Tetrahedron, 1964, Vol. 20, pp. 1625 to 1632. Pergamon Press Ltd. Printed in Northern Ireland

SYNTHESIS AND CHEMISTRY OF SEVERAL FLUORINATED *p*-XYLENES DESIGNED AS PRECURSORS FOR α,α,α′,α′-TETRAFLUORO-*p*-XYLYLENE

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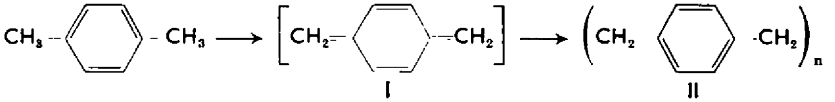
(*Received* 27 *January* 1964; *in revised form* 10 *March* 1964)

Abstract—Attempts to prepare and isolate α,α,α′,α′-tetrafluoro-*p*-xylylene (III) from several compounds designed as precursors were not successful. Pyrolysis of α,α,α′,α′-tetrafluoro-*p*-xylene (V) gave a mixture of β,β,*p*-trifluorostyrene (XIV) and 1,1,5-trifluorobenzocyclobutene (XIX). A novel synethsis of XIV was achieved.

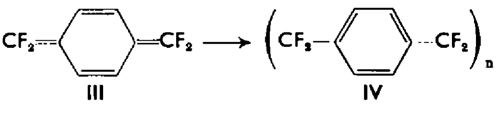
Among the organic compounds that have attracted theoretical interest prior to their actual synthesis is *p*-xylylene or quinodimethan (I). As early as 1945 Namiot *et al.*[3] discussed the compound, examined the relative stability of singlet and triplet forms, and concluded that the energy difference between the two was very small. Later, Szwarc[4] obtained evidence for the existence of I, and proposed it as an intermediate in the gas phase pyrolysis of *p*-xylene to form the polymer (II).



He proved the existence of I by injecting iodine into the gas stream and isolating *p*-xylylene diiodide.

It was not until 1957 that a practical method of preparing I was developed. Errede and Landrum[5] isolated solutions of I using a modification of the Szwarc pyrolysis procedure, and were able to study its properties and reactions. Although *p*-xylylene in the condensed phase was unstable at −190°, frozen hexane solutions at this temperature proved to be stable indefinitely. The half-life of these solutions at −78° was 21 hours.

The work on *p*-xylylene aroused our interest in the possibility of preparing fluorinated derivatives, particularly α,α,α′,α′-tetrafluoro-*p*-xylylene or 7,7,8,8-tetrafluoroquinodimethan (III). This compound might then be polymerized under controlled conditions to give the poly-*p*-xylylene structure (IV). Calculations by the molecular orbital method



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[1] Deceased.

[2] To whom inquiries should be addressed.

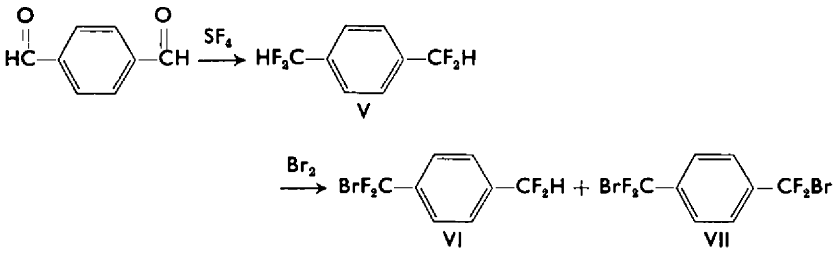
[3] A. J. Namiot, M. E. Dyatkina, and Ya. K. Syrkin, *C. R. Acad. Sci., U.S.S.R.* **48**, 267 (1945).

[4] M. Szwarc, *J. Chem. Phys.* **16**, 128 (1948).

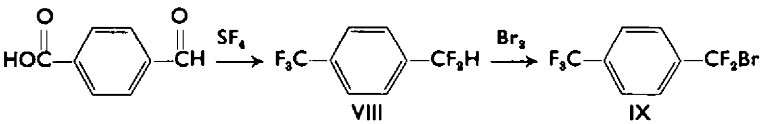
[5] L. A. Errede and B. F. Landrum, *J. Amer. Chem. Soc.* **79**, 4952 (1957).

were made in an attempt to determine the relative stability of III as compared to I. These calculations indicated that the resonance energy of III would be greater than I, that III should have a greater energy difference between the singlet and triplet states, and that the "free valence" of the terminal carbon atoms in III should be less. From these results, it was concluded that III should have a lower susceptibility toward radical attack than the unfluorinated species and thus be more stable in the liquid phase.[6]

Three precursors for the preparation of III were synthesized by the following sequence: terephthalaldehyde was treated with sulfur tetrafluoride to give α,α,α′,α′-tetrafluoro-*p*-xylene (V) which was brominated to give a readily separable mixture of α-bromo-α,α,α′,α′-tetrafluoro-*p*-xylene (VI), and α,α′-dibromo-α,α,α′,α′-tetrafluoro-*p*-xylene (VII). The latter compound was obtained in 27% overall yield from the commercially available terephthaldehyde. A very recent report[7] described the preparation of VII in 12% overall yield in three steps from 1,4,-dibromo-1,4-bis(trifluoromethyl)cyclohexane.



