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# THE REACTION OF ACID CHLORIDES WITH TRI-N-BUTYLTIN HYDRIDE. A STUDY ON SCOPE AND MECHANISM

BY

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B. S., Albany State College of Education, 1960

A THESIS

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Alexander R.

Kenneth K Andersen

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Date

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The author wishes to dedicate this thesis to his wife, Laureen.

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# INTRODUCTION

A review article on the reactions of organotin hydrides with organic compounds has recently been published.[1] In view of this fact, we shall concern ourselves mainly with those reductions which have immediate pertinence to this work.

In 1957, van der Kerk reported the first reduction of alkyl halides by organotin hydrides.[2] Since then several papers on reductions of this type, Eq. (1), in which $\underline{Sn}$ is a trisubstituted tin group, have appeared.[3]

$$R\text{-}X + \underline{Sn}\text{-}H \rightarrow R\text{-}H + \underline{Sn}\text{-}X \qquad (1)$$

Recently, Menapace and Kuivila[4] have provided evidence for a free radical chain mechanism for these reactions, Eq. (2) - (6).

$$\underline{Sn}\text{-}H + Q\cdot \rightarrow \underline{Sn}\cdot + Q\text{-}H \qquad (2)$$

$$\underline{Sn}\cdot + R\text{-}X \rightarrow \underline{Sn}\text{-}X + R\cdot \qquad (3)$$

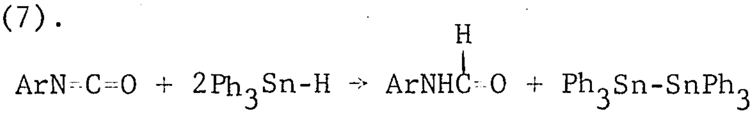
$$R\cdot + \underline{Sn}\text{-}H \rightarrow \underline{Sn}\cdot + R\text{-}H \qquad (4)$$

$$2\ \underline{Sn}\cdot \rightarrow \underline{Sn}\text{-}\underline{Sn} \qquad (5)$$

$$2\ R\cdot \rightarrow R\text{-}R \text{ or } R(+H) + R(-H) \qquad (6)$$

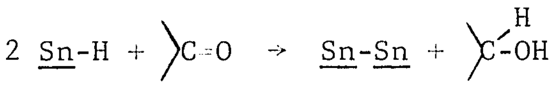
Aryl halides have also been found to undergo reduction with these hydrides.[5]

Certain carbonyl functions have been reduced with organotin hydrides. When phenyl or α-napthyl isocyanate was treated with two equivalents of triphenyltin hydride, the corresponding aryl formamides were produced in 40-50% yield[6], Eq. (7).



$$ArN{=}C{=}O + 2Ph_3Sn\text{-}H \rightarrow ArNH\overset{H}{C}{=}O + Ph_3Sn\text{-}SnPh_3 \qquad (7)$$

Aldehydes and ketones are reduced by organotin hydrides to the alcohol[7,8], Eq. (8). In this reaction a large variation in reactivity has been found[7] among the hydrides,



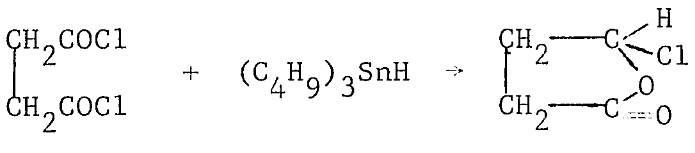
$$2\ \underline{Sn}\text{-}H + {>}C{=}O \rightarrow \underline{Sn}\text{-}\underline{Sn} + {>}\overset{H}{C}\text{-}OH \qquad (8)$$

the order of decreasing reactivity being $(C_6H_5)_2SnH_2 > (\underline{n}\text{-}C_4H_9)_2SnH_2 > \underline{n}\text{-}C_4H_9SnH_3 > (C_6H_5)_3SnH > (\underline{n}\text{-}C_4H_9)_3SnH$.

Acid chlorides have also been reduced by organotin hydrides. Van der Kerk, Noltes and Luijten[9] reported that benzaldehyde was obtained from the reduction of benzoyl chloride with triphenyltin hydride, Eq. (9).

$$(C_6H_5)_3SnH + C_6H_5COCl \rightarrow (C_6H_5)_3SnCl + C_6H_5CHO \qquad (9)$$

Kuivila[10] found that when one mole of tri-n-butyltin hydride was added to a mole of succinyl dichloride at 40°, the only product found was γ-chloro γ-butyrolactone, Eq. (10).



(10)

When phthalyl dichloride was reduced under the same conditions with two moles of the hydride, a 55% yield of phthalide was isolated.

# RESULTS AND DISCUSSION

## SCOPE

### General

In our study of the reaction of acid chlorides with tri-n-butyltin hydride it has been found that the production of the expected aldehyde is not the only course that the reaction takes, Eq. (11). Indeed in some cases, the production of ester is the predominant route, Eq. (12). The relative yields of ester and aldehyde are dependent upon the

$$\mathrm{RCOCl} + \underline{\mathrm{Sn}}\text{-H} \rightarrow \mathrm{RCHO} + \underline{\mathrm{Sn}}\text{-Cl} \tag{11}$$

$$2\ \mathrm{RCOCl} + 2\ \underline{\mathrm{Sn}}\text{-H} \rightarrow \mathrm{RCO_2CH_2R} + 2\ \underline{\mathrm{Sn}}\text{-Cl} \tag{12}$$

acid chloride used as well as the experimental conditions employed. In Table I are compiled the results of reductions of the acid chlorides studied.

When an acid chloride is mixed with tri-n-butyltin hydride at room temperature, an exothermic reaction frequently results and the ester is often the main product. The reaction is usually complete within 20 hrs. Notable exceptions are ethyl and benzyl chloroformates. These are extremely unreactive substrates and, when not undergoing fragmentation (see below), yield only the primary reduction product, the formate ester. The reaction of ethyl chloroformate and tri-n-butyltin hydride is not complete even after five weeks at ambient temperature. The same type of low reactivity is found with benzyl chloroformate, the reaction going to completion in about two weeks.

Only two acid bromides have been investigated, and

## TABLE I

The Reaction of Acid Halides with Tri-*n*-butyltin Hydride Neat and in Solution (0.63 M) at Ambient Temperature[a]

| | Neat | | | Solution | |
|---|---|---|---|---|---|
| R-in R-COCl | % Yield RCHO | % Yield $RCO_2CH_2R$ | Solvent | % Yield RCHO | $RCO_2CH_2R$ |
| $CH_3$ | 5 | 95 | | | |
| $C_2H_5$ | 1[b] | 87[c] | DMB | 75 | 25 |
| | | | MeOAc | 90 | 10 |
| | | | (*n*-$C_4H_9)_3$Sn-Cl | 27 | 73 |
| *n*-$C_4H_9$ | 19 | 81 | DMB | 91 | 9 |
| *i*-$C_3H_7$ | 36 | 64 | DMB | 52 | 48 |
| *t*-$C_4H_9$[e] | 56 | 33 | | | |
| $PhCH_2$ | | | $C_6H_5CH_3$ | 55 | 45 |
| Ph | 65 | 35 | *m*-xylene | 85 | 15 |
| $Ph_3C$[f] | | | *m*-xylene | 90 | 1[b] |
| $C_2H_5O$ | 95 | 1[b] | | | |
| $PhCH_2O$ | 61 | 1[b] | | | |
| RCOBr | | | | | |
| $C_2H_5$ | 79 | 21 | DMB | 60 | 40 |
| Ph | 99 | 1[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-dimethyl butane.

[e] Private communication, Henry G. Kuivila.

[f] Yield based on isolation experiment.

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

As the alkyl group becomes larger and more branched, the yield of aldehyde increases. When one goes from acetyl to 2,2-dimethylpropionyl chloride the aldehyde yield increases from 5% to 56% and the corresponding ester yield falls from 95% to 33%. The use of solvent exerts a profound influence upon the course of the reaction. When the reductions are carried out in 2,3-dimethyl butane, 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. Here, the neat reaction affords almost all ester, but when 2,3-dimethyl butane is employed as a solvent, only a 25% yield of ester is found. Valeryl chloride gives much the same results. The neat reaction produces an 81% yield of the ester but the same reaction conducted in 2,3-dimethyl butane gives only a 9% yield of the ester. An important exception to this solvent effect is that of tri-n-butyltin chloride which will be discussed later.

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; Eq. (13). For example, the addition of one mole

$$\mathrm{RCOCl} + {>}\mathrm{C{=}O} + \underline{\mathrm{Sn}}\text{-}\mathrm{H} \rightarrow \mathrm{RCHO} + \mathrm{RCOOCH_2R} + \underline{\mathrm{Sn}}\text{-}\mathrm{Cl} + \mathrm{RCO_2}\text{-}{>}\mathrm{C}\text{-}\mathrm{H} \tag{13}$$

of benzaldehyde to a mixture of a mole each of propionyl chloride and tri-n-butyltin hydride resulted in a 70% yield of benzyl propionate, Eq. (14). Here again the presence of

$$\mathrm{EtCOCl} + \underline{\mathrm{Sn}}\text{-H} + \mathrm{PhCHO} \rightarrow \mathrm{PhCH_2OOCEt} + \mathrm{EtCHO} + \mathrm{EtCH_2OOCEt} + \underline{\mathrm{Sn}}\text{-Cl} \quad (14)$$

solvent is felt. When this same reaction is conducted in solution (0.63 M) in either toluene or 2,3-dimethyl butane 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 reaction mixture, without solvent 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 conditions as determined by relative areas of <u>n</u>-propyl propionate to "mixed" ester in gas chromatographic analysis.

## TABLE II

### Yields of Esters from the Reaction of Acid Chlorides with a Tri-n-butyltin Hydride in the Presence of Added Carbonyl Compounds at Room Temperature

| ROCl | R'R"CO | Solvent (0.63M) | % Yield $RCO_2CH_2R$ | % Yield $RCO_2CHR'R''$ |
|---|---|---|---|---|
| $CH_3$ | 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 |
| $C_2H_5$ | $C_6H_5CHO$[a] | DMB[b] | c | 63 |
| $C_2H_5$ | $C_6H_5CHO$ | DMB | c | 34 |
| $C_2H_5$ | $C_6H_5CHO$ | $Et_2O$ | c | 13 |
| $C_2H_5$ | $C_6H_5CHO$ | Toluene | 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-$ClC_6H_4CHO$ | MeOAc | 14 | 5.1 |
| $C_2H_5$ | p-$CH_3OC_6H_4CHO$ | Toluene | c | 13 |
| $C_2H_5$ | p-$CH_3OC_6H_4CHO$ | $Et_2O$ | c | 20 |

[a] Trimethyltin hydride was used.

[b] 2,3-dimethyl butane.

[c] Yield not determined.

# MECHANISM OF THE FORMATION OF ALDEHYDE

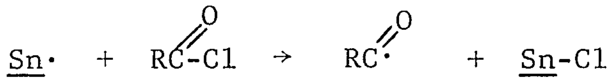
## General

The main purpose of this work was to attempt to elucidate the mechanism of the reaction between acid chlorides and tri-n-butyltin hydride. Several mechanisms can be considered since we must account for the formation of both aldehyde and ester. For the purpose of simplicity, we shall consider separately the mechanisms of aldehyde and ester formation.

## The Mechanism for the Formation of Aldehydes

It has been demonstrated recently that the reaction between alkyl halides and tri-n-butyltin hydride proceeds by a free radical chain mechanism[4] involving abstraction of the halogen atom by a tin radical and subsequent reaction of the alkyl radical with another mole of tin hydride to produce the reduced product and another tin radical, Eq. (3) and (4). Since the reaction of acid chlorides with the same hydride occurs readily in non-polar solvents, it was felt that a free radical mechanism may also be involved here. Results obtained in the study of this reaction are by and large consistent with a free radical mechanism. Equations (15) - (17),

$$Q\cdot + \underline{Sn}\text{-}H \rightarrow QH + \underline{Sn}\cdot \tag{15}$$



$$\underline{Sn}\cdot + RC(=O)\text{-}Cl \rightarrow RC(=O)\cdot + \underline{Sn}\text{-}Cl \tag{16}$$

$$RC(=O)\cdot + \underline{Sn}\text{-}H \rightarrow RC(=O)\text{-}H + \underline{Sn}\cdot \tag{17}$$

comprise our mechanistic hypothesis for the formation of the aldehyde. In this scheme Q· is some free radical possibly resulting 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 react by abstracting a chloride atom from the acid chloride generating an acyl free radical. The acyl radical can then react with another mole 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

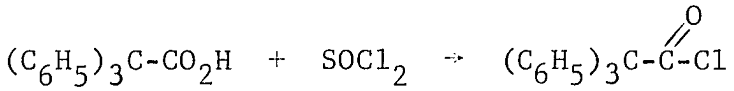
Acyl radicals have been shown to be intermediates in vapor phase decompositions of some ketones and aldehydes and are usually generated in solution by peroxides or photochemically.[11,12] Photolysis of acyl xanthates constitutes a new method for the preparation of these radicals which has recently been reported by Barton, et al.[13] Probably the most important reaction of acyl radicals is decarbonylation at moderately high temperatures.[11,14] They can therefore be used as intermediates in the formation of alkyl radicals, Eq. (18). Furthermore, the formation of carbon monoxide may

$$R\dot{C}{=}O \xrightarrow{\Delta} R\cdot + CO \qquad (18)$$

be taken to indicate the intermediacy of acyl radicals. Because tri-n-butyltin hydride is an efficient free radical trap, it was necessary to use an acid chloride whose derived acyl radical would decarbonylate with ease, i.e., one which would yield a particularly stable alkyl radical. The acid chloride selected for these experiments was triphenylacetyl chloride which was prepared according to the scheme below.

$$3\ C_6H_6 + CCl_4 \xrightarrow{AlCl_3} (C_6H_5)_3C\text{-}Cl$$

$$(C_6H_5)_3C\text{-}Cl + Mg \rightarrow (C_6H_5)_3C\text{-}Mg\text{-}Cl \xrightarrow[\text{(2) hydr.}]{\text{(1) } CO_2} (C_6H_5)_3C\text{-}CO_2H$$



$$(C_6H_5)_3C\text{-}CO_2H + SOCl_2 \rightarrow (C_6H_5)_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl$$

Numerous attempts were made by mixing together the acid chloride and hydride in xylene and heating the reaction mixture to 100-110° in a closed system attached to a gas burette. In every case the amount of gas collected was too small to give a good infrar-red spectrum. However, if the hydride was added slowly, thereby limiting the availability of this efficient trap, enough carbon monoxide was collected to give the characteristic infra-red spectrum.[15] The yield of the gas, as judged from the volume was 10-12%. A 5% yield of triphenylmethane was isolated along with a 90% yield of triphenylacetaldehyde. Eq. (19)-(22), account for these results.

$$Ph_3CCOCl + \underline{Sn}\cdot \rightarrow Ph_3C\dot{C}{=}O + \underline{Sn}\text{-}Cl \tag{19}$$

$$Ph_3C\dot{C}{=}O + \underline{Sn}\text{-}H \rightarrow Ph_3CCHO + \underline{Sn}\cdot \tag{20}$$

$$Ph_3C\dot{C}{=}O \rightarrow Ph_3C\cdot + CO \tag{21}$$

$$Ph_3C\cdot + \underline{Sn}\text{-}H \rightarrow Ph_3C\text{-}H + \underline{Sn}\cdot \tag{22}$$

A control experiment was run on the same scale under the same conditions as the experiment above with the organotin 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, may react with the hydride, Eq. (23) - (25). After 4.5 hrs. of heating there was no evolution of gas.

$$\mathrm{Ph_3CCOCl} + \underline{\mathrm{Sn}}\mathrm{-Cl} \rightarrow \mathrm{Ph_3C\overset{+}{C}{=}O} + \underline{\mathrm{Sn}}\mathrm{Cl_2^-} \tag{23}$$

$$\mathrm{Ph_3C\overset{+}{C}{=}O} \rightarrow \mathrm{Ph_3C^+} + \mathrm{CO} \tag{24}$$

$$\mathrm{Ph_3C^+} + \underline{\mathrm{Sn}}\mathrm{-H} \rightarrow \mathrm{Ph_3C{-}H} + \underline{\mathrm{Sn}}^+ \tag{25}$$

Another type of fragmentation was observed in the reduction of benzylchloroformate. The benzyloxycarbonyl 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; Eq. (26) - (29). Gas chromatographic anlysis indicated a 39% yield of toluene and a 61% yield of the benzoyl formate.

$$\mathrm{PhCH_2OCOCl} + \cdot\underline{\mathrm{Sn}} \rightarrow \mathrm{PhCH_2O\dot{C}{=}O} + \underline{\mathrm{Sn}}\mathrm{-Cl} \tag{26}$$

$$\mathrm{PhCH_2O\dot{C}{=}O} \rightarrow \mathrm{PhCH_2\cdot} + \mathrm{CO_2} \tag{27}$$

$$\mathrm{PhCH_2O\dot{C}{=}O} + \underline{\mathrm{Sn}}\mathrm{-H} \rightarrow \mathrm{PhCH_2OCHO} + \underline{\mathrm{Sn}}\cdot \tag{28}$$

$$\mathrm{PhCH_2\cdot} + \underline{\mathrm{Sn}}\mathrm{-H} \rightarrow \mathrm{PhCH_3} + \underline{\mathrm{Sn}}\cdot \tag{29}$$

This type of free radical fragmentation was first observed by Thynne and Gray[16], usually at higher temperatures, with the methoxycarbonyl free radical. This intermediate, at the temperature used, 120-185°, breaks down quantitatively to the methyl radical and carbon dioxide; Eq. (30) - (33).

$$(CH_3)_2O_2 \rightarrow 2\ CH_3O\cdot \qquad (30)$$

$$CH_3O\cdot + H\text{-}CO_2CH_3 \rightarrow CH_3OH + O{=}\dot{C}OCH_3 \qquad (31)$$

$$CH_3O\dot{C}{=}O \rightarrow CO_2 + CH_3\cdot \qquad (32)$$

$$CH_3\cdot + H\text{-}CO_2CH_3 \rightarrow CH_4 + O{=}\dot{C}OCH_3 \qquad (33)$$

At higher temperatures the amount of fragmentation of the benzyloxy radical would be expected to increase. In an experiment conducted at room temperature, the reaction was allowed to proceed for four days at which time it had only gone 30% of the way to completion as determined by infrared analysis. The reaction mixture was subjected to gas chromatographic analysis without quenching with the injection port at 180°. In this case the toluene was the major product with only small amounts of the formate indicated. The reaction had gone to completion in the injection port as evidenced by the very small peak corresponding to starting material in the chromatogram. This is in contrast to the reaction described above which was conducted at room temperature until all the hydride had been consumed.

## Free Radical Catalysis

Free radical catalysis has been dramatically demonstrated with the ethylchloroformate. This acid chloride reacts very slowly at 80° with tri-*n*-butyltin hydride so it provides a particularly good model for catalysis. This reaction was found to be subject to free radical catalysis as is shown by the fact that ethylchloroformate undergoes only 5% reduction in three hours at 80°, whereas under the same conditions in the presence of 1.6 mole per cent of azobisisobutyronitrile the reaction is complete, see Table III. The products in each case are ethylformate and tri-n-butyltin chloride.

## TABLE III

Catalyzed and Uncatalyzed Reaction of Ethylchloroformate with Tri-n-butyltin Hydride at 80° in Sealed Ampoules

| Time | Catalyzed[a] % Completed | Uncatalyzed % Completed |
|---|---|---|
| 0.5 hrs. | 30 | 0 |
| 1.5 hrs. | 98-100 | 2-4 |
| 3.0 hrs. | 100 | 5 |
| 18.5 hrs. | | 35 |

[a] 1.6 mole percent of azobisisobutyronitrile.

Free radical catalysis of the reaction of benzoyl chloride with the organotin hydride in m-xylene is not as clearly established for two reasons. One is that degree of catalysis is surprisingly small and the other is that slightly different ratios of aldehyde to ester are found in the catalyzed and uncatalyzed reactions. The azobisisobutyronitrile catalyzed reaction went only some 30-40% faster than the uncatalyzed reaction which was complete in about 20 hrs. at 80°. The catalyzed reaction produced slightly more than twice as much ester (30%) than the uncatalyzed reaction (13%). We cannot explain these observations at this time but, as will be brought out later, there seem to be at least two competing mechanisms for ester formation.

## Relative Reactivities of Acid Chlorides

The relative reactivities of the acid chlorides were determined by allowing each acid chloride to compete with an alkyl bromide for a deficiency of tri-n-butyltin hydride. After all the hydride had been consumed, the reaction mixture was analyzed by gas chromatography. The yield of hydrocarbon from the reduction of the alkyl bromide was determined. When this amount was subtracted from the amount of organotin hydride used, assuming 100% reaction, we obtained the amount of acid chloride which had reacted with the hydride. With this information it was possible to determine the final concentrations of each competitor.

The relative rates were determined by using the standard equation which was first described by Ingold and Stow [17], where $k_A/k_B$ represents the ratio of rate constants

$$\frac{\log A_o - \log A}{\log B_o - \log B} \qquad k_A/k_B \tag{34}$$

for abstraction of halide by the tin radical. $A_o$ and $B_o$ represent the initial concentrations of acid chloride and alkyl bromide respectively, and A and B are their respective final concentrations.

