919. *Organic Fluorides. Part XIV.* The Synthesis of Some Aromatic Fluoro- and Chloro-compounds.*

By L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow.

Aromatic compounds having $-CCl_3$ or $>CCl_2$ side chains react, in pyridine, with copper powder, with removal of chlorine and consequent dimerisation of the organic residues. In this way 1 : 1 : 2 : 2-tetrachloro- and 1 : 2-dichloro-1 : 2-diphenylethane and 1 : 2-dichloro-1 : 1 : 2 : 2-tetraphenylethane were made; further reaction with 1 : 2-dichloro-compounds gives olefins. $-CCl_3$ or $>CCl_2$ side chains adjacent to benzene nuclei are converted into the corresponding trifluoro- and difluoro-groupings by the use of hydrogen fluoride or antimony trifluoride. Difluorodi-*p*-fluorophenylmethane, 1 : 1 : 2 : 2-tetrafluoro-1 : 2-diphenylethane, bistrifluoromethylbenzene, and 1 : 3 : 5-tristrifluoromethylbenzene were prepared thus from the corresponding chloro-compounds. In the first of these compounds the fluorinated group is very readily hydrolysed; the last three compounds have stable side chains.

This paper summarises investigations carried out some years ago in order to provide aromatic chloro- and fluoro-hydrocarbon intermediates. Aromatic compounds with chlorinated side chains, from which the corresponding fluoro-compounds are derived most conveniently, were prepared in two ways. The usual non-catalysed direct side-chain chlorination was utilised for the production of certain compounds (Harvey, Smith, Stacey, and Tatlow, unpublished results), and others were made by application of a method described by Karrer, Wehrli, Biedermann, and Vedova (*Helv. Chim. Acta*, 1928, **11**, 233). In the latter process, the chloro-compound, in pyridine, is treated with copper powder, whereupon two molecules are linked together, one chlorine atom from each molecule being eliminated. Although this method is not applicable widely, it is shown herein to be very useful in certain cases. 1 : 1 : 2 : 2-Tetrachloro-1 : 2-diphenylethane was prepared readily from benzotrichloride in this way, and from dichlorodiphenylmethane 1 : 2-dichloro-1 : 1 : 2 : 2-tetraphenylethane was obtained. Under rather more drastic conditions, compounds having chlorine atoms on adjacent carbon atoms are dechlorinated to give olefins in this reaction: from the first process above, when reaction was allowed to proceed further, 1 : 2-dichloro-1 : 2-diphenylethylene was obtained, in the second process tetraphenylethylene, and, from treatment of (pentachloroethyl)benzene, αββ-trichlorostyrene. This reaction with copper powder and pyridine is limited to compounds having reactive chlorine atoms; only poor conversions of benzylidene chloride into 1 : 2-dichloro-1 : 2-diphenylethane were given, and benzyl chloride and nuclear-halogen derivatives such as chlorobenzene were unaffected. Pyridine plays an important rôle in this reaction, since copper powder alone reacts slowly in the cold with chloro-compounds such as those mentioned above, but in the presence of pyridine the reaction is often spontaneous, heat being evolved, and a blue crystalline material, reported by Karrer *et al.* (*loc. cit.*) to be a cupric chloride–pyridine complex, is precipitated. It may well be that polychloro-compounds with labile chlorine atoms, such as those which react in this process, form to some extent a quaternary pyridinium chloride, and that this is the reactive intermediate.

Fluorobenzene, in a Friedel–Crafts reaction with carbon tetrachloride promoted by aluminium chloride, gave dichlorodi-*p*-fluorophenylmethane, which was hydrolysed rapidly in aqueous alcohol to 4 : 4′-difluorobenzophenone. Bergmann, Hoffmann, and Meyer (*J. pr. Chem.*, 1932, **135**, 245) first prepared the ketone, using a similar process, but did not isolate the intermediate dichloro-compound. From the reaction of the latter, in pyridine, with copper powder, there was obtained tetra-*p*-fluorophenylethylene; the pure intermediate dichloro-compound could not be isolated in this case. The structure of the olefin was confirmed by its oxidation to 4 : 4′-difluorobenzophenone.