Two additional precursors for the preparation of III were obtained by treating 4-carboxybenzaldehyde with sulfur tetrafluoride to give α,α,α,α′,α′-pentafluoro-*p*-xylene (VIII), and by brominating VIII to get α-bromo-α,α,α′,α′α′-pentafluoro-*p*-xylene (IX). A byproduct of the sulfur tetrafluoride reaction was *p*-difluoromethylbenzoyl fluoride which was characterized as the dimethylamide.



All of the synthesized precursors were pyrolyzed under a wide variety of conditions. The bromine-containing precursors were treated with quinoline zinc, magnesium, lithium, and sodium under refluxing conditions, and also in sealed tubes. They were also pyrolyzed over zinc. A careful examination of all products by gas chromatography failed to provide any evidence for the presence of III. In most cases an ill-defined mixture of polymeric materials was obtained. In view of the extensive rearrangements that might occur during these reactions (see below), it would seem rash to describe the polymeric material as a poly-*p*-xylylene structure, even though some of the elemental analyses were roughly in agreement with such an assumption.

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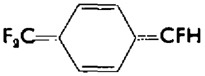
[6] These calculations were carried out by Dr. Dale E. Van Sickle of these laboratories.

[7] W. R. Herter, *J. Amer. Chem. Soc.* **28**, 2877 (1963).

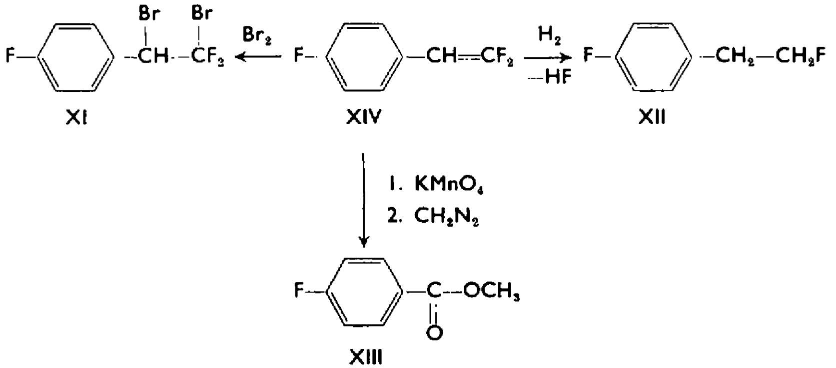
An unsuccessful attempt to isolate III from a pyrolysate of VII has recently been reported.[7]

A sample of α,α,α′,α′-tetrafluoro-*p*-xylene (V) was pyrolyzed by passing the vapor through a Vycor tube filled with Vycor chips at 850–925° at 3–5 mm. The components of the condensate were separated by gas chromatography. The major component, A, had a molecular weight of 158 (mass spectrometer) which corresponds to loss of HF. The IR spectrum showed a strong peak at 5·74 μ. The proton NMR spectrum showed four protons at 2·62–3·19 τ and one proton as four peaks at 4·72 τ. On treatment of this compound with t-butyl perbenzoate at 100° for 60 hr, a polymer was obtained, which could be precipitated from benzene solution with methanol. The white solid polymer had a molecular weight of about 5700, and gave carbon, hydrogen, and fluorine values that corresponded approximately to those calculated for $(C_8H_5F_3)_n$, the polymer expected from X. These data and the elemental analysis were at first taken as evidence for a monomer of structure X, α,α,α′-trifluoro-*p*-xylene. Long-range coupling with the ring *ortho* protons was invoked to explain the splitting of the proton at 4·72 τ.



X

Further investigation, however, revealed that component A was in fact the product of a drastic rearrangement. Bromination of component A gave α,β-dibromo-β,β,*p*-trifluoroethylbenzene (XI). Hydrogenation gave β,*p*-difluoroethylbenzene (XII), and permanganate oxidation followed by treatment with diazomethane gave methyl *p*-fluorobenzoate (XIII). Component A was therefore β,β,*p*-trifluorostyrene (XIV).



