RESULTS OF VISCOSITY MEASUREMENTS

Compound	t, °C.	Kinematic viscosity, centistokes	ASTM slope
$[-O_2C(CF_2)_3CO_2(CH_2)_3-]_n$[11]	0.2	5365	
	19.0	934.3	0.68
	76.4	39.3	
	99.5	17.27	
After standing for 64 days	0.2	4346	
	25.6	464.0	0.68
$[-O_2C(CF_2)_3CO_2(CH_2)_3-]_n$[12]	18.2	5190	
	21.9	3519	0.68
	76.6	91.95	
$[-O_2C(CF_2)_3CO_2(CH_2)_6-]_n$	0.0	4480	
	23.4	748	0.59
	27.4	578	
	75.8	57.5	

In a 200-ml. round bottom flask equipped with a modified Dean and Stark apparatus used as a phase separator and a reflux condenser to which a drying tube containing Drierite was attached, was placed 42.8 g. (0.2 mole) of heptafluorobutyric acid (Minnesota Mining and Manufacturing Co.), 10.4 g. (0.1 mole) of 1,5-pentanediol (du Pont Electrochemical), 30 ml. of redistilled toluene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for four hours. The reaction was followed by the rate of formation of water, which was carried over into the phase separator as an azeotrope with toluene. The theoretical amount of water (3.6–3.65 ml.) was obtained. The reaction mixture was allowed to cool, washed with a 5% solution of potassium carbonate, dried over anhydrous sodium sulfate and distilled. There was obtained 46.0 g. (92.7%) of diester, b.p. 103–104° (4 mm.). This reaction was also carried out and with similar results without the use of the inorganic acid catalyst.

Perfluorofatty Acid Chlorides.—The method used was described in the previous paper of this series.[2] The acid was mixed with phosphorus pentachloride, the reaction mixture heated under reflux for three to four hours and the product separated by distillation from the phosphorus oxychloride formed in the reaction. Yields of 59–90% were thus obtained. Perfluorocapryl chloride distilled at 174–175° at 747 mm., m.p. 27–28°.

Anal. Calcd. for $C_{10}F_{19}OCl$: Cl, 6.66. Found: Cl, 6.53.

Crude perfluorocaproyl chloride distilled at 90–100°.

Diesters from Perfluorofatty Acid Chlorides and Polymethylene Glycols.—In a 100-ml. round-bottom flask fitted with a water-cooled condenser vented through a drying tube containing Drierite was placed 43.3 g. (0.1 mole) of perfluorocaprylyl chloride and 6.2 g. (0.06 mole) of 1,5-pentanediol. There was no observed evolution of hydrogen chloride upon mixing. The reaction mixture was gently refluxed for six hours with evolution of hydrogen chloride. At first the reaction mixture consisted of two immiscible liquids which gradually formed a yellow, then finally a dark brown solution. After washing with 10% potassium carbonate solution until the upper, aqueous layer was free of chloride ion, the reaction mixture was washed with water, dried over anhydrous sodium sulfate and distilled. The yield of pure diester, b.p. 158–160° (mostly 159–160°) at 7 mm., was 26.4 g. (59%).

Diesters of Octafluoroadipic Acid and Hexafluoroglutaric Acid with Unfluorinated Alcohols.—This method is illustrated by the preparation of diisobutyl octafluoroadipate.

In a 200-ml. round bottom flask equipped with a modified Dean and Stark apparatus used as a phase separator and a water-cooled reflux condenser to which a drying tube was attached, was placed 29.0 g. (0.1 mole) of octafluoroadipic acid, 14.8 g. (0.2 mole) of isobutyl alcohol, 35 ml. of dry benzene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for two hours by which time the theoretical amount of water had been formed. After the benzene and excess alcohol had been removed by distillation, the crude ester was washed with 5% sodium bicarbonate, then with water, dried over anhydrous sodium sulfate and distilled, yielding 35.0 g. (87.1%) of diester, b.p. 117–118° at 8 mm.

Acknowledgment.—The authors wish to express their appreciation to Mr. Richard Sneed and Mrs. Lois Cook for technical assistance during this investigation, and to Minnesota Mining and Manufacturing Co. for their gift of some of the perfluorinated acids.

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[11] Prepared by the reaction of silver perfluoroglutarate and trimethylene diiodide.

[12] Prepared by condensation polymerization of perfluoroglutaric acid and trimethylene glycol.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The Synthesis and Polymerization of Some Fluorinated Styrenes[1]

BY MAURICE PROBER

RECEIVED MAY 13, 1952

A series of fluorinated styrenes, α,β,β-trifluorostyrene, β,β-difluorostyrene, α,β-difluorostyrene and α-chloro-β-fluorostyrene, was prepared starting with sodium difluoroacetate. α,β,β-Trifluorostyrene was also prepared by the direct reaction of chlorotrifluoroethylene and benzene. Good conversion to a high softening polymer was obtained with α,β,β-trifluorostyrene.

Discussion

Interest in the properties of the fluorinated polymers prompted an investigation into the synthesis and polymerization of fluorinated styrenes in which the fluorine was substituted in the vinyl side chain. When the problem was begun in this Laboratory, the only styrenes of this class described in the literature were β-fluorostyrene[2] and dichlorofluorostyrene,[3] neither of which was fully characterized. Recently the preparation of α,β,β-trifluorostyrene, α-chloro-β,β-difluorostyrene[4] and β-chloro-α,β-difluorostyrene[5] has been described, but no information concerning polymerization has appeared.

This paper consists of three parts: the synthesis of α,β,β-trifluorostyrene, α-chloro-β-fluorostyrene, α,β-difluorostyrene and β,β-difluorostyrene by the following reaction sequence; the direct synthesis of α,β,β-trifluorostyrene; and the polymerization behavior of these olefins.

