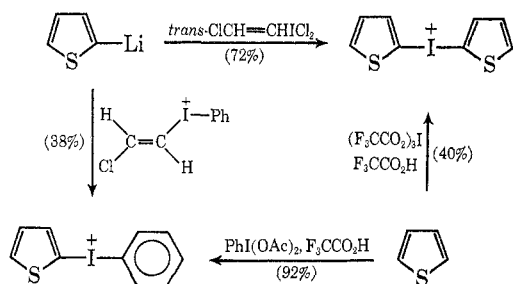
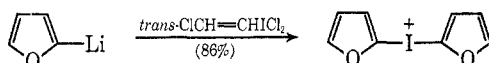


yields, respectively, by the reaction of 2-thienyllithium with *trans*-chlorovinylidioso dichloride and phenyl(*trans*-chlorovinyl)iodonium chloride.



By this method it has been possible to prepare for the first time an iodonium salt from furan. The mixed



iodonium chloride-bromide, isolated as soon as the reaction mixture warmed to room temperature, could not be successfully recrystallized, but metathesis to the iodide gave a pure salt. Attempts to prepare phenyl(2-furanyl)iodonium salts from phenyl(2-chlorovinyl)iodonium chloride with 2-furanyllithium were unsuccessful.

Pyridyliodonium salts could not be prepared by the use of 2-pyridyllithium with the iodoso and iodonium reagents. It is not known whether the difficulty lay in an inherent shortcoming of the synthesis or in the instability of 2-pyridyliodonium salts.

In attempts to form iodonium salts with one or two bonds to sp^3 carbon, the same iodoso and iodonium reagents containing the *trans*-chlorovinyl masking group were treated with neopentyllithium and with 1-bicyclo[2.2.1]heptyllithium but gave no iodonium salt. Also, unsuccessful were reactions using vinylolithium, 1-cyclohexenyllithium, 1-perfluoroheptyllithium, and 3,3,3-trifluoropropynyllithium; the causes of these failures are not known.

Experimental Section

Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Gas chromatography was done on 6-ft columns, packed with 20% SE-30 on Chromosorb W (DMCS-treated), with an Aerograph 1520-A gas chromatograph. Melting points⁵ were taken in capillary tubes on a Thomas-Hoover apparatus and corrected.

Neopentyllithium.—Since the low-temperature (10°) synthesis of neopentyllithium^{6,7} could not be repeated, a new procedure at higher temperature⁸ was developed. A 250-ml round-bottom three-necked flask equipped with a septum cap, reflux condenser, and pressure-equalizing addition funnel was flushed well with argon, flamed, charged with 8.0 g of lithium dispersion⁹ and 80 ml of benzene, and kept under a positive pressure of argon. Neopentyl chloride (21.32 g, 200 mmol) in 40 ml of benzene was placed in the addition funnel. After approximately 20% of the alkyl chloride solution had been added, the temperature was raised slowly to the point of exotherm (usually between 75 and

80°), at which time the heat was removed, and gentle reflux was maintained (about 82°) by regulating the rate of addition of the alkyl halide. After this addition, the mixture was heated overnight under reflux. The cooled reaction mixture was filtered through sintered glass under argon. Titration of aliquots from different runs showed a variation from 60 to 90% in the yield of neopentyllithium. Neopentyl bromide gave much lower yields, about 10%.

Di-2-thienyliodonium Iodide and Di-2-furanyliodonium Iodide.—These reactions were carried out at Dry Ice-acetone temperatures as described³ for diphenyliodonium iodide, except that they were terminated immediately upon warming to room temperature. Work-up was rapid, and all salts were stored below 0° . Di-2-thienyliodonium iodide was obtained in 72% yield, mp 131 – 136° dec, lit.⁴ 135 – 136° .

Di-2-furanyliodonium iodide was similarly obtained in 86% yield, mp 114 – 116° dec.¹⁰

Anal. Calcd for $C_8H_6O_2I_2$: C, 24.77; H, 1.56; I, 65.43. Found: C, 24.92; H, 1.45; I, 65.36.

