tion for 8.5 min. The rate of gas flow was 11.55 l./hr. The suspended solid gradually dissolved in the solvent as the fluorination proceeded and after 5 min the material was completely dissolved. After the fluorination was completed, the system was flushed with helium for 20 min to remove the residual fluorine. A wet solid residue remained after the solvent was evaporated. This material was vacuum sublimed at room temperature and 0.005 mm. A flaky white solid was obtained, 0.142 g (26.4%),<sup>14</sup> mp 56-57.5° (mixture melting point with product from difluoramine reaction was 57.5-58°).

product from diffuoramine reaction was  $57.5-58^{\circ}$ ). Anal. Calcd for C<sub>8</sub>H<sub>12</sub>FNO<sub>2</sub>: C, 55.50; N, 8.09; F, 10.98; mol wt, 173. Found: C, 55.22; N, 7.94; F, 11.4; mol wt, 198.

The infrared spectrum and the proton and fluorine nmr spectra were identical with the respective spectra of the product obtained in the difluoramine reaction.

**Registry No.**—I, 933-52-8; difluoramine, 10405-27-3; III, 18993-54-9.

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(14) Optimum conditions for the fluorination were not determined and the percentage yield was based upon the recovery of 0.5 g of starting material. Over fluorination in this reaction resulted only in the formation of base-soluble products.

## The Reaction of Acyl Halides with Organotin Hydrides. The Effect of Halide and Hydride Structure on Product Distribution<sup>1</sup>

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In our previous studies of the scope and mechanism of this reaction we have concentrated on the reduction of acid chlorides with tri-*n*-butyltin hydride.<sup>2,3</sup> When the reductions were carried out neat most of these chlorides gave mainly ester with varying amounts of aldehyde. The aldehyde, however, was often the main product when the reaction was carried out in solution. We indicated that the two acid bromides observed displayed behavior quite different from that of the acid chlorides<sup>2</sup> since the yield of aldehyde in the neat reactions was considerably higher suggesting that a different mechanism may be operative when bromides are used.

 $3\mathrm{RCOX} + 3\mathrm{R'}_3\mathrm{SnH} \rightarrow \mathrm{RCHO} + \mathrm{RCO}_2\mathrm{CH}_2\mathrm{R} + 3\mathrm{R'}_3\mathrm{SnX}$ 

Kupchik and Kiesel<sup>4,5</sup> have demonstrated that reductions of certain acid chlorides, neat or in solution, gave predominantly ester when they employed triphenyltin hydride indicating that the structure of the hydride may also be of importance in product distribution.

We have examined the reactions of other acid chlorides, bromides and two fluorides with trimethyl and tri-n-butyltin hydride and have found that the product distribution is sensitive to the type of halide and hydride employed. In Table I we report the reduction of acid chlorides with trimethyltin hydride; the reduction of acid bromides and an aromatic and aliphatic acid fluoride with both hydrides. The acid bromides are reduced by tri-n-butylin hydride to give predominantly aldehyde whereas trimethyltin hydride reductions gave mainly ester products. The reduction of acid fluorides affords only ester in both cases studied.

The acid fluorides were comparatively unreactive with either trimethyl or tri-*n*-butyltin hydride. When they hydride and benzoyl fluoride were mixed, neat at ambient temperature, no discernible reaction occurred even after 5 days. In a 0.6 M solution of refluxing benzene the reaction can be completed in 5 days while under the same conditions with an added 2 mol % of AIBN the reaction is finished within 31 hr. Both reactions gave only benzylbenzoate and tri-*n*-butyltin fluoride as the products.

The reasons for the differences in product distribution with respect to type of organotin hydride and acid halide used are obscure at this point but we feel it probably is due to changes in the ester-forming process which can be complicated.<sup>3</sup>

## **Experimental Section**

All infrared spectra were determined on a Perkin-Elmer Model 337 double-beam spectrophotometer. Gas chromatographic analysis was carried out on a dual column F & M Scientific Co., Model 720 gas chromatograph.

Materials.—The acid bromides and chlorides were obtained commercially in high purity. The acid fluorides<sup>6</sup> and tin hydrides<sup>2</sup> were prepared by previously described methods.

**Reduction of Acid Bromides.**—Owing to the vigor of this reaction, the hydride was added to an equimolar amount of bromide in an ice bath. As the reaction subsided the system was flushed with nitrogen and stoppered. These reactions were complete within 20 hr as evidenced by the disappearance of the Sn-H band at  $1810 \text{ cm}^{-1}$  in the infrared region. The reaction mixtures were then examined by gas chromatography and the products were identified by comparison of their retention times with those of authentic samples.

