tone and collected on a filter. The residue (or filter cake) was extracted with boiling ethyl acetate and air dried. The following data show the intrinsic viscosity of solutions to be inversely proportional to the α,α'-azobisisobutyronitrile concentration used.

(c) *N-(Acetamidomethyl)acrylamide.* N-Hydroxymethylacetamide was prepared from 177.0 g. (3.0 moles) of acetamide and 93.0 g. (3.1 moles) of 94% paraformaldehyde in 300 cc. of ethyl acetate at 50–54°, using 4 cc. of 25% alcoholic potassium hydroxide as catalyst. After 0.5 hr. an additional 2.0 cc. of catalyst solution was added and stirring was continued for 2 hr. A layer of N-hydroxymethylamide separated on standing overnight. Stirring was resumed while 213 g. (3.0 moles) of acrylamide and 6.0 cc. of concd. hydrochloric acid were added. After 3 hr. at 53°, 4.0 cc. of concd. hydrochloric acid was added to lower the pH to 1–2. After 2 hr. the solution began to thicken, and crystalline product

separated. The slurry was cooled to 30°, 1.0 g. of sodium nitrite was added, and the solid collected on a Büchner funnel. The filter cake was washed with 100 cc. of ethyl acetate and air dried; its weight was 143.1 g. and m.p. (sinter 148°) 152–156°. Recrystallization from 1:1 ethyl acetate–methanol raised the m.p. to 166–167°. Polymerization occurred in a heated capillary tube at the melting point. Analyses are listed in Table II. The mother liquors gave 164 g. of less pure product (total yield 69%).

(d) *Polymerization of N-(acetamidomethyl)acrylamide.* Polymerization occurred readily in a 10% solution in water with 1% hydrogen peroxide at 40–60°. The polymer invariably formed a gel which was soluble in alcohol-water mixtures, but was insoluble in acetone. The dried polymer was a white, brittle solid which did not melt at 300°.

WILMINGTON, DEL.

The Reaction of Alkyl Halides with Carboxylic Acids and Phenols in the Presence of Tertiary Amines

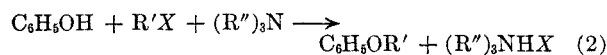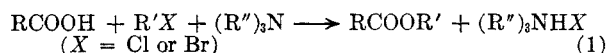ROBERT L. MERKER AND MARY JANE SCOTT

The preparation of a number of esters of aliphatic and aromatic carboxylic acids and of mixed aromatic-aliphatic ethers has been carried out through the reaction of tertiary amine salts of carboxylic acids or phenolic compounds with alkyl halides. In addition to other advantageous factors, the rather large solubility of the amine carboxylates in a variety of organic solvents leads to a wide possible choice of solvent systems and reaction temperatures which are not always obtainable when employing conventional esterification methods.

The use of pyridine to discourage side reactions in the preparation of esters from acid chlorides and alcohols has been reported by Norris and Rigby.[2] In a variation of this procedure Mills[3] carried out this reaction in the presence of excess pyridine in an inert solvent.

The preparation of some *p*-phenylphenacyl esters through reaction of methylammonium carboxylates with *p*-phenylphenacyl bromide has been reported by Drake and Bronitsky.[4] In a similar reaction Cromwell and Starks[5] reported the synthesis of α-acetoxy-β-piperidinobenzylacetophenone from α-bromo-β-piperidinobenzylacetophenone and triethylamine acetate in benzene solution. More recently Moreland[6] has described the preparation of a number of esters from phenacyl bromide, *p*-phenylphenacyl bromide, and *p*-nitrobenzyl chloride through reaction with triethylamine carboxylates.