Phenyl(2-thienyl)iodonium chloride was prepared as described previously for phenyl-1-naphthylidoniochloride **3**, except that it was worked up immediately upon reaching room temperature, giving 1.6 g (38%), mp 149 – 150.5° dec, lit.⁴ 140 – 141° .

Attempts to Prepare Alkylidoniochloride Salts.—The unsuccessful reactions of various alkyl- and perfluoroalkyllithium reagents with *trans*-chlorovinylidioso dichloride and phenyl(*trans*-chlorovinyl)iodonium chloride were run like the successful preparations of diaryliodonium salts.³ With these salts neopentyllithium gave no iodonium salt and no neopentyl halides. However, with phenyliodoso dichloride,¹¹ neopentyllithium gave neopentyl chloride and iodide (trace) along with iodobenzene.

When 1-bicyclo[2.2.1]heptyllithium was allowed to react with *trans*-chlorovinylidioso dichloride, while no solid was formed, vpc confirmed the presence of both bridgehead iodide and chloride (ratio of *ca.* 5:1). Presumably, the bridgehead iodide results from nucleophilic addition of the bicycloheptyl group to iodine in the iodoso or iodonium reagent.

Reactions of phenyliodoso dichloride and of phenyl(*trans*-chlorovinyl)iodonium chloride with 1-cyclohexenyllithium were equally unsuccessful. In the latter reaction quenching at low temperature with magnesium bromide etherate, with triphenylboron, and with methanol, in an attempt to help break the chlorovinylidioso bond, was also unsuccessful. In all three cases phenyl(*trans*-chlorovinyl)iodonium chloride was recovered.

Registry No.—*trans*-Chlorovinylidioso dichloride, 24472-17-1; di-2-furanyliodonium iodide, 24472-18-2.

(10) Previously unknown compound.

(11) J. Dehn, Jr., Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1964.

Reactions of 1,1-Bis(trifluoromethyl)alkenols in Sulfuric Acid

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We have recently had an interest in the preparation of fluorinated monomers, including 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene. At least two attempts to prepare this or similar compounds have appeared in the literature.^{1,2} Plakhova and Gambaryan² reported the preparation of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene by the phosphorus pentoxide or sulfuric acid dehydration of 1,1-bis(trifluoromethyl)-1-buten-3-ol, but this work may be in doubt (*vide infra*).

(1) M. H. Kaufman and J. D. Brown, *J. Org. Chem.*, **31**, 3090 (1966).

(2) V. F. Plakhova and N. P. Gambaryan, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **4**, 681 (1962).

(5) The technique involved in taking melting points of iodonium salts has been discussed previously: F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *J. Amer. Chem. Soc.*, **81**, 342 (1959).

(6) D. E. Applequist and D. F. O'Brien, *ibid.*, **85**, 743 (1963).

(7) H. Gilman, H. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *ibid.*, **71**, 1499 (1949).

(8) H. Gilman, F. W. Moore, and O. Baine, *ibid.*, **68**, 2479 (1941).

(9) A dispersion of lithium containing 0.5% sodium in mineral oil. Due to the nonhomogeneity of the dispersion the exact amount of metal in the reaction mixture was unknown. The amount used, however, was in excess of stoichiometry.

These data suggest that reduction of 4 to 5 is competitive with reduction of 3 to 4. It is difficult to rationalize the reported yields of 4 using 0.5 mol of lithium aluminum hydride.

Dehydration of the ether azeotrope from reduction of 3 is the reported final step in the preparation of 1. We have attempted the sulfuric acid dehydration of 5, which we obtained under the reported reduction conditions, to determine if a product corresponding to the reported 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene would obtain. There was only extensive degradation. In our hands the reaction sequence does not lead to the reported compounds, and we can neither confirm the work nor suggest alternative products.