Relative reactivities of substituted benzoyl chlorides are consistent with our mechanistic hypotheses with one step in which the tin radical abstracts a chlorine atom from an acid chloride, Table IV.

The relative reactivities show a Hammett correlation with a rho of 2.61, in m-xylene, Fig. I. The fact that electron withdrawing groups facilitate the reaction rules out an acylium ion mechanism and is consistent with the conventional manner of visualizing polar contributions to the transition state in free radical reactions. Structure I depicts the

## TABLE IV

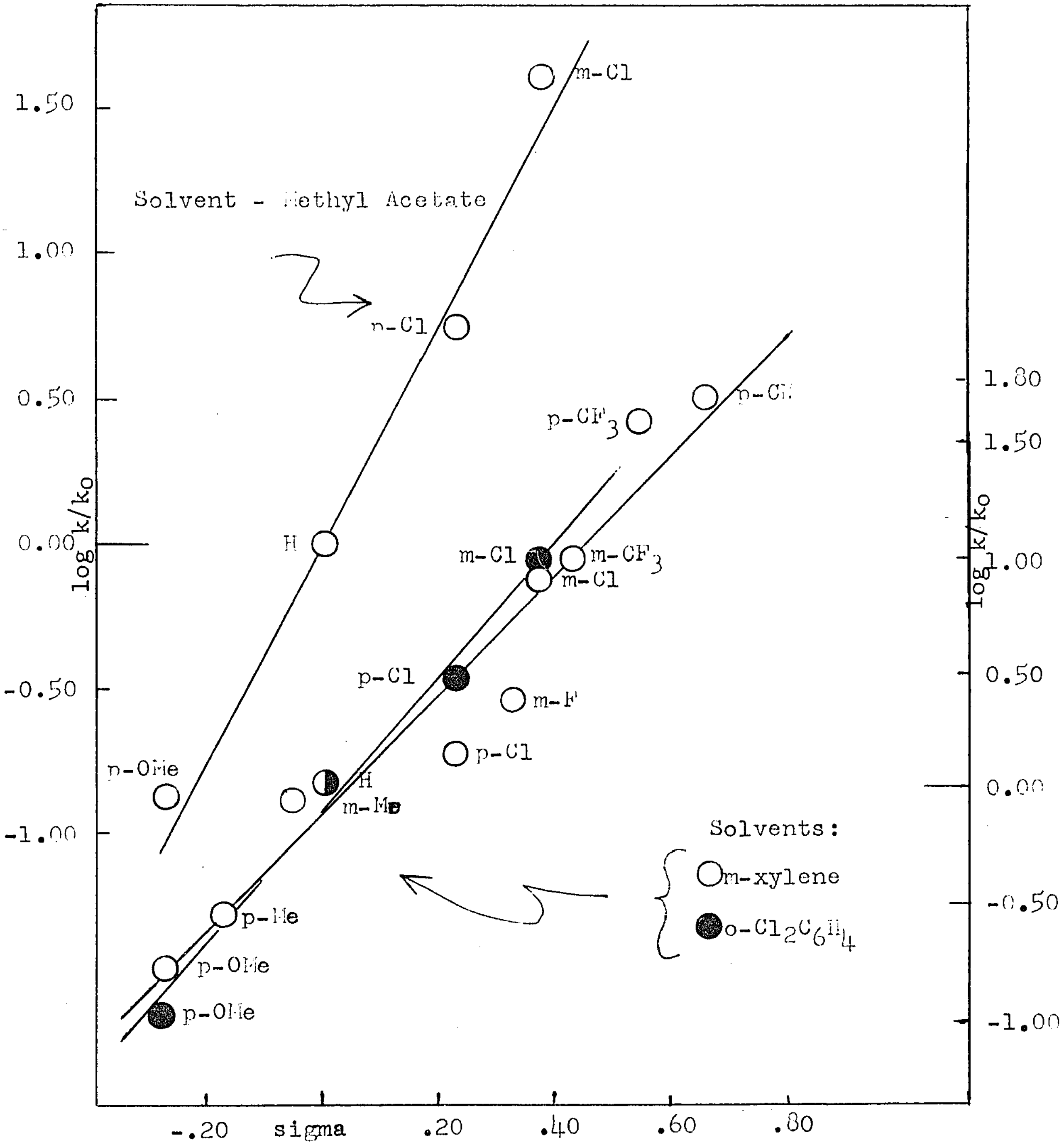
### Relative Reactivities of Acyl Halides Toward Tri-n-butyltin Hydride at 25° in Solution (0.63M)[a]

| Benzoyl Chloride | Relative Rate in m-xylene | Relative Rate in MeOAc | Relative Rate in DCB[b] | sigma[19] |
|---|---|---|---|---|
| p-cyano | 61.40 | | | .660 |
| p-trifluoromethyl | 38.10 | | | .540 |
| m-trifluoromethyl | 9.50 | | | .430 |
| m-chloro | 8.20 | 42.20 | 9.70 | .373 |
| m-fluoro | 2.34 | | | .337 |
| p-chloro | 1.27 | 5.56 | 2.92 | .227 |
| H | 1.00 | 1.00 | 1.00 | |
| m-methyl | 0.937 | | | -.069 |
| p-methyl | 0.290 | | | -.170 |
| p-methoxy | 0.166 | 0.116 | 0.084 | -.268 |
| Benzoyl Bromide | 331 | | | |
| Benzyl Bromide | 28.78 | | | |
| sec. Oct. Br | 2.07 | | | |
| Propionyl Chloride | 5.63 | | | |

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

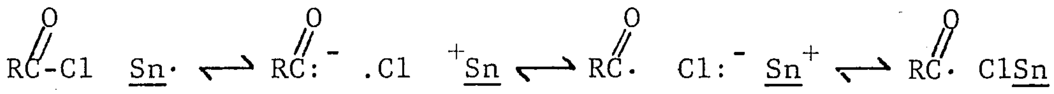
[b] o-Dichlorobenzene

Figure I



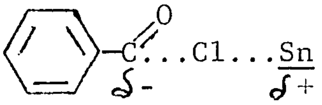
Hammett plots for the reaction of substituted benzoyl chlorides with Sn• in three different solvents at 25°.

transition state as a resonance hybrid in which polar structures make a significant contribution. Structure II is an alternative shorthand representation of the same transition state.



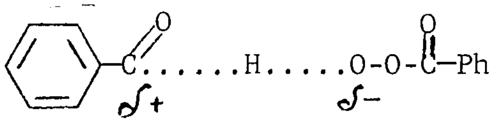
$$\mathrm{R\overset{O}{\overset{\|}{C}}{-}Cl}\quad \underline{\mathrm{Sn}}\cdot \longleftrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}{:}^-}\quad \mathrm{.Cl}\quad {}^{+}\underline{\mathrm{Sn}} \longleftrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}\cdot}\quad \mathrm{Cl{:}^-}\quad \underline{\mathrm{Sn}}^{+} \longleftrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}\cdot}\quad \mathrm{Cl\underline{Sn}}$$

I



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 previous work, the source of the acyl radical has been the reaction of an aldehyde with the electrophilic species, the benzoyloxy radical.[18] In such cases the acyl carbon assumes acylium ion character in the transition state, structure III.



III

The Hammett correlation appears to be better with $\sigma$ than with $\sigma^-$. Values of the correlation coefficient, r[19], are 0.963 and 0.955, respectively. The value of $\rho$ for the correlation is 2.61 as shown in Fig. I. The $\rho$ value based on $\sigma^-$ values was 2.02.

The effect of solvent in this Hammett correlation has been studied briefly. It can be seen from Table IV the nature of the solvent can exert a profound effect. The rho value in methyl acetate, 4.0, is considerably greater than that in m-xylene or o-dichlorobenzene. The nature of this effect can be rationalized on the basis of the work done in these three solvents. Two effects can be operable here. One, as predicted by Howard and Ingold[20], would be that an increase in the polarizability or dielectric constant of the solvent would tend to stabilize a charged transition state and thereby increase the rho value. We do not think that this is the explanation for the solvent effect of methyl acetate, because, although it 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 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.[21] It is known that the reactivity, i.e., selectivity, of the chlorine radical toward primary, secondary and tertiary carbon-hydrogen bonds is profoundly altered in aromatic solvents and carbon disulfide as compared with alkanes. A pi complex between the electrophilic Cl· and the electron donating aromatic nucleous is formed; Eq. (35). The chlorine radical then becomes more selective and attack upon the tertiary car-

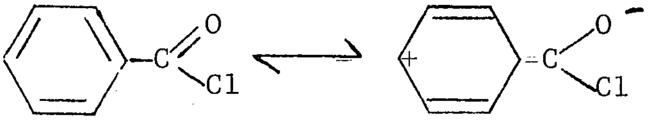
(35)

bon-hydrogen bonds is favored. Although there has not been any detailed study of solvent effects in free radical reactions involving an electropositive free radical, it seems reasonable to postulate the same type of effect for these radicals with solvents of opposite properties. The specific solvent effect of methyl acetate may be tentatively explained by complexing of the organotin radical with a methyl acetate solvent molecule. A complex between the electropositive tin radical and the electron accepting methoxycarbonyl group is depicted by Eq. (36). This effect, by analogy with electro-

$$CH_3CO_2CH_3 + \underline{Sn}\cdot \rightleftharpoons \left[CH_3CO_2CH_3\cdot\underline{Sn}\right]^{\bullet} \qquad (36)$$

philic radicals and donor molecules, should serve to stabilize the organotin radical thus making it more selective in its reaction with substituted benzoyl chlorides. The more stable radical would then experience a greater energy of activation in its reaction with benzoyl chlorides. The greater the energy of activation, the more bond breaking will occur in the transition state.[23] Therefore, as the reactivity of the organotin radical decreases the amount of bond breaking in the transition state will increase and the transition state will be more nearly described by its polar contributors. This will make the reaction more susceptible to polar influences, thus increasing the rho value of the Hammett correlation.

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 it may seem surprising that the benzoyl compound is slower than the aliphatic one. However, the aromatic nucleus can often function as an electron donating group, especially when it is in conjugation with an electron-withdrawing seat of unsaturation, structure IV. The relative reactivity of the benzoyl halides



IV

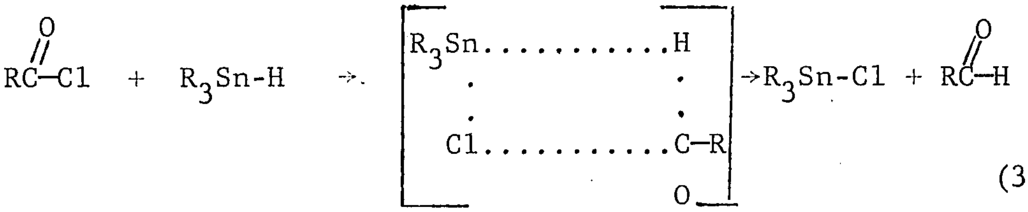
would be diminished by the increased electron density in the chlorocarbonyl group. This same effect is found in the competition of aldehydes, as n-heptaldehyde is almost twice as reactive as benzaldehyde, Table V.

Since benzyl bromide and sec-octyl bromide have been allowed to compete against benzoyl chloride, it is possible to derive a relative rate constant for these bromides. This can be compared with that found by Menapace and Kuivila[4] in their study of the free radical reaction of these compounds with organotin hydrides. We have found that the rate ratio $k_{C_6H_5CH_2Br}/k_{2\text{-}BrC_8H_{17}} = 13.90$ at 25°, while Menapace and Kuivila found a value of 12.70 at 45°. This is good agreement since a small increase in selectivity may be expected at a lower temperature.

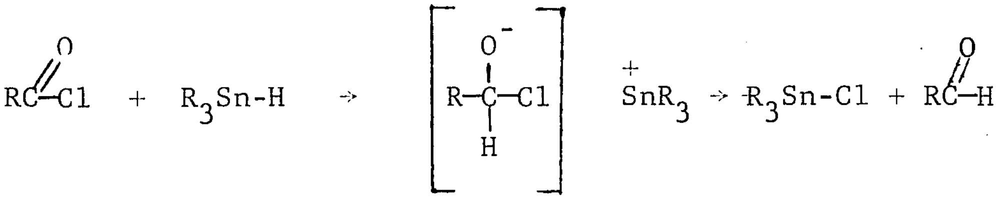
## Other Mechanisms for Aldehyde Formation

Although ionic processes cannot be ruled out, unequivocally, certainly one involving formation of the acylium ion can be, in view of the substituent effects found for substituted benzoyl chlorides. The Hammett correlation shows that the reaction of acid chlorides is facilitated by electron withdrawal.

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, Eq. (37) and (38).



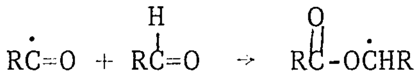
(37)



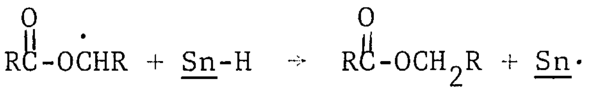
(38)

## MECHANISM OF ESTER FORMATION

The study of the mechanism of ester formation turned out to be much more complicated than that for the formation of aldehyde. However, we propose that the ester in our reaction is also formed by a free radical process, Eq. (39)-(40).



$$R\dot{C}{=}O + R\overset{H}{\overset{|}{C}}{=}O \rightarrow R\overset{O}{\overset{\|}{C}}\text{-}O\dot{C}HR \qquad (39)$$



$$R\overset{O}{\overset{\|}{C}}\text{-}O\dot{C}HR + \underline{Sn}\text{-}H \rightarrow R\overset{O}{\overset{\|}{C}}\text{-}OCH_2R + \underline{Sn}\cdot \qquad (40)$$

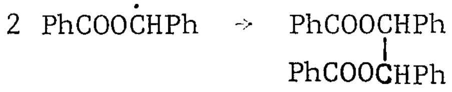
Here, the acyl radical, instead of abstracting a hydrogen atom from a mole of the hydride, attacks the oxygen atom of a previously formed aldehyde molecule to form an α'-acyloxy radical which reacts with another mole of organotin hydride to produce the ester and another tin radical.

This reaction of the acyl radical is not without precedent. Rust, Seubold and Vaughan[24] reported that the benzoyl radical generated in the presence of benzaldehyde had a great facility for attacking the carbonyl oxygen atom of the aldehyde molecule to form the α'-acyloxy radical which then coupled to give the diester of the glycol, Eq. (41)-(44).

$$({}^{t}Bu)_2O_2 \rightarrow 2\ {}^{t}BuO\cdot \qquad (41)$$

$${}^{t}BuO\cdot + PhCHO \rightarrow {}^{t}BuOH + Ph\dot{C}{=}O \qquad (42)$$

$$Ph\dot{C}{=}O + PhCHO \rightarrow PhCOO\text{-}\dot{C}HPh \qquad (43)$$



$$2\ PhCOO\dot{C}HPh \rightarrow \begin{array}{l} PhCOOCHPh \\ \qquad\quad | \\ PhCOOCHPh \end{array} \qquad (44)$$

We do not observe coupling of this type, presumably because the organotin hydride is too efficient a free radical trap. The benzoyl radical has also been shown to attack the carbonyl oxygen of quinones.[25]

The main emphasis in testing the validity of this mechanism has been upon the study of the relative rates of ester formation of added carbonyl compounds. From this study we have been able to infer that the acyl radical is an intermediate in the formation of the ester.

## Relative Reactivities of Added Carbonyl Compounds

The acyl radical should display its electropositive nature[11] when it becomes the attacking radical and reacts with a carbonyl compound. We have measured the efficiencies of several substituted benzaldehydes as traps for the acyl radical. Aldehydes were allowed to compete in pairs and the reaction product mixture was analyzed by gas chromatography, using the internal standard method which is described by Keulemans.[26] Results were calculated using the standard equation of Ingold and Stow[17], Eq. (34).

In the derivation of the above expression for the determination of relative rate constants, it is assumed that both competing reactions are irreversible and proceed by the same mechanism and therefore have the same kinetic order. To give an indication that this assumption is sound and to demonstrate the reproducibility in these systems, a competitive experiment was studied at different relative concentrations, Table V. As can be seen from this table, there is no definite trend in the relative rate constants over the limited range of concentrations used.

The results obtained from the competitive experiments are gathered in Table VI and a Hammett plot is found in Figure II. The value of rho is 0.48. Electron withdrawing groups in the aldehyde facilitate the reaction. The acyl radical as

## TABLE V

### Effect of Varying Concentrations on the Relative Rate Constants for p-Methyl Benzaldehyde and Benzaldehyde[a]

| Initial Conc. p-Methyl Benzald. (mmoles) | Initial Conc. Benzald. (mmoles) | $k_{p\text{-Methyl Benzald.}}/k_{\text{benzald.}}$ |
|---|---|---|
| 4.10 | 3.80 | 1.25 |
| 7.98 | 3.70 | 1.25 |
| 3.86 | 4.26 | 1.27 |
| 4.24 | 3.90 | 1.20 |

---

[a] Reactions run at 25° in 2,3-dimethylbutane (0.63 M) with 3.78 mmoles of $(\underline{n}\text{-}C_4H_9)_3SnH$ and propionyl chloride.

## TABLE VI

Relative Reactivities of Aldehydes and Ketones with Propionyl Radical at 25° in 2,3-Dimethyl Butane, (0.63M)

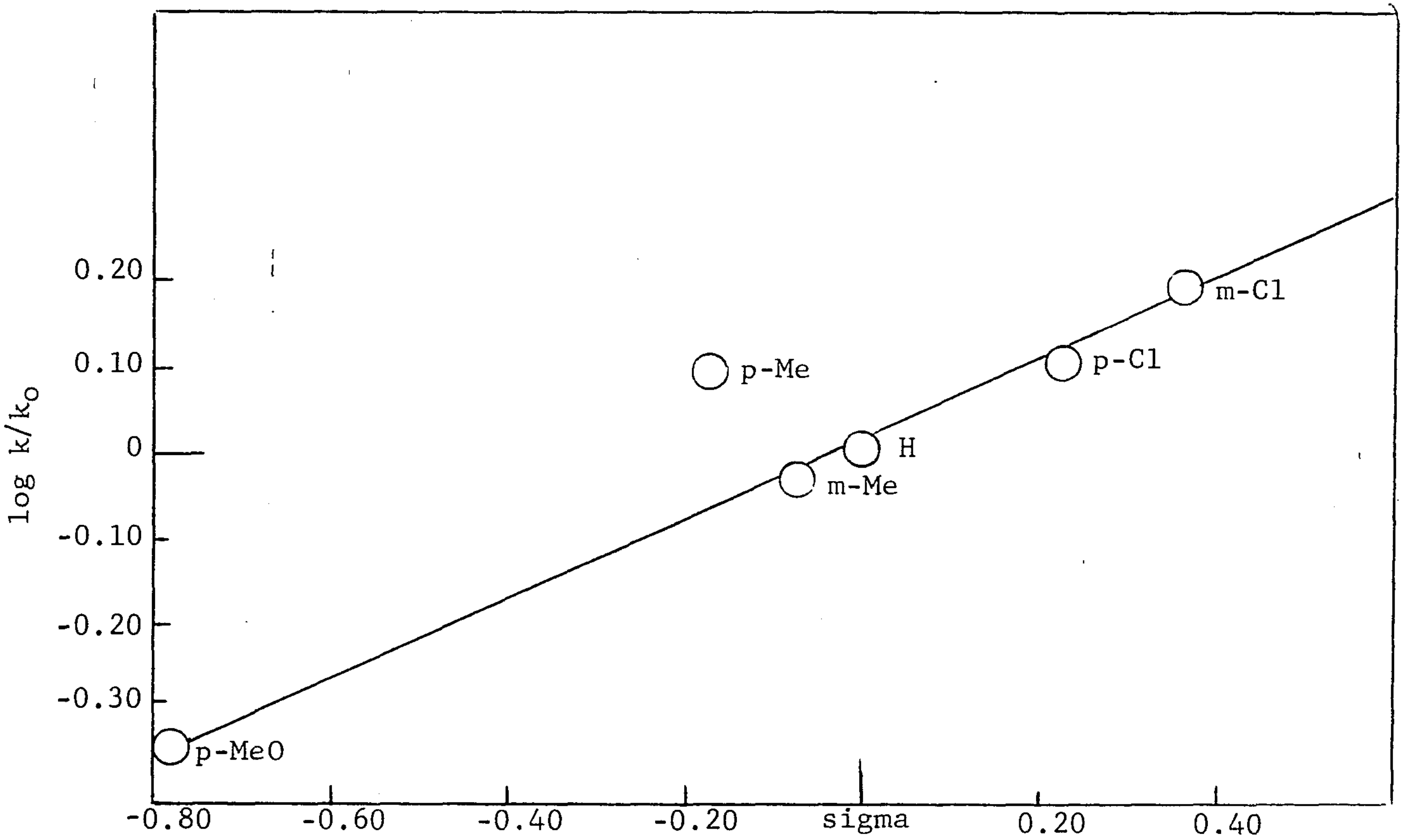
| Carbonyl Compound | Relative Reactivity[a] | Sigma[19] |
|---|---|---|
| n-heptaldehyde | 1.62 | |
| m-chlorobenzaldehyde | 1.57 | .373 |
| p-chlorobenzaldehyde | 1.26[b] | .227 |
| p-methylbenzaldehyde | 1.25 | -.170 |
| benzaldehyde | 1.00 | 0.00 |
| m-methylbenzaldehyde | 0.94 | -.069 |
| p-methoxybenzaldehyde | 0.468 | -.268 (-.778)[c] |
| cyclohexanone[d] | 0.093 | |
| cyclopentanone[d] | 0.005 | |

[a] Based on at least two determinations. The relative rate constants were reproducible within 4%.

