307. *Aromatic Polyfluoro-compounds. Part IX.*[1] *Perfluoro-*o*-xylene, Perfluoro-*p*-xylene, and Tetrafluoro-phthalic and -terephthalic Acid.*

By B. Gething, C. R. Patrick, and J. C. Tatlow.

Defluorination of perfluoro-1,2- and -1,4-dimethylcyclohexane by iron at 450—500° has given perfluoro-*o*- and -*p*-xylene respectively. With concentrated sulphuric acid these gave respectively tetrafluoro-phthalic and -terephthalic acid. The former was converted into its anhydride and imide and thence into tetrafluoroanthranilic acid. By decarboxylation each phthalic acid gave the expected tetrafluorobenzene.

This paper describes the preparation of perfluoro-*o*- and -*p*-xylene by defluorination [2,3] of the corresponding perfluoro-alicyclic compounds, perfluoro-1,2- and -1,4-dimethylcyclohexane.[4] These were prepared by the vapour-phase fluorination of *o*- and *p*-xylene respectively with cobalt trifluoride at 300—350° in a stirred reaction vessel.[5] They were defluorinated by passage over iron gauze heated to about 450—500°, giving perfluoro-*o*- and -*p*-xylene, respectively. About 35% of the starting materials were recovered, yields being 40—45% based on that consumed. The yields and ease of formation of these compounds from the respective dimethylcyclohexanes are similar to those of perfluorotoluene from perfluoromethylcyclohexane,[2] and show a considerable improvement over the case of perfluorocyclohexane.[3] Thus it appears that, although the introduction of a tertiary carbon atom into an alicyclic fluorocarbon, as in perfluoromethylcyclohexane, reduces the difficulty of defluorination of the compound, a second tertiary atom, as in the perfluorodimethylcyclohexanes, has little further effect.

The trifluoromethyl groups of perfluoro-*o*- and -*p*-xylene were hydrolysed by fuming sulphuric acid at 150°, to give respectively, in good yield, tetrafluorophthalic and tetrafluoroterephthalic acid. The *o*-acid gave di-*S*-benzylthiouronium and disilver salts, but only a monoanilinium salt, despite the use of an excess of aniline. Tetrafluoroterephthalic acid gave di-salts with the same three bases and also a dimethyl ester.

Tetrafluorophthalic acid was converted into its anhydride by treatment with trifluoroacetic anhydride. Unlike phthalic anhydride, tetrafluorophthalic anhydride reacted readily with water. It dissolved almost instantaneously to give a solution that could be titrated with alkali just as though it were one of the free acid. The ease of hydrolysis

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[1] Part VIII, Barbour, Buxton, Coe, Stephens, and Tatlow, *J.*, 1961, 808.

[2] Gething, Patrick, Stacey, and Tatlow, *Nature*, 1959, **183**, 588.

[3] Coe, Patrick, and Tatlow, *Tetrahedron*, 1960, **9**, 240.

[4] Fowler, Burford, Hamilton, Sweet, Weber, Kasper, and Litant, *Ind. Eng. Chem.*, 1947, **39**, 292.

[5] Stacey and Tatlow, " Advances in Fluorine Chemistry," Butterworths, London, Vol. I, **1960**, p. 166.

of this anhydride parallels the rapidity of the hydrolysis of anhydrides of aliphatic perfluoro-acids, such as trifluoroacetic anhydride. Perfluoro-aromatic acids also should be strong acids [pentafluorobenzoic acid has a high dissociation constant (p*K* 0·8) [6]], and the ready hydrolysis of tetrafluorophthalic anhydride is in keeping with the high strength of the acid from which it is derived, the carbon atoms of the carbonyl groups being susceptible to attack by nucleophilic reagents. With ammonia, tetrafluorophthalic anhydride gave tetrafluorophthalimide. As is generally the case with amides, this was less readily hydrolysed than was the related anhydride. Tetrafluorophthalimide was converted into the xanthhydrol derivative and also, by the action of sodium hypobromite, into 3,4,5,6-tetrafluoroanthranilic acid.

By the action of heat on tetrafluorophthalic acid, and on tetrafluoroterephthalic acid, in admixture with soda lime, 1,2,3,4- and 1,2,4,5-tetrafluorobenzene, respectively, were obtained in good yield. These were characterised by infrared spectroscopy and their formation confirms that there had been no migration of substituent groups in the sequence of reactions from the hydrocarbon starting materials. In view of the value of bromo-aromatic compounds in synthetic work an attempt was made to convert the disilver salts of the tetrafluorophthalic acids into the corresponding dibromotetrafluorobenzenes by the Hunsdiecker reaction with bromine; this type of conversion has been very useful in the perfluoro-aliphatic series. However, when the reaction mixtures were worked up, only the appropriate tetrafluorophthalic acid could be isolated. In this process,[7] disilver phthalate gave very little dibromide, some acid being recovered, whilst disilver terephthalate was virtually unattacked.