The UV spectrum of component A, with its strongest peak at 237 mμ (ε = 14,200) and its typical benzenoid absorption peaks between 270 mμ and 290 mμ, was certainly more consistent with a styrene structure (XIV) than with a conjugated hexatriene structure (X).

The mechanism for the drastic rearrangement V → XIV is not known. Quite possibly it may proceed through a cyclooctatetraene intermediate. Both cyclooctatetraene and styrene have been found in pyrolysis products from *p*-xylene.[8]

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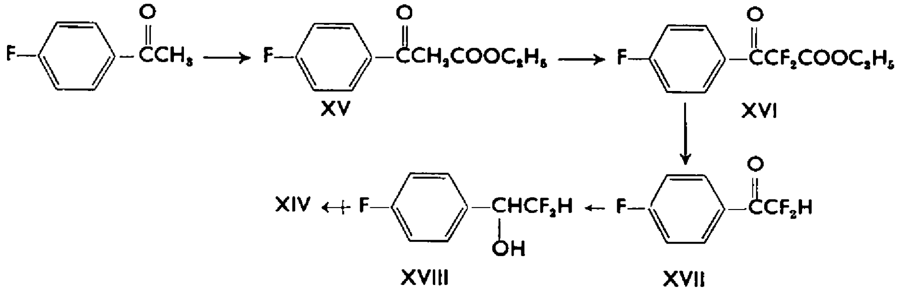
[8] L. A. Errede and F. De Maria, *J. Phys. Chem.* **66**, 2664 (1962).

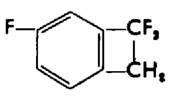
In order to obtain an authentic sample of XIV, the following sequence was devised.



Condensation of *p*-fluoroacetophenone with ethyl carbonate and sodium hydride gave ethyl *p*-fluorobenzoylacetate (XV) which, on treatment with perchloryl fluoride in pyridine (hazard! see Experimental) yielded ethyl *p*-fluorobenzoyldifluoroacetate (XVI). Hydrolysis of XVI and simultaneous decarboxylation by refluxing in glacial acetic acid–hydrochloric acid solution gave α,α,*p*-trifluoroacetophenone (XVII). Reduction of XVII with sodium borohydride gave β,β,*p*-trifluoro-α-hydroxyethylbenzene (XVIII). This compound resisted all attempts at dehydration to XIV.

A novel one-step synthesis of XIV was finally achieved[9] by refluxing a mixture of *p*-fluorobenzaldehyde, sodium chlorodifluoroacetate, and triphenylphosphine in 1,2-dimethoxyethane. The IR and NMR spectra of the compound thus synthesized were identical with those of the pyrolysis product XIV.

The gas chromatogram of the pyrolysis products from α,α,α′,α′-tetrafluoro-*p*-xylene (V) showed a smaller peak (component B) beyond that ascribed to XIV; the area ratio of the former to the latter peak was about 1:4. The compound represented by the smaller peak was isomeric with XIV. Spectral evidence (see Experimental) indicated a benzenoid structure for this compound, but precluded an olefinic bond as did its inertness toward hydrogen, bromine, and permanganate. The only structure we could write for component B that was consonant with the history and the spectral and chemical evidence was 1,1,5-trifluorobenzocyclobutene (XIX).



XIX

Attempts to obtain XIX by pyrolysis of XIV were unsuccessful.

Pyrolysis of α,α,α,α′,α′-pentafluoro-*p*-xylene (VIII) gave a mixture of at least eleven compounds. Four of these compounds had a molecular weight of 176 (loss of HF from starting material) by mass spectrometry, but were not further investigated.

EXPERIMENTAL

IR spectra were obtained on a Perkin-Elmer 221 or a Beckman IR5 instrument; NMR spectra on a Varian HR-60; UV spectra on a Cary Model 14 M; and mass spectra on a Consolidated Electrodynamics Corp. Model 21-103C. The C—H stretching bands in the IR spectra were not reported because they were generally weak and not informative.

α,α,α′,α′-Tetrafluoro-p-xylene V. According to the method of Hasek *et al.*,[10] 125 g (0·932 mole) terephthalaldehyde (Aldrich) and 437 g (3·64 moles 90% sulfur tetrafluoride in an 825 ml stainless

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[9] Further details and extensions of this synthesis will be reported elsewhere.

steel bomb were heated at 150° and rocked for 13 hr at 1300 p.s.i. The reaction products were washed with pentane onto 40 g NaF, filtered, and passed through a short column of alumina. The light-yellow pentane solution was concentrated at red. press., and the residual oil fractionally distilled to yield 133 g (80%) of a colorless oil, b.p. 83–84° (30 mm) n_D^{25} 1·4382, d_4^{25} 1·312. An analytical sample prepared from another batch boiled at 90°/40 mm, n_D^{25} 1·4378; it gave a single peak on a DEGS gas chromatography column.

