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## Cleavage of Carboxylic Acid Esters to Acid Chlorides with Dichlorotriphenylphosphorane<sup>1</sup>

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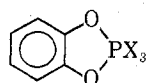
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The scope and mechanism of the cleavage of carboxylic acid esters RCOOR' to RCOCl and R'Cl with Ph<sub>3</sub>PCl<sub>2</sub> (2) was investigated. The reaction was rapid in refluxing CH<sub>3</sub>CN with the methyl esters of halogenated acids, such as CF<sub>3</sub>COOH, but was retarded considerably by steric hindrance in the alkoxy fragment. Esters of nonhalogenated acids were more effectively cleaved with Ph<sub>3</sub>PCl<sub>2</sub>+BF<sub>3</sub>Cl<sup>-</sup> (3). A mechanism involving initial nucleophilic cleavage of the alkyl-oxygen bond with Cl<sup>-</sup> is proposed for halogenated esters (CF<sub>3</sub>COOR), whereas an initial electrophilic attack by Ph<sub>3</sub>PCl<sup>+</sup> on the carbonyl oxygen is proposed for the cleavage of nonhalogenated esters (CH<sub>3</sub>COOR).

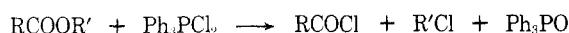
The direct conversion of an ester to an acid halide has the obvious advantage that the otherwise necessary steps of hydrolysis and isolation of the acid are obviated. An aqueous hydrolysis may indeed be precluded because of sensitivity of other functionalities in the molecule to water or acids and bases. A one-step regeneration of an active acid derivative from an ester, initially generated for the purpose of masking an acid halide or carboxyl group, would also be of value in a multistep synthesis.

Ester cleavage to an acid halide has previously been observed with reagents such as BCl<sub>3</sub>,<sup>2</sup> COCl<sub>2</sub>,<sup>3</sup> PCl<sub>5</sub>,<sup>4</sup> CHCl<sub>2</sub>OCH<sub>3</sub>,<sup>5</sup> and catechylphosphotrihalides<sup>6</sup> 1.



1, X = Br, Cl

We have observed ester cleavage with Ph<sub>3</sub>PCl<sub>2</sub> 2 and have investigated the scope and mechanism of this reaction.<sup>8</sup>



## Results and Discussion

**Scope.** Preliminary experiments showed that esters of halogenated acids were cleaved more readily than those of nonhalogenated acids. The cleavage of trifluoroacetic acid esters (CF<sub>3</sub>COOR) with Ph<sub>3</sub>PCl<sub>2</sub> or Ph<sub>3</sub>PBr<sub>2</sub> in refluxing CH<sub>3</sub>CN was very sensitive to the steric requirements of R; the methyl ester cleaved very rapidly (90% consumption after 2 hr of reflux) whereas secondary alkyl esters reacted sluggishly (cf. Table I). Cleavage was also suppressed by substitution of electron-withdrawing groups in R (Table II), a result not unexpected if in the cleavage process a nucleophilic attack by halide ion occurs at the alkoxy carbon.<sup>9</sup>

The effect of electron withdrawal in the acyl fragment of an ester is evident from the results presented in Table II. The successive substitution of the α hydrogens in the acyl portion of ethyl acetate with halogens results in an increasing susceptibility of the ester to cleavage. The lack of electron-withdrawing substituents in the acyl fragment necessitates the use of vigorous conditions to effect cleavage. Phthalide, for example, was only cleaved to the extent of 11% after 39-hr reflux with 2 in CH<sub>3</sub>CN. When the reaction

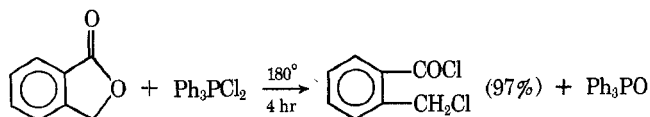
Table I  
Effect of Steric Hindrance in the Alkoxy Fragment

$$\text{CF}_3\text{COOR} + \text{Ph}_3\text{PX}_2 \xrightarrow[\text{reflux}]{\text{CH}_3\text{CN}} \text{CF}_3\text{COX} + \text{RX} + \text{Ph}_3\text{PO}$$

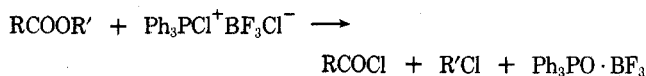
R	X	Reflux, hr	CF <sub>3</sub> COX, <sup>a</sup> %	RX, <sup>a</sup> %
CH <sub>3</sub> <sup>b</sup>	Cl	9	79	
<i>n</i> -C <sub>4</sub> H <sub>9</sub> <sup>c</sup>	Cl	72	78	68
<i>i</i> -C <sub>3</sub> H <sub>7</sub> <sup>d</sup>	Cl	97	16	17
CH <sub>3</sub> (C <sub>6</sub> H <sub>13</sub> )CH <sup>e</sup>	Cl	132	10 <sup>f</sup>	44
CH <sub>3</sub> <sup>g</sup>	Br	14	93	
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	Br	95		87
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	Br	95	11	11
CH <sub>3</sub> (C <sub>6</sub> H <sub>13</sub> )CH	Br	336	15 <sup>g</sup>	38

<sup>a</sup> Yields are based on the amount of ester initially present and were obtained by GLC analysis. The acid halide was determined as its derivative butyl ester or by titration of its aqueous hydrolysis products. <sup>b</sup> Registry no., 431-47-0. <sup>c</sup> Registry no., 367-64-6. <sup>d</sup> Registry no., 3974-99-0. <sup>e</sup> Registry no., 332-83-2. <sup>f</sup> The ratio of phosphorane to ester was 1.5:1.0 in this experiment. <sup>g</sup> The derivative ester (CF<sub>3</sub>COOBu-*n*) of the acid halide was subject to losses by evaporation during long reaction periods.

was repeated in the absence of solvent and at an elevated temperature, an almost quantitative conversion to acid chloride resulted.

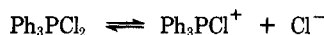


It was found that nonhalogenated esters were more effectively cleaved by a modification of 2 involving its complexation with a Lewis acid. When a heterogeneous solution of 2 in CH<sub>2</sub>Cl<sub>2</sub> was treated with BF<sub>3</sub>, a homogeneous solution resulted which gave a nearly quantitative yield of Ph<sub>3</sub>PCl<sup>+</sup>BF<sub>3</sub>Cl<sup>-</sup> 3 when the solvent and excess BF<sub>3</sub> were removed under vacuum. A comparison of the reactivities of 2 and 3 with those of a few nonhalogenated esters showed that 3 was a much more active cleavage agent<sup>10</sup> (Table III).



3 also displayed the advantage of being less reactive toward acid chlorides. Thus, when 2 was heated with ClCH<sub>2</sub>COCl in CH<sub>3</sub>CN for 4 hr at 150°, an 80% consumption of the acid chloride resulted. Under the same conditions, ClCH<sub>2</sub>COCl was recovered in 97% yield after being heated with 3.

**Mechanism. Halogenated Esters.** Experiments were carried out to ascertain the role of chloride ion in the cleavage of halogenated esters, since 2 is dissociated appreciably in organic solvents such as CH<sub>3</sub>CN.<sup>11</sup>



It was found that (*n*-Bu)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> was indeed a more effective cleavage agent than 2 with halogenated esters. When CF<sub>3</sub>COOBu-*n* was heated in separate ampoules with 2 and (*n*-Bu)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> in CH<sub>3</sub>CN at 150° for 3 hr, a 100% consumption of ester was obtained in the ammonium salt ampoule, while an 87% consumption was found in the phosphorane ampoule. These results suggest that an SN<sub>2</sub> displacement of carboxylate ion by chloride ion is occurring at the alkoxy carbon as a first step in the phosphorane cleavage of halogenated esters.

The carbonyl carbon offers an obvious alternate site of attack by Cl<sup>-</sup>.