[b] Solvent - methyl acetate.

[c] Sigma plus value.

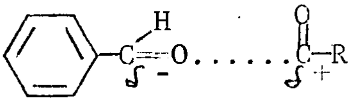
[d] Run at 45°; ($k_{cyclohexanone}/k_{cyclopentanone} = 17.82$).



Hammett plot for the trapping of the propionyl radical by substituted benzaldehydes at 25°.

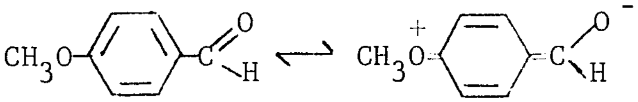
Figure II

expected functions as a nucleophile, assuming acylium ion character, when it attacks the normally nucleophilic oxygen of the carbonyl group[11], structure V.



V

The correlation includes the p-methoxy substituent only if the sigma-plus constant is employed. This is probably a consequence of conjugation between the formyl and methoxy groups leading to contributing structures such as VI in the ground state. This same kind of deviation was found by Huyser and Neckers[27] in their study of the peroxide

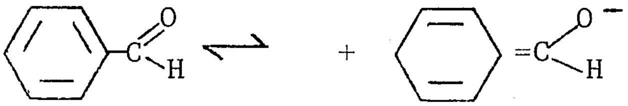


VI

induced reaction of substituted acetophenones with 2-butanol in which they got a good correlation with all substituents except p-methoxy. The rho value for this free radical reaction is also positive and it appears that the correlation is better if the sigma-plus constant for the p-methoxy substituent is used.

The reason why the point for p-methylbenzaldehyde lies above the best line is not known. The greater reactivity of n-heptaldehyde over benzaldehyde also presents some difficulty. There is evidence available that the benzene ring and the aldehyde group are coplanar in benzaldehyde as would be required for maximum contribution from a structure such as

VII.[28] This effect, if not overbalanced by the inductive

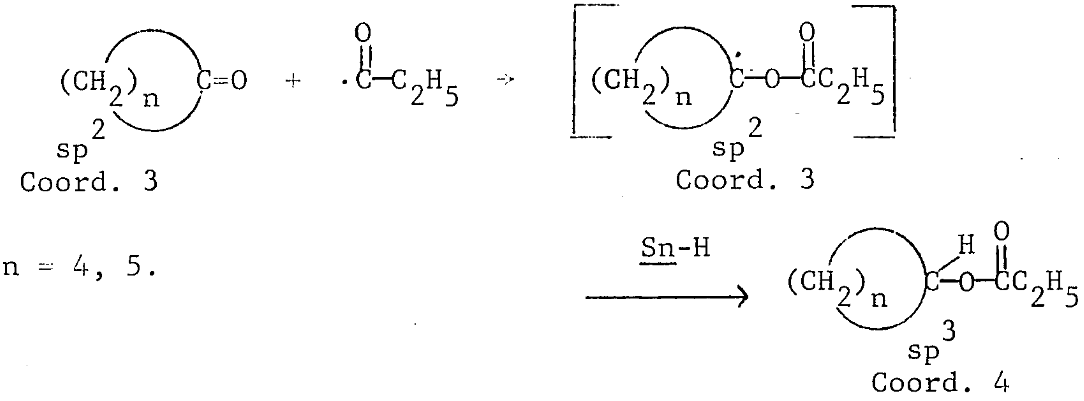


VII

effect of the phenyl group, could lead to a higher electron density on the carbonyl oxygen in benzaldehyde than in *n*-heptaldehyde and, therefore, lower reactivity.

The greater reactivity of cyclohexanone over cyclopentanone can be interpreted in terms of the Brown I-strain theory[29] if it is assumed that the carbonyl carbon is developing $sp^3$ hybridization in the transition state, with concomitant development of new eclipsing interactions in the five-membered ring.

The cyclohexyl ring, which is free of strain, opposes coordination changes of 4 → 5 or 4 → 3, but a coordination change of 3 → 4, as in our case, is favored since it involves a decrease in internal strain, Eq. (45).



n = 4, 5.

(45)

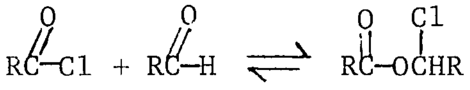
On the other hand, five-membered rings are under some strain. Introduction of an atom with a preferred 120° angle, as there is in cyclopentanone, leads to a decrease in internal strain. In the cyclopentyl ring, therefore, coordination changes 4 → 3 are favored while 3 → 4 are not.

As previously mentioned it was found that ketones in general are not as good traps for the acyl radical as aldehydes. It is likely that ketones are less reactive because of the greater electron release provided by the second alkyl group, and steric factors probably also play some role.

# STUDIES OF OTHER POSSIBLE MECHANISMS FOR ESTER FORMATION

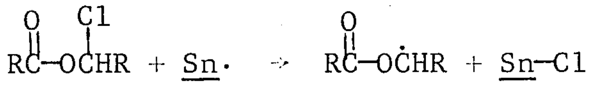
## The α'-chloroester Process

It has been known for some time that acid chlorides will react slowly with aldehydes to give the α'-chloroester[30], Eq. (46). In the aliphatic series catalysis by zinc chloride

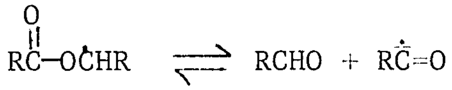


$$R\overset{O}{\overset{\|}{C}}-Cl + R\overset{O}{\overset{\|}{C}}-H \rightleftharpoons R\overset{O}{\overset{\|}{C}}-O\overset{Cl}{\overset{|}{C}}HR \qquad (46)$$

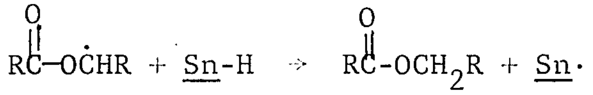
is a necessity but with the corresponding aromatic compounds catalysis is a convenience. It was necessary for us to study this reaction from two points of view. It is, of course, a possible step in formation of esters in the reaction of acid chlorides with organotin hydrides if one assumes the α'-chloroester formed is easily reduced to the unsubstituted ester. Secondly, it would be a model compound for determining if the addition of the acyl radical to an aldehyde is reversible, Eq. (47) - (49). Once the chlorester is prepared we



$$R\overset{O}{\overset{\|}{C}}-O\overset{Cl}{\overset{|}{C}}HR + \underline{Sn}\cdot \rightarrow R\overset{O}{\overset{\|}{C}}-O\dot{C}HR + \underline{Sn}-Cl \qquad (47)$$



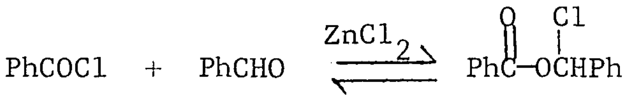
$$R\overset{O}{\overset{\|}{C}}-O\dot{C}HR \rightleftharpoons RCHO + R\dot{C}{=}O \qquad (48)$$



$$R\overset{O}{\overset{\|}{C}}-O\dot{C}HR + \underline{Sn}-H \rightarrow R\overset{O}{\overset{\|}{C}}-OCH_2R + \underline{Sn}\cdot \qquad (49)$$

could allow it to react with tri-n-butyltin hydride, thereby forming the intermediate α'-acyloxy radical. If aldehyde can be detected in the reaction products under the proper conditions this would be good evidence for an equilibrium such as denoted in Eq. (48). On the other hand, if no aldehyde is apparent then we can assume that the addition reaction of the acyl radical is essentially irreversible or that reaction (49) is much faster than reaction (48).

The α'-chloroester of benzyl benzoate was prepared according to a modification of the method reported by Adams and Vollweiller[30,31], Eq. (50). The product was isolated as

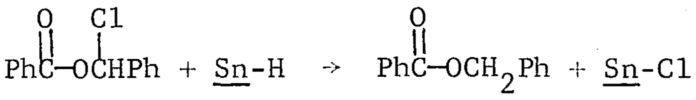


$$\mathrm{PhCOCl} + \mathrm{PhCHO} \overset{ZnCl_2}{\rightleftharpoons} \mathrm{Ph}\overset{O}{\overset{\|}{C}}{-}\mathrm{O}\overset{Cl}{\overset{|}{C}}\mathrm{HPh} \qquad (50)$$

a white, fluffy solid in nearly quantitative yield. It showed all ester absorptions in infra-red and the complete absence of both aldehyde and acid chloride absorptions. The compound is not stable in solution. It is particularly unstable in the presence of tri-n-butyltin chloride. Isomerization in a 12% solution of 2,3-dimethyl butane is very slow but when an equimolar amount of the organotin chloride is added the rate of isomerization increases. When the organotin chloride is added neat to the ester, a 50/50 mixture of ester and aldehyde is detected in the infra-red spectrum within fifteen minutes.

This isomerization brought about by dissolving the chloroester or, even more quickly by the addition of tri-n-butyltin chloride, detracts from this system as a model for the study of the reversible reaction between benzoyl radical and aldehyde since a certain amount of benzoyl chloride and benzaldehyde will be present before reduction of the chloroester is complete.

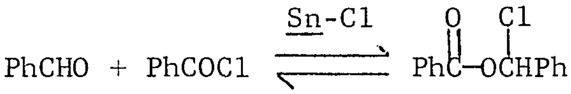
When α'-chlorobenzyl benzoate was reduced with tri-n-butyltin hydride in a 12% solution in 2,3-dimethyl butane or neat, only very small amounts of benzaldehyde could be detected by gas chromatography and infra-red analysis, Eq. (51).



$$\mathrm{Ph}\overset{O}{\overset{\|}{C}}{-}\mathrm{O}\overset{Cl}{\overset{|}{C}}\mathrm{HPh} + \underline{\mathrm{Sn}}\text{-}\mathrm{H} \rightarrow \mathrm{Ph}\overset{O}{\overset{\|}{C}}{-}\mathrm{OCH_2Ph} + \underline{\mathrm{Sn}}\text{-}\mathrm{Cl} \qquad (51)$$

At least 80% of the product was benzyl benzoate.

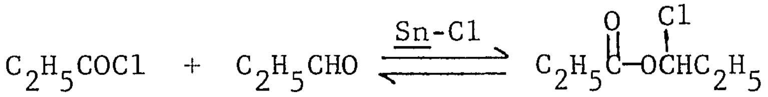
It was necessary, now, to examine the reaction of an aldehyde and an acid chloride in the presence of tri-n-butyltin chloride to see if this reaction is fast enough to compete with the reduction of acid chlorides by organotin hydrides. When equimolar amounts of benzaldehyde, benzoyl chloride and a one-half molar amount of tri-n-butyltin chloride were mixed together, neat, the reaction was only about 50% complete after twenty-four hours, whereas the acid chloride reaction under essentially the same conditions is complete in 15 hrs. or less, Eq. (52).



$$\mathrm{PhCHO} + \mathrm{PhCOCl} \xrightleftharpoons{\mathrm{Sn\text{-}Cl}} \mathrm{Ph}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\mathrm{O}\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{HPh} \qquad (52)$$

When tri-n-butyltin hydride was added to this mixture the remaining benzoyl chloride reacted preferentially with the hydride as evidenced by the fact that it was no longer detectable, 24 hrs. later, in the infra-red spectrum, whereas the α'-chloroester was.

A similar study with aliphatic reactants, propionaldehyde and propionyl chloride, indicated that this reaction was slower than the benzaldehyde-benzoyl chloride reaction, Eq. (53). Furthermore, the α'-chloroester of ethyl acetate



$$\mathrm{C_2H_5COCl} + \mathrm{C_2H_5CHO} \xrightleftharpoons{\mathrm{Sn\text{-}Cl}} \mathrm{C_2H_5}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}\mathrm{O}\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{HC_2H_5} \qquad (53)$$

was prepared and its reaction with tri-n-butyltin hydride appeared to be much slower than the benzoate reaction giving again the ester as the predominant product.

On the basis of the above information we conclude that the α'-chloroester mechanism can be discarded as the major pathway to ester formation in the reduction of acid chlorides.

## Alcohol as an Intermediate in Ester Formation

It can be postulated that alcohol is formed in these reactions and this reacts with the acid chloride to produce the ester. The alcohol could conceivably arise by two different processes. One would involve the reduction of the acid chloride directly to the alcohol, Eq. (54) - (56). This

$$RCOCl + 3\underline{Sn}\text{-}H \rightarrow RCH_2OH + \underline{Sn}\text{-}Cl + \underline{Sn}\text{-}\underline{Sn} \qquad (54)$$

$$RCH_2OH + RCOCl \rightarrow RCH_2O_2CR + HCl \qquad (55)$$

$$HCl + \underline{Sn}\text{-}H \rightarrow H_2 + \underline{Sn}\text{-}Cl \qquad (56)$$

process can be eliminated on three grounds: (1) the stoichiometry for the formation of ester requires three moles of hydride for two moles of acid chloride, but only two are used; (2) the hydrogen chloride formed would be expected to react with the hydride, leading to the formation of hydrogen gas which is not observed; (3) no ditins ($\underline{Sn}$-$\underline{Sn}$) have been observed among the reaction products.

The other process leading to alcohol formation could be the reduction of the aldehyde formed in this reaction by the hydride, Eq. (57) - (59). This process can be eliminated

$$RCOCl + \underline{Sn}\text{-}H \rightarrow RCHO + \underline{Sn}\text{-}Cl \qquad (57)$$

$$RCHO + 2\underline{Sn}\text{-}H \rightarrow RCH_2OH + \underline{Sn}\text{-}\underline{Sn} \qquad (58)$$

$$RCH_2OH + RCOCl \rightarrow RCH_2O_2CR + HCl \qquad (59)$$

on the same grounds as the previous process. In addition, it has been found in separate experiments that aldehydes in the presence of tri-n-butyltin hydride with or without added tri-n-butyltin chloride, are reduced too slowly, under our experimental conditions to account for the ester in these reactions. For example, a neat mixture of benzaldehyde and tri-n-butyltin hydride takes about nine days to go to completion while under the same conditions the benzoyl chloride reaction with the hydride is complete in 15 hrs.

## The Organotin Alkoxide as an Intermediate in Ester Formation

There was one other likely candidate as an intermediate in the ester formation process, and that was the organotin alkoxide formed by addition of tin hydride to the carbonyl double bond. It could give ester by reacting with acid chloride. It has been demonstrated that the reaction between aldehydes and organotin hydrides to form alkoxides, Eq. (60), can be brought about at moderate temperatures in the presence of azobisisobutyronitrile[32] or zinc chloride[33]

$$\underline{Sn}\text{-H} + \text{RCHO} \rightarrow \underline{Sn}\text{-OCH}_2\text{R} \qquad (60)$$

and photochemically.[34] This reaction can take place, it seems, by either a polar pathway or a free radical process. The free radical process is depicted by Eq. (61) - (62).

$$\underline{Sn}\cdot + \text{RCHO} \rightarrow \text{R}\dot{\text{C}}\text{H-O-}\underline{Sn} \qquad (61)$$

$$\text{R}\dot{\text{C}}\text{H-O-}\underline{Sn} + \underline{Sn}\text{-H} \rightarrow \text{RCH}_2\text{-O-}\underline{Sn} + \underline{Sn}\cdot \qquad (62)$$

In our reactions we have postulated the formation of the tin radical and, although it seems unlikely that the tin radical would react preferentially with the aldehyde over the acid chloride, and it was not known if these alkoxides would react with acid chlorides with any facility, we undertook a study of this possibility. One additional piece of information that made this pathway seem unlikely was the observation of Sawyer[35] that organotin alkoxides can be reduced by organotin hydrides, Eq. (63), yielding the alcohol which has been

$$\underline{Sn}\text{-H} + \underline{Sn}\text{-O-CH}_2\text{R} \rightarrow \underline{Sn}\text{-}\underline{Sn} + \text{RCH}_2\text{OH} \tag{63}$$

shown not to be an intermediate in ester formation.

The overall process accounting for ester by the alkoxide intermediate is described by Eq. (64) - (70). As

$$\text{RCOCl} + \underline{Sn}\cdot \rightarrow \text{R}\dot{\text{C}}\text{=O} + \underline{Sn}\text{-Cl} \tag{64}$$

$$\text{R}\dot{\text{C}}\text{=O} + \underline{Sn}\text{-H} \rightarrow \text{RCHO} + \underline{Sn}\cdot \tag{65}$$

$$\text{RCHO} + \underline{Sn}\cdot \rightarrow \text{R}\dot{\text{C}}\text{H-O-}\underline{Sn} \tag{66}$$

$$\text{R}\dot{\text{C}}\text{H-O-}\underline{Sn} + \underline{Sn}\text{-H} \rightarrow \text{RCH}_2\text{O}\underline{Sn} + \underline{Sn}\cdot \tag{67}$$

$$\text{RCH}_2\text{O}\underline{Sn} + \text{RCOCl} \rightarrow \text{RCH}_2\text{O}_2\text{CR} + \underline{Sn}\text{-Cl} \tag{68}$$

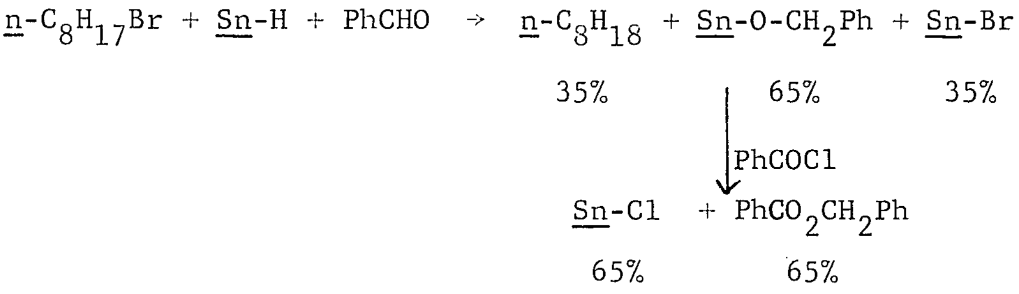
$$\text{RCH}_2\text{O}\underline{Sn} + \underline{Sn}\text{-H} \rightarrow \text{RCH}_2\text{OH} + \underline{Sn}\text{-}\underline{Sn} \tag{69}$$

$$\text{RCH}_2\text{OH} + \text{RCOCl} \rightarrow \text{RCH}_2\text{O}_2\text{CR} + \text{HCl} \tag{70}$$

can be seen, the stoichiometry is identical to that which we have found in our study of this reaction, and is a possible mechanism, if reaction (68) is much faster than reaction (69).

We generated the radical $\underline{Sn}\cdot$, by a known free radical process[4] in the presence of benzaldehyde and found extensive alkoxide formation. The reaction of primary octyl bromide with tri-*n*-butyltin hydride in the presence of benzaldehyde was used as a method for generating the organotin radical in the absence of acid chloride. The reaction was run neat and was complete in about five days. The infra-red spectrum of the reaction mixture indicated some remaining benzaldehyde by the carbonyl absorption at 1700 $\text{cm.}^{-1}$. There was also a prominent band at 1050 $cm.^{-1}$ indicating C-O bond.

Gas chromatographic analysis indicated less than 5% of benzyl alcohol and a 35% yield of n-octane. Also present in the chromatogram were peaks due to unreacted octyl bromide and organotin bromide, Eq. (71).



$$\begin{array}{lcccccc}
\underline{n}\text{-}C_8H_{17}Br + \underline{Sn}\text{-}H + PhCHO & \rightarrow & \underline{n}\text{-}C_8H_{18} & + & \underline{Sn}\text{-}O\text{-}CH_2Ph & + & \underline{Sn}\text{-}Br \\
 & & 35\% & & 65\% & & 35\% \\
 & & & & \Big\downarrow{\scriptstyle PhCOCl} & & \\
 & & \underline{Sn}\text{-}Cl & + & PhCO_2CH_2Ph & & \\
 & & 65\% & & 65\% & &
\end{array}$$

(71)

When benzoyl chloride was added to the reaction product mixture, a large amount of heat was generated and the infra-red spectrum was taken immediately. Now an ester carbonyl at 1730 $cm.^{-1}$ dominated the carbonyl region. The C-O stretch at 1050 $cm.^{-1}$ was absent. The reaction of the alkoxide with acid chloride must be extremely fast, much faster than the reaction of the alkoxide with the organotin hydride as evidenced by the small amount of benzyl alcohol found. Gas chromatographic analysis indicated a large amount of benzyl benzoate, and a three-to-one ratio of organotin chloride to organotin bromide peak areas.

Here is a mechanistic pathway which is feasible and can be demonstrated to occur in the absence of acid chlorides. A study was then undertaken to learn more about this reaction so that we might at least gain some ideas as to the importance of the alkoxide as an intermediate in the reaction of acid chlorides with tri-n-butyltin hydride.

Table VII indicates the role of different aldehydes in one case and the role of the reactivity of the halide used in the amount of alkoxide formed. These reactions were conducted at room temperature by mixing equimolar amounts of the bromide, aldehyde, hydride and the internal standard. The yields were determined using the internal standard method by gas chromatography. The amount of alkoxide was determined by adding propionyl chloride, after all the hydride had been consumed, and analyzing for the appropriate propionate ester.

