0.25 mole) in ether (970 ml.) was added to a cooled solution of 6-fluoronicotinic acid[21] (35.1 g., 0.25 mole) in ether (1.5 l.). When the mixture became colorless, the ether was evaporated, and the remaining solid (36.4 g., 94% yield, m.p. 47–49.5°) was vacuum sublimed (50°, 0.1 mm.) to give methyl 6-fluoronicotinate; yield, 34.8 g. (90%), m.p. 49–50°. Recrystallization from petroleum ether and chloroform raised the melting point to 49.5–50.5°.

Anal. Calcd. for $C_7H_6FNO_2$: C, 54.19; H, 3.90; N, 9.03. Found: C, 53.98; H, 4.07; N, 9.21.

Methyl 6-Hydrazinonicotinate (IIc).—Anhydrous hydrazine (4.1 g., 0.13 mole) in methanol (40 ml.) was added dropwise during 40 min. to a stirred solution of methyl 6-fluoronicotinate (20.0 g., 0.13 mole) in methanol (80 ml.). The mixture was heated under reflux for 15 min., cooled, and the crude product (10.3 g., m.p. 134.5–136°) was collected and washed with cold methanol. An additional amount of product (10.6 g.) was obtained when the mother liquor was evaporated. The crude combined product was recrystallized from methanol, Norit being used to give white needles of methyl 6-hydrazinonicotinate; yield, 10.4 g. (48%), m.p. 138–139°.

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.18; H, 5.38; N, 25.08.

Methyl 6-Methoxynicotinate.—Methyl 6-fluoronicotinate (10.0 g., 64 mmoles) was added to sodium methoxide (8.1 g., 0.15 mole, prepared from 3.5 g. of sodium) in anhydrous methanol (50 ml.). The mixture was heated under reflux for 2 hr., cooled, and evaporated. The remaining solid was washed three times with hot carbon tetrachloride. These washings were combined and evaporated to give a white solid (8.3 g., m.p. 50–51°). This was vacuum sublimed (50°, 0.1 mm.) to give pure methyl 6-methoxynicotinate; yield, 7.1 g. (66%), m.p. 51–52°. Recrystallization from petroleum ether gave white plates, m.p. 51–51.8°.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.21; H, 5.44; N, 8.37.

6-Methoxynicotinic Hydrazide.—Following the procedure used in the preparation of 6-fluoropicolinic hydrazide, hydrazine (1.0 g., 31 mmoles) in methanol (10 ml.) was added to methyl 6-methoxynicotinate (2.0 g., 12 mmoles) in methanol (20 ml.). Evaporation of this mixture gave the crude product (1.7 g.) which was recrystallized from methanol to give white micro needles of 6-methoxynicotinic hydrazide; yield, 0.93 g. (47%), m.p. 156.5–157.5°.

Anal. Calcd. for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.32; H, 5.34; N, 24.97.

3-Amino-6-fluoropyridine (IIIc).—Sodium hydroxide (6.6 g., 0.16 mole) was dissolved in water (80 ml.) and cooled to 0°, whereupon bromine (8.4 g., 52 mmoles) was added. 6-Fluoronicotinamide[21] (6 g., 40 mmoles) was added and the solution mechanically stirred for 15 min. at ice bath temperature. The ice bath then was replaced by a water bath at 75° and the solution was held at this temperature for 45 min. During the heating period a color change from yellow to dark red was observed.

The solution was allowed to cool to room temperature, acidified with acetic acid, and then made alkaline by addition of dilute sodium hydroxide. This solution was saturated with sodium chloride and continuously extracted with ether for 24 hr. in a liquid–liquid extractor. After the extract had been dried overnight, the ether was evaporated and a red residue was obtained (crude yield, 4 g.). Purification was effected by vacuum sublimation; yield 1.6 g. (35%), m.p. 87–87.5°.

Anal. Calcd. for $C_5H_5FN_2$: N, 24.99. Found: N, 24.96; F, positive by calcium chloride test.[19b]

3-Acetamido-6-fluoropyridine.—A small amount of 3-amino-6-fluoropyridine was dissolved in anhydrous ether. Ketene was bubbled through the solution for 30 min. without any noticeable effect. Removal of the ether gave a product which was recrystallized from water. When no crystals formed after the product had stood for 2 days, the solution was found to be acid to litmus. It was made basic and, after it had stood overnight in an ice bath, deposited long, white needles, m.p. 131–132°.

