replaced by 250 ml. of ether, and the ether solution refluxed for 22 hr. The reaction mixture was decomposed by the addition of cold, 2 *M* hydrochloric acid and worked up as usual. Acidification of the sodium carbonate extracts yielded an oil which was taken up in ether and the solvent removed to give 1.5 g. (3.7%) of oily acid, neut. equiv., 272 (theory for half-ester, 268.3). Distillation of the neutral fraction yielded 29% recovery of di-*t*-butyl glutarate, and a 63% yield of residual hydroxy diester whose infrared spectrum was identical to that of the similar hydroxy diester obtained from the general procedure in 84% yield.

Proof of Structure of 5,5-Diphenyl-4-pentenoic Acid.[13]—To a solution of 19.7 g. (0.125 mole) of potassium permanganate in 250 ml. of water at 35° was added in three increments over 5 min., a solution of 12.6 g. (0.05 mole) of the acid, m.p. 78–78.5°, obtained by acidic hydrolysis of diester V, dissolved in 100 ml. of water containing 4.0 g. of potassium hydroxide. The permanganate color disappeared as the last was added, and the temperature rose to a maximum of 68°. After stirring for 2 hr. at room temperature, the manganese dioxide was filtered off, stirred with three portions of ether, and each of these were then used to extract the aqueous filtrate. The solvent was removed from the dried ether extracts to yield 5.0 g. of benzophenone, m.p. 46–48°, m.m.p. with an authentic sample, 46–47.5°. The basic aqueous filtrate was evaporated to dryness in a rotating evaporator under water pump vacuum at 140°, the residue was dissolved in 35 ml. of water, acidified with concentrated hydrochloric acid, and cooled. The mother liquor was decanted from the potassium chloride which first precipitated and cooled further to yield a mixture of inorganic and organic precipitate. This was warmed with 50 ml. of absolute ethanol, filtered, and the solvent removed to yield 3.0 g. of succinic acid, m.p. 186–188°, m.m.p. with an authentic sample, 188–189°.

Proof of Structure of α-(1-Cyclohexenyl)glutaric Acid.—This was carried out using 7.0 g. (0.033 mole) of the acid, m.p. 109.5–110°, obtained by acidic hydrolysis of diester VIII, and 10.5 g. (0.067 mole) of potassium permanganate. The acid was added all at once, and an excess of permanganate was not used, so as to prevent any further oxidation of cyclohexanone if it were formed. An ether extract was not made of the aqueous layers, but instead these were distilled at atmospheric pressure to remove cyclohexanone as an azeotrope. None was found, and the distillation was stopped after removing 25 ml. The residual aqueous solution was then evaporated to dryness as before, taken up in water, and acidified. Gas evolution was noted during the acidification and a precipitate formed at once. This was filtered off at room temperature to yield 3.4 g. of white crystals, m.p. 114.5–115.5°. After one recrystallization from water, they gave m.p. 115–115.2° and neut. equiv., 108.2 (reported[14] m.p. for 5-oxodecanedioic acid, 116°, calcd. neut. equiv., 108.1). The semicarbazone was prepared and gave m.p. 177.5–178.5°, neut. equiv., 136.4 (reported[14] m.p. 179–180°, calcd. neut. equiv., 136.6).

Acknowledgment.—The author gratefully expresses his appreciation to the National Science Foundation for a grant (NSF-G11318) which supported this research.

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[13] This and the following oxidation were done by the general procedure as given by J. W. Hill and W. L. McEwen, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 53.

[14] W. Huckel, *Ann.*, **441**, 1 (1925).

α-Fluorostyrene: Preparation, Properties, and Polymerization

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α-Fluorostyrene, a new vinyl monomer, was prepared by the pyrolysis of α,α-difluoroethylbenzene. The latter was obtained by the reaction of hydrogen fluoride with phenylacetylene or with α-chlorostyrene. α-Fluorostyrene was polymerized in neutral or basic emulsion systems to a high molecular weight homopolymer. The polymer had the striking property of evolving hydrogen fluoride abruptly and quantitatively when heated to 225–235°, forming poly(phenylacetylene).

Among the five isomers of fluorostyrene the only one not recorded in the literature is α-fluorostyrene.[1] As a result of our interest in the effect of substituents on the properties of vinyl polymers, a study of the preparation and polymerization of α-fluorostyrene was undertaken. A number of routes to α-fluorostyrene were tried but the most satisfactory one was a two-step procedure of which the first step was the synthesis of α,α-difluoroethylbenzene by one of the methods shown in equations 1–4.

$$C_6H_5C{\equiv}CH + 2HF \xrightarrow[0°]{\text{Ether solvent}} C_6H_5CF_2{-}CH_3 \quad (1)$$

$$C_6H_5C{\equiv}CH + 2HF \xrightarrow[150°]{\text{13–14\% HgO on act. carbon}} C_6H_5CF_2{-}CH_3 \quad (2)$$

$$C_6H_5CCl{=}CH_2 + 2HF \xrightarrow[0°]{\text{Ether solvent}} C_6H_5CF_2{-}CH_3 + HCl \quad (3)$$

$$C_6H_5CCl{=}CH_2 + 2HF \xrightarrow{\text{13–14\% HgO on act. carbon}} C_6H_5CF_2{-}CH_3 + HCl \quad (4)$$

