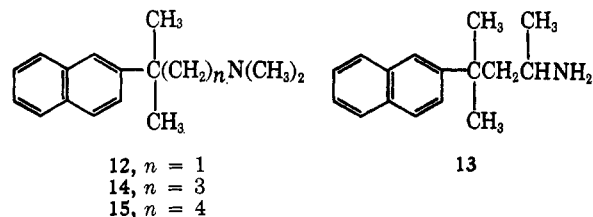


For veratrole, anhydrous hydrogen fluoride was the only satisfactory condensation medium found. Again, the 4 isomer was the exclusive product (16–18), identified by the characteristic low-frequency infrared spectrum (770, 810, and 855 cm$^{-1}$), similar to that of 3-hydroxy-4-methoxy- and 4-hydroxy-3-methoxy-*t*-butylbenzene.[7]

(1) (a) Supported by Merck Sharp and Dohme Research Laboratories. (b) Inquiries may be addressed to W. D. B.: U. S. Army Natick Laboratories, Natick, Mass.

(2) C. M. Suter and A. W. Ruddy, *J. Am. Chem. Soc.*, **65**, 762 (1943).

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(4) J. English, Jr., and K. D. Bliss, *ibid.*, **78**, 4057 (1956).

(5) "The Sadtler Standard Spectra," Midget ed, Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 5335.

(6) Reference 5, Spectrum No. 8153.

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