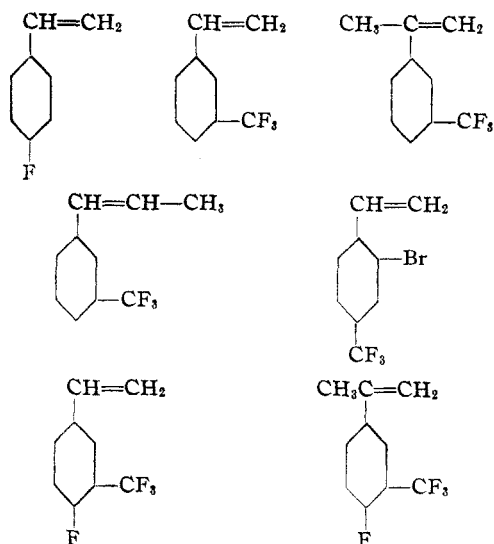


[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Monomers and Polymers. I. Fluorinated Styrenes^{1,2}

BY G. BRYANT BACHMAN AND LEONDA L. LEWIS

This paper reports the synthesis of seven fluorinated styrenes and gives a brief summary of their polymerization and copolymerization characteristics.



4-Fluorostyrene and 3-trifluoromethylstyrene have been prepared previously by methods other than those described in this paper. The others are new.

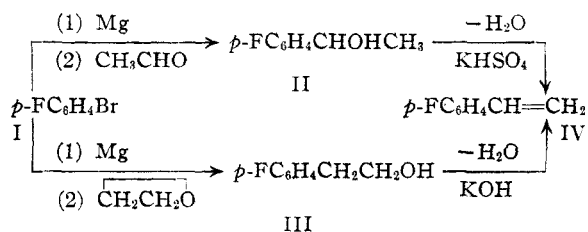
The general approach to these compounds involved preparing the corresponding fluorobromobenzenes, converting them *via* Grignard reagents to the corresponding primary, secondary or tertiary alcohols, and then dehydrating the alcohols to the desired styrenes. Careful studies were made of the dehydrating conditions in each case, since considerable variations in yields were experienced. In general the secondary and tertiary alcohols dehydrated most satisfactorily with acid catalysts (KHSO_4 , P_2O_5) while the primary alcohols dehydrated best with strong bases (KOH) as catalysts. The temperature, pressure and rate of dehydration were important. Optimum conditions are given in the experimental part.

The polymerization characteristics of the fluorinated styrenes are especially interesting. Those without α -methyl or β -methyl groups polymerize readily with peroxide catalysts to give brilliantly-

clear, hard polymers. All except the β -methylstyrene copolymerize with butadiene to give rubbers which appear to be equal or superior to GR-S in preliminary tests. On the basis of the information obtained further studies on fluorinated styrenes in plastics and rubbers would appear to be desirable.

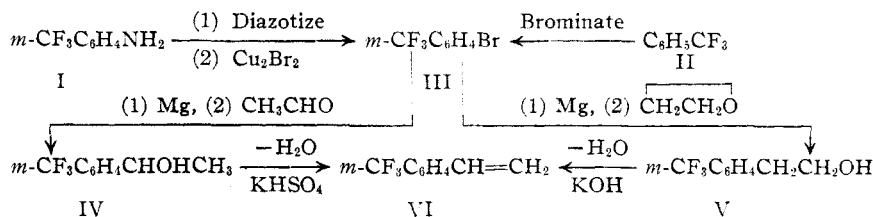
Acknowledgment.—The authors are indebted to the General Tire and Rubber Company for financial support and for the synthetic rubber evaluations.

Experimental

4-Fluorostyrene^{3,4}

4-Fluoro- α -methylbenzyl Alcohol⁵ (II).—The Grignard reagent from 209 g. of I⁵ in 585 ml. of ether was added to 56.5 g. of acetaldehyde in 435 ml. of ether. The addition product was decomposed with 190 ml. of 25% ammonium chloride solution, the mixture filtered, and the solution distilled. There resulted 110.5 g. (66% yield) of product, b. p. (20 mm.) 104–110°, d_{25}^{25} 1.1333, n_D^{25} 1.5035.