Anal. Calcd. for $C_7H_7FN_2O$: N, 18.18. Found: N, 18.38; F, positive by calcium chloride test.[19b]

Attempted Preparation of 2,5-Difluoropyridine.—All attempts to prepare 2,5-difluoropyridine from 2-fluoro-5-aminopyridine by methods identical to those previously described failed. On one trial, some apparent diazonium fluoborate was obtained and it appeared fairly stable, although the yield was rather poor. Thermal decomposition proceeded smoothly, but the product obtained from steam distillation was lost before it was characterized. Several more trials under the same conditions did not yield the diazonium fluoborate.

Reactions of Trihalogenated Esters with Triethylamine and Anions[1]

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The reactions of several trihalogenated esters with triethylamine were studied at room temperature. All the trihalogenated esters formed quaternary ammonium compounds with triethylamine. In the case of the trifluoro esters, the formation of N,N-diethyltrifluoroacetamide and an ether was a competing reaction. Amide formation was not observed for the tribromo and trichloro esters, at room temperature, but occurred with methyl thioltrichloroacetate. During this study, it was observed that methyl trichloroacetate behaved as an alkylating agent toward sodium phenoxide, while ethyl trifluoroacetate behaved as an acylating agent. A significant feature of this work is the alkylating ability of alkyl trichloroacetates, at room temperature. This property makes methyl trichloroacetate a potentially useful methylating agent to replace toxic compounds such as diazomethane or dimethyl sulfate.

Our interest in the reactions of primary and secondary amines with trihalogenated acetates[3] has led us to investigate the behavior of triethylamine with similar esters. The purpose of the present work was to determine the products formed when triethylamine reacted with some trihalogenated esters at room temperature.

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(1) Abstracted in part from the Ph.D. dissertation of A. C. Pierce, University of Pennsylvania, 1962.

(2) Recipient of W. T. Taggart and E. F. Smith Memorial Scholarships, 1961–1962.

(3) (a) M. M. Joullié and A. R. Day, *J. Am. Chem. Soc.*, **76**, 2990 (1954); (b) M. M. Joullié, *ibid.*, **77**, 6662 (1955); (c) A. C. Pierce, Ph.D. dissertation, University of Pennsylvania, 1962.

The reaction of tertiary amines with ordinary esters has been studied by several workers, particularly because it was of interest as an alkylation reaction. At temperatures between 80–160°, the product formed was shown to be an ammonium salt.[4] Hammett and Pfluger studied the rate of reaction of trimethylamine with methyl esters in methanol at 100°.[5] These authors found that the rate of methylation of trimethylamine by various esters increased with increasing strength of the corresponding acid and that the rate of the reaction did not appear to be affected by steric hindrance. The reactions appeared to involve a nucleophilic displacement of the same type as the cleavage of methyl esters by methoxide ion.[6]

Important and extensive studies of nucleophilic catalysis have included tertiary amines. The catalytic action of trimethylamine in the hydrolysis of *p*-nitrophenyl acetate is believed to depend upon the formation of an acyltrimethylammonium intermediate.[7] Quaternary ammonium intermediates have also been postulated for reactions involving triethylamine,[8] in spite of the larger steric requirements of this amine.

The data found in the literature for reactions of tertiary amines and esters support a nucleophilic attack by the amine on both the alkoxyl group and the carbonyl group of the ester. We have investigated both possibilities in our systems. The study of Courtauld models of addition compounds formed by addition of triethylamine to the carbonyl group of a trihalogenated ester showed that such an intermediate is possible for trifluoro esters and triethylamine. A tribromo- or trichloromethyl group introduces considerable steric hindrance to the addition of triethylamine to the ester.

Discussion and Results

The reactions of triethylamine with trihalogenated esters were first studied in the absence of solvents to determine which products might be formed at room temperature after twenty-four hours. Under these conditions ethyl acetate did not react while the trihalogenated esters reacted within three minutes. The infrared absorption spectrum of a given reaction mixture, as a film, showed the decrease in absorbance of the ester carbonyl absorption band and the appearance of a band typical of the trihalogenated carboxylic acid anion accompanied by weak bands in the 2800–2400-cm.$^{-1}$ region characteristic of the quaternary ammonium ion. In order to follow the amount of ester that reacted with triethylamine, the absorbances of the carbonyl groups of the esters chosen were measured in carbon tetrachloride solution. Beer's law curves were constructed for each compound. Since Beer's law was approximately valid, the quantity of ester which had lost its carbonyl function could be calculated. The infrared absorption frequencies of the trihalogenated esters used and the corresponding acetate ions were measured accurately and are reported in Table I. The per cent of ester remaining after twenty-four hours in all the reactions studied is also shown in Table I.

