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 $k_{\mathrm{PhCH_2Br}}/k_{\mathrm{2\text{-}BrC_8H_{17}}} = 13.8$ 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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Contribution from the Department of Chemistry, University of New Hampshire, Durham, New Hampshire, and the Gates and Crellin Laboratories, California Institute of Technology, Pasadena, California. *Received August 12, 1965*

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 ($\mathrm{Sn^*} = (C_4H_9)_3Sn$) probably serve as chain-carrying steps.[5]

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[1] This research was supported in part by the National Science Foundation under Grant NSF G-10,000.

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

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

[4] (a) This work was begun during the tenure of a John Simon Guggenheim 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.

$$\mathrm{Sn^{*}\cdot + RCOCl \longrightarrow Sn^{*}Cl + R\dot{C}{=}O} \qquad (1)$$

$$\mathrm{R\dot{C}{=}O + Sn^{*}H \longrightarrow Sn^{*}\cdot + RCHO} \qquad (2)$$

Since esters are also formed in these reductions, and may indeed be major products, it was of interest to ascertain the mechanism of their formation. We report here the results of the first phase of an investigation which lead to the conclusion that at least two mechanisms are probably involved, although one of these is strongly predominant under the usual reaction conditions. We shall present four plausible mechanisms and examine them in the light of our experimental observations.

The α′-Chloro Ester Route. It has been long known that acid chlorides will react with aldehydes to produce α′-chloro esters (eq. 3).[6] In the aliphatic series,

$$\mathrm{RCOCl + RCHO \longrightarrow RCOOCHClR} \qquad (3)$$

catalysis by a Lewis acid such as zinc chloride appears to be necessary, but catalysis is not needed in the aromatic series. It would be expected that tri-*n*-butyltin chloride could function as a Lewis acid, albeit, not as effectively as zinc chloride. Thus aldehyde formed by the reduction of acid chloride could react with unreacted acid chloride to form α′-chloro ester, which, in turn, could be reduced to the ester by the generally accepted mechanism for reduction of alkyl halides involving the chain-carrying steps 4 and 5.

$$\mathrm{RCOOCHClR + Sn^{*}\cdot \longrightarrow RCOO\underset{\cdot}{C}HR + Sn^{*}Cl} \qquad (4)$$

$$\mathrm{RCOO\underset{\cdot}{C}HR + Sn^{*}H \longrightarrow RCOOCH_2R + Sn^{*}\cdot} \qquad (5)$$

A modification of the method of Adams and Vollweiller, was used for the preparation of α′-chlorobenzyl benzoate in virtually quantitative yield. The infrared spectrum showed all of the bands expected and none of the bands due to aldehyde or acid chloride. In 2,3-dimethylbutane solution the product reverts slowly to an equilibrium with the reactants. On the other hand, use of tri-*n*-butyltin chloride as solvent results in a solution containing equimolar amounts of ester, aldehyde, and acid chloride within 15 min. When the chloro ester was reduced with tri-*n*-butyltin hydride without solvent or in 2,3-dimethylbutane, the product contained at least 80% benzyl benzoate and a small amount of benzaldehyde. Reduction of benzoyl chloride under the same conditions in the absence of solvent led to product containing 65% benzaldehyde. Thus the chloro ester could be an intermediate in the reduction if it is formed rapidly enough and is reduced rapidly enough by the organotin hydride. These possibilities were tested.

When 1 mole each of benzaldehyde and of benzoyl chloride were mixed with 0.5 mole of tri-*n*-butyltin chloride, conversion to α′-chloro ester was about 50% complete in 24 hr. When tri-*n*-butyltin hydride was added to this mixture, the benzoyl chloride was completely consumed within another 24 hr., while the chloro ester was still present. Furthermore, the reduction of benzoyl chloride with the hydride is complete within 15 hr. under these conditions. It can be concluded that both the formation and reduction of the chloro ester are too slow for it to be a significant intermediate in the reaction.

Similar experiments with propionyl chloride and propionaldehyde revealed that formation of the corresponding chloro ester proceeds even more slowly than in the example above. Propionyl chloride is reduced nearly six times as rapidly as is benzoyl chloride.[5] Clearly the chloro ester cannot be an important intermediate in this case either.