Table II  
Effect of Electron Withdrawal in the Acyl and Alkoxy Fragments

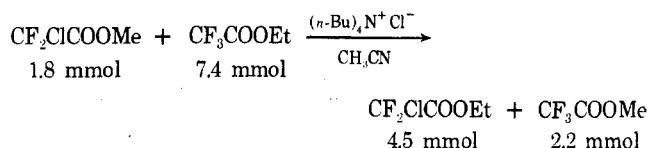
$$\text{RCOOR}' + \text{PhPCl}_2 \xrightarrow[\text{-Ph}_3\text{PO}]{\text{CH}_3\text{CN}} \text{RCOCl} + \text{R}'\text{Cl}$$

R	R'	Time, hr	Temp, °C	RCOCl, <sup>b</sup> %	R'Cl, <sup>b</sup> %
CH <sub>2</sub> Cl	CH <sub>2</sub> CH <sub>3</sub>	4	150	8.5	28
CHCl <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	4	150		70
CHF <sub>2</sub>	CH <sub>2</sub> CH <sub>3</sub>	4	150		58
CF <sub>3</sub>	CH <sub>2</sub> CH <sub>3</sub>	48	80	69	17 <sup>c</sup>
CF <sub>3</sub>	CH <sub>2</sub> CF <sub>3</sub>	48	80	12	14

<sup>a</sup> Registry numbers are, respectively, 105-39-5, 535-15-9, 454-31-9, 383-63-1, 407-38-5. <sup>b</sup> Yields are based on the amount of ester initially present and were obtained with NMR or GLC analysis by comparison to an internal standard. <sup>c</sup> The volatile EtCl was at times inefficiently trapped in systems at atmospheric pressure, as opposed to ampoule reactions where the measurement of EtCl is considered to be quite reliable.



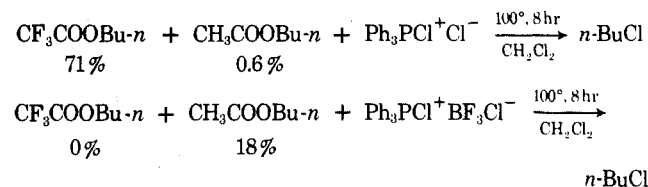
Evidence for this type of reaction was obtained when extensive transesterification was observed between CF<sub>3</sub>COOEt (10.0 mmol) and CF<sub>2</sub>ClCOOMe (10.0 mmol) after 1.5 hr of reflux in CH<sub>3</sub>CN in the presence of (*n*-Bu)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>. GLC analysis indicated the following solution composition.<sup>12</sup>



The silyl ether, Me<sub>3</sub>SiOEt, was detected in solution when CF<sub>2</sub>ClCOOEt was heated in CH<sub>2</sub>Cl<sub>2</sub> with (*n*-Bu)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> and Me<sub>3</sub>SiCl.

**Nonhalogenated Esters.** In the case of nonhalogenated esters (*n*-Bu)<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> was found to be unreactive under conditions where cleavage was obtained with 2. The nonhalogenated esters also exhibited markedly different behavior with 2 and 3 as compared to the halogenated esters. When equal amounts of each type of ester were heated with 2 in CH<sub>2</sub>Cl<sub>2</sub>, the halogenated ester was consumed almost exclusively, whereas the opposite result was obtained with 3.

The cleavage behavior of nonhalogenated esters was further compared to that of halogenated esters with respect to steric effects. Equimolar amounts of the ethyl and butyl esters of acetic acid and of 2 were heated in CH<sub>2</sub>Cl<sub>2</sub> in an ampoule. Measurement of the amounts of unreacted esters after ca. 35% reaction showed the relative reactivity of the ethyl to butyl ester to be 0.92. In a similar experiment with the ethyl and butyl esters of chlorodifluoroacetic acid competing for 2, a reactivity ratio of 1.24 (Et/Bu) was found.

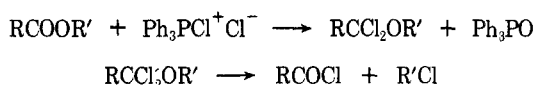


In further investigation of the mechanism of nonhalogenated ester cleavage, the possible intermediacy of an α,α-dichloro ether was considered.

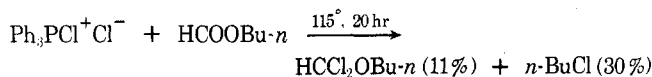
Table III  
Cleavage of Esters with  $\text{Ph}_3\text{PCl}_2$  and with  $\text{Ph}_3\text{PCl}^+\text{BF}_3\text{Cl}^-$

Ester	Reagent	Time, hr	Temp, °C	Ester consumed, % <sup>a</sup>	Acid chloride, % <sup>b</sup>	Ethyl chloride, % <sup>c</sup>
( <i>E</i> )-PhCH=CHCOOEt <sup>d</sup>	$\text{Ph}_3\text{PCl}_2$	8	150	77	69	20
( <i>E</i> )-PhCH=CHCOOEt	$\text{Ph}_3\text{PCl}^+\text{BF}_3\text{Cl}^-$	0.8	150	90	77	78
( <i>E</i> )-PhC(CF <sub>3</sub> )=CHCOOEt <sup>e</sup>	$\text{Ph}_3\text{PCl}_2$	12	180	73	42	75
( <i>E</i> )-PhC(CF <sub>3</sub> )=CHCOOEt	$\text{Ph}_3\text{PCl}^+\text{BF}_3\text{Cl}^-$	5	150	~100	97 <sup>f</sup>	54
( <i>E</i> )-PhC(CF <sub>3</sub> )=CHCOOEt	$\text{Ph}_3\text{PCl}^+\text{BF}_3\text{Cl}^-$	1.5	150	89	92	67

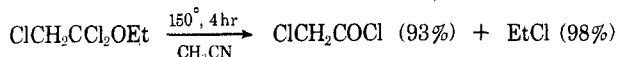
<sup>a</sup> The measurements of the amounts of acid chloride and ester were made by NMR analysis, following their removal from the reaction flask by distillation. <sup>b</sup> No isomerization of the double bond was noted. <sup>c</sup> The efficiency of trapping the volatile EtCl (bp 12°) was variable. <sup>d</sup> Registry no., 4192-77-2. <sup>e</sup> Registry no., 56210-74-3. <sup>f</sup> The *Z* acid chloride was formed in ca. 3% yield.



This replacement of the carbonyl oxygen with two chlorine atoms was observed by Gross in the reaction of 1 (X = Cl) with alkyl formates.<sup>13</sup> This type of reaction occurred with 2 and HCOOBu-*n*.

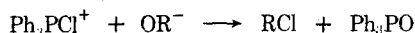
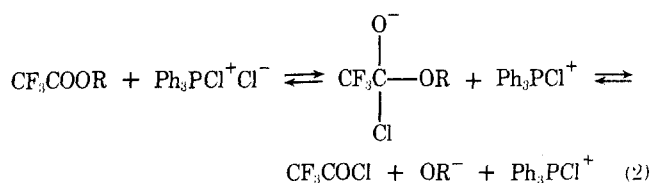
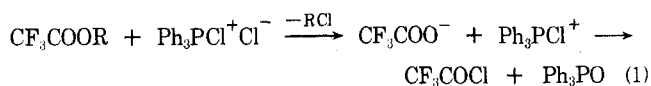


In an attempt to extend evidence of ether formation to acetate esters, it was found that ClCH<sub>2</sub>CCl<sub>2</sub>OEt could not be detected in the cleavage of ClCH<sub>2</sub>COOEt with 2 under a variety of reaction conditions. It was demonstrated that the α,α-dichloro ether expected from ClCH<sub>2</sub>COOEt would decompose to yield acid chloride in high yield.