EXPERIMENTAL

*Preparation of Perfluoro-*o- *and* -p-*xylene.*—Perfluoro-1,2-dimethylcyclohexane (9 g.) was passed in a stream of nitrogen flowing at 2 l./hr. through the defluorination tube [2,3] which was heated to 460°. The product (6 g.) was separated by preparative-scale gas chromatography [8] (column A, temp. 110°) to give starting material (3·1 g.) and *perfluoro-*o*-xylene* (1·8 g.), b. p. 128°, n_D^{19} 1·3670 (Found: C, 33·2; F, 66·2. C_8F_{10} requires C, 33·6; F, 66·4%). Mass spectrometry: principal mass peaks: 286, C_8F_{10}; 267, C_8F_9; 217, C_7F_7. Light absorption in ethanol (*c*, 0·085 g./l.): $\lambda_{max.}$ 2720 (ε 1753).

Perfluoro-1,4-dimethylcyclohexane (9·0 g.) was treated as described above (reactor temperature 460°, the value quoted earlier [2] should also have been 460°). The product (6·0 g.), separated as before, gave starting material (3·5 g.) and perfluoro-*p*-xylene (1·65 g.), b. p. 122°, n_D^{17} 1·3621 (Found: C, 33·9; F, 66·3%). Light absorption in ethanol (*c*, 0·047 g./l.): $\lambda_{max.}$ 2850 (ε 2590).

Preparation of Tetrafluorophthalic Acid.—Perfluoro-*o*-xylene (6·4 g.) and fuming sulphuric acid (20% of sulphur trioxide; 4 ml.) were heated at 150° and shaken in a sealed tube for 12 hr. The tube was cooled in liquid air, then opened, and its contents were poured on ice. The resulting solution was made alkaline, extracted with ether, and acidified. The acid solution was extracted continuously with ether for 12 hr. and the extract was decolorised (charcoal), dried ($MgSO_4$), and evaporated to leave a white solid (5·8 g.), m. p. 151—153°, which was recrystallised from *o*-xylene to give *tetrafluorophthalic acid* (5·0 g.), m. p. 153—154° (Found: C, 40·3; H, 1·0; F, 31·6%; equiv., 117. $C_8H_2F_4O_4$ requires C, 40·3; H, 0·8; F, 31·9%; equiv., 119). The infrared spectrum showed a strong band at 1735 cm.$^{-1}$ (C=O).

The acid (0·3 g.) gave in the usual way *di-*(S*-benzylthiouronium) tetrafluorophthalate* (0·2 g.), m. p. 205° (decomp.) (from water) (Found: C, 50·8; H, 4·0; F, 13·4. $C_{24}H_{22}F_4N_4O_4S_2$ requires C, 50·5; H, 3·9; F, 13·3%). Treatment of the acid (0·2 g.) with an excess of aniline in ether in the usual way gave *anilinium hydrogen tetrafluorophthalate* (0·2 g.), m. p. 204—205° (decomp.) (from acetone–chloroform) (Found: C, 50·8; H, 2·9. $C_{14}H_9F_4NO_4$ requires C, 50·8; H, 2·7%). A solution of tetrafluorophthalic acid (5·5 g.) in water (20 ml.) was neutralised with aqueous

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[6] Alsop, Burdon, and Tatlow, unpublished work.
[7] Oldham, *J.*, 1950, 100.
[8] Stephens, Tatlow, and Wiseman, *J.*, 1959, 148.

sodium carbonate. A solution of silver nitrate (20 g.) in water (50 ml.) was added and the precipitated *disilver salt* (9·5 g.) filtered off (Found: C, 21·4. $C_8Ag_2F_4O_4$ requires C, 21·2%).

Tetrafluorophthalic Anhydride.—Tetrafluorophthalic acid (2·4 g.) was refluxed with trifluoroacetic anhydride (5 ml.) for 2 hr. Trifluoroacetic acid and trifluoroacetic anhydride were removed by distillation under reduced pressure, and the residue was sublimed at 80°/0·05 mm., to yield *tetrafluorophthalic anhydride* (2·0 g.), m. p. 94—95·5° (Found: C, 43·4%; equiv., 110. $C_8F_4O_3$ requires C, 43·6%; equiv., 110). The infrared spectrum showed a band at 1805 cm.$^{-1}$ (C=O).