TABLE I

CARBONYL INFRARED ABSORPTION FREQUENCIES[a] OF TRIHALOGENATED ESTERS AND REACTION PRODUCTS AND PER CENT OF ESTER REMAINING AFTER 24 HR.[b]

Esters	% Unchanged ester after 24 hr. (1:1 ratio of reagents in CCl$_4$)	ν_{max} cm.$^{-1}$, CCl$_4$		
		Ester	Amide	Acetate
$Br_3C_2O_2C_2H_5$	96.3[c]	1757		1653
$Cl_3C_2O_2CH_3$	87.6	1773		1661
$Cl_3C_2OSCH_3$	92.0	1699	1740[j]	1650
$Cl_3C_2O_2C_2H_5$	90.0[d]	1769[h]		1665
$Cl_3C_2O_2CH_2C_6H_5$	93.1	1769		1681
$Cl_3C_2O_2C(CH_3)_3$	94.9[e]	1764		1662
$Cl_3C_2O_2C_6H_5$	80.3[f]	1789		1667
$F_3C_2O_2C_2H_5$	71.2[g]	1789[i]	1684[k]	1671
$F_3C_2O_2CH_2C_6H_5$	84.9	1787	1684	1671
$F_3C_2O_2C(CH_3)_3$	94.0	1781	1688	1675
$F_3C_2O_2C_6H_5$	70.3	1802	1694	1674

[a] All measurements were reproducible to ±2 cm.$^{-1}$. [b] Duplication of the runs were reproducible to within ±4%. [c] 69.6% when an excess of triethylamine is used. [d] 79.4% in acetonitrile. [e] 79.6% when an excess of triethylamine is used. [f] 52.0% when an excess of triethylamine is used; 37.6% after 48 hr. [g] 15% in acetonitrile; 48.4% when an excess of triethylamine is used. [h] 1758 cm.$^{-1}$ in acetonitrile. [i] 1782 cm.$^{-1}$ in acetonitrile. [j] $\nu_{max}^{C=O}$ for N,N-diethyltrichloroacetamide is 1742 cm.$^{-1}$ as observed in the reaction mixture of ethyl trichloroacetate and diethylamine. [k] 1691 cm.$^{-1}$ in acetonitrile.

The data reported in Table I showed that the amount of ester which reacted with triethylamine was proportional to the strength of the corresponding acid. Under similar conditions, the equilibrium was shifted to the right in the increasing order $Br_3CCO_2R < Cl_3CCO_2R < F_3CCO_2R$ for esters which have the same alkoxyl groups.

The presence of quaternary ammonium ions in these reactions was established by infrared spectroscopy and by the isolation of Reinecke salt derivatives of these ions. Most Reinecke salt derivatives were obtained analytically pure except for the derivative of the triethylphenylammonium ion, although the presence of this ion was established by other means.

It is possible that these Reinecke salt derivatives resemble some quaternary ammonium polyborates prepared by Petersen, Finkelstein, and Ross.[9]

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(5) L. P. Hammett and H. L. Pfluger, *J. Am. Chem. Soc.*, **55**, 4079 (1933).

(6) J. F. Bunnett, M. M. Robinson, and F. C. Pennington, *ibid.*, **72**, 2378 (1950).

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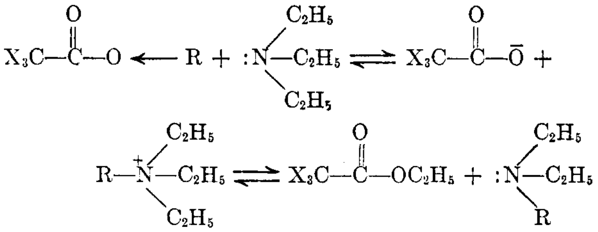
(9) R. C. Petersen, M. Finkelstein, and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 3264 (1959).

These authors found that in the preparation of quaternary ammonium polyborates, the nature of the cation determined whether the salt crystallized without water of hydration, with one or more molecules of water of hydration or with one molecule of boric acid. It was not clear just what features of the cation were significant but the authors concluded that the size and symmetry of the quaternary ammonium ion dictated the nature of the spaces in the crystal lattice. If the nature of the Reinecke salt derivatives of the ammonium ions were determined by these factors, the failure to obtain an analytically pure sample of the tetraethylphenylammonium derivative could be explained.