IR λ film: 6·98, 7·28, 8·19, 8·89, 9·35, 9·65, 11·88, 12·3, 14·7. NMR, τ. 2·47 (singlet, 4 protons), 3·42 (triplet, J_{HF} = 57 c/s, 2 protons), NMR, F^{19}, φ. + 112·5 (doublet, J_{HF} = 57 c/s). UV, mμ (ε), isooctane, 210 (6500), 216 (4800, sh), 258 (440, sh), 264 (610), 270 (550). (Found: C, 53·55; H, 3·52. Calc. for $C_8H_6F_4$: C, 53·94; H, 3·40%).

*α-Bromo-α,α,α'α'-tetrafluoro-*p*-xylene* VI, *and α,α'-dibromo-α,α,α',α'-tetrafluoro-*p*-xylene* VII. A mixture of 26·2 g (0·147 mole) α,α,α',α'-tetrafluoro-*p*-xylene and 11·5 ml (36 g; 0·113 mole) Br_2 in 25 ml CCl_4 was refluxed and irradiated for 5·5 hr with a 250 watt UV lamp and for 8 hr with a 300 watt incandescent bulb. The disappearance of starting material and the appearance of the two bromination products were followed by gas chromatography. Both light sources seemed about equally effective. The reaction solution was washed with dil. $NaHCO_3$ aq and then with dil. $Na_2S_2O_3$. Fractionation through an 18" spinning band column gave recovered starting material and 16·9 g (45%) α-bromo-α,α,α',α'-tetrafluoro-*p*-xylene (VI), b.p. 93–95°/30 mm. A middle cut of this fraction, b.p. 94·5–95°/30 mm, n_D^{25} 1·4716, gave a single peak on a DEGS gas chromatography column.

IR, μ. 6·99, 7·12, 7·81, 8·17, 8·74, 9·3, 9·5, 11·2, 11·6, 12·2, 12·6, 14·35. NMR F^{19} φ. + 45·53 (singlet, $2F^{19}$), + 112·9 (doublet, J_{HF} = 57, $2F^{19}$). (Found: C, 36·97; H, 1·89; Br, 31·9. Calc. for $C_8H_5BrF_4$: C, 37·38; H, 1·96; Br, 31·1%).

Continued fractionation gave 11·4 g (34%) α,α'-dibromo-α,α,α',α'-tetrafluoro-*p*-xylene (VII), b.p. 101–108·5°/29 mm. Most of this fraction (8·7 g) boiled at 107–108·5°/29 mm, n_D^{25} 1·4987. An analytical fraction was prepared by trapping from a DEGS gas chromatography column. IR λ film. 7·05, 7·82, 8·72, 9·11, 9·40, 9·50, 9·81, 11·12, 11·23, 11·49, 12·06, 12·30, 13·93. NMR, φ. + 46·06 (singlet). (Found: C, 28·44; H, 1·47; Br, 46·90. Calc. for $C_8H_4Br_2F_4$: C, 28·60; H, 1·20; Br, 47·55%).

*α,α,α,α',α'-Pentafluoro-*p*-xylene* VIII. A mixture of 110·0 g (0·732 mole) 4-carboxybenzaldehyde (Aldrich) and 445 g (3·70 mole) 90% sulfur tetrafluoride were reacted at 150° and 1100 p.s.i. in a 825 ml stainless steel bomb for 13 hr. The product was worked up as described for V. Fractional distillation gave 67·5 g (47%) of a colorless liquid, b.p. 59·5–60°/33 mm, n_D^{25} 1·4060. IR λ film. 6·98, 7·22, 7·5, 8·17, 8·5–8·9, 9·2–9·6, 9·79, 11·4–12·1, 13·0, 14·7. UV, mμ (ε), isooctane. 209 (6150), 213 (4720, sh), 2·57 (570, sh), 263 (830), 269 (790). NMR, τ. 2·28 (singlet, 4 protons) 4·02 (triplet, J_{HF} = 57 cs, 1 proton). NMR, F^{19}, φ. + 63·94 (singlet, $3F^{19}$), + 113·1 (doublet, J_{HF} = 57, $2F^{19}$). (Found: C, 49·0; H, 2·57. Calc. for $C_8H_5F_5$: C, 49·0; H, 2·57%).

p-Difluoromethylbenzoyl fluoride. Another preparation starting with 36·0 g 4-carboxybenzaldehyde gave 8·0 g of a higher boiling fraction b.p. 95–98°/31 mm, which on standing in a stoppered flask turned yellow, evolved HF fumes, and developed a precipitate. This fraction represented a 19% yield of *p*-difluoromethylbenzoyl fluoride, characterized as the dimethylamide.

