C=CH); mass spectrum, *m/e* 258 (M^+).

Anal. Calcd for $C_{18}H_{26}O$: C, 83.66; H, 10.14. Found: C, 83.58; H, 10.11.

N,N-Dimethylaniline (15 g, 0.12 mol) 2 mL of concentrated HCl and 15 mL of xylene were refluxed to remove the water. The mixture was cooled, and 15 g (0.1 mol) of isophorone dimer was added. The mixture was refluxed at 158 °C for 20 h; no water formed, and GC showed that no reaction had occurred.

Dimer 1 and Aniline. Isophorone dimer (126 g, 0.46 mol), 85 g (0.91 mol) of aniline, 24 g (0.18 mol) of aniline hydrochloride, and 75 mL of toluene were refluxed, and the water was collected as it formed in a Dean-Stark trap. In 5 h, only 30% of the theoretical amount of water had collected. GC showed the presence of dimer **1**, isophorone anil, and product **2**. In 15 h, 90% of the theoretical amount of water had formed. The reaction was worked up in the usual way to give 170 g of crude product from which 70 g (53%) of **2** was obtained by recrystallization from hexane (by mixture melting point and IR). Isophorone dimer (20 g, 0.07 mol) and 80 g (0.86 mol) of aniline were stirred and heated at 160 °C for 6 h. GC showed that no reaction had occurred.

Xylene (50 mL), 13 g (0.12 mol) of *N*-methylaniline, and 2 mL of concentrated HCl were refluxed, and the water was removed in a Dean-Stark trap. Isophorone dimer (15 g, 0.1 mol) was added and the mixture refluxed at 144–148 °C for 24 h. GC showed that no reaction had occurred.

p-Toluenesulfonic acid (2 g) and 50 mL of xylene were refluxed for 3 h, and the water was collected as it formed in a Dean-Stark trap. Isophorone dimer 1 (10 g, 0.036 mol) was added, and the mixture was refluxed for 10 h at 143 °C. Samples were taken every 2 h and analyzed by GC. Dimer 1 was found to be slowly but completely converted into a number of higher boiling materials. No isophorone was detected.

Acknowledgment. We would like to thank Charles P. Jacobs for assisting in the experiment work and K. Welch for the mass spectral work.

Registry No.—**1**, 6244-16-2; **2**, 68936-70-9; **2** reduction product, 68928-14-3; isophorone-*m*-toluidine condensation product, 68928-15-4; 3,5-dimethylcyclohexen-1-one–aniline condensation product, 68928-16-5; (*E*)-isophorone anil, 68928-17-6; (*Z*)-isophorone anil, 68928-18-7; (*E*)-*N*-(3,5,5-trimethyl-2-cyclohexenylidene)cyclohexylamine, 68928-19-8; (*Z*)-*N*-(3,5,5-trimethyl-2-cyclohexenylidene)-cyclohexylamine, 68928-20-1; 3-[(3,5,5-trimethylcyclohexenylidene)methyl]-5,5-dimethyl-2-cyclohexen-1-one, 68928-21-2; isophorone, 78-59-1; aniline, 62-53-3; isophorone anil, 36755-22-3; aniline hydrochloride, 142-04-1; *m*-toluidine, 108-44-1; 3,5-dimethylcyclohexen-1-one, 1123-09-7; cyclohexylamine, 108-91-8.

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Esterification of Carboxylic Acids with Trialkyloxonium Salts

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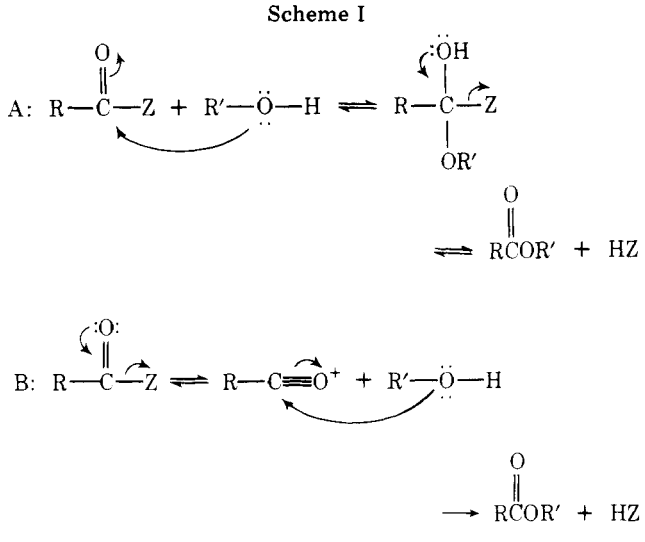
The preparation of methyl and ethyl esters of a variety of carboxylic acids using trimethyl- and triethyloxonium tetrafluoroborate has been explored. This method has been found to be successful for a broad series of carboxylic acids including sterically hindered and polyfunctional carboxylic acids. Mild conditions are employed and the reaction is quite rapid in the absence of steric hindrance. Carboxylic acids can be esterified by this procedure in excellent yield to afford products with a high degree of purity.