The difluoroacetophenone (I) was prepared in

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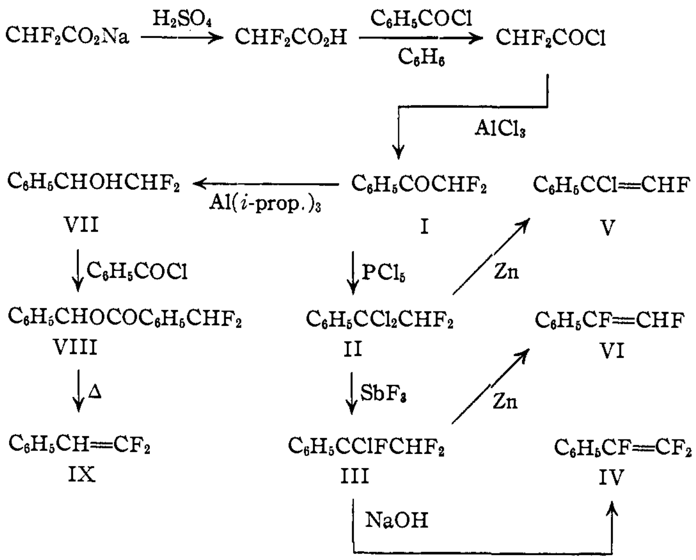
[1] Presented at the 120th Meeting of the American Chemical Society, New York, N. Y., September, 1951.

[2] F. Swarts, *Bull. soc. chim.*, [4] **25**, 145 (1919).

[3] V. Weinmayr, U. S. Patent 2,398,483 (June 19, 1945).

[4] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, THIS JOURNAL, **71**, 3439 (1949).

[5] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, *ibid.*, **72**, 3952 (1950).



69% yield by a procedure similar to that of Cohen, Wolosinski and Scheuer.[4] This ketone reacts with 2,4-dinitrophenylhydrazine and gives negative tests with Tollens reagent and neutral permanganate. Unlike acetophenone, it forms a crystalline solid with aqueous sodium bisulfite. This ketone is not soluble in sodium bicarbonate or carbonate, but is soluble in sodium hydroxide requiring one mole of base to dissolve one mole of ketone. The enol test with ferric chloride is negative and the reaction of the ketone with sodium is slow at room temperature, indicating that enolization is not responsible for the base solubility of the ketone. A possible explanation of this solubility behavior is the formation of a soluble sodium salt of the dihydroxy compound, for Simons and Ramler[6] have shown that α,α,α-trifluoroacetophenone, where enolization cannot take place, could be dissolved without cleavage in base, and dihydroxy structures of hexafluoroacetyl acetone have been isolated.[7]

The formation of α,α-dichloro-β,β-difluoroethylbenzene (II) is favored by slow heating with phosphorus pentachloride. Rapid heating results in some dehydrohalogenation. The pure dichloride hydrolyzes slowly in contrast to benzal chloride. However, the slightly lower boiling dehydrohalogenation product becomes strongly acid on exposure to air and this is the reason for the reported instability[4] of the dichloride.

In preparing III by reaction of the dichloride with antimony trifluoride, it was necessary to distil out the monochloride as rapidly as it was formed. The tetrafluoride and unreacted starting material predominated when this reaction was carried out under total reflux with a trace of antimony pentafluoride and the stoichiometric quantity of antimony trifluoride for replacement of a single chlorine atom. The monofluoride reacts very slowly with warm alcoholic silver nitrate, but more rapidly with alcoholic potassium hydroxide. The latter reaction results in a complex mixture of saturated and unsaturated ethers.

In testing the stability of II and III toward metals, considerable reaction was noted with zinc. This proved to be an unusual type of dehalogenation involving chlorine and fluorine on adjacent carbon atoms which has been observed with phenoxy-2,2-dichloro-1,1-difluoroethane.[8] This dehalogenation resulted in α-chloro-β-fluorostyrene (V) and α,β-difluorostyrene (VI).

Dehydrohalogenation of III was the most difficult step of the sequence. Reactions with tertiary amines, aqueous and nonaqueous basic solutions and ferric chloride did not produce the desired reaction. The trifluorostyrene (IV) was prepared in low yield by adding III to molten sodium hydroxide. This olefin as well as the other fluorostyrenes described in this paper have characteristic sweetish odors, quite unlike that of styrene. These fluoroölefins are also readily oxidized by neutral permanganate in acetone.

The Meerwein–Ponndorf–Verley reduction of the difluoroacetophenone to VII gave excellent yields if prolonged refluxing with aluminum isopropoxide was avoided. This alcohol is somewhat acidic, being soluble in 5% potassium hydroxide, but insoluble in 5% potassium carbonate. This alcohol reacts with sodium, reacts very slowly with neutral permanganate, gives a very weak ceric nitrate test and a negative secondary alcohol test with the zinc chloride–hydrochloric acid reagent.

As with other β-fluorinated alcohols,[9] the direct dehydration of (VII) was unsuccessful with such reagents as sulfuric acid, zinc chloride, phosphorus pentoxide, sirupy phosphoric acid, alumina and potassium hydroxide. However, pyrolysis of the esters gave the desired β,β-difluorostyrene. The acetate and benzoate esters were formed readily by reaction with the acid chloride. These esters are quite stable and it was necessary to operate above 600° to produce the olefin. The benzoate yielded a cleaner reaction product, but there was considerable carbonization and ketone (I) formation.