Experimental Section⁵

I. Preparation of 1,1-Bis(trihalomethyl)alken-1-ols. $AlCl_3$ -Catalyzed Reaction of 1-Alkenes and Hexahaloacetone.—The procedure for the preparation of the alkene-hexahaloacetone adducts is already described for the reaction between hexafluoroacetone and propylene⁶ and consists of allowing a cold (-30°) mixture of 2 mol of propylene, 1 mol of hexafluoroacetone, and a catalytic amount of $AlCl_3$ in 1 l. of pentane to warm slowly to 0° and then stirring for 2 hr.

The reagents used are given as follows in the order yield, boiling point, and product composition.

Propylene and hexafluoroacetone: 72%; 97–100°; 60% 1,1-bis(trifluoromethyl)-2-buten-1-ol, 3% *cis*-1,1-bis(trifluoromethyl)-3-buten-1-ol, and 37% *trans*-1,1-bis(trifluoromethyl)-3-buten-1-ol.^{5a}

1-Butene and hexafluoroacetone: 79%; 114–117°; 59% *trans*-1,1-bis(trifluoromethyl)-2-penten-1-ol, 8% *cis*-1,1-bis(trifluoromethyl)-3-penten-1-ol, and 33% *trans*-1,1-bis(trifluoromethyl)-3-penten-1-ol.^{5a}

Propylene and chloropentafluoroacetone: 82%; 127–130°; 50% 1-trifluoromethyl-1-chlorodifluoromethyl-2-buten-1-ol, 40% *trans*-1-trifluoromethyl-1-chlorodifluoromethyl-3-buten-1-ol, and 10% *cis*-1-trifluoromethyl-1-chlorodifluoromethyl-3-buten-1-ol.⁷ *Anal.* (for mixture). Calcd for $C_6H_8ClF_5O$: C, 32.53; H, 2.69. Found: C, 32.08; H, 2.73.

1-Hexene and hexafluoroacetone: 79%; 150–153°; 50% *trans*-1,2-bis(trifluoromethyl)-2-hepten-1-ol, 10% *cis*-1,1-bis(trifluoromethyl)-3-hepten-1-ol, and 40% *trans*-1,1-bis(trifluoromethyl)-3-hepten-1-ol.⁷ *Anal.* (for mixture). Calcd for $C_9H_{12}F_6O$: C, 43.24; H, 4.72. Found: C, 43.24; H, 4.91.

1-Octene and hexafluoroacetone: 64%; 119–124° (70 mm); 60% *trans*-1,1-bis(trifluoromethyl)-2-nonen-1-ol, 10% *cis*-1,1-bis(trifluoromethyl)-3-nonen-1-ol, and 30% *trans*-1,1-bis(trifluoromethyl)-3-nonen-1-ol.⁸ *Anal.* (for mixture). Calcd for $C_{11}H_{16}F_6O$ (mixture): C, 47.49; H, 5.78. Found: C, 47.60; H, 5.68.

(5) All boiling and melting points are uncorrected. Infrared spectra were obtained as films or Nujol smears using a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were obtained using a Varian Associates Model HA-100 spectrometer using chloroform as solvent and TMS as internal standard. For fluorine spectra trifluoroacetic acid was used as an external standard. Spectra were run using field frequency lock at 94.1 MHz using a modification described by Douglas.⁹ Spectra at both frequencies are accurate to ± 0.02 ppm. Glpc work was done on an F & M Model 720 gas chromatograph using a 9-ft column filled with a 20% Carbowax 20M on Chromosorb P packing. Molecular weights were determined by one of two methods depending on the magnitude of the value. For polymer in the range of 5000 (M_n) the Mechrolab membrane osmometer, Model 501, was employed. Values greater than 50,000 were determined with a Mechrolab vapor pressure osmometer. Elemental analyses were performed by Huffman Laboratories Inc., Wheatridge, Col.

(6) A. W. Douglas, Abstracts of papers presented at the 7th Experimental Nmr Conference, Pittsburgh, Pa., Feb 1966.