Determination of Aldehyde with 2,4-Dinitrophenylhydrazine.—The procedure used was essentially that developed by Iddles.<sup>7</sup> An aliquot was taken from the reaction mixture, dissolved in 25 ml of ethanol and added to a 300-ml saturated solution of 2,4-dinitrophenylhydrazine in 2 M HCl. The precipitate was then collected on a tared filtering funnel, dried at

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TABLE 1											
Тне	Neat	Reactions	OF .	Acid	HALIDES	WITH	Organotin	Hydrides	АT	Ambient	TEMPERATURES
		3H	RCOX	x + :	3R' <sub>s</sub> SnH -	$\rightarrow$ RC	HO + RCC	$_{2}CH_{2}R +$	3R	∕₃SnX	

	% yield%									
	<u> </u>	Сн	R' =	n-Bu	$R' = C_6H_5$					
	Aldehyde	Ester	Aldehyde	Ester	Aldehyde	Ester				
			RCOCl							
CHa	15	85	$5^{b}$	95 <sup>6</sup>						
$C_2H_5$				875	14°	50°				
Me <sub>2</sub> CHCH <sub>2</sub>	10	90								
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>			550	450	6.6°					
C <sub>6</sub> H <sub>5</sub>				99d.e		997				
p-MeC <sub>6</sub> H <sub>4</sub>	g	99								
p-MeOC <sub>6</sub> H <sub>4</sub>	25	75								
m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	g	99								
			RCOBr							
CH <sub>3</sub>	12	88	69	31						
$C_2H_5$	16	84	65	35						
Me <sub>2</sub> CHCH <sub>2</sub>	54	46	40	60						
$C_6H_5$	40	63*	97	h						
			RCOF							
$C_6H_5$	g	99i	g	99i						
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	Ŭ		ģ	991						

<sup>a</sup> Aldehyde yields were determined from the 2,4-dinitrophenyldhydrazone derivitive. The ester yields were ascertained by difference from theoretical and identified by infrared and glpc as the only other reduction product. <sup>b</sup> Reported yield.<sup>2</sup> • Reference 5. <sup>d</sup> We were unable to duplicate a previous result<sup>2</sup> of 65% benzaldehyde. • Yield based on isolation. <sup>f</sup> Reference 4. • None observed. <sup>b</sup> Trace. <sup>i</sup> 0.6 M benzene solution.

 $100^{\circ}$  and weighed. The precipitate was then carefully recrystallized from an ethanol-ethyl acetate mixture and weighed again.

Isolation Experiment.—A 0.33-mol scale reduction of benzoyl bromide with triethyltin hydride in 250 ml of absolute ether was carried out. Fractional distillation of the reaction mixture gave a pure fraction of benzyl benzoate which amounted to a 63% yield. The yield of benzaldehyde by difference was 37%. A duplicate reaction which was run concurrently and analyzed by the 2,4-dinitrophenylhydrazine method gave a benzaldehyde yield of 43% before recrystallization.

## The Influence of Silver Acetate on the Oxymercuration-Demercuration of Olefins

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The oxymercuration-demercuration reaction is a well-known method of preparation of alcohols from olefins.<sup>1-3</sup> Bordwell<sup>4</sup> has demonstrated that the cyclization of 4-cycloocten-1-ol is pH dependent. He has also demonstrated that the demercuration is pH dependent.

However, no work has been done on the influence of metallic cations on the oxymercuration-demercuration reaction.

In an effort to study the competition of silver ion and mercuric ion for the exocyclic double bond of 4-vinylcyclohexene, a mercuric acetate solution was added to 4-vinylcyclohexene in tetrahydrofuran (THF) in the presence of silver acetate. After alkaline treatment with sodium borohydride, followed by extraction, the product was analyzed by gas chromatography. In addition to the expected alcohol, 4-acetylcyclohexene was obtained. The ketone/alcohol ratio was 2:3.

The oxymercuration-demercuration reaction in the presence of silver acetate was studied with various olefins (see Table I). The addition of the aqueous mercuric acetate solution to the THF-olefin-silver acetate mixture produced only a transitory yellow color which disappeared quickly. The reaction appeared to be at least as rapid as normal oxymercuration.

Demercuration must be preceded by the addition of base to the reaction mixture. When the demercuration was carried out without this step only the alcohol was obtained. The oxymercuration reaction is quantitative; however, the demercuration reaction results in a great deal of regenerated olefins. Consequently, the absolute yields of ketone as prepared by this method are poor. The reaction is useful to the extent that exocyclic double bonds are converted into ketones, while endocyclic double bonds are relatively inert, and the reaction conditions are mild enough to leave the most easily oxidized groups unaffected.

The realization that acyclic olefins yield a greater

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