767. *Studies of Trifluoroacetic Acid. Part VI.* Trifluoroacetyl Derivatives of Amines.*

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A series of trifluoroacetylated amines has been prepared by using trifluoroacetic anhydride. Those derived from primary aromatic amines and from 2 : 2 : 2-trifluoroethylamine may be titrated with aqueous alkali and recovered when the solutions are acidified. Aniline reacts with trifluoroacetic anhydride–acetic acid, and with trifluoroacetic acid–acetic anhydride, to give both the *N*-acetyl and *N*-trifluoroacetyl derivatives. Acetanilide and *N*-*cyclo*hexylbenzamide give diacyl derivatives when treated with trifluoroacetic anhydride.

Apart from Swarts's original paper on trifluoroacetic acid (*Bull. Acad. roy. Belg., Classe Sci.*, 1922, **8**, 343) in which he described the amide and the anilide, little has been reported about the chemistry of *N*-trifluoroacetyl derivatives, although a few of these compounds

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have been mentioned briefly in other connections (cf. Park, Englert, and Meek, *J. Amer. Chem. Soc.*, 1951, **73**, 5898; Shine and Niemann, *ibid.*, 1952, **74**, 97; Weygand and Csendes, *Angew. Chem.*, 1952, **64**, 136; Dickey, U.S.P. 2,436,100). We have made certain of these compounds by treatment of amines with trifluoroacetic anhydride, reactions which, as expected, proceeded extremely readily (see Table 1). With an excess of amine (method A) the trifluoroacetate salt (isolated in some cases) was formed as well as the amide; with an excess of anhydride (method B) this salt was itself trifluoroacetylated. That the trifluoroacetyl groups of the products from aromatic amines were in fact carried on the amino-groups and not on the aromatic nuclei was proved by hydrolysis of the amides with dilute alkali and formation of the known *N*-benzoyl derivatives.

Though they were unaffected during 3—4 hours in boiling dry methyl alcohol (cf. the trifluoroacetate esters; Bourne, Tatlow, and Tatlow, *J.*, 1950, 1367), the trifluoroacetylamines were decomposed fairly readily by aqueous alkali (keeping them for an hour with N-sodium hydroxide caused extensive hydrolysis). It was found also that some of them dissolved readily in aqueous alkali and, if the solutions were acidified without long delay, the unchanged amides were reprecipitated. Accordingly, the trifluoroacetylated amines, acetanilide, and 2 : 5-dichloroacetanilide were titrated, in aqueous-alcoholic solution, against approx. 0·1N-sodium hydroxide. The two acetylated amines, the trifluoroacetylated secondary amines, *N*-*cyclo*hexyltrifluoroacetamide, and *N*-benzyltrifluoroacetamide did not take up alkali under these conditions, whereas the trifluoroacetylated primary aromatic amines and *N*-(2 : 2 : 2-trifluoroethyl)trifluoroacetamide did (end-points *ca.* pH 11—11·5); the equivalents thus determined showed these amides to be monobasic (see Table 2). Acidification of each solution regenerated the amide, showing that the alkali take-up was due to the formation of a sodio-derivative and was not caused by hydrolysis.

It is evident that the strongly electrophilic trifluoromethyl group is primarily responsible for this display of acidity by the amido-function because, although analogous acetyl compounds give sodio-derivatives with metallic sodium in inert solvents (see, for example, Hepp, *Ber.*, 1877, **10**, 327), they do not in general give them with aqueous bases. Further, in order to be acidic the substituted trifluoroacetamide must have an amine component which possesses a suitable electrophilic residue (*e.g.*, a phenyl or trifluoroethyl group). It is also of interest that the amides containing aromatic nuclei become progressively more acidic, as indicated by the steeper slopes at the end-points of the titration curves, with increasing electrophilic character of the nuclear substituents; in this way a general method might be developed for comparison of the basic strengths of weak amines.

That the trifluoroethyl group has a profound influence on the reactions of the amino-group in 2 : 2 : 2-trifluoroethylamine has been demonstrated previously, for with nitrous acid, the amine gives 2 : 2 : 2-trifluorodiazoethane (Gilman and Jones, *J. Amer. Chem. Soc.*, 1943, **65**, 1458). Our sample of trifluoroethylamine was prepared in good yield by reduction of trifluoroacetamide with lithium aluminium hydride. Previous methods have involved reduction of the nitrile (Gilman and Jones, *loc. cit.*) or treatment of 1-chloro-2 : 2 : 2-trifluoroethane with ammonia (Benning and Park, U.S.P. 2,348,321).