(7) The product composition is based on the glpc scan which shows three peaks in the ratios shown and by analogy with the product mixture from propylene and hexafluoroacetone or 1-butene and hexafluoroacetone for which the exact compositions have been determined.^{5a}

(8) The product composition is based on the ^{19}F nmr scan which shows three peaks in the ratio shown at -1.8 , -1.6 , and -0.8 ppm. Assignments are based on the analogy to the products from the reaction of 1-butene and hexafluoroacetone for which the exact composition has been determined.^{5a}

II. The Thermal Reaction.—The reaction was carried out as shown in the literature³ by heating equimolar amounts of olefin and hexafluoroacetone in a sealed tube at 150° for 16 hr.

Reagents used are given as follows in the order, yield, boiling point, and product composition.

Propylene and hexafluoroacetone: 82%; 94–95°; 100% 1,1-bis(trifluoromethyl)-3-buten-1-ol (lit.^{3a} 97–98°).

1-Butene and hexafluoroacetone: 74%; 117–119°; 20% *cis*-1,1-bis(trifluoromethyl)-3-penten-1-ol and 80% *trans*-1,1-bis(trifluoromethyl)-3-penten-1-ol.^{3a}

III. Reactions of 1,1-Bis(trihalomethyl)alken-1-ols in Sulfuric Acid. 1,1-Bis(trihalomethyl)alken-1-ols from the $AlCl_3$ -Catalyzed Reaction of 1-Alkenes and Hexahaloacetone (~60% 2-Alken-1-ol and 40% 3-Alken-1-ol).—The procedure is, in general, similar to that with the 1,1-bis(trifluoromethyl)buten-1-ols below and consists of dissolving the alcohol in sulfuric acid and heating at *ca.* 100° while distilling product (under vacuum if needed).

1,1-Bis(trifluoromethyl)buten-1-ols.—The mixture of isomeric alcohols prepared (above) by the aluminum chloride catalyzed reaction of propylene and hexafluoroacetone (272 g, 1.3 mol) was dissolved in 400 ml of sulfuric acid and heated at 100 – 110° ; 150 g (59%) of essentially pure 1,1,1-trifluoro-1-trifluoromethyl-2,4-pentadiene was distilled (bp 70 – 72°). The infrared spectrum shows vinyl CH (3100), $C=CH_2$ (1630), and $C=C(CF_3)_2$ (1660 cm^{-1}), while aliphatic CH absorption is absent (2800–3000 cm^{-1}). The 1H nmr spectrum shows only vinyl protons as complex groups at 6.5–7.1 ppm (area = 2), 5.6 (1), and 5.9 (1). The ^{19}F spectrum shows a pair of quartets at -14.5 and -20.6 ppm ($J = 7$ Hz). *Anal.* Calcd for $C_6H_4F_6$: C, 38.34; H, 2.35; F, 60.12. Found: C, 38.11; H, 2.26; F, 59.97.

The pot temperature was then raised to 220° yielding a product which on redistillation afforded 15 g (5%) of 1,1-bis(trifluoromethyl)tetrahydrofuran (bp 106 – 107°). The infrared spectrum is consistent, showing no OH, vinyl CH, $C=C$ absorption. The 1H nmr spectrum shows two protons at 4.10 ppm (triplet, $J = 6$ Hz) and four protons as a complex multiplet at 2.0–2.5 ppm, while the ^{19}F spectrum shows a single peak at -0.2 ppm. *Anal.* Calcd for $C_6H_8F_6O$: C, 34.87; H, 3.03; F, 54.77. Found: C, 34.62; H, 2.91; F, 54.76.