The Alcohol Route. This mechanism would involve reduction of the aldehyde formed in reaction 2 to the alcohol, which could react with acid chloride to form ester (reactions 6 and 7). It could be shown that

$$\mathrm{RCHO + 2Sn^{*}H \longrightarrow RCH_2OH + Sn^{*}\text{–}Sn^{*}} \qquad (6)$$

$$\mathrm{RCH_2OH + RCOCl \longrightarrow RCH_2OCOR + HCl} \qquad (7)$$

$$\mathrm{HCl + Sn^{*}H \longrightarrow H_2 + Sn^{*}Cl} \qquad (8)$$

(6) is catalyzed by tri-*n*-butyltin chloride, but even the catalyzed reaction was much slower than reduction of the acid chloride. Furthermore, any hydrogen chloride formed would be expected to react with the hydride according to (8) to form hydrogen and waste hydride. No hydrogen was detected. The stoichiometry for the sequence 1, 2, 6, 7 requires 3 moles of hydride per mole of acid chloride, whereas only 2 moles are required even when large amounts of ester are formed. Finally, there was no indication of significant amounts of ditin in the reaction product mixtures. This mechanism can be discarded with confidence.

The Organotin Alkoxide Route. Present evidence shows that reaction 6 is almost certainly a composite of two reactions, 9 and 10. Reaction 9 can be brought

$$\mathrm{Sn^{*}H + RCHO \longrightarrow Sn^{*}OCH_2R} \qquad (9)$$

$$\mathrm{Sn^{*}OCH_2R + Sn^{*}H \longrightarrow HOCH_2R + Sn^{*}\text{–}Sn^{*}} \qquad (10)$$

about at moderate temperatures in the presence of azobisisobutyronitrile[7] or zinc chloride[8] or photochemically.[9] It appears, therefore, that the reaction can proceed by either a free-radical chain mechanism with chain-carrying steps 11 and 12 or by a polar mechanism which is catalyzed by Lewis acids. Sawyer and Neumann, *et al.*, have shown that reaction 10 occurs readily.[10] Since organotin radicals are formed under the

$$\mathrm{Sn^{*}\cdot + RCHO \longrightarrow Sn^{*}O\underset{\cdot}{C}HR} \qquad (11)$$

$$\mathrm{Sn^{*}O\underset{\cdot}{C}HR + Sn^{*}H \longrightarrow Sn^{*}OCH_2R + Sn^{*}\cdot} \qquad (12)$$

reaction conditions, the extent to which eq. 11 and 12 occur depends upon how fast reaction 11 is in comparison with reaction of these radicals with other species such as the acid chloride. The organotin alkoxide would be expected to react readily with the acid chloride to form the ester (reaction 13); the over-all reaction would have the observed stoichiometry and no hydride would be wasted in either alcohol or hydrogen formation.

$$\mathrm{Sn^{*}OCH_2R + RCOCl \longrightarrow RCH_2OCOR + Sn^{*}Cl} \qquad (13)$$

We sought to determine how reaction 11 compares in rate with the reaction of the organotin radical with

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(5) H. G. Kuivila and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, **87**, 571 (1965).

(6) H. E. French and R. Adams, *ibid.*, **43**, 651 (1921); R. Adams and E. H. Vollweiller, *ibid.*, **40**, 1732 (1918).

(7) W. P. Neumann, H. Niermann, and R. Sommer, *Angew. Chem.*, **73**, 768 (1963); *Ann.*, **659**, 27 (1962); **683**, 11 (1965).

(8) W. P. Neumann and E. Heymann, *Angew. Chem.*, **75**, 166 (1963); *Ann.*, **683**, 24 (1965).

(9) R. Calas, J. Valade, and J. C. Pommier, *Compt. rend.*, **255**, 1450 (1962); J. Valade and J. C. Pommier, *Bull. soc. chim. France*, 199 (1963).