The α,α-difluoroethylbenzene, a previously unreported compound, was then pyrolyzed to give the desired α-fluorostyrene plus hydrogen fluoride.

$$C_6H_5CF_2{-}CH_3 \xrightarrow{350–400°} C_6H_5CF{=}CH_2 + HF \quad (5)$$

Reactions of the types represented by equations 1–4 have not previously been applied successfully with phenylacetylene or α-chlorostyrene. Certain

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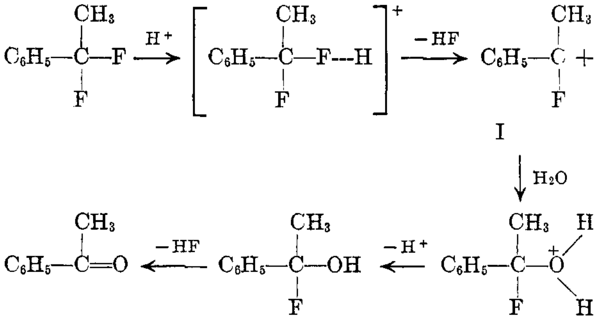
[1] For *o*,*m*,*p*-fluorostyrenes see L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944). Also see M. W. Renoll, *ibid.*, **68**, 1159 (1946), and G. B. Bachman and L. L. Lewis, *ibid.*, **69**, 2022 (1947), for *p*-fluorostyrene. For β-fluorostyrene see F. Swarts, *Bull. soc. chim.*, [4] **25**, 145 (1919); F. Bergmann, A. Kalmus, and E. Breuer, *J. Am. Chem. Soc.* **80** 4540 (1958).

other alkynes[2,3] and chloroölefins,[4–8] however, are known to react with anhydrous hydrogen fluoride in the liquid phase to give difluoroalkanes as the usual products. A closely related reaction, the liquid phase addition of a single molecule of hydrogen fluoride to some alkynes[2,3] and chloroölefins,[4,6–8] has been reported. Oxygenated solvents such as ether or acetone have been used to moderate some hydrogen fluoride additions.[3] In the vapor phase over heterogeneous catalysts, hydrogen fluoride has been added to alkynes to give difluoroalkanes[9–13] and monofluoroölefins.[9–14] In the only reported study of the reaction of phenylacetylene with hydrogen fluoride, Plueddeman obtained tars at temperatures from −80–0°.[3,15] When the reaction was moderated in ether solution at 0° and the product was steam distilled, a small quantity of acetophenone was obtained, suggesting to Plueddeman that hydrogen fluoride had added to the phenylacetylene. However, neither *α,α*-difluoroethylbenzene nor *α*-fluorostyrene was isolated. The reaction of a mixture of *α*-chlorostyrene and *β*-chlorostyrene with anhydrous hydrogen fluoride at 60° for two hours and then 90° for three hours was reported to give tar exclusively.[6,15]

Of our four methods for preparing *α,α*-difluoroethylbenzene, the second (equation 2) was the most convenient and gave yields of 40–45% at phenylacetylene conversion levels of almost 100%. These results were obtained at a space velocity of approximately 600 liters gas (S.T.P.)/liter catalyst/hour and an $HF/C_6H_5C{\equiv}CH$ mole ratio of 4–5:1. When this mole ratio was reduced in an attempt to prepare *α*-fluorostyrene directly, some *α*-fluorostyrene was obtained but the main result was a decrease in the over-all amount of phenylacetylene converted. The preparation of *α,α*-difluoroethylbenzene by the method of equation 1 gave best results (18% yield) when a 16:4:1 mole ratio of hydrogen fluoride–ether–phenylacetylene was employed. In addition to polymer, some acetophenone was formed as side product, probably by hydrolysis of the difluoroethylbenzene primarily during work-up. Some *α,α*-difluoroethylbenzene was obtained with a 4:1:1 mole ratio of hydrogen fluoride–ether–phenylacetylene, but practically no reaction occurred with a 1:1:1 ratio. When *α*-chlorostyrene was treated with hydrogen fluoride in ether solution (equation 3) using an 8:3:1 mole ratio of hydrogen fluoride–ether–*α*-chlorostyrene, a 28% yield of *α,α*-difluoroethylbenzene was obtained. Some unchanged *α*-chlorostyrene was recovered when the ratio was changed to 3:1:1.

α,α-Difluoroethylbenzene is a mobile, colorless liquid with b.p. 64.6–66.0° (40 mm.). It is stable in the presence of bases such as tetramethylguanidine at 160° and molten moist sodium hydroxide at 235°. In the presence of dilute aqueous solutions of strong acids, however, it is readily hydrolyzed to acetophenone. We believe that this facile hydrolysis proceeds in a manner such as the following:



$$C_6H_5C(CH_3)F_2 \xrightarrow{H^+} [C_6H_5C(CH_3)F{-}F{-}H]^+ \xrightarrow{-HF} C_6H_5\overset{+}{C}(CH_3)F \;(\text{I}) \xrightarrow{H_2O} C_6H_5C(CH_3)(F){-}\overset{+}{O}H_2 \xrightarrow{-H^+} C_6H_5C(CH_3)(F)OH \xrightarrow{-HF} C_6H_5C(CH_3){=}O$$

