The Reaction of Acyl Halides with Organotin Hydrides. The Mechanism of Aldehyde Formation[1,2]

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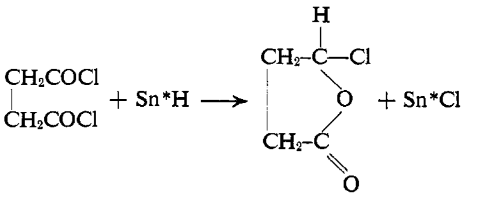
Abstract: Acid chlorides and acid bromides react with organotin hydrides to yield aldehydes and esters. The distribution of the two products depends on electronic and steric effects of R and the nature of X in RCOX. A free-radical mechanism for aldehyde formation is indicated by free-radical catalysis, fragmentation of the acyl radicals postulated as intermediates, and the effect of R on the reactivities of acid chlorides. The Hammett ρ value for the reaction of tri-*n*-butyltin radicals with substituted benzoyl chlorides is 2.6 in *m*-xylene, 2.7 in *o*-dichlorobenzene, and 4.0 in methyl acetate.

Organotin hydrides have been found to react with a variety of organic functional groups including halides.[5,6] The reduction of alkyl halides (eq. 1), in which Sn* is a trisubstituted tin group, has been studied with regard to scope and mechanism.[6]

$$\text{R–X} + \text{Sn*–H} \longrightarrow \text{R–H} + \text{Sn*–X} \qquad (1)$$

van der Kerk, Noltes, and Luijten[7] reported that benzaldehyde was obtained from the reduction of benzoyl chloride with triphenyltin hydride (eq. 2). Kuivila[8] found that when 1 mole of tri-*n*-butyltin hydride was added to 1 mole of succinyl dichloride, the only product isolated was γ-chloro-γ-butyrolactone (eq. 3, Sn* = $(n\text{-}C_4H_9)_3Sn$), and when phthalyl dichloride was reduced under the same conditions with 2 moles of the hydride a 55% yield of phthalide was isolated.

$$(C_6H_5)_3SnH + C_6H_5COCl \longrightarrow C_6H_5CHO + (C_6H_5)_3SnCl \qquad (2)$$



(3)

Since then we have reported[5] that the reduction of benzoyl chloride with tri-*n*-butyltin hydride in ether provided a 54% yield of benzaldehyde but that the major product was benzyl benzoate in the absence of a solvent. Recently, Kupchik and Kiesel[9] have reported that the reduction of benzoyl chloride with triphenyltin hydride, with or without solvent, gave benzyl benzoate as the only product.

Results and Discussion

When an acid chloride is mixed with tri-*n*-butyltin hydride at room temperature, an exothermic reaction frequently results. The reaction is usually complete within 20 hr. Our results show that formation of the expected aldehyde (eq. 4) is usually accompanied by formation of ester (eq. 5). The relative yields of ester and aldehyde are dependent upon the acid chloride used, the experimental conditions employed, and the hydride used. Our results on the reduction of several acyl halides are presented in Table I.

$$\text{Sn*H} + \text{RCOCl} \longrightarrow \text{RCHO} + \text{Sn*Cl} \qquad (4)$$

$$2\text{SnH} + 2\text{RCOCl} \longrightarrow \text{RCOOCH}_2\text{R} \qquad (5)$$

Table I. The Reaction of Acyl Halides with Tri-*n*-butyltin Hydride Neat and in Solution (0.63 *M*) at Ambient Temperatures[a]

	Yield (neat), %			Yield (soln.), %	
R	RCHO	RCO_2-CH_2R	Solvent	RCHO	RCO_2-CH_2R
RCOCl					
CH_3	5	95			
C_2H_5	...[b]	87[c]	DMB[d]	75	25
			MeOAc	90	10
			$(n\text{-}C_4H_9)_3SnCl$	27	73
$n\text{-}C_4H_9$	19	81	DMB	91	9
$i\text{-}C_3H_7$	36	64	DMB	52	48
$t\text{-}C_4H_9$	56	33			
$PhCH_2$			$C_6H_5CH_3$	55	45
Ph	65	35			
Ph_3C[e]			*m*-Xylene	90	...[b]
C_2H_5O	95	...[b]			
$PhCH_2O$	61	...[b]			
RCOBr					
C_2H_5	79	21	DMB	60	40
Ph	99	...[b]			

[a] All yields reported in this table, except those noted, have been determined by g.l.c. analysis. [b] None observed. [c] 80% by isolation. [d] 2,3-Dimethylbutane. [e] Yield based on isolation.

Ethyl and benzyl chloroformates are notably unreactive. The former was not completely reduced in 5 weeks at ambient temperature and gave ethyl formate as the only product. The latter was completely reduced in about 2 weeks and yielded only benzyl formate and fragmentation products (see below).