(10) A. K. Sawyer, *J. Am. Chem. Soc.*, **87**, 537 (1965); W. P. Neumann, *et al.*, *Angew. Chem.*, **76**, 849, 891 (1964).

the acid chloride. 2-Bromooctane is 2.3 times as reactive as 1-bromooctane toward the tri-*n*-butyltin radical and 2.1 times as reactive as benzoyl chloride.[11] Thus 1-bromooctane and benzoyl chloride have virtually the same reactivity. We therefore generated organotin radicals in the presence of benzaldehyde by mixing equimolar amounts of 1-bromooctane, benzaldehyde, and the organotin hydride. When all of the organotin hydride was consumed, the infrared spectrum had a modest carbonyl absorption of benzaldehyde at 1710 cm.$^{-1}$, and a band at 1050 cm.$^{-1}$ due to a carbon–oxygen stretching vibration. Gas chromatographic analysis showed less than 5% benzyl alcohol and 35% *n*-octane as well as peaks due to unreacted 1-bromooctane and tri-*n*-butyltin bromide. Treatment of the mixture with benzoyl chloride resulted in a highly exothermic reaction. The product showed a band due to an ester carbonyl at 1730 cm.$^{-1}$ and no band at 1050 cm.$^{-1}$. Gas chromatographic analysis revealed much benzyl benzoate, and tri-*n*-butyltin chloride in concentration twice that of tri-*n*-butyltin bromide. These results are interpreted in terms of reaction sequence 14.

$$n\text{-}C_8H_{17}Br + PhCHO + Sn^*H \longrightarrow$$

$$\underset{35\%}{n\text{-}C_8H_{18}} + \underset{65\%}{Sn^*OCH_2Ph} + \underset{35\%}{Sn^*Br} \qquad (14)$$

$$\Big\downarrow \text{PhCOCl}$$

$$\underset{65\%}{Sn^*Cl} + \underset{65\%}{PhCOOCH_2Ph}$$

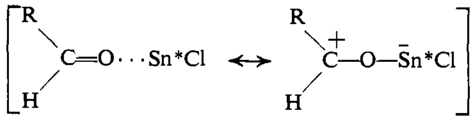
Several other similar experiments were carried out with the results given in Table I. As expected, the effectiveness of the bromides in competing with benzaldehyde for the organotin radical increases in the order 1-bromooctane < 2-bromooctane < benzyl bromide.

Table I. Yields of Hydrocarbon and Esters[a] (Alkoxides) from the Reaction of Alkyl Halides with Tri-*n*-butyltin Hydride in the Presence of Aldehydes[b]

R-Br	Aldehyde	Yield, % R-H	Yield, % C_2H_5-CO_2CH_2R
1-BrC_8H_{17}	C_6H_5CHO	30	65
1-BrC_8H_{17}	$(CH_3)_2CHCHO$	85-95	5
2-BrC_8H_{17}	C_6H_5CHO	50	49
$C_6H_5CH_2Br$	C_6H_5CHO	69	37

[a] Formed after treatment of reaction product with propionyl chloride. [b] Neat; ambient temperature.

In the absence of solvent the reduction of benzaldehyde by tri-*n*-butyltin hydride requires about 10 days for completion, whereas the reduction of benzoyl chloride under the same conditions is complete in about 15 hr. This would indicate that the alkoxide path cannot be significant in the formation of ester. However, addition of 5 mole % of either propionyl chloride or 1-bromooctane to the mixture of benzaldehyde and hydride results in a definite enhancement in rate of reduction of the aldehyde. Addition of 5 mole % of tri-*n*-butyltin chloride also enhances the rate, and addition of an equimolar amount increases the rate to virtually that of the reduction of benzoyl chloride. The organotin chloride catalyzes the reaction most probably because of its ability to function as a Lewis acid as Neumann has suggested for zinc chloride.[8] Coordination with the oxygen of the carbonyl group would make the carbonyl carbon sufficiently electrophilic so that it could abstract a hydride ion from the hydride to initiate the addition reaction. This electrophilic catalysis accounts for the observation reported earlier[5] that reduction of propionyl chloride in dimethylbutane or methyl acetate yielded aldehyde as major product, while use of tri-*n*-butyltin chloride as solvent provided the ester as the major product.



Further study is needed in order to determine if propionyl chloride and 1-bromooctane catalyze only by virtue of the organotin halides formed when they are reduced, or if another catalysis mechanism is also involved.