1-Trifluoromethyl-1-chlorodifluoromethylbuten-1-ols.—A mixture of the isomeric alcohols prepared (above) by the aluminum chloride catalyzed reaction of propylene and chloropentafluoroacetone (22.4 g, 0.10 mol) was dissolved in 90 g of sulfuric acid and heated at 100° (50 mm) yielding a dark oil which on washing with water and redistilling afforded 1.2 g (6%) of 1-chloro-1,1-difluoro-2-trifluoromethyl-2,4-pentadiene (bp 101 – 102°). The infrared spectrum shows vinyl CH (3000–3100), $C=CH_2$ (1600), and $C=C(CF_3)(CF_2Cl)$ (1660 cm^{-1}). The proton nmr spectrum shows vinyl hydrogens as three complex groups at 6.9 ppm (area = 2), 5.8 (1), and 5.9 (1). The ^{19}F nmr spectrum shows that the product is an equimolar mixture of *cis* and *trans* isomers. The *trans*-1-chloro-1,1-difluoro-2-trifluoromethyl-2,4-pentadiene shows a trifluoromethyl group at -14.6 ppm as a pure triplet ($J = 7$ Hz) and a CF_2Cl - group at -37.7 ppm as a quartet ($J = 7$ Hz) split slightly (*ca.* 1 Hz by the *trans* vinyl proton⁹). The *cis* isomer shows the trifluoromethyl group at -20.7 ppm [triplet ($J = 7$ Hz) of doublets ($J = 1$ Hz)]. The CF_2Cl - appears as a pure quartet ($J = 7$ Hz) centered at -26.5 ppm. *Anal.* Calcd for $C_6H_4ClF_5O$: C, 35.00; H, 1.94. Found: C, 34.97; H, 2.10.

IV. 1,1-Bis(trifluoromethyl)penten-1-ols, -hepten-1-ols, and -nonen-1-ols.—The reactions of these materials were carried out in the same manner as with the buten-1-ols above. The starting material used are given as follows in the order product, yield, boiling point, and spectroscopic data.

1,1-Bis(trifluoromethyl)penten-1-ols: 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran, 68%, bp 115 – 117° , n_D^{20} 1.3340. The nmr and infrared spectra are identical with those of the previously authenticated material.^{5a}

1,1-Bis(trifluoromethyl)hepten-1-ols: 1,1-bis(trifluoromethyl)-4-propyltetrahydrofuran, 87%, bp 67% (30 mm). The infrared and nmr spectra are consistent with the latter described as follows: HCO, 4.2 (complex); $-(CH_2)_2-$ 1.2–2.5 (complex); CH_3- , 0.91 ppm (triplet, $J = 7$ Hz). *Anal.* Calcd for $C_9H_{12}F_6O$: C, 43.26; H, 4.81; F, 45.57. Found: C, 43.24; H, 4.83; F, 45.74.

(9) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Spectroscopy," Vol. II, Pergamon Press Inc., Elmsford, N. Y., 1966, p 913.

1,1-Bis(trifluoromethyl)nonen-1-ols: 1,1-bis(trifluoromethyl)-4-pentyltetrahydrofuran, 72%, bp, 184°. The infrared and nmr spectra are consistent with the latter described as follows: HCO, 4.2 (complex); $-(CH_2)_2-$, 1.2-2.4 (complex); CH_3- 0.89 ppm (triplet, $J = 7$ Hz). *Anal.* Calcd for $C_{11}H_{16}F_6O$: C, 47.48; H, 5.79. Found: C, 47.83; H, 5.56.

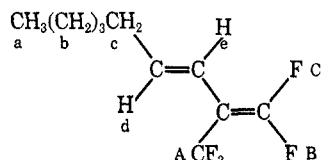
V. 1,1-Bis(trifluoromethyl)-3-alken-1-ols from the Thermal Reaction of 1-Alkenes and Hexafluoroacetone.—Reactions were carried out in a manner identical with those above. The 1,1-bis(trifluoromethyl)-3-buten-1-ols gave a 61% yield of 1,1,1-trifluoro-2-trifluoromethyl-2,4-pentadiene while the 1,1-bis(trifluoromethyl)-3-penten-1-ols yielded 71% 1,1-bis(trifluoromethyl)-4-methyltetrahydrofuran.

VI. Reactions of 1,1,1-Trifluoro-2-trifluoromethyl-2,4-pentadiene (1). Polymerization. In Bulk.—A mixture of 1.90 g (0.10 mol) of 1 and 0.010 g of benzoyl peroxide was placed in a vial, flushed with nitrogen, and heated at 60° for 66 hr. After distilling excess monomer *in vacuo* the residue (0.5 g, 25%) had a molecular weight of 4500. The infrared spectrum shows aliphatic CH (2800-3000), vinyl CH (3000-3100), and $C=C(CF_3)_2$ (1680 cm^{-1}). These characteristics and the absence of other $C=C$ absorption indicate that polymerization occurs to a large extent across the less substituted double bond by 1,2 addition.