The following reaction scheme is consistent with the observed results:



R = CH_3, C_2H_5, $C(CH_3)_3$, $CH_2C_6H_5$, C_6H_5[a]
X = F,[b] Cl, Br

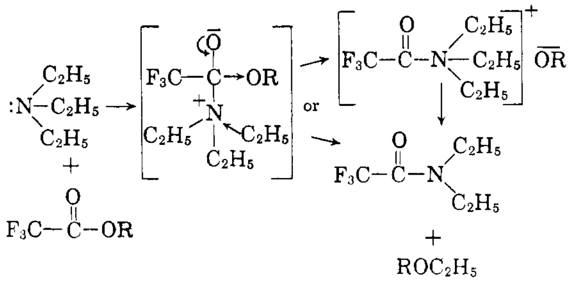
[a] The first step is not reversible. [b] No ethyl trifluoroacetate was found in the reaction mixture of ethyl trifluoroacetate and triethylamine.

Evidence for the equilibrium shown was established in several ways. The presence of ethyl trichloroacetate, in the reaction mixture obtained by mixing benzyl trichloroacetate and triethylamine, could not be noticed in the spectrum of the reaction mixture because ethyl and benzyl trichloroacetates have the same carbonyl infrared absorption. However the presence of both esters was established by gas-liquid chromatography and benzyl trichloroacetate was found to predominate. Infrared studies on the quaternary ammonium salt obtained from the reaction of benzyl trichloroacetate and triethylamine showed an increase in ester carbonyl absorbance from zero to 0.55 upon standing for forty-eight hours at room temperature. Tetraethylammonium trichloroacetate prepared by an unequivocal synthesis was shown to form ethyl trichloroacetate on standing.

Ethyl tribromo- and *t*-butyl trichloroacetate behaved in the same manner as ethyl and benzyl trichloroacetates.

When the reaction mixture of phenyl trichloroacetate and triethylamine was studied by gas–liquid chromatography, after four months, the only ester present in the reaction mixture was ethyl trichloroacetate. The corresponding N,N-diethylaniline was identified from the infrared spectrum of the reaction mixture and by gas–liquid chromatographic analysis. This observation was of considerable interest since the presence of these products was good evidence for the formation of an intermediate quaternary ammonium salt. The absence of phenyl trichloroacetate indicated that no migration of the phenyl group from the quaternary ammonium ion had occurred.

Ethyl, benzyl, and *t*-butyl trifluoroacetates reacted with triethylamine in the same manner as their trichloro analogs and the presence of the intermediate quaternary ammonium salts was demonstrated by the same techniques used for the trichloro esters. In addition to alkylation, an acylation reaction predominated to yield N,N-diethyl trifluoroacetamide and an ether. The reaction probably proceeds *via* a direct addition of triethylamine to the carbonyl group of the ester to yield a tetrahedral intermediate which breaks down to give the desired products. The tetrahedral intermediate may break down immediately to give the products or it may form a quaternary ammonium compound similar to the one postulated for the reaction of benzenesulfonyl chloride and tertiary amines in ether solution. The electron-withdrawing power of the benzenesulfonyl group is believed to aid the separation of one of the alkyl groups as an electron-deficient group. The trifluoroacetyl group could act similarly.



Some evidence for the belief that triethylamine added to the carbonyl carbon atom of the trifluoro esters was obtained from a comparison of the amount of amide formed in the reaction of this amine with ethyl and *t*-butyl trifluoroacetates. If the reaction involved addition of the amine to the carbonyl carbon atom of these esters, steric hindrance should be greater in the case of the *t*-butyl ester as evidenced by a study of the Courtauld models of intermediates. After one month reaction time ethyl trifluoroacetate yielded 52% N,N-diethyltrifluoroacetamide while *t*-butyl trifluoroacetate yielded 15.6% of this amide, under the same conditions.

Methyl thioltrichloroacetate also formed a quaternary ammonium salt when treated with triethylamine. Although the reaction occurred to a lesser extent than with the corresponding oxygenated ester, this observation is interesting since ordinary thiol esters show no tendency to behave as alkylating agents. Few examples of alkyl–sulfur fission in thiolesters have been reported in the literature.[10] In the case of methyl thioltrichloroacetate, the cleavage of the alkyl–sulfur bond is aided by the electron-withdrawing effect of the trichloroacetyl group.

After triethylamine reacted with methyl thioltrichloroacetate at room temperature for one week, the infrared spectrum of the reaction mixture had a new band which was identified as the carbonyl absorption band of N,N-diethyltrichloroacetamide. This observation is of interest since it is in agreement with the behavior noted for acylated coenzyme A.[11] The corresponding oxygenated ester did not yield any amide under similar conditions.

A comparative study of the relative susceptibility of oxygenated esters and thiol esters towards simple nucleophiles has been carried out by Bender and Connors.[12] These authors believe that because of hybridization with the sulfur *d*-orbitals the electron distribution of the carbonyl group of thiol esters is sufficiently altered so that the approach of a nucleophile is not controlled by the carbonyl group alone.

