CCXCIII.—*The Nature of the Alternating Effect in Carbon Chains. Part XXVIII. The Preparation and some Properties of Benzyl Fluoride.*

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Although benzyl chloride, bromide, and iodide are familiar substances, the preparation of benzyl fluoride has not yet been described, and, in view of the importance of the benzyl halides for the study of serial relationships in the electrochemical behaviour of the halogen elements in organic chemistry, we attempted to devise a satisfactory method for the formation of the missing member of the series. Recent imperfectly successful attempts have been recorded by Tronov (*J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1270), who treated benzyl chloride with silver fluoride and obtained only toluene, and by Swarts (*Bull. Soc. chim.*, 1924, **35**, 1533), who, by some method not stated, obtained "with great difficulty" a small quantity of a liquid which was neither purified nor analysed, and quickly decomposed.

In their study of the decomposition of quaternary ammonium salts, Hanhart and Ingold (J., 1927, 997) showed that under structural conditions antagonistic to the formation of an olefin, the alkyl radical most tolerant to a positive charge is ejected and subsequently combines with the anion of the salt. The order of toleration given included the inequality $C_6H_5 \cdot CH_2 > CH_3$, and the present application is that the distillation of a quaternary ammonium fluoride such as benzyltrimethylammonium fluoride, containing only benzyl and methyl groups, should yield a predominating proportion of benzyl fluoride. We have prepared benzyl fluoride from several salts of this type (yields about 60% after complete rectification) and have taken the opportunity to study its properties.

Benzyl fluoride is a colourless liquid with an odour which is quite unlike that of its analogues, and rather resembles that of benzene. The m. p. is − 35°, and the b. p. 139·9°/760 mm. is of interest in relation to those of toluene, benzal fluoride, and benzotrifluoride. The series $C_6H_5 \cdot CH_3$(110·8°), $C_6H_5 \cdot CH_2F$(139·9°), $C_6H_5 \cdot CHF_2$(133·5°), $C_6H_5 \cdot CF_3$(103·5°) shows a maximum at the boiling point of benzyl fluoride, and this is noteworthy in relation to Arkel and de Boer's theory respecting the boiling points of organic compounds (*Physica, Nederlandsch Tijdsch. Natuurkunde*, 1924, **4**, 392; 1925, **5**, 134; *Rec. trav. chim.*, 1925, **44**, 675). According to these authors, the boiling points of halogenohydrocarbons are additive in the sense that they can be expressed as a simple function of the sum of a number of terms ("$\sqrt{\alpha}$-values") corresponding to the contributions of the atoms to the external molecular field and hence to the internal pressure of the liquid. For compounds belonging to the same hydrocarbon type the $\sqrt{\alpha}$-values of the halogens are constant; *e.g.*, for methane derivatives the values are F 23, Cl 47·5, Br 60·8, I 81·3. On the other hand, the $\sqrt{\alpha}$-value for hydrogen is variable and depends upon the degree of incipient ionisation induced by the halogen atoms attached to the same carbon atom. The degree of incipient ionisation produced by different halogens is substantially the same, and therefore the main factor which determines the $\sqrt{\alpha}$-value for hydrogen is the number of halogen atoms attached to the carbon atom to which it is linked. The following $\sqrt{\alpha}$-values for hydrogen illustrate this (X = halogen) : CH_4 16·2, CH_3X 21·4, CH_2X_2 25·2, CHX_3 26·1. The peculiarity of fluorine is that its $\sqrt{\alpha}$-value lies within the range of values which hydrogen may assume, and hence the possibility arises that whilst the replacement of one hydrogen atom in a hydrocarbon by fluorine may cause an increase in $\Sigma\sqrt{\alpha}$ and thus an increase in boiling point, the replacement of succeeding hydrogen atoms attached to the same carbon atom may lead to a decrease both in $\Sigma\sqrt{\alpha}$ and in the b. p. The series of b. p.'s given above forms a striking illustration of this deduction, and is the first complete series of the kind. As already stated, the $\sqrt{\alpha}$-values vary slightly from type to type, and it must be assumed that the value for side-chain hydrogen crosses the fluorine figure on passing from toluene to benzyl fluoride, thus producing a maximum b. p. at this member of the series.