TABLE VII

Yields of Hydrocarbon and Esters[a] (Alkoxides) in the Reaction of Alkyl Halides with Tri-n-butyltin Hydride in the Presence of Aldehydes, Neat and at Ambient Temperatures

| R-Br | Aldehyde | % Yield R-H | % Yield $C_2H_5COOCH_2R$ |
|---|---|---|---|
| 1-Br$C_8H_{17}$ | $C_6H_5CHO$ | 30 | 65 |
| 1-Br$C_8H_{17}$ | $(CH_3)_2CHCHO$ | 85-95 | 5 |
| 2-Br$C_8H_{17}$ | $C_6H_5CHO$ | 50 | 49 |
| $C_6H_5CH_2Br$ | $C_6H_5CHO$ | 69 | 37 |

[a] Formed after treatment of reaction product with propionyl chloride.

We have found that when benzaldehyde is mixed, neat, with tri-n-butyltin hydride at room temperature the ensuing reaction takes some 9 to 10 days for completion. The benzoyl chloride and tin hydride reaction takes on the order of 15 hrs. under the same conditions. However, we have also found that, upon addition of 5 mole % of either propionyl chloride or primary octyl bromide to the mixture of benzaldehyde and tri-n-butyltin hydride, a definite catalysis is observed. In attempting to determine with certainty the nature of this catalysis an additional complication was encountered. We found that, upon addition of an equimolar amount of tri-n-butyltin chloride to the benzaldehyde-tri-n-butyltin hydride mixture catalysis results to such an extent that it is difficult to distinguish between the rate of this reaction and the rate of the neat reaction of benzoyl chloride with the hydride. Addition of 5 mole % of the tin chloride also catalyzes the aldehyde-organotin hydride reaction, but not to the extent that an equimolar quantity does.

As Neumann[32] has found, the formation of alkoxides from aldehydes and organotin hydrides is apparently catalyzed by either free radical or ionic catalysts. We feel that formation of alkoxide under trialkyltin chloride catalysis is most likely a polar process, with the chloride acting as a Lewis acid. The chloride may complex with the aldehyde molecule with subsequent attack by the organotin hydride molecule, Fig. III. This would make the carbonyl carbon more susceptible to nucleophilic attack by the hydride.

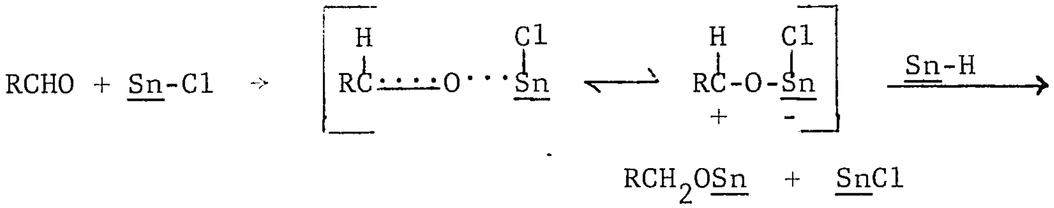


Fig. III

To ascertain if the polar process is the most important pathway for the formation of ester in our reactions of acid chlorides, we have compared the rates of three reactions under standard conditions and followed the reactions by infra-red analysis, Table VIII

## TABLE VIII[a]

A Comparison of Rates of Selected Reductions in Diethyl Ether (0.63M) at Ambient Temperature.

| Hrs. After Mixing | Experiment[b] Number | % of Reaction[c] |
|---|---|---|
| 19 | I | $>79$ |
| 19 | II | $>80$ |
| 19 | III | $\sim 35$ |
| 91 | I | $>90$ |
| 91 | II | $>85$ |
| 91 | III | $\sim 50$ |

[a] Results presented in this table are those of H. G. Kuivila. Reactions I and III were repeated by author and were in accord with the above results.

[b] Each experiment contained equimolar amounts (0.0038 moles) of reactants and catalyst where used. The hydride employed in each case was tri-n-butyltin hydride. Other reactants and catalysts were:

| | |
|---|---|
| I | $(CH_3)_2CHCOCl$ |
| II | $(CH_3)_2CHCOCl$ and $(n\text{-}C_4H_9)_3SnCl$ |
| III | $(CH_3)_2CHCHO$ and $(n\text{-}C_4H_9)_3SnCl$ |

[c] Determined by infra-red analysis.

The results, given in Table VIII, show that the polar organotin chloride catalyzed process is not fast enough to be a part of the main path of ester formation. It is also of interest to note that the tin chloride does not catalyze the acid chloride-organotin hydride reaction noticeably.

## Relative Rates of Alkoxide Formation

It was felt that the study of the relative rates of alkoxide formation should be informative in the assessment of the role of the alkoxide intermediate in our reactions of acid chlorides with tri-*n*-butyltin hydride. We can compare the relative rates of ester formation from added aldehydes in the propionyl chloride system with the relative rates of alkoxide formation. If the alkoxide is an intermediate in the formation of ester in the reduction of acid chlorides then we would expect to obtain a rho value from a Hammett plot of substituted benzaldehydes in these experiments essentially identical to that found in the propionyl chloride system. That this is not the case is evident from the results gathered in Table IX.

These reactions were conducted by allowing aldehydes to compete in pairs for an insufficient amount of tri-*n*-butyltin hydride in the reaction between either primary or secondary octyl bromide and the hydride. The alkoxide yields were determined by adding propionyl chloride after all hydride had been consumed and analyzing the reaction mixture by gas chromatography using the internal standard method for the propionates. The relative rate constants were calculated, using Eq. (34).

The relative reactivities in the octyl bromide induced

## TABLE IX

Relative Rates of Alkoxide and of Ester Formation[a]

| Aldehyde | Rel.Rate[b] $C_2H_5COCl$ | Rel.Rate[c] $C_8H_{17}Br$ | Rel.Rate[d] Sn-Cl | Rel.Rate[e] $CHCl_3$ |
|---|---|---|---|---|
| $CH_3(CH_2)_5CHO$ | 1.62 | 2.15 ±.04 | | |
| *m*-$ClC_6H_4CHO$ | 1.57 | 5.42 ±.42<br>(4.02 ±.16)[f] | 3.65 ±.04 | 4.72 ±.10 |
| *p*-$ClC_6H_4CHO$ | 1.26[g] | 1.93 ±.06[g] | | |
| *p*-$CH_3C_6H_4CHO$ | 1.25 | 1.18 ±.01 | 1.05 ±.04 | |
| $C_6H_5CHO$ | 1.00 | 1.00 | 1.00 | 1.00 |
| *m*-$CH_3C_6H_4CHO$ | 0.94 | 1.03 ±.03 | | |
| *p*-$CH_3OC_6H_4CHO$ | 0.47 | $<$0.16 | | |

[a] As conducted in 2,3-dimethyl butane, (0.63M) at 25°.

[b] As reported in Table VI.

[c] As determined in reactions with equimolar amounts (0.0038 moles) of primary or secondary bromide with tri-*n*-butyltin hydride in the presence of a pair of aldehydes. Alkoxide yields were determined by adding $C_2H_5COCl$ when reaction was complete, and then analyzing for the propionates by g.l.c.

[d] As determined in tri-*n*-butyltin chloride catalyzed reactions by allowing aldehydes to compete for tri-*n*-butyltin hydride; analysis as in b.

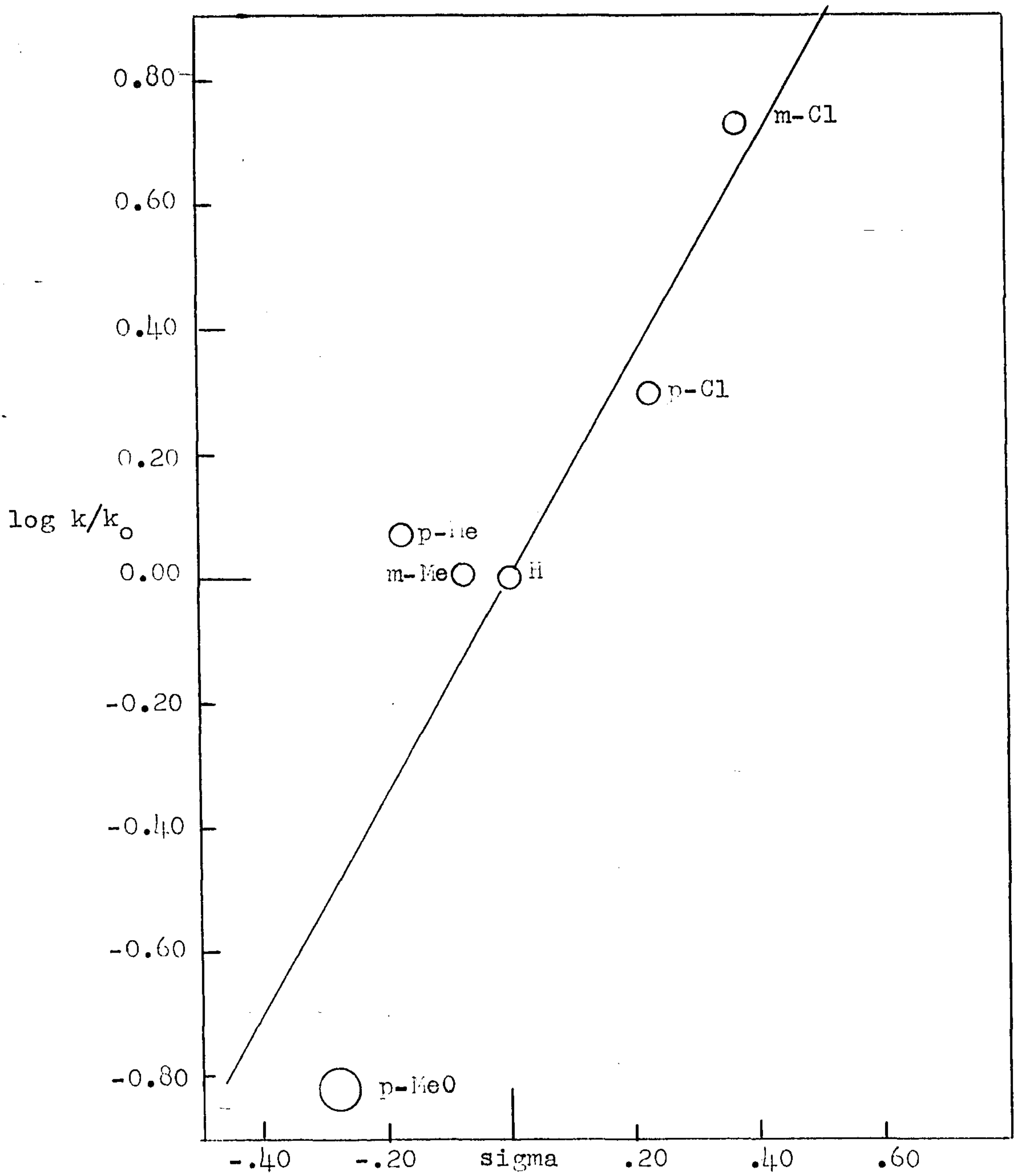
[e] As determined in the reaction with chloroform and tri-*n*-butyltin hydride in the presence of a pair of aldehydes; analysis as in b.

[f] This reaction was run in the same manner as described in b, with the exception of solvent. Here 3 ml. of 2,3-dimethyl butane and 2 ml. tri-*n*-butyltin chloride were used.

[g] Solvent - methyl acetate.

reaction yielded a Hammett correlation which gave a rho of approximately 1.85, Fig. IV.

Note that in all four cases studied organotin chloride catalysis serves to lower the relative rate constants with respect to those determined in the octyl bromide reaction. The relative rate for m-chlorobenzaldehyde as determined in the chloroform system is within experimental error of that found in the sec-octyl bromide system. This could be interpreted as meaning that the organotin radical is responsible in each case for the formation of alkoxide. It is impossible to draw any definite conclusions as to relative contributions of the organotin radical and organotin halide catalyzed reactions in the formation of the alkoxide in these experiments. One thing, however, is clear from these results: the relative rates of alkoxide formation are significantly different from the relative rates of ester formation in the propionyl chloride system. We infer from these results that the alkoxide intermediate route is not the main pathway in the formation of ester. It is felt, however, that under certain conditions the alkoxide intermediate mechanism could be a major pathway to ester formation. From the data in Table I it is obvious that the use of solvent drastically reduces the yield of ester in all cases save the one in which tri-n-butyltin chloride is used as a solvent. In this case some three times as much ester is formed as in 2,3-dimethyl butane. This effect of added chloride in increasing the yield of ester has also been observed in the benzoyl chloride reaction, Table X.



Hammett plot for alkoxide formation of substituted benzaldehydes at 25°.

Figure IV

## TABLE X

The Effect of Added Tri-*n*-butyltin Chloride on the Yield of Benzyl Benzoate in the Reaction Between Benzoyl Chloride and Tri-*n*-butyltin Hydride at 60-65°[a]

| Solvent | Area/Area Ester/I.S. (x Moles I.S.) | % Yield of Ester |
|---|---|---|
| 5 ml Toluene | .00087 | 20 |
| 4.5 ml Toluene<br>0.5 ml *Sn*-Cl | .00155 | 36 |
| 4 ml Toluene<br>1.0 ml *Sn*-Cl | .00172 | 40 |
| 3.5 ml Toluene<br>1.5 ml *Sn*-Cl | .00141 | 33 |

[a] 0.0038 mole of each reactant used; analysis by g.l.c.

# EFFECT OF TRI-N-BUTYLTIN CHLORIDE ON ALDEHYDES

## General

We have presented in the previous section evidence that tri-n-butyltin chloride has a profound catalytic effect in the reaction of aldehydes with tri-n-butyltin hydride. We have also found that aldehydes in the presence of the chloride are not quantitatively accounted for by gas chromatography owing to what appears to be a polymerization reaction of the aldehyde in the injection port. We have also found that tri-n-butyltin chloride catalyzes acetal formation in mixtures of propionaldehyde and ethanol.

## Problems Encountered in Gas Chromatographic Analysis of Aldehydes.

This problem was first observed during study of the effect of temperature on the trapping efficiency of cyclohexanone in the reaction of propionyl chloride with tri-n-butyltin hydride. The first experiment was carried out when there was no apparent difficulty in determining the aldehyde yield, Table XI. Aldehyde peaks of reasonable size were noted in these chromatograms. In later experiments, however, it became obvious that little if any aldehyde was indicated on the chromatograms, Table XII, even though the infra-red spectrum of these reaction mixtures indicated the presence of propionaldehyde. The yields of the aldehyde in Table XII are therefore those determined by difference assuming 100% reaction. To test the validity of determining yield by difference we have compared the relative areas of n-propyl propionate and propionaldehyde peaks in Table XI with what should have been observed in the repeated work since these were all done under the same conditions.

We obtained from this comparison a hypothetical area for the aldehyde based on the known area of the ester which, when compared to the area given by the internal standard, gave yields of propionaldehyde very close to those found by difference in Table XII, 25° - 5.4%; 45° - 19%; 90° - 33%.

## TABLE XI

A Study of the Trapping of Cyclohexanone at Different Temperatures in the Reaction of Propionyl Chloride and Tri-n-butyltin Hydride, Neat[a]

| Temperature | Area ratio: $C_2H_5COO(CH_2)_2CH_3/C_2H_5CHO$ | Area ratio: $C_2H_5COO(CH_2)_2CH_3/C_2H_5CO_2C_6H_{11}$ |
|---|---|---|
| 25° | 13.20 | 4.80 |
| 45° | 2.88 | 2.29 |
| 90° | 1.20 | 0.90 |

[a] Run on a 0.0038 mole scale with equimolar quantities of each reactant.

Internal standard curves of aldehydes have been prepared in the absence of the organotin chloride. Using these curves to analyze aldehydes in the presence of the chloride in synthetic mixtures, we found that we could only account for a part of the aldehyde, sometimes only 40-50%.

## TABLE XII

### A Study of the Trapping of Cyclohexanone at Different Temperatures in the Reaction of Propionyl Chloride and Tri-n-butyltin Hydride, Neat[a]

| Temperature °C | % Yield[b] $C_2H_5CHO$ | % Yield $C_2H_5CO_2C_3H_7$ | % Yield $C_2H_5CO_2C_6H_{11}$ | % Yield of Recovered Cyclohexanone |
|---|---|---|---|---|
| 25 | 10 | 78 | 12 | 85 |
| 45 | 18 | 69 | 13.2 | 93 |
| 90 | 36 | 50 | 13.5 | 84 |

[a] This experiment is a repeat of that described in Table XI.

[b] Yield determined by difference, assuming 100% reaction since little, if any, propionaldehyde was discernable in the gas chromatograph.

## Tri-_n_-butyltin Chloride as a Catalyst in Acetal Formation

We could find no evidence of complex formation between aldehydes and tri-_n_-butyltin chloride in the infrared spectrum or in the ultra-violet region in solvents such as _n_-hexane or ethyl acetate. When this system was studied in ethanol, however, we observed definite catalysis of acetal formation from propionaldehyde and ethanol by the chloride. The results are reported in Table XIII.

## TABLE XIII

## The Effect of Tri-n-butyltin Chloride on the Carbonyl Absorption of Propionaldehyde in Ethanol[a]

System: $C_2H_5CHO$ (0.105M)
Sn-Cl

| Absorbance | $\lambda$ mu ($\epsilon$) | Time After Mixing |
|---|---|---|
| .379 | 280 (3.60) | 0 hr. |
| .390 | 280 (3.70) | 1 hr. |
| .368 | 282 (3.50) | 3.7 hr. |
| .354 | 280 (3.37) | 5.5 hr. |
| .354 | 282 (3.37) | 22.8 hr. |

System: $C_2H_5CHO$ (0.090M)

| Absorbance | $\lambda$ mu ($\epsilon$) | Time After Mixing |
|---|---|---|
| 1.154 | 286 (13 ) | 0 hr. |
| .765 | 284 (8.5 ) | 1 hr. |
| .499 | 280 (5.55) | 3.7 hr. |
| .362 | 280 (4.02) | 5.5 hr. |
| .202 | 275 (2.24) | 22.8 hr. |
| .176 | 275 (2.00) | 30 hr. |
| .182 | 275 (2.03) | 35 hr. |

[a] As read on a Beckman D. U. Spectrophotometer.

## EXPERIMENTAL

All experiments involving organotin hydrides were conducted in an atmosphere of prepurified nitrogen. The infra-red spectra were determined with a Perkin-Elmer Model 21 or 337, recording double-beam spectrophotometer with sodium chloride optics. Experiments involving gas chromatography were carried out by using an F. and M. Scientific Company, Model 300 gas chromatograph.

## MATERIALS

### Acid Chlorides

In many cases the acid chlorides used were commercially available in high purity. When not available they were readily prepared in quantitative yields from the appropriate carboxylic acid and thionyl chloride.

### Solvents

In all cases, the solvents used were commercially available with an excellent degree of purity.

### Aldehydes

All aldehydes used were commercially available. Their purity was checked periodically by gas chromatography after distillation. All aldehydes were stored under nitrogen in the refrigerator.

### Esters

Some esters were commercially available, but in most cases they were prepared by lithium aluminum hydride reduction of the appropriate aldehyde or carboxylic acid to form the alcohol portion which was then acylated by the appropriate acid chloride. After distillation, the purity of the ester was determined by gas chromatography and infra-red spectroscopy. The purity in each case was at least 95%.

## Organotin Hydrides

The organotin hydrides were prepared by reduction of the appropriate organotin chlorides with lithium aluminum hydride. Tri-n-butyltin hydride was also prepared by reduction of bis(tri-n-butyltin) oxide. The tri-n-butyltin chloride and the bis-oxide were obtained through the courtesy of Metal and Thermit Chemicals, Inc.

### Tri-n-butyltin Hydride from Tri-n-butyltin Chloride.[7]

A 500 ml. flask in an ice bath was fitted with a stirrer, dropping funnel and a nitrogen inlet was charged with 150 ml. of anhydrous diethyl ether, there was added 3.8 g. (0.1 moles) of finely divided lithium aluminum hydride. Tri-n-butyltin chloride, 65.0 g. (0.2 moles) in 150 ml. of anhydrous ether was added over a period of about an hour with stirring. When addition was complete, the ice bath was removed and the mixture was allowed to stir at room temperature under nitrogen for from three to nine hours. The mixture was then hydrolyzed with ice water and the ether layer separated. The ether layer was then washed about six times with water and finally three times with a concentrated solution of calcium chloride in water. The ether layer was then dried over magnesium sulfate for at least three hours. The magnesium sulfate was filtered and the solvent removed on a rotary evaporator. The residue was distilled at 81-83°/0.5 mm. Yields were in the range of 60-80%. The hydride was then stored in carefully cleaned, evacuated ampoules.

Tri-*n*-butyltin Hydride from *Bis*(tri-*n*-butyltin) Oxide. The procedure followed was that of Considine and Ventura[36] and was essentially the same as that from the chloride with the exception that the stoichiometry is different. Two moles of the hydride are produced for every mole of oxide. The yields obtained were generally higher than in the above method, being on the order of 90%.