Preliminary polymerization results with trifluorostyrene were interesting and a more direct synthesis of this monomer was desired. This was accomplished by the intermolecular dehydrochlorination between benzene and chlorotrifluoroethylene. The reaction was carried out at an elevated temperature, 550°, using a flow type of apparatus with an unpacked Pyrex glass tube. With a mole ratio of chlorotrifluoroethylene to benzene of 1.3:1 and a contact time of 12.5 seconds, about half of the starting materials were recovered unreacted. The yield of styrene was 5.2% based on reacted chlorotrifluoroethylene and 7.9% based on the reacted benzene. The addition of small amounts of boron trifluoride increased the yield of the desired styrene. Under comparable conditions about 60% of the starting materials had reacted, and the yield of styrene was 6.6 and 9.5% based on the reacted chlorotrifluoroethylene and benzene, respectively.

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(6) J. H. Simons and E. O. Ramler, THIS JOURNAL, 65, 389 (1943).

(7) B. G. Schultz and E. M. Larsen, *ibid.*, 71, 3250 (1949).

(8) E. T. McBee and R. O. Bolt, *Ind. Eng. Chem.*, 39, 412 (1947).

(9) K. N. Campbell, J. O. Knobloch and B. N. Campbell, THIS JOURNAL, 72, 4380 (1950).

The position of the fluorine atoms in the styrene was proven by comparison of the physical constants with the literature values and by oxidation to benzoic acid.

Some of the compounds which are produced when chlorotrifluoroethylene and benzene are pyrolyzed individually were also found. Monochloropentafluoropropene, dichlorotetrafluoropropene, dichlorohexafluorobutene and 1,2-dichlorohexafluorocyclobutane were isolated. These compounds have been reported in the hot tube reaction of chlorotrifluoroethylene.[10] Biphenyl, a product of the benzene pyrolysis,[11] also was isolated.

Trifluoroethylene likewise was found and was formed probably by the reaction of chlorotrifluoroethylene and hydrogen, the latter arising from formation of biphenyl. In addition there were three higher boiling benzene derivatives containing unsaturated halogenated side chains. Analytical data suggest that these compounds resulted from the intermolecular dehydrochlorination of benzene and the halogenated propenes and butene.

The bulk polymerization of trifluorostyrene with several free radical catalysts was studied over the temperature range 65–130°. The yields of high melting polymer were below 10%. In working up the unreacted monomer, it was apparent that a significant side reaction, namely, dimerization of the trifluorostyrene, had taken place. This dimer was also isolated from the still pot residue of a vacuum distillation of the monomer. This dimer does not contain any simple olefinic bonds, and its ready formation at low temperature suggests that it also possesses the cyclobutane structure which has been observed with tetrafluoroethylene,[12] chlorotrifluoroethylene[13] and 1,1-dichloro-2,2-difluoroethylene.[13]

Emulsion polymerization resulted in satisfactory yields of high polymer. Using a potassium persulfate catalyst and dodecylamine hydrochloride emulsifier, an 83% conversion was obtained. This polymer has an intrinsic viscosity of 1.0 at 20° in toluene and has a softening point about 10° higher than that of the commercially available high molecular weight chlorotrifluoroethylene polymer (Kel-F, NST-300). This fluorinated styrene polymer, however, is brittle and is soluble in aromatic solvents. It undergoes slow cross-linking at 225°. It has good dielectric strength, a dielectric constant of 3.6 and a power factor which ranges from 0.002 to 0.005 over the range of 1 kilocycle to 1 megacycle.

The polymerization of the other styrenes was studied briefly. β,β-Difluorostyrene gives low yields of a thermally stable polymer which softens about 10° below the trifluorostyrene polymer. α,β-Difluorostyrene is polymerized rapidly by boron trifluoride, but the polymer is thermally unstable. α-Chloro-β-fluorostyrene does not polymerize.

Experimental

Difluoroacetyl chloride was prepared in 83% yield by treating sodium difluoroacetate[14] with concd. sulfuric acid followed by treating the acid with excess benzoyl chloride, b.p. 28.0–28.3° at 753 mm.; reported b.p. 25°[15] and 32–35°.[4]

Anal. Calcd. for C_2HOClF_2: Cl (hydrolyzable), 30.97; neut. equiv., 57.24. Found: Cl (hydrolyzable), 31.0; neut. equiv., 57.4.

The acid chloride was also obtained in 65% yield by reaction of the potassium salt directly with benzoyl chloride.

α,α-Difluoroacetophenone was obtained in 69% yield by a procedure similar to that reported for α,α,α-trifluoroacetophenone[4]; b.p. 86–87° at 30 mm., b.p. 185–186° at 754 mm., m.p. 9°, $n^{20}\mathrm{D}$ 1.4982; reported b.p. 83–85° at 29 mm.,[16] and 84–87° at 26–27 mm.[4]

Anal. Calcd. for $C_8H_6OF_2$: C, 61.54; H, 3.87; mol. wt., 156.1. Found: C, 61.8; H, 4.0; mol. wt., 155, 157.

The qualitative tests were carried out according to the procedures of Shriner and Fuson.[17]

α,α-Dichloro-β,β-difluoroethylbenzene was prepared in 91% yield by a slow reaction with a 10% excess of phosphorus pentachloride, followed by vigorous stirring with water to remove the phosphorus halides; b.p. 107–108° at 30 mm., 211–212° at 753 mm., m.p. −13°, d^{20}_4 1.384, $n^{20}\mathrm{D}$ 1.5086; reported b.p. 96–97° at 26–27 mm., $n^{30}\mathrm{D}$ 1.5046.[4]

Anal. Calcd. for $C_8H_6Cl_2F_2$: C, 45.53; H, 2.87; Cl, 33.60; mol. wt., 211.0. Found: C, 45.8, 45.4; H, 3.1, 2.9; Cl, 33.0; mol. wt., 209, 211.

The dichloride reacts slowly with alcoholic silver nitrate but rapidly with warm alcoholic potassium hydroxide.

