Studies of Trifluoroacetic Acid. Part XII. Acyl Trifluoroacetates and their Reactions.*

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Acetyl, benzoyl, and phenylacetyl trifluoroacetates have been made from the corresponding carboxylic acid–trifluoroacetic anhydride mixtures, and by the interaction of the symmetrical carboxylic anhydrides with trifluoroacetic anhydride. Infra-red analysis showed that in these systems the equilibria favour the unsymmetric anhydrides. In general, the reactions of the acyl trifluoroacetates resemble those of carboxylic acid–trifluoroacetic anhydride mixtures, but it appears that the acylating (as distinct from trifluoroacetylating) activity of the latter media is enhanced by the trifluoroacetic acid liberated as the unsymmetric anhydrides are formed.

It is now well established that acylations of hydroxy-compounds, and of reactive aromatic nuclei, by many carboxylic acids can be promoted by trifluoroacetic anhydride. The mechanisms that have been advanced to explain these reactions have postulated the establishment of the following inter-related equilibria:

$$R{\cdot}CO_2H + (CF_3{\cdot}CO)_2O \rightleftharpoons R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3 + CF_3{\cdot}CO_2H \quad . \quad . \quad . \quad (1)$$

$$R{\cdot}CO_2H + R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3 \rightleftharpoons (R{\cdot}CO)_2O + CF_3{\cdot}CO_2H \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$(R{\cdot}CO)_2O + (CF_3{\cdot}CO)_2O \rightleftharpoons 2R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It has been assumed further that the unsymmetric anhydride can ionise to a slight extent into acylium ($R{\cdot}CO^+$) and trifluoroacetate ($CF_3{\cdot}CO_2^-$) ions, the former being the principal acylating species (Bourne, Randles, Tatlow, and Tedder, *Nature*, 1951, **168**, 942; Bourne, Henry, Tatlow, and Tatlow, *J.*, 1952, 4014; Bourne, Randles, Stacey, Tatlow, and Tedder, *J. Amer. Chem. Soc.*, in the press). These postulates are in accord with the earlier experimental results, and also with the recently described additions of carboxylic acid–trifluoroacetic anhydride systems to olefins and to acetylenes (Henne and Tedder, *J.*, 1953, 3628). Other evidence in support of the hypothesis has been obtained from cryoscopic (Morgan, *J. Amer. Chem. Soc.*, 1951, **73**, 860) and conductivity measurements (Randles, Tatlow, and Tedder, *J.*, 1954, 436). Since, however, unsymmetric anhydrides had not been isolated from carboxylic acid–trifluoroacetic anhydride mixtures, we began a further study of three such systems, and we have isolated from them the expected intermediates, and have investigated some of their reactions; we now record these observations. The preparation, from silver trifluoroacetate and the appropriate acyl chloride, of several of these acyl trifluoroacetates was reported recently by Ferris and Emmons (*J. Amer. Chem. Soc.*, 1953, **75**, 232); no reactions of the compounds were described.

Since much of our work has involved acetylation processes, we studied first the system $CH_3{\cdot}CO_2H$–$(CF_3{\cdot}CO)_2O$; direct distillation of such a mixture gave no definite products (see also Morgan, *loc. cit.*). However, the addition of pyridine to acetic acid–trifluoroacetic anhydride in ether caused the precipitation of a solid, which was shown to be pyridinium trifluoroacetate, and distillation of the residue afforded the desired unsymmetric anhydride, acetyl trifluoroacetate. Further, distillation of an equimolar mixture of acetic and trifluoroacetic anhydrides gave only acetyl trifluoroacetate. These results suggested that the unsymmetric anhydride had but little tendency to disproportionate, and this conclusion was amply confirmed by infra-red analysis. Measurements were made of the unsymmetric anhydride itself (it has a characteristic band at 1072 cm.$^{-1}$), and of the rate of its formation from the two symmetric anhydrides [equilibrium (3)]. Other systems analysed were (*a*) $CH_3{\cdot}CO_2H$–$(CF_3{\cdot}CO)_2O$ and $CF_3{\cdot}CO_2H$–$CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3$, and (*b*) $(CH_3{\cdot}CO)_2O$–$CF_3{\cdot}CO_2H$ and $CH_3{\cdot}CO_2H$–$CH_3{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3$. The strengths of the band at 1072 cm.$^{-1}$ and bands due to the symmetric anhydrides indicated that acetyl trifluoroacetate was present in