Several experiments were conducted in order to ascertain if the organotin chloride catalyzed alkoxide route might be a major pathway for ester formation under normal reduction conditions. Results are presented in Table II. Two facts are evident: the organotin chloride has little effect on the rate of reduction of the acid chloride; and the aldehyde is reduced more slowly in the presence of the organotin chloride than is the acid chloride in its absence. Therefore, it may be concluded that, although the alkoxide route undoubtedly provides some of the ester that is formed, it cannot be the major pathway and is probably of minor importance under normal reaction conditions.

Table II. Relative Rates of Reduction of an Acid Chloride and an Aldehyde[a]

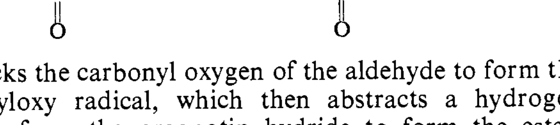
Reaction time, hr.	Expt.[b]	% reaction[c]
19	I	79
19	II	80
19	III	35
91	I	90
91	II	85
91	III	50

[a] Each addend 0.63 *M* in ethyl ether; ambient temperature. [b] (I) Tri-*n*-butyltin hydride and isobutyryl chloride; (II) tri-*n*-butyltin hydride, isobutyryl chloride and tri-*n*-butyltin chloride; (III) tri-*n*-butyltin hydride, isobutyraldehyde and tri-*n*-butyltin chloride. [c] Determined by intensity of Sn*–H band at 1810 cm.$^{-1}$.

The α-Acyloxy Radical Route. In the preceding paper we presented evidence that the acyl radical is an intermediate in aldehyde formation.[5] This radical could also be implicated in ester formation by the chain sequence shown in eq. 15 and 16. The acyl radical attacks the carbonyl oxygen of the aldehyde to form the α-acyloxy radical, which then abstracts a hydrogen atom from the organotin hydride to form the ester. If (15) is irreversible, the amounts of ester and alde-

 (15)

$$R\text{—}\dot{C}\text{=}O + RCHO \longrightarrow R\text{—}\underset{\underset{O}{\|}}{C}\text{—}O\dot{C}HR \qquad (15)$$

 (16)

$$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}O\dot{C}HR + Sn^*H \longrightarrow R\text{—}\underset{\underset{O}{\|}}{C}\text{—}OCH_2R + Sn^*\cdot \qquad (16)$$

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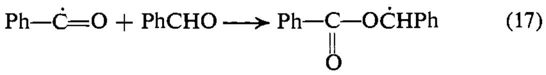
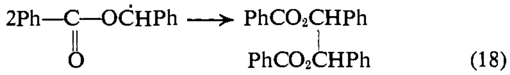
[11] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

hyde depend upon the relative effectiveness with which aldehyde and organotin hydride compete in reaction with the acyl radical.

The reaction of an acyl radical with a carbonyl oxygen has been observed before. Rust and coworkers[12] have shown that decomposition of di-*t*-butyl peroxide in benzaldehyde yields 85% of the dibenzoate of 1,2-diphenylethylene glycol. They attributed its formation to the reaction between the benzoyl radical and benzaldehyde to form the α-benzoyloxybenzyl radical (eq. 17), followed by coupling (eq. 18). The benzoyl radical has also been shown to attack the carbonyl oxygen of quinones.[13]



$$\mathrm{Ph{-}\dot{C}{=}O + PhCHO \longrightarrow Ph{-}\underset{\underset{O}{\|}}{C}{-}O\dot{C}HPh} \qquad (17)$$



$$2\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}O\dot{C}HPh \longrightarrow \begin{array}{l} PhCO_2CHPh \\ \quad\;\; | \\ PhCO_2CHPh \end{array}} \qquad (18)$$

As a means of testing the plausibility of the reaction sequence 15 and 16, we have examined the relative effectiveness of several carbonyl compounds in competition for the acyl radical (eq. 15). It would be expected that the acyl radical would act as a nucleophile if polar factors are of any consequence, because the acyl radical could assume acylium ion character in the transition state as shown below.[14] The carbonyl compounds were added in pairs to a reaction mixture containing limited amounts of propionyl chloride and tri-*n*-butyltin hydride. Yields of the two mixed esters were determined by g.l.c. and the relative rate constants for the two competitors computed by the equation of Ingold and Stow.[15] Results are displayed in Table III.