Sulphonamides derived from primary amines have long been known to be alkali-soluble (Hinsberg, *Ber.*, 1890, **23**, 2962), though, unlike the trifluoroacetamides, they are hydrolysed by alkali only with difficulty (cf. Schreiber and Shriner, *J. Amer. Chem. Soc.*, 1934, **56**, 114).

Recent work in this department has shown that trifluoroacetic anhydride promotes reactions between carboxylic acids and hydroxy-compounds or activated aromatic compounds (Bourne, Stacey, Tatlow, and Tedder, *J.*, 1949, 2976; 1951, 718). Accordingly, it was of interest to examine the reactions of such anhydride–acid mixtures with amines; the reactions were found, however, to be more complex in this case. Aniline, treated with an excess of an equimolecular mixture of acetic acid and trifluoroacetic anhydride, gave roughly equal proportions of acetanilide and of trifluoroacetanilide, and excess of aniline treated with the mixture in carbon tetrachloride solution gave more of the trifluoroacetyl derivative. With acetic anhydride–trifluoroacetic acid both products were again given; by use of a mixture of benzoic acid and trifluoroacetic anhydride, benzanilide and trifluoroacetanilide were obtained. The separation of the anilide mixtures into pure components was difficult, even by utilisation of the preferential solubility of the trifluoro-derivative in alkali, so that the yields recorded are probably low. With aniline trifluoroacetate, trifluoroacetic anhydride gave trifluoroacetanilide, acetic anhydride gave acetanilide, and a mixture of acetic acid and trifluoroacetic anhydride gave the trifluoroacetyl derivative, all in good yield.

The mechanism suggested for the reactions of acetic acid–trifluoroacetic anhydride (Bourne, Randles, Tatlow, and Tedder, *Nature*, 1951, **168**, 942) involved the formation of the unsymmetric anhydride, $CF_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3$, which can be formed also from mixtures of trifluoroacetic acid and acetic anhydride. This unsymmetric anhydride would be expected to react, if in the molecular form, to give trifluoroacetyl derivatives preferentially [compare Emery and Gold (*J.*, 1950, 1443, 1447, 1455) for reactions of unsymmetric anhydrides of acetic and chloroacetic acids]. However, conductivity measurements suggest that ionization of the unsymmetric anhydride occurs to a small extent to give $CH_3{\cdot}CO^+$ and $CF_3{\cdot}CO_2^-$, and that it is the acetylium cation which reacts preferentially with hydroxy-compounds and activated aromatic compounds (Bourne, Randles, Tatlow, and Tedder, *loc. cit.*). On the other hand, the acetyl and trifluoroacetyl derivatives which are formed from amines with acetic anhydride–trifluoroacetic acid and acetic acid–trifluoroacetic anhydride would seem to arise mainly from the unsymmetric anhydride in its molecular form. The probable reason for this is that the basicity of the amine suppresses the slight ionization of the unsymmetric anhydride; for example, the addition of a base to acetic acid–trifluoroacetic anhydride (*i.e.*, $CF_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + CF_3{\cdot}CO_2H$) would, by a proton transfer, rapidly produce a considerable concentration of $CF_3{\cdot}CO_2^-$ ions, thus greatly reducing the concentration of the $CH_3{\cdot}CO^+$ cations. The same result would occur if the unsymmetric anhydride reacted with $CF_3{\cdot}CO_2^-$ ions to give $CH_3{\cdot}CO_2^-$ ions and $(CF_3{\cdot}CO)_2O$. Further, molecular anhydrides appear to acylate amines more rapidly than hydroxy-compounds and these factors together would mean that the molecular unsymmetric anhydride should play an important part in the reaction with amines. Thus, these considerations lead to the conclusion that, in accordance with experimental results, a mixture of anilides, with the trifluoroacetylated product predominating, would be expected. It is significant that the treatment of aniline trifluoroacetate with acetic acid–trifluoroacetic anhydride gave a good yield of trifluoroacetanilide, no acetanilide being isolated.

