Palladium-Catalyzed Reaction of Tributyltin Hydride with Acyl Chlorides. A Mild, Selective, and General Route to Aldehydes

P. Four and F. Guibe*

Groupe de Recherche No. 12, CNRS, 94320 Thiais, France

Received April 10, 1981

Tetrakis(triphenylphosphine)palladium(0), various palladium(II) complexes, and even $PdCl_2$ in the presence of triphenylphosphine catalyze the reaction of acyl chlorides with tri-*n*-butyltin hydride to specifically give aldehydes under very mild conditions and in very good yields. The reaction is quite general and tolerates the presence of many other reducible groups on the acyl chloride. Tetrakis(triphenylphosphine)palladium(0) also catalyzes the tributyltin hydride reduction of α,β-unsaturated carbonyl compounds to saturated carbonyl compounds; however, α,β-unsaturated acyl chlorides may be reduced to α,β-unsaturated aldehydes with a very good selectivity. The mechanism of the catalytic reductions is discussed.

Several methods are available for the partial reduction of carboxylic acids or their derivatives to aldehydes.[1,2] Besides the Rosenmund catalytic reduction of acyl chlorides[3-5] and some related reactions,[6,7] most of them use complex metallic hydrides[8] as the reducing agents. Acids, phenyl esters, aliphatic esters, and carboxamides, especially acyl aziridines and dimethylamides, are reduced to aldehydes by means of various aluminum hydrides.[8,9] The reduction of 3-acylthiazolidine-2-thione by diisobutoxyaluminum hydride and by lithium tri-*tert*-butoxyaluminum hydride has recently been reported.[10] The reduction of acyl chlorides to aldehydes can be carried out with lithium tri-*tert*-butoxyaluminum hydride[11] and with complex copper tetrahydroborate or complex copper cyanotrihydroborate salts.[12-14] Sodium tetrahydroborate in dimethylformamide can also be used, either at low temperature[15] or in the presence of cadmium dichloride[16] which acts as a moderator. The conversion of acyl chlorides to aldehydes has also been achieved with anionic ironcarbonyl complexes.[17,18]

Many of these methods are not exempt from some disadvantages such as a limited scope of applicability, the contamination of the aldehyde by further reduction products, or an incompatability with the presence of other reducible groups in the molecule.

In a preliminary communication,[19] we have shown that tributyltin hydride, in the presence of a palladium catalyst, is an effective reagent for the conversion of acyl chlorides to aldehydes. This reaction can be related to the palladium-, platinum-, or rhodium-catalyzed reduction of acyl chlorides by silicon hydrides[6,7] on one hand and to the palladium-catalyzed conversion of acyl chlorides to ketones by tetraorganotin compounds on the other hand.[20] We report here a more detailed study of the catalytic reduction of acyl chlorides to aldehyde by tributyltin hydride which, owing to its mildess of conditions, its great selectivity, and its wide scope, appears quite attractive.

Results and Discussion

Tributyltin hydride is known to reduce,[21] probably by a free-radical chain mechanism, acyl chlorides to a mixture of aldehydes and esters according to eq 1. Owing to the

$$\mathrm{RCOCl} \xrightarrow[-\mathrm{Bu_3SnCl}]{\mathrm{Bu_3SnH}} \mathrm{RCHO} + \mathrm{RCOOCH_2R} \qquad (1)$$

competitive formation of the ester, this reaction is not very useful for the synthesis of aldehydes. However, if small amounts of palladium catalysts such as tetrakis(triphenylphosphine)palladium(0) are added to the medium, the reaction is made much more rapid and completely selective toward the formation of aldehyde (eq 2). The

$$\mathrm{RCOCl} + \mathrm{Bu_3SnH} \xrightarrow[\text{room temp}]{\mathrm{Pd(PPh_3)_4}} \mathrm{RCHO} + \mathrm{Bu_3SnCl} \qquad (2)$$

catalytic reduction is conveniently run at room temperature by adding tributyltin hydride (1.1 equiv) over a period of a few minutes to a mixture of the acyl chloride and the palladium catalyst (usually 10^{-2} equiv) in a solvent. The reaction is exothermic and usually complete within a very short time.[22] The end of the reaction is usually signaled by a darkening of the reaction mixture and frequently by some gas evolution due to the decomposition of the tributyltin hydride in excess (eq 3). With some exceptions

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(22) The increase in the rate of the reduction brought about by the palladium catalyst is considerable. Thus benzoyl chloride in 1 M benzene solution at room temperature is completely reduced within 5 min in the presence of 10^{-2} equiv of tetrakis(triphenylphosphine)palladium(0). Without the catalyst only ca. 10% of the aldehyde is formed after 2 h. See also ref 19.