We have studied the refraction and the dispersion of benzyl fluoride, both because these data will ultimately be required for the calculation of the molecular dipole moment of this substance, and also because the effect of the substituent (F) on the optical dispersion of a substance forms a partial measure of its effect on the rigidity of the electrons in the molecule. To facilitate an accurate comparison of the refraction constants of fluorine relative to those of hydrogen, the densities and refractive indices of highly purified toluene have been measured with the same apparatus. The data are in the following table, in which the bottom row contains the differences between $[R_L]$ for benzyl fluoride and for toluene :

		λ 6563.	λ 5893.	λ 5461.	λ 4861.	λ 4358.	λ 4340.
Benzyl fluoride	$n^{25\cdot3^\circ}$	1·48481	1·48919	1·49294	1·50014	1·50927	1·50967
$d_{4^\circ}^{25\cdot3^\circ}$ 1·02278	$[R_L]$	30·829	31·067	31·269	31·656	32·144	32·165
Toluene	$n^{23\cdot9^\circ}$	1·48876	1·49331	1·49720	1·50454	1·51402	1·51436
$d_{4^\circ}^{23\cdot9^\circ}$ 0·86140	$[R_L]$	30·833	31·077	31·285	31·676	32·177	32·195
(F) − (H)		−0·004	−0·010	−0·016	−0·020	−0·033	−0·030

Eisenlohr's (1910) values for the refraction constant of hydrogen being used, the contributions to the molecular refractions attributable to fluorine in benzyl fluoride are in the following table, in which Eisenlohr's values for the other halogens are included for comparison :

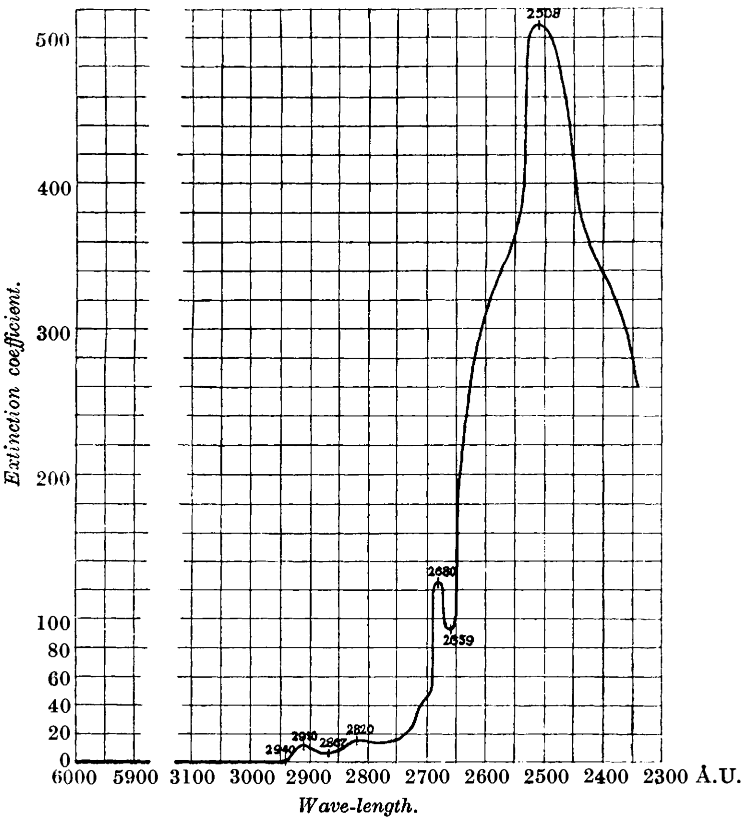
	H_α.	D.	H_β.	H_γ.	$H_\beta - H_\alpha$.	$H_\gamma - H_\alpha$.
F(BzF)	1·088	1·090	1·095	1·092	0·007	0·004
Cl	5·933	5·967	6·043	6·101	0·110	0·168
Br	8·803	8·865	8·999	9·152	0·196	0·349
I	13·757	13·900	14·224	14·521	0·467	0·764

It will be seen that fluorine has by far the lowest refraction values and that it differs sharply from the other halogens in contributing practically nothing to dispersion, and we conclude that amongst the four benzyl halides the halogen in benzyl fluoride exerts the strongest positive field over the aromatic nucleus. For *o*-, *m*-, and *p*-fluorotoluene Swarts (*J. Chim. phys.*, 1922, **20**, 30) obtained results which, when reduced in the same way, give — 0·034 (mean) for the contribution by fluorine to the dispersion (H_γ—H_α). For fluorobenzene the corresponding figure was — 0·045, and the marked contrast between these figures and that now derived (+ 0·004) for benzyl fluoride shows that the introduction of a fluorine atom into the aromatic nucleus causes a larger restraint on the electrons and hence a larger increase in the frequency governing dispersion than that produced by the entrance of a fluorine atom into the side chain.