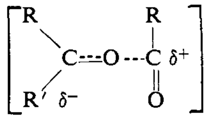


Table III. Relative Reactivities of Aldehydes and Ketones with Propionyl Radical at 25° in 2,3-Dimethylbutane

Carbonyl compd.	Relative[a] reactivity	σ^{+b}
n-Heptaldehyde	1.62	
m-Chlorobenzaldehyde	1.57	0.399
p-Chlorobenzaldehyde	1.26[c]	0.114
p-Methylbenzaldehyde	1.25	−0.311
Benzaldehyde	1.00	0.00
m-Methylbenzaldehyde	0.94	−0.066
p-Methoxybenzaldehyde	0.468	−0.778
Cyclohexanone[d]	0.093	
Cyclopentanone[d]	0.005	

[a] Based on at least two determinations. The relative rate constants were reproduced within ±4%. [b] From H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). [c] In methyl acetate. [d] At 45°.

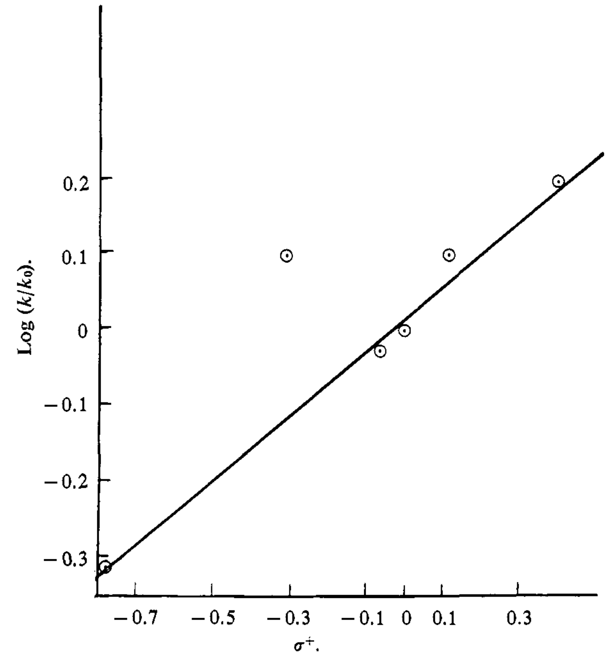
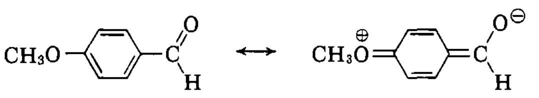


Figure 1. Hammett plot for ester formation from benzaldehydes in the reduction of propionyl chloride with tri-*n*-butyltin hydride.

A Hammett plot for the substituted benzaldehydes is shown in Figure 1. If σ^+ is used an excellent correlation with a ρ value of 0.43 is obtained for five of the substituents. The deviation for *p*-tolualdehyde is real, but the reason for this is obscure. If the normal σ values are used, the point for *p*-methoxy falls *below* the best line for the other substituents. This is attributable to conjugation between the methoxy and the formyl groups in the ground states, the energy of which must be overcome in passing to the transition state. A similar deviation was observed by Huyser and Neckers in the reaction of 2-hydroxy-2-butyl radicals with substituted acetophenones.[16] It is likely that such conjugation also exists in benzaldehyde itself. Since the reaction is facilitated by electron withdrawal in the carbonyl compound, one might expect benzaldehyde to be more effective than *n*-heptaldehyde because the phenyl group is more electron withdrawing than the *n*-hexyl group. *n*-Heptaldehyde is 62% more effective than benzaldehyde, however. Conjugation between the ring and the formyl group for which evidence has been presented[17] has two consequences: greater thermodynamic stability and a higher electron density at the carbonyl group. The present data do not permit a partition of the result between these two factors.