### Trimethyltin Hydride from Trimethyltin Chloride.

Twenty g. of the chloride in 30 ml. of di-*n*-butyl ether was added from an addition funnel to a stirring suspension of 4 g. of lithium aluminum hydride in 30 ml. of the dibutyl ether under nitrogen at a temperature of 100°. The trimethyltin hydride distilled from the reaction mixture as it was formed. The hydride prepared in this manner was used immediately. The main fraction distilled at 60° at atmospheric pressure, and the yields were on the order of 50-60 %.

## REDUCTION OF ACID HALIDES

### Procedure

Reductions were carried out in ordinary laboratory equipment and, for the most part, at room temperature. The acid chloride was placed in a glass-stoppered Erlenmeyer flask followed by solvent when used. The organotin hydride was usually added by pipet. The flask was then flushed with prepurified nitrogen immediately and the stopper securely fastened. If the reaction was exothermic, the flask was cooled in an ice bath in most cases. Yields were determined usually by gas chromatography although a few isolation experiments were carried out.

Phenylacetyl Chloride - To a solution containing 3.7 g. (0.024 moles) of the acid chloride in 15 ml. toluene was added slowly 6.6 g. (0.024 moles) of the hydride. The reaction flask was flushed with nitrogen and stoppered. After a few minutes the reaction mixture became warm and was cooled in an ice bath. The reaction was allowed to proceed at room temperature for five days. Distillation at reduced pressure yielded 1.58 g., 55% of phenylacetaldehyde, m.p. 33-34°, and 5 g. of tri-*n*-butyltin chloride. The residue was identified as the ester β-phenylethyl phenylacetate. This was an oil whose infra-red spectrum was identical to that of a pure synthetic sample. The yield of the ester was 2.3 g., 40%.

Acetyl Chloride - To 0.30 g. (0.0038 moles) of the acid chloride was added 1.1 g. (0.0038 moles) of the tri-*n*-butyltin hydride. The reaction became very exothermic and was immediately cooled in an ice bath. The reaction was complete within 24 hrs. and was analyzed by gas chromatography.

The yield of aldehyde and ester in Table I was found by comparing the peak areas of the respective products.

Isobutyryl Chloride (Neat) - To a solution containing 0.3680 g. (0.00367 moles) of n-heptane, and 0.3870 g. (0.00364 moles) of the acid chloride, was added 1.1 g. of tri-n-butyltin hydride. The reaction was exothermic at room temperature. Gas chromatographic analysis gave a yield of 0.00117 moles, 64% of the ester, isobutyl isobutyrate. The balance, 36%, was given as the yield of isobutyraldehyde.

Isobutyryl Chloride (Solution) - To a solution containing 0.3822 g. (0.00381 moles) of n-heptane, 0.3881 g. (0.00365 moles) of the acid chloride and 5.0 ml. of 2,3-dimethyl butane was added 1.1 g. (0.0038 moles) of tri-n-butyltin hydride. This reaction, at room temperature afforded a yield of 0.00088 moles, 48% of the ester, as determined by gas chromatography. A 52% yield of the aldehyde was determined by difference.

Valeroyl Chloride (Neat) - To 0.3745 g. (0.00374 moles) of n-heptane and 0.4473 g. (0.00371 moles) of the acid chloride was added 1.1 g. of the hydride. The reaction was slightly exothermic. This reaction, at room temperature afforded 0.00150 moles, 81% of the ester, as determined by gas chromatography, using the internal standard method. The difference, 19% was the yield for the aldehyde.

Valeroyl Chloride (Solution) - To a solution of 0.3660 g. (0.00365 moles) of n-heptane, 0.4485 g. (0.00373 moles) of the acid chloride and 5.0 ml. of 2,3-dimethyl butane was added 1.1 g. of the hydride. Gas chromatographic analysis gave a yield of 0.00016 moles, 9% of the ester, hence a 91% yield of the aldehyde.

Ethyl Chlorocarbonate - To 4.9 g. (0.045 moles) of the chlorocarbonate was added 13.2 g. (0.045 moles) of tri-*n*-butyltin hydride. The reaction, which was not exothermic, was allowed to proceed at room temperature for approximately six weeks. The reaction was not complete at this time, but distillation of the mixture yielded only two products, ethyl formate and the organotin chloride. A significant amount of chloroformate was also isolated. When this reaction was allowed to go to completion, ethyl formate was produced in nearly quantitative yields.

Benzoyl Chloride (Neat) - To 0.50 g. (0.0036 moles) of the acid chloride was added 1.1 g. (0.0038 moles) of tri-*n*-butyltin hydride. The exothermic reaction was complete within 24 hrs. at room temperature. The infra-red indicated the presence of both the ester, 1730 cm.$^{-1}$ and the aldehyde, 1700 cm.$^{-1}$. Gas chromatographic analysis also indicated both products. A 35% yield of the ester was determined by comparing the peak areas of the organotin chloride and benzyl benzoate. The 65% yield of aldehyde was determined by difference from 100% reaction.

Benzoyl Chloride (Solution) - This reaction was carried out in the same manner as the neat reaction and with essentially the same molar quantities except 5.0 ml. of *m*-xylene was added to the reaction mixture. Gas chromatography gave a yield of 20% of the benzyl benzoate and 80% of benzaldehyde determined in the same manner as in the neat reaction.

Propionyl Chloride (Neat) - To a solution of 0.3500 g. (0.0038 moles) of propionyl chloride and 0.4808 g. (0.0048 moles) of the internal standard, *n*-heptane, was added 1 ml. (0.0038 moles) of the hydride. The reaction mixture, after being flushed with nitrogen and stoppered, was placed in a 25°

constant temperature bath. After six days the reaction mixture was analyzed by gas chromatography. There was no evidence of propionaldehyde. An 87% yield of n-propyl propionate was realized under these conditions.

Propionyl Chloride (Isolation Experiment) - To 4.2 g. (0.045 moles) of the acid chloride was added with external cooling 13.2 g. (0.045 moles) of tri-n-butyltin hydride. After 24 hrs. the reaction mixture was distilled at aspirator pressure and most of the product collected in a dry ice trap. The substance collected, 2.5 g. (80%), was n-propyl propionate with only a trace of the aldehyde as indicated by gas chromatography.

Propionyl Chloride in Methyl Acetate - To a solution containing 0.3872 g. (0.00386 moles) of n-heptane, 0.3042 g. (0.00329 moles) of the acid chloride and 5.0 ml. of the solvent was added 1.1 g. (0.0038 moles) of the hydride. Gas chromatographic analysis indicated a yield of 0.00015 moles, 9% of the ester and a 91% yield of the aldehyde, determined by difference.

Propionyl Chloride in Tri-n-butyltin Chloride - To a solution containing 0.3874 g. (0.00387 moles) of n-heptane, 0.3305 g. (0.00357 moles) of the acid chloride and 5.0 ml. of the solvent was added 1.1 g. of the hydride. After the reaction was complete, there was a noticeable separation of tin metal. The reaction mixture was centrifuged and the solution decanted. Gas chromatographic analysis of the clear solution gave a yield of 0.00120 moles of the ester, 73%. The balance, 27%, was aldehyde.

Propionyl Bromide (Neat) - To a mixture of 0.3656 g. (0.00365 moles) of n-heptane and 0.6395 g. (0.00466 moles) of the acid bromide was added 1.1 g. of tri-n-butyltin hydride. This reaction was very exothermic and was allowed to proceed at room temperature. Gas chromatographic analysis using the internal standard method showed a yield of 0.00080 moles of n-propyl propionate. This corresponds to 21% yield of the ester. The remaining 79% was attributed to the aldehyde.

Propionyl Bromide (Solution) - To a solution of 0.3958 g. (0.0395 moles) of n-heptane and 0.6082 g. (0.00444 moles) of the acid bromide in 5.0 ml. of 2,3-dimethyl butane was added 1.1 g. of the hydride. This reaction also was very exothermic and was allowed to go to completion at room temperature. Gas chromatographic analysis gave a yield of 0.00077 moles, 41% of the ester and a 59% yield of the aldehyde by difference.

Benzoyl Bromide - To 0.71 g. of the acid bromide (0.0038 moles) was added 1.1 g. of tri-n-butyltin hydride (0.0038 moles). The reaction was very exothermic and was placed in a 25° temperature bath. Gas chromatographic analysis indicated only two products, the organotin bromide and benzaldehyde.

## REACTIONS OF ACID CHLORIDES IN THE PRESENCE OF AN ADDED CARBONYL COMPOUND

Acetyl Chloride in the Presence of Cyclohexanone. To a cooled solution of 0.3758 g. (0.0038 moles) of cyclohexanone, .30 g. (0.0038 moles) acetyl chloride and 0.4382 g. (0.0039 moles) of the internal standard, chlorobenzene was added 1 ml. (0.0038 moles) of tri-n-butyltin hydride. After the reaction mixture was flushed with nitrogen and stoppered, it was placed in a constant temperature bath at 25°. It was analyzed by gas chromatography five days later in the usual manner. The yields obtained were: 5% of cyclohexyl acetate, 31% of ethyl acetate, and 64% acetaldehyde by difference. The yield of acetaldehyde actually shown on the chromatogram was 10%.

Propionyl Chloride in the Presence of Benzaldehyde. To a solution of 0.3445 g. (0.0037 moles), of propionyl chloride, 0.4142 g. (0.0039 moles) of benzaldehyde, and .3320 g. (0.0033 moles) of the internal standard, n-heptane, was added 1 ml. of tri-n-butyltin hydride. About a week later the reaction mixture was analyzed by gas chromatography by the usual method. Again the aldehyde peak was missing, but was estimated by difference, since the infra-red spectrum (No. 4510) showed the characteristic aldehyde absorption for propionaldehyde at 2800, 1720 and 1430 cm.$^{-1}$. The yields were: 10% n-propyl propionate, 70% benzyl propionate and 20% propionaldehyde.

Acetyl Chloride in the Presence of Benzaldehyde. To a mixture of 0.3223 g. (0.0041 moles) of acetyl chloride, 0.4220 g. (0.0041 moles) of benzaldehyde and 0.4422 g. (0.0038 moles) of the internal standard, chlorobenzene, was added 1 ml. of tri-n-butyltin hydride. The reaction flask was cooled in an ice bath for a moment, flushed with nitrogen, stoppered securely and placed in a 25° constant temperature bath. Thirty-six hours later the reaction mixture gave a negative hydride test. The mixture was analyzed by gas chromatography. The yields were: 18% acetaldehyde (52% by difference), 25% ethyl acetate and 23% benzyl acetate.

Acetyl Chloride in the Presence of Anisaldehyde. This reaction was carried out as above using 0.298 g. (0.0038 moles) of acetyl chloride, 0.5436 g. (0.0040 moles) of anisaldehyde and 0.4141 g. (0.0037 moles) of the internal standard, chlorobenzene. After 36 hrs. the reaction mixture was analyzed in the same manner as the experiment above. The yields as determined were: 8% acetaldehyde,(57% by difference), 63% anisaldehyde remaining (which again points up our difficulty in analyzing for aldehydes), 22% of ethyl acetate, and 21% of anisyl acetate.

Amounts of Trapping in the Propionyl Chloride Reaction with Tri-n-butyltin Hydride in the Presence of an Added Carbonyl Compound Under Standard Conditions. Approximately equimolar quantities, 0.0038 moles, of the acid chloride, internal standard, n-heptane and added carbonyl compound were dissolved in 5.0 ml. of solvent. To this mixture 1.0 ml. of the hydride was added. The reaction flask was flushed with nitrogen, the stopper securely fastened and placed in a constant temperature bath at 25°. The flask remained in the bath until all the organotin hydride was consumed. The solution was tested for the presence of hydride by removing an aliquot and adding it to an ethereal solution of sulfuric acid. Evolution of gas, hydrogen, constitutes a positive test for the presence of hydride. The yield of the ester resulting from the added carbonyl compound was determined by gas chromatography utilizing the internal standard method. Pertinent data for these experiments are given in Table XIV.

## TABLE XIV

Amounts of Trapping in the Propionyl Chloride (0.0038 moles) Reaction with Tri-n-butyltin Hydride (0.0037 moles) in the Presence of an Added Carbonyl Compound under Standard Conditions, (0.63M), 25°C

| Added Carbonyl Compound | RCHO (mmoles) | $C_2H_5COCl$ (mmoles) | Internal Standard (mmoles) | Solvent | $C_2H_5CO_2CH_2R$[a] % yield (mmoles) |
|---|---|---|---|---|---|
| cycloheptanone | 3.88 | 3.64 | 3.40 | DMB[b] | 3.2 (.12) |
| $C_6H_5CHO$ | 4.16 | 4.16 | 3.79 | DMB | 63.4[c] (260) |
| $C_6H_5CHO$ | 4.05 | .35 ml. | 3.73 | $(C_2H_5)_2O$ | 13 (.49) |
| $C_6H_5CHO$ | 3.81 | .40 ml. | 3.84 | $C_6H_5CH_3$ | 34.6 (1.31) |
| $C_6H_5CHO$ | 3.77 | .30 ml. | 3.93 | DMB | 33.7 (1.18) |
| $(CH_3)(CH_2)_5CHO$ | 3.84 | 3.84 | 3.83 | DMB | 22[d] (1.43) |
| m-$ClC_6H_4CHO$ | 3.81 | 3.52 | 3.79 | DMB | 38.7 (1.36) |
| p-$CH_3C_6H_4CHO$ | 3.52 | 3.65 | 3.84 | DMB | 38.7 (1.36) |
| p-$CH_3OC_6H_4CHO$ | 3.79 | .35 ml. | 3.76 | $(C_2H_5)_2O$ | 20 (.75) |
| p-$CH_3OC_6H_4CHO$ | 3.95 | .40 ml. | 3.82 | $C_6H_5CH_3$ | 13 (.50) |
| p-$CH_3OC_6H_4CHO$ | 3.84 | .32 ml. | 3.84 | $C_6H_5CH_3$ | 14 (.52) |
| p-$ClC_6H_4CHO$ | 3.76 | .40 ml. | 3.72 | MeOAc | 5.1[e] (.19) |
| m-$CH_3C_6H_4CHO$ | 3.04 | .32 ml. | 3.75 | DMB | 19 (.53) |

continued -

TABLE XIV - continued

[a] Yield based on acid chloride unless amount of aldehyde was less than 0.0037 moles. In most cases the yield of _n_-propyl propionate was small. Main reaction product was propionaldehyde.

[b] 2,3-dimethyl butane.

[c] Reduction was carried out with $(CH_3)_3Sn\text{-}H$.

[d] 75% _n_-propyl propionate.

[e] 14% _n_-propyl propionate.

## PREPARATION OF TRIPHENYLACETYL CHLORIDE

Preparation of Triphenylmethyl Chloride. This compound was prepared by the method described by Vogel[37] from benzene and carbon tetrachloride in 40-50% yields.

Preparation of Triphenylacetic Acid. Triphenylmethyl chloride was treated with powdered magnesium to form the Grignard reagent and this in turn was carboxylated with carbon dioxide gas according to the method described by Zook[38]. Subsequent hydrolysis and recrystallization of the product resulted in an 86% yield.

Preparation of Triphenylacetyl Chloride. The carboxylic acid was then allowed to react with thionyl chloride to form the acid chloride in quantitative yields. The product was recrystallized in the manner described by Norris and Cresswell.[39]

## FRAGMENTATION EXPERIMENTS

The Reaction of Triphenylacetyl Chloride with Tri-*n*-butyltin Hydride. - Into a 50 ml. flask attached to a gas buret and a dropping funnel containing 6.6 g. (0.022 moles) of hydride in 5 ml. of xylene, was placed 5.5 g. (0.018 moles) 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 two hours. After a total of four hours the collected gas was transferred into a previously evacuated gas cell and its infra-red spectrum, (No. 3535),was taken. Characteristic carbon monoxide absorptions at 2250 and 2000 cm.$^{-1}$ served to identify the gas. The volume of the gas collected, 45 ml., corresponds to a 10% yield. On cooling the reaction mixture, a white precipitate formed. This was 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 strong carbonyl absorption at 1720 cm.$^{-1}$, an aldehydic hydrogen stretch between 2900 and 2800 cm.$^{-1}$ (2 bands) and a characteristic aldehyde absorption at 1445 cm.$^{-1}$, (No. 3603). The mother liquor was subjected to column chromatography on acidic alumina. Three fractions were found on eluting with mixtures of petroleum ether (30-60°) and 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 triphenylacetaldehyde, m.p. 102-105°. This brought the total weight of the aldehyde to 4.4 g. which is a 90% yield. The last fraction was tri-n-butyltin chloride.

The Behavior of Triphenylacetyl Chloride and Tri-n-butyltin Chloride.- In a reaction system identical to the one described in the decarbonylation reaction, 5.5 g. (0.018 moles) of the acid chloride was dissolved in 50 ml. of xylene. Into the addition funnel was placed 5.6 g. (0.018 moles) of the chloride in 5-8 ml. of xylene. The closed system was heated to 105-110° for one-half hour to equilibrate the system and the expanded gas was expelled. The solution of the chloride was added over a period of one hour and the reaction mixture was heated for an additional 3 1/2 hrs. with no apparent evolution of gas.

Benzyl Chloroformate. - To 0.62 g. (0.0040 moles) of the chloroformate was added 1.1 g. (0.0038 moles) of the hydride. The reaction was not exothermic and at room temperature took about two weeks to go to completion in a flask with a Bunsen valve. When the reaction was complete 0.3459 g. (0.00345 moles) of the internal standard, n-heptane was added and the reaction mixture was analyzed by gas chromatography, using the internal standard method. A yield of 0.00145 moles (39%) of toluene and 0.00231 moles (61%) of benzyl formate was found.

## CATALYSIS BY AZOBISISOBUTYRONITRILE

Catalysis of the Reduction of Ethyl Chloroformate.- The reaction mixture for the uncatalyzed reaction consisted of 1.48 g. (0.014 moles) of ethyl chloroformate, 4.4 g. (0.015 moles) 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 moles) 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 time 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.

Catalysis of Benzoyl Chloride Reduction. - A solution containing 1.239 g. (0.0088 moles) of benzoyl chloride and 2.2 g. (0.0078 moles) of tri-n-butyltin hydride in 10.0 ml. of m-xylene was divided into two equal parts. To one part was added 0.039 g. (0.0002 moles) of azobisisobutyronitrile. Several 1 ml. portions were removed from each part, placed in an ampoule, flushed with nitrogen and sealed. All ampoules were placed simultaneously in an 80° oil bath. Ampoules were removed at intervals and analyzed by infra-red spectroscopy. The reaction was monitored by observing the bands at 1810 cm.$^{-1}$ (organotin hydride), 1780 cm.$^{-1}$ (acid chloride), 1730 cm.$^{-1}$ (ester), and 1700 cm.$^{-1}$ (aldehyde). The results of this experiment are presented in Table XV.

## TABLE XV

AIBN Catalyzed and Uncatalyzed Reaction of Benzoyl Chloride and Tri-n-butyltin Hydride in m-xylene at 80°

| Time After Mixing | Intensity of Absorption at 1810 cm.$^{-1}$ | |
|---|---|---|
| | Uncatalyzed | Catalyzed |
| 0.5 hr. | strong | strong |
| 2 hr. | .50 | .35 |
| 4 hr. | .45 | .15 |
| 7.5 hr. | .15 | .07 |

The uncatalyzed reaction was complete in about 10 hrs. The infra-red spectrum indicated that in the catalyzed reaction there was much more ester formed than in the uncatalyzed reaction. This observation was confirmed by gas chromatography by comparing the areas under the peaks of the organotin chloride and the ester. The uncatalyzed reaction gave a yield of 13% ester while the catalyzed reaction afforded a 30% yield of benzyl benzoate.

The Reaction of Benzaldehyde with Tri-n-butyltin Hydride with Free Radical Catalysis. - This reaction was conducted under the conditions described by Neumann.[32] To a mixture of 0.833 g. (0.00785 moles) of benzaldehyde and 0.038 g. (0.00023 moles) of azobisisobutyronitrile was added 2.2 g. (0.0076 moles) of the hydride. The reaction mixture was placed in glass ampoules, flushed with nitrogen, sealed and placed in an oil bath at 80°. After 24 hrs. the mixture still showed a very strong hydride band at 1810 cm.$^{-1}$. A large amount of alcohol was also indicated in the spectrum. After 48 hrs. the reaction was still not complete and the absorption of the alcohol indicated strongly that alcohol was a major product in this reaction.

## RELATIVE RATE DETERMINATIONS ON ACID CHLORIDES

### Procedure

The relative rate constants of the acid chlorides listed in Table IV were determined by allowing each acid chloride to compete with an alkyl bromide for an insufficient amount of tri-_n_-butyltin hydride. When all the hydride was consumed the reaction mixture was analyzed for the hydrocarbon resulting from the reduction of the alkyl bromide by gas chromatography using a 4-foot by 1/4 inch column packed with 10% Silicone rubber on 60-80 mesh Chromosorb P.

The two competitors, the internal standard, _n_-heptane and the hydride were weighed out into the reaction flask. The solvent was then added by means of a pipette. The flask was then flushed with nitrogen, tightly stoppered and placed in a constant temperature bath at 25 ± 0.01°C.