Methods for effecting the synthesis of carboxylic acid esters from the corresponding acid can be envisioned in terms of two general schemes: nucleophilic attack on the *carboxyl carbon* atom of the carboxylic acid or on one of its derivatives by an alcohol (Scheme I); or alkylation of the *carboxyl oxygen* atom of a carboxylic acid or carboxylate anion by an appropriate alkylating agent (Scheme II).

The direct esterification of a carboxylic acid by an alcohol (Scheme IA, Z = OH) proceeds at a reasonable rate only in the presence of acid catalysts[1] and thus severe problems are usually encountered in the esterification of acid-sensitive compounds. Furthermore, this reaction is reversible, often exhibiting an unfavorable equilibrium constant.[2] Therefore, it is frequently necessary to remove water and/or use a large excess of alcohol in order to achieve reasonable yields of product.[3] Finally, sterically crowded carboxylic acids are not readily esterified by this procedure because of increased steric interaction in the tetrahedral intermediate.[4]

Conversion of a carboxylic acid to a more reactive derivative

Scheme I



0022-3263/79/1944-1149$01.00/0

Table I. Esterification of Carboxylic Acids with Trimethyl- and Triethyloxonium Tetrafluoroborate[a]

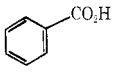
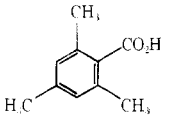
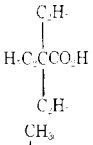
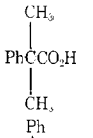
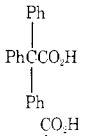
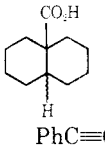
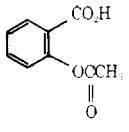
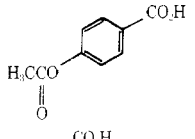
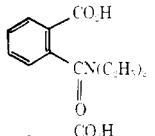
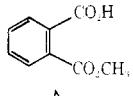
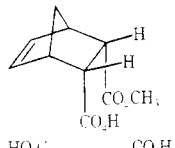
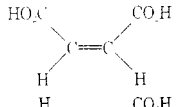
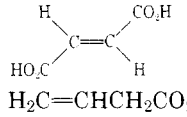
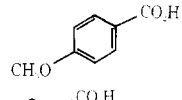
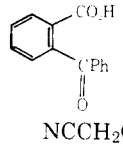
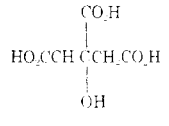
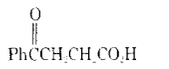
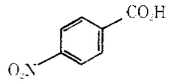
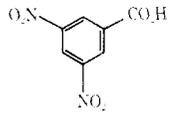
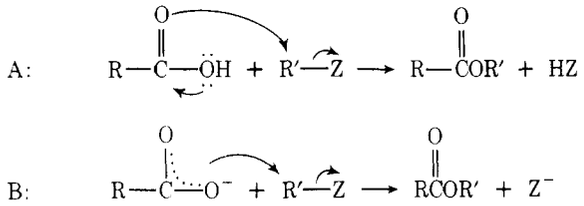
no.	compd	registry no.	methyl ester % yield[b]	methyl ester % purity[c]	registry no.	ethyl ester % yield[b]	ethyl ester % purity[c]	registry no.
1		65-85-0	92	>99	93-58-3	91	>99	93-89-0
2		480-63-7	90	>99	2282-84-0	90	>99	1754-55-8
3		813-58-1	95	>99	10250-49-4	90	>99	34666-17-6
4		826-55-1	88	>99	57625-74-8	86	>99	2901-13-5
5		595-91-5	97	(mp 182–183 °C)	5467-21-0	81	(mp 115–116 °C)	5467-22-1
6			93	>99		89	>99	
7	$PhC{\equiv}CCO_2H$	637-44-5	91	>99		91	>99	2216-94-6
8		50-78-2	85	>99	580-02-9	89	>99	529-68-0
9		2345-34-8	95	>99	24262-66-6	95	>99	13031-45-3
10		4166-52-3	86	>99	26593-44-2	88	>99	24677-02-9
11		4376-18-5	86	>99	131-11-3	87	>99	34006-77-4
12		4883-79-8	93	>99	39589-98-5	91	>99	7288-32-6
13		110-16-7	74[d]	>99	624-48-6	70[d]	>99	141-05-9
14		110-17-8	80[d]	>99	624-49-7	77[d]	>99	623-91-6
15	$H_2C{=}CHCH_2CO_2H$	625-38-7	73[e]	98[f]	3724-55-8	80[e]	98[f]	1617-18-1
16		100-09-4	88	>99	121-98-2	93	>99	94-30-4
17		85-52-9	95	>99	606-28-0	95	>99	604-61-5
18	$NCCH_2CO_2H$	372-09-8	82	95	105-34-0	91	>99	105-56-6
19		77-92-9	70[d]	>99	1587-20-8	86	>99	77-93-0