The increased bond length between carbon and sulfur in thiol esters as compared to oxygenated esters decreases the steric hindrance around the carbonyl carbon atom. If amide formation is assumed to occur *via* an attack on the carbonyl carbon atom, an explanation for the greater ease of amide formation with the thiol ester is available. It is possible that both increased bond length and increased polarizability of the sulfur atom can account for the easier addition of triethylamine to the carbonyl carbon atom of methyl thioltrichloroacetate, at room temperature.

When the reaction of phenyl trifluoroacetate and triethylamine was investigated both by infrared studies and gas–liquid chromatography, after four months' reaction time, no ethyl trifluoroacetate was present although initially the presence of a quaternary ammonium compound had been ascertained by infrared spectroscopy. Less than 2% phenyl trifluoroacetate was found. N,N-Diethyl trifluoroacetamide and phenyl ethyl ether were present in large amounts, indicating that acylation was the predominant reaction.

To strengthen further the belief that trichloro esters behaved as alkylating agents while trifluoro esters, although being capable of behaving similarly, also behaved as acylating agents, the reactions of these esters with some anions were studied. Methyl trichloroacetate reacted with sodium phenoxide to yield anisole in good yields. No products which might result from ester interchange were found. The methylating ability of methyl trichloroacetate was also shown by the fact that it reacted with sodium diethyl malonate to yield diethyl methylmalonate in good yields.

Phenyl trichloroacetate did not behave as a phenylating agent toward sodium phenoxide. Phenyl ether could not be found in the reaction mixture. Only phenyl trichloroacetate was present. This fact does not preclude the possibility of ester interchange through addition to the carbonyl carbon atom since the ester would be the same in this case. A study of Courtauld models for an intermediate addition compound resulting from addition of phenoxide ion to the carbonyl group shows that such an intermediate is possible. Ethyl trifluoroacetate did not form any phenetole when treated with sodium phenoxide. The only product which was formed was phenyl trifluoroacetate which resulted from ester interchange. This is evidence for the addition of the phenoxide ion to the carbonyl group of the ester.

Table II summarizes the data obtained by gas–liquid chromatographic analysis and infrared analysis as to the presence of absence of certain products in various reaction mixtures.

Experimental

Materials.—Triethylamine was dried over potassium hydroxide for 1 week. The drying agent was removed by filtration and the filtrate distilled through a column 2 cm. by 30 cm. packed with glass helices, b.p. 87–89°, n^{20}_{D} 1.4003, lit.,[13] b.p. 89.5°, n^{25}_{D} 1.40032. Carbon tetrachloride was purified in the same manner, b.p. 77°, n^{25}_{D} 1.4590, lit.,[14] b.p. 76.8°, n^{15}_{D} 1.46305. Anisole, phenetole, phenyl ether, benzyl ether, diethyl methylmalonate, and diethylaniline were obtained commercially and used as such. The physical constants of all the esters prepared in this study and the pertinent references are listed in Table III. Methyl thioltrichloroacetate was prepared from methyl thioalcohol and trichloroacetyl chloride. Benzyl trifluoroacetate was prepared by direct esterification of trifluoroacetic acid with benzyl alcohol. N,N-Diethyl trifluoroacetamide was prepared from diethylamine and ethyl trifluoroacetate, b.p. 30° (2 mm.), n^{25}_{D} 1.3780, lit.,[15] b.p. 30° (2 mm.), n^{25}_{D} 1.3780.

Analytical Techniques.—The reactions of triethylamine with the trihalogenated esters were followed by infrared spectroscopy. The infrared spectra were determined either with a Perkin-Elmer Model 421 double-beam recording infrared spectrophotometer, or a Perkin-Elmer Infracord. Matched sodium chloride cells 1.0 mm. in thickness were employed. Films were run between sodium chloride disks. The Model 421 was used for quantitative measurements. All absorption bands in the 1900–1600-cm.$^{-1}$ region were read from the meter. Beer's law curves were constructed for each of the esters listed and were essentially linear. The carbonyl absorbance of an approximately 0.05 *M* carbon tetrachloride solution of the ester studied was measured. The absorbance of the same solution was measured again, 24 hr. later, after triethylamine (0.01 g., 0.005 *M*) had been added to the solution. The difference in absorbance before and after the reaction, multiplied by 100, was assumed to be the per cent reaction after 24 hr. at room temperature.