The yield of hydrocarbon was determined by the internal standard method.[26] Calibration curves were prepared by chromatographing synthetic mixtures containing the pure component, whose concentration was to be determined in the reaction mixtures, and an internal standard in three or four accurately known proportions. The ratios of the areas of the peaks for the component and the internal standard were then plotted against the ratios of the amounts actually present. The reaction mixture, which contained a known amount of the internal standard, was then chromatographed and the ratio of the component to the internal standard peak areas was determined. The concentration of the component was then calculated. The areas were determined by multiplying the peak height by the peak width at the mid-point. The number of moles of the hydrocarbon was subtracted from the number of moles of the hydride used giving the number of moles of acid chloride which had reacted with the organotin hydride assuming 100% reaction.

The relative rate constants were determined using the equation of Ingold and Stow[17]:

$$\frac{\log \frac{A_o}{A}}{\log \frac{B_o}{B}} = k_A/k_B$$

in which: $A_o$ = the initial concentration of halide A
$A$ = the final concnetration of halide A
$B_o$ = the initial concentration of halide B.
$B$ = the final concentration of halide B

The relative rate constants obtained for each set of competitors is given in Table XVI. Initial and final concentrations for all competitive reactions are given in Table XVII.

## TABLE XVI

Relative Rates of Acid Chlorides, Bromides and Alkyl Bromides with Tri-n-butyltin Hydride at 25°C (0.63M)

| Exp. No. | Competitor A | Competitor B | Solvent | $k_A/k_B$ |
|---|---|---|---|---|
| 1 | $C_6H_5COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.442 |
| 2 | $C_6H_5COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.524 |
| 3 | p-Cl$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.651 |
| 4 | p-Cl$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.645 |
| 5 | $C_6H_5COBr$ | 2-Br$C_8H_{17}$ | m-xylene | 97.77 |
| 6 | m-Cl$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 4.05 |
| 7 | m-Cl$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 3.87 |
| 8 | p-CN$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 33.27 |
| 9 | p-CN$C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 25.95 |
| 10 | $C_6H_5COBr$ | $C_6H_5CH_2Br$ | m-xylene | 10.51 |
| 11 | $C_6H_5COBr$ | $C_6H_5CH_2Br$ | m-xylene | 12.38 |
| 12 | m-$CH_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.426 |
| 13 | m-$CH_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.481 |
| 14 | p-$CH_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.127 |
| 15 | p-$CH_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.152 |
| 16 | p-$CH_3OC_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.090 |
| 17 | p-$CH_3OC_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 0.069 |
| 18 | p-$CF_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 21.10 |
| 19 | p-$CF_3C_6H_4COCl$ | 2-Br$C_8H_{17}$ | m-xylene | 15.70 |

TABLE XVI - continued

| Exp. No. | Competitor A | Competitor B | Solvent | $k_A/k_B$ |
|---|---|---|---|---|
| 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 | 29.65 |
| 29 | $C_6H_5CH_2Br$ | $C_6H_5COCl$ | m-xylene | 27.90 |
| 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 | 24.20 |
| 35 | m-$ClC_6H_4COCl$ | 2-$BrC_8H_{17}$ | MeOAc | 20.65 |
| 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 |

TABLE XVI - continued

| Exp. No. | Competitor A | Competitor B | Solvent | $k_A/k_B$ |
|---|---|---|---|---|
| 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 |

## TABLE XVII

### Initial and Final Concentrations of Substrates Used in Relative Rate Determinations of Acid Chlorides

| Exp. No. | Initial Conc. R-$C_6H_4COX$ (mmoles) | Initial Conc. R-Br (mmoles) | Initial Conc. $(C_4H_9)_3Sn$-H (mmoles) | Conc. I.S. n-heptane (mmoles) |
|---|---|---|---|---|
| 1 | 3.84 | 5.19 | 3.79 | 3.30 |
| 2 | 3.80 | 3.85 | 3.80 | 3.63 |
| 3 | 5.06 | 5.24 | 3.72 | 3.67 |
| 4 | 3.94 | 3.77 | 3.52 | 3.83 |
| 5 | 3.85 | 7.63 | 3.76 | 3.64 |
| 6 | 3.85 | 3.84 | 3.7[illegible] | 3.76 |
| 7 | 4.08 | 3.84 | 3.52 | 3.93 |
| 8 | 3.79 | 7.75 | 3.79 | 3.70 |
| 9 | 3.67 | 5.36 | 3.58 | 3.79 |
| 10 | 3.81 | 7.46 | 3.67 | 3.82 |
| 11 | 3.77 | 8.66 | 3.56 | 4.13 |
| 12 | 3.93 | 3.79 | 3.69 | 3.84 |
| 13 | 3.99 | 3.71 | 3.62 | 3.87 |
| 14 | 3.89 | 3.67 | 3.80 | 3.97 |
| 15 | 3.94 | 3.80 | 3.51 | 3.87 |
| 16 | 7.87 | 3.87 | 3.83 | 3.95 |
| 17 | 8.18 | 3.77 | 3.60 | 3.97 |
| 18 | 3.88 | 7.74 | 3.71 | 4.17 |
| 19 | 3.73 | 7.76 | 3.49 | 3.78 |
| 20 | 3.73 | 7.74 | 3.83 | 3.62 |
| 21 | 3.72 | 7.80 | 3.67 | 3.85 |
| 22 | 3.81 | 4.00 | 3.64 | 4.02 |
| 23 | 3.84 | 5.14 | 3.66 | 3.83 |
| 24 | 3.87 | 3.76 | 3.67 | 3.73 |

TABLE XVII - continued

| Exp. No. | Peak Areas R-H/I. S. | R-H (mmoles) | (mmoles) R-$C_6H_4$COX reacted | Final Conc. R-$C_6H_4$COX (mmoles) | Final Conc. R-Br (mmoles) |
|---|---|---|---|---|---|
| 1 | .913 | 2.67 | 1.12 | 2.72 | 2.52 |
| 2 | .710 | 2.29 | 1.31 | 2.49 | .156 |
| 3 | .706 | 2.29 | 1.43 | 3.63 | 2.95 |
| 4 | .590 | 1.99 | 1.53 | 2.41 | 1.78 |
| 5 | .060 | 0.20 | 3.56 | 0.29 | 7.43 |
| 6 | .288 | 1.00 | 2.78 | 1.07 | 2.84 |
| 7 | .250 | 0.87 | 2.65 | 1.43 | 2.97 |
| 8 | .148 | 0.05 | 3.29 | .47 | 7.25 |
| 9 | .117 | 0.04 | 3.18 | .49 | 4.96 |
| 10 | .180 | 0.86 | 2.81 | 1.00 | 6.60 |
| 11 | .166 | 0.87 | 2.69 | 1.08 | 7.79 |
| 12 | .660 | 2.25 | 1.44 | 2.49 | 1.54 |
| 13 | .636 | 2.19 | 1.43 | 2.56 | 1.52 |
| 14 | .852 | 3.00 | 0.80 | 3.09 | 0.69 |
| 15 | .816 | 2.81 | 0.70 | 3.24 | 0.99 |
| 16 | .840 | 2.94 | 0.89 | 6.98 | 0.93 |
| 17 | .815 | 2.86 | 0.72 | 7.46 | 0.89 |
| 18 | .162 | 0.58 | 3.13 | 0.75 | 7.16 |
| 19 | .190 | 0.64 | 2.85 | 0.88 | 7.12 |
| 20 | .472 | 1.52 | 2.31 | 1.42 | 6.22 |
| 21 | .417 | 1.43 | 2.24 | 1.48 | 6.37 |
| 22 | .495 | 1.77 | 1.87 | 1.94 | 2.23 |
| 23 | .595 | 2.01 | 1.65 | 2.19 | 3.13 |
| 24 | .635 | 2.09 | 1.58 | 2.29 | 1.67 |

TABLE XVII - continued

| Exp. No. | Initial Conc. R-$C_6H_4COX$ (mmoles) | Initial Conc. R-Br (mmoles) | Initial Conc. $(C_4H_9)_3Sn$-H (mmoles) | Conc. I.S. *n*-heptane (mmoles) |
|---|---|---|---|---|
| 25 | 3.89 | 3.76 | 3.59 | 3.70 |
| 26 | 7.54 | 3.41 | 3.73 | 3.52 |
| 27 | 6.90 | 4.11 | 3.76 | 3.80 |
| 28 | 8.30 | 3.60 | 3.87 | 3.61 |
| 29 | 8.81 | 3.76 | 3.75 | 3.81 |
| 30 | 4.08 | 3.82 | 3.73 | 2.78 |
| 31 | 3.69 | 3.88 | 3.94 | 3.90 |
| 32 | 3.80 | 3.81 | 3.73 | 3.66 |
| 33 | 3.95 | 3.94 | 4.08 | 4.08 |
| 34 | 3.80 | 4.81 | 3.77 | 3.89 |
| 35 | 3.82 | 4.70 | 3.65 | 3.76 |
| 36 | 7.52 | 3.78 | 3.80 | 3.75 |
| 37 | 8.36 | 3.73 | 4.00 | 3.87 |
| 38 | 4.09 | 3.74 | 3.74 | 3.76 |
| 39 | 3.86 | 3.79 | 3.72 | 3.81 |
| 40 | 3.85 | 3.81 | 3.71 | 3.77 |
| 41 | 3.85 | 3.81 | 3.79 | 3.69 |
| 42 | 7.48 | 3.67 | 3.74 | 3.86 |
| 43 | 8.04 | 3.76 | 3.74 | 3.94 |
| 44 | 3.71 | 4.89 | 3.73 | 3.84 |
| 45 | 3.84 | 4.74 | 3.49 | 3.74 |

## TABLE XVII - continued

| Exp. No. | Peak Areas R-H/I. S. | R-H (mmoles) | (mmoles) R-$C_6H_4COX$ reacted | Final Conc. R-$C_6H_4COX$ (mmoles) | Final Conc. R-Br (mmoles) |
|---|---|---|---|---|---|
| 25 | .613 | 2.02 | 1.57 | 2.32 | 1.74 |
| 26 | .530 | 2.32 | 1.41 | 6.13 | 1.09 |
| 27 | .523 | 2.51 | 1.25 | 5.65 | 1.60 |
| 28 | .717 | 3.23 | 0.64 | 7.66 | 0.37 |
| 29 | .670 | 3.18 | 0.57 | 8.24 | 0.58 |
| 30 | .988 | 2.21 | 1.52 | 2.56 | 1.61 |
| 31 | .697 | 2.42 | 1.52 | 2.17 | 1.46 |
| 32 | .347 | 1.14 | 2.59 | 1.21 | 2.67 |
| 33 | .374 | 1.35 | 2.73 | 1.22 | 2.59 |
| 34 | .119 | 0.41 | 3.36 | 0.44 | 4.40 |
| 35 | .121 | 0.41 | 3.24 | 0.58 | 4.29 |
| 36 | .876 | 3.01 | 0.79 | 6.73 | 0.77 |
| 37 | .924 | 3.17 | 0.83 | 7.53 | 0.56 |
| 38 | .563 | 1.88 | 1.86 | 2.23 | 1.86 |
| 39 | .608 | 2.10 | 1.62 | 2.24 | 1.69 |
| 40 | .391 | 1.32 | 2.39 | 1.46 | 2.49 |
| 41 | .445 | 1.46 | 2.33 | 1.52 | 2.35 |
| 42 | .885 | 3.03 | 0.72 | 6.76 | 0.64 |
| 43 | .853 | 2.99 | 0.75 | 7.29 | 0.77 |
| 44 | .274 | 0.94 | 2.79 | 0.92 | 3.95 |
| 45 | .234 | 0.79 | 2.70 | 1.14 | 3.95 |

# RELATIVE RATE DETERMINATIONS OF ALDEHYDES IN THE PROPIONYL CHLORIDE REACTION

## Procedure

The relative rate constants for the aldehydes listed in Table VI were determined by allowing the aldehydes to compete in pairs for an insufficient amount of the postulated acyl radical and analyzing the resultant reaction mixture for the appropriate propionate ester. The reactions were conducted at 25 ± 0.01°C. The procedure, analysis and calculation of the relative rate constants was the same as that described for the determination of the relative rate constants of the acid chlorides.

The relative rate constants obtained for each set of competitors is given in Table XVIII. Initial and final concentrations for all these competitive reactions are given in Table XIX. The data used in plotting the calibration curves are given in Table XXII. Two internal standard curves have been reproduced (pages 90 and 91).

# TABLE XVIII

Competitive Experiments at 25° in 5 ml. of Solvent on a 0.0038 Mole Scale Using Propionyl Chloride and Tri-n-butyltin Hydride

| Exp. No. | Competitor A | Competitor B | Solvent | $k_A/k_B$ | Internal Standard Curve No. |
|---|---|---|---|---|---|
| 1 | cyclohexanone | cyclopentanone | DMB[a] | 12.30[b] | 18, 19 |
| 2 | cyclohexanone | cyclopentanone | DMB | 17.71[b] | 18, 19 |
| 3 | cyclohexanone | cyclopentanone | DMB | 17.94[b] | 18, 19 |
| 4 | $C_6H_5CHO$ | cyclohexanone | DMB | 11.00[c] | 22, 23 |
| 5 | $C_6H_5CHO$ | cyclohexanone | DMB | 10.54[c] | 22, 23 |
| 6 | $CH_3(CH_2)_5CHO$ | $C_6H_5CHO$ | DMB | 1.53 | 22, 24 |
| 7 | $CH_3(CH_2)_5CHO$ | $C_6H_5CHO$ | DMB | 1.70 | 22, 24 |
| 8 | m-$ClC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.57 | 22, 26 |
| 9 | m-$ClC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.57 | 22, 26 |
| 10 | p-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.26 | 22, 27 |
| 11 | p-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.25 | 22, 27 |
| 12 | p-$ClC_6H_4CHO$ | $C_6H_5CHO$ | MeOAc | 1.25 | 30, 33 |
| 13 | p-$ClC_6H_4CHO$ | $C_6H_5CHO$ | MeOAc | 1.27 | 30, 33 |
| 14 | $C_6H_5CHO$ | cyclohexanone | DMB | 10.86 | 30, 32 |
| 15 | m-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 0.92 | 30, 37 |
| 16 | m-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 0.96 | 30, 37 |
| 17 | $CH_3(CH_2)_5CHO$ | p-$MeOC_6H_4CHO$ | $C_6H_5CH_3$ | 5.16 | 30, 31 |
| 18 | $CH_3(CH_2)_5CHO$ | p-$MeOC_6H_4CHO$ | $C_6H_5CH_3$ | 2.81 | 30, 31 |

TABLE XVIII - continued

| Exp. No. | Competitor A | Competitor B | Solvent | $k_A/k_B$ | Internal Standard Curve No. |
|---|---|---|---|---|---|
| 19 | $CH_3(CH_2)_5CHO$ | p-$MeOC_6H_4CHO$ | $C_6H_5CH_3$ | 3.85 | 30, 36 |
| 20 | $CH_3(CH_2)_5CHO$ | p-$MeOC_6H_4CHO$ | $C_6H_5CH_3$ | 3.06 | 30, 36 |
| 21 | p-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.27 | 29, 30 |
| 22 | p-$MeC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.20 | 29, 30 |
| 23 | m-$ClC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.84 | 40, 30 |
| 24 | m-$ClC_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.69 | 40, 30 |

[a] 2,3-dimethyl butane

[b] 45°C

[c] Trimethyltin Hydride was used.

## TABLE XIX

### Initial and Final Concentrations of Added Carbonyl Compounds Used in Relative Rate Determinations[a]

| Exp. No. | Initial Conc. Competitor A (mmoles) | Conc. I. S. (mmoles) | Peak Areas Product A/IS | (mmoles) ester from A | (mmoles) Final Conc. of A |
|---|---|---|---|---|---|
| 1 | 3.88 | 3.36 | .27 | 0.87 | 3.01 |
| 2 | 3.91 | 3.41 | .33 | 1.09 | 2.82 |
| 3 | 3.83 | 3.52 | .17 | 0.58 | 3.25 |
| 4 | 3.77 | 4.04 | .57 | 1.92 | 1.85 |
| 5 | 3.82 | 3.85 | .66 | 2.15 | 1.67 |
| 6 | 5.85 | 3.79 | .47 | 1.25 | 4.60 |
| 7 | 8.79 | 3.80 | .56 | 1.50 | 7.29 |
| 8 | 3.34 | 3.80 | .31 | 0.97 | 2.37 |
| 9 | 4.01 | 3.80 | .34 | 1.06 | 2.98 |
| 10 | 4.10 | 3.80 | .21 | 0.67 | 3.43 |
| 11 | 7.98 | 3.79 | .24 | 0.76 | 7.22 |
| 12 | 3.48 | 3.86 | .04 | 0.14 | 3.33 |
| 13 | 6.86 | 3.80 | .066 | 0.23 | 6.63 |
| 14 | 3.87 | 3.77 | .13 | 0.40 | 3.47 |
| 15 | 3.56 | 3.95 | .166 | 0.47 | 3.09 |
| 16 | 4.17 | 3.82 | .185 | 0.54 | 3.63 |
| 17 | 3.81 | 3.85 | .138 | 0.38 | 3.46 |
| 18 | 3.85 | 3.92 | .072 | 0.20 | 3.65 |
| 19 | 3.69 | 3.74 | .147 | 0.37 | 3.32 |
| 20 | 3.81 | 3.89 | .086 | 0.23 | 3.58 |
| 21 | 3.86 | 3.96 | .157 | 0.55 | 3.31 |
| 22 | 4.24 | 3.81 | .20 | 0.65 | 3.59 |
| 23 | 3.28 | 3.76 | .22 | 0.75 | 2.53 |
| 24 | 4.00 | 3.72 | .19 | 0.67 | 3.33 |

[a] 0.0038 moles of $R_3Sn$-H and ETCOCl were used in each case.

TABLE XIX - continued

| Exp. No. | Initial Conc. Competitor B (mmoles) | Peak Areas Product B/IS | (mmoles) of ester from B | (mmoles) Final Conc. B |
|---|---|---|---|---|
| 1 | 3.72 | .02 | 0.07 | 3.65 |
| 2 | 3.69 | .022 | 0.08 | 3.61 |
| 3 | 17.90 | .045 | 0.16 | 17.74 |
| 4 | 7.50 | .14 | 0.49 | 7.01 |
| 5 | 8.35 | .12 | 0.46 | 7.89 |
| 6 | 3.85 | .17 | 0.55 | 3.30 |
| 7 | 3.86 | .13 | 0.42 | 3.44 |
| 8 | 5.25 | .32 | 1.03 | 4.22 |
| 9 | 6.47 | .36 | 1.14 | 5.35 |
| 10 | 3.80 | .16 | 0.50 | 3.30 |
| 11 | 3.70 | .09 | 0.28 | 3.42 |
| 12 | 4.17 | .04 | 0.14 | 4.03 |
| 13 | 3.80 | .035 | 0.11 | 3.69 |
| 14 | 7.54 | .02 | 0.08 | 7.46 |
| 15 | 3.87 | .167 | 0.53 | 3.34 |
| 16 | 3.58 | .181 | 0.55 | 3.03 |
| 17 | 7.73 | .047 | 0.15 | 7.58 |
| 18 | 9.97 | .058 | 0.20 | 9.77 |
| 19 | 7.85 | .060 | 0.20 | 7.65 |
| 20 | 9.35 | .057 | 0.19 | 9.16 |
| 21 | 4.26 | .144 | 0.48 | 3.78 |
| 22 | 3.90 | .17 | 0.51 | 3.39 |
| 23 | 5.12 | .238 | 0.71 | 4.41 |
| 24 | 6.50 | .21 | 0.67 | 5.83 |

# RELATIVE RATE DETERMINATIONS OF ALDEHYDES IN THE ALKYL BROMIDE REACTION

## Procedure

The relative rate constants for the aldehydes listed in Table IX were determined by allowing the aldehydes to compete in pairs in the reaction between an alkyl bromide and tri-n-butyltin hydride for an insufficient amount of the hydride. The organotin alkoxides resulting from the respective aldehydes were analyzed as the propionate esters after an excess of propionyl chloride was added to the reaction mixture after all the hydride had been consumed. The reactions were conducted at 25 ± 0.01°C. The procedure, analysis, and calculation of the relative rate constants was the same as that described for the determination of the relative rate constants of the acid chlorides.

The relative rate constants obtained for each set of competitors is given in Table XX. Initial and final concentrations for all these competitive reactions are given in Table XXI.