Table I (*Continued*)

no.	compd	registry no.	methyl ester % yield[b]	methyl ester % purity[c]	registry no.	ethyl ester % yield[b]	ethyl ester % purity[c]	registry no.
20		2051-95-8	85	>99	25333-24-8	99	>99	6270-17-3
21		62-23-7	90	(mp 93–94 °C)	619-50-1	87	(mp 54–55 °C)	99-77-4
22		99-34-3	85	(mp 109–110 °C)	2702-58-1	88	(mp 91–92 °C)	618-71-3

[a] Esterifications were performed at room temperature over a period of 18–24 h. [b] Isolated yield after Kugelrohr distillation or recrystallization. [c] Estimated by GLC. [d] Lower yields in this case are due to water solubility of the product. [e] Lower yields in this case are due to the high volatility of the product. [f] Contaminated by trace amounts of the crotonate (<2%).

Scheme II



such as the acid chloride, followed by alcoholysis (Scheme I; Z = Cl), overcomes problems associated with reversibility. Nevertheless, these methods are often rather harsh and side reactions can result. The formation of ketenes in the preparation of acid chlorides provides an example.[5,6] Furthermore, these methods require an additional synthetic step for the conversion of carboxylic acids into esters; hence, a concomitant decrease in overall yield is to be expected.

Methods which rely on the formation and subsequent alcoholysis of acylium ions (Scheme IB) are useful for the esterification of hindered carboxylic acids because formation of a tetrahedral intermediate is avoided. Included in these methods is the treatment of a carboxylic acid with 100% sulfuric acid followed by alcoholysis (Scheme IB; Z = H_2O).[7] In fact, hindered carboxylic acids can often be esterified through the acid chloride presumably by formation of the acylium ion (Scheme IB; Z = Cl).[8] These methods, although useful in many cases, require extremely harsh acidic conditions and have other limitations as well. The utilization of 100% sulfuric acid, for example, succeeds with only a limited number of carboxylic acids (i.e., only those aromatic acids which readily yield a stable acylium ion under the reaction conditions). This method fails, for example, with benzoic acid.[7]

Esterification methods based on the alkylation of the carboxyl group of a carboxylic acid (Scheme II) do not suffer from problems associated with reversibility. Furthermore, these methods are generally applicable to the esterification of sterically hindered carboxylic acids since a tetrahedral intermediate is not involved. Examples of this approach include alkylation of carboxylate salts with alkyl halides in hexamethylphosphoric triamide (HMPT) and other solvents,[9] alkylation of carboxylate salts with dialkyl sulfates,[10] alkyl chlorosulfites,[11] alkyl phosphates,[12] and quaternary ammonium salts,[13] and treatment of carboxylic acids with acetals of *N*,*N*-dimethylformamide,[14] alkyl phosphites,[15] alkyl-*p*-tolyltriazenes,[16] and diazomethane.[17]

These methods are valuable in many instances but are also subject to limitations. For example, in many cases the reagents or solvents are either toxic or carcinogenic, as is the case with HMPT,[18] methyl iodide,[19] dimethyl sulfate,[20] and methyl-*p*-tolyltriazene.[21] Some of the reagents are dangerous due to the fact that they are likely to undergo explosive decomposition. Such is the case with methyl-*p*-tolyltriazene[16] and diazomethane.[22] Alkylation of metal carboxylates often requires their preparation, which can be tedious. Still other methods require harsh conditions such as the pyrolytic treatment necessary for the reaction of carboxylate salts with either tetramethylammonium salts[13] or *n*-butyl chlorosulfite[11] to produce esters.