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$$2Bu_3SnH \xrightarrow{Pd(PPh_3)_4} H_2 + Bu_3SnSnBu_3 \quad (3)$$

(vide infra) the rate of the addition of tributyltin hydride is not an important factor of the reaction; in most cases the reduction may also be performed by adding the catalyst to a performed mixture of the acyl chloride and the tin hydride without any appreciable change in the outcome of the reaction.

Benzene, toluene, diethyl ether, and THF may be used as solvents; methylene chloride gave inconsistent results, having been used with success with benzoyl chloride, for example, but not with crotonyl chloride.

Tetrakis(triphenylphosphine)palladium(0) was the most often used catalyst throughout this work, but benzylchlorobis(triphenylphosphine)palladium(II), benzoylchlorobis(triphenylphosphine)palladium(II), dichlorobis(triphenylphosphine)palladium(II) plus two molecules of triphenylphosphine, and even $PdCl_2$ plus four or five molecules of triphenylphosphine were also used with success. Use of additional phosphines in the two latter cases, especially the $PdCl_2$ one, is necessary to avoid competitive tributyltin hydride decomposition. Palladium on charcoal gave poor results as a catalyst.

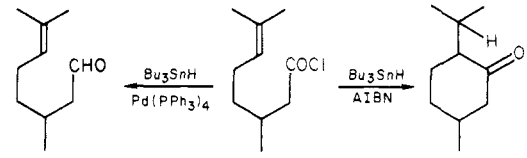
Aside from the aldehyde, the reaction produces tributyltin chloride and some amount of hexabutyldistannane. Liquid aldehydes are conveniently isolated by distillation. If necessary, tributyltin chloride [bp 98 °C/(0.45 mmHg)] may be first removed through conversion to the highly insoluble tributyltin fluoride.[20,23] Solid aldehydes can be isolated by precipitation with hexane, both tin compounds being miscible in that solvent, or by chromatography on a short column; it is then more convenient to first remove tributyltin chloride as it tends to trail on chromatography.

In many cases, a good part of the catalyst may be recovered by precipitation. Most reactions have been performed under an inert atmosphere and in degassed solvents, but some scattered experiments indicate that those precautions should not be necessary in general; however, the use of an inert atmosphere avoids the decomposition of the palladium complexes at the end of the reaction, when recovery of the catalyst is desired.

Scope of the Reaction. The palladium-catalyzed reduction with tributyltin hydride was carried out on a series of 26 representative acyl chlorides. The results in Table I show that the reaction may be applied to a wide range of acyl chlorides, aliphatic or aromatic, and tolerates the presence of many other reducible functions in the molecule. On the whole, the yields of aldehydes are consistently better than those in the palladium- or the platinum-catalyzed reductions of acyl chlorides by organosilicon hydrides.[6,7] In no cases could any appreciable amount of ester (eq 1) or alcohol be detected.

In the series of substituted benzoyl chlorides the yield of aldehyde was not affected by the nature of the para substituent. No reduction of the nitro or of the cyano groups was detected. 4-Methoxybenzoyl chloride yielded only 4-methoxybenzaldehyde, to the exclusion of 4,4′-dimethoxybenzophenone which is the main product of the rhodium-catalyzed reduction with organosilicon hydrides.[7] 4-Bromobenzoyl chloride did not undergo hydrogenolysis of the carbon bromine bond to an appreciable extent even when an excess of tributyltin hydride was used: in that case, mainly decomposition of the hydride (eq 3) was observed. This is to be compared with the palladium-catalyzed reaction of 4-bromobenzoyl chloride with tetramethyltin[20] which affords a mixture of 4-bromoacetophenone and 4-methylacetophenone in a ratio of about 2.5:1. Competitive experiments (entries 8 and 9) were carried out on equimolar mixtures of allyl acetate or allyl bromide on one hand and acyl chlorides on the other hand. Allyl bromine was found to be reduced more rapidly than benzoyl chloride but the less reactive allyl acetate did not compete in the reduction of benzoyl or 2-methylbenzoyl chlorides. 3-Pyridinecarbonyl chloride (entry 10a) was readily reduced to 3-pyridinecarboxaldehyde. A one-pot reduction of 3-pyridinecarboxylic acid to aldehyde was also performed via 3-pyridinecarbonyl chloride hydrochloride (entry 10b).