α-Chloro-α,β,β-trifluoroethylbenzene.—A flask equipped with a total condensation partial take-off head was charged with 21.6 g. (0.121 mole) of antimony trifluoride and α,α-dichloro-β,β-difluoroethylbenzene (76.5 g., 0.0363 mole). The flask was heated to oil-bath temperature, 220–230°, and the distillate boiling at 185–190° was collected. It was washed with dilute hydrochloric acid, water and dried over calcium chloride. Rectification yielded 1.9 g. of α,α,β,β-tetrafluoroethylbenzene, 35.7 g. of α-chloro-α,β,β-trifluoroethylbenzene, b.p. 92–94° at 55 mm., 173–174° at 763 mm., d^{20}_4 1.328, $n^{20}\mathrm{D}$ 1.4686, and 23.5 g. of recovered starting material; yield of monochloride, 51% (67% based on reacted dichloride).

Anal. Calcd. for $C_8H_6ClF_3$: C, 49.38; H, 3.11; Cl, 18.22; mol. wt., 194.6. Found: C, 49.6, 50.0; H, 3.4, 3.2; Cl, 18.5, 18.4; mol. wt., 193, 196.

α,α,β,β-Tetrafluoroethylbenzene.—α,α-Dichloro-β,β-difluoroethylbenzene (105.6 g., 0.500 mole), antimony trifluoride (29.9 g., 0.167 mole) and antimony pentachloride (2.9 g., 0.0097 mole) and 100 cc. of Freon-113 were refluxed with stirring for six hours. The Freon solution was decanted off and the solid washed with fresh solvent. The solution was washed with dilute hydrochloric acid, water, dried and rectified, yielding 28.8 g. of the tetrafluoride, b.p. 67–68° at 60–61 mm., 139–140° at 756 mm., d^{20}_4 1.277, $n^{20}\mathrm{D}$ 1.4258, 11.1 g. of the monochloride, and 21.2 g. of starting material; yield of tetrafluoride 32% (40% based on reacted dichloride). A 54% yield of tetrafluoride was obtained with equal molar quantities of reactants without antimony pentachloride and solvent.

Anal. Calcd. for $C_8H_6F_4$: C, 53.94; H, 3.40; mol. wt., 178.1. Found: C, 53.5, 53.9; H, 3.6, 3.5; mol. wt., 177, 182.

The tetrafluoride did not undergo dehydrohalogenation with quinoline, aqueous potassium hydroxide, molten sodium hydroxide or the potassium iodide, zinc, acetamide procedure of McBee and Bolt.[3]

α,β,β-Trifluorostyrene.—A flask was charged with 40.7 g. of sodium hydroxide (containing 2% water), and heated to bath temperature 230–250°. α-Chloro-α,β,β-trifluoro-

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[10] C. Slesser, "Preparation, Properties, and Technology of Fluorine and Organic Fluorine Compounds," National Nuclear Energy Series VII-I, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 595–600, 665–667.

[11] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 545.

[12] J. Harmon, U. S. Patent 2,404,374 (July 23, 1946).

[13] A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 281 (1947).

[14] Obtained from Columbia Organic Chemicals Co., Columbia, S. C.

[15] F. Swarts, *Chem. Zentr.*, **74**, II, 710 (1903).

[16] J. H. Simons and D. F. Herman, THIS JOURNAL, **65**, 2064 (1943).

[17] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940.

ethylbenzene (33.0 g., 0.170 mole) was added dropwise to the stirred molten base. The distillate was diluted with Freon-113 to reduce mechanical loss, dried over calcium chloride and rectified (*t*-butylcatechol added to still-pot) yielding 3.4 g. of α,β,β-trifluorostyrene; b.p. 67–68° at 70 mm., $n^{20}\text{D}$ 1.4731, and 7.9 g. of unreacted monochloride; reported b.p. 68–70° at 75 mm., $n^{20}\text{D}$ 1.4741[4]; yield 13% (17% based on reacted monochloride).

Anal. Calcd. for $C_8H_5F_3$: C, 60.76; H, 3.19. Found: C, 60.4; H, 3.1.

α-Chloro-β-fluorostyrene.—α,α-Dichloro-β,β-difluoroethylbenzene (42.2 g., 0.200 mole), zinc dust (26.1 g., 0.400 mole) and 200 cc. of dry dioxane were refluxed with stirring for seven hours, and then steam distilled. The aqueous solution was extracted with chloroform, which was combined with the organic phase. After drying over calcium sulfate, the solution was rectified and there was obtained 16.4 g. (52% yield) of the desired product; b.p. 93–94° at 29 mm., $n^{20}\text{D}$ 1.5401.

Anal. Calcd. for C_8H_6ClF: C, 61.35; H, 3.86; Cl, 22.64. Found: C, 60.7; H, 4.0; Cl, 22.5.

α,β-Difluorostyrene.—α-Chloro-α,β,β-trifluoroethylbenzene (38.9 g., 0.200 mole), zinc dust (52.2 g., 0.798 mole) and 180 cc. of dry dioxane reacted for 27 hours according to the previously described procedure. Rectification gave 11.5 g. (41% yield) of α,β-difluorostyrene, b.p. 88–90° at 60 mm., $n^{20}\text{D}$ 1.5061.

Anal. Calcd. for $C_8H_6F_2$: C, 68.57; H, 4.32. Found: C, 68.7; H, 4.5.

This olefin polymerized on long standing at room temperature, probably due to acid formed by hydrolysis.

α-Phenyl-β,β-difluoroethanol.—α,α-Difluoroacetophenone (88.0 g., 0.563 mole), aluminum isopropoxide (0.353 mole) and 480 g. of isopropyl alcohol were refluxed under a short fractionating column. At the end of 5.5 hours, 280 cc. of distillate was collected and the acetone test[18] was negative. Excess isopropyl alcohol was removed under vacuum, the sirupy residue hydrolyzed with dilute hydrochloric acid and the aqueous solution extracted with ether. Rectification gave 80.0 g. (90% yield) of the alcohol, b.p. 107–108° at 19–20 mm., 212–213° at 758 mm., $n^{20}\text{D}$ 1.4942.