We believed that the utilization of trialkyloxonium salts for the alkylation of the carboxyl group of carboxylic acids would afford a method of esterification which would be general in its applicability, convenient, mild, and which would not require the use of hazardous materials. Although it had previously been demonstrated that trialkyloxonium salts are capable of esterifying metal carboxylates in aqueous solution, particularly those derived from amino acids and peptides, a large excess of oxonium salt must be employed as a result of the rapid, although not instantaneous, reaction of trialkyloxonium salts with water.[23] We have previously described the preparation of ethyl esters of sterically hindered carboxylic acids using equivalent amounts of triethyloxonium tetrafluoroborate in dichloromethane[24] and have applied this method to the preparation of methyl and ethyl 4-acetoxybenzoate.[25]

Our approach has relied upon the in situ generation of the carboxylate anion in dichloromethane by use of the sterically hindered base *N*,*N*-diisopropylethylamine; not only is the alkylation of this amine by trialkyloxonium salts quite slow but the ammonium carboxylates which are rapidly formed via proton transfer are in general quite soluble in dichloromethane. Subsequent alkylation of the carboxylate anion by the trialkyloxonium salt produces the desired ester.

In order to assess the advantages of our approach over previously existing methods of esterification, we undertook a study which would allow us to determine the generality of our procedure and clearly define the reaction parameters. We now report the results of our studies on the esterification of a broad series of carboxylic acids with trimethyl- and triethyloxonium tetrafluoroborate. We demonstrate that much shorter reaction times are needed than were used previously and that the effects of steric hindrance on yield and reaction time are clearly delineated.

Results and Discussion

The esterification of carboxylic acids with trimethyl- and triethyloxonium tetrafluoroborate proceeds in nearly quantitative yield with both simple and hindered carboxylic acids. Polyfunctional carboxylic acids are readily esterified without interference from other functional groups. Furthermore, the procedure is extremely convenient; esterification is effected

by allowing a dichloromethane solution of carboxylic acid, oxonium salt, and *N,N*-diisopropylethylamine to stand at room temperature for 1–24 h. Extraction with dilute acid and dilute base followed by evaporation of the solvent and purification by simple procedures such as bulb-to-bulb (Kugelrohr) distillation provides the desired ester in excellent yield and in pure form (usually >99% by GLC). Workup of the reaction mixture is greatly facilitated by use of the water immiscible, low boiling solvent, dichloromethane. Table I summarizes the results for a wide variety of carboxylic acids. The yields reported are isolated yields after purification by Kugelrohr distillation or by recrystallization.

As Table I demonstrates, monofunctional carboxylic acids including sterically hindered examples, such as 2,4,6-trimethylbenzoic acid (**2**) and triethylacetic acid (**3**), are esterified in high yield. Polyfunctional carboxylic acids containing acid-labile functionality such as 2-acetoxybenzoic acid (**8**), *N,N*-diethylphthalamic acid (**10**), methyl hydrogen phthalate (**11**), and 3-(methoxycarbonyl)-5-norbornene-2-carboxylic acid (**12**) are esterified smoothly without affecting the acid-sensitive functional groups. The direct acid-catalyzed esterification process would be expected to fail in these cases as a consequence of neighboring group assisted side reactions. However, close proximity of the carboxyl group to a second sensitive functional group is not a prerequisite for failure of the normal acid-catalyzed esterification reaction. For example, our attempted production of methyl 4-acetoxybenzoate from the acid-catalyzed reaction between 4-acetoxybenzoic acid (**9**) and methanol afforded only methyl 4-hydroxybenzoate in which the phenolic ester had been cleaved by transesterification. In contrast, esterification of 4-acetoxybenzoic acid (**9**) with trialkyloxonium salts leads to production of methyl or ethyl 4-acetoxybenzoate in excellent yield.

Unsaturated carboxylic acids do not undergo isomerization as a result of our procedure. For example, maleic acid (**13**) does not undergo cis/trans isomerization nor does 3-butenoic acid (**15**) undergo appreciable isomerization to the more stable crotonate.[26] In each case, integrity of the olefinic linkage is maintained. In contrast to our procedure, the acid-catalyzed esterification process can cause isomerization of a carbon–carbon double bond to take place.[26]

Carboxylic acids containing other functional groups which are known to be alkylated by trialkyloxonium salts[27] are, nevertheless, smoothly esterified by the present method without affecting the other functionality. A variety of such functional groups which may be present are illustrated by examples in Table I: alkoxy [4-methoxybenzoic acid (**16**)]; acyl [2-benzoylbenzoic acid (**17**), 3-benzoylpropionic acid (**20**)]; cyano [cyanoacetic acid (**18**)]; hydroxyl [citric acid (**19**)]; and carboxamide [*N,N*-diethylphthalamic acid (**10**)]. Several of these functional groups would be expected to be more reactive toward alkylation by trialkyloxonium salts than carboxylic acids themselves.[27] Consequently, the success of our procedure with such polyfunctional acids is unquestionably due to the in situ conversion to the more reactive carboxylate salt. Interference by proximal functional groups does not appear to present any problems in the esterification with trialkyloxonium salts. Even in the case of 2-benzoylbenzoic acid (**17**), which is particularly susceptible to intramolecular cyclization reactions,[28] the esterification with trialkyloxonium salts proceeds without complication.