Further evidence pointing in a similar direction was obtained by a study of the ultra-violet absorption of the substance, and the results are of interest in connexion with the parallelism which appears to subsist between the selective absorption of simply constituted aromatic compounds and their nuclear reactivity. It is known (Baly and Collie, J., 1903, **87**, 1332) that the conversion of aniline into a salt causes the selective absorption to be displaced in the direction of shorter wave-lengths, and this effect, manifestly connected with the increased electronic restraints produced by the positive charge, may be correlated with the inhibited nuclear reactivity and tendency to *m*-orientation of the salt. The opposite influence of a negative charge is displayed when phenol is converted into a salt, and the displacement of the selective absorption to a region of greater wave-lengths finds its counterpart in largely increased nuclear reactivity and very strong *op*-orientation. Spectrographic studies with benzene, toluene, ethylbenzene, and the three xylenes in alcoholic solution (Baly and Collie, *loc. cit.*) have shown that the introduction of alkyl groups into the aromatic nucleus displaces the absorption maximum towards the red, and quantitative data are available in the case of *p*-xylene (Henri, " Études de

Photochimie," 1919); the effect corresponds to *op*-orientation associated with increased nuclear reactivity (Ingold and Shaw's "Case I," J., 1927, 2918). If, however, the side-chain hydrogen atoms of toluene are replaced by atoms which attract electrons strongly, the circumstances of Ingold and Shaw's "Case I" pass into those of their "Case II," and continuously decreasing nuclear reactivity is associated with increasing *m*-orientation. Benzyl fluoride, benzaldehyde, and benzoic acid represent progressive stages in this process, and it is therefore of interest to compare the positions and intensities of the principal ultra-violet absorption maxima of these substances with those of benzene and *p*-xylene. The curve representing the extinction coefficients for benzyl fluoride in $M/100$- to $M/1600$-ethyl-alcoholic solution is shown in the diagram, and a comparison of the wave-length of the maximum with those recorded by Henri (*loc. cit.*) for the other substances

FIG. 1.



shows that benzyl fluoride falls into place as a somewhat feebly *m*-orienting member of the series. The trend of the ε-values (minimum at benzene) suggests that electrical dissymmetry in the molecule favours photoelectronic excitation.

	p-Xylene.	Benzene.	Benzyl fluoride.	Benz-aldehyde.	Benzoic acid.
λ	2684	*2547*	2508	2,440	2,302
ε	750	*210*	508	16,260	44,700

It is not to be expected that the basis here indicated for the correlation of colour with constitution will be capable of a more general application until it has been considerably elaborated, and a more extended discussion of the effect of polar influences on colour must await further experimental studies.

The above reference to the *m*-orienting power of the fluoromethyl group is based on our observation that on nitration in acetic anhydride solution benzyl fluoride yields mononitro-derivatives in the following proportions: ortho- 28·1, meta- 17·5, para- 54·4%. Comparison of these figures with those which have been obtained by Miss F. R. Shaw in these laboratories for the nitration of benzyl chloride, namely, ortho- 32·0, meta- 15·5, para- 52·5%, shows that there is more *m*-substitution in the former case, and that therefore the electron-attraction (inductive + direct effects, $-I$ $-D$) of the halogen in benzyl fluoride is greater than in benzyl chloride.

According to Ingold and Vass (this vol., p. 417; see also Lapworth and Robinson, *Mem. Manchester Phil. Soc.*, 1928, **72**, No. 4) the direct effect is one of the main factors controlling the ortho/para ratio in aromatic substitution, and conversely this ratio, or the related ratio para/½ortho, may be taken to indicate the relative intensities of the external fields of the halogen atoms in the above cases, provided that the possibility of complications arising from steric hindrance is not disregarded. The ratios for benzyl fluoride and chloride are 3·89 and 3·28 respectively, showing that the direct effect of fluorine is stronger than that of chlorine, since steric hindrance should produce a difference in the opposite direction. This is confirmed by the halogenobenzene ratios (Holleman), namely, PhF 13·76, PhCl 4·64, PhBr 3·30, PhI 2·85, which indicate that the complete sequence is $D_F > D_{Cl} > D_{Br} > D_I$. It is natural that the ratios for the phenyl compounds should be greater than for the corresponding benzyl compounds, because not only will the field over the nucleus be stronger in the former case owing to the proximity of the halogen atom, but also the difference between the distances of the ortho- and para-positions from the directing atom will be relatively greater. The fact that the difference between the values for fluorobenzene and chlorobenzene is greater than that between the values for benzyl fluoride and benzyl chloride can be similarly explained, and it may also be a contributing circumstance that in the phenyl compounds a tendency towards sharing additional electrons with the nucleus (residuum of the tautomeric effect $+T$) in the order $Cl > F$ increases the disparity between the external fields produced by these atoms.