Cyclohexanone is less reactive toward the propionyl radical than the aldehydes, and cyclopentanone is still less reactive. The lower reactivity of these ketones, and of acetone and acetophenone,[5] can be attributed to electron release by the alkyl groups. The greater reactivity of cyclohexanone over cyclopentanone can be interpreted if it is assumed that the α-acyloxy free

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(12) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, 70, 3258 (1948).

(13) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953); A. Schonberg and A. Mustafa, *Chem. Rev.*, 40, 181 (1947).

(14) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., p. 273 ff.

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

(16) E. S. Huyser and D. C. Neckers, *J. Am. Chem. Soc.*, **84**, 3641 (1963).

(17) F. A. L. Anet and M. Ahmad, *ibid.*, **86**, 120 (1964); E. A. Braude in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press Inc., New York, N. Y., 1955, p. 172 ff.; H. C. Brown and K. Ichikawa, *J. Am. Chem. Soc.*, **84**, 373 (1962).

Table IV. Relative Rates of Alkoxide Formation[a]

	Relative rate			
Aldehyde	C_2H_5COCl[b]	$C_8H_{17}Br$	Sn*Cl	$CHCl_3$
$CH_3(CH_2)_5CHO$	1.62	2.15 ± 0.04		
m-ClC_6H_4CHO	1.57	5.42 ± 0.42 (4.02 ± 0.16)[c]	3.65 ± 0.04	4.72 ± 0.10
p-ClC_6H_4CHO	1.26[d]	1.93 ± 0.06		
p-$CH_3C_6H_4CHO$	1.25	1.18 ± 0.01	1.05 ± 0.04	
C_6H_5CHO	1.00	1.00	1.00	1.00
m-$CH_3C_6H_4CHO$	0.94	1.03 ± 0.03		
p-$CH_3OC_6H_4CHO$	0.47	<0.16		

[a] In 2,3-dimethylbutane, (0.63 *M*) at 25°. [b] From Table III. [c] Solvent: 60% 2,3-dimethylbutane and 40% tri-*n*-butyltin chloride. [d] In methyl acetate.

radical has a tetrahedral configuration. Conversion from trigonal to tetrahedral in a carbon atom of the five-membered ring will lead to increased strain due to the establishment of new eclipsing inter-nonbonded interactions.[18]

It was of interest to compare the results described above with those obtainable for the formation of alkoxide by the free-radical mechanism or the Lewis acid catalyzed mechanism or both. For this study approximately equimolar amounts of 1-bromooctane or 2-bromooctane, tri-*n*-butyltin hydride, and each of two competing aldehydes were allowed to react until the hydride was consumed. The reaction mixture was treated with propionyl chloride, the concentrations of the two propionate esters were determined by g.l.c., and the relative rates of reaction of the aldehydes (to form the alkoxides) were computed. Two experiments were carried out with chloroform instead of octyl bromide and three with tri-*n*-butyltin chloride. The latter should give the largest amount of alkoxide by the polar mechanism. Results are given in Table IV, along with those for the corresponding reactions with propionyl chloride. A Hammett plot for the octyl bromide reactions is shown in Figure 2 with regular σ values, and the value of ρ is about 1.85. It is clear from the data in the table that the organotin chloride serves to lower the value of ρ. This suggests, rather surprisingly, that the Lewis acid catalyzed alkoxide formation is less sensitive to polar factors than is the free-radical reaction.

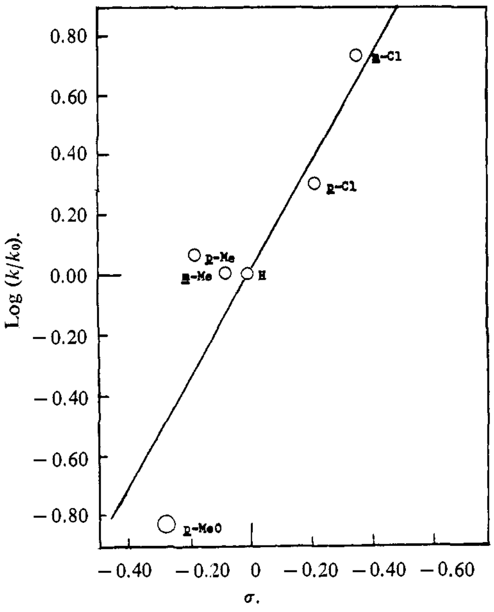

Figure 2. Hammett plot for alkoxide formation from substituted benzaldehydes at 25°.