N,N-*Dimethyl*-p-*difluoromethylbenzamide.* The fraction of *p*-difluoromethylbenzoyl fluoride (8·0 g) from above was dissolved in ether and slowly treated with dimethylamine for about 1 hr. During this time the mixture became yellowish-orange and a precipitate collected in the flask. On standing overnight, the ether evaporated, leaving a solid. Water was added, and the aqueous mixture was extracted with ether. Removal of the ether, after drying, gave 7·4 g of yellow oil, which crystallized into well-formed needles. Three recrystallizations from a pentane–ether mixture gave colorless needles, m.p. 49–50°. IR λ melt. 6·10, (C=O), 7·15, 7·90, 8·20, 9·25, 9·75, 11·75–12·0, 13·05. NMR, F^{19}, φ. + 112·0 (doublet, J_{HF} = 57). (Found: C, 61·9; H, 5·72; N, 6·76. Calc. for $C_{10}H_{11}F_2NO$: C, 60·29; H, 5·57; N, 7·03%).

*α-Bromo-α,α,α',α',α'-pentafluoro-*p*-xylene* IX. A solution of 6·75 g (0·0344 mole) VIII and 3·55 ml (0·0346 mole) Br_2 in 20 ml CCl_4 was irradiated for 5 hr with a 250 watt UV source, for 55 hr with a 300 watt incandescent bulb, and for 5 hr with sunlight. The course of the reaction was followed by gas chromatography. The reaction mixture was extracted with dil. $NaHCO_3$ aq, dil. $Na_2S_2O_3$ aq and water. Fractionation through an 18" spinning band column gave 6·20 g (65%) of colorless

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[10] W. R. Hasek, W. C. Smith and V. A. Englehardt, *J. Amer. Chem. Soc.* **82**, 547 (1960).

liquid, b.p. 69·5–70°/28 mm, n_D^{25} 1·4395. This material gave a single peak on a Dow 11 gas chromatography column. IR λ film. 7·05, 7·51, 7·83, 8·50, 8·76, 9·06, 9·32, 9·48, 9·97, 11·20, 12·00, 12·89, 13·49, 14·42. (Found: C, 34·95; H, 1·87; Br, 28·94. Calc. for $C_8H_4F_6Br$: C, 34·93; H, 1·47; Br, 29·06%).

*Pyrolysis of α,α,α′,α′-tetrafluoro-*p*-xylene* V. The pyrolysis apparatus consisted of a 25 ml pear-shaped flask connected through a capillary (0·5 mm), stopcock, pyrolysis tube, and dry ice-acetone trap to a vacuum line. The pyrolysis tube was Vycor tubing (10·5 mm O.D.) loosely packed with Vycor chips. The length of tube heated by the furnace was 30 cm.

For pyrolysis, 6·57 g α,α,α′,α′-tetrafluoro-*p*-xylene V was placed in the flask and the apparatus was flushed with N_2. With the stopcock closed, the pyrolysis tube was evacuated and heated to 850°. The stopcock was opened and the sample allowed to pass through the tube under autogenous press. of 3–5 mm. Occasional warming of the flask was necessary to ensure complete volatilization, which occurred over a seven-hour period. Considerable carbonization was evident in the tube. A brown product (5·50 g) collected in the trap. This was solid at −78° but became a fuming liquid on warming to room temp. It was chromatographed in 1 ml portions through a Beckman GC-2 "preparative" gas chromatograph, using a 10′ × ⅜″ silicone column (30% Silicone DC 550 on Chromasorb W). The mixture consisted of two components which were collected together, and starting tetrafluoro-*p*-xylene with small amounts of minor products. The two components which were collected together were cleanly separated on a 10′ × ⅜″ column (25% diethylene glycol succinate, DEGS, on firebrick), and each component was collected as a pure material. The area of the first peak (component A) was four times the area of the second peak (component B). The product corresponding to the first peak (A) was β,β,*p*-trifluorostyrene (XIV). The product corresponding to the second peak (B) was 1,1,5-trifluorobenzocyclobutene (XIX).