These considerations, combined with conclusions previously reached on other grounds (Ingold and Shaw, *loc. cit.*; Ingold and Vass, *loc. cit.*), show that, whereas in regard to the tautomeric effect the halogens are in the order $I > Br > Cl > F$, they stand in the reverse order with respect to both their inductive and direct effects, and one of the most interesting problems in the chemistry of the benzyl halides arises in connexion with the reconciliation of the above analysis of their nuclear reactivity with the available data relating to their side-chain transformations. According to Ingold and Rothstein (this vol., p. 1217) the side-chain substitutions of benzene derivatives are of four types, which, for the benzyl halides, may be exemplified by the reactions with (1) amines, water, and alcohols, (2) halogens (high temperatures), (3) reducing agents, (4) powerful alkalis. These types are divisible into two groups, since the mechanism of the reactions of which (2) is an example may be regarded as a variant of that of the reactions of category (1): the latter involve the ionisation $C_6H_5{\cdot}\overset{+}{C}H_2\}\overset{-}{X}$ (X = halogen). Similarly, reactions of type (4) proceed by a mechanism closely allied to that which obtains in class (3), and these reactions involve the opposite process $C_6H_5{\cdot}\overset{-}{C}H_2\}\overset{+}{X}$. Now, if the above considerations relating to the inductive and direct effects produced by halogens be taken as indicating the electrical states of these atoms, then the sequence $F > Cl > Br > I$ should connote the order of negativity of halogen substituents in corresponding compounds, that is, the degree of pre-formation of the halide anions. It follows that the relative ease of reactions involving the separation of the halide anions should accord with the above sequence, and the facility of those which require the separation of a real or potential halous kation should follow the opposite order. There exists much evidence indicating that the latter statement corresponds to reality so far as concerns the three previously-known benzyl halides and we have shown that benzyl fluoride falls into the sequence, since, under conditions in which benzyl chloride is reduced [reaction (3)], the fluoride remains unaffected, and furthermore, the conversion of the fluoride into benzyl ethyl ether by treatment with sodium ethoxide [reaction (4)] is much more difficult to bring about than is the corresponding reaction of the chloride. On the other hand, general experience shows that benzyl iodide and bromide are *more* reactive towards tertiary bases and acid hydrolytic and alcoholytic agents than is the chloride, and we have shown that benzyl fluoride reacts with trimethylamine and with ethyl alcohol much less readily than does benzyl chloride. Thus it appears that in reactions requiring the separation of a halide anion, the reactivities of the benzyl halides are in the opposite order to that which might be expected from a consideration of the influences of halogens on nuclear aromatic substitutions, and we are therefore compelled to suppose that the primary condition affecting the reactivity of the halogen substituents themselves is not so much the average or actual electrical condition of these atoms, but rather the extent to which they *are capable* of temporary electrical polarisation by the external fields of reagent molecules; * in other words, the fundamental condition is the magnitude of the restoring forces brought into play when the electrons of the carbon–halogen linking are displaced in either direction; or, again, the matter might be expressed in terms of energy relations, since the restoring force (f) referred to will be connected, through the integral $\int_0^\infty f dx$, to the critical energy increment of ionisation. It seems a reasonable assumption that the relative displaceability of the shared electrons of the four halogens in corresponding halides will run parallel with that of the unshared halogen electrons, and there is an accumulation of evidence that whilst the unshared electrons which combine most readily with a positive charge are those of iodine (example : formation of iodinium salts), the electrons of the outer shell of iodine are also those which are most easily displaced by a combining anion (example : hydrolysis of *p*-iodoxynitrobenzene). Combining this evidence with facts such as those underlying Fajan's theory of covalency formation and Sidgwick's theory of the production of higher groups of valency electrons, it is but a short step to the inference that the shared halogen electrons in corresponding halogenohydrocarbons are most easily displaced *in both directions* in the case of the iodo-derivative and least easily in the case of the fluoride. Thus the probable order of decreasing restoring forces is F, Cl, Br, I, and this is the sequence required to account for the observations referred to above relating to the side-chain reactivity of the benzyl halides.