**Modes of Cleavage.** The results obtained from the mechanistic experiments suggest that different modes of cleavage are operative for halogenated (CF<sub>3</sub>COOR) and nonhalogenated (CH<sub>3</sub>COOR) esters. In the case of halogenated esters a mechanism involving an initial nucleophilic attack on the ester seems most reasonable (Scheme I),

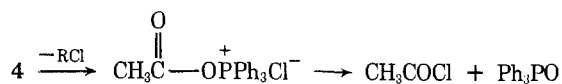
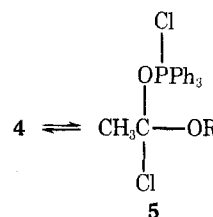
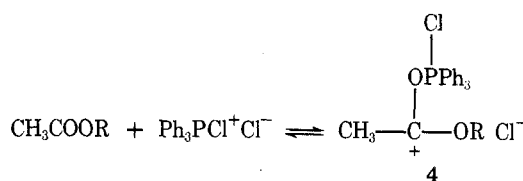
#### Scheme I Halogenated Esters



whereas in the case of nonhalogenated esters an initial electrophilic attack appears most consistent with the data (Scheme II).

An initial BAL<sup>2</sup><sup>14</sup> cleavage with chloride ion seems to be the main pathway toward acid chloride formation in the case of halogenated esters. This mode of cleavage would be consistent with the steric sensitivity observed for these reactions. The formation of a carboxylate anion is also consistent with an instance of decarboxylation observed with a

#### Scheme II Nonhalogenated Esters

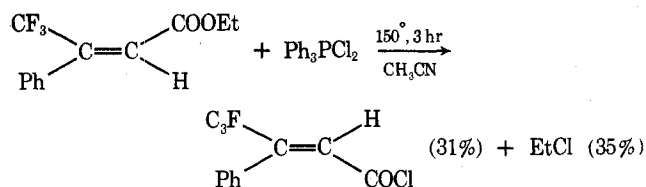


halogenated ester. Reaction of 2 with CCl<sub>3</sub>COOCH<sub>3</sub> for 0.8 hr at 150° resulted in a 23% yield of CO<sub>2</sub>.

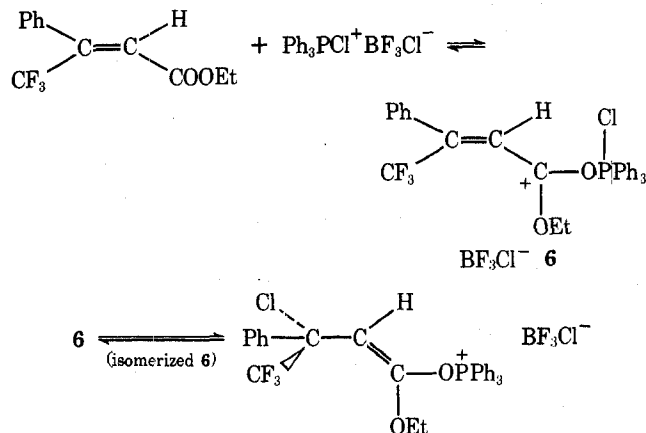
The equilibrium exchange of chloride and alkoxide at the carbonyl carbon (mechanism 2) is considered as a possible cleavage mechanism based on the extensive Cl<sup>-</sup>-catalyzed transesterification observed between CF<sub>3</sub>COOEt and CF<sub>2</sub>ClCOOMe. This type of reaction has rarely been documented in the literature. Halide ions are normally considered insufficiently nucleophilic to attack the carbonyl carbon of esters,<sup>15</sup> and this type of equilibrium would be expected to lie far to the left. Even a small production of alkoxide ions by this equilibrium would be sufficient, however, to cause efficient transesterification because these ions are regenerated in the transesterification reaction. In the phosphorane ester cleavage reactions a slow exchange of Cl<sup>-</sup> for OR<sup>-</sup> would be insufficient to achieve an appreciable rate of cleavage, since a chain reaction would not be operative. The exchange mechanism is thus considered to be a minor pathway of halogenated ester cleavage.

Cleavage of nonhalogenated esters with 2 is proposed to proceed by an initial electrophilic attack by Ph<sub>3</sub>PCl<sup>+</sup> at the carbonyl oxygen to give species 4. Consistent with this observation is the fact that the reactivity of 2 is increased by complexing it with a Lewis acid (BF<sub>3</sub>), presumably because the availability of the Ph<sub>3</sub>PCl<sup>+</sup> cation is thereby increased. A comparison of the results obtained from the cleavage of (*Z*)-CF<sub>3</sub>PhC=CHCOOEt with 2 and 3 gives support to this mechanism. Reagent 2 produced only isomerized acid chloride, and 14% of the unreacted ester was isomerized to the

*E* isomer. Reagent 3 similarly produced only isomerized acid chloride, but the isomerization of unreacted ester in-



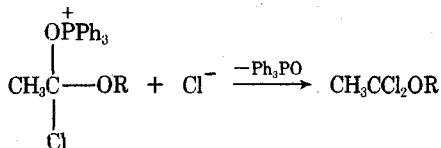
creased to 85%. The extensive isomerization of the unreacted ester with 3 is suggested to occur via the ion pair formed from the ester and the phosphonium cation.<sup>16</sup> The fact that



less isomerization of unreacted ester is observed with 2 is in agreement with the lower concentration of an ion pair of type 6 expected for this less electrophilic reagent. Production of only the *E* isomer of the acid chloride from the reaction of *Z* ester with 2 or 3 is apparently due to the isomerization of cation 6 being faster than its decomposition to acid chloride and ethyl chloride.

An electrophilic attack on the carbonyl oxygen by a phosphonium cation was also proposed by Green and Thorp in the cleavage of esters with  $\text{PCl}_5$ .<sup>17</sup> They found that esters labeled with oxygen-18 in the alkoxy fragment gave acid chlorides containing labeled oxygen.

The equilibration of 4 and 5 may be nonproductive, or it may lead to cleavage products by ionization of the P-Cl bond in 5 with subsequent formation of an  $\alpha,\alpha$ -dichloro ether.



The question of the possible intermediacy of  $\alpha,\alpha$ -dichloro ethers has not been resolved by the results of this work. It is possible that formate esters are unique in the formation of these ethers,<sup>18</sup> or it is possible that the ethers are formed in the phosphorane cleavage of other esters but the conditions necessary for their formation result in their immediate decomposition to acid chloride and alkyl chloride.

### Summary

The data obtained in this study of the cleavage of carboxylic esters with 2 show that this reaction proceeds most readily when the ester contains electron-withdrawing substituents on the  $\alpha$  carbon of the acyl fragment, whereas the presence of these groups on the  $\beta$  carbon of the alkoxy frag-

ment retards cleavage. The effect of steric hindrance in the alkoxy fragment of the esters of halogenated acids is significant; secondary alkyl esters cleave very slowly. The esters of nonhalogenated acids are most effectively cleaved with 3. The cleavage of both types of esters is favored by the use of polar solvents such as  $\text{CH}_3\text{CN}$  or  $\text{PhCN}$ .

The mechanism of cleavage is dependent on the effects of electron withdrawal in the acyl fragment of the ester. Esters derived from halogenated acids appear to cleave by an initial nucleophilic displacement of carboxylate by halide ion. In the absence of these electron-withdrawing substituents, an initial electrophilic attack by  $\text{Ph}_3\text{PCl}^+$  occurs at the carbonyl oxygen to form a species which then is converted to cleavage products by reaction with halide ion.

### Experimental Section<sup>19</sup>

**Materials.**  $\text{Ph}_3\text{P}$  was obtained from Cincinnati Milacron. Unless otherwise indicated, the esters used in this work were either prepared by standard procedures from the acid and alcohol or were obtained from commercial sources and distilled before use.  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$  (Eastman) was dried at  $50^\circ$  in vacuo.  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{CN}$  were dried by distillation from  $\text{P}_2\text{O}_5$  and stored over molecular sieves.

**Procedures.** Reactions which involved the use of moisture-sensitive materials such as dihalophosphoranes,  $\alpha,\alpha$ -dichloro ethers, hygroscopic salts, etc., were carried out under a  $\text{N}_2$  atmosphere. The reaction apparatus was oven dried, assembled while hot, and flushed with  $\text{N}_2$  prior to introduction of the solvent and reagents. The dry solvents were transferred by syringe or pipet, and the reagents were handled by syringe or were transferred in a  $\text{N}_2$ -filled glovebag.