In another experiment, 56·0 g (0·314 mole) α,α,α′,α′-tetrafluoro-*p*-xylene was pyrolyzed, and the condensate (35 g) was distilled through an 18″ spinning band column. The β,β,*p*-trifluorostyrene XIV fraction (6·46 g) was collected at 52°/28 mm. The 1,1,5-trifluorobenzocyclobutene (XIX) fraction (1·41 g) was collected at 63–78·5°/28 mm. Ten grams of starting material was recovered.

The following physical data are given for β,β,*p*-trifluorostyrene (XIV). n_D^{25} 1·4700. IR λ film 5·74, ($CH = CF_2$), 6·20, 6·58, 7·39, 8·00, 8·59, 10·61, 11·84 (*p*-disubstituted benzene). UV, mμ (ε), isooctane. 207 (7180), 237 (14,200), 274 (670), 278 (680), 281 (720), 284 (620), 291 (500). NMR, τ. 2·6–3·2 (multiplet, 4 proton), 4·72 (2 pairs, $J_{HF\ trans} = 24$ c/s, $J_{HF\ cis} = 5$ c/s, 1 proton). NMR, F^{19}. φ. + 85 (6 peaks, $2F^{19}$), + 114·8 (singlet, $1F^{19}$). Mass spectrum. Calc.[11] for $C_8H_5F_3$: Parent mass 158, parent − 1, 8·73% of parent, parent + 2, 0·33%, of parent. Found: Parent mass 158, parent + 1, 8·7% of parent, parent + 2, 0·4% of parent; base mass 158. (Found: C, 60·77; H, 3·21; F, 36·25. Calc. for $C_8H_5F_3$: C, 60·76; H, 3·19; F, 36·04%).

The following physical data are given for 1,1,5-trifluorobenzocyclobutene (XIX). IR λ film. 6·17, 6·23, 6·76, 6·98, 7·48, 7·83, 7·90, 8·52, 9·14, 9·50, 10·03, 11·06, 11·19, 11·63 (*o*-disubstituted benzene ring), 12·13 (*o*-disubstituted benzene ring). UV, mμ (ε), isooctane. 209 (5520), 260 (1370), 263 (1560), 265 (1630), 268 (2310), 273 (2280). NMR, τ. 2·6–3·2 (multiplet, 3 protons), 6·32 (3 peaks, $J_{HH} = 3·8$, 2 protons). NMR, F^{19}, φ. + 99·95 (singlet, $2F^{19}$), + 105·3 (singlet, $1F^{19}$). Mass spectrum. The parent, parent − 1, parent + 2, and the base peak are identical with those given for XIV. The fragmentation patterns for XIV and XIX are very similar. (Found: C, 60·84; H, 3·39; F, 36·18. Calc. for $C_8H_5F_3$: C, 60·76; H, 3·19; F, 36·04%).

*Polymerization of β,β,*p*-trifluorostyrene* XIV. A sample of XIV was sealed under He in a glass vial and irradiated for 25 hr with a Co^{60} source (total dose $11·3 \times 10^6$ rads, 10·5 megareps). At the end of this period, the sample was still liquid. The vial was opened, 1% of t-butyl perbenzoate added, and the vial was resealed under He and heated at 100° for 60 hr. The sample (viscous at room temp) was dissolved in benzene, and polymer was precipitated by addition of methanol. The white precipitate was removed by centrifuging and decanting, and was dried at 100° at 1 mm. The white polymer had a softening range of 200–210°, and had a mol. wt. of about 5700. IR λ film. 6·23, 6·63, 7·40, 7·88, 8·15, 8·50, 8·61, 9·60, 9·35, 9·86, 11·30, 11·90, 12·45, 13·67. (Found: C, 61·94; H, 3·58; F, 34·51. Calc. for $(C_8H_5F_3)_n$: C, 60·76; H, 3·19; F, 36·04%).

*Bromination of β,β,*p*-trifluorostyrene* XIV. Approximately 20 mg XIV was treated in the dark at room temp. for 24 hr with excess Br_2 in CCl_4. Gas chromatography (6′ × ¼″, 15% Dow 11, 190°,

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[11] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, p. 9, J. Wiley, New York (1963).

25 ml/min) gave a single cut which identified as α,β-dibromo-β,β,*p*-trifluoroethylbenzene XI. IR λ film. 6·22, 6·59, 8·08, 8·42, 9·03, 9·11, 9·97, 10·58, 10·75, 11·56, 11·92, 12·54, 13·04, 13·81. NMR, τ. 2·40–3·12 (multiplet, 4 protons), 4·72 (2 pairs, hindered rotation $J_{HF} = 17$ and 5 c/s, 1 proton). IR λ film. 6·22, 6·61, 8·08, 8·42, 9·00, 9·12, 9·97, 10·58, 10·76, 11·57, 11·93, 12·56, 13·05, 13·82, 15·00. Mol. wt. (mass spectrometer) 318.