(6)

Although the dehydrofluorination of *α,α*-difluoroethylbenzene to *α*-fluorostyrene is not feasible by treatment with base, it is smoothly accomplished by vapor phase pyrolysis (equation 5). Similar pyrolytic dehydrofluorinations of *gem*-difluoroalkanes are well known.[16–18] The preparation of *α*-fluorostyrene was best effected by a two-pass procedure in which the vapors of *α,α*-difluoroethylbenzene, diluted with an equal volume of nitrogen, were passed through the pyrolysis zone of a stainless steel or Monel metal reactor at 350–400° with a space velocity of about 25 liters gas (S.T.P.)/liter volume of pyrolysis zone/hour. For best results a clean metal wall appeared to be necessary. A 53% yield of *α*-fluorostyrene was obtained at 83% over-all conversion of *α,α*-difluoroethylbenzene. There was also obtained a small amount of phenylacetylene which resulted from overcracking. At higher pyrolysis temperatures the formation of resinous material and of phenylacetylene was favored, with a corresponding decrease in the yield of *α*-fluorostyrene.

The isolation of pure *α*-fluorostyrene from the pyrolysis product is difficult because the boiling points of *α*-fluorostyrene and *α,α*-difluoroethylbenzene are so similar that fractional distillation is

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(2) A. V. Grosse and C. B. Linn, *J. Am. Chem. Soc.*, **64**, 2289 (1942); U. S. Patent 2,287,934 (1943).

(3) A. L. Henne and E. P. Plueddeman, *ibid.* **65**, 587 (1943).

(4) A. L. Henne and F. W. Haekl, *ibid.*, **63**, 2692 (1941).

(5) M. W. Renoll, *ibid.*, **64**, 1115 (1942); U. S. Patent 2,364,818 (1944).

(6) A. L. Henne and E. P. Plueddeman, *ibid.* **65**, 1271 (1943).

(7) A. L. Henne and J. B. Hinkamp, *ibid.*, **67**, 1194 (1945).

(8) A. L. Henne and E. G. DeWitt, *ibid.*, **70**, 1548 (1948).

(9) J. Söll, British Patent 469,421 (1937); U. S. Patent 2,118,901 (1938).

(10) G. M. Whitman, U. S. Patent 2,401,850 (1946).

(11) D. D. Coffman and L. F. Salisbury, U. S. Patent 2,451,612 (1948).

(12) J. C. Hillyer and J. F. Wilson, U. S. Patent 2,471,525 (1949).

(13) J. C. Hillyer and J. F. Wilson, U. S. Patent 2,574,480 (1951).

(14) A. L. Barney, U. S. Patent 2,437,148 (1948).

(15) E. P. Plueddeman, Ph.D. dissertation, The Ohio State University, 1942.

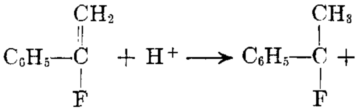
(16) F. B. Downing, A. F. Benning, and R. C. McHarness, U. S. Patent 2,480,560 (1949).

(17) P. R. Austin, U. S. Patent 2,585,529 (1952); P. R. Austin, D. D. Coffman, H. H. Hoehn, and M. S. Raasch, *J. Am. Chem. Soc.*, **75**, 4834 (1953).

(18) C. F. Feasly and W. A. Stover, U. S. Patent 2,627,529 (1953).

impractical. Furthermore, distillation in apparatus containing Monel metal or stainless steel is accompanied by decomposition with evolution of hydrogen fluoride. A chromatographic procedure employing a basic alumina was developed which accomplished the separation after several passes.

α-Fluorostyrene is a colorless liquid with b.p. 45.0–45.4°(14 mm.). Since many monofluorinated organic compounds are extremely toxic,[19] the toxicity of α-fluorostyrene was determined before larger quantities were made for polymerization studies. A single oral dose rat LD_{50} of 838 mg./kg. was obtained which indicated that α-fluorostyrene is only slightly toxic. The hydrolytic behavior of α-fluorostyrene is similar to that of α,α-difluoroethylbenzene. α-Fluorostyrene is stable in aqueous alkali at 100° but is even more readily hydrolyzed than α,α-difluoroethylbenzene to acetophenone in the presence of acids. The sequence depicted in equation 6 would account for this difference since carbonium ion I probably is formed more rapidly from α-fluorostyrene than from α,α-difluoroethylbenzene:



$$C_6H_5-\overset{\overset{CH_2}{\|}}{\underset{F}{C}} + H^+ \longrightarrow C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{\text{I}}{F}}{C}}{}^+ \qquad (7)$$

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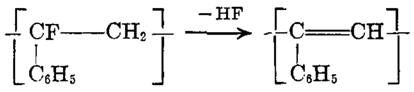
A number of procedures to prepare the homopolymer of α-fluorostyrene were tried. Bulk polymerizations with azobisisobutyronitrile at 70° and with ultraviolet light at room temperature yielded dark mixtures from which hydrogen fluoride was evolved. Only small amounts of a yellow, unsaturated polymer were isolated from these mixtures. It appeared that some of the monomer was polymerized but the polymer underwent dehydrofluorination to give a polyconjugated material in the manner:



$$\left[\underset{C_6H_5}{\underset{|}{CF}}-CH_2\right] \xrightarrow{-HF} \left[\underset{C_6H_5}{\underset{|}{C}}=CH\right] \qquad (8)$$

Since hydrogen fluoride evolution was suspected of being autocatalytic, several emulsion polymerizations were tried under buffered neutral or alkaline conditions. It was found that a high molecular weight polymer containing the theoretical amount of fluorine could be prepared in such systems.[20] Two convenient procedures were developed, one employing a potassium persulfate catalyst buffered at pH 7, in which the persulfate was decomposed thermally at 50°, and a second in which the initiating system was ammonium persulfate activated with triethanolamine buffered at pH 9. It was necessary to employ a non-ionic emulsifier which would tolerate the high salt concentrations of the buffers.