Gas–liquid chromatography was used to analyze the reaction mixtures. All analyses were carried out using a 250-mm. column, 12 mm. in diameter packed with 15% silicone oil on chromosorb 30–60 regular mesh packing at various temperatures and various rates of helium flow. A Burrell Kromo-Tog Model Kl was employed. When gas–liquid

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TABLE II

SUMMARY OF EXPERIMENTAL DATA

Triethylamine and trihalogenated esters (1:1 ratio)	Substances present (+) or absent (−) after 4 mo. at room temp.	t_R[a]	Temp., °C.	He flow, ml./min.	Yield,[b] %
$F_3C_2O_2C_2H_5$	$F_3C_2O_2C_2H_5(+)$	0.75	210	120	47
	$C_2H_5OC_2H_5(+)$[c]	6.0	38	150	52
	$F_3C_2ON(C_2H_5)_2(+)$	1.6	217	120	52
$F_3C_2O_2CH_2C_6H_5$	$F_3C_2O_2CH_2C_6H_5(+)$	2.31	213	100	30
	$F_3C_2O_2C_2H_5(+)$	...	...	...	10
	$C_6H_5CH_2OCH_2C_6H_5(-)$	10.9	240	160	...
	$F_3C_2ON(C_2H_5)_2(+)$	...	...	...	50
$F_3C_2O_2C(CH_3)_3$	$F_3C_2O_2C(CH_3)_3(+)$	1.0	210	120	60
	$F_3C_2O_2C_2H_5(+)$	...	...	...	10
	$F_3C_2ON(C_2H_5)_2(+)$	...	...	...	15.6
$F_3C_2O_2C_6H_5$	$F_3C_2O_2C_6H_5(+)$	1.8	210	120	<2
	$F_3C_2O_2C_2H_5(-)$	...	...	...	...
	$C_6H_5OC_2H_5(+)$	3.0	210	120	80
	$F_3C_2ON(C_2H_5)_2(+)$	...	...	...	80
$Cl_3C_2O_2CH_2C_6H_5$	$Cl_3C_2O_2CH_2C_6H_5(+)$	24.6	225	120	60
	$Cl_3C_2O_2C_2H_5(+)$	2.75	210	120	30
$Cl_3C_2O_2C_6H_5$	$Cl_3C_2O_2C_6H_5(-)$	14.3	210	120	...
	$Cl_3C_2O_2C_2H_5(+)$	...	...	...	80
	$C_6H_5N(C_2H_5)_2(+)$	2.5	245	160	5.5
$Cl_3C_2OSCH_3$[d]	$Cl_3C_2OSC_2H_5(+)$	2.0	245	160	6
	$Cl_3C_2OSCH_3(+)$	1.6	245	160	...
	$Cl_3C_2ON(C_2H_5)_2(+)$	2.5	245	160	4
Anions and trihalogenated esters					
$F_3C_2O_2C_2H_5 + C_6H_5\overset{-}{O}\overset{+}{N}a$	$F_3C_2O_2C_6H_5(+)$	...	...	...	...
	$C_6H_5OC_2H_5(-)$	...	...	...	...
$Cl_3C_2O_2CH_3 + C_6H_5\overset{-}{O}\overset{+}{N}a$	$Cl_3C_2O_2C_6H_5(-)$	...	...	...	...
	$C_6H_5OCH_3(+)$	2.8	210	78	...
$Cl_3C_2O_2CH_3 + Na^+\acute{C}H(CO_2C_2H_5)_2$	$CH_3CH(CO_2C_2H_5)_2(+)$	2.75	230	120	...
$Cl_3C_2O_2C_6H_5 + C_6H_5\bar{O}Na^+$	$C_6H_5OC_6H_5(-)$	14.3	210	120	...

[a] Retention time (t_R) in minutes. [b] Duplications of the runs were reproducible to within ±8%. [c] The presence of the products were verified after 1 week. [d] After 24 hr.

chromatography was used as a quantitative tool, an Otts planimeter Type 31 was used to measure the area of an unknown volume of a known compound. This relative area was compared with the relative area (obtained in the same manner) of a known volume of the compound. This ratio multiplied by 100, was assumed to be the per cent yield of that particular compound. This method is limited by a precision of ±3–5%. When gas-liquid chromatography was used in the identification of the components of a mixture, each component was identified by comparing its retention time to that of an authentic sample and by addition of an authentic sample of a given component to the reaction mixture in varying amounts (*i.e.*, 20:80; 50:50; 80:20).

Reactions of Trihalogenated Esters with Triethylamine.—These reactions were carried out by mixing equimolecular amounts of amine and ester at room temperature. All reactions occurred to some extent within 3 min. in the absence of a solvent. The reaction was slower in carbon tetrachloride solution. In solution, the ammonium ion absorption is too weak and broad to be of value but the acetate anion absorption could be recorded except when acetonitrile was used as a solvent. The reactions of triethylamine with trifluoro esters also yielded N,N-diethyltrifluoroacetamide in addition to a quaternary ammonium compound. The carbonyl absorption band of the amide was also recorded. The reactions of ethyl trichloro- and trifluoroacetate with triethylamine were also studied in 0.05 *M* acetonitrile.