Finally, the presence of electron-withdrawing substituents, as in 4-nitrobenzoic acid (**21**) and 3,5-dinitrobenzoic acid (**22**), does not appear to decrease the effectiveness of our procedure.

Reaction Rates. In our initial studies,[24,25] we were concerned with the possibility that the rate of esterification might vary considerably depending upon the nature of the particular carboxylic acid. Consequently, we adopted the convenient general procedure of allowing the reaction mixture to stand at room temperature overnight (i.e., 16–24 h). A cursory examination of reaction rates has demonstrated that this procedure was highly conservative and that, in the absence of steric hindrance, the reaction is very rapid. When the reaction of benzoic acid with triethyloxonium tetrafluoroborate was monitored by GLC, the reaction was essentially complete as soon as the reactants were mixed when the concentrations of the reactants were the same as those used in the synthetic procedure.

In order to assess whether shorter reaction times were sufficient for preparative work, a variety of carboxylic acids were subjected to esterification with trimethyl- and triethyloxonium tetrafluoroborate under the same conditions employed for the acids listed in Table I but using a reaction time of only 1 h. Table II summarizes the results. Of the carboxylic acids studied, only 2,4,6-trimethylbenzoic acid (**2**) appears to require reaction times longer than 1 h, and only then in the reaction with triethyloxonium tetrafluoroborate. Thus, in the absence of steric hindrance, reaction times >1 h appear to present no advantage, although it may occasionally be more convenient to employ longer reaction times.

Handling of Trialkyloxonium Salts. Since one of the major aims of our work on esterification reactions was to develop a procedure which was both general and convenient, the stringent handling requirements associated with the use of trialkyloxonium salts was of some concern to us (e.g., in some procedures the use of a drybox is recommended).[29] However, we have found such tedious techniques to be totally unnecessary. After large-scale preparation of trimethyl- and triethyloxonium tetrafluoroborate according to convenient *Organic Syntheses* procedures,[30,31] both salts were stored in the freezing compartment of a refrigerator (ca. −20 °C) in tightly stoppered bottles. Triethyloxonium tetrafluoroborate was stored under diethyl ether and, therefore, exhibited a greater capacity for storage over long periods of time. Both salts were handled in the open atmosphere and we have performed successful esterifications, without any apparent decrease in yield or purity of the products, with triethyloxonium tetrafluoroborate that had been stored for up to 1 year and trimethyloxonium tetrafluoroborate that had been stored for up to 6 months.

We do recommend that some caution be taken in the handling of trialkyloxonium salts since adequate testing for the toxicity of these substances has not yet been undertaken. While we are unaware of any reports which indicate that these oxonium salts are carcinogenic, the carcinogenic properties of other potent alkylating agents are well documented.[19] Any such dangers associated with trialkyloxonium salts are certainly minimized by the fact that these compounds are water-soluble, nonvolatile, crystalline solids which are rapidly solvolyzed in aqueous solution.[27]

Conclusion

We believe that the esterification of carboxylic acids by trialkyloxonium salts is a superior method of esterification in terms of generality, convenience, and mildness of conditions rivaled only perhaps by methods which employ diazomethane or acetals of *N,N*-dimethylformamide. However, the present method is superior to methods which employ diazomethane in that methyl and ethyl esters, and in principle other esters as well,[27] may be prepared without the toxicity and explosion hazard of diazomethane. The method presented here is also superior to those employing acetals of *N,N*-dimethylformamide in that the preparation of such acetals ultimately involves the use of trialkyloxonium salts[27] and acetals of dimethylformamide condense readily with active methylene compounds.[14] For example, in contrast to our procedure (see Table I), cyanoacetic acid (**18**) cannot be esterified in good

Table II. Esterification of Carboxylic Acids with Trimethyl- and Triethyloxonium Tetrafluoroborate[a]

	methyl ester		ethyl ester	
no.	% yield[b]	% purity[c]	% yield[b]	% purity[c]
1	90	>99	96	>99
2	92	>99	81[d]	>99
9	93	>99	95	>99
15	70[e]	98[f]	78[e]	98[f]
22	83	(mp 109–110 °C)	89	(mp 91–92 °C)