The samples of poly-α-fluorostyrene were white and of appreciable molecular weight, indicated by intrinsic viscosity measurements in the range 0.8 to 1.2 dl./g. These samples were soluble in the usual solvents for polystyrene and clear films could be cast from solvents such as chloroform. The polymer was found to be stable below its softening point (145–150°), but on prolonged heating above its softening point, hydrogen fluoride was evolved. When the pure polymer, contained in a porcelain crucible, was subjected to a programmed heating at 10°/min. under nitrogen in a thermogravimetric balance, it underwent no weight change to 220°, but lost 15.5% of its weight very abruptly between 225 and 235°. The fact that this weight loss corresponded to a quantitative evolution of hydrogen fluoride (theoretical weight loss = 15.57%) was confirmed in a separate experiment in which the sample was cooled immediately after being heated to this point. The residual sample had acquired a brick-red color and contained less than 0.4% fluorine.[21] Its infrared spectrum no longer contained the carbon–fluorine or methylene bands and was identical with the spectrum of poly(phenylacetylene) prepared in these laboratories from phenylacetylene according to a procedure described by Natta[22] and with the spectrum published recently by other workers.[23] Other fluorine-containing polymers, such as polyvinyl fluoride, polyvinylidene fluoride, and polytrifluoroethylene, are known to eliminate hydrogen fluoride on pyrolysis,[24,25] but there are no observations reported of abrupt, quantitative hydrogen fluoride evolution without chain fragmentation. The pyrolysis of poly-α-fluorostyrene of known structure and molecular weight would therefore appear to be a good synthesis for the conjugated polymer of phenylacetylene.

Experimental

Boiling points and melting points are uncorrected. Gas-liquid chromatographic analyses were performed with helium carrier gas on a Wilkins Model A-90-C chromatograph equipped with a 10-ft. column containing 20% of either Silicone GE SF-96 grease or Apiezon L grease on firebrick, or on an F & M Model 119-A chromatograph equipped with an 8-ft. column of Dow Corning high vacuum silicone grease on Chromosorb W solid support. The infrared spectra were recorded on Perkin-Elmer Model 137B or Model 21 spectro-

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[19] See F. L. M. Pattison, "Toxic Aliphatic Fluorine Compounds," Elsevier Publishing Co., New York, N. Y., 1959.

[20] Under the same conditions, we found that α-chlorostyrene could not be polymerized successfully because hydrogen chloride was eliminated, destroying the effectiveness of the initiator. Other workers have reported hydrogen chloride elimination during the polymerization of α-chlorostyrene; see C. S. Marvel, G. E. Inskeep, R. Deanin, A. E. Juve, C. H. Schroeder, and M. M. Goff, *Ind. Eng. Chem.*, **39**, 1486 (1947), and J. P. Regeaud, *Chim. mod.*, **4**, No. 27, 91 (1959).

[21] The accuracy of the analysis was ±0.3%.

[22] Montecatini, Australian Patent 215,925 (1956).

[23] Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellman, and W. Brenner, *Chem. Ind.* (London), 2004 (1961). In the spectrum obtained by these workers the phenyl absorptions at 755 and 698 $cm.^{-1}$ were blanked out by some unspecified chlorinated solvent.

[24] S. L. Madorsky, V. E. Hart, S. Strauss, and V. A. Sedlak, *J. Res. Natl. Bur. Std.*, **51**, 327 (1953).

[25] S. L. Madorsky and S. Strauss, *ibid.*, **63A**, 261 (1959).

photometers. The n.m.r. spectra were obtained with a Varian V4300B spectrometer operating at 56.4 Mc.; the samples were dissolved in carbon tetrachloride in approximately 10% concentration together with small amounts of tetramethylsilane or trichlorofluoromethane as internal references.

Materials.—Anhydrous hydrogen fluoride was obtained in cylinders from the Matheson Co., Inc. Phenylacetylene was obtained from Farchan Research Laboratories. α-Chlorostyrene was prepared from acetophenone and phosphorus pentachloride.[26]