Concurrent with the above work, a number of silylmethyl esters[7] were synthesized in this labora-

tory through reaction of chloromethylsilicon compounds with various triethylamine carboxylates. This present paper gives examples of the extension of this general method of esterification to halogen compounds in which the halogen is not activated by an adjacent carbonyl group or aromatic ring as well as its application for the preparation of mixed aliphatic-aromatic ethers.

$$\begin{array}{c} RCOOH + R'X + (R'')_3N \longrightarrow RCOOR' + (R'')_3NHX \\ (X = Cl \text{ or } Br) \hfill (1) \end{array}$$

$$C_6H_5OH + R'X + (R'')_3N \longrightarrow \\ C_6H_5OR' + (R'')_3NHX \quad (2)$$

In general, the procedure for conducting these reactions consisted of adding stoichiometric quantities of the reactants either to an excess of the particular carboxylic acid reactant or an appropriate solvent. The reaction mixture was then refluxed or held at some other temperature for a suitable period of time after which the tertiary amine hydrohalide was either filtered or washed from the reaction mixture. The products were isolated by distillation. Yields varied from about 50 to 93%. Full investigation of variables leading to optimum yields for each reaction system was not attempted, but the results of the reactions carried out proved the method to be most attractive.

Using triethylamine as the tertiary amine in

(1) Multiple Fellowship on Silicones sustained by the Dow Corning Corp. and Corning Glass Works.

(2) J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.,* **54,** 2088 (1932).

(3) J. A. Mills, *J. Chem. Soc.,* 2332, 1951.

(4) N. L. Drake and J. Bronitsky, *J. Am. Chem. Soc.,* **52,** 3715 (1930).

(5) N. H. Cromwell and F. W. Starks, *J. Am. Chem. Soc.,* **72,** 4108 (1950).

(6) W. T. Moreland, *J. Org. Chem.,* **21,** 820 (1956).

(7) R. L. Merker, U. S. Patent **2,833,802,** May, 1958.

reaction 1, no difficulties were encountered in the preparation of the benzyl and hexyl esters of benzoic acid, the benzyl ester of acetic acid, and the allyl ester of acetic acid. Another interesting application of this method of esterification is its use in the preparation of the bissilylmethyl esters of acetic acid, methacrylic acid, and formic acid from bischloromethyltetramethyldisiloxane.

The reaction of cyclohexyl bromide and acetic acid in the presence of triethylamine yielded if any, only trace amounts of cyclohexyl acetate, the major product being cyclohexene. Under similar conditions, t-butyl chloride, acetic acid, and triethylamine failed to react to form either t-butyl acetate or the expected 3-methylpropene. Also, no reaction occurred between bromobenzene, acetic acid, and triethylamine. The reaction of benzyl chloride, phenol, and triethylamine yielded benzylphenyl ether.

While the reactions described in this paper are limited to those employing triethylamine as the tertiary amine, other tertiary amines have been examined in a qualitative manner and found to be satisfactory. For some purposes it certainly should be possible and even preferable to employ other tertiary amines or perhaps even secondary or primary amines. Secondary and primary amines were not used in the present study because of their possible side-reaction with alkyl halides to form tertiary amine hydrohalides and secondary amine hydrohalides, respectively.
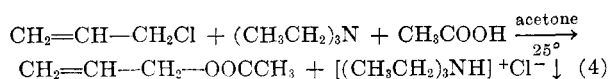
As some esterifications by this method propose separate and distinct problems requiring different reaction conditions, the advantage of a wide range of possible solvents with different boiling points, polarities, and other characteristics is readily seen. For the less reactive alkyl halides, solvents of higher boiling points which permit higher reaction temperatures are preferable.

A side reaction involving the reaction of the alkyl halide with the tertiary amine, to form the

$$R'X + R''_3N \longrightarrow (R_3''R'N)^+X^- \qquad (3)$$
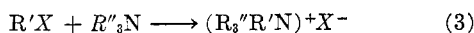
quaternary ammonium halide occurred to some extent in the reactions studied. The nature of the alkyl halide, the tertiary amine, the carboxylic acid, the solvent medium, the reaction temperature, $etc.$, all conceivably play a significant role in determining the relative extent of ester formation and quaternary ammonium salt formation. While the study of these variables is beyond the scope of this present paper, it was of interest to investigate the possibility of such quaternary ammonium salts functioning as reaction intermediates in the formation of esters.