One consequence of the assumption that it is the external molecular fields of adjacent reagent molecules which polarise the carbon–halogen linking sufficiently to lead to side-chain substitutions of benzyl halides is that reagents of many kinds, including

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* This statement may be expected to apply with a considerable degree of generality to substituents in carbon compounds.

those which are employed for nuclear substitutions, must (since they will also possess external molecular fields) bring about similar, if smaller, temporary electron displacements in the side chain. Concerning the effect of these side-chain polarisations on the result of nuclear substitution, it will be obvious that everything must depend on their duration, and the fact that a change of reagent has little influence on the proportions of the nuclear substitution products (provided that covalency formation does not take place between the side chain and the reagent) shows that the duration of the side-chain polarisations must be small. Nevertheless we believe that the cause here indicated is one of the principal factors which contribute to the small differences which have been observed in the proportions of nuclear substitutions by different reagents, and we deduce that the nuclear substitution of an iodo-compound should be more sensitive to a change of reagent than that of the corresponding bromo-derivative, and so forth ($I > Br > Cl > F$). Thus the interesting distinction between the state of polarisation and the polarisability of the halogens and other substituents should be capable of independent investigation along these lines.

EXPERIMENTAL.

Preparation of Benzyl Fluoride.—Benzyl chloride (60 c.c.) and a 33% solution of trimethylamine in ethyl alcohol (120 c.c.) were mixed in an open flask at the ordinary temperature and the mixture was shaken and cooled externally as long as was necessary to prevent the temperature from rising above 40° (about 15 mins.). A further 60 c.c. of benzyl chloride and 120 c.c. of trimethylamine solution were then added and the action was regulated as before. The flask was thereafter closed with a drying tube, kept for 1 hour, and heated at 45° for several hours (usually over-night) to complete the reaction. About 2 l. of dry ether were added and the hygroscopic benzyltrimethylammonium chloride was rapidly collected, washed with ether, and dissolved in water. The solution was treated (stirring) with a suspension of excess of silver oxide and filtered. The combined filtrate and washings were neutralised with 20% hydrofluoric acid and evaporated on the steam-bath to a viscous syrup. A third of the syrup thus obtained was distilled in a water-pump vacuum from a water-bath until the crystals of benzyltrimethylammonium fluoride, at first transparent, had dried and become opaque through efflorescence, and then with a free flame (the better to control frothing), through an ice-water condenser, into 400 c.c. of 10% hydrochloric acid cooled below 0°, in which the benzyl fluoride collected as an oil. A tower containing a small amount of hydrochloric acid cooled below 0° served to scrub a further small quantity of benzyl fluoride from the methyl fluoride which passed into the pump. After the remainder of the syrup had been similarly distilled in two portions into the same receiver, the oil in this and the scrubber was extracted with ether, and the extract washed three times with 10% hydrochloric acid and twice with aqueous sodium hydrogen carbonate, and dried with sodium sulphate. The residue which remained after removal of the ether gave (*a*) 4 g. of distillate, b. p. up to 69°/65 mm.; (*b*) 54 g., b. p. 69—71°/65—66 mm.; (*c*) 4 g., b. p. 71—77°/65—66 mm.; and (*d*) about 4 g. of a yellow, less volatile residue. Redistillation of fractions (*a*) and (*c*) augmented (*b*) to 60 g. The hydrochloric acid solution was evaporated to a paste, which was distilled with concentrated aqueous potassium hydroxide to expel the trimethylamine; this was dried, collected in alcohol, and used again. The benzyldimethylamine which remained as an oil was also recovered for use in the following method.

The recovered benzyldimethylamine was treated with the theoretical quantity of benzyl bromide, about half of which was introduced slowly with shaking and external cooling. Just before the mass became inconveniently viscous the remainder was added quickly, the reaction then proceeding rapidly to completion with a large evolution of heat. The crystalline dibenzyldimethylammonium bromide was, without purification, converted into the hydroxide and thence into the fluoride, which was decomposed by distillation as in the first method (yield, about 60%). The recovered bases consisted of benzyldimethylamine and dibenzylmethylamine. The former on treatment with benzyl bromide, and the latter on treatment with methyl iodide, yielded quaternary salts from which a further stock of dibenzyldimethylammonium fluoride, and thence of benzyl fluoride, was obtained.

Gram-molecular quantities of tribenzylamine and methyl iodide were kept in a sealed flask at 45° (in a thermostat) for 10 days. The sparingly soluble tribenzylmethylammonium iodide was finely ground and well-stirred for 16 hours with 4·5 l. of an aqueous suspension of silver oxide at 80—90°. The hydroxide was converted into the fluoride, which was decomposed in the usual way, yielding 35 g. of benzyl fluoride. Dibenzylmethylamine and some tribenzylamine were recovered and used again.