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equilibrium (3) to the extent of *ca.* 97% of the maximum possible concentration, in systems of type (*a*) to the extent of *ca.* 95%, and in type (*b*) to about 40%. These results are given in Table 1.

Treatment of benzoic acid–trifluoroacetic anhydride, in ether, with pyridine, and distillation of the filtrate, afforded benzoyl trifluoroacetate. Also, direct distillation of benzoic acid–trifluoroacetic anhydride gave first trifluoroacetic acid, and then the unsymmetric anhydride; in addition, the latter was made by distillation of an equimolar mixture of benzoic and trifluoroacetic anhydrides. Application of the last two processes enabled phenylacetyl trifluoroacetate to be prepared, and it appears that each of the three methods constitutes a fairly general process for the synthesis of acyl trifluoroacetates, and, probably, of other acyl perhalogenocarboxylates also. Infra-red measurements on benzoyl and phenylacetyl trifluoroacetates confirmed the earlier conclusions. Many unsymmetric anhydrides are known to disproportionate fairly readily (Emery and Gold, *J.*, 1950, 1443, and earlier references quoted therein; Brown and Trotter, *J.*, 1951, 87); however, the stability of acyl trifluoroacetates during distillation was noted by Ferris and Emmons (*loc. cit.*), though they found that disproportionation was catalysed by silver trifluoroacetate.

Reactions of acetyl trifluoroacetate with a number of hydroxy-compounds gave acetyl esters in good yield (see Table 2). However, with some of the lower aliphatic alcohols the reaction was more complex than this, both acetates and trifluoroacetates being formed. In these cases, since the ester products were liquid, they were converted into the corresponding anilides with anilinomagnesium iodide, according to Hardy's procedure (*J.*, 1936, 398; it was shown that ethyl acetate and ethyl trifluoroacetate gave acetanilide and trifluoroacetanilide, respectively, in this way in excellent yield). The mixture of anilides was then separated chromatographically on an alumina column. Though the total yield of anilides obtained was not quantitative, averaging *ca.* 65%, the method gave a general indication of the relative proportions of acetyl and trifluoroacetyl esters originally produced. In Table 3 are recorded the proportions of acetyl and trifluoroacetyl esters formed in the reaction of acetyl trifluoroacetate with *n*-, *sec.*-, and *tert.*-butyl alcohol, and in the first case the effect of the prior addition of trifluoroacetic acid to the unsymmetric anhydride. The decrease in the proportion of trifluoroacetate in the products, both with increased substitution of the hydroxylated carbon of the butanol, and as trifluoroacetic acid was added in the reaction with the primary alcohol, is noteworthy.

The reaction of acetyl trifluoroacetate with thiophen gave the 2-acetyl derivative, whilst with phenetole (see Table 4) *p*-ethoxyacetophenone was formed in moderate yield (30%) after 46 hr. The use of nitromethane as a solvent gave the same yield in only 3 hr., but addition of sodium trifluoroacetate or acetate to the anhydride prevented ketone formation, whilst acetic acid had little apparent effect. A mixture of acetyl trifluoroacetate and trifluoroacetic acid, however, gave an excellent yield (90%) of ketone in only 3 hr., 1 mol. of acid being necessary to give the best results.