The reaction of allyl chloride, triethylamine, and acetic acid in acetone solution to yield allyl acetate was chosen for this study. Reaction was stopped

$$CH_2{=}CH{-}CH_2Cl + (CH_3CH_2)_3N + CH_3COOH \xrightarrow[25°]{acetone}$$
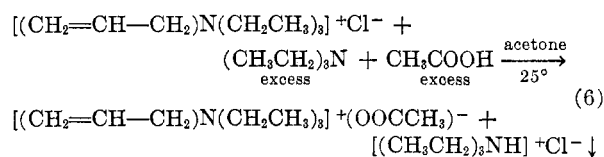$$CH_2{=}CH{-}CH_2{-}OOCCH_3 + [(CH_3CH_2)_3NH]^+Cl^- \downarrow \quad (4)$$

after approximately 65.4% of the triethylamine had been converted to the triethylamine hydrochloride.

At this point in the reaction, analysis revealed that only 35.8% of the allyl chloride had been converted to allyl acetate. The apparent discrepancy in these two values was resolved when allyltriethylammonium chloride synthesized by the reaction,
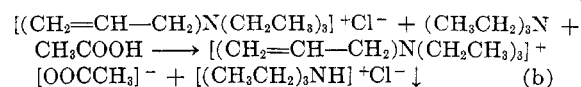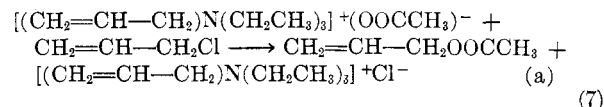
$$CH_2{=}CH{-}CH_2Cl + (CH_3CH_2)_3N \xrightarrow[25°]{acetone}$$
$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+Cl^- \quad (5)$$
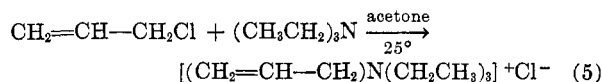
was added to a system analogous to reaction 4 except that no allyl chloride was present. The

$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+Cl^- +$$
$$(CH_3CH_2)_3N + CH_3COOH \xrightarrow[25°]{acetone}$$
$$\underset{excess}{} \quad \underset{excess}{}$$
$$(6)$$
$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+(OOCCH_3)^- +$$
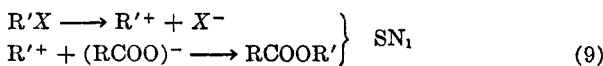$$[(CH_3CH_2)_3NH]^+Cl^- \downarrow$$

rather surprising conversion of the quaternary ammonium chloride to the corresponding acetate in the above system reflects the tendency of allyltriethyl ammonium chloride and acetate to form soluble acid salts, a tendency not manifested by triethylamine hydrochloride which precipitates from the solvent system. Both reaction 4, as written, leading to ester formation and reaction 5, during the early stages of the reaction when acetic acid and triethylamine are still present, yield triethylamine hydrochloride. As both are occurring simultaneously in the preparation of allyl acetate via synthesis 4 the discrepancy between the amounts of triethylamine hydrochloride and allyl acetate obtained is reconciled.

As no allyl acetate was formed in reaction 6 even after long standing, it was concluded that the formation of allyltriethyl ammonium acetate and its subsequent decomposition to triethylamine and allyl acetate is not the mechanism by which ester formation occurs. Once formed, however, allyltriethyl ammonium acetate, being the salt of a strong base and weak acid and hence manifesting a greater transfer of electrons to the carboxylate ion than occurs in the triethylamine acetate, could exert a marked catalytic effect on the esterification reaction.

$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+(OOCCH_3)^- +$$
$$CH_2{=}CH{-}CH_2Cl \longrightarrow CH_2{=}CH{-}CH_2OOCCH_3 +$$
$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+Cl^- \qquad (a)$$
$$(7)$$
$$[(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+Cl^- + (CH_3CH_2)_3N +$$
$$CH_3COOH \longrightarrow [(CH_2{=}CH{-}CH_2)N(CH_2CH_3)_3]^+$$
$$[OOCCH_3]^- + [(CH_3CH_2)_3NH]^+Cl^- \downarrow \qquad (b)$$

The extent to which ester formation proceeds through reaction 7 or through the direct reaction of triethylamine acetate with allyl chloride as shown in reaction 4 is not known at the present time. At any rate the above experiments and the nature of the products formed in the reactions

carried out so far in this investigation suggest that ester formation appears to proceed by typical nucleophilic replacement mechanisms.

$$(RCOO)^- + R'X \longrightarrow RCOOR' + X^- \quad SN_2 \quad (8)$$

$$\left.\begin{array}{l} R'X \longrightarrow R'^+ + X^- \\ R'^+ + (RCOO)^- \longrightarrow RCOOR' \end{array}\right\} \quad SN_1 \quad (9)$$

The degree to which the reaction occurs by the SN_1 mechanism just as in other nucleophilic replacement reactions would be expected to increase with increasing electron repulsion of R' and increasing ionizing power of the solvent medium. Obviously, kinetic studies are needed to elucidate these factors.