Fluorination of chloroalkyl-aromatic compounds was effected by the use of antimony

---

* Part XIII, *J.*, 1952, 3830.

trifluoride (Swarts, *Bull. Acad. roy. Belg.*, 1898, **35**, 375) or of anhydrous hydrogen fluoride (Osswald, Müller, and Steinhäuser, G.P. 575,593; B.P. 395,227). Thus prepared were bistrifluoromethylbenzene (cf. McBee, Hass, *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 298; Murray, Beanblossom, and Wojcik, *ibid.*, p. 302), 1 : 3 : 5-tristrifluoromethylbenzene (cf. McBee and Leech, *ibid.*, p. 393), and fluoro-chloro-compounds derived from (pentachloroethyl)benzene (cf. McBee, Hass, *et al.*, *ibid.*, p. 384; Simons and Herman, *J. Amer. Chem. Soc.*, 1943, **65**, 2064).

It is noteworthy that 1 : 3 : 5-tristrifluoromethylbenzene has a b.p. of *ca.* 120°, which is lower than that of perfluoro-(1 : 3 : 5-trimethyl*cyclo*hexane) for which Fowler *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 292) gave b. p. 124·7—125·1°, and Haszeldine and Smith (*J.*, 1950, 3617) 124·6°. This effect may well be due to the suppression of intermolecular association such as hydrogen bonding in the mesitylene derivative because of the positions and size of the trifluoromethyl groups. 1 : 3 : 5-Tristrifluoromethyl*cyclo*hexane has b. p. 157° (Gilbert and Bigelow, *J. Amer. Chem. Soc.*, 1950, **72**, 2411).

Dichlorodi-*p*-fluorophenylmethane gave, with antimony trifluoride, difluorodi-*p*-fluorophenylmethane, which, as expected by analogy with difluorodiphenylmethane (Henne and Leicester, *ibid.*, 1938, **60**, 864), was hydrolysed very readily to 4 : 4′-difluorobenzophenone. 1 : 1 : 2 : 2-Tetrafluoro-1 : 2-diphenylethane was produced from the corresponding tetrachloride by treatment with antimony trifluoride–antimony pentachloride, or preferably by Henne's method (*ibid.*, p. 1569; hydrogen fluoride and mercuric oxide). The fluorine atoms in this compound were tightly bound, though they were removed by concentrated sulphuric acid at 100°, this reaction giving benzil; the conversion of $>CF_2$ groups linked to aromatic rings into keto-groups with sulphuric acid is to be expected since Le Fave (*ibid.*, 1949, **71**, 4148) observed that aromatic $-CF_3$ groups give carboxylic acids when thus treated.

Though direct linkage to an aromatic nucleus causes some decrease in the stability of $-CF_3$ groups, in comparison with most aliphatic compounds, yet, in general, reactions occur only with sulphuric acid and other drastic reagents. The same effect seems to apply when $\cdot CF_2\cdot CF_2\cdot$ groups are joined to benzene rings. However, when two aromatic groups are joined directly to a $>CF_2$ group, in the stability of the grouping is considerably reduced, and the fluorine is readily replaced.

EXPERIMENTAL

*Preparation of Dichlorodi-*p*-fluorophenylmethane.*—Fluorobenzene (19·2 g.) in carbon tetrachloride (29·0 g.) was added during 1 hour to a suspension of powdered anhydrous aluminium chloride (13·5 g.) in carbon disulphide (30 c.c.). Reaction ensued, and after 16 hours at 15° the mixture was poured into ice-water, the organic layer extracted with ether, and the extracts were washed with aqueous sodium hydrogen carbonate, then with water, and dried ($MgSO_4$). Contact of the organic layer with water was kept to a minimum. After removal of low-boiling material from the extracts, distillation under diminished pressure gave *dichlorodi-*p*-fluorophenylmethane* (59%), b. p. 180—182°/26 mm. (Found: Cl, 25·7; F, 13·8. $C_{13}H_8Cl_2F_2$ requires Cl, 26·0; F, 13·9%).