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[2] Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[3] (a) This work was begun during the tenure of a John Simon Guggenheim Memorial Foundation Fellowship at the California Institute of Technology, 1959; (b) author to whom inquiries should be addressed: Department of Chemistry, State University of New York at Albany, Albany, N. Y.

[4] U. S. Public Health Service Predoctoral Fellow, 1962–1964.

[5] H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964), and references therein.

[6] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

[7] G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, **7**, 356 (1957).

[8] H. G. Kuivila, *J. Org. Chem.*, **25**, 284 (1960).

[9] E. J. Kupchik and R. J. Kiesel, *ibid.*, **29**, 3690 (1964).

The two acid bromides investigated indicate that the behavior of the bromides is different from that of the corresponding chlorides. These reactions are also exothermic, but the yields of aldehydes are higher and yields of the ester are lower than those obtained from the acid chlorides.

As the alkyl group becomes larger and more branched, the yield of the aldehyde increases. When one goes from acetyl to 2,2-dimethylpropionyl chloride, the yield of aldehyde increases from 5 to 56% and the yield of ester falls from 95 to 33%. The use of a solvent exerts a profound influence upon the course of the reaction. When the reductions are carried out in 2,3-dimethylbutane, toluene, *m*-xylene, or methyl acetate, the yield of aldehyde increases at the expense of the ester. A good example of this is the propionyl chloride reaction; the neat reaction affords ester almost exclusively, but, when 2,3-dimethylbutane is employed as a solvent, only a 25% yield of ester is realized. Valeryl chloride gives much the same results; the neat reaction produces 81% of the ester, but the same reaction conducted in 2,3-dimethylbutane gives only 9%. An important exception to this solvent effect is observed with tri-*n*-butyltin chloride in which a substantial yield of ester is obtained from propionyl chloride. A reasonable explanation of this is given in the accompanying paper.[10]

It has been observed that if an aldehyde or a ketone is added to the reaction mixture a "mixed" ester, whose alkoxy fragment is derived from the added carbonyl compound, is formed. For example, the addition of 1 mole of benzaldehyde to a mixture of 1 mole each of propionyl chloride and tri-*n*-butyltin hydride resulted in a 70% yield of benzyl propionate (eq. 6). Here

$$C_2H_5COCl + C_6H_5CHO + Sn^*\text{-}H \longrightarrow C_2H_5CHO + C_3H_7O_2CC_2H_5 + Sn^*\text{-}Cl \quad (6)$$

again the role of solvent is important. When this reaction is conducted in solution (0.63 *M*) in either toluene or 2,3-dimethylbutane, only a 34% yield of benzyl propionate is realized. These and other examples are listed in Table II. Ketones in general appear not to be as reactive in these reactions as aldehydes. When cyclohexanone is added to the neat reaction mixture under the same conditions as in the experiment with benzaldehyde, only a 12% yield of cyclohexyl propionate is found. Acetone and acetophenone give somewhat smaller yields of "mixed" ester under these same conditions.[11]

Table II. Yields of Esters from the Reaction of Acid Chlorides with Tri-*n*-butyltin Hydride in the Presence of Equimolar Amounts of Carbonyl Compounds at Room Temperature

			Yield, %	
RCOCl	R′R″CO	Solvent[a]	RCO_2-CH_2R	RCO_2-CHR′R″
CH_3	Cyclohexanone	Neat	31	5
C_2H_5	Cyclohexanone	Neat	78	12
CH_3	C_6H_5CHO	Neat	25	23
C_2H_5	C_6H_5CHO	Neat	10	70
CH_3	*p*-$CH_3OC_6H_4CHO$	Neat	22	21
C_2H_5	C_6H_5CHO[b]	DMB	...[c]	63
C_2H_5	C_6H_5CHO	DMB	...[c]	34
C_2H_5	C_6H_5CHO	$(C_2H_5)_2O$	...[c]	13
C_2H_5	C_6H_5CHO	$C_6H_5CH_3$	...[c]	35
C_2H_5	Cyclopentanone	DMB	...[c]	3.2
C_2H_5	*n*-Heptaldehyde	DMB	75	22
C_2H_5	*p*-$CH_3C_6H_4CHO$	DMB	...[c]	39
C_2H_5	*m*-$CH_3C_6H_4CHO$	DMB	...[c]	19
C_2H_5	*m*-ClC_6H_4CHO	DMB	...[c]	39
C_2H_5	*p*-ClC_6H_4CHO	CH_3COOCH_3	14	5.1
C_2H_5	*p*-$CH_3OC_6H_4CHO$	$C_6H_5CH_3$	...[c]	13
C_2H_5	*p*-$CH_3OC_6H_4CHO$	$(C_2H_5)_2O$	...[c]	20

[a] Concentration 0.63 *M* when solvent was used. DMB = 2,3-dimethylbutane. [b] Trimethyltin hydride was used. [c] Yield not determined.