Anal. Calcd. for $C_8H_8OF_2$: C, 60.75; H, 5.10. Found: C, 60.5; H, 5.2.

α-Phenyl-β,β-difluoroethyl Acetate.—α-Phenyl-β,β-difluoroethanol (78.5 g., 0.497 mole) and acetyl chloride (47.2 g., 0.601 mole) were mixed and, after the initial reaction, heated at 110° for four hours. The product was washed with dilute potassium hydroxide, water, dried and rectified. There was obtained 87.8 g. (88% yield) of the acetate; b.p. 114–116° at 20 mm., 225–227° at 758 mm., $n^{20}\text{D}$ 1.4715.

Anal. Calcd. for $C_{10}H_{10}O_2F_2$: C, 60.00; H, 5.04; mol. wt., 200.2. Found: C, 60.5, 60.5; H, 5.3, 5.3; mol. wt., 199, 206.

α-Phenyl-β,β-difluoroethyl Benzoate.—α-Phenyl-β,β-difluoroethanol (146.3 g., 0.925 mole) and benzoyl chloride (143 g., 1.02 moles) were heated at 140° for two hours and the reaction product washed with dilute potassium hydroxide, water, dried and distilled under vacuum. There was obtained 228.0 g. (94% yield) of benzoate; b.p. 161–163° at 6.3 mm., $n^{20}\text{D}$ 1.5361.

Anal. Calcd. for $C_{15}H_{12}O_2F_2$: C, 68.70; H, 4.61; F, 14.49. Found: C, 68.9; H, 4.9; F, 14.6.

The ester was obtained as a viscous supercooled liquid, which crystallized when the container was accidentally jarred, m.p. 48–49°; recrystallized from heptane, m.p. 49–50°.

β,β-Difluorostyrene.—α-Phenyl-β,β-difluoroethylbenzoate (171.6 g., 0.655 mole) was passed through a 58 × 2 cm. Pyrex glass packed tube in seven hours. A 38-cm. section was heated at 625–636°. The reaction product was washed with dilute base, water, dried and vacuum distilled to give 26.5 g., b.p. 65–103° at 73 mm. This fraction was rectified, and there was obtained 8.8 g. (10% yield) of β,β-difluorostyrene; b.p. 65–66° at 61–62 mm., $n^{20}\text{D}$ 1.4925. Rectification of the residue gave 9.1 g. of α,α-difluoroacetophenone, b.p. 84–87° at 30 mm., $n^{20}\text{D}$ 1.4978, and 42.2 g. of unreacted benzoate (13% yield of styrene based on reacted benzoate).

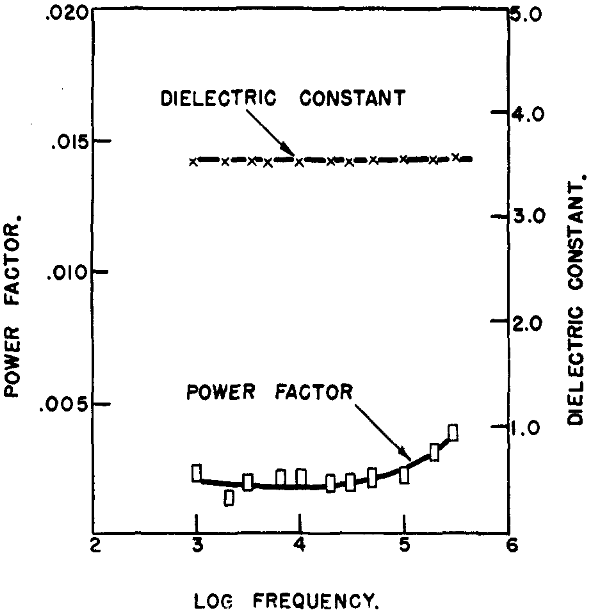

Fig. 1.—Dielectric properties of trifluorostyrene polymer.

Anal. Calcd. for $C_8H_6F_2$: C, 68.57; H, 4.32. Found: 68.8; H, 4.3.

The Direct Synthesis

The reactor was an unpacked 78 × 2.8 cm. Pyrex glass tube. A 30-cm. section of the tube was regulated at 550° by a Brown Pyrometer Controller with the thermocouple midway in the heated zone. The reactor was followed by a trap with a water-cooled condenser and two Dry Ice traps. The chlorotrifluoroethylene,[19] which had been scrubbed free of inhibitor by sulfuric acid, was metered through a calibrated rotameter, and the flow rate was constant to ±2%. The benzene (C.P. grade, thiophene-free) was added through a calibrated constricted capillary, and the rate of addition was constant to ±5%. The apparatus was first swept out with nitrogen and 234 g. (2.01 moles) of chlorotrifluoroethylene and 117.9 g. (1.51 moles) of benzene were passed into the tube in 4.5 hours. The water cooled trap contained 163.6 g., and the Dry Ice traps 172.6 g. There were also some very volatile acidic products not retained by the Dry Ice traps, which gave positive chloride and fluoride tests. The Dry Ice condensate was distilled through a potassium hydroxide solution, dried over calcium chloride and recondensed. The residue from this simple distillation was combined with the product in the water cooled trap, the solution diluted with methylene chloride to reduce mechanical loss, washed with dilute potassium hydroxide and rectified. After removing solvent, the following fractions were obtained: (a) 40–77.0°, 15.0 g.; (b) 77–80°, benzene, 34.5 g.; (c) 34–35° at 148 mm., benzene, 31.1 g.; (d) 35° at 148 mm.–66° at 69 mm., 3.1 g.; (e) 66–69° at 69 mm., α,β,β-trifluorostyrene, 8.4 g.; (f) 69° at 69 mm. to 98° at 68 mm., 4.1 g.; (g) 98–114° at 68 mm., 17.1 g.; (h) 69–114° at 10 mm., 10.2 g.; (i) 114–117° at 10 mm., 4.1 g.; (j) residue, 22.8 g. The low boiler was rectified through a 45 × 1 cm. helix packed low temperature column yielding (k) −50 to −30°, 6.8 g.; (l) −30 to −25°, chlorotrifluoroethylene, 112.9 g.; (m) −26 to 35°, 10.6 g.; (n) residue, 12.4 g.