**Phosphorane Reagents.**  $\text{Ph}_3\text{PCl}_2$  (2) or  $\text{Ph}_3\text{PBr}_2$  were prepared by adding an equimolar amount of the halogen to a solution of the phosphine in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  at  $0^\circ$ . The solvent was then removed under reduced pressure if the reaction was to be carried out neat. Stock solutions of 2 were prepared in  $\text{CH}_3\text{CN}$  or  $\text{CH}_2\text{Cl}_2$  in concentrations of ca. 0.8 and 0.4 M, respectively.<sup>20,21</sup> The solutions were conveniently dispensed by syringe and assayed for phosphorane content by base titration of the HCl released upon hydrolysis of aliquots of the solutions in  $\text{H}_2\text{O}$ . Solutions of 2 in  $\text{CH}_3\text{CN}$  (0.758 M) and  $\text{CH}_2\text{Cl}_2$  (0.423 M) exhibited single absorptions at  $-47.4$  and  $-57.4$  ppm, respectively, in their phosphorus NMR spectra.

**$\text{Ph}_3\text{PCl}^+\text{BF}_3\text{Cl}^-$  (3).**  $\text{BF}_3$  (16.5 g, 0.244 mol) was bubbled into a magnetically stirred slurry of 0.210 mol of 2 in 100 ml of  $\text{CH}_2\text{Cl}_2$  while a positive pressure of  $\text{N}_2$  was maintained in the system by means of a bubbler. The solution became homogeneous after the addition of 12.9 g of  $\text{BF}_3$ . With the further addition of 3.6 g of  $\text{BF}_3$ , fumes appeared at the bubbler and the addition was stopped. The flask was heated and the solvent and excess  $\text{BF}_3$  were removed under reduced pressure (maximum bath temperature of  $90^\circ$ , minimum pressure of 7 mm) to give 84.4 g (97%) of 3, mp  $89.4$ – $91.0^\circ$ .

A  $^{31}\text{P}$  NMR of a 1.15 M solution<sup>22</sup> of 3 in  $\text{CH}_2\text{Cl}_2$  showed one absorption only, at  $-59.7$  ppm. The  $^{19}\text{F}$  NMR showed absorptions at  $\phi^* 105$  (q,  $J_{\text{B-F}} = 51$  Hz), 126 (broad peak), 144 (s), and 151 ppm (broad peak). At  $-30^\circ$  the peak at 126 ppm became a quartet with  $J_{\text{B-F}} = 24$  Hz, and the broad peak at 151 ppm sharpened markedly. The peaks at 105, 126, and 151 ppm correspond to the  $\text{BF}_2\text{Cl}_2^-$ ,  $\text{BF}_3\text{Cl}^-$ , and  $\text{BF}_4^-$  absorptions expected for a mixture resulting from disproportionation of the  $\text{BF}_3\text{Cl}^-$  ion in solution.<sup>23</sup> The absorption at 144 ppm (small area) is due to  $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ , apparently resulting from exposure of 3 to traces of moisture.<sup>24</sup>

**$\text{PhCF}_3\text{C}=\text{CHCOOEt}$ .**<sup>25</sup> Trifluoroacetophenone<sup>26</sup> (43.5 g, 0.250 mol) was added dropwise (0.3 hr) to a refluxing solution (mechanically stirred) of 87.0 g (0.250 mol) of  $\text{Ph}_3\text{P}=\text{CHCOOEt}$ <sup>27</sup> in 300 ml of dry benzene under a  $\text{N}_2$  atmosphere. The solution was refluxed overnight. The resultant heterogeneous solution was subjected to reduced pressure (aspirator) on a rotary evaporator. The residual slurry was suction filtered, and the white solid was washed with hexane to give 59.6 g (86%) of  $\text{Ph}_3\text{PO}$  (mp  $158$ – $158.5^\circ$ , lit.<sup>28</sup> mp  $156.5$ – $157.0^\circ$ ). The solution of combined filtrates was distilled through an 11-cm Vigreux column to give two fractions of  $\text{PhCF}_3\text{C}=\text{CHCOOEt}$ : (1) 45.4 g (bp  $88$ – $92^\circ$ , 27 mm) of 96.4% *E* and 3.6% *Z*; (2) 4.8 g (bp  $92$ – $100^\circ$ , 27 mm) of 41.0% *E* and 59.0% *Z*, for total yields of 75% *E* and 7% *Z*. The pure isomers were obtained by a spinning band distillation (63-cm Nester-Faust column) at 18 mm.

The pure *E* isomer had the following properties:  $n_D^{20}$  1.4646; micro bp 220° (747 mm); ir (film) 1715 (C=O) and 1645  $\text{cm}^{-1}$  (C=C);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  7.30 (m, 5,  $\text{C}_6\text{H}_5$ ), 6.54 (q, 1,  $J_{\text{CF}_3, \text{H}} = 1.33$  Hz, vinyl H), 3.94 (q, 2,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ ), and 1.00 ppm (t, 3,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{19}\text{F}$  NMR ( $\text{CCl}_4$ )  $\phi^*$  68.02 ppm (d,  $J_{\text{CF}_3, \text{H}} = 1.29$  Hz,  $\text{CF}_3$ ); uv max (95% EtOH) 244 nm ( $\epsilon$  3160).

Anal. Calcd for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_2$ : C, 59.01; H, 4.54. Found: C, 59.26; H, 4.92.

Isomer *Z* contained 2.5% isomer *E* by GLC analysis and had the following properties:  $n_D^{20}$  1.4769; micro bp 243.5° (740 mm); ir (film) 1736 (C=O) and 1650  $\text{cm}^{-1}$  (C=C);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  7.35 (m, 5,  $\text{C}_6\text{H}_5$ ), 6.24 (s, 1, vinyl H), 4.22 (q, 2,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ ), and 1.31 ppm (t, 3,  $J = 7.2$  Hz,  $\text{CH}_2\text{CH}_3$ );  $^{19}\text{F}$  NMR ( $\text{CCl}_4$ )  $\phi^*$  60.82 ppm (s,  $\text{CF}_3$ ); uv max (95% EtOH) 247 nm ( $\epsilon$  7540).

Anal. Calcd for  $\text{C}_{12}\text{H}_{11}\text{F}_3\text{O}_2$ : C, 59.01; H, 4.54. Found: C, 59.26; H, 4.82.

**Cleavage of  $\text{CF}_3\text{COOR}$  in Refluxing  $\text{CH}_3\text{CN}$ .** The cleavage of  $\text{CF}_3\text{COOMe}$  will be described as an example of the procedure used for trifluoroacetate esters.

A homogeneous solution of 9.66 g (75.4 mmol) of  $\text{CF}_3\text{COOMe}$  and 75.4 mmol of **2** in 100 ml of  $\text{CH}_3\text{CN}$  was prepared under  $\text{N}_2$  in a flask equipped with a magnetic stirring bar, septum-covered inlet, and reflux condenser. The volatile  $\text{CF}_3\text{COCl}$  generated during the reaction was carried by a slow flow of  $\text{N}_2$ , passing through a glass "T" set atop the condenser, into a gas bubbling apparatus containing 100 ml of  $\text{H}_2\text{O}^{29}$  followed by a cold trap. Rapid bubbling ensued in the water trap as the reaction solution was brought to reflux temperature. GLC analysis indicated that the reaction was 90% complete after 2 hr of reflux. After 9 hr of reflux 98% of the ester was consumed. The solution was diluted to 250 ml. Hydrolysis of a 25-ml aliquot of this solution in a mixture of 130 ml of  $\text{H}_2\text{O}$  and 100 ml of benzene, followed by the addition of excess  $\text{AgNO}_3$  to the aqueous layer, gave 0.20 g ( $\pm 0.00$ ) of  $\text{AgCl}$  for two trials, indicating a 91% consumption of **2**. Titration of the water trap for  $\text{CF}_3\text{COOH}$  and  $\text{HCl}$  with standardized base indicated that a 79% yield of  $\text{CF}_3\text{COCl}$  was obtained.