With aniline, acetyl trifluoroacetate gave mainly trifluoroacetanilide, together with a little acetanilide (10%). The latter yield was increased (to 25%) when nitromethane was employed as a solvent. The unsymmetric anhydride and aniline in excess of trifluoroacetic acid gave almost pure trifluoroacetanilide, only a trace (0·5%) of acetanilide being detected.

Benzoyl trifluoroacetate appears to have more tendency to effect trifluoroacetylation than does acetyl trifluoroacetate. Phenols readily gave benzoate esters, but only the trifluoroacetate was obtained with *p*-nitrobenzyl alcohol, though the benzoate was formed when trifluoroacetic acid was added to the anhydride. Trifluoroacetanilide only was detected in the product of the reaction with aniline, and from anisole no ketone was obtained, though *p*-methoxybenzophenone was formed when trifluoroacetic acid was present.

Phenylacetyl trifluoroacetate seems to occupy an intermediate position. Again, phenols gave the phenylacetates almost exclusively, but with *p*-nitrobenzyl alcohol some phenylacetate was isolated, and the presence of a strong acid in the mother-liquors suggested that the trifluoroacetate had been formed as well.

The results obtained so far show that acyl trifluoroacetates ($R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CF_3$) can be

obtained from carboxylic acid–trifluoroacetic anhydride mixtures, and that they can function, in many cases, as acylating agents, *i.e.*, for the introduction of R·CO–. However, they are also trifluoroacetylating agents in some cases. Further work on their reactions is in progress to confirm and extend the preliminary results, the mode of attack on different types of hydroxy-compounds under varying conditions being of particular interest. Whilst we prefer to await the results of these further investigations before forming definite conclusions on the reaction mechanisms utilised by acyl trifluoroacetate and carboxylic acid–trifluoroacetic anhydride systems, it appears that our earlier hypotheses are largely in accord with the present observations. The existence of acyl trifluoroacetates in the equilibrium mixtures seems to be established. Tentatively, we suggest that the reactions of these unsymmetric anhydrides themselves may be explained if it is assumed, in accordance with the electronic theory, that in the molecular form they are principally trifluoroacetylating agents [cf. the work of Emery and Gold (*J.*, 1950, 1443, 1447, 1455) on anhydrides from acetic and the chloroacetic acids], whilst the alternative type of acylation is due largely to the acylium ion ($R{\cdot}CO^+$). Thus, the amines and the lower primary alcohols may be simultaneously acylated by the ion and trifluoroacetylated by the molecular anhydride, which, of course, is present in much greater concentration, whilst with the more complex alcohols, the phenols, and aromatic compounds reaction with the latter species may be too slow to be important. The effects of bases and of nitromethane on the reactions of the acyl trifluoroacetates resemble those with $R{\cdot}CO_2H$–$(CF_3{\cdot}CO)_2O$ (Bourne, Henry, Tatlow, and Tatlow; Bourne, Randles, Stacey, Tatlow, and Tedder, *locc. cit.*) and may be explained similarly. Though acyl trifluoroacetates are present in $R{\cdot}CO_2H$–$(CF_3{\cdot}CO)_2O$ mixtures and the reactivity of the latter may arise principally from their presence, it seems clear that the trifluoroacetic acid also produced enhances considerably the acylating activity of these anhydrides. Quantitative work on the various aspects of the problem is necessary before these tentative ideas can be established firmly.

Since this manuscript was prepared a note has appeared in which Emmons, McCallum, and Ferris (*J. Amer. Chem. Soc.*, 1953, **75**, 6047) describe the preparation of several acyl trifluoroacetates by distillation of carboxylic acid–trifluoroacetic anhydride mixtures. Infra-red measurements were used to show that acyl trifluoroacetates were formed almost quantitatively when certain carboxylic acids were treated with trifluoroacetic anhydride. The frequencies employed for this analysis were in the ranges 688—714 cm.$^{-1}$ and 1832—1873 cm.$^{-1}$. No reactions of the materials were reported.

Experimental

Unless otherwise stated, dry reagents and anhydrous conditions were employed.