In Emulsion.—A mixture of 11.8 g (0.06 mol) of 1, 34 ml of water, 0.060 g of potassium persulfate, and 0.36 g of Duponol (surfactant) was placed in a vial, flushed with nitrogen, and heated at 50-60° with vigorous stirring for 20 hr. Evaporation of the water yielded 7.9 g (67%) of a clear, tough polymer having a molecular weight of 83,000. The infrared spectrum is similar to that of the polymer from the bulk reaction.

VII. Hydrogenation.—Diene 1 (48 g), 50 ml of acetic acid, and 0.5 g of 5% Pd-C were placed in a Parr apparatus and hydrogenated at 50 psig. The theoretical amount of hydrogen was quickly absorbed. Filtration and distillation of the product solution yielded 37 g (77%) of 1,1-bis(trifluoromethyl)butane (bp 66-67°). The 1H nmr spectrum shows three complex envelopes at 0.7-1.4 ppm (area = 3), 1.4-2.2 (4), and 2.6-3.2 (1). The ^{19}F spectrum shows a doublet at -9.88 ppm ($J = 7$ Hz). *Anal.* Calcd for $C_6H_8F_6$: C, 37.12; H, 4.15. Found: C, 37.47; H, 3.90.

VIII. Reaction with *n*-Butyllithium.—A solution (1.6 M, 19 ml) of *n*-butyllithium in hexane (0.030 mol) was added slowly to a cold (0°) solution of 5.7 g (0.030 mol) of 1 in hexane. After stirring for 1 hr, the reaction was hydrolyzed with 5% hydrochloric acid, and after drying over sodium sulfate the organic layer was distilled (8-in. Vigreux) to yield 3.10 g (45%) of *trans*-1,1-difluoro-2-trifluoromethyl-1,3-nonadiene, bp 148-150°. The infrared spectrum is consistent, showing bands at 1630 ($-CH=CH-$) and 1710 cm^{-1} ($C=CF_2$). The nmr spectra are described below.

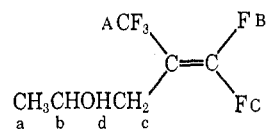


1H (δ , ppm): a, 0.90; b, 1.3 (complex); c, 2.0-2.3 (complex); d, 5.8-6.2 (complex); e, 5.70 (doublet, $J_{de} = 16$ Hz). ^{19}F (ϕ , ppm): A, -17.88 (two doublets, $J_{CA} = 28$ Hz, $J_{BA} = 10$ Hz); B, +1.1 (two quartets, $J_{AB} = 10$ Hz, $J_{CB} = 10$ Hz); C, -0.3 (two quartets, $J_{AC} = 28$ Hz, $J_{BC} = 10$ Hz). *Anal.* Calcd for $C_{10}H_{13}F_4O$: C, 52.67; H, 5.81. Found: C, 52.70; H, 5.91.

4,4-Bis(trifluoromethyl)-3-buten-2-one.—Triphenylphosphineacetemethylene, mp 201-203° (lit.⁴ 205-206°), was prepared according to the method of Ramirez and Dershowitz⁴ and allowed to react with a slight excess of hexafluoroacetone as outlined by Plakhova and Gambaryan.² The yield of 4,4-bis(trifluoromethyl)-3-buten-2-one was 90%, bp 109-111° [lit.² bp 68° (135 mm)]. The infrared spectrum shows $C=O$ (1720) and $C=C$ (1670 cm^{-1}). The 1H nmr spectrum shows sharp singlets for the vinyl proton (6.97 ppm) and the three methyl protons (2.38 ppm).