4-Fluorostyrene^{3,4} (IV).—Dropwise addition of 145 g. of III⁶ to potassium hydroxide pellets in a copper flask held at 250–255° in a metal bath followed by recovery and distillation of the organic product gave 17.6 g. (22.5% yield) of the styrene, b. p. 44–45° (15 mm.), d_{25}^{25} 1.022, n_D^{25} 1.5131. The same product was obtained in better yields (62%) from II by Brooks³ procedure.

3-Trifluoromethylstyrene^{4,7}

3-Bromo- α -trifluorotoluene^{8,9,10} (III).—This compound was prepared from I by a procedure described by Hartwell¹¹ for the conversion of 2-chloroaniline to 2-bromochloro-

(3) Brooks, *THIS JOURNAL*, **66**, 1295 (1944).(4) Renoll, *ibid.*, **68**, 1159 (1946).(5) Schiemann and Pillarsky, *Ber.*, **64**, 1340–1345 (1931).(6) Suter and Weston, *THIS JOURNAL*, **63**, 602–605 (1941).(7) Marvel, Overberger, Allen and Saunders, *ibid.*, **68**, 736–738 (1946).(8) Finger and Kalinowski, *Trans. Illinois State Acad. Sci.*, **37**, 66–68 (1944).(9) Gilman and Tolman, *THIS JOURNAL*, **68**, 426–428 (1946).(10) Simons and Ramler, *ibid.*, **65**, 689–692 (1943).(11) Hartwell, "Organic Syntheses," **24**, 22–24 (1944).

(1) Read before the Organic Division at the Atlantic City Meeting of the American Chemical Society, April, 1946.

(2) From the Ph.D. thesis of L. L. Lewis. Present address: E. I. du Pont de Nemours Company, Buffalo, New York.

benzene. From 1100 g. (6.84 moles) of I there was obtained 1328 g. (5.9 moles, 86.4% yield) of III; b. p. 154–156°, d_{25}^{25} 1.6371, n_D^{25} 1.4713.

3-Bromo- α -trifluorotoluene was also prepared by the bromination of α -trifluorotoluene according to a method of Graham.¹² From 1750 g. (12 moles) of α -trifluorotoluene there was obtained 1809 g. (73% yield) of III, b. p. 73–74.5° (45 min.). One mole (147 g.) of α -trifluorotoluene was recovered. From this reaction there was also obtained 147 g. of a material boiling at 88–90° (10 mm.). This fraction was subsequently found to be a mixture of 3,4- and 2,5-dibromo- α -trifluorotoluenes. The experimental part of this identification is given in the section dealing with the preparation of 2-bromo-4-trifluoromethylstyrene.

3-Trifluoromethylphenethyl Alcohol (V).—This alcohol was prepared by a method similar to that used by Bachmann and Thomas¹³ for the preparation of 3-methoxyphenethyl alcohol. From 101 g. (0.45 mole) of III there was obtained 57.4 g. (0.302 mole, 67% yield) of V; b. p. 85–90° (4 mm.), d_{25}^{25} 1.2608, n_D^{25} 1.4623.

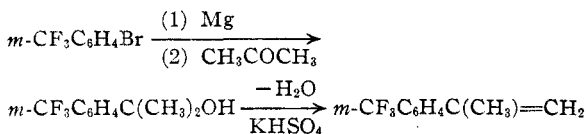
*Anal.*¹⁴ Calcd. for $C_9H_9OF_3$: F, 29.97. Found: F, 29.4, 29.4.

3-Trifluoromethylstyrene (VI).—Dehydration of 8.9 g. of V with 0.8 g. of potassium hydroxide at 180–200° (oil-bath) and 125 mm. pressure followed by fractionation of the product gave 4.85 g. (72% yield) of the styrene, b. p. 70–71° (40 mm.), d_{25}^{25} 1.1628, n_D^{25} 1.4635.

Anal. Calcd. for $C_9H_7F_3$: C, 62.79; H, 4.10. Found: C, 62.61, 62.75; H, 4.10, 4.00.

Dehydration of 190 g. of IV⁷ by heating with 4 g. of hydroquinone and 8.8 g. of phosphorus pentoxide at 145–170° (oil-bath) and 130–140 mm. pressure over a period of four hours, followed by rectification of the product gave 129 g. (79% yield) of VI.

