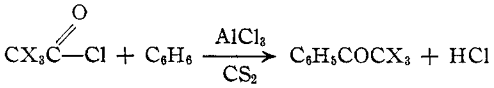
[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

α,β,β-Trifluorostyrene and α-Chloro-β,β-difluorostyrene[1]

BY SAUL G. COHEN, HENRY T. WOLOSINSKI AND PAUL J. SCHEUER[1a]

Consideration of the useful properties of the polymers of tetrafluoroethylene, $CF_2{=}CF_2$,[1b] and chloro trifluoroethylene, $CF_2{=}CFCl$,[2] has indicated to us the desirability of preparing and studying the phenyl derivatives of these compounds. There are now in the literature several references to styrenes which contain fluorine or trifluoromethyl substituents in the benzene ring,[3] but apparently only one reference to a phenylperchlorofluoroethylene[4] and that to a monofluorodichlorostyrene with its exact structure unspecified. Recently an unsuccessful attempt to prepare β-fluorostyrene has been reported.[5] In this paper, we are reporting the preparation of α,β,β-trifluorostyrene, $C_6H_5CF{=}CF_2$ (I) and α-chloro-β,β-difluorostyrene, $C_6H_5CCl{=}CF_2$ (II).

In the course of this work, chlorodifluoroacetophenone, $C_6H_5COCClF_2$, trifluoroacetophenone, $C_6H_5COCF_3$, and difluoroacetophenone, $C_6H_5COCHF_2$ were prepared by the Friedel–Crafts reactions of the corresponding acid chlorides with benzene in the presence of aluminum chloride.



$$CX_3C(=O)-Cl + C_6H_6 \xrightarrow[CS_2]{AlCl_3} C_6H_5COCX_3 + HCl$$

Trifluoroacetyl chloride[6] and monofluoroacetyl chloride[5,7] have been used in this type of reaction, while treatment of benzene with chlorofluorocarbons and aluminum chloride has been unsuccessful.[8] Optimum conditions for carrying out this Friedel–Crafts reaction are described under the preparation of trifluoroacetophenone. Single attempts to prepare this compound by treatment of diphenylcadmium with trifluoroacetyl chloride[9] and by the Friedel–Crafts reaction of trifluoroacetic acid and benzene failed.

Each of the three ketones was converted to the corresponding dichloride by reaction with phosphorus pentachloride, leading to the compounds $C_6H_5CCl_2CClF_2$, (IV) $C_6H_5CCl_2CF_3$,[6] (V) and $C_6H_5CCl_2CHF_2$.

$$C_6H_5COCX_3 + PCl_5 \longrightarrow C_6H_5CCl_2CX_3 + POCl_3$$

Use of 50 mole per cent.[6] excess phosphorus pentachloride and long heating under reflux was found desirable. Removal of the excess phosphorus pentachloride, whether by filtration or washing,[6] was inconvenient and either was incomplete or led to diminished yields. Treatment of the reaction mixture with a quantity of acetone equivalent to the excess phosphorus pentachloride converted it to phosphorus oxychloride, from which the desired products were readily separated and isolated in 85–90% yield. This greatly facilitated our preparation of compounds IV and V.

The compounds IV and V, $C_6H_5CCl_2CClF_2$ and $C_6H_5CCl_2CF_3$, were each treated with one-third mole of antimony trifluoride and catalytic quantities of bromine at 140–170°.

$$C_6H_5CCl_2CX_3 + {}^1/_3SbF_3 \xrightarrow{Br_2} C_6H_5CClFCX_3 + {}^1/_3SbCl_3$$

The products were mixtures which appeared to contain both starting materials and the products of replacement of two chlorine atoms by fluorine as well as the desired products of replacements of one chlorine atom by fluorine, $C_6H_5CClFCClF_2$ (VI) and $C_6H_5CClFCF_3$[10] (VII). The latter compounds were isolated in about 35% yield.

The desired α,β,β-trifluorostyrene (I) and α-chloro-β,β-difluorostyrene (II) were prepared by the zinc dechlorination of the corresponding pentahaloethylbenzenes.

$$C_6H_5CClFCClF_2 + Zn \xrightarrow[\text{ethanol}]{\text{absolute}} C_6H_5CF{=}CF_2\ (I) + ZnCl_2$$

$$C_6H_5CCl_2CClF_2 + Zn \xrightarrow[\text{ether}]{\text{anhydrous}} C_6H_5CCl{=}CF_2\ (II) + ZnCl_2$$

α,β,β-Trifluorostyrene (I) was obtained in 48% yield, b. p. 68–69° (75 mm.), $n^{20}D$ 1.4741, m. p. -23.0 to $-22°$. Its formation in this way supplies evidence for the assigned structure of the intermediate, $C_6H_5CClFCClF_2$. α-Chloro-β,β-difluorostyrene (II) was obtained in 70% yield, b. p. 100° (100 mm.), $n^{20}D$ 1.5080.