## TABLE XX

### Relative Rates of Aldehydes in Alkoxide Formation[a]

| Exp. No. | RX | Competitor A | Competitor B | Solvent | $k_A/k_B$ | Internal Standard Curve No. |
|---|---|---|---|---|---|---|
| 1 | 1-BrC$_8$H$_{17}$ | *p*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | MeOAc | 1.99 | 33, 30 |
| 2 | 1-BrC$_8$H$_{17}$ | *p*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | MeOAc | 1.86 | 33, 30 |
| 3 | 2-BrC$_8$H$_{17}$ | *p*-CH$_3$C$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB[b] | 1.17 | 29, 30 |
| 4 | 2-BrC$_8$H$_{17}$ | *p*-CH$_3$C$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 1.19 | 29, 30 |
| 5 | 2-BrC$_8$H$_{17}$ | *m*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 5.84 | 40, 30 |
| 6 | 2-BrC$_8$H$_{17}$ | *m*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 5.00 | 40, 30 |
| 7 | 2-BrC$_8$H$_{17}$ | *m*-CH$_3$C$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 1.05 | 37, 30 |
| 8 | 2-BrC$_8$H$_{17}$ | *m*-CH$_3$C$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 1.00 | 37, 30 |
| 9 | 2-BrC$_8$H$_{17}$ | *n*-heptaldehyde | C$_6$H$_5$CHO | DMB | 2.11 | 36, 30 |
| 10 | 2-BrC$_8$H$_{17}$ | *n*-heptaldehyde | C$_6$H$_5$CHO | DMB | 2.18 | 36, 30 |
| 11 | CHCl$_3$ | *m*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 4.64 | 40, 30 |
| 12 | CHCl$_3$ | *m*-ClC$_6$H$_4$CHO | C$_6$H$_5$CHO | DMB | 4.84 | 40, 30 |

TABLE XX - continued

| Exp. No. | RX | Competitor A | Competitor B | Solvent | $k_A/k_B$ | Internal Standard Curve No. |
|---|---|---|---|---|---|---|
| 13 | 2-Br$C_8H_{17}$ | m-ClC$_6$H$_4$CHO | $C_6H_5CHO$ | 3 ml DMB<br>2 ml Sn-Cl | 4.18 | 40, 30 |
| 14 | 2-Br$C_8H_{17}$ | m-ClC$_6$H$_4$CHO | $C_6H_5CHO$ | 3 ml DMB<br>2 ml Sn-Cl | 3.85 | 40,30 |
| 15 | 2-Br$C_8H_{17}$ | n-heptaldehyde | p-$CH_3OC_6H_4CHO$ | DMB | 10.0[c] | 36, 31 |
| 16 | 2-Br$C_8H_{17}$ | n-heptaldehyde | p-$CH_3OC_6H_4CHO$ | DMB | 10.0[c] | 36, 31 |
| 17 | SnCl | m-ClC$_6$H$_4$CHO | $C_6H_5CHO$ | DMB | 3.62 | 40, 30 |
| 18 | SnCl | m-ClC$_6$H$_4$CHO | $C_6H_5CHO$ | DMB | 3.68 | 40, 30 |
| 19 | SnCl | p-$CH_3C_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.01 | 29, 30 |
| 20 | SnCl | p-$CH_3C_6H_4CHO$ | $C_6H_5CHO$ | DMB | 1.09 | 29, 30 |

[a] These reactions were catalyzed by the alkyl bromide reaction with tri-n-butyltin hydride or by tri-n-butyltin chloride at 25°, (0.63M).

[b] 2,3-dimethyl butane

[c] not precisely determined; 10.0 is a minimum.

## TABLE XXI

### Initial and Final Concentrations of Added Carbonyl Compounds Used in Relative Rate Determinations[a]

| Exp. No. | RX Conc. (mmoles) | Initial Conc. Competitor A (mmoles) | Conc. I.S. (mmoles) | Peak Areas Product A/I.S. | (mmoles) ester from A | (mmoles) Final Conc. of A |
|---|---|---|---|---|---|---|
| 1 | 3.69 | 3.66 | 3.84 | .143 | 0.55 | 3.11 |
| 2 | 3.76 | 6.72 | 3.78 | .280 | 0.98 | 5.74 |
| 3 | 3.76 | 4.15 | 3.88 | .150 | 0.58 | 3.57 |
| 4 | 3.75 | 3.99 | 3.74 | .193 | 0.62 | 3.37 |
| 5 | 3.80 | 3.76 | 3.67 | .535 | 1.84 | 1.92 |
| 6 | 3.76 | 4.01 | 3.92 | .470 | 1.71 | 2.30 |
| 7 | 3.81 | 4.39 | 3.76 | .299 | 0.83 | 3.56 |
| 8 | 3.81 | 5.00 | 3.77 | .319 | 0.89 | 4.11 |
| 9 | 3.82 | 5.59 | 3.79 | .372 | 0.95 | 4.64 |
| 10 | 3.77 | 8.78 | 3.66 | .488 | 1.21 | 7.57 |
| 11 | 3.80 | 3.69 | 2.79 | .746 | 1.93 | 1.76 |
| 12 | 3.80 | 4.04 | 3.75 | .560 | 1.95 | 2.09 |
| 13 | 3.75 | 3.49 | 3.78 | .620 | 2.17 | 1.32 |
| 14 | 3.90 | 3.98 | 3.89 | .513 | 1.85 | 2.13 |
| 15 | 3.86 | 3.68 | 3.75 | .328 | 0.75 | 2.93 |

## TABLE XXI

Initial and Final Concentrations of Added Carbonyl Compounds Used in Relative Rate Determinations[a]

| Exp. No. | Initial Conc. Competitor B (mmoles) | Peak Areas Product B/I.S. | (mmoles) of ester from B | (mmoles) Final Conc. of B |
|---|---|---|---|---|
| 1 | 4.30 | .096 | 0.31 | 3.99 |
| 2 | 3.70 | .085 | 0.27 | 3.43 |
| 3 | 3.76 | .140 | 0.45 | 3.31 |
| 4 | 3.91 | .172 | 0.52 | 3.39 |
| 5 | 4.96 | .174 | 0.51 | 4.45 |
| 6 | 6.71 | .220 | 0.71 | 6.00 |
| 7 | 4.00 | .240 | 0.73 | 3.27 |
| 8 | 4.14 | .234 | 0.72 | 3.42 |
| 9 | 3.99 | .109 | 0.34 | 3.65 |
| 10 | 3.84 | .079 | 0.24 | 3.60 |
| 11 | 5.38 | .348 | 0.78 | 4.60 |
| 12 | 6.46 | .270 | 0.83 | 5.63 |
| 13 | 5.09 | .357 | 1.10 | 3.99 |
| 14 | 6.40 | .310 | 0.97 | 5.43 |
| 15 | 7.64 | - | - | - |

## TABLE XXI - continued

| Exp. No. | RX Conc. (mmoles) | Initial Conc. Competitor A (mmoles) | Conc. I.S. (mmoles) | Peak Areas Product A/I.S. | (mmoles) ester from A | (mmoles) Final Conc. of A |
|---|---|---|---|---|---|---|
| 16 | 3.72 | 3.72 | 3.93 | .307 | 0.83 | 2.89 |
| 17[b] | 1 ml | 3.84 | 3.88 | .596 | 2.13 | 1.71 |
| 18[b] | 1 ml | 4.07 | 3.82 | .586 | 2.10 | 1.97 |
| 19[b] | 1 ml | 3.90 | 3.77 | .460 | 1.49 | 2.41 |
| 20[b] | 1 ml | 4.01 | 3.73 | .498 | 1.59 | 2.42 |

[a] 0.0038 moles of $(C_4H_9)_3Sn\text{-}H$

[b] These experiments were catalyzed by $(C_4H_9)_3Sn\text{-}Cl$.

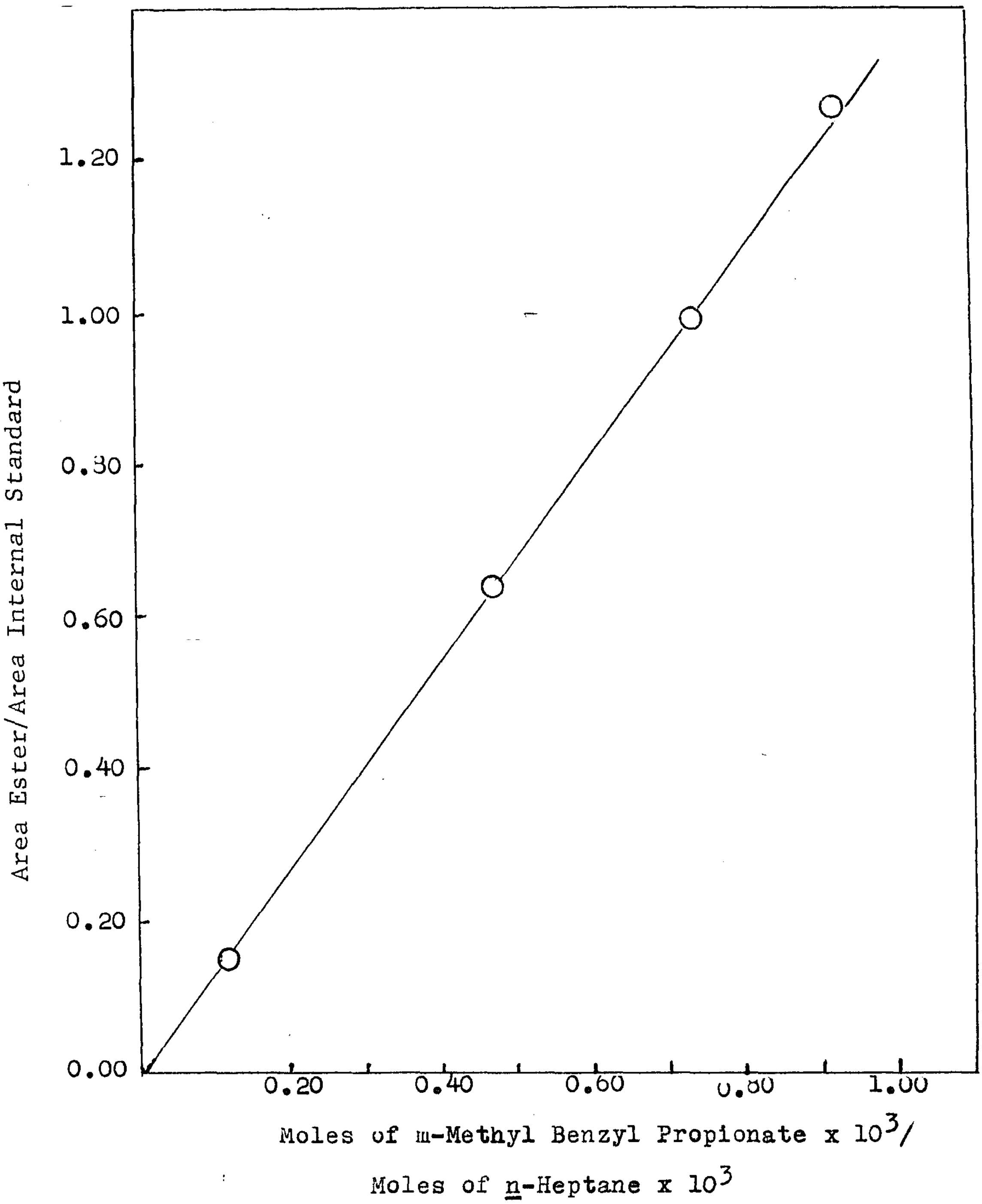
TABLE XXI - continued

| Exp. No. | Initial Conc. Competitor B (mmoles) | Peak Areas Product B/I.S. | (mmoles) of ester from B | (mmoles) Final Conc. of B |
|---|---|---|---|---|
| 16 | 9.45 | - | - | - |
| 17[b] | 5.64 | .369 | 1.13 | 4.51 |
| 18[b] | 6.82 | .390 | 1.22 | 5.60 |
| 19[b] | 3.87 | .487 | 1.47 | 2.40 |
| 20[b] | 3.82 | .474 | 1.42 | 2.40 |

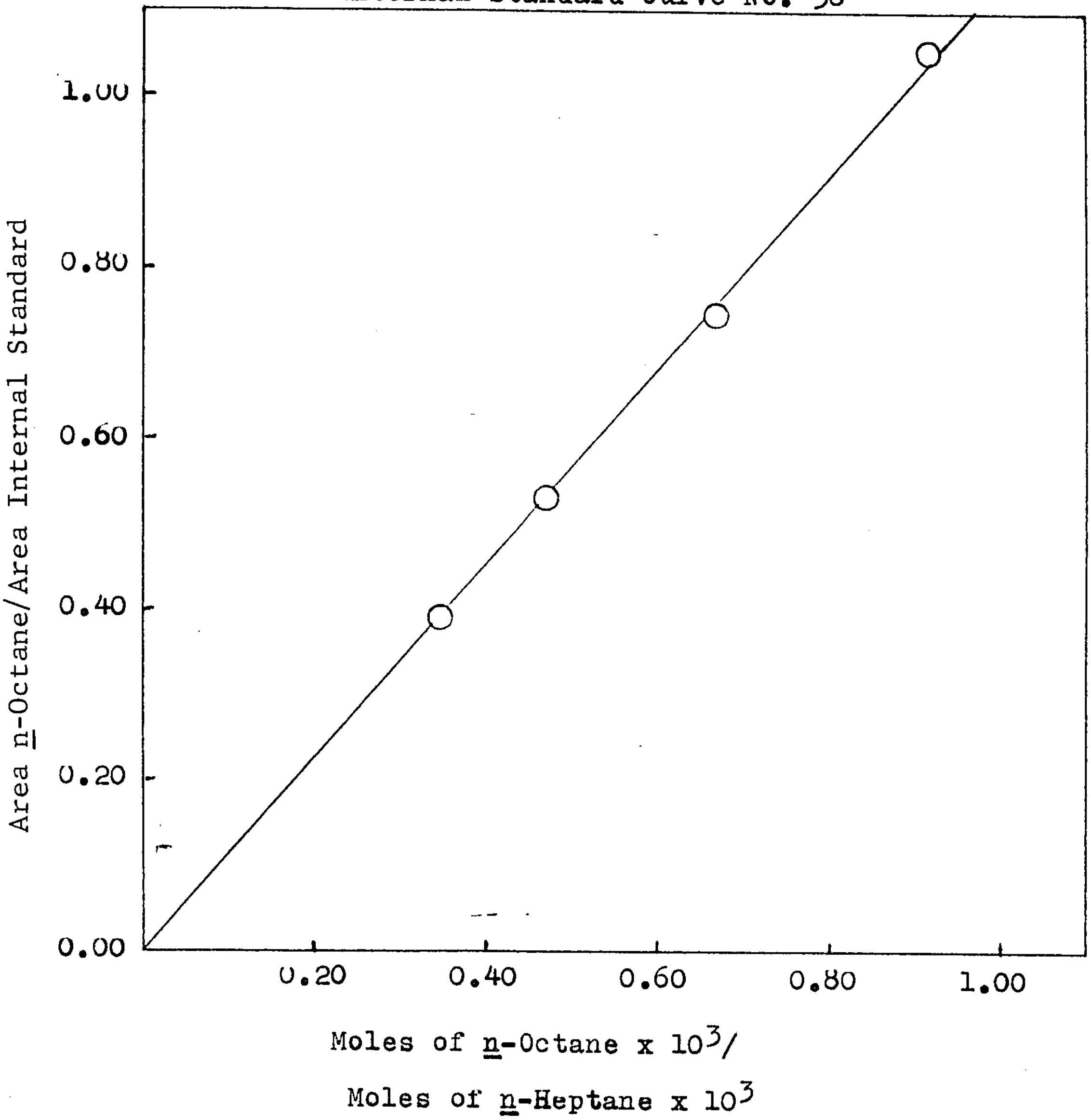
[a] 0.0038 moles of $(C_4H_9)_3Sn\text{-}H$

[b] These experiments were catalyzed by $(C_4H_9)_3Sn\text{-}Cl$

Internal Standard Curve No. 37



Internal Standard Curve No. 38



## TABLE XXII

### Internal Standard Curve Data

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles)I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| A | 1 | isobutyl isobutyrate | toluene | .805 | 1.50 |
| | | | | .500 | 0.700 |
| | | | | .250 | 0.320 |
| | | | | .160 | 0.220 |
| A | 2 | isobutyraldehyde | toluene | 1.19 | 1.15 |
| | | | | 0.390 | 0.290 |
| | | | | 0.280 | 0.206 |
| | | | | 0.110 | 0.074 |
| A | 3 | acetaldehyde | chlorobenzene | 1.08 | 0.42 |
| | | | | 0.35 | 0.12 |
| | | | | 0.37 | 0.11 |
| | | | | 0.22 | 0.09 |
| A | 4 | ethylacetate | chlorobenzene | 1.08 | 0.82 |
| | | | | 0.63 | 0.43 |
| | | | | 0.43 | 0.31 |
| | | | | 0.31 | 0.21 |
| A | 5 | benzaldehyde | chlorobenzene | 1.06 | 0.95 |
| | | | | 0.63 | 0.55 |
| | | | | 0.52 | 0.47 |
| | | | | 0.34 | 0.29 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles)I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| A | 6 | benzyl acetate | chlorobenzene | 1.03 | 1.31 |
| | | | | 0.65 | 0.78 |
| | | | | 0.49 | 0.58 |
| | | | | 0.31 | 0.38 |
| A | 7 | propionaldehyde | *n*-heptane | 1.11 | 0.49 |
| | | | | 0.52 | 0.23 |
| | | | | 0.36 | 0.16 |
| | | | | 0.79 | 0.38 |
| A | 8 | *n*-propyl propionate | *n*-heptane | 0.95 | 0.86 |
| | | | | 0.50 | 0.44 |
| | | | | 0.35 | 0.31 |
| | | | | 0.81 | 0.75 |
| A | 9 | cyclohexanone | *n*-heptane | 0.92 | 0.73 |
| | | | | 0.50 | 0.41 |
| | | | | 0.37 | 0.27 |
| | | | | 0.82 | 0.67 |
| A | 10 | cyclohexyl propionate | *n*-heptane | 0.915 | 1.07 |
| | | | | 0.505 | 0.60 |
| | | | | 0.356 | 0.42 |
| | | | | 0.78 | 0.97 |
| A | 11 | anisaldehyde | chlorobenzene | 0.975 | 1.06 |
| | | | | 0.52 | 0.558 |
| | | | | 0.336 | 0.384 |
| | | | | 0.723 | 0.80 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles) I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| A | 12 | cyclohexyl acetate | chlorobenzene | 0.936 | 1.13 |
| | | | | 0.50 | 0.592 |
| | | | | 0.342 | 0.43 |
| | | | | 0.725 | 0.80 |
| A | 13 | anisyl acetate | chlorobenzene | 0.98 | 0.90 |
| | | | | 0.515 | 0.57 |
| | | | | 0.329 | 0.377 |
| | | | | 0.664 | 0.77 |
| A | 14 | benzyl propionate | *n*-heptane | 1.16 | 1.17 |
| | | | | 0.72 | 0.85 |
| | | | | 0.50 | 0.57 |
| | | | | 0.36 | 0.39 |
| A | 15 | *n*-heptyl propionate | *n*-heptane | 1.26 | 1.08 |
| | | | | 0.734 | 0.657 |
| | | | | 0.608 | 0.55 |
| | | | | 0.544 | 0.447 |
| | | | | 0.315 | 0.286 |
| A | 16 | *n*-heptaldehyde | *n*-heptane | 1.010 | 0.727 |
| | | | | 0.705 | 0.530 |
| | | | | 0.588 | 0.393 |
| | | | | 0.540 | 0.330 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles) I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| B | 17 | isobutyraldehyde | *n*-heptane | 0.945 | 0.460 |
| | | | | 0.728 | 0.350 |
| | | | | 0.574 | 0.240 |
| | | | | 0.320 | 0.134 |
| B | 18 | cyclopentyl propionate | *n*-heptane | 0.984 | 1.06 |
| | | | | 0.789 | 0.870 |
| | | | | 0.585 | 0.650 |
| | | | | 0.384 | 0.400 |
| B | 19 | cyclohexyl-propionate | *n*-heptane | 1.000 | 1.05 |
| | | | | 0.810 | 0.86 |
| | | | | 0.585 | 0.634 |
| | | | | 0.380 | 0.382 |
| B | 20 | cyclohexanone | *n*-heptane | 0.98 | 0.670 |
| | | | | 0.795 | 0.552 |
| | | | | 0.562 | 0.404 |
| | | | | 0.387 | 0.253 |
| B | 21 | *n*-propyl-propionate | *n*-heptane | 1.03 | 0.929 |
| | | | | 0.792 | 0.716 |
| | | | | 0.510 | 0.451 |
| B | 22 | cyclohexyl-propionate[1] | *n*-heptane | 1.03 | 1.27 |
| | | | | .708 | .787 |
| | | | | .502 | .604 |
| | | | | .347 | .424 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles) I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| B | 23 | benzyl propionate | _n_-heptane | 1.13 | 1.36 |
| | | | | .820 | 1.00 |
| | | | | .565 | .670 |
| | | | | .419 | .506 |
| B | 24 | _n_-heptyl propionate | _n_-heptane | 1.02 | 1.49 |
| | | | | .733 | 1.01 |
| | | | | 0.500 | .797 |
| | | | | .384 | .505 |
| B | 25 | _n_-propyl propionate[2] | _n_-heptane | 1.01 | .945 |
| | | | | .724 | .666 |
| | | | | .506 | .483 |
| | | | | .347 | .325 |
| B | 26 | _m_-chloro-benzyl propionate | _n_-heptane | 1.02 | 1.25 |
| | | | | .71 | .94 |
| | | | | .49 | .58 |
| | | | | .32 | .26 |
| B | 27 | _p_-methyl-benzyl propionate | _n_-heptane | 1.00 | 1.22 |
| | | | | .696 | .885 |
| | | | | .469 | .523 |
| | | | | .326 | .339 |
| B | 28 | toluene | _n_-heptane | .930 | .750 |
| | | | | .507 | .400 |
| | | | | .314 | .256 |

## TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles)I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| B | 29 | n-heptane | toluene | 1.07 | 1.33 |
| | | | | .493 | .618 |
| | | | | .238 | .300 |
| C | 30 | benzyl propionate | n-heptane | 1.00 | 1.17 |
| | | | | .727 | .900 |
| | | | | .495 | .614 |
| | | | | .346 | .425 |
| C | 31 | anisyl propionate | n-heptane | 1.01 | 1.21 |
| | | | | .730 | .906 |
| | | | | .503 | .616 |
| | | | | .350 | .425 |
| C | 32 | cyclohexyl propionate | n-heptane | 1.01 | 1.18 |
| | | | | .735 | .895 |
| | | | | .497 | .593 |
| | | | | .355 | .409 |
| C | 33 | p-chloro-benzyl propionate | n-heptane | .945 | .930 |
| | | | | .675 | .720 |
| | | | | .324 | .380 |
| C | 34 | n-propyl propionate | n-heptane | 1.01 | .935 |
| | | | | .733 | .710 |
| | | | | .505 | .493 |
| | | | | .353 | .360 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles) I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| C | 35 | toluene | *n*-heptane | .892 | .706 |
| | | | | .703 | .570 |
| | | | | .477 | .376 |
| | | | | .355 | .285 |
| C | 36 | *n*-heptyl propionate | *n*-heptane | 1.13 | 1.69 |
| | | | | .708 | 1.02 |
| | | | | .464 | .697 |
| | | | | .346 | .503 |
| C | 37 | *m*-methyl-benzyl propionate | *n*-heptane | 0.920 | 1.27 |
| | | | | .734 | .995 |
| | | | | .476 | .646 |
| | | | | .121 | .155 |
| C | 38 | *n*-octane | *n*-heptane | .913 | 1.04 |
| | | | | .670 | .750 |
| | | | | .468 | .531 |
| | | | | .350 | .394 |
| C | 39 | *p*-methyl-benzyl propionate | *n*-heptane | 1.04 | 1.20 |
| | | | | .440 | .520 |
| | | | | .349 | .329 |
| C | 40 | *m*-chloro-benzyl propionate | *n*-heptane | .944 | 1.17 |
| | | | | .460 | .512 |
| | | | | .331 | .333 |

TABLE XXII - continued

| Column | Curve No. | Substrate | Internal Standard | (mmoles) Substrate/ (mmoles)I.S. | Peak Area Substrate/ Peak Area I.S. |
|---|---|---|---|---|---|
| C | 41 | *n*-pentyl pentoate | *n*-heptane | .637 | .933 |
| | | | | .454 | .637 |
| | | | | .335 | .473 |
| C | 42 | isobutyl isobutyrate | *n*-heptane | .676 | .792 |
| | | | | .457 | .525 |
| | | | | .330 | .385 |
| C | 43 | benzyl formate | *n*-heptane | .911 | .782 |
| | | | | .462 | .356 |
| | | | | .000 | .000 |

A 2 ft. 20% Silicone Rubber on 60-80 Chromosorb P

B 4 ft. 20% Silicone Rubber on 60-80 Chromosorb P

C 4 ft. 10% Silicone Rubber, Se -30 on 60-80 P. (F & M Scientific Co.)