Acetyl Trifluoroacetate from Acetic Acid–Trifluoroacetic Anhydride.—A mixture of acetic acid (2·10 g.) and trifluoroacetic anhydride (7·41 g.) was kept at 20° for 15 min., and then ether (5 c.c.) was added. Pyridine (2·78 c.c.) in ether (5 c.c.) was introduced dropwise, with cooling and vigorous stirring. The hygroscopic crystalline precipitate, collected by filtration, was *pyridinium trifluoroacetate* (4·63 g.), m. p. 82—83° alone and on admixture with a sample prepared from pyridine and trifluoroacetic acid in ether (Found: F, 28·9%; equiv., 193. $C_7H_6O_2NF_3$ requires F, 29·5%; equiv., 193). Distillation of the filtrate through a short Vigreux column gave ether, and then *acetyl trifluoroacetate* (2·81 g.) as a colourless liquid, b. p. 94—95°, n_D^{25} 1·3253, d 1·38 (Found: C, 31·0; H, 2·0; F, 36·1%; equiv., 79. $C_4H_3O_3F_3$ requires C, 30·8; H, 2·0; F, 36·5%; equiv., 78).

To determine the equivalent, the unsymmetric anhydride (0·0461 g.), in water, was titrated (pH meter) against 0·05N-sodium hydroxide. Two end-points were observed, one at pH 3·34, corresponding to neutralisation of the trifluoroacetic acid (5·82 c.c.), and the other at pH 8·55, representing neutralisation of the total acidity (11·65 c.c.). Thus the anhydride gave acetic and trifluoroacetic acids in equimolecular proportions.

Acetyl Trifluoroacetate from Acetic Anhydride–Trifluoroacetic Anhydride.—A mixture of acetic anhydride (1·26 g.) and trifluoroacetic anhydride (2·59 g.), distilled through a short Vigreux column, gave, as the only fraction, acetyl trifluoroacetate (2·32 g.), b. p. 95—96°, n_D^{25} 1·3255 (Found: equiv., 80). The infra-red spectrum of the product, in carbon tetrachloride

solution, was identical, over the frequency range 1000—1250 cm.$^{-1}$, with that of the sample of acetyl trifluoroacetate described above.

Benzoyl Trifluoroacetate from Benzoic Acid–Trifluoroacetic Anhydride.—(*a*) A solution of benzoic acid (5·01 g.) in trifluoroacetic anhydride (9·58 g.) was kept at 40° for 30 min. before ether (5 c.c.) was added, followed by pyridine (3·30 c.c.) in ether (5 c.c.), as before. The pyridinium trifluoroacetate (4·34 g.), m. p. and mixed m. p. 81—82°, was removed by filtration. From the filtrate, benzoyl trifluoroacetate (1·90 g.) was obtained as a colourless oil, b. p. 54°/2·5 mm., n_D^{25} 1·4487 (Found: C, 49·8; H, 2·3%; equiv., 107. Calc. for $C_9H_5O_3F_3$: C, 49·6; H, 2·3%; equiv., 109). Ferris and Emmons (*loc. cit.*) gave b. p. 57—58°/1·7 mm., n_D^{20} 1·4524.

(*b*) A solution of benzoic acid (2·50 g.) in trifluoroacetic anhydride (4·86 g.) was kept at 40° for 30 min., and the liberated trifluoroacetic acid was removed under diminished pressure. The residual liquid was distilled to give benzoyl trifluoroacetate (2·23 g.), b. p. 55—56°/3·8 mm., n_D^{25} 1·4486 (Found: equiv., 109).

Benzoyl Trifluoroacetate from Benzoic Anhydride–Trifluoroacetic Anhydride.—A solution of benzoic anhydride (4·65 g.) in trifluoroacetic anhydride (4·33 g.) was kept at 40° for 90 min., and then distilled, to give benzoyl trifluoroacetate (5·40 g.), b. p. 56—57°/3·5 mm., n_D^{25} 1·4488. The infra-red spectra of all three samples of benzoyl trifluoroacetate, in carbon tetrachloride solution, were identical over the frequency range 1000—1250 cm.$^{-1}$.