*4 : 4′-Difluorobenzophenone from Dichlorodi-*p*-fluorophenylmethane.*—A solution of the chloro-compound (1·00 g.) in aqueous ethyl alcohol was boiled for a few minutes and then cooled. The deposited solid, recrystallised from light petroleum (b. p. 60—80°), gave 4 : 4′-difluorobenzophenone (95%), m. p. 107—108° (Found: C, 71·7; H, 3·7; F, 17·4. Calc. for $C_{13}H_8OF_2$: C, 71·6; H, 3·7; F, 17·4%). Bergmann, Hoffmann, and Meyer (*loc. cit.*) reported m. p. 109°.

This ketone (5·53 g.), when refluxed for 2 hours with phosphorus pentachloride (5·25 g.), gave back the corresponding dichloro-compound (79%), b. p. 158°/15 mm.

*Difluorodi-*p*-fluorophenylmethane.*—Dichlorodi-*p*-fluorophenylmethane (10·0 g.), antimony trifluoride (4·4 g.), and antimony pentachloride (0·5 g.) were heated to 160° for 4 minutes. The product was cooled and extracted with ether, and the ethereal extracts were washed very quickly with dilute hydrochloric acid and then with water, and dried ($MgSO_4$), and the ether was removed. The residue, on distillation under diminished pressure, gave fractions (*a*) difluorodi-*p*-fluorophenylmethane (2·6 g.), b. p. 134—136°/15 mm., and (*b*) (3·7 g.), b. p. 165—170°/15 mm. Fraction (*b*) solidified and when recrystallised from ethyl alcohol gave 4 : 4′-difluorobenzophenone,

m. p. and mixed m. p. 107—108°. Fraction (*a*), which did not contain chlorine, was hydrolysed extremely readily by moist air, water, or aqueous alcohol, with evolution of hydrogen fluoride, and formation of 4 : 4′-difluorobenzophenone.

1 : 1 : 2 : 2-*Tetrachloro*-1 : 2-*diphenylethane*. (This was mentioned by Karrer *et al.*, *loc. cit.*, but without details.)—Benzotrichloride (50·0 g.) was added to pyridine (200 c.c.), the mixture darkening and fumes being evolved; dry pyridine usually gives the best results, but is not essential. Copper powder (8·05 g.), prepared by addition of zinc dust to copper sulphate solution, was added gradually to the solution with stirring, so that, despite the vigorous reaction, the temperature remained below 70°. When cold, the solution was filtered from the mass of blue-green crystals of pyridine-cupric chloride complex, the precipitate was washed thoroughly with excess of ether, and the combined filtrates were washed with dilute hydrochloric acid, then water, dried ($MgSO_4$), filtered, and distilled, to give a solid residue. (Alternatively the copper complex was washed with acetone, the combined filtrates were poured into excess of water, and the precipitate was filtered off, washed, and dried). The crude solid, recrystallised twice from alcohol, gave 1 : 1 : 2 : 2-tetrachloro-1 : 2-diphenylethane (65%), m. p. 161—162° (Found : Cl, 44·2. Calc. for $C_{14}H_{10}Cl_4$: Cl, 44·3%). Onufrowicz (*Ber.*, 1884, **17**, 833) recorded m. p. 162°.