α -Methyl-3-trifluoromethylstyrene



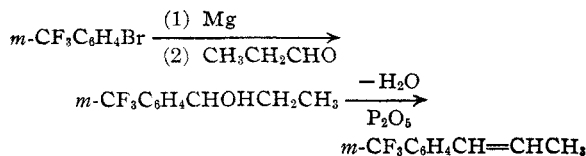
α,α -Dimethyl-3-trifluoromethylbenzyl Alcohol.—A solution of 107 g. of acetone in 500 ml. of ether was added to the Grignard reagent from 375 g. of 3-bromo- α -trifluorotoluene in 1200 ml. of ether. The mixture was treated with 264 ml. of 25% ammonium chloride solution, filtered and rectified to give 246 g. (72% yield) of the alcohol, b. p. 91.5° (10 mm.), d_{25}^{25} 1.2039, n_D^{25} 1.4572.

Anal. Calcd. for $C_{10}H_{11}OF_3$: C, 58.81; H, 5.43. Found: C, 58.65, 58.55; H, 5.59, 5.51.

α -Methyl-3-trifluoromethylstyrene.—Dehydration of 86.4 g. of the above alcohol with 4.4 g. of potassium acid sulfate under nitrogen at 175–195° (oil-bath) followed by fractionation of the product gave 69.3 g. (86% yield) of the corresponding styrene, b. p. 83–84° (40 mm.), d_{25}^{25} 1.1358, n_D^{25} 1.4625.

Anal. Calcd. for $C_{10}H_9F_3$: C, 64.50; H, 4.87. Found: C, 64.41, 64.40; H, 4.87, 4.89.

β -Methyl-3-trifluoromethylstyrene



(12) Graham, unpublished work, Purdue University.

(13) W. E. Bachmann and Thomas, *THIS JOURNAL*, **64**, 94–97 (1942).

(14) Analysis by A. M. Ribley, Purdue University.

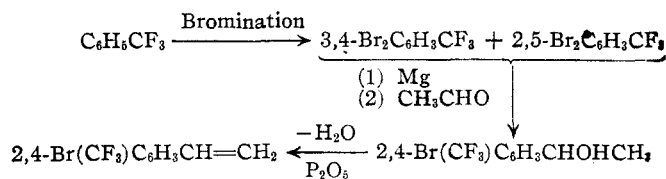
α -Ethyl-3-trifluoromethylbenzyl Alcohol.—A solution of 128 g. of propanal in 300 ml. of ether was added to the Grignard reagent from 450 g. of 3-bromo- α -trifluorotoluene in 2000 ml. of ether. Addition of 317 ml. of 25% ammonium chloride solution, filtration, and rectification gave 300 g. (73% yield) of the alcohol, b. p. 85–88° (5 mm.), d_{25}^{25} 1.197, n_D^{25} 1.4562.

Anal. Calcd. for $C_{10}H_{11}OF_3$: C, 58.81; H, 5.43. Found: C, 58.80, 58.71; H, 5.42, 5.45.

β -Methyl-3-trifluoromethylstyrene.—Dehydration of 172 g. of the above alcohol with 8 g. of phosphorus pentoxide under nitrogen at 175–195° (oil-bath) followed by distillation gave 87 g. (70% yield) of the styrene, b. p. 93–95° (40 mm.), d_{25}^{25} 1.136, n_D^{25} 1.4724.

Anal. Calcd. for $C_{10}H_9F_3$: C, 64.50; H, 4.87. Found: C, 64.42, 64.31; H, 4.89, 4.95.

2-Bromo-4-trifluoromethylstyrene



2,5- and 3,4-Dibromo- α -trifluorotoluene.— α -Trifluorotoluene was dibrominated according to the method of Graham¹² to give a product which, on distillation, separated into about equal amounts of solid and liquid phases. The solid was removed by filtration and recrystallized from an alcohol-water mixture. Large, white needles were formed, m. p. 49–50°; not changed by further recrystallization.

*Anal.*¹⁴ Calcd. for $C_7H_5Br_2F_3$: Br, 52.59; F, 18.75. Found: Br, 52.8, 53.1; F, 19.1, 18.8.