Preparation of α,α-Difluoroethylbenzene. 1. Reaction of Phenylacetylene with Hydrogen Fluoride in Ether Solution.—Eighty-one milliliters (80 g., 4.0 moles) of anhydrous hydrogen fluoride, cooled to Dry Ice temperature, was added during 10 min. to 105 ml. (74.3 g., 1.0 mole) of anhydrous ether stirred at Dry Ice–acetone temperature in a Monel metal flask equipped with a sealed stainless steel stirrer. Heat was evolved during the addition. The hydrogen fluoride–ether solution was then protected from atmospheric moisture and the Dry Ice bath was replaced by an ice–water bath. After the hydrogen fluoride–ether solution reached ice-water temperature, 25.5 g. (0.250 mole) of phenylacetylene was added dropwise during 1 hr. with vigorous stirring. Stirring was continued for another hour in the ice bath. Seventy-five milliliters of ether was then added, and the cold mixture was poured into 200 ml. of cracked ice and 100 ml. of water contained in a stainless steel beaker. The resulting mixture was cooled and stirred while sufficient 33% (by weight) aqueous potassium hydroxide solution was added to make the aqueous phase basic. The ether layer was separated and dried over anhydrous magnesium sulfate. The ether was removed by distillation at atmospheric pressure on the steam bath. The residue was distilled on a Widmer glass-spiral column ($^1/_2$ in. × 12 in.) to give: (1) 4.3 g., b.p. 64.6° (40 mm.); (2) 2.0 g., b.p. 64.6–66.0° (40 mm.); (3) 0.9 g., b.p. 66.0–110.2° (40 mm.); (4) 7.2 g., b.p. 110.2° (40 mm.). Gas-liquid chromatographic analysis (Dow Corning silicone, 170°) and infrared spectra showed that fractions 1 and 2 were practically pure α,α-difluoroethylbenzene and fractions 3 and 4 were practically pure acetophenone.[27] The yield of α,α-difluoroethylbenzene was 6.3 g. (0.044 mole) or 18% based on 0.250 mole of phenylacetylene. The infrared spectrum of α,α-difluoroethylbenzene shows absorptions (cm.$^{-1}$) at 1388 for CH_3 and 1182 for CF_2.

Anal. Calcd. for $C_8H_8F_2$: C, 67.61; H, 5.67; F, 26.74. Found: C, 67.94; H, 5.70; F, 27.08.

2. Reaction of α-Chlorostyrene with Hydrogen Fluoride in Ether Solution.—Using the procedure described in part 1 for the reaction of phenylacetylene with hydrogen fluoride, 20.0 g. (0.144 mole) of α-chlorostyrene was added to 23 g. (1.2 moles) of anhydrous hydrogen fluoride dissolved in 44 ml. (35 g., 0.42 mole) of anhydrous ether. Distillation gave: (1) 4.5 g., b.p. 67.1° (47 mm.); (2) 1.6 g., b.p. 67.1–105° (47 mm.); (3) 1.5 g., b.p. 105° (47 mm.). Gas-liquid chromatographic analysis (Dow Corning silicone, 170°) showed that fraction 1 was α,α-difluoroethylbenzene, fraction 2 was 80% α,α-difluoroethylbenzene, and fraction 3 was predominantly acetophenone. The yield of α,α-difluoroethylbenzene was 5.8 g. (0.041 mole) or 28% based on 0.144 mole of α-chlorostyrene.

3. Reaction of Phenylacetylene with Hydrogen Fluoride in the Vapor Phase.—A catalyst comprising charcoal-supported mercury compounds was prepared by a procedure similar to that given by Salisbury.[28] Elemental analysis showed that the catalyst contained 13.4% mercury and 1.1% nitrogen.

One hundred milliliters of the catalyst formed a 3-in. bed when placed in the center of a vertical reactor constructed of a 24-in. length of 2-in. iron pipe (1.61 in. i.d.). The reactor contained a coaxially mounted thermocouple well of $^1/_4$-in. steel tubing. The entire length of the reactor was jacketed with an electric furnace segmented for separate heating of top, center, and bottom. The top of the reactor was equipped with a pre-heater having separate entrance ports for liquid phenylacetylene and a mixture of gaseous anhydrous hydrogen fluoride and prepurified nitrogen; provision was made just before the pre-heater for mixing nitrogen with the phenylacetylene. The temperature of the preheater and the interior temperature of the catalyst bed were measured with thermocouples. The flow rates of nitrogen and liquid phenylacetylene were measured with rotameters and the flow rate of hydrogen fluoride gas was measured with a flow-meter of the type described by Peterson.[29] The effluent from the bottom of the reactor was passed into the bottom of an ice-cooled scrubber containing 150 ml. of hexane and 1400 ml. of an aqueous solution of 450 g. of potassium hydroxide. The gas from the top of the scrubber was led through a trap cooled in Dry Ice–acetone and then through a wet-test meter which was connected to a water aspirator regulated to lower slightly the pressure on the outlet side of the reactor so as to maintain the feed side at atmospheric pressure.

Before starting the reaction, the system was swept with nitrogen and the pre-heater temperature was raised to 170° while the reactor temperature was raised to approximately 75°. The hydrogen fluoride–nitrogen mixture was then turned on at a rate of 0.659 l. (S.T.P.)/min. of hydrogen fluoride and 0.105 l. (S.T.P.)/min. of nitrogen. The catalyst temperature rose sharply, especially at the top. During the next 25 min., the furnace was adjusted to bring the top portion of the reactor to 150°, the bottom to 85°, and the catalyst (top) to 135°. The phenylacetylene–nitrogen mixture was then turned on at a rate of 0.00778 mole/min. of phenylacetylene and 0.111 l. (S.T.P.)/min. of nitrogen. The space velocity was 630 l. gas (S.T.P.)/l. catalyst/hr. After 40 min. the catalyst temperatures were: top, 170°; center, 155°; bottom, 150°. These temperatures were maintained approximately during the next 105 min., after which the phenylacetylene and hydrogen fluoride were shut off. The total amounts of reactants fed were 147 g. (1.44 moles) of phenylacetylene and 5.41 moles of hydrogen fluoride. The total nitrogen fed was 1.79 moles, 40.0 l. (S.T.P.); the off-gases measured by the wet-test meter were 37.9 l. (S.T.P.); the off-gases measured by the wet-test meter were 37.9 l. (S.T.P.).