Acetanilide and *N*-*cyclo*hexylbenzamide formed *N*-acetyl-*N*-trifluoroacetylaniline and *N*-benzoyl-*N*-trifluoroacetyl*cyclo*hexylamine, respectively, when treated with trifluoroacetic anhydride. These diacyl products were very readily hydrolysed and were susceptible also to methanolysis, the trifluoroacetyl residue being removed in each case, leaving the original acylated amine. *N*-Acetyl-*N*-trifluoroacetylaniline reacted with 2 : 5-dichloroaniline to give 2 : 5-dichlorotrifluoroacetanilide and acetanilide. Infra-red measurements of the trifluoroacetylated benzamide and acetamide derivative, carried out in collaboration with Dr. D. H. Whiffen, suggested that they did, in fact, contain two acyl groups as such [cf. Hunter and Reynolds (*J.*, 1950, 2857) who found no evidence for the existence of imidol forms in various diacyl types]. Diacyl derivatives could not be isolated when trifluoroacetanilide was treated with acetic anhydride, trifluoroacetic anhydride, or acetic acid–trifluoroacetic anhydride, or when benzanilide was treated with trifluoroacetic anhydride, though in the last case there were indications that a very unstable product may have been formed. It appears that the formation of diacyl derivatives from substituted amides is rendered progressively more difficult by the presence of increasingly electrophilic substituents.

At present, the evidence suggests that trifluoroacetic anhydride will be less useful for promoting *N*-acylation by carboxylic acids than it is for effecting *O*-acylation. It may be possible, however, in certain cases to arrange that a significant amount of *N*-acylation does occur, and thus to promote, for example, peptide synthesis.

EXPERIMENTAL

Trifluoroacetylation of Amines.—(*a*) *General methods.* (A) A solution of trifluoroacetic anhydride (1 mol.) in about twice its volume of a dry inert solvent was added at 0° to a solution of the amine (2 mol.) in the minimum volume of the same solvent. After 10—60 minutes, the volatile matter was removed by distillation under diminished pressure, ice-water was added to the residue, and the precipitated amide was collected and recrystallised.

(B) The amine (1 mol.) was treated with trifluoroacetic anhydride (1—6 mols.) and, after being warmed if necessary to effect solution and then kept for 10—60 minutes, the mixture was evaporated under diminished pressure, several portions of carbon tetrachloride being added successively to, and distilled under diminished pressure from, the residue before it was recrystallised.

TABLE 1. *Trifluoroacetylation of amines.*

No.	Parent	Amine (g.)	$(CF_3{\cdot}CO)_2O$ (g.)	Solvent used	Method	Yield (g.)	Solvent for recrystn.*	M. p.
I	NH_2Ph	12·02	13·4	Et_2O	A	7·37	$EtOH-H_2O$	88·5—90°
		0·66	4·5	CCl_4	B	1·24	Pet B	89—90
II	2 : 5 : 1-$C_6H_3Cl_2{\cdot}NH_2$	2·35	1·5	Et_2O	A	0·71	$EtOH-H_2O$	67—68
		0·51	1·2	None	B	0·71	Pet A	67—68·5
III	*p*-$C_6H_4Cl{\cdot}NH_2$	10·00	8·5	Et_2O	A	6·00	$EtOH-H_2O$	123—124·5
IV	*p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$	0·49	4·5	Et_2O	B	0·71	,,	151·5—153
V	$[CH_2]_5{>}CH{\cdot}NH_2$	1·43	1·5	Et_2O	A	0·62	,,	93—95
		5·00	10·4	Et_2O	B	7·82	Pet C	94—95
VI	*p*-$C_6H_4Me{\cdot}NH_2$	1·65	1·5	Et_2O	A	1·01	,,	111—112
VII	$CH_2Ph{\cdot}NH_2$	1·96	3·9	Et_2O	B	2·75	,,	73·5—75
VIII	NHPhMe	1·95	2·1	Et_2O	A	1·32	Pet A	26—27
IX	*p*-$MeO{\cdot}C_6H_4{\cdot}NH_2$	9·99	8·6	$CHCl_3$	A	4·84	Pet C	112·5—115
X	*p*-$EtO{\cdot}C_6H_4{\cdot}NH_2$	1·97	1·5	Et_2O	A	0·75	,,	141—143
XI	β-$C_{10}H_7{\cdot}NH_2$	2·07	1·5	Et_2O	A	1·05	,,	146—148
XII	$NHPh_2$	2·44	1·5	Et_2O	A	0·90	$EtOH-H_2O$	71—72
		0·51	3·7	None	B	0·73	,,	71—72
XIII	*p*-$Ph{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NH_2$	0·51	3·0	Et_2O	B	0·53	Pet C	176—178

* Pet = light petroleum, b. p. (A) 40—60°, (B) 60—80°, (C) 80—100°.