EXPERIMENTAL

Commercial materials were used without further purification in this work. The triethylamine was supplied by Eastman Organic Chemicals. Glacial reagent grade carboxylic acids were used.

A. Benzyl benzoate. For 4 hr., 50 g. (0.39 mole) of benzyl chloride, 48.1 g. (0.39 mole) of benzoic acid, 39.8 g. (0.39 mole) of triethylamine, and 100 cc. of xylene were refluxed, temperature range 148°–167°. The reaction mixture was then washed with water, dried over anhydrous sodium sulfate, and distilled. Benzyl benzoate, n_D^{25} 1.5668 (lit.[8] n_D^{20} 1.5681) in a yield of 65.8 g., 79%, was obtained.

B. Hexyl benzoate. For 11 hr., 50 g. (0.41 mole) of hexyl chloride, 50.6 g. (0.41 mole) of benzoic acid, 42 g. (0.41 mole) of triethylamine, and 105 cc. of xylene were refluxed in the temperature range 134°–141°. The reaction mixture was then washed with water and dilute sodium hydroxide. After drying over anhydrous sodium sulfate, the mixture was fractionally distilled to yield 40.3 g. of hexyl benzoate, 47.2 %, b.p. 166°/50 mm.; n_D^{25} 1.4902; d_4^{25} 0.971.

C. Benzyl acetate. For 2 hr. at about 147° were refluxed 50 g. (0.39 mole) of benzyl chloride, 47.3 g. (0.79 mole) of acetic acid, and 39.8 g. (0.39 mole) of triethylamine. The mixture was then poured into excess hexane, and the triethylamine hydrochloride which had formed in 93% yield was removed by filtration. The filtrate was washed with water and distilled to yield 44.4 g., 75% yield, of benzyl acetate. The refractive index of the product was measured at 25° as 1.4994 but all literature sources consulted report this property ranging in value from 1.5232 to 1.5242. NMR analysis, preparation of the benzyl alcohol derivative, and Eastman highest purity benzyl acetate (n_D^{25} 1.4998) confirmed the structure and purity of the benzyl acetate prepared in this laboratory. Properties: b.p. 134°/102 mm.; n_D^{25} 1.4994; d_4^{25} 1.050; R_D, found, 0.2799; R_D calcd., 0.2804; Literature values: n_D^{25} 1.5232,[8,9] 1.5242[10,11] d_4^{16} 1.057.[8]

D. Tetramethyldisiloxane-1,3-bismethylacetate. A solution of 36 g. (0.6 mole) of acetic acid, 55 g. (0.55 mole) of triethylamine, and 58 g. (0.25 mole) of bischloromethyltetramethyldisiloxane in 60 cc. of xylene was refluxed for 18 hr. The precipitate which had formed was removed by filtration; 68 g., 100% of triethylamine hydrochloride. Distillation of the filtrate gave a 93% yield of tetramethyldisiloxane-1,3-bismethylacetate, b.p. 171°/760 mm., d_4^{25} 1.00, n_D^{25} 1.4215 (lit.[12] n_D^{25} 1.4215, d_4^{25} 0.993).

E. Tetramethyldisiloxane-1,3-bismethylmethacrylate. In 110 g. of xylene with 3 g. of hydroquinone were dissolved 51 g. (0.6 mole) of glacial methacrylic acid, 55.5 g. (0.55 mole)

of triethylamine, and 57.8 g. (0.25 mole) of bischloromethyltetramethyldisiloxane; the mixture was refluxed for 8 hr. The precipitate which had formed was removed by filtration; 68.5 g., 99%, of triethylamine hydrochloride. The filtrate was distilled yielding 37 g., 45%, of tetramethyldisiloxane-1,3-bismethylmethacrylate, b.p. 127°/3 mm.; n_D^{25} 1.4472; d_4^{25} 0.996 (lit.[13] n_D^{25} 1.44 d_4^{25}72; 0.996).