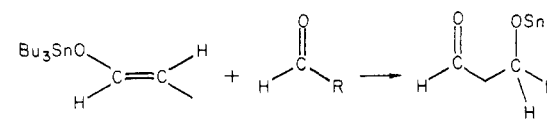
The reduction of olefinic acyl chlorides was studied in some detail. 10-Undecenoyl chloride (entry 11) yielded exclusively and in very good yield 10-undecenal. No aldehydes with an internal olefinic bond could be detected either by ^{13}C or by ^1H NMR spectroscopy. On the contrary, extensive double bond migration, together with some double bond hydrogenation, has been reported in the Rosenmund reduction of 10-undecenoyl chloride.[24] The catalytic reduction of citronellyl chloride (entry 12) which possesses a double bond in the 5–6 position gave only citronellal while the azobis(isobutyronitrile) (AIBN)-initiated radical reduction has been reported to give the cyclized product menthone[25] (eq 4) 4-Pentenoyl chloride



(4)

(entry 13) afforded reasonable yields of the corresponding aldehyde only if enough catalyst (5%) was used and if the tin hydride was slowly added to the cooled mixture (5 °C) of the acyl chloride and the catalyst; otherwise, mainly tin hydride decomposition was observed, and most of the acyl chloride was left unreacted. 5-Methyl-4-hexenoyl chloride, on the other hand, reacted normally (entry 14), which shows that coordination of palladium by the unsubstituted terminal double bond is probably responsible for the unusual behavior of 4-pentenoyl chloride. In neither case could any significant amount of cyclic ketones (cyclopentanone or its 2,2-dimethyl analogue) be detected; this result will be discussed later on.

α,β-Unsaturated acyl chlorides (entries 15 and 16) reacted with 1 equiv of tributyltin hydride to give the α,β-unsaturated aldehydes in good yields and almost free of the saturated aldehydes. Use of additional equivalents (one or two) of tributyltin hydride led to the total disappearance of the unsaturated aldehyde, probably as the result of a palladium-catalyzed conjugate addition of tributyltin hydride. However, we never succeeded in obtaining good yields of the saturated aldehydes. Possibly the tin enolate produced by the conjugate addition reacts with free aldehydes present in the medium to give aldol-type condensations (eq 5). Aldol condensations have



(5)

already been proposed to account for the low yields obtained in the alkylation of aldehyde tin enolates.[26]

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(24) J. English, Jr., and S. F. Velick, *J. Am. Chem. Soc.*, **67**, 1413 (1945).
(25) Z. Ceković, *Tetrahedron Lett.*, 749 (1972).
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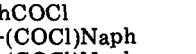
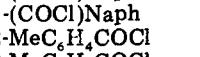
Table I. Catalytic Reduction of RCOCl with Bu_3SnH