The objective of our work has been to elucidate aspects of the mechanisms of these reactions between acid halides and organotin hydrides. In this paper we shall discuss the mechanism of aldehyde formation. The reactions which lead to esters are discussed in the accompanying paper.[10]

Mechanism of Aldehyde Formation. It has recently been demonstrated[6] that the reaction between alkyl halides and tri-*n*-butyltin hydride proceeds by a free-radical chain mechanism probably involving abstraction of the halogen atom by a tin radical, followed by reaction of the alkyl radical with another mole of tin hydride to produce the reduced product and another tin radical (eq. 7 and 8) as chain-carrying steps. Since

$$Sn^*\cdot + R\text{-}X \longrightarrow Sn^*\text{-}X + R\cdot \quad (7)$$

$$R\cdot + Sn^*\text{-}H \longrightarrow Sn^*\cdot + R\text{-}H \quad (8)$$

the reaction of acid chlorides with the hydrides occurs readily in nonpolar solvents, it was thought that a free-radical mechanism may also be involved here. Results obtained in the study of this reaction indicate that this is so. Equations 9–11 comprise our mechanistic

$$Q\cdot + Sn^*H \longrightarrow Sn^*\cdot + QH \quad (9)$$

$$Sn^*\cdot + RCOCl \longrightarrow R\dot{C}{=}O + Sn^*Cl \quad (10)$$

$$R\dot{C}{=}O + Sn^*H \longrightarrow RCHO + Sn^*\cdot \quad (11)$$

hypothesis for the formation of the aldehyde. In this scheme Q· is some free radical arising from a bimolecular reaction between the hydride and the acid chloride or by other means. This free radical abstracts a hydrogen atom from the organotin hydride molecule producing an organotin free radical. The tin radical can then abstract a chlorine atom from the acid chloride, generating an acyl free radical which can then react with another molecule of organotin hydride to form the aldehyde and another organotin radical. Evidence for this mechanism comes from studies on fragmentation, free radical catalysis, and substituent effects.

Fragmentation. Acyl radicals have been shown to be intermediates in vapor phase decompositions of some aldehydes and ketones, and their formation in solution is usually initiated by photolysis or by reaction of aldehydes with alkoxy radicals.[12,13] Two new methods for generating these radicals have been reported by Barton[14] and Waters[15] and co-workers. These involve photolysis of acyl xanthates and azodibenzoyl compounds, respectively. Probably the most important reaction of acyl radicals is decarbonylation at moder-

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(10) E. J. Walsh, Jr. and H. G. Kuivila, *J. Am. Chem. Soc.*, **87**, 576 (1965).

(11) As approximated from relative areas of *n*-propyl propionate and "mixed" ester peaks in gas chromatograms.

(12) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., pp. 273–285, 325.

(13) B. G. Tucker and E. Whittle, *Proc. Chem. Soc.*, 93 (1963).

(14) D. H. Barton, *et al.*, *J. Am. Chem. Soc.*, **84**, 1967 (1962).

(15) D. MacKay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 4793 (1964).

ately high temperatures.[12,16] They can therefore be used as intermediates in the formation of alkyl radicals (eq. 12). Furthermore, the formation of carbon monoxide may be taken to indicate the intermediacy of acyl radicals.

$$R\dot{C}{=}O \xrightarrow{\Delta} R\cdot + CO \qquad (12)$$

Decarbonylation cannot compete with reaction 11 in most cases because tri-*n*-butyltin hydride is highly efficient as a hydrogen donor. In order to foster the competition we sought to use an acid chloride which would decarbonylate with relative ease, *i.e.*, one which would yield a particularly stable alkyl radical. Triphenylacetyl chloride was selected. Numerous attempts were made by mixing the acid chloride and hydride in xylene and heating the reaction mixture to 100–110° in a system attached to a gas buret. In every case the amount of gas collected was too small to give a good infrared spectrum. However, if the hydride was added slowly, thereby limiting its availability, enough carbon monoxide (10–12%) was collected to give the characteristic infrared spectrum.[17] A 5% yield of triphenylmethane was isolated along with a 90% yield of triphenylacetaldehyde; eq. 13–16 account for these results.

$$(C_6H_5)_3CCOCl + Sn^*\cdot \longrightarrow (C_6H_5)_3C\dot{C}{=}O + Sn^*Cl \qquad (13)$$

$$(C_6H_5)_3C\dot{C}{=}O + Sn^*H \longrightarrow (C_6H_5)_3CCHO + Sn^*\cdot \qquad (14)$$

$$(C_6H_5)_3C\dot{C}{=}O \longrightarrow (C_6H_5)_3C\cdot + CO \qquad (15)$$

$$(C_6H_5)_3C\cdot + Sn^*H \longrightarrow (C_6H_5)_3CH + Sn^*\cdot \qquad (16)$$

A control experiment was run on the same scale under the same conditions as the experiment above with tri-*n*-butyltin chloride and the acid chloride to test whether the chloride is a strong enough Lewis acid to generate the acylium ion which might decarbonylate to give the triphenylcarbonium ion which, in turn, would be expected to react with the hydride. There was no evolution of carbon monoxide.