1 : 2-*Dichloro*-1 : 2-*diphenylethane from Benzylidene Chloride*.—A mixture of the chloride (25·0 g.), pyridine (100 c.c.), and copper powder (4·93 g.) was heated under reflux for 10 minutes before being worked up as before. The ethereal extracts, on evaporation, gave a liquid residue, distillation of which under diminished pressure gave (*a*) unchanged benzylidene chloride (17·2 g.), b. p. 82—86°/15 mm., and (*b*) a solid (5·1 g.), b. p. 168—172°/15 mm. Fraction (*b*) after recrystallisation from ethyl alcohol gave *meso*-1 : 2-dichloro-1 : 2-diphenylethane, m. p. 193° (Found : Cl, 28·8. Calc. for $C_{14}H_{12}Cl_2$: Cl, 28·2%). Zincke (*Annalen*, 1879, **198**, 115) reported m. p. 192—193° for the *meso*-compound, and m. p. 93—94° for the racemic form.

1 : 2-*Dichloro*-1 : 1 : 2 : 2-*tetraphenylethane and Tetraphenylethylene*.—(*a*) Copper powder (1·33 g.) was added gradually, with stirring, to a cooled solution of dichlorodiphenylmethane (10·0 g.) in pyridine (40 c.c.). The mixture was filtered, the precipitate extracted with benzene–ether, and the combined filtered extracts were washed, dried ($MgSO_4$), filtered, and distilled to leave a residue, which after recrystallisation from benzene–ethanol gave 1 : 2-dichloro-1 : 1 : 2 : 2-tetraphenylethane (69%), m. p. 181° (Found : Cl, 17·3. Calc. for $C_{26}H_{20}Cl_2$: Cl, 17·6%). Schmidlin and von Escher (*Ber.*, 1910, **43**, 1153) recorded m. p. 186°.

(*b*) The above experiment was repeated but with copper powder (2·66 g.) added in one portion, and after the initial vigorous reaction had subsided the mixture was refluxed for 2 minutes. The product, isolated as above, was tetraphenylethylene (74%), m. p. 221° (Found : C, 93·8; H, 5·9. Calc. for $C_{26}H_{20}$: C, 93·9; H, 6·1%). Behr (*Ber.*, 1870, **3**, 751) gave m. p. 221°.

(*c*) 1 : 2-Dichloro-1 : 1 : 2 : 2-tetraphenylethane (5·0 g.), in pyridine (20 c.c.), treated with copper powder (0·79 g.) as in (*b*) above, gave tetraphenylethylene (90%), m. p. 221°.

Tetra-p-*fluorophenylethylene*.—Dichlorodi-*p*-fluorophenylmethane (1·79 g.), pyridine (10 c.c.), and copper powder (0·42 g.) were refluxed for 3 minutes. Isolation as before gave, after recrystallisation from alcohol, *tetra*-p-*fluorophenylethylene* (60%), m. p. 189—190° (Found : C, 77·2; H, 4·4; F, 18·6. $C_{26}H_{16}F_4$ requires C, 77·2; H, 4·0; F, 18·8%).

The olefin (0·15 g.) was boiled for 4 hours with chromic oxide (1 g.) in acetic acid (2 c.c.) and water (0·5 c.c.), and the mixture poured into water and extracted in the usual way, affording 4 : 4′-difluorobenzophenone (30%), m. p. and mixed m. p. 107°. Riemschneider (" Pharmazie," Beiheft 2, Ergänzungsband I, 1947, p. 99) mentioned this olefin, but without details.

1 : 1 : 2 : 2-*Tetrafluoro*-1 : 2-*diphenylethane*.—(*a*) Antimony trifluoride (7·5 g.), antimony pentachloride (0·75 g.), and 1 : 1 : 2 : 2-tetrachloro-1 : 2-diphenylethane (10·0 g.) were heated at 200° until completely liquid (*ca.* 2 min.). The product, when cool, was extracted with boiling ether, the extracts were washed with dilute hydrochloric acid, then water, and after being dried ($MgSO_4$) and filtered were distilled for removal of ether. Further distillation under diminished pressure gave 1 : 1 : 2 : 2-*tetrafluoro*-1 : 2-*diphenylethane* (46%), b. p. 145—150°/20 mm., m. p. 122° (from ethyl alcohol) (Found : C, 65·9; H, 4·0; F, 29·6. $C_{14}H_{10}F_4$ requires C, 66·1; H, 4·0; F, 29·9%).