entry	RCOCl[n]	catalyst[a]	solvent	reduction product[n]	yield,[b] % anal.	yield,[b] % isol
1a	PhCOCl	A	benzene	PhCHO	95	81
1b	PhCOCl	A	Et_2O	PhCHO	92	
1c	PhCOCl	D	benzene	PhCHO	95	
2	2-(COCl)Naph	A	benzene	2-(CHO)Naph	76	65
3	1-(COCl)Naph	A	benzene	1-(CHO)Naph	97	
4a	2-MeC_6H_4COCl	A	benzene	2-MeC_6H_4CHO	92	
4b	2-MeC_6H_4COCl	E	benzene	2-MeC_6H_4CHO	88	
5	4-$MeOC_6H_4COCl$	A	benzene	4-$MeOC_6H_4CHO$	75	
6	4-$NO_2C_6H_4COCl$	A	benzene	4-$NO_2C_6H_4CHO$	81	75
				PhCHO	traces	
7a	4-BrC_6H_4COCl	A	benzene	4-BrC_6H_4CHO	81	
				PhCHO	6	
7b	4-BrC_6H_4COCl	A	THF	4-BrC_6H_4CHO		78
				PhCHO		<5
8	PhCOCl +  (1 eq)	A	benzene	PhCHO	<5,[c] 93[d]	
9	2-MeC_6H_4COCl +  (1 eq)	A	benzene	PhCHO	83	
10a	3-(COCl)Pyr	A	benzene	3-(CHO)Pyr	90	
10b	3-(CO_2H)Pyr[e]	A	THF	3-(CHO)Pyr	75	
11	H_2C=$CH(CH_2)_8COCl$	A	benzene	H_2C=$CH(CH_2)_8CHO$		88
12	$(CH_3)_2C$= $CH(CH_2)_2CH(CH_3)CH_2COCl$	A	benzene	$(CH_3)_2C$= $CH(CH_2)_2CH(CH_3)CH_2CHO$	85	
13	H_2C=$CH(CH_2)_2COCl$	A[f,g]	benzene	H_2C=$CH(CH_2)_2CHO$	71	
14	$(CH_3)_2C$=$CH(CH_2)_2COCl$	A	benzene	$(CH_3)_2C$=$CH(CH_2)_2CHO$	92	
15a	PhCH=CHCOCl	A[f,h]	benzene	PhCH=CHCHO	73	
				$PhCH_2CH_2CHO$	7	
15b	PhCH=CHCOCl	A[i]	benzene	PhCH=CHCHO	0	
				$PhCH_2CH_2CHO$	15-35	
16a	CH_3CH=CHCOCl	A[h]	benzene	CH_3CH=CHCHO	85	
				$CH_3CH_2CH_2CHO$	<5	
16b	CH_3CH=CHCOCl	A	Et_2O	CH_3CH=CHCHO		62
				$CH_3CH_2CH_2CHO$		<5
17	n-$C_6H_{13}COCl$	A	benzene	n-$C_6H_{13}CHO$	81	77
18	n-$C_{15}H_{31}COCl$	A	benzene	n-$C_{15}H_{31}CHO$	97	
19a	$(CH_3)_2CHCOCl$	A	benzene	$(CH_3)_2CHCHO$	87	
19b	$(CH_3)_2CHCOCl$	B	Et_2O	$(CH_3)_2CHCHO$	95	
20a	c-$C_6H_{11}COCl$	A	benzene	c-$C_6H_{11}CHO$	85	
20b	c-$C_6H_{11}COCl$	E	benzene	c-$C_6H_{11}CHO$	98	
21	$Ph_2CHCOCl$	A	benzene	Ph_2CHCHO	75	
22a	$(CH_3)_3CCOCl$	B[f,g]	benzene	$(CH_3)_3CHO$	80	
22b	$(CH_3)_3CCOCl$	C[j]	THF	$(CH_3)_3CHO$	89	
22c	$(CH_3)_3CCOCl$	C[j]	toluene	$(CH_3)_3CHO$		65
23a	Ph_3CCOCl	A[f,j]	benzene	Ph_3CCHO	37	
				Ph_3CH	49	
23b	Ph_3CCOCl	B[f,j] + $5PPh_3$	benzene	Ph_3CCHO	71	
				Ph_3CH	19	
24a	4-$ClCOC_6H_4COCl$	A	benzene	4-$HCOC_6H_4CHO$	87	
24b	4-$ClCOC_6H_4COCl$	E	benzene	4-$HCOC_6H_4CHO$	82	
25	$ClCO(CH_2)_4COCl$	A	THF	$HCO(CH_2)_4CHO$	88	
26	$ClCO(CH_2)_2COCl$	A[d,j]	THF	4-Cl-4-Btl	[k]	
27	$PhCH_2OCOCl$	A[l]	benzene	$HCOOCH_2Ph$	17	
				$PhCH_3$[m]	11	