Physical properties. The *benzyl fluoride* (Found: C, 76·3; H, 6·3. C_7H_7F requires C, 76·4; H, 6·4%) prepared by these methods is a colourless mobile liquid, which does not fume in air and is not lachrymatory. On cooling, it sets to a mass of white needles, m. p. – 36° (uncorr.), and the b. p.'s observed during the preparation were 40—40·5°/14 mm., 55—56°/30—30·5 mm., 70—71°/

66 mm., 85—86°/118—119 mm., 100—100·5°/244—246 mm., 139—140°/ordinary pressure (all uncorr.). For more precise physical characterisation a sample boiling within a range of 1° was further purified by distillation, controlled by m. p. determinations. After the first distillation the m. p.'s were as follows: first, 20%, — 36·5°; middle, 60%, — 35·5°; last, 20%, — 37·5°. The middle fraction, on redistillation, gave a head fraction, m. p. — 35°, a main fraction, m. p. — 35°, and a tail fraction, m. p. — 36°. The main fraction on distillation gave only fractions having m. p. — 35° (corr.). The b. p. was 139·8°/753 mm. (corr.), which corresponds to 139·9°/760 mm. (corr.) if the small correction to standard pressure is made by means of the approximate vapour-pressure observations recorded above. The purified sample was used for the determinations of density and refractive index recorded on p. 2250, and for tracing the curve of extinction coefficients shown in the diagram. The toluene required for the former observations was carefully purified by freezing. The absorption curve is plotted from about 50 comparison photographs taken with a polarisation-photometer by Bellingham and Stanley, Ltd., and a spectrometer giving a dispersion at the plate of 80 Å.U. per cm. at λ 2500.

Action of Sulphuric Acid, Hydrofluoric Acid, and Certain Kinds of Glass.—Benzyl fluoride readily loses hydrogen fluoride under certain conditions and passes into a hydrocarbon, or mixture of hydrocarbons $(C_7H_6)_x$. When the liquid is touched with a rod moistened with concentrated sulphuric acid, a violent reaction sets in and rapidly spreads throughout the mass, much heat being generated and hydrogen fluoride copiously evolved. The product is an opaque white glass. It is sparingly soluble in alcohol and moderately easily soluble in benzene; but it could neither be distilled nor crystallised. It contained not more than a trace of fluorine, and analysis indicated the empirical composition C_7H_6, although the molecular weight is undoubtedly high. A similar product is obtained when benzyl fluoride is left in contact with concentrated hydrofluoric acid in a platinum vessel, but hydrochloric and nitric acids do not appear to induce the decomposition.

An identical, or closely similar, product, also giving analytical results in accordance with the formula $(C_7H_6)_x$, is obtained when benzyl fluoride decomposes spontaneously in glass vessels. The reaction, which may develop with almost explosive violence, appears to commence at the glass surface. In the earlier experiments it frequently occurred during distillation, commencing in the side tube, with etching of the glass, and spreading backwards into the distilling flask. The action seems to be autocatalytic, and when the pure stable liquid is deliberately contaminated with a trace of a decomposing specimen the whole decomposes even in platinum. The kind of glass is an important factor, and no losses have so far occurred when Jena glass vessels have been used for distillation. For storage, moulded bottles of uncertain history are to be avoided; the pure fluoride has, however, been kept for months without any sign of deterioration in Wood Bros.' flasks and Parkes' test-tubes.

Action of Potassium Carbonate.—Benzyl fluoride (11 g.) was boiled for 6 hours with 400 c.c. of 10% potassium carbonate solution; the product on distillation yielded 4·4 g. of recovered benzyl fluoride, b. p. 137—142°, 3·4 g. of benzyl alcohol, b. p. 200—208°, and an intermediate fraction containing both. Benzyl chloride (12·5 g.), treated similarly, yielded only benzyl alcohol.

Action of Zinc and Alcohol.—According to Tommasi (*Ber.*, 1874, 7, 826) benzyl chloride, on boiling with zinc dust and ethyl alcohol, is reduced to toluene. We have confirmed this, but find that benzyl ethyl ether is also formed. Benzyl fluoride (11 g.) on similar treatment yielded neither toluene nor benzyl ethyl ether in significant quantities, and over 90% was recovered unaltered.

Action of Alcoholic Trimethylamine.—Benzyl chloride readily reacts with 33% ethyl-alcoholic trimethylamine and combination is complete when a mixture of the theoretical quantities has been kept at about 45° for 3 hours. A mixture of benzyl fluoride and 33% alcoholic trimethylamine in the correct proportion was kept at 44° for 20 hours. The product, on being poured into water and extracted with ligroin, gave back 80% of the original benzyl fluoride, b. p. 138—140°. The aqueous solution was evaporated until it was neutral; the quaternary base was then precipitated as its picrate (m. p. and mixed m. p. with genuine benzyltrimethylammonium picrate, 169—170°). The yield was 5%, and since the picrate is very sparingly soluble, it is probable that this approximately represents the proportion of quaternary salt formed under the conditions used.