[a] Esterifications were performed at room temperature; reaction time 1 h. [b] Isolated yield after Kugelrohr distillation or recrystallization. [c] Estimated by GLC. [d] Yields of 90% (see Table I) could be obtained by increasing the reaction time to 4 h or longer. [e] Lower yields in this case are due to the volatility of the product. [f] Contaminated by trace amounts of the crotonate (<2%).

yield with *N,N*-dimethylformamide dimethyl acetal.[14] Finally, trialkyloxonium salts are convenient reagents. Although fairly expensive when purchased commercially, they can be prepared inexpensively and in substantial quantity by reliable procedures.[30,31]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Model 337 or a Perkin-Elmer Model 457 spectrophotometer. Nuclear magnetic resonance spectra were recorded on either a Varian Model A-60 or a Varian Model EM-360 spectrometer, and chemical shifts are reported in parts per million downfield from Me_4Si. Gas chromatographic analyses were performed on a Varian Model 2400 gas chromatograph equipped with flame ionization detectors and 5 ft × 0.125 in. (o.d.) columns packed with either 10% Carbowax 20M on Chromosorb W or 10% FFAP on Chromosorb W.

Benzoic acid (**1**), 2,4,6-trimethylbenzoic acid (**2**), triphenylacetic acid (**5**), phenylpropiolic acid (**7**), maleic acid (**13**), fumaric acid (**14**), 4-methoxybenzoic acid (**16**), 2-benzoylbenzoic acid (**17**), cyanoacetic acid (**18**), anhydrous citric acid (**19**), 4-nitrobenzoic acid (**21**), and 3,5-dinitrobenzoic acid (**22**) were all obtained commercially and used without subsequent purification. Triethylacetic acid[32] (**3**) was prepared according to a procedure previously reported in the literature.[33] 2-Methyl-2-phenylpropionic acid (**4**) was obtained from Wenzinger of the University of South Florida. This material exhibited an IR spectrum which was in agreement with the one reported in the literature.[34] 9-Decalincarboxylic acid (mixture of cis and trans) (**6**) was prepared via the reaction between carbon monoxide and the 9-decalyl cation generated from commercial decahydro-2-naphthol,[35] mp 98–110 °C (lit.[35] cis, 122–123 °C; trans, 135–136 °C). 2-Acetoxybenzoic acid (**8**) was prepared via the reaction between commercial 2-hydroxybenzoic acid and acetic anhydride.[36] 4-Acetoxybenzoic acid (**9**) was prepared by following the same procedure[36] as the one used for the preparation of 2-acetoxybenzoic acid (**8**), mp 186–188 °C (lit.[37] 189–190 °C). *N,N*-Diethylphthalamic acid (**10**) was prepared via the reaction between commercial phthalic anhydride and diethylamine.[38] Methyl hydrogen phthalate (**11**) was prepared via the reaction between commercial phthalic anhydride and anhydrous methanol.[39] 3-(Methoxycarbonyl)-5-norbornene-2-carboxylic acid (**12**) was prepared via the reaction between *endo-cis*-5-norbornene-2,3-dicarboxylic acid anhydride (prepared via the method of Diels and Alder[40]) and anhydrous methanol.[41] 3-Butenoic acid (**15**) was prepared by hydrolysis of commercial allyl cyanide.[42] 3-Benzoylpropionic acid (**20**) was prepared via the reaction between benzene and commercial succinic anhydride.[43]

Trimethyloxonium tetrafluoroborate was prepared by the method of Curphy.[30] Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein.[31] *N,N*-Diisopropylethylamine was purchased from Aldrich Chemical Co. and used without subsequent purification. Reagent grade dichloromethane was stored over Linde 4 Å molecular sieves and used without subsequent purification.

The general procedure which follows was used for all of the carboxylic acids studied. The NMR and IR spectra of methyl and ethyl benzoate, ethyl phenylpropiolate, methyl 2-acetoxybenzoate, dimethyl phthalate, dimethyl *endo-cis*-5-norbornene-2,3-dicarboxylate, dimethyl and diethyl maleate, dimethyl and diethyl furmarate, methyl and ethyl 3-butenoate, methyl and ethyl 2-benzoylbenzoate, methyl and ethyl 4-methoxybenzoate, methyl and ethyl cyanoacetate, trimethyl and triethyl citrate, methyl 3-benzoylpropionate, methyl and ethyl 4-nitrobenzoate, and methyl and ethyl 3,5-dinitrobenzoate were in agreement with published spectra.[44] The NMR and IR spectra of methyl and ethyl 2,4,6-trimethylbenzoate,[14] methyl 2-methyl-2-phenylpropionate,[45] methyl triphenylacetate,[46] methyl 9-decalincarboxylate,[47] methyl phenylpropiolate,[48] and ethyl 2-acetoxybenzoate[49] were in agreement with those reported in the literature.[14,45–49] Spectral data are listed below for those esters for which no comparison with published spectra could be made.