In the boron trifluoride run, the gas was passed through a bubble counter, the rate averaging 57 bubbles per second. The reaction conditions were similar to those of the previous experiment: 245 g. of chlorotrifluoroethylene and 121.6 g. of benzene were passed through the tube in 4.5 hours, and 176.6 and 162.9 g. were collected in the water-cooled and Dry Ice traps, respectively. The product was worked up as above and there were obtained (1) 50.7 g. of benzene, (2) 93.6 g. of chlorotrifluoroethylene, (3) 13.6 g. of α,β,β-trifluorostyrene, b.p. 66–69° at 70 mm.

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[18] R. Adams, Ed., "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 200.

[19] Obtained from Kinetic Chemicals, Inc., Wilmington, Delaware.

α,β,β-Trifluorostyrene.—The styrene fractions of several runs were combined and rectified. Eighty per cent. of the distillate boiled at 66.2–67.5° at 70 mm., $n^{20}\mathrm{D}$ 1.4732, m.p. −23 to −24°; reported[4] b.p. 68–70° at 75 mm., $n^{20}\mathrm{D}$ 1.4741, m.p. −22 to −23°.

Anal. Calcd. for $C_8H_5F_3$: C, 60.76; H, 3.19. Found: C, 61.1; H, 3.4.

The styrene was oxidized to benzoic acid by refluxing 1.0 g. of α,β,β-trifluorostyrene for two hours with a solution of 2.0 g. of potassium dichromate in 20 cc. of water with 10 cc. of concd. sulfuric acid. The solution was extracted with ether, the ethereal solution shaken with potassium hydroxide solution and the basic solution acidified. Benzoic acid, 0.34 g., was filtered off, m.p. 121–122°, reported[15] m.p. 121°, mixed m.p. 121–122°.

Dimer of α,β,β-Trifluorostyrene.—A 6.9-g. residue, 15% of original charge in the still-pot, was obtained in the styrene purification, and it was distilled, yielding 6.5 g. of dimer; b.p. 120–121° at 6 mm., $n^{20}\mathrm{D}$ 1.4973. The dimer was saturated to permanganate in acetone.

Anal. Calcd. for $C_{16}H_{10}F_6$: C, 60.76; H, 3.19; mol. wt., 316.2. Found: C, 60.4; H, 3.5; mol. wt., 315, 315.

Phenylchlorofluoropropenes and Butene.—Fractions corresponding to (f) and (g) of several runs were combined, rectified and three plateaus in the ratio of 1:2:2 were obtained in the distillation curve: (i) 81–84° at 70 mm., $n^{20}\mathrm{D}$ 1.4428, (ii) 99–102° at 70 mm., $n^{20}\mathrm{D}$ 1.4620, and (iii) 108–110° at 70 mm., $n^{20}\mathrm{D}$ 1.4418. These compounds are believed to be pentafluorophenylpropene (i), chlorotetrafluorophenylpropene (ii) and chlorohexafluorophenylbutene (iii). It is believed that they arise from the dehydrochlorination involving benzene and the allylic chlorine of the chlorofluoroölefins formed by the pyrolysis of chlorotrifluoroethylene. All of these fractions gave strong permanganate unsaturation tests. They were oxidized following the procedure for α,β,β-trifluorostyrene, and benzoic acid was obtained (0.26 g. from (i), 0.22 g. from (ii) and 0.19 g. from (iii)). The shape of the distillation curve indicated that sharp separation of these components was not achieved (probably due to smaller quantities of other unknown components), so that discrepancies in the analytical results are not surprising.

Anal. Calcd. for $C_9H_5F_5$: C, 51.93; H, 2.42; Cl, 0.00; F, 45.64; mol. wt., 208. Found: C, 55.4; H, 2.6; Cl, 0.0; F, 43.8; mol. wt., 217, 217. Calcd. for $C_9H_5ClF_4$: C, 48.49; H, 2.24; Cl, 15.79; F, 33.84; mol. wt., 224.6. Found: C, 49.8; H, 2.9; Cl, 13.9; F, 32.5; mol. wt., 220, 227. Calcd. for $C_{10}H_5ClF_6$: C, 43.74; H, 1.84; Cl, 12.91; F, 41.52; mol. wt., 274.6. Found: C, 45.5; H, 2.3; Cl, 11.9; F, 38.0; mol. wt., 283, 274.

Biphenyl.—Fraction (i) had the characteristic biphenyl odor and the b.p. 114–117° at 10 mm. is in good agreement with the reported b.p. 117° at 10 mm.[20] Solid recrystallized from ethanol-water, m.p. 69–70°, reported 70°,[15] mixed m.p. 69–70°.