The same procedure was used in the reactions with  $\text{Ph}_3\text{PBr}_2$  in place of **2**. The dibromophosphorane is less soluble than **2** in  $\text{CH}_3\text{CN}$ , however, and its reactions were performed in heterogeneous solution.

**$\text{ClCH}_2\text{COOEt}$  and **2**.** A 5-ml ampoule containing 0.2497 g (2.04 mmol) of  $\text{ClCH}_2\text{COOEt}$  and 2.8 ml (2.1 mmol) of 0.758 *M* solution of **2** in  $\text{CH}_3\text{CN}$  was sealed and heated in a 150° oil bath for 4 hr. An internal standard ( $\text{HCCl}_2\text{CCl}_2\text{H}$ ) was added, and the solution was analyzed by NMR to reveal a 36% consumption of ester together with an 8.5% yield of  $\text{ClCH}_2\text{COCl}$  and a 28% yield of  $\text{EtCl}$ .

The  $\text{HCCl}_2\text{COOEt}$  and  $\text{CF}_2\text{HCOOEt}$  cleavage reactions (Table II) were carried out in the same manner.

**Phthalide and **2**.** A flask containing 105 mmol of **2** and 13.4 g (100 mmol) of phthalide was heated in a 180° oil bath for 4 hr. The contents of the flask formed a homogeneous, black solution which was magnetically stirred. Analysis of two aliquots of a  $\text{CH}_3\text{CN}$  solution (100 ml) of the flask contents with NMR by comparison to an internal standard (dioxane) indicated a 97.4% ( $\pm 1.8$ ) yield of *o*-chloromethylbenzoyl chloride<sup>30</sup> and a 11.1% ( $\pm 0.8$ ) recovery of phthalide.

A sample of the acid chloride was obtained by distillation and had the following properties: ir (film) 1770  $\text{cm}^{-1}$  (C=O); NMR ( $\text{CCl}_4$ )  $\delta$  8.4–7.3 (m, 4,  $\text{C}_6\text{H}_4$ ) and 4.85 ppm (s, 2,  $\text{CH}_2\text{Cl}$ ); mass spectrum (70 eV) *m/e* (rel intensity) 188 (28,  $\text{M}^+$ ), 153 (100), 125 (76), 118 (36), and 105 (70).

**(*E*)- $\text{PhCF}_3\text{C}=\text{CHCOOEt}$  and **2**.** A flask containing 60.0 mmol of **2** was charged with 11.8 g (48.4 mmol) of (*E*)- $\text{PhCF}_3\text{C}=\text{CHCOOEt}$  and heated in an oil at 180° for 12 hr. These reagents were slow to form a homogeneous melt. At the end of the heating period there were still small particles of solid present in the black solution. Volatile materials were removed from the flask under reduced pressure (maximum bath temperature of 195°, minimum pressure of 0.25 mm) and collected in a Dry Ice cooled receiver to give 9.4 g of a pale-green distillate. A vapor trap attached to the flask during the heating period contained 2.3 g (75%) of  $\text{EtCl}$ .

A 10% solution of the distillate in  $\text{CCl}_4$  showed the vinyl hydrogen quartets at  $\delta$  6.79 and 6.54 expected for the *E* acid chloride and *E* ester, respectively. The downfield quartet disappeared with the addition of  $\text{EtOH}$ , while the intensity of the upfield quartet increased. The  $^{19}\text{F}$  spectrum showed the  $\text{CF}_3$  group of the acid chloride as a doublet ( $J_{\text{H}, \text{CF}_3} = 1.4$  Hz) which was slightly upfield of, but overlapping with, the  $\text{CF}_3$  doublet ( $J_{\text{H}, \text{CF}_3} = 1.3$  Hz) of the ester. These overlapping absorptions were centered at  $\phi^* 68$ . The distillate composition as indicated by the proton spectrum was 1.5

g of  $\text{CH}_2\text{Cl}_2$ ,<sup>31</sup> 3.2 g of unreacted ester (27% recovery), and 4.7 g (42%) of (*E*)- $\text{PhCF}_3\text{C}=\text{CHCOCl}$ .

**(*E*)- $\text{PhHC}=\text{CHCOOEt}$  and **3**.** A flask containing 56.0 mmol of **3** and 9.0 g (51.1 mmol) of (*E*)- $\text{PhHC}=\text{CHCOOEt}$  was heated in a 150° oil bath for 0.8 hr. The flask contents formed a homogeneous solution which frothed during the first 0.3 hr, while condensate collected rapidly in a vapor trap attached to the flask. The solution became black and viscous, and the bubbling ceased during the last 0.3 hr. The material in the flask cooled to a red solid which was broken up in 20 ml of dry  $\text{Et}_2\text{O}$ . The resultant mixture was pressure filtered with  $\text{N}_2$  through a sintered glass funnel. The solid was washed with three 10-ml portions of  $\text{Et}_2\text{O}$ , and the filtrates (red solution) were combined. The air-dried, white solid (mp 213–229°) weighed 19.3 g, representing a 100% yield of crude  $\text{Ph}_3\text{PO}\cdot\text{BF}_3$ . A sample was recrystallized from  $\text{CHCl}_3$  to give material with mp 235–239° (lit.<sup>32</sup> mp 239°). The  $\text{Et}_2\text{O}$  was removed from the combined filtrates, and the residue was distilled at reduced pressure (maximum bath temperature of 120°, minimum pressure of 0.25 mm) to give 7.5 g of a clear distillate and 0.2 g of solid residue. The vapor trap contained 2.6 g (78%) of  $\text{EtCl}$  and 0.5 g of  $\text{CH}_2\text{Cl}_2$ .<sup>33</sup>

Analysis of a sample of the distillate dissolved in  $\text{CCl}_4$  by NMR showed the vinyl hydrogen absorptions of unreacted ester and of acid chloride. The vinyl hydrogen doublets of the acid chloride appeared at  $\delta$  7.70 ( $J = 15.6$  Hz) and 6.51 ( $J = 15.4$  Hz). Addition of  $\text{EtOH}$  resulted in the disappearance of these doublets together with a corresponding increase in the absorptions of the ester. Three aliquots were withdrawn from the distillate and an internal standard (dioxane) was added to each. Analysis of these samples by NMR showed a 9.6% ( $\pm 1.8$ ) recovery of ester and a 77.0% ( $\pm 3.4$ ) yield of (*E*)- $\text{PhHC}=\text{CHCOCl}$ .

The reactions of (*E*)- $\text{PhHC}=\text{CHCOOEt}$  with **2** and (*E*)- $\text{PhCF}_3\text{C}=\text{CHCOOEt}$  with **3** were carried out as described for the above two experiments (Table III).

**$\text{ClCH}_2\text{COCl}$  and **2**.** A 5-ml ampoule was charged with 0.2202 g (1.95 mmol) of  $\text{ClCH}_2\text{COCl}$  and 2.8 ml (2.1 mmol) of a 0.758 *M* solution of **2** in  $\text{CH}_3\text{CN}$ . The ampoule was sealed and heated in a 150° oil bath for 4 hr. The black solution was analyzed with NMR by comparison to an internal standard ( $\text{HCCl}_2\text{CCl}_2\text{H}$ ) to reveal an 80% consumption of  $\text{ClCH}_2\text{COCl}$ .

In a similar experiment with  $\text{ClCH}_2\text{COCl}$  and **3**, the acid chloride was recovered in 97% yield.

**$\text{CF}_3\text{COOBu-}n$  and **2**.** A 5-ml ampoule containing 0.3473 g (2.04 mmol) of  $\text{CF}_3\text{COOBu-}n$  and 2.8 ml (2.1 mmol) of a 0.758 *M* solution of **2** in  $\text{CH}_3\text{CN}$  was sealed and heated in a 150° oil bath for 3 hr. The dark-brown solution was analyzed by GLC with the use of an internal standard (benzene) to reveal an 87% consumption of ester and an 87% yield of *n*- $\text{BuCl}$ .