F. Tetramethyldisiloxane-1,3-bismethylformate. For 12 hr., 97 g. (0.42 mole) of bischloromethyltetramethyldisiloxane, 43 g. (0.94 mole) of glacial formic acid, 90 g. (0.89 mole) of triethylamine, and 150 g. of xylene were refluxed. The triethylamine hydrochloride which had formed was removed by filtration and the filtrate distilled to give 84% yield of tetramethyldisiloxane-1,3-bismethylformate, b.p. 143°/40 mm., n_D^{25} 1.4228, d^{25} 1.034; R_D, found, 0.2461; R_D calcd., 0.2457.

G. Reaction of cyclohexyl bromide and acetic acid. For 4 hr., 50 g. (0.31 mole) of cyclohexyl bromide, 36.9 g. (0.61 mole) of acetic acid, and 31 g. (0.31 mole) of triethylamine were refluxed, temperature 125°–105°. The reaction mixture was washed with water, dried, and distilled; a yield of 65.5% of cyclohexene, b.p. 82°/740 mm. n_D^{25} 1.4435 (lit.[8] n_D^{25} 1.4451), was obtained. A small amount of higher-boiling impure material thought to be cyclohexyl acetate was also obtained. Further purification of this product was not attempted.

H. Attempted esterification of acetic acid with t-butyl chloride. In the usual way 50 g. (0.54 mole) of t-butyl chloride, 64.8 g. (1.08 mole) of acetic acid, and 54.6 g. (0.54 mole) of triethylamine were refluxed for several hours. The condenser was equipped with a Dry-Ice acetone trap to collect any 2-methylpropene (b.p. 6°) which might be formed. Nothing was collected in the trap and no evidence of reaction was seen.

I. Attempted esterification of acetic acid with bromobenzene. For 3.5 hr., 50 g. (0.32 mole) of bromobenzene, 38.2 g. (0.636 mole) of acetic acid, and 32.1 g. (0.32 mole) of triethylamine were refluxed. That no reaction occurred was evident upon pouring the mixture into excess hexane, at which point no triethylamine hydrobromide precipitated.

J. Benzyl phenyl ether. For 2 hr. 50 g. (0.39 mole) of benzyl chloride, 74.3 g. (0.79 mole) of phenol, and 40 g. (0.395 mole) of triethylamine were refluxed, temperature range 150° to 190°. The reaction mixture was then washed with water and dilute sodium hydroxide. After drying over anhydrous sodium sulfate, the mixture was distilled to yield 33.6 g. of benzyl phenyl ether, 46%. This product was recrystallized from 95% ethanol, melting point 38–39° (lit.[9] m.p., 40°). This structure was confirmed by NMR analysis.

K. Allyl acetate. A mixture of 101 g. (1.0 mole) of triethylamine, 60 g. (1.0 mole) of acetic acid, 76.5 g. (1.0 mole) of allyl chloride, 300 cc. of acetone, and 1 g. of potassium iodide was held at room temperature for 1 week. The precipitate which had formed was filtered, and weighed 89.9 g.; 65.4% of triethylamine hydrochloride. The filtrate was distilled and a yield of 35.8% of allyl acetate was obtained, b.p. 99–100°/atm. n_D^{25} 1.4018 (lit.[14] b.p. 104°/762 mm., n^{20} 1.4045).

L. Behavior of allyltriethylammonium chloride under esterification conditions. Allyltriethylammonium chloride was easily obtained as it precipitated on standing from an acetone solution which contained stoiciometric weights of triethylamine and allyl chloride plus a trace of potassium iodide. Four grams of the quaternary salt so prepared was placed in 12.0 g. of acetic acid, 10.1 g. of triethylamine, and 30 cc. of acetone. After 75 hr. at room temperature, the mixture was filtered and 2.6 g. of precipitate was obtained; theory for triethylamine hydrochloride, 3.1 g. Analysis of this precipitate showed it to be 94% triethylamine hydrochloride. No allyl acetate could be found in the filtrate.

PITTSBURGH, PA.

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