The reactions of trihalogenated esters with triethylamine were forced toward completion by using an excess of amine or a longer time of reaction. The amount of ester remaining was measured as previously described.

A comparison of amide formation or the reactions of triethylamine with ethyl and *tert*-butyl trifluoroacetates was carried out by analyzing the reaction mixtures by infrared spectroscopy in carbon tetrachloride solution. The per cent amide was calculated by considering the per cent absorbance, *A* of amide to that of the ester and amide, *i.e.*, *A* amide/(*A* amide + *A* ester) × 100. A reaction mixture containing triethylamine (1.01 g., 0.01 mole) and ethyl trifluoroacetate (1.42 g., 0.01 mole) was allowed to stand at room temperature for 1 month. The per cent amide formed was found to be 52%. A reaction mixture containing triethylamine (1.01 g., 0.01 mole) and *tert*-butyl trifluoroacetate (1.70 g., 0.01 mole) was also allowed to stand at room temperature for 1 month. The per cent amide formed was found to be 15.6%.

Derivatives of Some Quaternary Ammonium Compounds.—When the reaction mixture of triethylamine and benzyl trifluoroacetate was dissolved in methanol and treated with a saturated aqueous ammonium Reineckate solution, a derivative of the corresponding quaternary ammonium ion was obtained. A similar derivative was obtained when the reaction mixture of triethylamine and ethyl trichloroacetate was treated in the same manner. These stable derivatives gave correct analyses. $(C_2H_5)_3{}^+NCH_2C_6H_5$ $[Cr(NH_3)_2(SCN)_4]^-$. H_2O, m.p. 127–128° dec.

Anal. Calcd. for $C_{17}H_{30}N_7S_4OCr$: C, 38.61; H, 5.72; N, 18.55. Found: C, 38.74; H, 5.75; N, 18.55. $(C_2H_5)_4N^+$ $[Cr(NH_3)_2(SCN)_4]^-$. H_2O, m.p. 145–146° dec.

Anal. Calcd. for $C_{12}H_{28}OCrN_7S_4$: C, 30.88; H, 6.04; N, 21.01. Found: C, 31.15; H, 5.76; N, 20.70.

All the reaction mixtures of the ethyl trihalogenated esters and triethylamine gave an ammonium Reineckate derivative that melted at 145–146° dec. The reaction mixture of benzyl trichloroacetate and triethylamine gave an ammonium Reineckate derivative that melted at 127–128°, dec.

TABLE III

PHYSICAL CONSTANTS OF TRIHALOGENATED ESTERS

Ester	B.p.	Lit. b.p.	n^t_D	Lit. n^t_D	d^t	Lit. d^t
$Br_3C_2O_2C_2H_5$[a]	104 (15 mm.)	225 (760 mm.)	1.5430^{13}	1.5437^{13}		
$Cl_3C_2O_2CH_3$[b]	42.8 (8 mm.)	152–153 (760 mm.) 46.5–47.0 (11 mm.)	1.4547^{20}	1.4572^{20}		
$Cl_3COCSCH_3$[c]	44 (3 mm.) 34 (1 mm.)		1.5249^{25}			
$Cl_3C_2O_2C_2H_5$[b]	165–166 (760 mm.)	167–168 (760 mm.)	$1.4485^{25.2}$	1.4509^{20}		
$Cl_3C_2O_2CH_2C_6H_5$[d]	52–53 (10 mm.)	178 (760 mm.)	1.5259^{25}	$1.5288^{18.8}$		1.3887^{4}_{4}
$Cl_3C_2O_2C(CH_3)_3$[e]	41 (2 mm.)	37 (1 mm.)	$1.4395^{24.5}$	1.4398^{25}		1.2363^{25}_{4}
$Cl_3C_2O_2C_6H_5$[f]	90.5–91 (1.5 mm.)	122 (14 mm.)	1.5226^{25}	1.5233^{20}	$1.400^{24.8}_{24.8}$	
$F_3C_2O_2C_2H_5$[b]	61 (760 mm.)	60.3–60.6 (760 mm.)	1.3052^{25}	1.3072^{20}		
$F_3C_2O_2CH_2C_6H_5$[g]	50–52 (5 mm.) 178 (760 mm.)		1.4380^{25}		1.2419^{22}_{22}	
$F_3C_2O_2C(CH_3)_3$[h]	83 (760 mm.)	83 (760 mm.)	1.3310^{25}	1.3300^{25}		
$F_3C_2O_2C_6H_5$[i]	149 (760 mm.)	146.5–147 (760 mm.)	1.4195^{29}	1.4183^{25}	$1.274^{23.2}_{23.2}$	$1.269^{22.5}$