[a] A, Pd $(PPh_3)_4$; B, $PhCH_2PdCl(PPh_3)_2$; C, $PhCOPdCl(PPh_3)_2$; D, $PdCl_2(PPh_3)_2$ + $2PPh_3$; E, $PdCl_2$ + 4 to $5PPh_3$; 10^{-2} equiv of catalyst (based on RCOCl) unless otherwise indicated. [b] Based on RCOCl. Analytical yields by NMR integration of aldehydes peaks. [c] Propene was formed. [d] 2.2 equiv of Bu_3SnH added. [e] "One-pot" reduction of the acid via 3-pyridinecarbonyl chloride hydrochloride. Yield is based on the starting acid. See the Experimental Section. [f] 5×10^{-2} equiv of catalyst. [g] Slow addition of Bu_3SnH; see the Experimental Section. [h] Rigorously, 1 equiv of Bu_3SnH was added. [i] 2 or 3 equiv of Bu_3SnH added. [j] Special experimental conditions; see the text and the Experimental Section. [k] Not determined; no other products were detected. [l] 0.2 equiv of catalyst. [m] Other byproducts: $PhCH_2Cl$, 33%; $PhCH_2OH$, 5-10%; $PhCH_2OCOOCH_2Ph$, 3%. [n] Naph = naphthalene, Pyr = pyridine, and Btl = butyrolactone.

Tributyltin hydride reduces α,β-unsaturated ketones and aldehydes without any catalyst, but the reaction requires high temperatures or UV irradiation.[27] To check more accurately that tetrakis(triphenylphosphine)palladium(0) does catalyze such a reaction, we carried out the catalytic reduction of cyclohexenone for which no side reaction was expected. Cyclohexanone was effectively formed, but competitive decomposition of tributyltin hydride was also observed, probably because cyclohexenone is not reactive enough. Upon addition of 3.3 equiv of hydride, 68% of cyclohexanone was obtained together with 11% of unreacted cyclohexenone.

The sensitivity of the catalytic reduction to steric congestion was also investigated. Aliphatic acyl chlorides with a secondary α-carbon (entries 19–22) as well as 2-methylbenzoyl chloride (entry 4) were found to react normally. Wth pivaloyl chloride and with triphenylacetyl

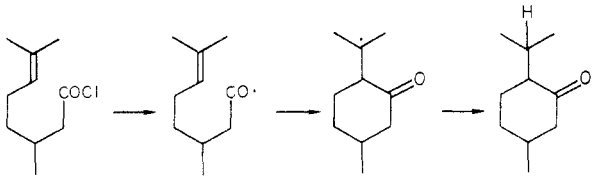
(27) M. Pereyre and J. Valade, *Bull. Soc. Chim. Fr.*, 1928 (1967).

chloride (entries 22–23) the aldehyde was obtained in good yields only if the tin hydride, diluted in benzene, was very slowly added to a warmed (60 °C) solution of the acyl chloride and tributyltin hydride, in order to keep the concentration of tributyltin hydride in the medium as low as possible. Otherwise, mainly the decomposition of the hydride (eq 3) was observed. When similar conditions were applied to triphenylacetyl chloride in the absence of catalyst, less than 10% of the acyl chloride was consumed. The free-radical reduction of triphenylacetyl chloride with tributyltin hydride involves heating in xylene at 110 °C for several hours.[28] In the catalytic reduction of triphenylacetyl chloride, triphenylmethane was always obtained as a byproduct. The relative amount of triphenylmethane although variable was always greater than the one (ca. 5%) obtained under free-radical conditions. On the other hand, triphenylmethane is the only product of the Rosenmund reduction of triphenylacetyl chloride.[3] We found that triphenylacetyl chloride and triphenylacetaldehyde were not decarbonylated in benzene at 60 °C in the presence of tetrakis(triphenylphosphine)palladium(0). Decarbonylation should therefore occur during the palladium-mediated reaction of triphenylacetyl chloride with tributyltin hydride. Another possibility is that the presence of tin compounds induces in some way the decomposition of triphenylacetyl chloride to trityl chloride. We checked to see that trityl chloride was rapidly reduced to triphenylmethane under our conditions.