General Procedure for the Preparation of Methyl Esters with Trimethyloxonium Tetrafluoroborate. To a suspension of 1.63 g (0.011 mol) of trimethyloxonium tetrafluoroborate in 75 mL of dichloromethane was added 0.010 mol of the carboxylic acid. The resulting suspension was stirred magnetically while 1.42 g (0.011 mol) of *N,N*-diisopropylethylamine was introduced with a syringe. For di- and triprotic acids, a corresponding increase in the number of equivalents of oxonium salt and amine was used. During the addition of the amine, a warming of the reaction mixture was observed; larger scale reactions require a dropping funnel and a reflux condenser. The flask was stoppered after the addition of the amine and the suspension was allowed to stir for 1–24 h. After approximately 1 h virtually all of the originally undissolved oxonium salt had gone into solution. After the end of the desired reaction time, the organic solution was extracted with three 50-mL portions of 1 N hydrochloric acid, three 50-mL portions of 1 N potassium bicarbonate, and a single portion of saturated sodium chloride. With maleic acid (**13**), fumaric acid (**14**), 3-butenoic acid (**15**), and citric acid (**19**), the HCl and the $KHCO_3$ solutions were back-extracted due to the water solubility of the corresponding esters. The organic solution was then dried over anhydrous sodium sulfate and the solvent was removed by evaporation under reduced pressure. The residue was purified by short-path (Kugelrohr) distillation or by recrystallization to afford 70–97% of the desired esters with purities of 95% or greater.

General Procedure for the Preparation of Ethyl Esters with Triethyloxonium Tetrafluoroborate. An ether slurry of triethyloxonium tetrafluoroborate was evaporated under reduced pressure to generally afford powdery material. However, in some cases, the oxonium salt appeared to be wet after removal of the ether. In these cases, addition of anhydrous ether followed by reevaporation of the ether slurry produced powdery material of sufficient purity to be used for esterifications.[50] To a solution of 2.09 g (0.011 mol) of the oxonium salt in 75 mL of dichloromethane was added 0.010 mol of the carboxylic acid. The resulting solution (suspension) was stirred magnetically while 1.42 g (0.011 mol) of *N,N*-diisopropylethylamine was introduced with a syringe. For di- and triprotic acids a corresponding increase in the number of equivalents of oxonium salt and amine was employed. During the addition of the amine, a warming of the reaction mixture was observed; larger scale reactions require the use of a dropping funnel and a reflux condenser. The flask was stoppered and the resulting solution was allowed to stand for 1–24 h. Workup as described above for the preparation of methyl esters afforded 70–99% of the desired esters with purities of 95% or greater.

Reaction of 4-Acetoxybenzoic Acid (9) with Methanol. To a solution of 1.00 g (5.56 mmol) of 4-acetoxybenzoic acid (**9**) in 20 mL of absolute methanol was added 0.5 mL of concentrated sulfuric acid, and the resulting solution was allowed to reflux for 24 h. The solution was then allowed to cool to room temperature and diluted with 50 mL of dichloromethane. The organic solution was extracted with three 50-mL portions of 1 N potassium bicarbonate and a single 50-mL portion of saturated sodium chloride. The organic solution was dried over anhydrous sodium sulfate and then evaporated under reduced pressure. Recrystallization of the residue from petroleum ether gave 0.51 g (60%) of methyl 4-hydroxybenzoate[51] with a melting point of 127–129 °C. This material exhibited NMR and IR spectra in agreement with published spectra.[44]

Reaction Rates. To a solution of 2.09 g (0.011 mol) of triethyloxonium tetrafluoroborate in 75 mL of dichloromethane was added 1.22 g (0.010 mol) of benzoic acid followed by 1.42 g (0.011 mol) of *N,N*-diisopropylethylamine, while the dichloromethane solution was stirred magnetically. After approximately 5 min the reaction mixture was worked up in the manner described above in the general procedure for the preparation of methyl esters. GLC analysis using naphthalene as an internal standard indicated quantitative conversion to ethyl benzoate.