Another type of fragmentation was observed in the reduction of benzyl chloroformate. The benzoyloxycarbonyl free-radical intermediate apparently dissociates rapidly, even at room temperature, to carbon dioxide and the more stable benzyl radical. The benzyl radical then reacts with the hydride to produce toluene as shown in eq. 17–20. Gas chromatographic analysis indicated a 39% yield of toluene and a 61% yield of benzyl formate.

$$C_6H_5CH_2OCOCl + Sn^*\cdot \longrightarrow C_6H_5CH_2O\dot{C}{=}O + Sn^*Cl \qquad (17)$$

$$C_6H_5CH_2\dot{O}C{=}O \longrightarrow C_6H_5CH_2\cdot + CO_2 \qquad (18)$$

$$C_6H_5CH_2O\dot{C}{=}O + Sn^*H \longrightarrow C_6H_5CH_2OCHO + Sn^*\cdot \qquad (19)$$

$$C_6H_5CH_2\cdot + Sn^*H \longrightarrow C_6H_5CH_3 + Sn^*\cdot \qquad (20)$$

This type of free-radical fragmentation was observed by Thynne and Gray[18] with the methoxycarbonyl free radical. This intermediate, at the temperature used, 120–185°, breaks down quantitatively to the methyl radical and carbon dioxide (eq. 21–24). On the other hand, ethyl chloroformate reduction by tri-*n*-butyltin hydride yielded only ethyl formate and no indication of carbon monoxide or ethane. Presumably the energy of activation for decarboxylation of the ethoxycarbonyl radical is sufficiently high that reaction with the hydride is its exclusive fate under the conditions used.

$$(CH_3)_2O_2 \xrightarrow{\Delta} 2CH_3O\cdot \qquad (21)$$

$$CH_3O\cdot + HCO_2CH_3 \longrightarrow CH_3OH + O{=}\dot{C}OCH_3 \qquad (22)$$

$$CH_3O\dot{C}{=}O \longrightarrow CO_2 + CH_3\cdot \qquad (23)$$

$$CH_3\cdot + HCO_2CH_3 \longrightarrow CH_4 + O{=}\dot{C}OCH_3 \qquad (24)$$

Free-Radical Catalysis. Ethyl chloroformate reacts very slowly at 80° with tri-*n*-butyltin hydride, so it served as a particularly good substrate for catalysis experiments. The reaction with tri-*n*-butyltin hydride was found to be subject to free-radical catalysis as is shown by the observation that ethyl chloroformate undergoes only 5% reduction in 3 hr. at 80°, whereas the reaction is complete under the same conditions in the presence of 1.6 mole % of azobisisobutyronitrile (see Table III). The products in each case were ethyl formate and tri-*n*-butyltin chloride.

Table III. Catalyzed and Uncatalyzed Reaction of Ethyl Chloroformate with Tri-*n*-butyltin Hydride at 80°

Time, hr.	% completed	
	Catalyzed[a]	Uncatalyzed
0.5	30	0
1.5	98–100	2–4
3.0	100	5
18.5		35

[a] 1.6 mole % of azobisisobutyronitrile.

A brief examination of the reduction of benzoyl chloride provided less clear-cut results. In experiments similar to those described above, the half-life of the uncatalyzed reaction was roughly twice that of the catalyzed reaction. However, the result was complicated by the observation that the catalyzed reaction produced 30% of ester while the uncatalyzed reaction produced only 13%. A detailed explanation of these results will not be attempted here, but, as is shown in the accompanying paper,[10] there seem to be at least two competing mechanisms for ester formation. This fact can complicate the problem of product distribution under varying conditions.

Relative Reactivities of Acid Chlorides. The relative reactivities of acid chlorides were determined by allowing each acid chloride to compete with a benzyl bromide or 2-bromooctane for a deficiency of tri-*n*-butyltin hydride at 25°. The reaction product was analyzed by gas chromatography using an internal standard. Satisfactory determinations of aldehyde and acid chloride concentrations could not be obtained, but that of the hydrocarbon produced from the alkyl halide could. The amount of acid chloride was then determined by difference assuming no wastage of the organotin hydride. Relative rate constants were computed by the method of Ingold and Stow.[19]

The fact that electron-withdrawing groups facilitate the reaction rules out an acylium ion mechanism,

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(16) See, *e.g.*, V. P. Grinn, *et al.*, *J. Org. Chem.*, **28**, 2643 (1963); W. A. Bonner and F. D. Mango, *ibid.*, **29**, 29 (1964); D. Schuster and J. D. Roberts, *ibid.*, **27**, 51 (1962); J. W. Wilt and A. A. Levin, *ibid.*, **27**, 2319 (1962).