No.	Formula	Required, % C	H	F	Found, % C	H	F
I	$C_8H_6ONF_3$	50·8	3·2	30·1	50·8	3·2	30·0
II	$C_8H_4ONCl_2F_3$	37·2	1·6	22·1	36·9	1·5	22·1
III	$C_8H_5ONClF_3$	43·0	2·3	—	43·1	2·4	—
IV	$C_8H_5O_3N_2F_3$	41·0	2·2	24·3	40·8	1·9	23·8
V	$C_8H_{12}ONF_3$	49·2	6·2	29·2	49·6	6·2	29·6
VI	$C_9H_8ONF_3$	53·2	4·0	—	53·0	3·9	—
VII	$C_9H_8ONF_3$	53·2	4·0	28·1	53·4	3·8	28·2
VIII	$C_9H_8ONF_3$	53·2	4·0	—	53·1	3·8	—
IX	$C_9H_8O_2NF_3$	49·3	3·7	—	49·1	3·7	—
X	$C_{10}H_{10}O_2NF_3$	51·5	4·3	—	51·4	4·2	—
XI	$C_{12}H_8ONF_3$	60·3	3·4	—	60·6	3·3	—
XII	$C_{14}H_{10}ONF_3$	63·4	3·8	—	63·0	3·9	—
XIII	$C_{14}H_{10}ON_3F_3$	57·3	3·4	19·4	57·2	3·2	19·2

Details of the trifluoroacetylated amines which were prepared are given in Table 1. Swarts (*loc. cit.*) reported m. p. 87·6° for trifluoroacetanilide; the other *amides* are new.

(*b*) *Trifluoroacetanilide from aniline hydrochloride.* Aniline hydrochloride (0·59 g.) and the anhydride (4·5 g.), treated as in method B, gave trifluoroacetanilide (0·68 g.).

(*c*) N-(2 : 2 : 2-*Trifluoroethyl*)*trifluoroacetamide.* 2 : 2 : 2-Trifluoroethylamine hydrochloride (1·16 g.) and trifluoroacetic anhydride (7·5 g.) were warmed at 50° for 30 minutes, and the mixture was then distilled under diminished pressure with ether (4 × 10 c.c.) and carbon tetrachloride (10 c.c.). The residual *amide* (XIV) (1·16 g.) had m. p. 51—52°, unchanged by recrystallisation (Found: C, 24·6; H, 1·5; F, 57·9. $C_4H_3ONF_6$ requires C, 24·6; H, 1·55; F, 58·45%). This amide is appreciably volatile, and unless care is taken handling losses are serious.

TABLE 2.

Compound no.		I	II	III	IV	VI	IX	X	XI	XIII	XIV
Equiv. :	Found	192	256	224	227	212	224	240	241	289	196
	Reqd.	189	258	224	234	203	219	233	239	293	195

Potentiometric Titrations of N-*Trifluoroacetylated Amines.*—Aqueous-alcoholic solutions of the amides (0·1—0·2 g.) were titrated against standard sodium hydroxide solution (*ca.* 0·1N), a Cambridge instrument being used to measure pH. In Table 2 are recorded the equivalents calculated from the titration curves for those amides which are acidic. The curves for acetanilide, 2 : 5-dichloroacetanilide, *N-cyclo*hexyltrifluoroacetamide, and *N*-benzyltrifluoroacetamide showed the complete absence of acidic groupings.

After each titration, the solution was acidified with dilute hydrochloric acid, and then extracted with chloroform. The original trifluoroacetylated amines were regenerated (recovery 80—95%), except that recovery of *p*-nitrotrifluoroacetanilide in good yield was difficult owing to rapid hydrolysis at the end-point of the titration.