A 1-g. sample of these crystals was hydrolyzed by refluxing for two hours with 80% sulfuric acid. The acid obtained, after recrystallization from an alcohol-water mixture, melted at 156–157°.

*Anal.*¹⁴ Calcd. for $C_7H_4O_2Br_2$: Br, 57.10. Found: Br, 57.3, 57.4.

The melting point and analysis of the acid agree with those of 2,5-dibromobenzoic acid. Reported by Koopal,¹⁵ m. p. 157°. The solid isomer resulting from the dibromination of α -trifluorotoluene must therefore be 2,5-dibromo- α -trifluorotoluene.

The liquid portion of the dibromination product was rectified at 10-mm. pressure and a material boiling at 81–87° was obtained. A sample of this fraction was hydrolyzed by refluxing for two hours with 80% sulfuric acid and an acid was obtained melting at 234–235°. Further recrystallization from an alcohol-water mixture did not change the melting point, which agrees with that of 3,4-dibromobenzoic acid.^{16,17} The liquid isomer resulting from the dibromination of α -trifluorotoluene has therefore been identified as 3,4-dibromo- α -trifluorotoluene. Simons and Ramler¹¹ reported this isomer only in their bromination studies; b. p. 102–104° (25 mm.).

2-Bromo- α -methyl-4-trifluoromethylbenzyl Alcohol (IV).—A Grignard reagent was prepared from 70.6 g. (2.91 moles) of magnesium, 425.6 g. of the mixture of 2,5- and 3,4-dibromo- α -trifluorotoluenes and 152.6 g. (1.4 moles) of ethyl bromide in two liters of absolute ether. The Grignard reagent reacted with 144.6 g. of freshly-distilled acetaldehyde and the resulting addition product was decomposed with 25% ammonium chloride. After filtering and drying, the ether solution was distilled at 3 mm. (Claisen flask). The crude product, b. p. 98–108°, was rectified under vacuum through a 10-inch Fenske

(15) Koopal, *Rec. trav. chim.*, **34**, 148 (1915).

(16) Neville and Winther, *Ber.*, **13**, 970 (1880), m. p. 232–233°.

(17) Miller, *J. Chem. Soc.*, **61**, 1033 (1892), m. p. 232°.

column, and 96 g. of pure IV was obtained; b. p. 105–107° (3 mm.), d_{25}^{25} 1.601, n_D^{25} 1.5060.

Anal. Calcd. for $C_9H_8OBrF_3$: C, 40.17; H, 3.00. Found: C, 40.29, 40.36; H, 2.92, 3.04.

This alcohol was identified as 2-bromo- α -4-trifluoromethylbenzyl alcohol by conversion first to the styrene, and then, by oxidation and acid hydrolysis, to 2-bromoterephthalic acid. The experimental part for this identification is found in the following sections.

2-Bromo-4-trifluoromethylstyrene (V).—This styrene was prepared from IV in a manner similar to that described for the preparation of 3-trifluoromethylstyrene. From 25 g. (0.093 mole) of IV there was obtained 17 g. (0.0677 mole, 72.8% yield) of the styrene; b. p. 72–73° (5 mm.), d_{25}^{25} 1.558, n_D^{25} 1.5228.

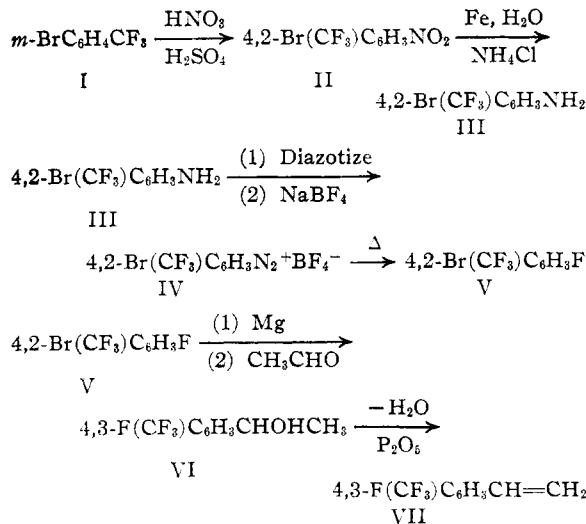
Anal. Calcd. for $C_9H_7BrF_3$: C, 43.05; H, 2.47. Found: C, 42.74, 42.87; H, 2.47, 2.53.