[a] A. Magnani and S. M. McElvain, *J. Am. Chem. Soc.*, **60**, 2211 (1938). [b] Purchased from Columbia Organic Chemical Co. and purified. [c] *Anal.* Calcd. for $C_3H_3Cl_3SO$: C, 18.62; H, 1.56; Cl, 54.97; S, 16.57. Found: C, 18.89; H, 1.63; Cl, 54.76; S, 16.41. [d] C. N. Hinshelwood and A. R. Legard, *J. Chem. Soc.*, 587 (1935); K. Seubert, *Ber.*, **21**, 283 (1888). [e] W. E. Scovill, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **66**, 1039 (1944). [f] W. Kuster and G. Koppenhoffer, *Ber.*, **60**, 1773 (1927). [g] *Anal.* Calcd. for $C_9H_7F_3O_2$: C, 52.94; H, 3.43; F, 27.94. Found: C, 53.17; H, 3.68; F, 27.79. [h] Ref. 15. [i] R. F. Clark and J. H. Simons, *J. Am. Chem. Soc.*, **75**, 6306 (1953).

Preparation of Tetraethylammonium Trichloroacetate.—Trichloroacetic acid was added to an anhydrous ether suspension (20 ml.) of tetraethylammonium bromide 10% by volume, until the evolution of hydrobromic acid had ceased. The solid was removed by filtration and washed with anhydrous ether. It darkened as soon as all the solvent was removed. The spectrum of this salt as a potassium bromide disk showed an absorption band which corresponded to that of ethyl trichloroacetate.

Reaction of Methyl Trichloroacetate with Sodium Diethyl Malonate.—Sodium diethyl malonate was prepared by adding diethyl malonate (8.00 g., 0.05 mole) to sodium (1.15 g., 0.05 g.-atom) in 100 ml. of carbon tetrachloride in a 250 ml. round-bottom two-necked flask fitted with a stirrer and water condenser with a calcium chloride drying tube. The reaction mixture was stirred and heated with steam for 1 hr. Methyl trichloroacetate (8.9 g., 0.05 mole) was added directly to the carbon tetrachloride solution of sodium diethyl malonate at room temperature. The reaction mixture was analyzed by gas–liquid chromatography and diethyl methylmalonate was shown to be present in 40% yield.

Reaction of Methyl Trichloroacetate with Sodium Phenoxide.—Sodium phenoxide (5.8 g., 0.05 mole) was prepared using the apparatus described in the previous experiment. Phenol (4.7 g., 0.05 mole) was added with stirring to sodium (1.2 g., 0.05 g.-atom) in 100 ml. of carbon tetrachloride. The reaction was warmed and stirred for 1 hr. The sodium phenoxide was removed by filtration. Methyl trichloroacetate (8.9 g., 0.05 mole) was added to a carbon tetrachloride mixture containing the sodium phenoxide and the resulting mixture was stirred at room temperature for 1 hr. After standing at room temperature for 17 hr., an infrared spectrum of the reaction mixture in carbon tetrachloride showed bands characteristic of anisole. Anisole could not be separated from unchanged methyl trichloroacetate since both compounds have the same boiling point. Gas–liquid chromatographic analysis could not accomplish a separation of the two compounds before saponification. The final identification of anisole was made by gas–liquid chromatographic analysis after the unreacted ester was destroyed by refluxing the reaction mixture with sodium hydroxide pellets (2.0 g., 0.05 mole) for 1 hr. Since separation of the two compounds could not be accomplished before processing the reaction mixture, no per cent yield of anisole could be calculated. No phenyl trichloroacetate could be observed before saponification by gas–liquid chromatographic analysis or infrared spectroscopy.

Reaction of Ethyl Trifluoroacetate with Sodium Phenoxide.—Sodium phenoxide (2.9 g., 0.05 mole) prepared as described in the previous experiment was reacted with ethyl trifluoroacetate (3.5 g., 0.025 mole) at room temperature. The reaction mixture was allowed to stand for 65 hr. An infrared spectrum of a carbon tetrachloride solution of the reaction mixture showed a strong band at 1802 ± 2 cm.$^{-1}$ attributed to the carbonyl group of phenyl trifluoroacetate. No bands which could be attributed to phenetole could be found. The reaction mixture was analyzed by gas–liquid chromatography and the observations derived from the infrared data proved to be correct. No phenetole was detected and phenyl trifluoroacetate occurred in 80% yield.