Spectral Data. Methyl triethylacetate: NMR ($CDCl_3$) δ 0.8 (t, J = 7 Hz, 9 H), 1.6 (q, J = 7 Hz, 6 H), 3.7 (s, 3 H); IR (thin film) 1740 cm^{-1}. Ethyl triethylacetate: NMR ($CDCl_3$) δ 0.8 (t, J = 7 Hz, 9 H), 1.2 (t, J = 8 Hz, 3 H), 1.7 (q, J = 7 Hz, 6 H), 4.1 (q, J = 8 Hz, 2 H); IR (thin film) 1740 cm^{-1}. Ethyl 2-phenyl-2-methylpropionate: NMR

($CDCl_3$) δ 1.1 (t, J = 8 Hz, 3 H), 1.6 (s, 6 H), 4.1 (q, J = 8 Hz, 2 H), 7.4 (s, 5 H); IR (thin film) 1740 cm^{-1}. Ethyl triphenylacetate: NMR ($CDCl_3$) δ 1.2 (t, J = 7 Hz, 3 H), 4.4 (q, J = 7 Hz, 2 H), 7.5 (s, 15 H); IR (thin film) 1740 cm^{-1}. Ethyl 9-decalincarboxylate: NMR ($CDCl_3$) δ 1.3 (m, 20 H), 4.3 (q, J = 7 Hz, 2 H); IR (thin film) 1740 cm^{-1}. Methyl 4-acetoxybenzoate: NMR ($CDCl_3$) δ 2.3 (s, 3 H), 3.9 (s, 3 H), 7.1 (d, J = 8 Hz, 2 H), 8.0 (d, J = 8 Hz, 2 H); IR (thin film) 1725, 1760 cm^{-1}. Ethyl 4-acetoxybenzoate: NMR ($CDCl_3$) δ 1.3 (t, J = 7 Hz, 3 H), 2.3 (s, 3 H), 4.4 (q, J = 7 Hz, 2 H), 7.2 (d, J = 8 Hz, 2 H), 8.1 (d, J = 8 Hz, 2 H). Methyl N,N-diethylphthalamate: NMR ($CDCl_3$) δ 1.0 (t, J = 7 Hz, 3 H), 1.3 (t, J = 7 Hz, 3 H), 3.1 (q, J = 7 Hz, 2 H), 3.5 (q, J = 7 Hz, 2 H), 3.8 (s, 3 H), 7.6 (m, 4 H); IR (thin film) 1650, 1735 cm^{-1}. Ethyl N,N-diethylphthalamate: NMR ($CDCl_3$) δ 1.0 (m, 9 H), 3.1 (q, J = 7 Hz, 2 H), 3.5 (q, J = 7 Hz, 2 H), 4.3 (q, J = 7 Hz, 2 H), 7.6 (m, 4 H); IR (thin film) 1650, 1735 cm^{-1}. Methyl and ethyl phthalate: NMR ($CDCl_3$) δ 1.3 (t, J = 7 Hz, 3 H), 3.9 (s, 3 H), 4.3 (q, J = 7 Hz, 2 H), 7.5 (m, 4 H); IR (thin film) 1730 cm^{-1}. Methyl and ethyl 5-norbornene-2,3-dicarboxylate: NMR ($CDCl_3$) δ 1.2 (m, 5 H), 3.2 (m, 4 H), 3.5 (s, 3 H), 4.0 (q, J = 7 Hz, 2 H), 6.1 (s, 2 H); IR (CCl_4) 1735 cm^{-1}. Ethyl β-benzoylpropionate: NMR ($CDCl_3$) δ 1.2 (t, J = 7 Hz, 3 H), 2.7 (t, J = 6 Hz, 2 H), 3.2 (t, J = 6 Hz, 2 H), 4.1 (q, J = 7 Hz, 2 H), 7.6 (m, 5 H); IR (thin film) 1700, 1740 cm^{-1}.

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Registry No.—Trimethyloxonium tetrafluoroborate, 420-37-1; triethyloxonium tetrafluoroborate, 368-39-8; *cis*-9-decalincarboxylic acid, 3021-73-6; *trans*-9-decalincarboxylic acid, 2543-75-1; methyl *cis*-9-decalincarboxylate, 4630-78-8; methyl *trans*-9-decalincarboxylate, 55498-75-4; ethyl *cis*-9-decalincarboxylate, 61242-66-8; ethyl *trans*-9-decalincarboxylate, 61242-65-7; 9-decalyl cation, 23373-80-0; 2-hydroxybenzoic acid, 69-72-7; 4-hydroxybenzoic acid, 99-96-7; phthalic anhydride, 85-44-9; *endo-cis*-5-norbornene-2,3-dicarboxylic acid, 3853-88-1; allyl cyanide, 109-75-1; benzene, 71-43-2; succinic anhydride, 108-30-5.

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