2-Bromo-4-trifluoromethylbenzoic Acid.—The structure of the above styrene was proven as follows. A sample was oxidized with potassium permanganate to the previously undescribed 2-bromo-4-trifluoromethylbenzoic acid. This acid, on recrystallization from an alcohol-water mixture, melted at 182–183°.

Anal. Calcd. for $C_9H_4O_2BrF_3$: C, 35.71; H, 1.50. Found: C, 35.65, 35.75; H, 1.62, 1.51.

A sample of the 2-bromo-4-trifluoromethylbenzoic acid was hydrolyzed with 80% sulfuric acid (two hours at reflux temperature) to give 2-bromoterephthalic acid, m. p. 296–298°. From the preceding considerations the structures of the alcohol (IV) and the styrene (V) must be as stated.

4-Fluoro-3-trifluoromethylstyrene



5-Bromo- α -trifluoro-2-nitrotoluene (II).—Nitration of 675 g. of I by a procedure analogous to that of Finger and Reed¹⁹ gave 753 g. (93% yield) of II, b. p. 95–100° (5 mm.), d_{25}^{25} 1.799, n_D^{25} 1.5180.

Anal. Calcd. for $C_7H_5O_2NBrF_3$: C, 31.14; H, 1.12. Found: C, 31.16, 31.28; H, 1.26, 1.16.

4-Bromo- α -trifluoro-*o*-toluidine (III).—Reduction¹⁹ of 753 g. of II gave 639 g. of III, b. p. 84–86° (5 mm.), d_{25}^{25} 1.712, n_D^{25} 1.5281.

Anal. Calcd. for $C_7H_5NBrF_3$: C, 35.02; H, 2.10. Found: C, 35.12, 35.01; H, 2.26, 2.17.

4-Bromo-2-trifluoromethylbenzenediazoniumfluoroborate (IV).—This diazonium salt was prepared from III accord-

(18) Fileti and Crosa, *Gazz. chim. ital.*, **16**, 300 (1876), m. p. 296–297°.

(19) Finger and Reed, *THIS JOURNAL*, **66**, 1972–1975 (1944).

ing to a similar procedure previously given¹⁹ for the preparation of 4-fluoro-2-trifluoromethylbenzenediazoniumfluoroborate. From 240 g. (1.0 mole) of III there was isolated 266 g. (0.785 mole) of the fluoroborate salt, yield 78.5%.

5-Bromo- α , α , α -2-tetrafluorotoluene (V).—Two hundred and sixty-two grams of the fluoroborate salt (IV) was decomposed by gentle heating in a 1-liter distilling flask fitted with a condenser set for downward distillation. Two 5000-ml. Erlenmeyer flasks, immersed in an ice-salt bath were used in series as receivers to insure complete condensation of the product. The distillate was washed several times with water, dried with calcium chloride and then distilled at 50 mm. pressure (Claisen flask). A colorless liquid (V), 162 g. (0.666 mole, 86% yield) was obtained; b. p. 78–83° (50 mm.), d_{25}^{25} 1.720, n_D^{25} 1.4580.

Anal. Calcd. for $C_7H_5BrF_4$: C, 34.59; H, 1.24. Found: C, 34.70, 34.60; H, 1.28, 1.22.

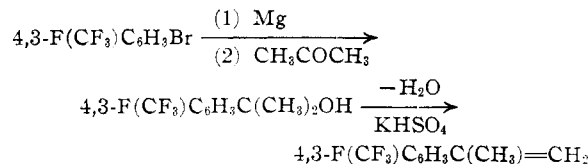
4-Fluoro- α -methyl-3-trifluoromethylbenzyl Alcohol (VI).—A solution of 9.5 g. of acetaldehyde in 50 ml. of ether was added to the Grignard reagent from 42 g. of V in 120 ml. of ether. Decomposition of the addition complex with 28 ml. of 25% ammonium chloride solution followed by filtration and rectification gave 22 g. (61% yield) of the alcohol, b. p. 86–87° (5 mm.), d_{25}^{25} 1.332, n_D^{25} 1.4461.