Reactions of Aniline with Acetic–Trifluoroacetic Acid–Anhydride Mixtures.—(*a*) A mixture of acetic acid (1·89 g., 6·0 mols.) and trifluoroacetic anhydride (6·70 g., 6·0 mols.) was added to aniline (0·49 g., 1·0 mol.), a vigorous reaction ensuing. After 15 minutes at 15°, the volatile constituents were distilled off *in vacuo* with several portions of carbon tetrachloride. A solution of the residue in chloroform was washed with 2N-sodium hydroxide and then with water, dried ($MgSO_4$), filtered, and distilled, to give a residue which, on recrystallisation from light petroleum (b. p. 100—120°), afforded acetanilide (0·155 g., 0·22 mol.), m. p. and mixed m. p. 114—115°. Acidification of the cooled alkaline extract gave trifluoroacetanilide (0·20 g., 0·20 mol.), m. p. and mixed m. p. 88—89°.

(*b*) Aniline (1·48 g., 3·0 mols.) in carbon tetrachloride (27 c.c.), was treated with a mixture of acetic acid (0·32 g., 1·0 mol.), trifluoroacetic anhydride (1·12 g., 1·0 mol.), and carbon tetrachloride (4 c.c.). After 5 minutes' refluxing, the precipitated aniline trifluoroacetate (1·52 g., 1·37 mols.), m. p. 124°, was collected. The solution was evaporated and the residue recrystallised from light petroleum (b. p. 60—80°) and then from aqueous alcohol, to give trifluoroacetanilide (0·488 g., 0·48 mol.); from the mother-liquors acetanilide (0·065 g., 0·09 mol.) was obtained.

(*c*) A mixture of trifluoroacetic acid (1·35 g., 2·2 mols.) and acetic anhydride (0·54 g., 1·0 mol.) was added to aniline (0·49 g., 1·0 mol.). Treatment as in (*a*) gave trifluoroacetanilide (0·119 g., 0·12 mol.) and acetanilide (0·273 g., 0·38 mol.). A similar reaction using aniline (1·0 mol.), acetic anhydride (2·0 mols.), and trifluoroacetic acid (4·0 mols.) gave acetanilide (0·29 mol.) and trifluoroacetanilide (0·33 mol.).

Acylations of Aniline Trifluoroacetate.—(*a*) The salt, treated with trifluoroacetic anhydride, as in method B (p. 4017), gave trifluoroacetanilide (85%).

(*b*) With acetic anhydride, the salt, in a similar process, gave acetanilide in 78% yield.

(*c*) The salt (1·11 g., 1 mol.), treated with a mixture of acetic acid (0·63 g., 2 mols.) and trifluoroacetic anhydride (2·2 g., 2 mols.), afforded trifluoroacetanilide (0·84 g., 83%).

Trifluoroacetylation of Aniline Acetate.—This salt, when treated with trifluoroacetic anhydride, gave trifluoroacetanilide in 68% yield.

N-*Acetyl*-N-*trifluoroacetylaniline.*—(a) *Preparation.* Trifluoroacetic anhydride (2·8 g.) and acetanilide (1·53 g.) were left together at 15° for 10 minutes. After evaporation of volatile constituents under diminished pressure with several portions of carbon tetrachloride, the residue was distilled, to give the *diacyl* compound (1·74 g., 67%) as a syrup, b. p. 121—125° (bath-temp.)/12 mm. (Found: C, 52·2; H, 3·3; F, 25·0; CF_3·CO, 41·9. $C_{10}H_8O_2NF_3$ requires C, 51·95; H, 3·5; F, 24·7; CF_3·CO, 42·0%).

(b) *Hydrolysis.* The titration liquors from the trifluoroacetyl determination (see Bourne, Tatlow, and Tatlow, *loc. cit.*) yielded acetanilide in 69% yield.

(c) *Methanolysis.* The diacyl compound (0·171 g.) was refluxed in magnesium-dried methyl alcohol (5 c.c.) for 40 minutes before the alcohol was distilled off and the solid residue recrystallised to give acetanilide (0·066 g., 66%).