[1] Differs in rate of program from Curve No. 19.

[2] Differs in rate of program from Curve No. 21.

## THE PREPARATION AND REACTIONS OF α'-CHLOROESTERS

Preparation of the α'-chloroester of Benzyl Benzoate.[30,31] In an Erlenmeyer flask 14.064 g. ( 0.100 moles) of benzoyl chloride was mixed with 10.627 g. (0.101 moles) of benzaldehyde. A pinch of freshly fused zinc chloride was added. The reaction flask was flushed with nitrogen and tightly stoppered. After about ten minutes, the reaction mixture took on an amber color and gave off a large amount of heat. It was allowed to stir at room temperature for about 24 hours. After this time it was refrigerated and small amounts of white solid began to form. 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 very unstable on standing at room temperature even under nitrogen. Infra-red spectrum (No. 903) of a 12% solution of the ester in 2,3-dimethyl butane indicated all ester absorptions, 1730, 1255, 1060 and 1080 $cm.^{-1}$. Acid chloride and aldehyde absorptions were absent. When this solution was allowed to stand for 24 hrs. small amounts of the acid chloride and aldehyde became visible in the infra-red spectrum (No. 904). Addition of a small amount of tri-*n*-butyltin chloride produced greater amounts of the acid chloride and aldehyde, (No. 905).

Behavior of α'-chlorobenzyl Benzoate in the Presence of Tri-*n*-butyltin Chloride. In Solvent. A solution containing 0.9432 g. (0.00381 moles) of the ester and 1.0 ml. of the organotin chloride in 10 ml. of 2,3-dimethyl butane was read immediately upon mixing. The infra-red spectrum (No. 906) indicated a significant amount of aldehyde was present from the absorption at 1700 $cm.^{-1}$. After about 20 min., a deep orange color pervaded the mixture.

Neat. When the same amount of the ester was mixed with 1.0 ml. of the organotin chloride, neat and the infrared spectrum (No. 907) read immediately a 50/50 mixture of ester and aldehyde was indicated.

The Reaction of α'-chlorobenzyl Benzoate with Tri-*n*-butyltin Hydride. To a solution of 0.9622 g. (0.00389 moles) of the ester in 10 ml. of 2,3-dimethylbutane was added 1.1 g. (0.00378 moles) of the hydride. The reaction was allowed to proceed for about two weeks under nitrogen. Infrared spectrum (No. 934) of the reaction mixture indicated a small amount of benzaldehyde by a shoulder at 1700 $cm.^{-1}$. Gas chromatographic analysis indicated again a small amount of the aldehyde with the predominant product certainly being benzyl benzoate. A neat reaction carried out with the same quantities and in the same way produced the same results.

The Tri-*n*-butyltin Chloride Catalyzed Reaction Between Benzaldehyde and Benzoyl Chloride. Equimolar amounts (0.0038 moles) of benzaldehyde, 0.40 g. and benzoyl chloride, 0.53 g. were mixed neat with 0.50 ml. of the organotin chloride and the reaction was monitored in the infra-red, by comparing intensities of bands at 1780 $cm.^{-1}$, acid chloride; 1730 $cm.^{-1}$, chloroester and 1700 $cm.^{-1}$, benzaldehyde. After 24 hrs. the reaction appeared to be a little over 50% complete and after 48 hrs. the reaction appeared to have gone to 75% of completion.

Propionyl Chloride and Propionaldehyde. Equimolar amounts (0.0038 moles) of the aldehyde and acid chloride were mixed with 0.5 ml. of the organotin chloride and the reaction was monitored periodically in the infra-red. After 48 hrs., the acid chloride carbonyl absorption at 1770 $cm.^{-1}$ still dominated absorptions in the carbonyl region indicating the reaction still had not gone to 50% of completion.

Preparation of α'-chloroethyl Acetate. This compound was prepared by the method described by Ulich and Adams[40] from acetyl chloride and paraldehyde in the presence of zinc chloride. The product distilled, in bantam-ware apparatus, 120-122° at atmospheric pressure. The infra-red spectrum (No. 1753) shows all ester absorptions.

The Reaction of α'-chloroethyl Acetate with Tri-*n*-butyltin Hydride. To 0.92 g. (0.0075 moles) of the chloro-ester was added 2.2 g. (0.0075 moles) of the hydride. No noticeable heat was evolved. Gas chromatographic analysis indicated that the reaction had still not gone to completion after three days as hydride was still in evidence. Major product, as identified by retention time, was the ester.

# THE REACTION OF ALKYL BROMIDES IN THE PRESENCE OF ALDEHYDES

## Procedure

These reactions were run on a 0.0038 mole scale. The alkyl bromide was allowed to react with tri-n-butyltin hydride in the presence of an equimolar amount of an aldehyde both neat and in solution. All these reactions were conducted at room temperature in tightly stoppered flasks under nitrogen. When all the hydride had been consumed, as evidenced by the lack of an absorption band in the infrared spectrum at 1810 cm.$^{-1}$, a 0.0038 mole amount of propionyl chloride was added to the reaction mixture. The reaction of the acid chloride with the organotin alkoxide always generated a large amount of heat. The mixture was analyzed by gas chromatography using the internal standard method. The yield of the hydrocarbon resulting from the reduction of the bromide was determined. The yield of the propionate ester resulting from the reaction of the acid chloride with the alkoxide was also determined and this yield was ascribed to the amount of alkoxide formed. Results pertinent to these experiments are found in Table XXIII.

## TABLE XXIII

Results of Reactions of Alkyl Bromides with Tri-*n*-butyltin Hydride (0.0038 moles) in the Presence of Aldehydes at Room Temperature[a]

| RBr (mmoles) | | RCHO (mmoles) | | I.S. (mmoles) | RH (mmoles) | RH (% yield) | Sn-OCH$_2$R (mmoles) | Sn-OCH$_2$R (% yield) | Solvent |
|---|---|---|---|---|---|---|---|---|---|
| 1-BrC$_8$H$_{17}$ | (3.97) | (CH$_3$)$_2$CHCHO | (3.74) | 3.97 | 3.46 | (93) | 0.18 | ( 5) | neat |
| 1-BrC$_8$H$_{17}$ | (3.90) | (CH$_3$)$_2$CHCHO | (3.87) | 3.90 | 3.13 | (84) | [c] | ($<$5) | DMB[d] |
| 1-BrC$_8$H$_{17}$ | (3.76) | C$_6$H$_5$CHO | (3.76) | 4.07 | 1.10 | (30) | 2.28 | (62) | neat |
| 1-BrC$_8$H$_{17}$ | (3.93) | C$_6$H$_5$CHO | (3.91) | 4.07 | 1.83 | (50) | 0.94 | (26) | DMB |
| 2-BrC$_8$H$_{17}$ | (3.83) | C$_6$H$_5$CHO | (3.91) | 3.73 | 1.83 | (50) | 1.79 | (49) | neat |
| C$_6$H$_5$CH$_3$ | (3.81) | C$_6$H$_5$CHO | (3.73 | 3.74 | 2.54 | (69) | 1.38 | (37) | neat |

[a] All yields were determined by g.l.c. analysis using the internal standard method.

[b] Yields of alkoxides were determined as the respective propionate by adding to the reaction mixture propionyl chloride.

[c] Peak area too small for an accurate determination.

[d] 2,3 dimethyl butane.

## A COMPARISON OF RATES OF VARIOUS TRI-N-BUTYLTIN HYDRIDE REACTIONS

### Time of Completion for Certain Reactions with Tri-n-butyltin Hydride.

Procedure. Neat reactions with the hydride were run to determine roughly the speed of the reaction involved. Equimolar quantities of hydride and substrate were mixed, the reaction flask was flushed with nitrogen and stoppered. The reaction was allowed to proceed at room temperature and was followed by infra-red spectroscopy. The results are gathered in Table XXIV.

### Comparison of Rates of Reaction of Isobutyryl Chloride and Isobutyraldehyde with Tri-n-butyltin Hydride.

This experiment is a qualitative check on the results presented in Table VIII. In the acid chloride reaction, equimolar amounts (0.0038 moles) of the hydride, 1.10 g. were mixed with 0.42 g. of the acid chloride in 5.0 ml. of diethyl ether. In the aldehyde reaction equimolar amounts (0.0038 moles) of the hydride, 1.10 g., 0.27 g. of the aldehyde and 1.23 g. of tri-n-butyltin chloride in 5.0 ml. of diethyl ether were mixed. The reaction flasks were flushed with nitrogen, stoppered and the reaction was allowed to proceed at room temperature. The reaction was followed by infra-red at certain time intervals. The speeds of the reactions were compared by comparing the ratio of the bands at 1810 and 1480 cm.$^{-1}$. The pertinent data is presented in Table XXV.

## TABLE XXIV

### Times of Completion for Certain Reactions with Tri-n-butyltin Hydride, Neat, at Room Temperature[a]

| Substrate | Time of Completion after mixing |
|---|---|
| $C_6H_5COCl$ | 18 hrs. |
| $C_2H_5COCl$ | 18 hrs. |
| $C_6H_5CHO$ | 9 - 10 da. |
| $C_2H_5CHO$ | 10 da. |
| $C_6H_5CHO$ (Sn-Cl)[b] | 18 - 19 hrs.[c] |
| $C_2H_5CHO$ (Sn-Cl)[b] | 18 - 19 hrs.[d] |

[a] Reaction followed in infra-red by Sn-H stretching 1810 cm.$^{-1}$. Equimolar amounts of substrate and hydride were used (0.0038 moles).

[b] 1 ml. of tri-n-butyltin chloride was added as a catalyst.

[c] Main reaction product was alkoxide with very small amounts of alcohol in evidence.

[d] Main product was alkoxide with a significant amount of alcohol present.

## TABLE XXV

Comparison of the Rate of Reaction of $(CH_3)_2CHCOCl$ with Tri-n-butyltin Hydride and $(CH_3)_2CHCHO$ with the Hydride in the Presence of Tri-n-butyltin Chloride.

| Time After Mixing | $\frac{\text{Intensities at 1810 cm.}^{-1}}{\text{Intensity at 1480 cm.}^{-1}}$ | |
|---|---|---|
| | $(CH_3)_2CHCOCl$ | $(CH_3)_2CHCHO$ |
| 9 hr. | 1.0 | 1.3 |
| 14.5 hr. | .93 | 1.5 |
| 19 hr. | .50 | .85 |
| 72 hr. | .10 | .53 |
| 95 hr. | .12 | .37 |

# CATALYZED REACTION OF ISOBUTYRALDEHYDE AND TRI-N-BUTYLTIN HYDRIDE

Catalysis by Primary Octyl Bromide. To a solution containing 0.3182 g. (0.00441 moles) of the aldehyde, 0.3855 g. (0.00385 moles) of n-heptane and 0.0406 g. (0.00021 moles) of the bromide was added 1.0 ml. of the hydride. The reaction flask was flushed with nitrogen and tightly stoppered. After five days the infra-red spectrum indicated that all the hydride had been consumed. There is a small amount of alcohol indicated in the spectrum. Addition of 0.4 ml. of propionyl chloride to the reaction mixture produced a highly exothermic reaction. Analysis by gas chromatography showed a yield of 0.00246 moles, 67% of the propionate.

Catalysis by Propionyl Chloride. This reaction was run on the same scale as above and in the same manner except 5 mole percent of propionyl chloride was used to catalyze the reaction. The infra-red spectrum after five days indicated that all the hydride had been consumed. After addition of excess propionyl chloride, gas chromatographic analysis showed a yield of 0.00286 moles, 77%, of the propionate.

## GAS CHROMATOGRAPHIC ANALYSIS OF ALDEHYDES

### Analysis of Synthetic Mixtures Containing Aldehydes and Tri-*n*-butyltin Chloride.

Procedure. Synthetic mixtures of ketones, esters and aldehydes were prepared. To these mixtures were added various amounts of tri-*n*-butyltin chloride. Areas of each substrate were measured against an internal standard and the number of moles of each component was determined from a previously prepared internal standard curve. The material balance of all substrates save aldehydes was good. Those of aldehydes by gas chromatography were good in the absence of tri-*n*-butyltin chloride. Pertinent data for these studies are gathered in Table XXVI.

### A Study of the Temperature Effect in Cyclohexanone Trapping Reaction with Propionyl Chloride and Tri-*n*-butyltin Hydride.

To a mixture of 0.95 g. (0.010 moles) of propionyl chloride and 0.95 g. (0.010 moles) of cyclohexanone was added 3 ml. (0.011 moles) of the hydride. Three one-ml. portions of this reaction mixture were removed, placed in ampoules, flushed with nitrogen, and sealed. One was placed in a 25° constant temperature bath, the other in a 45° bath and the Third one in a 90° constant temperature bath. After 53 hrs. the ampoules were removed and analyzed by gas chromatography. Aldehyde peaks were very prominent on the chromatograms. Since no internal standard was used, ratio of areas were determined as listed in Table XI.

## TABLE XXVI

### Analysis of Aldehydes in Gas Chromatography in Synthetic Mixtures Containing Tri-*n*-butyltin Chloride[a]

| Mixture | Substrate (mmoles) | Accounted for (mmoles) | Accounted for % | I. S. Curve No. |
|---|---|---|---|---|
| I | Cyclohexanone (3.78) | 3.65 | 97 | 9 |
| | Cyclohexyl propionate (3.75) | 3.80 | 100 | 10 |
| | *n*-propyl propionate (3.88) | 3.60 | 93 | 8 |
| | propionaldehyde (4.57) | 3.00 | 65 | 7 |
| | *Sn*-Cl (3.26) | | | |
| II | propionaldehyde (3.66) | 2.87 | 78 | 7 |
| | *Sn*-Cl (1.91) | | | |
| III | isobutyraldehyde (1.40) | .62 | 44 | 17 |
| | *Sn*-Cl (3.90) | | | |
| IV | isobutyraldehyde (2.76) | 2.35 | 85 | 17 |
| | *Sn*-Cl (7.90) | 2.29 | 83 | 17 |
| V[b] | benzyl acetate (1.6 ) | 1.8 | 100+ | 6 |
| | benzaldehyde (1.8 ) | 1.8 | 100[c] | 5 |
| | *Sn*-Cl | 1.0 | 58[d] | |

[a] Analysis by the internal standard method.

[b] This mixture was first checked against the appropriate I.S. Curves without added *Sn*-Cl and accountability was excellent. [c] Before; [d] after addition of *Sn*-Cl.

## The Reaction of Propionyl Chloride with Tri-n-butyltin Hydride in the Presence of Cyclohexanone at 25°.

To a cooled mixture of 0.3855 g. of cyclohexanone, (0.00392 moles), the internal standard, n-heptane, 0.3750 g., (0.00374 moles) and 0.3334 g., (0.00360 moles) of the acid chloride was added 1 ml., (0.0038 moles) of the hydride. The reaction flask was flushed with nitrogen, stoppered securely, and placed in a constant temperature water bath. After three days the reaction mixture was analyzed by gas chromatography. Only a trace of aldehyde was discernible on the chromatograms. The yields as established by the internal standard method were: n-propyl propionate - 78%, cyclohexyl propionate - 12% and recovered cyclohexanone - 85%.

## The Reaction of Propionyl Chloride with Tri-n-butyltin Hydride in the Presence of Cyclohexanone at 45°.

The procedure was the same as that employed for the reaction at 25° with 1 ml. of the hydride being used and 0.3880 g. (0.00395 moles), of cyclohexanone, 0.4096 g., (0.00410 moles) of n-heptane and 0.3533 g. (0.00382 moles) of the acid chloride. The reaction flask was placed in a constant temperature bath at 45°. Three days later the reaction mixture was analyzed by gas chromatography. Again only a trace of the aldehyde peak could be noticed on the chromatogram. The yields as established by the internal standard method were: n-propyl propionate, 69%; cyclohexyl propionate, 13.2%; recovered cyclohexanone, 93%.

### The Reaction of Propionyl Chloride with Tri-n-butyltin Hydride in the Presence of Cyclohexanone at 90°.

The procedure was the same as that used in the experiment at 25° with 1 ml. of the hydride being used, 0.3786 g. (0.00385 moles) of cyclohexanone, 0.3818 g. (0.00380 moles) of n-heptane and 0.3446 g. (0.00373 moles) of the acid chloride. The reaction flask was placed in a constant temperature bath. The yields as established by the internal standard method were: n-propyl propionate, 50%; cyclohexyl propionate, 13.5%; recovered cyclohexanone, 84%. Infra-red spectrum (No. 4511) showed definite aldehyde absorptions at 2800, 1720 and 1430 cm.$^{-1}$. Therefore the yield of the aldehyde was determined by difference from 100% reaction.

# SUMMARY

The reaction of acid chlorides with tri-n-butyltin hydride has been found to give as products, esters as well as aldehydes. The relative amount of these products is dependent upon the acid chloride used as well as the experimental conditions employed. The use of solvent enhances the yield of aldehyde at the expense of ester.

The mechanism of this reaction has been studied and evidence is presented for its free radical nature. In the formation of aldehyde, decarbonylation, decarboxylation and free radical catalysis have been observed. Relative reactivities of various acid chlorides have been determined and the Hammett correlation resulting from this work is consistent with the formation of an acyl radical. A study of solvent effects in the Hammett correlation of substituted benzoyl chlorides indicates that methyl acetate exerts a specific solvent effect in this reaction. The rho value of 2.61 found in m-xylene and o-dichlorobenzene is quite different from 4.0 which was found in methyl acetate. This effect has been attributed to complexing of the organotin radical with the carbonyl group of the acetate.

The formation of ester is also postulated to be a free radical process involving an attack by the acyl radical on the carbony oxygen of an aldehyde. When other carbonyl compounds are added to the reaction mixture of acid chlorides and the organotin hydride, one obtains along with the usual ester and aldehyde a "mixed" ester whose alkoxy fragment is derived from the added carbonyl compound. We have measured the efficiencies of several substituted benzaldehydes as traps

for the acyl radical. A Hammett correlation gave a rho value of 0.48. Other pathways to the formation of ester have been considered. Organotin hydrides add to carbonyl compounds to form organotin alkoxides, which react rapidly with acid chlorides. The relative rates of alkoxide formation from substituted benzaldehydes in the absence of acid chloride gave a rho value of 1.8, in contrast to the value 0.48 for ester formation in the presence of acid chloride.

Tri-n-butyltin chloride has been found to be an effective catalyst for the reaction between an aldehyde and tri-n-butyltin hydride. It also catalyzes acetal formation with propionaldehyde and ethanol and catalyzes $\alpha'$-chloroester formation from the reaction between an acid chloride and an aldehyde.

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