Phenylacetyl Trifluoroacetate from Phenylacetic Acid–Trifluoroacetic Anhydride.—A solution of phenylacetic acid (3·00 g.) in trifluoroacetic anhydride (5·62 g.) was kept at 50° for 20 min., and the liberated trifluoroacetic acid was removed under diminished pressure. Distillation of the residue gave phenylacetyl trifluoroacetate (1·32 g.) as a colourless oil, b. p. 98°/15 mm., n_D^{25} 1·4422 (Found: C, 51·8; H, 3·0%; equiv., 118. Calc. for $C_{10}H_7O_3F_3$: C, 51·7; H, 3·0%; equiv., 116). Ferris and Emmons (*loc. cit.*) gave b. p. 57—58°/0·3 mm., n_D^{20} 1·4445.

Potentiometric titration of the unsymmetric anhydride (0·0447 g.) against 0·05N-sodium hydroxide, as before, required 3·76 c.c. for neutralisation of the trifluoroacetic acid (end-point, pH 3·53), and another 3·79 c.c. for neutralisation of the phenylacetic acid (end-point, pH 8·55).

Phenylacetyl Trifluoroacetate from Phenylacetic Anhydride–Trifluoroacetic Anhydride.—A solution of phenylacetic anhydride (2·99 g.) in trifluoroacetic anhydride (3·04 g.) was kept at 50° for 1 hr., before being distilled to give phenylacetyl trifluoroacetate (2·38 g.), b. p. 98°/15 mm., n_D^{25} 1·4422 (Found: equiv., 116). The infra-red spectrum of this compound, in carbon tetrachloride solution, was identical, over the frequency range 1000—1250 cm.$^{-1}$, with that of the sample mentioned above.

Infra-red Spectra.—(*a*) The infra-red spectra of acetic anhydride, of trifluoroacetic anhydride, and of acetyl trifluoroacetate in carbon tetrachloride (concentration *ca.* 0·05M) were determined over the range 1000—1250 cm.$^{-1}$, by use of a Grubb-Parsons spectrometer with a rock-salt prism. The absorption band (at 1121 cm.$^{-1}$) of acetic anhydride, and the band (at 1041 cm.$^{-1}$) of trifluoroacetic anhydride, were entirely absent from the spectrum of acetyl trifluoro-

TABLE 1.

Original system (mol.)					Time after mixing	Components found (mol.)		
Ac_2O	AcOH	$(CF_3{\cdot}CO)_2O$	$CF_3{\cdot}CO_2H$	$Ac{\cdot}O{\cdot}CO{\cdot}CF_3$		Ac_2O (1121 cm.$^{-1}$)	$(CF_3{\cdot}CO)_2O$ (1041 cm.$^{-1}$)	$Ac{\cdot}O{\cdot}CO{\cdot}CF_3$ (1072 cm.$^{-1}$)
0·5	—	0·5	—	—	5 min.	0·12	0·10	0·75
0·5	—	0·5	—	—	15 min.	0·04	0·05	0·90
0·5	—	0·5	—	—	18 hr.	0·03	Nil	0·94
0·5	—	0·5	—	—	14 days	0·01	Nil	0·98
—	1·0	1·0	—	—	2 hr.	0·04	Nil	0·95
—	—	—	1·0	1·0	2 hr.	0·04	Nil	0·95
1·0	—	—	1·0	—	2 hr.	0·60	Nil	0·41
—	1·0	—	—	1·0	2 hr.	0·60	Nil	0·39

acetate, which itself showed a characteristic strong absorption band at 1072 cm.$^{-1}$. The calculated optical densities (1 mole/l. in a cell of thickness *ca.* 0·1 mm.) of the appropriate solutions (*ca.* 0·05M in CCl_4) were then used to estimate, by comparison, the proportion of each of these anhydride components in the following systems: acetic anhydride–trifluoroacetic anhydride, acetic acid–trifluoroacetic anhydride, acetyl trifluoroacetate–trifluoroacetic acid, acetic anhydride–trifluoroacetic acid, and acetyl trifluoroacetate–acetic acid. The results are recorded in Table 1. Acetic and trifluoroacetic acids did not show absorption peaks which interfered with those mentioned above. The accuracy of the method is estimated at ±5%.