Action of Sodium Ethoxide.—Benzyl chloride and sodium ethoxide react quantitatively and immediately at the boiling point of alcohol. Benzyl fluoride (11 g.) was boiled for 1 hour with a solution of sodium ethoxide prepared from 2·3 g. of sodium and 24 g. of ethyl alcohol. The product yielded unaltered benzyl fluoride (3·1 g., b. p. 139—144°), benzyl ethyl ether (2·2 g., b. p. 185—190°), and an intermediate fraction which contained a considerable amount of benzyl fluoride (sulphuric acid test).

Nitration.—Freshly distilled, absolute nitric acid (6·3 g.), freed from nitrous acid, was slowly mixed with acetic anhydride (16 g.) at 5°. After warming the solution to 25°, benzyl fluoride (11·0 g.) was added. Nitration proceeded at a convenient velocity, between

25° and 30°, and was controlled by cooling the mixture to 25° as often as the temperature mounted to 30°. When this ceased to occur, the flask was placed in a thermostat at 25° for 6 hours, after which its contents were shaken with ice and water to destroy the acetic anhydride. The straw-coloured oil was extracted with benzene, washed six times with water, which removed a trace of yellow dye, and once with aqueous sodium hydrogen carbonate, and dried with sodium sulphate. The benzene and any excess of benzyl fluoride were removed at 40—50°/14 mm. by a slow stream of dry air, and the nitration product was distilled under about 0·1 mm.; only an insignificant residue remained. The distillate (Expt. 1) had $n_D^{25°}$ 1·5385 (Found: C, 54·3; H, 3·8. Calc.: C, 54·2; H, 3·8%). The last few drops, collected separately, had $n_D^{25°}$ 1·5390, proving the absence of dinitration products. The corresponding figures for the product of Expt. 2 were $n_D^{25°}$ 1·5382; C, 54·2; H, 3·9%; and for the last drops of the distillate, $n_D^{25°}$ 1·5388.

These products partly crystallised at 0° and appeared to be wholly solid at − 33°. That obtained from Expt. 1 was filtered off at the temperature of ice (solid = A_1), again at that of liquid sulphur dioxide (solid = B_1), and again in an ice–salt mixture (solid = C_1; liquid = D_1). The product of Expt. 2 was similarly treated, the filtration at 0°, however, being omitted (fractions B_2, C_2, D_2). Fractions A_1, B_1, and B_2 remained solid at the ordinary temperature and on crystallisation from ether–ligroin below 0° yielded long, colourless needles, m. p. 38·5°, of pure p-*nitrobenzyl fluoride* (Found: C, 54·4; H, 3·9. $C_7H_6O_2NF$ requires C, 54·2; H, 3·8%), since oxidation with alkaline permanganate under the standard conditions described below yielded *p*-nitrobenzoic acid (m. p. 230—233° unpurified, mixed m. p. 233—234°). Fractions C_1 and D_1, which were liquid at the ordinary temperature, were drained on porcelain at the temperature of liquid ammonia (C_1' and D_1'); and fractions C_2 and D_2 were crystallised from ligroin containing a trace of ether at about − 40°, whereby, as was shown by oxidation, the *o*-nitro-compound was concentrated in the former (C_2') and the *m*-derivative in the latter (D_2'), so that these isomerides, although they could not be completely purified, were obviously produced in significant quantities.

For the estimation of the isomerides the mixed mononitro-derivatives were converted into the nitrobenzoic acids, which were estimated by separation (Baker and Ingold, J., 1926, 2462) and also by Baker's adaptation (J., 1927, 565) of Holleman's solubility method. Both methods were again standardised by application to artificial mixtures. The method of oxidation was different from those formerly employed, which proved unsatisfactory; the new method depended on the formation of nitrobenzyl alcohols which were rapidly oxidised with permanganate of low concentration. Conversions of about 90%, reproducible to 1%, were obtained, and deviations in the conversions of the individual isomerides were corrected for (Ingold, Ingold, and Shaw, J., 1927, 813).