(d) *Reaction with* 2 : 5-*dichloroaniline.* This amine (0·502 g.) and the above diacyl compound (0·718 g.) were heated together at 100° for 1 hour. The residue was extracted with boiling light petroleum (b. p. 40—60°), and the insoluble portion was recrystallised from light petroleum (b. p. 100—120°), to give acetanilide (0·310 g., 74%). The solution after concentration deposited 2 : 5-dichlorotrifluoroacetanilide (0·573 g., 71%), m. p. and mixed m. p. 68°.

N-*Benzoyl*-N-*trifluoroacetyl*cyclo*hexylamine.*—(a) *Preparation.* *N-cyclo*Hexylbenzamide (1·02 g.), trifluoroacetic anhydride (6·0 g.), and sodium trifluoroacetate (0·39 g.) were refluxed for 20 minutes and then distilled at 20 mm. with several portions of carbon tetrachloride. The solid residue was extracted with boiling light petroleum (b. p. 40—60°), and the extracts were concentrated and cooled; the deposit was recrystallised twice from the same solvent, to give the *diacyl* compound (0·443 g., 29%), m. p. 81—82° (Found: C, 60·2; H, 5·2; F, 18·7; CF_3·CO, 33·3. $C_{15}H_{16}O_2NF_3$ requires C, 60·2; H, 5·4; F, 19·0; CF_3·CO, 32·4%).

(b) *Hydrolysis.* The titration liquors afforded *N-cyclo*hexylbenzamide (96%), m. p. and mixed m. p. 148°.

(c) *Methanolysis.* The diamide (0·125 g.), refluxed in dry methyl alcohol (10 c.c.) for 90 minutes, gave *N-cyclo*hexylbenzamide (0·083 g., 98%).

Infra-red Measurements on the Diacyl Derivatives.—By means of a Grubb Parsons infra-red spectrometer with a rock-salt prism, and chloroform or carbon tetrachloride as solvents, the following carbonyl stretching frequencies (cm.$^{-1}$) were recorded : acetanilide 1690, trifluoroacetanilide 1734, *N*-acetyl-*N*-trifluoroacetylaniline 1734 (one band only), *N*-*cyclo*hexylbenzamide 1652, *N*-*cyclo*hexyltrifluoroacetamide 1718, and *N*-benzoyl-*N*-trifluoroacetyl*cyclo*hexylamine 1726 and 1703. It appears that in the last derivative, the presence of the $CF_3{\cdot}CO$ residue increases the carbonyl frequency due to the $C_6H_5{\cdot}CO$ group by 51 cm.$^{-1}$. A similar increase with *N*-acetyl-*N*-trifluoroacetylaniline would result in the carbonyl frequencies due to the $CH_3{\cdot}CO$ and $CF_3{\cdot}CO$ groups lying very close together so that they would not be resolved. No evidence for the presence of $C{=}N$ bonds was found from either diacyl derivative.

Preparation of 2 : 2 : 2-*Trifluoroethylamine* (with M. W. BUXTON).—Trifluoroacetamide (11·5 g.) in dry ether (40 c.c.) was added dropwise during 2 hours to a cooled and stirred suspension of lithium aluminium hydride (7·6 g.) in dry ether (120 c.c.). After 16 hours at 20° the mixture was cooled in ice and cautiously treated with an excess of water. The precipitate was removed (centrifuge), and the ethereal layer was separated. The solid and the aqueous solution were extracted with more ether, and the combined ethereal layers were dried ($CaCl_2$), filtered, and treated with hydrogen chloride. The resulting precipitate, recrystallised from absolute alcohol, gave the amine hydrochloride (11·1 g., 80%), subliming rapidly at 195° (Found : C, 17·7; H, 3·7; F, 41·4. Calc. for $C_2H_5NClF_3$: C, 17·7; H, 3·7; F, 42·1%).

The hydrochloride, treated in the usual way with benzoyl chloride and sodium hydroxide solution, the precipitate being recrystallised from aqueous methyl alcohol, gave *N*-(2 : 2 : 2-*trifluoroethyl*)*benzamide* (67%), m. p. 115—116° (Found: C, 53·2; H, 3·7. $C_9H_8ONF_3$ requires C, 53·2; H, 4·0%).

Analysis.—Carbon and hydrogen analyses were carried out by the method of Belcher and Goulden (*Mikrochem. Mikrochim. Acta*, 1951, **36/37**, 679), and fluorine analyses by the method of Belcher and Tatlow (*Analyst*, 1951, **76**, 593).

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