(*b*) The infra-red spectrum of benzoyl trifluoroacetate in carbon tetrachloride solution, determined over the same range of frequencies, showed a characteristic strong absorption band at 1086 cm.$^{-1}$. Comparative measurements of optical density showed that benzoyl trifluoroacetate was formed almost quantitatively when benzoic acid was dissolved in trifluoroacetic anhydride.

(*c*) The infra-red spectrum of phenylacetyl trifluoroacetate in carbon tetrachloride solution showed a characteristic absorption band at 1100 cm.$^{-1}$, which was entirely absent from the spectra of phenylacetic and trifluoroacetic anhydride.

Acetylations of Hydroxy-compounds with Acetyl Trifluoroacetate.—The hydroxy-compound (1 mol.) was treated with the unsymmetric anhydride (1·5 mol. per hydroxy-group) at *ca.* 20° for 30 min., and the mixture was poured into excess of sodium hydrogen carbonate solution, which was then extracted with chloroform. The extracts were washed with water, dried ($MgSO_4$), and evaporated, leaving a residue, which crystallised from aqueous alcohol. Three samples of the anhydride were used: (A), prepared as above, by using acetic acid–trifluoroacetic anhydride–pyridine; (B), prepared as above by distillation of an equimolecular mixture of acetic and trifluoroacetic anhydrides; and (C), which was simply an equimolecular mixture of acetic and trifluoroacetic anhydrides. The results are recorded in Table 2 for acetylations of *p*-nitrobenzyl alcohol, methyl α- and β-D-glucopyranoside, D-mannitol, and β-naphthol.

TABLE 2.

Ester produced	Anhydride sample	Properties of product: Yield (%)	M. p. and mixed m. p.	$[\alpha]_D^{20}$ in $CHCl_3$ (*c*, 1·0—2·8)
p-Nitrobenzyl acetate	A	80	77—78°	—
	B	75	78	—
	C	84	78	—
Methyl α-D-glucoside tetra-acetate	A	63	100—101	+129°
Methyl β-D-glucoside tetra-acetate	C	64	104	−19·1
D-Mannitol hexa-acetate	C	79	123—124	+25·1
β-Naphthyl acetate	A	81	70	—
	B	76	69	—
	C	81	69—70	—

Reactions of Acetyl Trifluoroacetate with the Butanols.—The alcohol (*ca.* 1·4 g.) in ether (3·0 c.c.) was treated with the unsymmetric anhydride (3·78 g.) and, after 30 min. at *ca.* 20°, ether (30 c.c.) was added. The solution was washed quickly with dilute aqueous sodium hydroxide (0·08N; the calculated volume for neutralisation of the liberated acid and the excess of anhydride was used; the pH of the aqueous phase was then *ca.* 7), then with water, dried ($MgSO_4$), and filtered. Most of the ether was removed by distillation through a 1′ column packed with Dixon gauze spirals. The residual solution was added to anilinomagnesium iodide which had been prepared from magnesium (1·0 g.), methyl iodide (2·9 c.c.), ether (20 c.c.), and aniline (4·0 c.c.), and the mixture was refluxed for 40 min. Water (10 c.c.) was added very cautiously down the condenser, followed by dilute hydrochloric acid. The ethereal layer and extracts of the aqueous phase were dried ($MgSO_4$), filtered, and evaporated. The residual anilides were separated chromatographically, and purified, as described later. The results obtained with *n*-, *sec.*-, and *tert.*-butanol, and from a reaction with *n*-butanol in which acetyl trifluoroacetate–trifluoroacetic acid was used, are given in Table 3.