(17) R. H. Pierson, A. N. Fletcher, and E. St. C. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

(18) J. C. J. Thynne and P. Gray, *Proc. Chem. Soc.*, **141**, 295 (1962); *Trans. Faraday Soc.*, **58**, 2403 (1962).

(19) C. K. Ingold and F. R. Stow, *J. Chem. Soc.*, 2918 (1927).

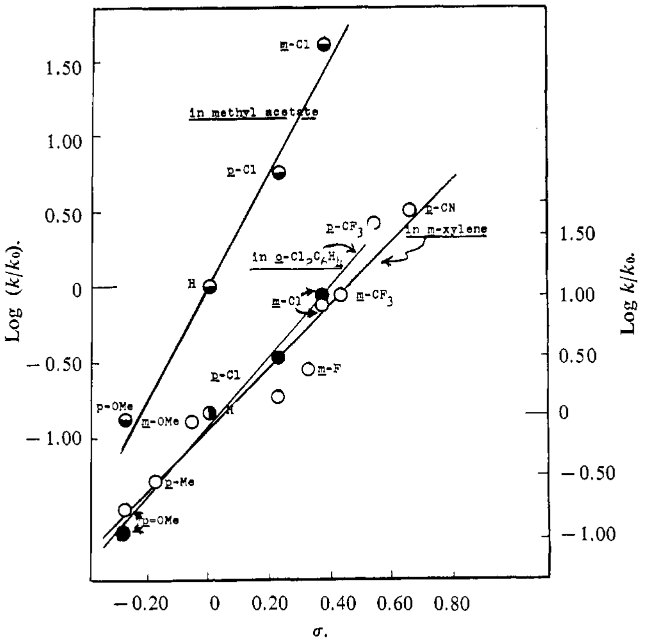


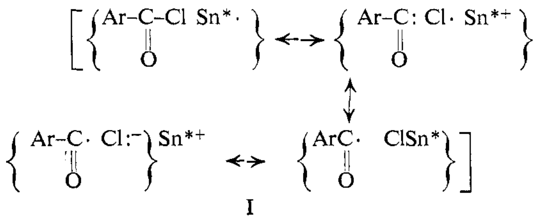
Figure 1. Hammet plots for the reaction of substituted benzoyl chlorides with the tri-*n*-butyltin radical.

(eq. 25 and 26). Reaction 25 would be facilitated by electron-releasing substitutents.

$$\text{RCOCl} + \text{Sn}^{*+} \longrightarrow \text{RC}^{+}{=}\text{O} + \text{Sn}^{*}\text{Cl} \qquad (25)$$

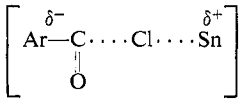
$$\text{RC}^{+}{=}\text{O} + \text{Sn}^{*}\text{H} \longrightarrow \text{RCHO} + \text{SN}^{*+} \qquad (26)$$

The results are consistent with the free-radical mechanism postulated with reaction 10 subject to substantial polar effects as depicted by the contributing structures in I or the shorthand representation II. The electropositive organotin radical functions as an electron donor to the electronegative chlorocarbonyl group. The carbonyl group assumes a degree of carbanionic character which is novel for reactions leading to the formation of the acyl radical. In much of the previous work, the source of the acyl radical has been the reaction of an aldehyde with an electrophilic species, such as the benzoyloxy radical.[20] In such cases the acyl carbon assumes acylium ion character in the transition state, structure III.



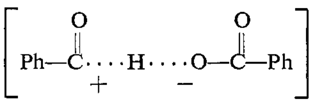
$$\left[\left\{\text{Ar}-\underset{\underset{\text{O}}{\|}}{\text{C}}-\text{Cl Sn}^{*}\cdot\right\} \longleftrightarrow \left\{\text{Ar}-\underset{\underset{\text{O}}{\|}}{\text{C}}:\text{Cl}\cdot\ \text{Sn}^{*+}\right\} \updownarrow \left\{\text{Ar}-\underset{\underset{\text{O}}{\|}}{\text{C}}\cdot\ \text{Cl}:^{-}\right\}\text{Sn}^{*+} \longleftrightarrow \left\{\text{Ar}\underset{\underset{\text{O}}{\|}}{\text{C}}\cdot\ \ \text{ClSn}^{*}\right\}\right]$$

I



$$\left[\text{Ar}-\overset{\delta^{-}}{\underset{\underset{\text{O}}{\|}}{\text{C}}}\cdots\text{Cl}\cdots\overset{\delta^{+}}{\text{Sn}}\right]^{\cdot}$$

II



$$\left[\text{Ph}-\underset{+}{\overset{\overset{\text{O}}{\|}}{\text{C}}}\cdots\text{H}\cdots\underset{-}{\text{O}}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{Ph}\right]^{\cdot}$$

III

The Hammett correlation appears to be better with σ than with σ^{-}. Values of r, the correlation coefficient, are 0.963 and 0.955, respectively. Corresponding values of ρ are 2.61 and 2.02, respectively.