*Oxidation of β,β,*p*-trifluorostyrene* XIV. A 2% $KMnO_4$ aq was added dropwise with shaking to 1 g of XIV until the pink color persisted when the mixture was warmed on the steam bath. The aqueous solution was cooled, acidified with dil. H_2SO_4 aq, and extracted with ether. The ether solution was extracted with a 2% NaOH aq. The aqueous solution was acidified and the white precipitate which formed was removed by filtration. One recrystallization from ethanol–water, followed by sublimation (130° at 1–2 mm) gave a white crystalline product, m.p. 177–182°. This acid (276 mg) was treated with diazomethane in ether. The ether solution was evaporated, and the residue was triturated with pentane. The pentane solution was evaporated, and the residual oil was distilled at 117° at 150 mm. The distillate gave a single peak on gas chromatography; it was identified as methyl *p*-fluorobenzoate XIII. The IR spectrum was identical with that of an authentic sample of the ester prepared from *p*-fluorobenzoic acid (Eastman). IR, λ film. 5·81 (C=O), 6·25, 6·64, 6·99, 7·81, 8·10, 8·67, 9·00, 9·18, 11·71, 11·82, 13·07, 14·58. NMR, τ. 1·90 (2 pairs $J_{HF} = 5·5$ c/s, $J_{HH} = 10·3$ c/s, 2 protons), 2·80 (triplet, $J_{HH} = J_{HF} = 10·3$ c/s, 2 protons) 6·10 singlet, 3 protons). Mass spectrum. Calc. for $C_8H_7O_2F$; Parent mass 154; parent + 1, 8·84% of parent; parent + 2, 0·74% of parent. Found: Parent mass 154; parent + 1, 9·1% of parent; parent + 2, 0·9% of parent; base mass 123.

*Hydrogenation of β,β,*p*-trifluorostyrene* XIV. A suspension of 1·4015 g XIV and 118 mg red. PtO_2 was stirred under H_2 overnight at room temp in a glass hydrogenation apparatus. Hydrogen absorption was 2·55 moles/mole. It was noted the mixture became acidic, and that the glass was etched. The hydrogenation product was isolated by gas chromatography and was identified as β,*p*-difluoroethylbenzene XII by its mass, and IR spectra. IR λ film. 6·23, 6·62, 8·18, 8·61, 9·08, 9·40, 9·87, 12·18. Mass spectrum. Calc. for $C_8H_8F_2$: Parent mass 142; parent + 1, 8·77% of parent; parent + 2, 0·34% of parent. Found: Parent mass 142; parent + 1, 8·7% of parent; parent + 2, 0·36% of parent; base mass 109.

*Ethyl-*p*-fluorobenzoylacetate* XV. A 1-l., 3-neck flask, fitted with a pressure-equalized dropping funnel, stirrer, condenser, and drying tube was flame-dried under N_2. To a stirred refluxed mixture in the dried flask of 45·3 g (1·0 mole) 53% NaH in oil (Metal Hydrides Inc.), 118·4 g (1·0 mole) ethyl carbonate (Matheson, Coleman and Bell), and 300 ml anhydrous ether, was added over a period of 30 min, 68·95 g (0·5 mole) *p*-fluoroacetophenone (Pierce Chemical Co.). Hydrogen evolution began immediately, and was monitored volumetrically. After all of the *p*-fluoroacetophenone had been added, the mixture suddenly became a very thick paste. Ether was added to thin the mixture, and refluxing and stirring were continued for another hour. The mixture was poured into ice water containing 100 ml acetic acid, and after thorough stirring, the ether layer was separated. The aqueous layer was extracted with ether, and the combined ether solution was washed successively with water, 5% $NaHCO_3$ aq, and water. The ether solution was dried, and concentrated on the steam bath to about 250 ml. Distillation through an 18″ spinning band column gave a small forerun of starting materials, and a main cut of 67·2 g (64%) at 104–105°/0·6 mm, n_D^{25} 1·5092. IR λ film. 5·73, 5·91, and 6·13 (β-ketoester), 6·25, 6·61, 7·00, 7·52, 7·90, 8·10, 8·35, 8·60, 9·05, 9·27, 9·66, 9·85, 9·98, 11·80, 12·44, 13·55. (Found: C, 64·2; H, 5·45; F, 8·78. Calc. for $C_{11}H_{11}FO_3$: C, 62·9; H, 5·28; F, 9·04%).