**$\text{CF}_3\text{COOBu-}n$  and (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$ .** A 5-ml ampoule containing 0.5664 g (2.04 mmol) of (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$ , 0.3264 g (1.92 mmol) of  $\text{CF}_3\text{COOBu-}n$ , and 2.8 ml of  $\text{CH}_3\text{CN}$  was sealed and heated in a 150° oil bath for 3 hr. The dark-brown solution effervesced when the ampoule was opened, indicating that some decarboxylation had occurred. Analysis by GLC showed no trace of unreacted ester.<sup>34</sup>

**$\text{CF}_2\text{ClCOOEt}$ ,  $\text{CF}_2\text{ClCOOBu-}n$ , and **2**.** A 10-ml ampoule containing 0.4881 g (2.62) mmol of  $\text{CF}_2\text{ClCOOBu-}n$ , 0.4145 g (2.62 mmol) of  $\text{CF}_2\text{ClCOOEt}$ , 0.1740 g of cyclohexane (internal standard), and 6.4 ml (2.71 mmol) of a 0.423 *M* solution of **2** in  $\text{CH}_2\text{Cl}_2$  was sealed and heated in a 100° oil bath for 4 hr. The colorless solution was analyzed by GLC<sup>35</sup> to reveal a 63.0% ( $\pm 0.0$ ) consumption of the ethyl ester and a 51.0% ( $\pm 0.6$ ) consumption of the butyl ester, for a consumption ratio ( $\text{Et}/\text{Bu}$ ) of 1.24 ( $\pm 0.02$ ).

**$\text{CF}_2\text{ClCOOMe}$ ,  $\text{CF}_3\text{COOEt}$ , and (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$ .** A 30-ml, one-necked flask equipped with a septum inlet was charged with 1.202 g (4.32 mmol) of (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$  under  $\text{N}_2$  (glovebag) and fitted with a reflux condenser, which was connected to a vapor trap. A solution which contained 1.455 g (10.0 mmol) of  $\text{CF}_2\text{ClCOOMe}$ , 1.422 g (10.0 mmol) of  $\text{CF}_3\text{COOEt}$ , 0.7655 g of *n*-hexane (internal standard), and 10 ml of  $\text{CH}_3\text{CN}$  was syringed into the flask. The flask was heated in a 85° oil bath for 6 hr. Analysis by GLC after 1.5 hr showed (mmol)  $\text{CF}_3\text{COOMe}$  (2.2),  $\text{CF}_3\text{COOEt}$  (7.4),  $\text{CF}_2\text{ClCOOMe}$  (1.8), and  $\text{CF}_2\text{ClCOOEt}$  (4.5). At the conclusion of the 6-hr reflux period the flask and condenser walls were washed down with solvent to correct for possible errors in analysis caused by fractionation of the solution components. The resultant solution showed only traces of the methyl esters together with  $\text{CF}_3\text{COOEt}$  (6.2 mmol) and  $\text{CF}_2\text{ClCOOEt}$  (3.8 mmol). The vapor trap contained 0.5 g (99%)<sup>36</sup> of  $\text{CH}_3\text{Cl}$ .

**$\text{CF}_2\text{ClCOOEt}$ , (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$ , and  $\text{Me}_3\text{SiCl}$ .** A 10-ml ampoule containing 0.6174 g (2.22 mmol) of (*n*- $\text{Bu}$ ) $_4\text{N}^+\text{Cl}^-$ , 0.3431 g (2.16

mmol) of  $\text{CF}_2\text{ClCOOEt}$ , 0.3324 g (3.06 mmol) of  $\text{Me}_3\text{SiCl}$ , and 5 ml of  $\text{CH}_2\text{Cl}_2$  was sealed and heated in an  $80^\circ$  oil bath for 3.5 hr. An internal standard (toluene) was added and the solution was analyzed by GLC to reveal 1.92 mmol (89% recovery) of  $\text{CF}_2\text{ClCOOEt}$  and 0.10 mmol (5% yield) of  $\text{Me}_3\text{SiOEt}$ .

**$\text{CF}_3\text{COOBu-n}$ ,  $\text{CH}_3\text{COOBu-n}$ , and 2.** A 10-ml ampoule containing 0.3058 g (2.63 mmol) of  $\text{CH}_3\text{COOBu-n}$ , 0.4478 g (2.63 mmol) of  $\text{CF}_3\text{COOBu-n}$ , and 6.4 ml (2.71 mmol) of a 0.423 M solution of 2 in  $\text{CH}_2\text{Cl}_2$  was sealed and heated in a  $100^\circ$  oil bath for 8 hr. GLC analysis (toluene internal standard) showed a 71% consumption of  $\text{CF}_3\text{COOBu-n}$  and a 0.6% consumption of  $\text{CH}_3\text{COOBu-n}$ .

**$\text{CF}_3\text{COOBu-n}$ ,  $\text{CH}_3\text{COOBu-n}$ , and 3.** A 10-ml ampoule containing 0.3022 g (2.60 mmol) of  $\text{CH}_3\text{COOBu-n}$ , 0.4434 (2.61 mmol) of  $\text{CF}_3\text{COOBu-n}$ , 4.0 ml of  $\text{CH}_2\text{Cl}_2$ , and 2.3 ml (2.64 mmol) of a 1.15 M solution of 3 in  $\text{CH}_2\text{Cl}_2$  was sealed and heated in a  $100^\circ$  oil bath for 8 hr. GLC analysis (toluene internal standard) showed a 0% consumption of  $\text{CF}_3\text{COOBu-n}$  and an 18% consumption of  $\text{CH}_3\text{COOBu-n}$ .

**$\text{CH}_3\text{COOEt}$ ,  $\text{CH}_3\text{COOBu-n}$ , and 2.** A 10-ml ampoule containing 0.2344 g (2.66 mmol) of  $\text{CH}_3\text{COOEt}$ , 0.3044 g (2.62 mmol) of  $\text{CH}_3\text{COOBu-n}$ , and 6.4 ml (2.71 mmol) of a 0.423 M solution of 2 in  $\text{CH}_2\text{Cl}_2$  was sealed and heated in a  $120^\circ$  oil bath for 40 hr. GLC analysis<sup>32</sup> (cyclohexane internal standard) showed a 34.8% ( $\pm 0.2$ ) consumption of the ethyl ester and a 37.6 ( $\pm 1.0$ ) consumption of the butyl ester, for a consumption ratio (Et/Bu) of 0.92 ( $\pm 0.02$ ).

**$\text{CH}_3\text{COOEt}$ ,  $\text{CH}_3\text{COOBu-n}$ , and  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ .** A 10-ml ampoule containing 0.2326 g (2.65 mmol) of  $\text{CH}_3\text{COOEt}$ , 0.3040 g (2.62 mmol) of  $\text{CH}_3\text{COOBu-n}$ , 0.7685 g (2.76 mmol) of  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ , and 6.4 ml of  $\text{CH}_2\text{Cl}_2$  was sealed and heated in a  $100^\circ$  oil bath for 30 hr. GLC analysis (toluene internal standard) showed a 98.5% recovery of the butyl ester and a 105% recovery of the ethyl ester.<sup>37</sup> There was no EtCl detected by GLC.

In comparison to the above results, 2 cleaved the same mixture of esters to the extent of ca. 10% for each ester under the same conditions.

**$\text{HCOOBu-n}$  and 2.** A heterogeneous mixture of 105 mmol of 2 and 10.2 g (100 mmol) of  $\text{HCOOBu-n}$  was magnetically stirred and heated in a  $115^\circ$  oil bath for 20 hr. The volatile materials were removed from the flask under reduced pressure (maximum bath temperature of  $125^\circ$ , minimum pressure of 0.5 mm) and collected in a Dry Ice cooled receiver to give 16.7 g of distillate. The presence of  $\text{HCCl}_2\text{OBu-n}$  was indicated by the fact that spiking of the distillate with an authentic sample<sup>38</sup> resulted in enhancement of the singlet at  $\delta$  7.35 ( $\text{CCl}_2\text{H}$ ) and triplet at  $\delta$  3.94 ( $-\text{OCH}_2\text{Pr}$ ). The addition of water to the distillate resulted in the disappearance of these signals and enhancement of the ester absorptions, as expected for hydrolysis of the dichloro ether to the corresponding ester. The mole percent composition of the distillate, obtained from its NMR spectrum, showed that  $n\text{-BuCl}$  and  $\text{HCCl}_2\text{OBu-n}$  were produced in 30 and 11% yields, respectively. A 66% recovery of  $\text{HCOOBu-n}$  was also indicated.