From the data now available, it is reasonable to conclude that the reduction of acid chlorides under ordinary conditions (a) does not proceed through the alcohol or α'-chloro ester routes to any significant extent, (b) probably proceeds through the organotin alkoxide route to a minor extent, and (c) most probably proceeds through the α-acyloxy radical as the major route.

Experimental Section

All reactions involving organotin hydrides were conducted in an atmosphere of prepurified nitrogen. Infrared spectra were determined with a Perkin-Elmer

Table V. Relative Rates of Ester Formation from Aldehydes and Ketones[a]

Expt. no.	Competitor A	Competitor B	Solvent	k_A/k_B
1	Cyclohexanone	Cyclopentanone	DMB[b]	12.30[c]
2	Cyclohexanone	Cyclopentanone	DMB	17.71[c]
3	Cyclohexanone	Cyclopentanone	DMB	17.94[c]
4	C_6H_5CHO	Cyclohexanone	DMB	11.00[d]
5	C_6H_5CHO	Cyclohexanone	DMB	10.54[d]
6	$CH_3(CH_2)_5CHO$	C_6H_5CHO	DMB	1.53
7	$CH_3(CH_2)_5CHO$	C_6H_5CHO	DMB	1.70
8	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	1.57
9	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	1.57
10	*p*-MeC_6H_4CHO	C_6H_5CHO	DMB	1.26
11	*p*-MeC_6H_4CHO	C_6H_5CHO	DMB	1.25
12	*p*-ClC_6H_4CHO	C_6H_5CHO	MeOAc	1.25
13	*p*-ClC_6H_4CHO	C_6H_5CHO	MeOAc	1.27
14	C_6H_5CHO	Cyclohexanone	DMB	10.86
15	*m*-MeC_6H_4CHO	C_6H_5CHO	DMB	0.92
16	*m*-MeC_6H_4CHO	C_6H_5CHO	DMB	0.96
17	$CH_3(CH_2)_5CHO$	*p*-$MeOC_6H_4CHO$	$C_6H_5CH_3$	5.16
18	$CH_3(CH_2)_5CHO$	*p*-$MeOC_6H_4$-CHO	$C_6H_5CH_3$	2.81
19	$CH_3(CH_2)_5CHO$	*p*-$MeOC_6H_4$-CHO	$C_6H_5CH_3$	3.85
20	$CH_3(CH_2)_5CHO$	*p*-$MeOC_6H_4$-CHO	$C_6H_5CH_3$	3.06
21	*p*-MeC_6H_4CHO	C_6H_5CHO	DMB	1.27
22	*p*-MeC_6H_4CHO	C_6H_5CHO	DMB	1.20
23	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	1.84
24	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	1.69

[a] 3.8 mmoles of propionyl chloride, tri-*n*-butyltin hydride, and each competitor in 5 ml. of solvent. [b] 2,3-Dimethylbutane. [c] 45°. [d] Trimethyltin hydride was used.

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(18) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Am. Chem. Soc.*, 73, 212 (1951).

Table VI. Relative Reactivities of Aldehydes in Alkoxide Formation[a]