Trifluoroethylene.—Rectification of (i) through a Podbielniak low temperature column yielded 2.9 g. of trifluoroethylene, b.p. −61–−60°; calcd. mol. wt., 82.0; found mol. wt., 82; reported b.p. −51°.[21] The mass spectrometer pattern of this compound was consistent with trifluoroethylene. The dibromide of the olefin was prepared, b.p. 74–75°, reported 76.5.[19]

Chloropentafluoropropene.—The pyrolysis of chlorotrifluoroethylene resulting in this and succeeding olefins has been fully described by Miller.[10,22] Rectification of fraction (m) gave chlorotrifluoroethylene and 3.3 g., b.p. 8–9°, which was unsaturated and contained chlorine and fluorine; reported for chloropentafluoropropene, 8.3°[10]; calcd. mol. wt., 166.5; found mol. wt., 166. The olefin was chlorinated to the trichloride, b.p. 73°, $n^{20}\mathrm{D}$ 1.3510; reported b.p. 73.7°, $n^{20}\mathrm{D}$ 1.3503.[10]

Dichlorotetrafluoropropene.—Fractions (a) and (n) were combined, and rectified, yielding 5.3 g., which was unsaturated and contained chlorine and fluorine, b.p. −1–0° at 100 mm., 46–48° at atmospheric pressure, $n^{20}\mathrm{D}$ 1.3520. Reported for dichlorotetrafluoropropene, b.p. 47–48°, $n^{20}\mathrm{D}$ 1.3509[11]; calcd. mol. wt., 233.0; found mol. wt., 232. The propene was chlorinated to the tetrachloride, b.p. 112–113°, $n^{20}\mathrm{D}$ 1.3949; reported[10] b.p. 114°, $n^{20}\mathrm{D}$ 1.3959.

1,2-Dichlorohexafluorocyclobutane.—The above distillation yielded 8.7 g., b.p. 9–10° at 100 mm. This fraction gave a weak unsaturation test and it was chlorinated. On redistillation, about nine-tenths of the product boiled at 59–60° at atmospheric pressure, $n^{20}\mathrm{D}$ 1.3348, contained chlorine and fluorine, and was saturated; reported for 1,2-dichlorohexafluorocyclobutane, b.p. 60.4°, $n^{20}\mathrm{D}$ 1.3340[10]; calcd. mol. wt., 233.0; found mol. wt., 232.

Dichlorohexafluorobutene.—The rectification gave 3.0 g. which contained chlorine and fluorine and was unsaturated, b.p. 14–15° at 100 mm., 66–67° at atmospheric pressure; reported for dichlorohexafluorobutene, b.p. 65–66°; calcd. mol. wt., 233.0; found mol. wt., 234. The olefin was chlorinated to a tetrachloride, b.p. 133–134°, $n^{20}\mathrm{D}$ 1.3844; reported for 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane, b.p. 134–134.6°, $n^{20}\mathrm{D}$ 1.3850.[10]

Polymerization

Bulk polymerizations were carried out for 72 hours with benzoyl peroxide at 70–75° and with boron trifluoride at 1–4°. The boron trifluoride was measured volumetrically and condensed in the polymerization tube with liquid nitrogen. The polymer was precipitated by addition of methanol and dried in a vacuum oven. The softening points were determined by placing some of the polymer powder between two cover glasses of a Fisher–Johns melting point apparatus and heating slowly. Pressure was exerted on the upper cover glass with a small spatula, and the temperature at which the edges of the particles began to clear was taken as the softening point. The results are summarized in Table I.

TABLE I

Olefin	Catalyst	Catalyst concn., wt. %	Polymer, %	Softening point, °C.
$C_6H_5CF{=}CF_2$	Benzoyl peroxide	2.9	9.7	185–190
	Boron trifluoride	1.2	0	
$C_6H_5CH{=}CF_2$	Benzoyl peroxide	3.5	.4	176–180
	Boron trifluoride	2.4	.4	127–130
$C_6H_5CF{=}CHF$	Benzoyl peroxide	2.7	.7	
	Boron trifluoride	2.8	39	Strong decomp. 225–230
$C_6H_5CCl{=}CHF$	Benzoyl peroxide	2.7	0	
	Boron trifluoride	3.2	0	

The bulk polymerization of α,β,β-trifluorostyrene was carried out using 0.3 mole % of catalyst and heating for 72 hours. The *first figure* following the catalyst is the reaction temperature and the second is the yield of polymer: benzoyl peroxide, 65–68°, 6.2%; bisazoisobutyronitrile, 65–68°, 3.5%; ultraviolet light and bisazoisobutyronitrile, approx. 45–50°, 4.0%; *t*-butyl hydroperoxide, 81–83°, 4.3%; *t*-butyl perbenzoate, 101–104°, 0.7%; di-*t*-butyl peroxide, 120–123°, 6.4%. The softening points of these polymers all fell in the range 210–225°.

The methanol-soluble polymers from the above polymerizations were obtained by heating at 75° in a vacuum oven followed by pumping with a high vacuum system. The residues were mobile saturated liquids; calcd. mol. wt. of dimer, 316; found mol. wt., 315.

The dimerization is a significant side reaction and the approximate yields found in two of the above polymerizations are: benzoyl peroxide, 50%, *t*-butyl perbenzoate, 85%. The other fluorinated styrenes underwent little if any dimerization in bulk polymerization.

In the emulsion polymerization of α,β,β-trifluorostyrene, the styrene was distilled in a vacuum system into 2 cc. of a degassed aqueous solution containing 0.040 g. of emulsifier and 0.0015 g. of potassium persulfate. The emulsifiers with the corresponding quantities of styrene were: (a) Ivory soap, 0.234 g. (aqueous solution contained 0.010 g. of sodium tetraborate decahydrate to keep it alkaline); (b) Aerosol OT, 0.463 g.; (c) dodecylamine hydrochloride, 0.340 g. The sealed tubes were shaken at 50–55° for 72 hours. (Visual inspection of the polymerization tubes indicated that most, if not all, of the polymerization was over in less than 24 hours.) Tubes (a) and (c) contained colloidal dispersions. The polymer had coagulated in (b). The polymer was precipitated with methanol, washed and dried. Conversions were (a) 67%, (b) 47%, (c) 83%. Larger scale experiments with dodecylamine hydrochloride gave

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[20] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[21] Reference 18, p. 80.