*Ethyl-*p*-fluorobenzoyldifluoroacetate* XVI. The reactor used for this type of reaction and the hazard involved have been described.[12] A solution of 69·9625 g (0·333 mole) ethyl-*p*-fluorobenzoylacetate (XV) and 50 ml pyridine in the reactor was cooled in an ice bath and stirred magnetically while a slow stream of perchloryl fluoride (Pennsalt) was bubbled through the sintered glass disc over a period of 6 hr. Treatment with perchloryl fluoride was continued for an additional 4 hr at room temp. The operation was carried out in a good hood behind a safety-glass barricade. The reaction product was poured into 1·5 l. water, and mixture was extracted twice with ether. The ether solution was washed successively with water, 10% HCl aq, water, 5% $NaHCO_3$ aq, and water. The ether solution was dried, the ether removed, and the residual oil (57·7 g) was distilled through an 18″ spinning band column. A cut of 9·4 g (11·5%) at 92–93°/1·2 mm (n_D^{25} 1·4698) gave a satisfactory

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[12] S. A. Fuqua and R. M. Silverstein, *J. Org. Chem.* **29**, 395 (1964).

combustion analysis and an IR spectrum in accord with that expected from the desired compound. A higher boiling fraction (26·5 g, 107–109°/1·2 mm) was starting material.

A subsequent attempt to improve the yield by refluxing the perchloryl fluoride from a cold finger resulted in a violent explosion. IR λ film. 5·63, (COOEt), 5·86 (φ—C=O), 6·25, 6·61, 7·06, 7·29, 7·62, 8·03, 8·62, 9·08, 9·88, 10·80, 10·96, 11·72, 11·90, 12·80, 13·04, 14·07. (Found: C, 54·9; H, 4·17; F, 22·5. Calc. for $C_{11}H_9F_3O_3$: C, 53·7; H, 3·69; F, 23·15%).

α,α,p-*Trifluoroacetophenone* XVII. A mixture of 7·6853 g (31·22 mmoles) ethyl *p*-fluorobenzoyldifluoroacetate (XVI), 30 ml glacial acetic acid, and 1 ml conc. HCl was refluxed 70 hr. The mixture was poured into 200 ml water and the aqueous mixture extracted twice with ether. The ether solution was washed with water and 5% $NaHCO_3$ aq, and was dried. Evaporation of the ether solution left 5·87 g of yellow oil. Distillation through an 8″ spinning band column gave 2·507 g (46%) of a fraction which distilled at 56–57° at 5 mm, and crystallized on standing, m.p. 35–36·5. IR λ film. 5·88 (C=O), 6·28, 6·62, 7·08, 7·42, 7·70, 8·09, 8·60, 8·81, 9·44, 10·20, 11·40, 11·73, 11·95, 13·05, 14·80, 15·35. (Found: C, 55·3; H, 3·2. Calc. for $C_8H_5F_3O$: C, 55·2; H, 2·90%).

β,β,p-*Trifluoro-α-hydroxyethylbenzene* XVIII. A solution of 1·5388 g (8·85 mmole) α,α,*p*-trifluoroacetophenone (XVII and 150 mg $NaBH_4$ in 20 ml ethanol was allowed to stand overnight at room temp and was poured into 200 ml 2% H_2SO_4. Extraction with ether gave 1·9575 g of an oil whose IR spectrum showed an OH peak but no carbonyl. The crude material was subjected to a variety of dehydration and ester-pyrolysis reactions which were monitored by gas chromatography. No trace of the desired product XII was found. IR λ film. 2·98 (strong, OH), no C=O, 6·22, 6·63, 8·17, 9·33, 9·54, 11·98, 12·68, 13·0.

Synthesis of β,β,p-*trifluorostyrene* XIV. The following compounds were dissolved in 100 ml anhydrous 1,2-dimethoxyethane (Arapahoe Chemical Co.), and the solution refluxed under N_2 for 24 hr: 13·45 g (0·0904 mole sodium chlorodifluoroacetate, 23·70 g (0·0904 mole) triphenylphosphine (M. and T. Chemicals Inc.), and 10·50 g (0·0846 mole) *p*-fluorobenzaldehyde (Pierce Chemical Co.). The cooled mixture was filtered to remove NaCl (5·90 g), and the filtrate was concentrated on the steam bath. The residue was distilled, and the desired fraction (8·095 g, 60%) was cut at 61–64°/50 mm. The IR and NMR spectra were identical with those of XIV from the pyrolysis of α,α,α′,α′-tetrafluoro-*p*-xylene (V).

Acknowledgment—This work was supported entirely by an internal research grant from Stanford Research Institute. The NMR and mass spectra were run at Stanford Research Institute by Mr. W. R. Anderson and Mrs. L. Peters respectively.