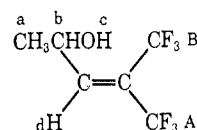
IX. Lithium Aluminum Hydride Reduction of 4,4-Bis(trifluoromethyl)-3-buten-2-one. Using 0.50 Mol of $LiAlH_4$.—A solution of 10.3 g (0.050 mol) of 4,4-bis(trifluoromethyl)-3-buten-2-one in 50 ml of ether was cooled to 0° and 0.95 g (0.025 mol) of finely crushed $LiAlH_4$ was added over a period of 1 hr. The reaction mixture was stirred at 0° for 1 hr and after hydrolysis

with 5% hydrochloric acid and drying over sodium sulfate, the solvent was removed from the product by careful distillation. The residue was distilled to yield 6.3 g (67%) of 5,5-difluoro-4-trifluoromethyl-4-penten-2-ol. The infrared spectrum shows OH absorption (3500 cm^{-1}) and also $C=CF_2$ (1740 cm^{-1}). The nmr spectra are described below.



1H (δ , ppm): a, 1.25 (doublet, $J_{ba} = 6$ Hz); b, 3.95 (complex); c, 2.3 (complex); d, 2.30. ^{19}F (ϕ , ppm): A, -17.84 (two doublets, $J_{BA} = 10$ Hz, $J_{CA} = 20$ Hz); B, -2.28 (broad multiplet); C, +0.18 (broad multiplet). *Anal.* Calcd for $C_6H_7F_5O$: C, 37.91; H, 3.60. Found: C, 37.77; H, 3.69.

Using 0.25 Mol of $LiAlH_4$.—The reduction was carried out as above using 0.475 g (0.0125 mol) of lithium aluminum hydride. Distillation gave 6.5 g of product, bp 118-134°. Glpc analysis (8-ft silicone grease column) showed the product yield to be starting material, 33%; 5,5-difluoro-4-trifluoromethyl-4-penten-2-ol, 21%; 4,4-bis(trifluoromethyl)-3-buten-2-ol, 12%. The first two materials were identified by comparison of the glpc retention times and infrared spectra with those of the respective authentic compounds. A sample of the third was obtained by preparative scale glpc techniques. The infrared spectrum is consistent, showing OH (3500 cm^{-1}) and $C=C(CF_3)_2$ (1680 cm^{-1}) absorptions. The nmr spectra are described below.



1H (δ , ppm): a, 1.38 (doublet, $J_{ba} = 7$ Hz); b, 4.9 (complex); c, 2.02 (singlet); d, 6.70 (doublet, $J_{bd} = 9$ Hz). ^{19}F (ϕ , ppm): A, -13.2 (quartet, $J_{BA} = 7$ Hz); B, -20.0 (quartet, $J_{AB} = 7$ Hz). *Anal.* Calcd for $C_6H_8F_6O$: C, 34.62; H, 2.90. Found: C, 34.81; H, 2.85.

Registry No.—1, 1422-33-9; *cis*-2, 24010-42-2; *trans*-2, 24010-43-3; 1,1-bis(trifluoromethyl)tetrahydrofuran, 24010-61-5; 1,1-bis(trifluoromethyl)-4-propyltetrahydrofuran, 24010-62-6; 1,1-bis(trifluoromethyl)-4-pentyltetrahydrofuran, 24010-63-7; 1,1-bis(trifluoromethyl)butane, 24010-64-8; *trans*,1,1-difluoro-2-trifluoromethyl-1,3-monadiene, 24010-44-4; 4,5-difluoro-4-trifluoromethyl-4-penten-2-ol, 24010-65-9; 4,4-bis(trifluoromethyl)-3-buten-2-ol, 656-80-4.

α, α' -Dianilino-stilbenes. The Cyanide Ion Catalyzed Dimerization of Aromatic Schiff Bases

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The alkali cyanide catalyzed dimerization of benzaldehyde anil (1a) in liquid ammonia has been described to give a fluorescent, yellow dimer to which the anilinoanil structure 2a was assigned because of the analogous formation of benzoin from benzaldehyde.¹ Since the dimerization product was found to be readily oxidized upon exposure to air to give benzil dianil (4a), structure 2a was suggested to be in equilibrium

(1) H. H. Strain, *J. Amer. Chem. Soc.*, **50**, 2218 (1928).