Diacyl chlorides were normally reduced to the corresponding dialdehydes when the two carbonyl functions were sufficiently far apart (entries 24 and 25). Succinyl chloride (entry 26), on the other hand, afforded exclusively 4-chloro-4-butyrolactone even when the catalyst was added to the preformed solution of the acyl chloride and tributyltin hydride; thus despite the high rate of the catalytic reduction, tautomerization of the acyl chloride–aldehyde monoreduction compound (either spontaneous or palladium mediated) cannot be avoided.

Attemps to extend the catalytic reduction to alkyl chloroformates were not successful. Thus benzyl chloroformate (entry 27) gave only 17% of benzyl formate together with benzyl chloride (33%) and small amounts of toluene (11%), benzyl alcohol, and dibenzyl carbonate. In the absence of tributyltin hydride, the palladium catalyst was found to decompose benzyl chloroformate over a period of 24 h to a mixture of benzyl chloride (ca. 75%) and dibenzyl carbonate (ca. 25%).

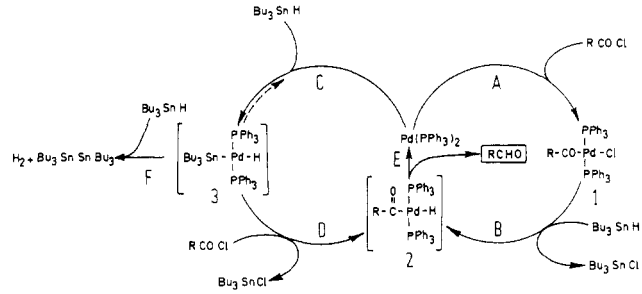
Mechanistic Aspects. As already mentioned, under AIBN-initiated free-radical conditions, citronellyl chloride is reduced to menthone instead of citronellal; the formation of menthone is explained by the addition of the initially formed acyl radical onto the double bond[25] (eq 6).



(6)

In the presence of palladium catalysts, on the contrary, citronellyl chloride yields exclusively citronellal. It may also be noted that 4-nitrobenzoyl chloride reacts readily with tributyltin hydride in our catalytic conditions while the same substrate is not reduced by triphenyltin hydride under free-radical conditions.[29] For those reasons, the possibility of a radical mechanism for the palladium-mediated reduction can confidently be discarded.

Scheme I



Two plausible, perhaps oversimplified, mechanisms are outlined in Scheme I. Both of them involve the acylhydridopalladium(II) complex **2** as the immediate precursor, through reductive elimination, of the aldehyde. Two ways are considered for the formation of complex **2**: either the oxidative addition of the acyl chloride onto $Pd(PPh_3)_2$ followed by a metathesis reaction between the resulting acylchloropalladium(II) complex **1** and tributyltin hydride (reaction sequence AB)[30] or the oxidative addition of tributyltin hydride onto $Pd(PPh_3)_2$ followed by a methathesis reaction between the oxidative addition adduct **3** and the acyl chloride (reaction sequence CD). Finally steps C and F could account for the competitive decomposition of tributyltin hydride observed with poorly reactive acyl chlorides.[31]

Steps A and B appear to be very fast processes. Thus we observed that benzoylchlorobis(triphenylphosphine)-palladium(II) in benzene at room temperature is immediately reduced to benzaldehyde in the presence of a stoichiometric amount of tributyltin hydride. Likewise, we found (infrared analysis) the oxidative addition of benzoyl and 2-methylbenzoyl chlorides to tetrakis(triphenylphosphine)palladium(0) to be quasi-instantaneous in benzene or THF at room temperature. We were able to get a rough estimate of the rate of the reaction between tetrakis(triphenylphosphine)palladium(0) and benzoyl chloride in THF at −38 °C. A half-reaction time of about 10 min was found for an initial concentration of 0.035 mol/L in palladium complex and of 0.032 mol/L in acyl chloride. Nor too much significance can be given to this result as the reactivity of tetrakis(triphenylphosphine)-palladium(0), owing to its dissociative properties, may depend on its concentration; besides, the palladium complex was only partially soluble under the conditions of the reaction. However, it is clear that the oxidative addition process A is a very fast one and is compatible with the rapidity of the catalytic reduction observed here. Meanwhile the alternative CDE sequence for aldehyde formation cannot be discarded either. By analogy with what has been proposed for the palladium- or rhodium-catalyzed hydrosilylation of dienes and α,β-unsaturated ketones,[32,33] it may

(28) H. G. Kuivila and E. J. Walsh, Jr., *J. Am. Chem. Soc.*, 88, 571, (1966).