**$\text{ClCH}_2\text{COOEt}$  and 2.** Equimolar amounts of  $\text{ClCH}_2\text{COOEt}$  and 2 (0.758 M solution) were heated together in  $\text{CH}_3\text{CN}$  at  $80^\circ$  for 4.5 hr and 4 days, and at  $150^\circ$  for 4 hr in an attempt to detect the presence of  $\text{ClCH}_2\text{CCl}_2\text{OEt}$  in the cleavage of this ester. Spiking of these solutions with an authentic sample<sup>39</sup> of the ether demonstrated that it could be detected in low concentration by NMR analysis. The ester and 2 were also heated together neat at  $110^\circ$  for 30 hr. None of these attempts were successful in detecting any trace of the  $\alpha,\alpha$ -dichloro ether.

**$\text{ClCH}_2\text{CCl}_2\text{OEt}$  and Heat.** A solution of 0.3470 g (1.96 mmol) of  $\text{ClCH}_2\text{CCl}_2\text{OEt}$  in 2.8 ml of  $\text{CH}_3\text{CN}$  was heated in a sealed, 5-ml ampoule at  $150^\circ$  for 4 hr. Analysis of the black solution by NMR, following the addition of an internal standard ( $\text{HCCl}_2\text{CCl}_2\text{H}$ ), showed a 96% consumption of the ether together with 98 and 93% yields of EtCl and  $\text{ClCH}_2\text{COCl}$ , respectively.

**$\text{CCl}_3\text{COOMe}$  and 2.** A mixture of 2 (197 mmol) and  $\text{CCl}_3\text{COOMe}$  (181 mmol) was heated in a flask at  $150^\circ$  for 0.8 hr. A  $\text{Ba}(\text{OH})_2$  bubbler connected to the flask collected 8.29 g of  $\text{BaCO}_3$ , representing a 23% yield of  $\text{CO}_2$ .

**$(Z)\text{-PhCF}_3\text{C}=\text{CHCOOEt}$  and 2.** A solution of 0.3100 g (1.27 mmol) of  $(Z)\text{-PhCF}_3\text{C}=\text{CHCOOEt}$  and 2.0 ml (1.5 mmol) of a 0.758 M solution of 2 in  $\text{CH}_3\text{CN}$  was heated at  $150^\circ$  for 3 hr in a 5-ml, sealed ampoule. GLC analysis showed the consumption of unreacted ester to be 86% *Z* isomer and 14% *E* isomer. Analysis with NMR by comparison to an internal standard ( $\text{CH}_2\text{Cl}_2$ ) showed 0.823 mmol of both ester isomers (65% recovery) and 0.442 mmol of EtCl (35% yield). Comparison of the areas of the vinyl hydrogen absorptions of the esters and acid chloride indicated a 31%

yield of  $(E)\text{-PhCF}_3\text{C}=\text{CHCOCl}$ . The *Z* isomer of the acid chloride was not detected by NMR or GLC analyses.

**$(Z)\text{-PhCF}_3\text{C}=\text{CHCOOEt}$  and 3.** A 5-ml ampoule containing 2.4 ml (1.6 mmol) of a 0.657 M solution of 3 in  $\text{CH}_3\text{CN}$  and 0.3203 g (1.31 mmol) of  $\text{PhCF}_3\text{C}=\text{CHCOOEt}$ , composed of 97.6% *Z* isomer and 2.4% *E* isomer, was sealed and heated in a  $150^\circ$  oil bath for 3 hr. GLC analysis showed the composition of unreacted ester to be 12.9% *Z* isomer and 87.1% *E* isomer. Comparison of the areas of the vinyl hydrogen absorptions of the esters and acid chloride indicated a 52% yield of  $(E)\text{-PhCF}_3\text{C}=\text{CHCOCl}$ . The *Z* isomer of the acid chloride was not detected by NMR or GLC analyses.

**$(Z)\text{-PhCF}_3\text{C}=\text{CHCOOEt}$  and  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ .** A 5-ml ampoule containing 0.3037 g (1.09 mmol) of  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ , 1.5 ml of  $\text{CH}_3\text{CN}$ , and 0.2371 g (0.971 mmol) of  $\text{PhCF}_3\text{C}=\text{CHCOOEt}$ , composed of 95% *Z* isomer and 5% *E* isomer, was sealed and heated in a  $150^\circ$  oil bath for 3 hr. Analysis with NMR by comparison to an internal standard ( $\text{CH}_2\text{Cl}_2$ ) showed a 97% recovery of ester having a composition of 91% *Z* isomer and 9% *E* isomer.

**Registry No.**—2, 2526-64-9; 3, 42957-71-1;  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$ , 1112-67-0;  $\text{CF}_2\text{ClCOOEt}$ , 383-62-0;  $\text{CF}_2\text{ClCOOBu-n}$ , 56210-76-5;  $\text{CF}_2\text{ClCOOMe}$ , 1514-87-0;  $\text{Me}_3\text{SiCl}$ , 75-77-4;  $\text{CH}_3\text{COOBu-n}$ , 123-86-4;  $\text{CH}_3\text{COOEt}$ , 141-78-6;  $\text{HCOOBu-n}$ , 592-84-7;  $\text{ClCH}_2\text{CCl}_2\text{OEt}$ , 56210-77-6;  $\text{CCl}_3\text{COOMe}$ , 598-99-2;  $\text{Ph}_3\text{PBr}_2$ , 1034-39-5; trifluoroacetophenone, 434-45-7;  $(Z)\text{-PhCF}_3\text{C}=\text{CHCOOEt}$ , 56210-75-4;  $\text{PH}_3\text{P}=\text{CHCOOEt}$ , 1099-45-2; phthalide, 87-41-2; *o*-chloromethylbenzoyl chloride, 42908-86-1;  $\text{ClCH}_2\text{COCl}$ , 79-04-9.

## References and Notes

- (1) (a) This paper is based on the Ph.D. Thesis of W.M.K., University of Iowa, 1972. Partial support for this work was obtained from Public Health Grant GM11809. (b) A preliminary account of this work has appeared: D. J. Burton and W. M. Koppes, *J. Chem. Soc., Chem. Commun.*, 425 (1973).
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- (7) J. Greenwald, Ph.D. Thesis, University of Iowa, Iowa City, Iowa, 1971.
- (8) A report on the use of  $\text{Ph}_3\text{PBr}_2$  for ester cleavage has recently appeared: A. G. Anderson, Jr., and D. H. Kono, *Tetrahedron Lett.*, 5121 (1973).
- (9) The synthesis of alkyl halides from 1,1-di-*H*-perfluoroalkyl tosylates, for example, requires more vigorous conditions than those required with unsubstituted alkyl tosylates; cf. G. V. D. Tiers, H. A. Brown, and T. S. Reid, *J. Am. Chem. Soc.*, 75, 5978 (1953).
- (10) Preliminary experiments have indicated that 3 is also a more effective reagent for ether cleavage than 2. Ether cleavage with  $\text{Ph}_3\text{PBr}_2$  has also been enhanced by its complexation with  $\text{BF}_3$ . Other salts such as  $\text{Ph}_3\text{PCl}^+\text{SbCl}_6^-$  would presumably also represent more reactive "phosphorane" reagents in many types of reactions, and other complexed phosphoranes will be tried in future work.
- (11) D. B. Denny, D. Z. Denny, and B. C. Chang, *J. Am. Chem. Soc.*, 90, 6332 (1968).
- (12) After 6 hr of reflux the methyl esters were completely cleaved to  $\text{CH}_3\text{Cl}$  (99% yield in vapor trap) and carboxylate anions, while the ethyl group was completely retained in solution as  $\text{CF}_3\text{COOEt}$  and  $\text{CF}_2\text{ClCOOEt}$ .
- (13) See ref 6b.
- (14) This type of alkyl-oxygen bond fission was denoted as BAL2 by Ingold to symbolize a mode of ester hydrolysis: C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y. 1969, p 1131.
- (15) D. P. N. Satchell and R. S. Satchell in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, New York, N.Y. 1969, p 393.
- (16) Isomerization by chloride ion alone (by carbanion formation from attack of  $\text{Cl}^-$  on the olefinic double bond) would account for only a small amount of the observed isomerization of the ester. The *Z* ester underwent only 4% isomerization with  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$  under the same conditions.
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- (19) GLC analyses were performed on a Hewlett-Packard Model 5750B chromatograph. Melting points were determined on a Thomas-Hoover apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer Model 21 instrument and calibrated with a polystyrene film. Ultraviolet spectra were obtained with a Cary 14 instrument. NMR spectra were determined with Varian A-60 and H-100 instruments using  $\text{Me}_4\text{Si}$  and  $\text{CCl}_3\text{F}$  as internal standards or 85%  $\text{H}_3\text{PO}_4$  as an external standard. Elemental analyses were performed in the analytical laboratory of the Chemistry Department at The University of Iowa.