[22] Abstracts of Papers, 119th Meeting, American Chemical Society, April, 1951, p. 33M.

similar results. The absence of considerable dimer in this experiment is attributed to the lower reaction temperature, and the slow rate of dimerization compared to emulsion polymerization.

The softening points for (a) and (b) were 240–245°. The initial clear temperature of (c) (procedure developed by Mr. D. W. Caird, New Product Development Laboratory, Pittsfield) was determined by compacting the polymer into a $^1/_8''$ cube, which is placed on a Fisher–Johns m.p. block. The upper cover glass supported a glass tube (held vertical in a bearing) which supported a 500-g. weight. The polymer was finally heated at 1° per minute, and the clear temperature defined as the temperature at which a translucent spot appeared at the center. This determination was reproducible to ±2°. The initial clear temperature of (c) was 237°. The initial clear temperature of Kel-F, NST-300, was 226°.

The polymer was soluble in aromatic solvents. Transparent films were cast from toluene solution, and they were about as brittle as polystyrene. The intrinsic viscosity of a toluene solution at 20.0° was 1.0 using concentrations in the range of 0.1–0.2 g. of polymer per 100 ml. This intrinsic viscosity probably corresponds to a mol. wt. in the range of 100,000 to 500,000.[23]

Strips of polymer were heat aged at 150–153°, 175–180° and 200–205° for 30 days in circulating air-ovens. The polymer had not discolored, fused, or become more brittle. Heat aging of polymer-powder under nitrogen at 225–230° for 33 days resulted in a weight loss of 0.7%, and some cross-linking, as evidenced by incomplete solubility of the polymer in excess toluene.

The electrical tests were run on a 5-mil sheet and the results are given below. The exact value of the AC dielectric strength could not be measured in the step-by-step test because of arcing around the edge of the samples, but it was greater than 1000 volts per mil.

The emulsion polymerization of β,β-difluorostyrene was carried out following the procedure described above. The emulsifier, per cent. conversion and softening points were: (a) Ivory soap, 3.5%, 207–211°; (b) Aerosol OT, 2.8%, 208–213°; *n*-dodecylamine hydrochloride, 7.3%, 220–225°. No decomposition was noted in these softening point determinations.

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SCHENECTADY, N. Y.

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[23] A. Weissberger, Ed., "Physical Methods of Organic Chemistry," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, p. 351.

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF LOUISVILLE SCHOOL OF MEDICINE]

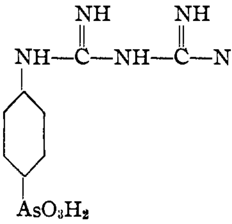
Some Derivatives and Analogs of 4-Biguanidophenylarsonic Acid[1]

BY ROBERT L. MCGEACHIN

RECEIVED SEPTEMBER 19, 1952

2-(4-Arsonophenylguanidino)-4,6-dimethylpyrimidine has been prepared from 4-biguanidophenylarsonic acid by condensation with pentanedione-2,4 and was found to have trypanocidal activity. 4-Biguanidobenzoic acid was prepared and also condensed with pentanedione-2,4 to give 2-(4-carboxyphenylguanidino)-4,6-dimethylpyridine, which proved to be highly toxic to rats.

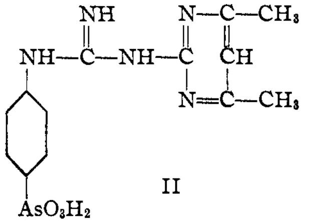
In the studies of preparation of protozoacidal organic arsenicals, 4-biguanidophenylarsonic acid



I

(I), previously reported by both Banks[2] and Sato,[3] was prepared by condensation of *p*-arsanilic acid and dicyandiamide. A modification of Sato's method was used since, in our hands, it gave more satisfactory results than those reported previously. Related compounds have been reported by Roy and Guha,[4] Bogert and Stickler[5] and Sweet, *et al.*[6]

Reports[7] that pentanedione-2,4 condenses with guanidines to give dimethylpyrimidines led us to attempt the condensation of I with pentanedione-2,4. Interest in this reaction was initially aroused by the report of Curd and Rose[8] who found that some of the pyrimidylguanidino compounds formed in the reaction of biguanides with ethyl acetoacetate had therapeutic value as antimalarials. It was also noted that the dimethylpyrimidino group expected from this reaction would be the same as that found in sulfamethazine. Condensation of I with pentanedione-2,4 in alkaline medium gave 2-(4-arsonophenylguanidino)-4,6-dimethylpyrimidine (II).



II

The condensation seems to involve only the terminal amidino group of the biguanido side-chain, two molecules of water being eliminated in the course of the reaction. One molecule of water is formed from the hydrogen of the imino group plus a hydroxyl from the enol form of pentanedione-2,4 and the other from the two hydrogens of the amino group plus the ketonic oxygen in the pentanedione-2,4. II is readily soluble in dilute alkali and mod-

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[1] This work was aided by a grant to the University of Louisville from the Kentucky State Medical Research Commission.

[2] C. K. Banks, J. Controulis and W. F. Holcomb, THIS JOURNAL, **68**, 2102 (1946).

[3] M. Sato, *J. Pharm. Soc. Japan*, **69**, 303 (1949).

[4] A. C. Roy and P. C. Guha, *J. Sci. Ind. Research (India)*, **9B**, 242 (1950).

[5] M. T. Bogert and W. T. Stickler, *Science*, **100**, 526 (1944).

[6] L. A. Sweet, *et al.*, THIS JOURNAL, **69**, 2258 (1947).

[7] Private communication from the Carbide and Carbon Chemicals Company.

[8] F. H. S. Curd and F. L. Rose, *J. Chem. Soc.*, 362 (1946).