Expt. no.	RX	Competitor A	Competitor B	Solvent	k_A/k_B
1	1-BrC_8H_{17}	*p*-ClC_6H_4CHO	C_6H_5CHO	MeOAc	1.99
2	1-BrC_8H_{17}	*p*-ClC_6H_4CHO	C_6H_5CHO	MeOAc	1.86
3	2-BrC_8H_{17}	*p*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB[b]	1.17
4	2-BrC_8H_{17}	*p*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB	1.19
5	2-BrC_8H_{17}	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	5.84
6	2-BrC_8H_{17}	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	5.00
7	2-BrC_8H_{17}	*m*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB	1.05
8	2-BrC_8H_{17}	*m*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB	1.00
9	2-BrC_8H_{17}	*n*-Heptaldehyde	C_6H_5CHO	DMB	2.11
10	2-BrC_8H_{17}	*n*-Heptaldehyde	C_6H_5CHO	DMB	2.18
11	$CHCl_3$	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	4.64
12	$CHCl_3$	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	4.84
13	2-BrC_8H_{17}	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB[c] Sn*Cl[d]	4.18
14	2-BrC_6H_{17}	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB[c] Sn*Cl[d]	3.85
15	2-BrC_8H_{17}	*n*-Heptaldehyde	*p*-$CH_3OC_6H_4CHO$	DMB	10.0[e]
16	2-BrC_8H_{17}	*n*-Heptaldehyde	*p*-$CH_3OC_6H_4CHO$	DMB	10.0[e]
17	Sn*Cl	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	3.62
18	Sn*Cl	*m*-ClC_6H_4CHO	C_6H_5CHO	DMB	3.68
19	Sn*Cl	*p*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB	1.01
20	Sn*Cl	*p*-$CH_3C_6H_4CHO$	C_6H_5CHO	DMB	1.09

[a] These reactions were catalyzed by the reaction of the alkyl bromide with tri-*n*-butyltin hydride or by tri-*n*-butyltin chloride at 25° (0.63 *M*). [b] 2,3-Dimethylbutane. [c] 3 ml. [d] 2 ml. [e] Not precisely determined owing to the extremely small amount of anisyl propionate present; 10.0 is a minimum value.

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 and *n*-heptane were used as internal standards with a 4-ft. stainless steel column packed with 10% silicone rubber (Se-30) on Chromosorb P, 60–80 mesh (F&M Scientific Co.).

Materials. The acid chlorides, solvents, and aldehydes used were all commercially available and of high purity as shown by gas chromatography. The aldehydes were stored under nitrogen in a refrigerator and their purity was checked periodically by gas chromatography. The esters and the organotin hydrides used were prepared as described in the previous paper.[5]

Preparation of α-Chlorobenzyl Benzoate.[6,19] Into an erlenmeyer flask were place 14.06 g. of benzoyl chloride, 10.63 g. of benzaldehyde, and a pinch of freshly fused zinc chloride. The flask was flushed with nitrogen and tightly stoppered; after about 10 min., the reaction mixture took on an amber color as a highly exothermic reaction ensued. It was then allowed to stand at room temperature for about 24 hr. Addition of *n*-hexane to this mixture produced large amounts of a white fluffy precipitate which was filtered quickly and stored under nitrogen in the refrigerator. This compound is unstable on standing at room temperature even under nitrogen. A 12% solution of the ester in 2,3-dimethylbutane indicated all ester absorptions: 1730, 1255, 1060, and 1080 cm.$^{-1}$. Acid chloride and aldehyde absorptions were absent.

Relative Reactivities of Carbonyl Compounds in Propionate Ester Formation. Known amounts of two competing carbonyl compounds were mixed with an equimolar amount of propionyl chloride and the organotin hydride. Both carbonyl compounds were in excess of the amount of hydride used. 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 all the hydride had been consumed; it was then analyzed by gas chromatography. The yields of the propionates were determined by the internal standard method.[15] The relative rate constants were calculated by the equation of Ingold and Stow[15]

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

in which A_0 and A and B_0 and B are initial and final concentrations of the competing carbonyl compounds. The final concentrations of the carbonyl compounds were found by subtracting the yield of the ester from the initial concentration of the corresponding compound. The relative rate constants obtained for the competition experiments are given in Table V.

Relative Reactivities of Aldehydes in Tri-n-butyltin Alkoxide Formation. Known amounts of two competing aldehydes were mixed with an equimolar amount of an alkyl halide and tri-*n*-butyltin hydride. Both aldehydes were in excess of the amount of hydride used. 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 all the hydride had been consumed. An excess of propionyl chloride was added, the resultant mixture was analyzed by gas chromatography, and the amounts of the respective propionate esters were determined by g.l.c. using an internal standard.[15] The relative rate constants were calculated in the same way as described for the competitive experiments with propionyl chloride and are given in Table VI.

(19) We are indebted to P. R. Jones and R. Nadeau for this procedure and a description of this compound.