After sweeping the system with nitrogen for 0.5 hr., the scrubber and cold trap were dismantled and the contents combined. The dark organic layer was separated, washed three times with a saturated aqueous potassium chloride solution made slightly basic with ammonium hydroxide, and then dried over anhydrous magnesium sulfate. The solution was distilled to remove the hexane at 140 mm. and to collect 90.3 g. of a liquid with b.p. 64–67° (48 mm.). Gas-liquid chromatography (Apiezon L, 100°) showed that the distillate consisted of 4.2 g. (0.041 mole) of phenylacetylene and 86.1 g. (0.606 mole) of α,α-difluoroethylbenzene. The conversion of phenylacetylene was 97.2% and the yield of α,α-difluoroethylbenzene was 43.3%.

4. Reaction of α-Chlorostyrene with Hydrogen Fluoride in the Vapor Phase.—The procedure was the same as that used with phenylacetylene (see part 3), except that only 100 ml. of hexane was used in the scrubber and the temperatures were: pre-heater, 220°; reactor top, 170°; reactor bottom, 170°, catalyst top 155°; catalyst center, 152°; catalyst bottom, 150°. The flow rates (S.T.P.) were: hydrogen fluoride–nitrogen, 0.551 l./min.–0.157 l./min.; α-chlorostyrene–nitrogen, 0.00686 mole/min.–0.153 l./min. The space velocity was 611 l. gas (S.T.P.)/l. catalyst/hr. The reaction time was 150 min., during which 1.03 moles of α-chlorostyrene, 3.69 moles of hydrogen fluoride, and 2.08 moles, 46.5 l. (S.T.P.), of nitrogen were fed; the gas

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(26) J. U. Nef, *Ann.*, **308**, 264 (1899).

(27) In order to minimize hydrolysis to acetophenone, the neutralization procedure could probably be improved by adding the reaction mixture to excess base, rather than the reverse as described.

(28) L. F. Salisbury, U. S. Patent 2,519,199 (1950).

(29) W. S. Peterson, *Ind. Eng. Chem., Anal. Ed.*, **17**, 54 (1945).

measured by the wet-test meter was 44.3 l. (S.T.P.). After washing and drying, the hexane solution was given a one-plate distillation at 3-mm. pressure; 137 g. of distillate was collected, leaving 19 g. of a black tarry pot residue. After accounting for the original 66 g. of hexane, gas-liquid chromatography (Silicone GE SF-96, 150°, and Apiezon L, 100°) showed that the distillate consisted of 61.9 g. (0.45 mole) of α-chlorostyrene and 9.2 g. (0.065 mole) of α,α-difluoroethylbenzene. The conversion of α-chlorostyrene was 56% and the yield of α,α-difluoroethylbenzene was 11%. The poor material balance was caused by the formation of tar which drained from the reactor but was insoluble in the hexane.

Preparation of α-Fluorostyrene. 1. Pyrolysis of α,α-Difluoroethylbenzene.—A vertically mounted reactor was constructed of stainless steel pipe with internal diameter of 2.08 in. and length of 12 in. to provide a volume of 668 ml. The reactor was jacketed with an electric furnace and the internal temperature at 1 in. from the bottom could be measured with a thermocouple. The top of the reactor was equipped with a pre-heater in which liquid α,α-difluoroethylbenzene was vaporized and mixed with a stream of prepurified nitrogen. The pre-heater led to a pipe descending to three inches from the bottom of the reactor. An exit port at the top of the reactor led through a heated tube to the bottom of an ice-cooled scrubber containing 25 ml. of hexane and a solution of 178 g. of potassium hydroxide in 250 ml. of water. The gas from the top of the scrubber went through a trap cooled in Dry Ice–acetone.

After the apparatus was flushed with nitrogen, the preheater and exit line were maintained at 200° and the reactor was heated at 400°. During 143 min., a mixture of 113 g. (0.795 mole) of α,α-difluoroethylbenzene and 7.2 g. (0.071 mole) of phenylacetylene was passed at a constant rate into the reactor together with 19.4 l. (S.T.P.) (0.866 mole) of nitrogen. The space velocity was 24.4 l. gas (S.T.P.)/l. vol. of pyrolysis zone/hour. After sweeping the system with nitrogen for 0.5 hr., the scrubber and cold trap were dismantled and the contents combined. The organic layer was separated and washed three times with saturated aqueous potassium chloride solution made slightly basic with ammonium hydroxide. A small quantity of hydroquinone was added and the product was dried over anhydrous magnesium sulfate. The solution was distilled to remove the hexane at 140 mm. and to collect 88.5 g. of a liquid with b.p. 66.1–68.2° (47 mm.); the pot residue was 9 g. and smelled of acetophenone. Gas-liquid chromatography (Apiezon L, 100°) showed that the distillate consisted of 50.4 g. (0.355 mole) of α,α-difluoroethylbenzene, 29.2 g. (0.239 mole) of α-fluorostyrene, and 8.9 g. (0.0872 mole) of phenylacetylene. The conversion of α,α-difluoroethylbenzene was 55.4%, the yield of α-fluorostyrene was 54.3%, and the yield of phenylacetylene was 3.6%.