Table IV. Relative Reactivities of Acyl Halides toward Tri-*n*-butyltin Hydride at 25° in Solution (0.63 *M*)[a]

Acyl halide	Relative rate in *m*-Xylene	MeOAc	DCB[b]	σ
Benzoyl chloride				
p-Cyano	61.40			0.660
p-Trifluoromethyl	38.10			0.540
m-Trifluoromethyl	9.50			0.430
m-Chloro	8.20	42.20	9.70	0.373
m-Fluoro	2.34			0.337
p-Chloro	1.27	5.56	2.92	0.227
H	1.00	1.00	1.00	0
m-Methyl	0.937			−0.069
p-Methyl	0.290			−0.170
p-Methoxy	0.166	0.116	0.084	−0.268
Benzoyl bromide	331			
Benzyl bromide	28.78			
sec-Octyl bromide	2.07			
Propionyl chloride	5.63			

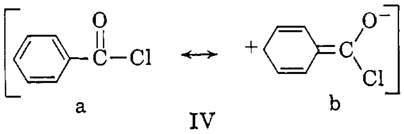
[a] As determined by competition with *sec*-octyl bromide for an insufficient amount of the hydride. [b] *o*-Dichlorobenzene.

The effect of solvent on the Hammett correlation has been studied briefly. It can be seen from Table IV and Figure 1 that the nature of the solvent can exert a profound effect. The ρ value in methyl acetate (4.0) is considerably greater than that in *m*-xylene or *o*-dichlorobenzene (2.7). Two effects could be operable here. One, proposed by Howard and Ingold,[21] would be due to the polarizability or dielectric constant of the solvent, an increase in which would tend to stabilize a charged transition state and thereby increase the ρ value. This is not the explanation for the solvent effect here, because, although methyl acetate has a higher dielectric constant (6.68) than *m*-xylene (2.37), *o*-dichlorobenzene has an even higher dielectric constant of 9.93 and substituent effects in this solvent are similar to those obtained in *m*-xylene.

The other effect may be a specific solvent effect which is not unknown in free-radical chemistry.[22] We do not feel, however, that we can describe this effect in our system with any certainty on the basis of the three solvents used.

The results of other competitive experiments listed in Table IV show a much greater reactivity of benzoyl bromide than benzoyl chloride as would be expected from a consideration of the respective bond dissociation energies. An interesting result is the greater reactivity of propionyl chloride over benzoyl chloride. From the polar effects in the reduction of benzoyl chlorides this may seem surprising.

However, the aromatic nucleus can often function as an electron-releasing seat of unsaturation, structure IV. The relative reactivity of the benzoyl halides would be



IV

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[20] C. Walling and E. McElhill, *J. Am. Chem. Soc.*, 73, 2927 (1951).

[21] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **41**, 1744 (1963).

[22] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958); **79**, 2997 (1957); *J. Org. Chem.*, **24**, 300 (1959); G. A. Russell, A. Ito, and D. G. Hendry, *J. Am. Chem. Soc.*, **85**, 2976 (1963); **86**, 2368 (1964); C. Walling and M. Mayaki, *ibid.*, **81**, 1485 (1959); C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

diminished by the increased electron density in the chlorocarbonyl group owing to contributions from IVb.

Four-centered and nucleophilic displacement mechanisms seem unlikely on the basis of the observations of free-radical catalysis, decarbonylation, and decarboxylation, as well as the inferred trapping of the acyl radical by added carbonyl compounds.[10]

Experimental Section

All reactions involving organotin hydrides were conducted in an atmosphere of prepurified nitrogen. Infrared spectra were determined with a Perkin-Elmer Model 21 or 337 recording double-beam spectrophotometer. Experiments involving gas chromatography were carried out using a F&M Scientific Co., Model 300, gas chromatograph. Toluene, chlorobenzene, and *n*-heptane were used as internal standards with a 4-ft. column packed with 10% silicone rubber (Se-30), on Chromosorb P, 60–80 mesh (F&M Scientific Co.).

Materials. In many cases the acid chlorides used were commercially available in high purity. When not available, they were prepared in essentially quantitative yields from the appropriate carboxylic acid and thionyl chloride. In all cases the solvents employed were commercially available with an excellent degree of purity. All aldehydes used were commercially available. Their purity was checked periodically by gas chromatography after distillation. These aldehydes were stored under nitrogen in the refrigerator. Some of the esters needed were commercially available, but in most cases they were prepared by lithium aluminum hydride reduction of the appropriate aldehyde or carboxylic acid to the alcohol which was then acylated by the appropriate acid chloride. Tri-*n*-butyltin hydride was prepared by lithium aluminum hydride reduction of the chloride[23] or the bis oxide[24] which was obtained through the courtesy of M&T Chemicals, Inc. Trimethyltin hydride was prepared by the lithium aluminum hydride reduction of the chloride in di-*n*-butyl ether at 100°. Under these conditions the organotin hydride distilled at 60° as it was formed.