Anal. Calcd. for $C_9H_8OF_4$: C, 51.93; H, 3.87. Found: C, 51.69, 51.80; H, 3.67, 3.78.

4-Fluoro-3-trifluoromethylstyrene (VII).—Dehydration of 107 g. of VI with 5 g. of phosphorus pentoxide and 1 g. of picric acid at 140–170° and 90–100 mm. pressure followed by rectification gave 65 g. (70% yield) of VII, b. p. 77–78° (40 mm.), d_{25}^{25} 1.263, n_D^{25} 1.4522.

Anal. Calcd. for $C_9H_7F_4$: C, 56.85; H, 3.18. Found: C, 56.68, 56.83; H, 3.21, 3.16.

4-Fluoro- α -methyl-3-trifluoromethylstyrene



α , α -Dimethyl-4-fluoro-3-trifluoromethylbenzyl Alcohol.—A solution of 41.5 g. of acetone in 100 ml. of ether was added to the Grignard reagent from 162 g. of 5-bromo- α , α , α -2-tetrafluorotoluene in 900 ml. of ether. Decomposition with 100 ml. of 25% ammonium chloride solution, filtration and rectification gave 102 g. (70% yield) of the alcohol, b. p. 80–84° (5 mm.), d_{25}^{25} 1.285, n_D^{25} 1.4475.

Anal. Calcd. for $C_{10}H_{10}OF_4$: C, 54.11; H, 4.54. Found: C, 54.04, 54.15; H, 4.33, 4.47.

4-Fluoro- α -methyl-3-trifluoromethylstyrene.—This styrene was prepared from the above alcohol in a manner similar to that described for the preparation of α -methyl-3-trifluoromethylstyrene. From 100.6 g. (0.452 mole) of the alcohol there was obtained 70.5 g. (83% yield) of the styrene; b. p. 89–91° (40 mm.), d_{25}^{25} 1.230, n_D^{25} 1.4530.

Anal. Calcd. for $C_{10}H_9F_4$: C, 58.83; H, 3.95. Found: C, 58.67, 58.71; H, 3.95, 3.91.

Polymerization of Fluorinated Styrenes.—Samples of 4-fluorostyrene, 3-trifluoromethylstyrene, α -methyl-3-trifluoromethylstyrene, 2-bromo-4-trifluoromethylstyrene, 4-fluoro-3-trifluoromethylstyrene, 4-fluoro- α -methyl-3-trifluoromethylstyrene, and 4-fluoro- β -methyl-3-trifluoromethylstyrene containing 0.5% benzoyl peroxide were placed in small stoppered test-tubes (1 × 5 cm.) and heated in an oven at 70°. After three days the styrenes containing no methyl group on the α and β carbon had completely polymerized. The polymers were hard, tough, colorless, crystal clear materials. The α and β methylstyrenes failed to polymerize even after several weeks at 70°.

Pearl Polymerization of 3-Trifluoromethylstyrene.—The procedure was analogous to that described by Hohenstein, Vingiello and Mark²⁰ for styrene. Adjustment of the specific gravity of the aqueous phase with salt was necessary because of the high density of the fluorinated styrene. A mixture of 25 g. of 3-trifluoromethylstyrene, 0.25 g. of benzoyl peroxide, 500 g. of water, 76.5 g. of sodium chloride and 2.6 g. of talc was agitated slowly by means of a propeller-type stirrer at 80–85° for five hours. The resulting pearls were hard and translucent with an average diameter of 1–2 mm.; molecular weight 9370 (viscosity method, $K = 0.45 \times 10^4$, Kemp and Peters²¹).

Emulsion Polymerization of 3-Trifluoromethylstyrene.—Mixtures of 75 g. of 3-trifluoromethylstyrene, 450 ml. of water, 5 ml. of Tergitol Penetrant No. 4 and 0.15 g. (0.2%) of $K_2S_2O_8$ in each of 3 quart bottles were rotated in a polymerization bath at 40° for six days. The polymer was then coagulated by a saturated salt solution, washed, and dried. A molecular weight determination gave a value of 74,000 (Kemp and Peters²¹ equation).