The interior of the reactor was cleaned by heating at 700° while purging with air for 3 hr. and steam for 3 hr. The mixture obtained from the first-pass pyrolysis was pyrolyzed as before, except that the reactor temperature was lowered to 350°. The mixture was passed into the reactor together with 15.3 l. (S.T.P.) (0.681 mole) of nitrogen during 104 min. The space velocity was 26.5 l. gas (S.T.P.)/l. vol. of pyrolysis zone/hour. Distillation of the product gave 72.9 g. of liquid with b.p. 65–69° (49 mm.); the pot residue was 2.9 g. Gas-liquid chromatography showed that the distillate consisted of 19.0 g. (0.134 mole) of α,α-difluoroethylbenzene, 43.0 g. (0.352 mole) of α-fluorostyrene, and 10.9 g. (0.107 mole) of phenylacetylene. After two passes, the conversion of α,α-difluoroethylbenzene was 83.3%, the yield of α-fluorostyrene was 53.2%, and the yield of phenylacetylene was 5.4%.

The product mixture was chromatographed on a 4.9 cm. × 50 cm. basic alumina column (Alcoa, grade F-20, freshly activated by heating at 205° for 18 hr.).[30] Elution with 750 ml. of hexane gave a solution greatly enriched in α-fluorostyrene but still containing some α,α-difluoroethylbenzene and phenylacetylene. Because the separation among the three components was not complete, some α-fluorostyrene was left on the column. After two more chromatographic purifications, gas-liquid chromatography showed only α-fluorostyrene; distillation (hydroquinone inhibitor) gave 12.0 g. (0.0984 mole) with b.p. 45.0–45.4° (14 mm.).

The infrared spectrum of α-fluorostyrene shows absorptions (cm.$^{-1}$) at 1655 for C=C, 1278 and 930 for C—C—F, and 847 for =CH$_2$. The n.m.r. spectrum of α-fluorostyrene shows that the F^{19} chemical shift is +107.9 ϕ and the H^1 chemical shifts are +5.18 τ and +5.02 τ. The F—H and the H—H coupling constants are all consistent with values given in the literature for similar compounds.[31]

Anal. Calcd. for C_8H_7F: C, 78.69; H, 5.78; F, 15.56. Found: C, 78.57; H, 5.73; F, 15.54.

2. Reaction of Phenylacetylene with Hydrogen Fluoride in the Vapor Phase.—The catalyst and procedure were the same as for the preparation of α,α-difluoroethylbenzene from phenylacetylene (see part 3, above), except that 100 ml. of toluene was used in the scrubber and the temperatures were: pre-heater 165°; reactor top, 160°; reactor bottom, 80°; catalyst top, 160°; catalyst center, 160°; catalyst bottom, 155°. The flow rates (S.T.P.) were: hydrogen fluoride–nitrogen, 0.466 l./min.–0.113 l./min; phenylacetylene–nitrogen, 0.0137 mole/min.–0.111 l./min. The space velocity was 598 l. gas (S.T.P.)/l. catalyst/hour. The reaction time was 101 min., during which 1.38 moles of phenylacetylene, 2.10 moles of hydrogen fluoride, and 1.01 moles, 22.6 l. (S.T.P.) of nitrogen were fed; the off-gases measured by the wet-test meter were 20.9 l. (S.T.P.). After washing and drying, the toluene solution (230 g.) was analyzed by gas-liquid chromatography (Apiezon L, 105°) which showed a weight ratio phenylacetylene–α,α-difluoroethylbenzene–α-fluorostyrene of 8.8:2.8:1.0.

Preparation of Poly-α-fluorostyrene.—Just before polymerization, the α-fluorostyrene was freed of hydroquinone inhibitor by passing through a column of activated basic alumina (Alcoa, grade F-20). The polymerization was accomplished by one of the following procedures.

1. Into a 100-ml. three-necked flask, equipped with a stirrer, a nitrogen inlet tube, a reflux condenser, and a gas exit tube, were placed 20 ml. of an aqueous buffer[32] at pH 7 and 0.11 g. of a non-ionic emulsifier.[33] The system was stirred and swept with prepurified nitrogen for 15 min. The nitrogen flow was discontinued, 2.2 g. of α-fluorostyrene was added, and the stirring was continued. When the milky appearance of the mixture indicated that an emulsion had formed, 0.030 g. of $K_2S_2O_8$ was added, and the system was stirred at 50° for 20 hr. The reaction mixture was poured into 500 ml. of methanol, and the precipitated polymer was filtered, washed with methanol, dissolved in benzene, and reprecipitated. The dried polymer (0.45 g.) was a fluffy, white solid, softening point 145–150°, with an intrinsic viscosity in benzene of 0.84 dl./g. A polymer film of 0.5-mil thickness showed absorptions in the infrared (cm.$^{-1}$) at 1357 for CH$_2$ and 1238 and 1134 for C—C—F.