Reduction of Acid Chlorides. General. These reductions were carried out at ambient temperature in ordinary laboratory apparatus. Except for a few isolation experiments the yields were determined by gas chromatography using the internal standard method described by Keulemans.[25] Because aldehydes in the presence of organotin chloride gave consistently low results (as determined from known mixtures with and without added organotin chloride), the aldehyde yield was determined as the difference between the yield of ester and the amount of organotin hydride used. When propionyl chloride was reduced in the presence of an added carbonyl compound, both esters were analyzed by this method.

Decarbonylation of Triphenylacetyl Chloride. Into a 50-ml. flask attached to a gas buret and a dropping funnel containing 6.6 g. (0.022 mole) of the hydride in 5 ml. of xylene, was placed 5.5 g. (0.018 mole) of the acid chloride dissolved in 50 ml. of xylene. The flask was preheated to 100° and the expanded gas in the buret was removed. While maintaining the temperature at 100–110°, the hydride was added slowly over a period of 2 hr. After a total of 4 hr. the collected gas was transferred to a gas cell and its infrared spectrum showed the characteristic carbon monoxide absorptions at 2250 and 2000 cm.$^{-1}$. The volume of this gas, 45 ml., corresponds to about a 10% yield. On cooling the reaction mixture, a white precipitate formed. This was filtered off and found to be triphenylacetaldehyde contaminated by triphenylmethane. The solvent was stripped off under reduced pressure and the residual solid material was filtered and recrystallized from ethanol. The white, fluffy material, 4.3 g., m.p. 102–104°, showed all the characteristic aldehyde absorptions for triphenylacetaldehyde in the infrared. The mother liquor was subjected to column chromatography on acidic alumina. Three fractions were found on eluting with mixtures of petroleum ether (b.p. 30–60°) and

Table V. Relative Reactivities of Acid Chlorides and Bromides and Alkyl Bromides with Tri-*n*-butyltin Hydride at 25° (0.63 *M*)

Expt. no.	Competitor A	Competitor B	Solvent	k_A/k_B
1	C_6H_5COCl	2-BrC_8H_{17}	*m*-Xylene	0.442
2	C_6H_5COCl	2-BrC_8H_{17}	*m*-Xylene	0.524
3	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	0.651
4	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	0.645
5	C_6H_5COBr	2-BrC_8H_{17}	*m*-Xylene	97.7
6	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	4.05
7	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	3.87
8	*p*-CNC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	33.2
9	*p*-CNC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	25.9
10	C_6H_5COBr	$C_6H_5CH_2Br$	*m*-Xylene	10.5
11	C_6H_5COBr	$C_6H_5CH_2Br$	*m*-Xylene	12.3
12	*m*-$CH_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.426
13	*m*-$CH_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.481
14	*p*-$CH_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.127
15	*p*-$CH_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.152
16	*p*-$CH_3OC_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.090
17	*p*-$CH_3OC_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.069
18	*p*-$CF_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	0.674
19	*p*-$CF_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	15.7
20	*m*-$CF_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	4.30
21	*m*-$CF_3C_6H_4COCl$	2-BrC_8H_{17}	*m*-Xylene	4.85
22	*m*-FC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	1.12
23	*m*-FC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	1.13
24	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	0.647
25	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*m*-Xylene	0.672
26	$C_6H_5CH_2Br$	C_2H_5COCl	*m*-Xylene	5.50
27	$C_6H_5CH_2Br$	C_2H_5COCl	*m*-Xylene	4.72
28	$C_6H_5CH_2Br$	C_6H_5COCl	*m*-Xylene	29.6
29	$C_6H_5CH_2Br$	C_6H_5COCl	*m*-Xylene	27.9
30	C_6H_5COCl	2-BrC_8H_{17}	MeOAc	0.532
31	C_6H_5COCl	2-BrC_8H_{17}	MeOAc	0.535
32	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	MeOAc	3.22
33	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	MeOAc	2.71
34	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	MeOAc	24.2
35	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	MeOAc	20.6
36	*p*-$MeOC_6H_4COCl$	2-BrC_8H_{17}	MeOAc	0.070
37	*p*-$MeOC_6H_4COCl$	2-BrC_8H_{17}	MeOAc	0.053
38	C_6H_5COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	0.750
39	C_6H_5COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	0.674
40	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	2.22
41	*p*-ClC_6H_4COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	1.93
42	*p*-$MeOC_6H_4COCl$	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	0.058
43	*p*-$MeOC_6H_4COCl$	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	0.062
44	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	7.11
45	*m*-ClC_6H_4COCl	2-BrC_8H_{17}	*o*-$Cl_2C_6H_4$	6.71

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(24) W. J. Considine and J. J. Ventura, *Chem. Ind.* (London), 1683 (1962).