(*b*) Anhydrous hydrogen fluoride was passed into a mixture of the tetrachloride (40·0 g.), mercuric oxide (68·0 g.), and benzene (320 c.c.) which was stirred in a nickel vessel cooled in water at 15—20°. After 16 hours' stirring, the mixture was poured into ice-water and neutralised with sodium hydroxide, and the precipitate filtered off, dried, and extracted with boiling benzene. The extracts and the original benzene layer were combined, washed, dried ($MgSO_4$), and distilled. The residue was sublimed at 15 mm. and the sublimate recrystallised from ethyl alcohol to give 1 : 1 : 2 : 2-tetrafluoro-1 : 2-diphenylethane (56%), m. p. 122—123°, identical with the material prepared as in (*a*). Balon and Tinker (U.S.P. 2,238,242) recorded that treatment of this tetrachloro-compound with anhydrous hydrogen fluoride at 100° gave a product with the same m. p. (122—123°), which they claimed was 1 : 2-difluorodiphenylethylene.

(*c*) 1 : 1 : 2 : 2-Tetrafluoro-1 : 2-diphenylethane (0·26 g.) was heated at 100° for 2 hours with concentrated sulphuric acid (1·0 c.c.). Pouring into water, etc., and recrystallisation from ethyl alcohol gave benzil (23%), m. p. and mixed m. p. 94° (Found : C, 79·9; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%).

Bistrifluoromethylbenzenes and 1 : 3 : 5-*Tristrifluoromethylbenzene*.—Bistrichloromethylbenzene (0·3—1 mol.), prepared by chlorination of commercial xylene, gave bistrifluoromethylbenzene by treatment in an autoclave with anhydrous hydrogen fluoride (about 50% excess) at 150—200° for 15—20 hours. The product (yield, 25%) had b. p. 114—118° (Found : F, 53·1. Calc. for $C_8H_4F_6$: F, 53·25%). Murray *et al.* (*loc. cit.*) gave b. p. 113—116·5°. The use of antimony trifluoride or antimony trifluoride + antimony pentachloride for the fluorination gave the same product in poorer yields.

1 : 3 : 5-Tristrifluoromethylbenzene, prepared (yield 18%) from the chloro-compound with antimony trifluoride–antimony pentachloride, had b. p. 118—120° (Found : F, 60·0. Calc. for $C_9H_3F_9$: F, 60·6%). McBee and Leech (*loc. cit.*) reported b. p. 119·6°.

Chlorofluoro-derivatives of Ethylbenzene.—(Pentachloroethyl)benzene (100 g.) treated with antimony trifluoride (80 g.) and antimony pentachloride (8 g.) at 250°, the product being worked up in the usual way, gave (dichlorotrifluoroethyl)benzene (21%), b. p. 78—82°/15 mm. (Found : Cl, 31·0; F, 24·5. Calc. for $C_8H_5Cl_2F_3$: Cl, 31·0; F, 24·9%), and (trichlorodifluoroethyl)-benzene (47%), b. p. 98—102°/15 mm. (Found : Cl, 43·2; F, 15·6. Calc. for $C_8H_5Cl_3F_2$: Cl, 43·3; F, 15·5%). From a similar reaction at 150°, there was isolated, in addition to the latter product (60%),(tetrachlorofluoroethyl)benzene (6%), b. p. 118—122°/15 mm. (Found : Cl, 53·9; F, 7·4. Calc. for $C_8H_5Cl_4F$: Cl, 54·1; F, 7·3%). Simons and Herman (*loc. cit.*) gave b. p.s 94—95°/42 mm., 100—102°/15 mm., and 123—126°/14 mm. respectively for these products.

The authors acknowledge their indebtedness to the late Professor Sir Norman Haworth, F.R.S., for his interest in this work.

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

[*Received, July* 25*th*, 1952.]