- (20)  $\text{Cl}_2$  was first condensed into a tared cold trap from which it was re-evaporated and condensed into the phosphine solution via a Dry Ice condenser. Alternatively, the  $\text{Cl}_2$  was delivered as a solution in  $\text{CH}_3\text{CN}$ , the concentration of which was determined by iodometric titration.
- (21) These concentrations represent the approximate limit of solubility of **2** in these solvents.
- (22) Solutions of **3** were prepared in a volumetric flask with solid **3** and  $\text{CH}_2\text{Cl}_2$ ; in situ preparation of a solution was not feasible because of difficulty in removal of any excess  $\text{BF}_3$ . A 1.15 M solution of **3** in  $\text{CH}_2\text{Cl}_2$  was assayed by hydrolysis in 0.1 M NaOH ( $\sim 0.75$  equiv) followed by titration of this aqueous solution with dilute NaOH to a phenolphthalein endpoint. Two trials gave a molarity of 1.16 M ( $\pm 0.00$ ), based on the release of 5 mol of acid per mole of **3**.
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- (29) Alternatively, *n*-BuOH was used as a trap for  $\text{CF}_3\text{COCl}$ , in which case the amount of  $\text{CF}_3\text{COOBU-}n$  was determined by GLC analysis.
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- (31) Residual solvent from the preparation of **2**.
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- (33) Residual solvent from the preparation of **3**.
- (34) The amount of *n*-BuCl in the solution was not calculated because of the interference from decomposition of the ammonium salts in the gas chromatograph, which also produces *n*-BuCl.
- (35) The average of two to three analyses is given followed by, in parentheses, the average deviation.
- (36) This yield is based on the amount of  $\text{CF}_2\text{ClCOOMe}$  initially present. It indicates that decarboxylation of  $\text{CF}_2\text{ClCOO}^-$  occurred with the release of  $\text{Cl}^-$ , since the amount of  $(n\text{-Bu})_4\text{N}^+\text{Cl}^-$  present is insufficient to account for all the  $\text{CH}_2\text{Cl}$  formed.
- (37) The butyl chloride peak due to decomposition of the ammonium salts in the gas chromatograph tailed slightly into the ethyl ester peak.
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## Stereochemistry and Mechanism of Ionic Cyclopropane Ring Cleavage by Arenesulfenyl Chloride Addenda in Quadricyclene Systems

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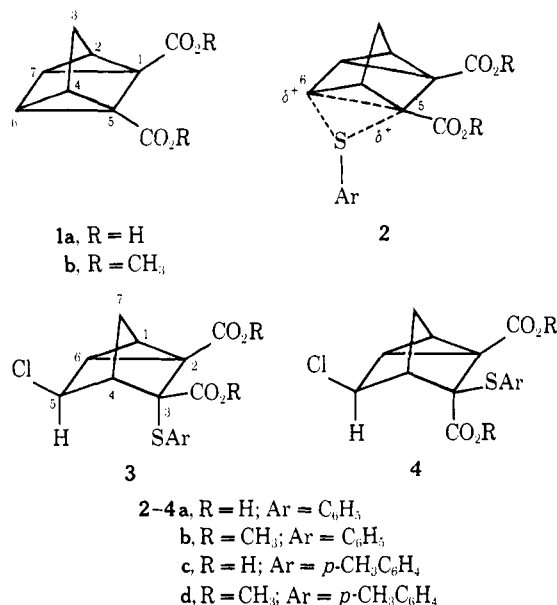
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Addition of benzenesulfenyl chloride to quadricyclenedicarboxylic acid (**1a**) and to the corresponding dimethyl ester (**1b**) gave adducts [*exo*-5-chloro-*endo*-3-phenylthiotricyclo[2.2.1.0<sup>2,6</sup>]heptane-2,*exo*-3-dicarboxylic acid (**3a**) and the *C*-3 epimer (**4a**) from **1a** and the corresponding dimethyl esters from **1b**, **3b**:**4b**, ca. 1:1]; these are the result of electrophilic cleavage of a cyclopropane ring in this system by retention and inversion processes (in nearly equal amounts). The addition of toluenesulfenyl chloride to **1b** gives analogous results. All such results demonstrate the lack of bridged sulfonium ions (e.g., **2**) as the sole product precursors and indicate that corner-attached electrophilic addition intermediates, relative to the corresponding edge-attached species, may have a far greater importance than previously suspected. The stereochemistry of the adducts was confirmed by spectral (largely proton magnetic resonance) and chemical (lactone formation) studies.

Although the ionic cleavage of cyclopropanes has been the subject of a large amount of research,<sup>1</sup> the stereochemical role of the electrophile has not been totally established. The vast majority of studies show that cyclopropane ring cleavages by nucleophile have occurred by inversion,<sup>1,2</sup> whereas electrophilic ring cleavage stereochemistry has been reported to involve each of retention,<sup>1,3,4</sup> inversion, and mixed retention-inversion processes.<sup>1,5,6</sup> Completion of our work<sup>5</sup> on the ionic cleavage of a cyclopropane in quadricyclenedicarboxylic acid with hydrogen chloride implied that the stereochemistry of new proton position in our final adduct was not a result of *direct* cyclopropane ring cleavage. We thus decided to investigate the arenesulfenyl chloride cyclopropane ring cleavage of quadricyclenedicarboxylic acid (**1a**, tetracyclo[3.2.0.0<sup>2,7</sup>.0<sup>4,6</sup>]heptane-1,5-dicarboxylic acid) and ultimately its dimethyl ester (**1b**). This combination seemed ideal because of the known propensity for  $\text{C}_5\text{-C}_6$  ( $\text{C}_1\text{-C}_7$ ) bond cleavage in this system<sup>5,7</sup> and the great driving force for sulfenyl halides to add via a bridged sulfonium ion.<sup>8</sup> We felt that the possibility of the latter would enhance the chances of direct electrophilic attack on the carbon atoms of the cyclopropane ring skeleton, perhaps to the exclusive formation of ion **2**, which should result in the exclusive formation of **3**.<sup>9</sup> The work described below shows that such an exclusive pathway is *not* the case, but that one, in all cases, obtains quantities of **4** essentially equivalent to the amount of **3** formed. This implies, as far as comparisons can be made between theoretical considerations of protonated cyclopropanes and cyclopropane cleavage intermediates involving other electrophiles, that the balance

may lie much more heavily toward corner-attached species (as opposed to edge-attached species) than previously suspected.<sup>1,10,11</sup>



The preparation of the quadricyclene diacid (**1a**) was carried out as has been described earlier.<sup>5,12</sup> Treatment of diacid **1a** (in dioxane at room temperature) with benzenesulfenyl chloride<sup>13</sup> resulted in quantitative yields of ad-