The solubility characteristics of this polymer were determined and compared with those of polystyrene (mol. wt. 47,700). Under comparable conditions, polytrifluoromethylstyrene and polystyrene were soluble in chloroform, trichloroethylene, toluene, benzotrifluoride

(20) Hohenstein, Vingiello and Mark, *India Rubber World*, **110**, 291–294 (1944).

(21) Kemp and Peters, *Ind. Eng. Chem.*, **34**, 1097 (1942).

and dioxane. Benzene and carbon tetrachloride swelled the fluorinated polymer and dissolved polystyrene. Acetone, ethyl alcohol and ether dissolved the fluorinated polystyrene while polystyrene was insoluble. Petroleum ether swelled the fluorinated styrene and did not dissolve polystyrene, while nitroethane dissolved the polyfluorostyrene but only swelled the polystyrene.

Copolymerizations.—Copolymers of the fluorinated styrenes with vinyl acetate, methyl methacrylate, styrene and maleic anhydride were prepared by heating the mixed monomers at 70° in the presence of benzoyl peroxide. Typical, hard, transparent or translucent polymers resembling polystyrene were obtained in all cases except those involving α - or β -methylstyrenes with vinyl acetate, which failed to copolymerize. Elastic copolymers with butadiene were prepared using the usual GR-S synthetic rubber emulsion system with styrene replaced by the fluorinated styrenes. Only the β -methylstyrene failed to copolymerize. The properties of these copolymers will be described elsewhere.

Summary

1. The preparation of seven fluorinated styrenes, five of which are new, is described.
2. A study has been made of the polymerization and copolymerization characteristics of these styrenes.

LAFAYETTE, INDIANA

RECEIVED FEBRUARY 8, 1947

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

A Precise Method for the Determination of the Ionization Constants of Some Weak Organic Acids¹

BY RICHARD S. STEARNS² AND GEORGE W. WHELAND

Introduction

The present investigation has as its purpose the determination, by a spectrophotometric method, of the ionization constants of 4,4',4''-trinitrotriphenylmethane, 2,4-dinitrodiphenylamine, 2,4-dinitroaniline, and 4-nitrodiphenylamine in ethanol, and of *p*-nitrobenzyl cyanide in water.

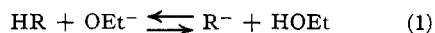
Theory of the Method

The method chosen for the determination of the ionization constants of the weak acids investigated here depends upon the fact that there is a difference between the positions of the absorption maxima of the undissociated compound, HR, and ion, R^- . This shift in the absorption maximum is illustrated in Fig. 1, where the curves for the absorption of light by 2,4-dinitroaniline in neutral and alkaline ethanol are plotted. This pronounced shift in the absorption maximum on ionization allows the concentration of the negative ion to be determined by standard spectrophotometric methods, provided Beer's law is obeyed and provided that the extinction coefficient of the colored ion is known.

(1) This paper comprises a part of the subject matter of a thesis submitted by Richard S. Stearns in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago.

(2) Present address: Chemical and Physical Research Laboratories, Firestone Tire and Rubber Company, Akron, Ohio.

The compounds investigated here are so weakly acidic that it is impossible to force the equilibrium of the reaction



so far to the right that virtually all of the compound HR is in the form of the ion R^- . Consequently, the extinction coefficient of the ion can not be calculated directly from the relation

$$kd = \log \frac{I_0}{I} / [R^-] \quad (2)$$

where k is equal to the molar extinction coefficient, $[R^-]$ is the concentration of R^- in moles per liter, d is the length of light path in centimeters, and I_0/I is the reciprocal of the fraction of light transmitted. Here, and throughout the remainder of this paper, the extinction coefficient of the ion R^- is assumed to be much greater, at the wave length used, than that of the un-ionized acid HR. In order to overcome the difficulty just referred to, a formula was developed which expresses an apparent extinction coefficient as a function of the concentration of base, and allows the true extinction coefficient at a given wave length to be determined by a short extrapolation.

If the concentration of the solvent ethanol is assumed constant, the equilibrium expression for the reaction written in equation 1 above is

$$K_e = (R^-)/(HR)(OEt^-) \quad (3)$$