TABLE 3.

Butanol: Isomer	Butanol: G.	$CF_3 \cdot CO_2H$ (g.)	Product: (*a*) Acetanilide (mol.)	Product: (*b*) Trifluoroacetanilide (mol.)
n	1·46	—	0·11	0·51
n	1·45	2·75	0·45	0·14
sec.	1·43	—	0·39	0·21
tert.	1·44	—	0·67	0·02

M. p. and mixed m. p. (*a*) 114°, (*b*) 88—89° in all cases.

Reaction of Acetyl Trifluoroacetate with Aniline.—(*a*) A solution of aniline (0·523 g.) and acetyl trifluoroacetate (1·06 g., 1·20 mol.) in ether (6 c.c.) was kept at *ca.* 20° for 10 min., diluted with ether (30 c.c.), washed with sodium hydrogen carbonate solution, and then with water, dried ($MgSO_4$), and evaporated. The residue was dissolved in benzene, and subjected to chromatographic separation on a column (15 × 2·5 cm.) of alkali-free aluminium oxide. The

column was eluted with benzene, and then with ether–ethanol (1 : 1, by vol.). Evaporation of the benzene solution, and recrystallisation of the residue from light petroleum (b. p. 60—80°), gave trifluoroacetanilide (0·58 mol.), m. p. and mixed m. p. 88—89°. The solute from the ether–ethanol, recrystallised from light petroleum (b. p. 80—100°), gave acetanilide (0·10 mol.), m. p. and mixed m. p. 114°.

(*b*) The experiment was repeated, with nitromethane (4 c.c.) instead of ether (6 c.c.) during the initial reaction. The products were trifluoroacetanilide (0·36 mol.) and acetanilide (0·25 mol.).

(*c*) When the experiment was repeated with trifluoroacetic acid (3 c.c.) instead of ether (6 c.c.) during the initial reaction, the products were trifluoroacetanilide (0·81 mol.) and acetanilide (0·005 mol.).

Acetyl Trifluoroacetate in Ketone Synthesis.—(a) p-*Ethoxyacetophenone.* A mixture of phenetole (0·483 g.) and acetyl trifluoroacetate (0·94 g.; 1·50 mol.) was kept at 10—15° for 18 hr. After dilution of the solution with water (1 c.c.), and neutralisation with sodium hydroxide, the ketone was isolated as its semicarbazone (21%), m. p. 182° (Found : C, 59·9; H, 6·9. Calc. for $C_{11}H_{15}O_2N_3$: C, 59·7; H, 6·8%). Unger (*Annalen*, 1933, **504**, 267) gave m. p. 181·5°.

The experiment was repeated with the same quantities of phenetole and acetyl trifluoroacetate, but with different reaction times, and in the presence of certain other compounds (see Table 4).

TABLE 4.

Addend												
Formula	—	—	—	$CH_3{\cdot}CO_2H$			$CF_3{\cdot}CO_2H$		$CH_3{\cdot}CO_2Na$	$CF_3{\cdot}CO_2Na$	$CH_3{\cdot}NO_2$
Mol.	—	—	—	1·50			0·45	1·50	1·50	1·50	19
Reaction time (hr.) ...	3	18	46	3	16	46	3	3	48	48	3
Yield (%)	0	21	30	11	15	33	45	90	0	0	29

(b) 2-*Acetylthiophen.* A mixture of thiophen (0·26 g.) and acetyl trifluoroacetate (0·75 g.) was kept at 45° for 2 hr., diluted with water (1 c.c.), and neutralised with sodium hydroxide. The ketone was isolated as its semicarbazone (88%), m. p. 189—190° (Found : C, 46·2; H, 5·0. Calc. for $C_7H_9ON_3S$: C, 45·9; H, 5·0%). Steinkopf and Jaffé (*Annalen*, 1917, **413**, 333) gave m. p. 190—191°.