Acknowledgment.—The authors wish to acknowledge helpful discussions with Dr. E. R. Blout.

Experimental

Sodium trifluoroacetate was obtained from the Hooker Electrochemical Company. **Sodium difluoromonochloroacetate** was obtained from Columbia Organic Chemicals, Inc.

Barium difluoroacetate and **sodium difluoroacetate** were prepared in 37% yield and 28% yield, respectively, by oxidation of 1,2-dichloro-3,3-difluoro-1-propene by a procedure similar to that described for the oxidation of the

---

[1] This work was sponsored by the Signal Corps, Department of the Army, and A. M. C., Electronics Subdivision, U. S. Air Force.

[1a] Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts.

[1b] Renfrew and Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).

[2] Anonymous, *Modern Plastics*, **26**, 168 (1948).

[3] Bachman and Lewis, THIS JOURNAL, **69**, 2022 (1947); Brooks, *ibid.*, **66**, 1295 (1944); Renoll, *ibid.*, **68**, 1159 (1946); Brooks and Nazzewski, U. S. Patent 2,406,319.

[4] Weinmayr, U. S. Pat. 2,398,483.

[5] Truce and Sack, THIS JOURNAL, **70**, 3959 (1948).

[6] Simons and Ramler, *ibid.*, **65**, 389 (1943).

[7] Gryszkiewicz-Trochimowski, Sporzynski and Wnuk, *Rec. trav. chem.*, **66**, 419 (1947).

[8] Henne and Newman, THIS JOURNAL, **60**, 1697 (1938).

[9] Jones, *ibid.*, **70**, 143 (1948).

[10] Simons and Herman, *ibid.*, **65**, 2064 (1943).

isomeric 1,1-dichloro-3,3-difluoro-1-propene.[11] 1,2-Dichloro-3,3-difluoro-1-propene was obtained from Halogen Chemicals, Inc.

Chlorodifluoroacetyl chloride was prepared by the interaction of sodium chlorodifluoroacetate (0.65 mole) and phosphorus trichloride (0.59 mole) for 2.5 hours at 100° under reflux. The product was distilled out, 77.5 g., (80% yield) boiling under 40°. A sample was converted to the amide, m. p. 76.5°. This chloride has been prepared by the chlorination of difluoroethanol,[12] b. p. 34°.

Trifluoroacetyl chloride[6] was prepared in 90% yield by the interaction of sodium trifluoroacetate (1.24 mole) and phosphorus oxychloride (1.83 moles) for twenty-one hours at 100° under reflux, the product condensing in a dry ice trap. A sample was converted to the amide, m. p. 74–75°.

Difluoroacetyl chloride was prepared by interaction of sodium difluoroacetate (0.312 mole) and phosphorus trichloride (0.69 mole) under reflux for twenty-one hours. The product boiled at 32–35°, 69% yield. The reported boiling point is 25°.[13]

α,α,α-Trifluoroacetophenone.[6]—Trifluoroacetyl chloride (180 g., 1.35 moles) was distilled over a period of four hours into a well stirred, cooled suspension of aluminum chloride (1.60 moles) in benzene (1.60 moles) and carbon disulfide (490 cc.). The reaction started at 10°, was run at 2–3°, and finally at room temperature for a short time. The complex was decomposed in 335 cc. of concentrated hydrochloric acid and 1900 g. of ice. The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were combined, filtered free from a black precipitate which was then further extracted. The extracts were dried and distilled, leading to trifluoroacetophenone, 150.6 g., 64% yield, b. p. 66–67° (37 mm.), n^{20}D 1.4576.

α,α,α-Difluorochloroacetophenone was prepared similarly, 68% yield, b. p. 95–97° (37 mm.), n^{20}D 1.4954. *Anal.* Calcd. for $C_8H_5OClF_2$: Cl, 18.6. Found: Cl, 18.2. This compound has been obtained in 8% yield in the fluorination of trichloroacetophenone.[10]

α,α-Difluoroacetophenone was prepared, 58% yield, b. p. 84–87° (26–27 mm.), in a standard Friedel–Crafts procedure in carbon disulfide at 10°. This compound has been prepared by the fluorination of acetophenone and the fluorination of dibromoacetophenone.[10]

α,α-Dichloro-β,β,β-trifluoroethylbenzene, $C_6H_5CCl_2$-CF_3.[6]—Trifluoroacetophenone (25 g., 0.14 mole) and phosphorus pentachloride (44 g., 0.21 mole) were heated under reflux for twenty-one hours, oil-bath temperature, 175°. Acetone (4.1 g., 0.07 mole) was added to the cooled reaction mixture, and, after the vigor of the ensuing reaction subsided, the product was fractionated and the desired material was obtained, 29 g., 90% yield, b. p. 88–90° (37 mm.), n^{20}D 1.4767. *Anal.* Calcd. for $C_8H_5Cl_2F_3$: Cl, 31.0. Found: Cl, 31.5.