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diethyl ether. The first fraction, 0.25 g., 5% yield, was identified as triphenylmethane. It melted at 92–94° and showed no melting point depression when mixed with an authentic sample. The second fraction, 0.1 g., was the aldehyde, m.p. 102–105°. This brought the total weight of the aldehyde recovered to 4.4 g. which is a 90% yield. The last fraction was tri-*n*-butyltin chloride.

Reduction of Benzyl Chloroformate. To 0.62 g. (0.0040 mole) of the chloroformate was added 1.1 g. (0.0038 mole) of tri-*n*-butyltin hydride. The reaction took about 2 weeks at room temperature to go to completion. Gas chromatographic analysis, using the internal standard method, gave 0.0015 mole (39%) of toluene and 0.0023 mole (61%) of benzyl formate.

Catalysis of the Reduction of Ethyl Chloroformate. The reaction mixture for the uncatalyzed reaction consisted of 1.48 g. (0.014 mole) of the chloroformate and 4.4 g. (0.015 mole) of tri-*n*-butyltin hydride. Four 1-ml. portions were removed to glass ampoules, flushed with nitrogen, and sealed. Samples for the catalyzed reaction were prepared in the same way except that 0.0395 g. (0.00024 mole) of azobisisobutyronitrile was added to the initial reaction mixture. All ampoules were immersed simultaneously in an oil bath at 80°. The ampoules were removed, in pairs, at appropriate intervals and analyzed directly by gas chromatography. The extent of reaction was determined by the relative areas of peaks due to starting material, the chlorocarbonate, and the formate. Results of this experiment are found in Table III.

Relative Reactivities of Acyl Halides. Known amounts of 2-bromooctane or benzyl bromide, the acyl halide, and tri-*n*-butyltin hydride were transferred into a reaction flask. The amount of hydride was sufficient to reduce about one-half of the total halide. Solvent was added; the flask was flushed with nitrogen, stoppered, and placed in a constant temperature bath at 25.0°. The mixture was allowed to stand until the hydride was all consumed, and it was then analyzed by gas chromatography using a 4-ft. × 0.25-in. column packed with 10% silicone rubber on 60–80 mesh Chromosorb P. The yield of *n*-octane or toluene was determined by the internal standard method using *n*-heptane as the standard.[26] This was a measure of the amount of alkyl halide consumed. The amount of acyl halide consumed was determined by difference assuming quantitative consumption of the hydride in reducing halides. The relative rate constants were calculated by the equation of Ingold and Stow[19]

$$\frac{\log (A_0/A)}{\log (B_0/B)} = k_A/k_B$$

in which A_0 and A and B_0 and B are initial and final concentrations of the competing halides. The relative rate constants obtained for the various sets of competitors are given in Table V. These results are reasonably reliable since comparison of expt. 1 and 2 with expt. 28 and 29 yields $k_{PhCH_2Br}/k_{2\text{-}BrC_8H_{17}} = 13.8$ as compared with the value 12.7 obtained by Menapace and Kuivila.[6] Comparison of the results of expt. 5 with expt. 11 and 12 gives a value of only 8.6, but this may be a reflection of the large difference in the reactivity of the competitors in expt. 5 which makes the value obtained subject to relatively large error.

The Reaction of Acyl Halides with Organotin Hydrides. Mechanisms of Ester Formation[1,2]

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Abstract: Reduction of acid chlorides by tri-*n*-butyltin hydride yields aldehydes and esters as products. Four pathways for the formation of ester have been considered: (a) reduction of the acid chloride to aldehyde and to alcohol, followed by reaction of the alcohol with acid chloride; (b) reaction between aldehyde and acid chloride to form α'-chloroester, followed by its reduction to ester; (c) addition of organotin hydride to the carbonyl group of the aldehyde to form ester and organotin chloride; (d) reaction of intermediate acyl radicals with the aldehyde to form α-acyloxy radical, followed by hydrogen abstraction from organotin hydride to form ester and organotin radical. Although each pathway is feasible, the first three are shown to be unimportant under ordinary reaction conditions, leaving (d) as the most likely one. The rates of reaction of substituted benzaldehydes with the presumed intermediate acyl radicals are correlated by the Hammett equation with $\rho = 0.43$.

In the preceding paper we presented evidence that the formation of aldehydes by the reaction of acyl chlorides with tri-*n*-butyltin hydride proceeds by a free-radical process in which reactions 1 and 2 ($Sn^* = (C_4H_9)_3Sn$) probably serve as chain-carrying steps.[5]

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[2] Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 3S.

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