Tetrafluorophthalimide.—The temperature of a mixture of tetrafluorophthalic anhydride (2·5 g.) and aqueous ammonia (*d* 0·88; 3 ml.) was gradually increased to 280° during 1 hr. The solid product (2·5 g.) sublimed at 120°/0·05 mm., to give *tetrafluorophthalimide* (1·5 g.), m. p. 210—211° (Found: C, 44·2; H, 0·8; F, 34·5. $C_8HF_4NO_2$ requires C, 43·8; H, 0·5; F, 34·7%).

This imide (0·3 g.) was added to a solution of xanthhydrol (0·3 g.) in glacial acetic acid (3 ml.) and heated in a boiling water bath for 30 min. The precipitate was recrystallised from dioxan–water (3 : 2) to give the *derivative* (0·15 g.), m. p. 255—256° (Found: C, 63·3; H, 2·3. $C_{21}H_9F_4O_3N$ requires C, 63·2; H, 2·3%).

Preparation of 3,4,5,6-*Tetrafluoroanthranilic Acid.*—To a cooled solution of sodium hydroxide (1·7 g.) and bromine (1·3 g.) in water (10 ml.) was added finely powdered tetrafluorophthalimide (1·7 g.). A solution of sodium hydroxide (1·1 g.) in water (5 ml.) was added rapidly and the resulting solution heated to 80° for 1 min. and then cooled to 15°. The solution was acidified with concentrated hydrochloric acid, and the resulting precipitate (1·0 g.), m. p. 135—139°, removed by filtration. Reprecipitation from alkaline solution and recrystallisation from water gave 3,4,5,6-*tetrafluoroanthranilic acid* (0·5 g.), m. p. 141—142° (Found: C, 40·5; H, 1·6. $C_7H_3F_4NO_2$ requires C, 40·2; H, 1·4%). The infrared spectrum showed bands at 1675 (C=O), 3400, 3620 (N–H), and 3000 cm.$^{-1}$ broad (O–H).

The acid (0·2 g.) gave in the usual way S-*benzylthiouronium* 3,4,5,6-*tetrafluoroanthranilate* (0·15 g.), m. p. 205° (Found: C, 48·2; H, 3·7. $C_{15}H_{13}F_4N_3O_2S$ requires C, 48·0; H, 3·5%).

Tetrafluoroterephthalic Acid.—Perfluoro-*p*-xylene (6·0 g.) was treated with concentrated sulphuric acid (6 ml.) as for its isomer. Recrystallisation from water of the solid obtained gave *tetrafluoroterephthalic acid* (4·0 g.), m. p. 283—284° (Found: C, 40·2; H, 0·7; F, 31·5%), $\nu_{max.}$ 1725s cm.$^{-1}$ (C=O).

The acid (0·2 g.) gave a *di*-(S-*benzylthiouronium*) *salt* (0·3 g.), m. p. 211—212° (Found: C, 50·7; H, 4·1%).

With aniline in ether the acid (0·26 g.) afforded a *dianilinium salt* (0·20 g.) (from acetone–chloroform), m. p. 205° (decomp.) (Found: C, 56·6; H, 3·6. $C_{20}H_{16}F_4N_2O_4$ requires C, 56·6; H, 3·8%).

Disilver tetrafluoroterephthalate was prepared as was its isomer (Found: C, 21·1%).

The acid (1·1 g.) and concentrated sulphuric acid (1·0 ml.) were refluxed for 5 hr. in methanol (10 ml.). When cooled, the precipitate which formed was filtered off and recrystallised from methanol to give *dimethyl tetrafluoroterephthalate* (0·7 g.), m. p. 79—80° (Found: C, 45·4; H, 2·0. $C_{10}H_6F_4O_4$ requires C, 45·1; H, 2·3%).

Decarboxylations of the Tetrafluorophthalic Acids.—Tetrafluorophthalic acid (0·43 g.) and soda-lime (1·0 g.) were mixed intimately and the temperature increased gradually to 300°. The distillate (0·20 g.) was shown by infrared spectroscopy to be 1,2,3,4-tetrafluorobenzene.[8,9]

In an analogous fashion, tetrafluoroterephthalic acid (0·51 g.) afforded 1,2,4,5-tetrafluorobenzene [10] (0·22 g.) with a correct infrared spectrum.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

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[9] Pummer, Florin, and Wall, *J. Res. Nat. Bur. Stand.*, 1959, **62**, 113.

[10] Finger, Reed, Burness, Fort, and Blough, *J. Amer. Chem. Soc.*, 1951, **73**, 145.