α,α,β-Trichloro-β,β-difluoroethylbenzene, $C_6H_5CCl_2$-$CClF_2$, was prepared similarly from difluorochloroacetophenone, 78% yield, b. p. 98–99° (15 mm.), n^{20}D 1.5106. *Anal.* Calcd. for $C_8H_5Cl_3F_2$: Cl, 43.5. Found: Cl, 42.4.

α,α-Dichloro-β,β-difluoroethylbenzene, $C_6H_5CCl_2$-CF_2H, was prepared similarly except that excess phosphorus pentachloride was removed by repeated filtration. The product was obtained in about 70% yield, fuming liquid, b. p. 96–97° (26–27 mm.), n^{30}D 1.5046.

α-Chloro-α,β,β,β-tetrafluoroethylbenzene, C_6H_5CCl-FCF_3.[10]—α,α-Dichloro-β,β,β-trifluoroethylbenzene was treated with one-third mole of antimony trifluoride and 10 mole per cent. of bromine at 150–170° for two hours with stirring. The product was cooled, washed, dried and distilled. Redistillation of the middle fraction, which boiled at 84–109° (100 mm.), led to the product, 35% yield, b. p. 85–86° (100 mm.), n^{20}D 1.4463. *Anal.* Calcd. for $C_8H_5ClF_4$: Cl, 16.7. Found: Cl, 16.0.

α,β-Dichloro-α,β,β-trifluoroethylbenzene, C_6H_5CFCl-CF_2Cl.—α,α,β-Trichloro-β,β-difluoroethylbenzene, C_6H_5-CCl_2CClF_2 (51 g. 0.21 mole), antimony trifluoride (12.5 g., 0.070 mole) and bromine (0.56 g., 0.0035 mole) were heated under reflux with stirring for one hour at 140°. The product was taken up in ether, washed dried and distilled. The desired product was obtained, 17.8 g., 37% yield, b. p. 92–94° (38 mm.), n^{20}D 1.4766. *Anal.* Calcd. for $C_8H_5Cl_2F_3$: Cl, 30.8. Found: Cl, 30.3. Some starting material was recovered, 10.5 g., b. p. 101° (16–17 mm.), $n^{25.4}$D 1.5075.

α-Chloro-β,β-difluorostyrene, $C_6H_5CCl{=}CF_2$.—α,α,β-Trichloro-β,β-difluoroethylbenzene (20 g., 0.081 mole) was treated with acid-washed zinc dust (5.55 g., 0.0854 mole) and one crystal of dried zinc chloride in 20 g. of anhydrous ether with stirring, under reflux. The solution was decanted from the residual zinc (0.014 g.), washed with dilute hydrochloric acid and water, dried and distilled through a 36″ wire spiral column at 10/1 reflux ratio. The product was obtained, 9.9 g., 70% yield, b. p. 100–100.5° (100 mm.), n^{20}D 1.5080. *Anal.* Calcd. for $C_8H_5ClF_2$: C, 55.0; H, 2.9; Cl, 20.3; F, 21.7. Found: C, 54.8; H, 3.0; Cl, 20.1; F, 21.8, 22.3.

α,β,β-Trifluorostyrene, $C_2H_5CF{=}CF_2$.—α,β-Dichloro-α,β,β-trifluoroethylbenzene (12.9 g., 0.056 mole), acid washed zinc (3.8 g., 0.059 mole) and a few crystals of dried zinc chloride in 15 cc. of absolute ethanol were boiled under reflux for two hours with occasional shaking. The solution was decanted from residual solid (0.37 g.), washed with 10% hydrochloric acid and water, dried and distilled. The product was obtained, 4.3 g., 48% yield, b. p. 68–70° (75 mm.), m. p. −23 to −22°, n^{20}D 1.4741. *Anal.* Calcd. for $C_8H_5F_3$: C, 60.8; H, 3.2; F, 36.0. Found: C, 60.7; H, 3.2; F, 35.7. This material appeared to contain about 0.4% Cl. Treatment with zinc at 120° for one hour and redistillation from the zinc led to a product which contained less than 0.2% Cl.

Summary

α,β,β-Trifluorostyrene, $C_6H_5CF_2{=}CF_2$, and α-chloro-β,β-difluorostyrene, $C_6H_5CCl{=}CF_2$ have been prepared by the dechlorination of α,β-dichloro-α,β,β-trifluoroethylbenzene, C_6H_5CClF-$CClF_2$, and α,α,β-trichloro-β-β-difluoroethylbenzene, $C_6H_5CCl_2CClF_2$, respectively.

CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 21, 1949

---

[11] A. L. Henne, T. Alderson and M. S. Newman, *ibid.*, **67**, 918 (1945).

[12] Swarts, *Mém. couronnés acad. roy. Belg.*, 51 (1895).

[13] Swarts, *Chem. Centr.*, **7**, II, 710 (1903).