Reaction of Benzoyl Trifluoroacetate with Hydroxy-compounds.—(a) *Phenol.* Treatment of phenol (0·256 g.) with benzoyl trifluoroacetate (0·877 g.) at 60° for 30 min., and isolation of the product as for acetate esters, gave phenyl benzoate (80%), m. p. and mixed m. p. 68°.

(b) β-*Naphthol.* In the same way, β-naphthol (0·300 g.) and benzoyl trifluoroacetate (0·644 g.) afforded β-naphthyl benzoate (88%), m. p. and mixed m. p. 105°.

(c) p-*Nitrobenzyl alcohol.* *p*-Nitrobenzyl alcohol (0·303 g.) was treated with benzoyl trifluoroacetate (0·603 g.), as before, and the oil which remained on evaporation of the chloroform extract was recrystallised from light petroleum (b. p. 40—60°) to give *p*-nitrobenzyl trifluoroacetate (46%), m. p. and mixed m. p. 46—47°. The rest of the product could not be purified; no *p*-nitrobenzyl benzoate could be isolated.

Treatment of *p*-nitrobenzyl alcohol (0·294 g.) with a mixture of benzoyl trifluoroacetate (0·603 g.) and trifluoroacetic acid (0·447 g.) at 60° for 30 min., isolation of the product as before, and crystallisation from aqueous alcohol, gave *p*-nitrobenzyl benzoate (80%), m. p. and mixed m. p. 89°.

Reaction of Benzoyl Trifluoroacetate with Aniline.—A solution of benzoyl trifluoroacetate (1·47 g., 1·2 mol.) and aniline (0·515 g.) in ether (4 c.c.) was kept at 20° for 1 hr., diluted with ether (30 c.c.), and washed, etc., as before. Recrystallisation of the product from light petroleum (b. p. 60—80°) afforded trifluoroacetanilide (0·75 mol.), m. p. and mixed m. p. 88—89°; no benzanilide was detected.

p-*Methoxybenzophenone.*—Anisole (0·25 g) was treated with a mixture of benzoyl trifluoroacetate (0·754 g.) and trifluoroacetic acid (0·447 g.) at 60° for 5 hr., before being poured into aqueous sodium hydrogen carbonate, and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and evaporated; recrystallisation of the residue from light petroleum (b. p. 60—80°) gave *p*-methoxybenzophenone (64%), m. p. and mixed m. p. 61—62°.

In a second experiment, from which the trifluoroacetic acid was omitted, no residue was obtained from the chloroform extract.

Reaction of Phenylacetyl Trifluoroacetate with Hydroxy-compounds.—(a) *Phenol.* Treatment of phenol (0·203 g.) with phenylacetyl trifluoroacetate (0·600 g.) at 20° for 30 min., and isolation of the ester in the usual way, afforded phenyl phenylacetate (73%), m. p. and mixed m. p. 41°.

(b) p-*Cresol.* In the same way, *p*-cresol (0·205 g.) and phenylacetyl trifluoroacetate (0·510 g.) gave *p*-tolyl phenylacetate (84%), m. p. and mixed m. p. 74—75°.

(c) p-*Nitrobenzyl alcohol.* Likewise, *p*-nitrobenzyl alcohol (0·200 g.) and phenylacetyl trifluoroacetate (0·364 g.) yielded *p*-nitrobenzyl phenylacetate (36%), m. p. and mixed m. p. 64°. The aqueous-alcoholic mother-liquors from the crystallisation were titrated against 0·05N-sodium hydroxide (9·03 c.c. required). This acidity was probably due to trifluoroacetic acid liberated on hydrolysis of *p*-nitrobenzyl trifluoroacetate (cf. Bourne, Tatlow, and Tatlow, *J.*, 1950, 1367).

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