Anal. Calcd. for C_8H_7F: C, 78.69; H, 5.78; F, 15.56. Found: C, 78.71; H, 6.21; F, 15.37.

2. In the 100-ml. three-necked flask, equipped as described in procedure 1, were placed 20 ml. of a buffer[32] of pH 9 and 0.11 g. of a non-ionic emulsifier.[33] The emulsion was prepared with 2.2 g. of α-fluorostyrene and deaerated as before. An initiation system of 0.035 g. $(NH_4)_2S_2O_8$ and 0.022 g. of triethanolamine was added, and the polymerization was allowed to proceed for 24 hr. at 35°. The polymer, iso-

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[30] The use of certain less basic grades of alumina caused decomposition on the column.

[31] C. N. Banwell and N. Sheppard, *Proc. Roy. Soc.* (London), **263A**, 136 (1961).

[32] Commercially available buffers were used, either Fisher Certified Reagent or Beckman.

[33] Triton X-305, a polyethylene oxide type emulsifier, available from Rohm and Haas.

lated and dried as before, weighed 1.3 g. and had an infrared spectrum identical to the analytically pure sample prepared by procedure 1.

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Ortho Substitution Rearrangement *vs.* Elimination Reaction of Ring-substituted Benzyldimethylethylammonium Ions[1]

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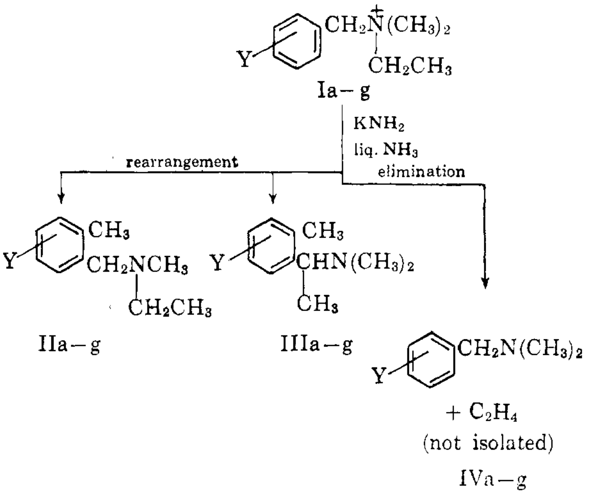
Treatment of 2-, 3-, and 4-methoxy- and -fluoro-substituted benzyldimethylethylammonium iodides with potassium amide in liquid ammonia was found to afford varying mixtures of the corresponding benzyldimethylamines and the two possible ortho substitution rearrangement products. The 2- and 4-methoxy substituents favored rearrangement almost to the exclusion of elimination. The 3-methoxy substituent had no appreciable effect, compared to the unsubstituted compound. The 2- and 3-fluoro substituents favored elimination. The rearrangement products consisted mainly of the corresponding methyl derivatives but contained smaller amounts of the methylene derivatives. These results are of interest from the theoretical and synthetic standpoints.

Recently[2] the benzyldimethylethylammonium ion (Ia) and certain other benzyldimethylalkylammonium ions having β-hydrogen were shown to undergo both the ortho substitution rearrangement and an elimination reaction with sodium amide in liquid ammonia. The relative extents of these two types of reaction were observed to depend on the nature of the alkyl group in the side chain. We have now found that the relative extents of the two types of reaction are also dependent on substituents in the aromatic ring. Thus treatment of quaternary ammonium ions Ia–g with five[3] molecular equivalents of potassium amide in liquid ammonia afforded various proportions of the rearrangement and elimination products. The former type of product consisted of mixtures of isomeric amines IIa–g and IIIa–g and presumably ethylene (Scheme A).



Ia. Y = H
Ib. Y = 2-OCH$_3$
Ic. Y = 2-F
Id. Y = 4-OCH$_3$
Ie. Y = 4-F
If. Y = 3-OCH$_3$
Ig. Y = 3-F

Scheme A

In Table I are summarized the proportions of rearrangement products to elimination products and calculated yields of products. These proportions were determined by vapor phase chromatography. A sample of the crude amine product from each reaction was passed through a short, nonselective column which separated the elimination product IV from the rearrangement products II and III, but which did not separate isomers II and III. The composition of the mixture was estimated from this chromatogram. When possible, the proportions of products were determined more accurately by comparison of the areas under the peaks corresponding to elimination and rearrangement products with the areas under these peaks of a known mixture of pure elimination product and a mixture of essentially pure rearranged amines II and III, obtained by distillation of the crude reaction product. Each analysis was reproducible to within 2%.

From the results shown in Table I and the weights of the crude amine products were calculated the yields of rearrangement product mixtures containing amines of types II and III and the yields of the elimination products of type IV (see Table I). In the reactions of the methoxy-substituted quaternary ions, only the above mentioned products were detected, the total yields being 88–93%. However, in the reactions of the fluoro-substituted quaternary ions, the amine products were con-

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(1) Supported by the Army Research Office (Durham).

(2) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 1542 (1962).

(3) Although only one molecular equivalent of the alkali amide is required, this large excess was employed to reduce possible concentration effects during the course of addition of the quaternary halide.