The nitration product (Expt. 3 : $n_D^{25^\circ}$ 1·5387; C, 54·3; H, 3·9%) was boiled with 50 parts of 10% aqueous potassium carbonate, and an equal volume of the same solution containing 3% of potassium permanganate was added in 75 equal parts at such a rate as to keep pace with the decolorisation as exactly as possible. The acids were isolated in 89·4% yield in the usual way (*M* by titration, 167·2; benzoic acid by sublimation, nil), and on separation gave 55·0% of *p*-nitrobenzoic acid, m. p. 234—235° unpurified, mixed m. p. 235—236°, and 17·6% of *m*-nitrobenzoic acid, m. p. 133—137°, mixed m. p. 138—140°, the recorded yields being corrected for the solubility of the *p*-acid in chloroform and of the *m*-barium salt in water. The yield of crude *o*-acid, m. p. 130—140° (containing *m*-acid), brought the total recovery to 99·7%. For the determination of the *m*-isomeride (18·0%) by solubility it was necessary to extend the reference curve given by Baker (*loc. cit.*) and the following additional determinations were made :

Meta added (mg.)	70·1	107·1	133·9	162·3	164·9
Meta found (mg.)	74·7	125·0	168·7	190·8	191·8

Fraction C_1' oxidised under the standard conditions gave nitrobenzoic acids in 89·0% yield (*M* by titration, 166·7; benzoic acid, nil), which on separation yielded 42·3% of *p*-nitrobenzoic acid, m. p. 231—234°, mixed m. p. 234—235°. The proportion of *m*-acid was determined by the solubility method to be 2·7%. Fraction C_2' yielded 88·8% of mixed nitrobenzoic acids, which on separation gave 29·2% of *p*-nitrobenzoic acid; the proportion of *m*-nitrobenzoic acid, determined by solubility, was zero. Fraction D_1' gave 90·9% of mixed acids (*M*, 167·3; benzoic acid, nil), which on separation yielded 14·5% of *p*-nitrobenzoic acid, m. p. 230—232°, mixed m. p. 232—234°, and 47·8% of *m*-nitrobenzoic acid, m. p. 131—136°, mixed m. p. 136—139°; the figure 47·8% was also obtained by the solubility method. Fraction D_2' yielded 91·2% of mixed acids, which on separation gave 8·0% of *p*-nitrobenzoic acid, m. p. 229—233°, mixed m. p. 230—234°; the proportion of *m*-nitrobenzoic acid was found by the solubility method to be 65·1%. *p*-Nitrobenzyl fluoride gave nitrobenzoic acid in 89·6, 90·0% yields. The mean conversions are calculated to be ortho 88·4%, meta 92·9%, para 89·8%, and hence the proportions of *o*-, *m*-, and *p*-nitrobenzyl fluorides are : ortho 27·9%, meta 17·1%, para 55·0% (separation), meta 17·5% (solubility). Expts. 4, 5, and 6 were carried out in like manner and the results are included in the following table :

		Nitrobenzoic acids.			Nitrobenzyl fluorides.			
		Separation.		Solubility.	Separation.			Solubility.
Nitration No.	Conversion into acids (%).	Para (%).	Meta (%).	Meta (%).	Ortho (%).	Meta (%).	Para (%).	Meta (%).
3	89·4	55·0	17·6	18·0	27·9	17·1	55·0	17·5
4	89·5	54·0	18·2	18·1	28·4	17·6	54·0	17·5
5	89·0	54·1	17·9	18·4	28·4	17·4	54·2	17·9
6	90·1	54·5	17·5	17·9	28·5	17·0	54·5	17·5
				Mean	*28·3*	*17·3*	*54·4*	*17·6*

Distillation of o-, m-, *and* p-*Nitrobenzyltrimethylammonium Fluorides.*—*p*-Nitrobenzyltrimethylammonium fluoride, which was prepared from *p*-nitrobenzyl chloride and trimethylamine *via* the quaternary chloride and hydroxide, yielded a crystalline neutral distillate when a water-pump was used, and a solid, together with an oil which contained combined fluorine, when the distillation was conducted with an oil-pump-backed two-stage diffusion pump and a charcoal–liquid-air trap. In each case the solid proved to be *p*-nitrobenzaldehyde (Found : C, 55·8; H, 3·6. Calc.: C, 55·6; H, 3·3%). In the vacuum of the diffusion pump the *o*- and *m*-nitro-salts gave oily distillates, from which aqueous semicarbazide acetate at once precipitated the semicarbazones of *o*- and *m*-nitrobenzaldehydes. In each case a very small amount of an oil containing fluorine was obtained by washing the crude semicarbazones with a mixture of equal parts of ether and ligroin. Energetic decomposition with charring occurred under all conditions and effective control could not be maintained.

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