(29) E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, **29**, 3690 (1964). On the other hand, we found that tributyltin hydride does react with 4-nitrobenzoyl chloride in the absence of catalyst. After several hours in boiling benzene, a mixture of 4-nitrobenzaldehyde and 4-nitrobenzyl 4-nitrobenzoate was obtained.

(30) This reaction sequence is analogous to the one proposed for the palladium-catalyzed conversion of acyl chlorides to ketones by tetraorganotin compounds.[20]

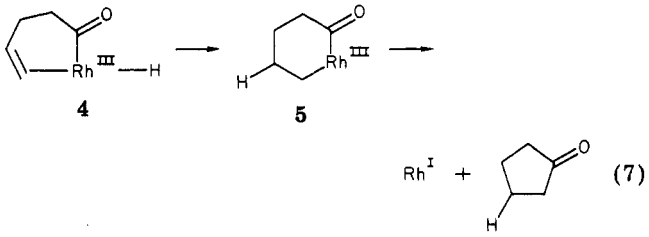
(31) The propension of tributyltin for decomposing in the presence of various metallic impurities is well-known, and we do not exclude other possible reactions for its decomposition.

(32) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nagatsugawa, and Y. Nagai, *J. Organomet. Chem.*, **94**, 449 (1975).

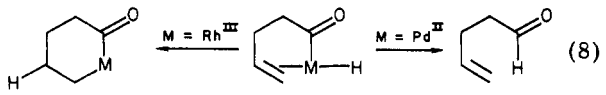
(33) J. Tsuji, "Organic Synthesis with Palladium Compounds, Reactivity and Structure Concepts in Organic Chemistry", Vol. 10, Springer-Verlag, West Berlin, Heidelberg, New York, 1980, pp 102, 103.

be assumed that the palladium-catalyzed reductions (hydrostannation) of α,β-unsaturated carbonyl compounds with tributyltin hydride involve an intermediate hydridotinpalladium compound similar to **3**. As the conditions for the catalytic reductions of the α,β-unsaturated carbonyl compounds and the acyl chlorides are the same, formation of the aldehyde throught the CDE reaction sequence is quite conceivable. Finally, the mechanism of the reaction might depend on the exact experimental conditions: the slower the addition of the tin hydride, the more likely is the reaction sequence ABE to operate.

Whatever the true reaction pathway, ABE or CDE, both of them involve a transient acylhydridopalladium(II) intermediate. We hoped to get some evidence as to its formation by studying the reduction of 4-pentenoyl chloride. It has recently been shown[34,35] that chlorotris(triphenylphosphine)rhodium(I) (Wilkinson complex) catalyzes the cyclization of 4-pentenal to cyclopentanone. The proposed mechanism (eq 7) involves the formation of the



acylhydridorhodium(III) complex **4**, the intramolecular insertion of the double bond into the rhodium–hydrogen bond of **4**, and the liberation of cyclopentanone from **5** through reductive elimination. From the foregoing, it could be expected that the palladium-catalyzed reduction of 4-pentenoyl chloride would afford cyclopentanone. As already pointed out, however, the catalytic reduction only afforded 4-pentenal. A stoichiometric reaction between (4-pentenoyl)chlorobis(triphenylphosphine)palladium(II) [the oxidative addition adduct of 4-pentenoyl chloride and tetrakis(triphenylphosphine)palladium(0)] was also performed; again, only 4-pentenal was obtained. While those results do not, of course, give any support for the intermediacy of an acylhydridopalladium(II) complex, they do not represent a real proof against either. The acylhydridopalladium(II) complex in contrast with its rhodium(III) analogue could very well undergo reductive elimination faster than double bond insertion (eq 8).



Conclusion

Tributyltin hydride, in the presence of soluble palladium catalysts, reduces acyl chlorides specifically to aldehydes under very mild conditions and in very good yields. The method is quite general and very selective. No further reduction of the aldehyde formed is observed; among the other reducible groups investigated here, only a bromine atom (but not an acetoxy group) allylic to a double bond was found to compete with the acyl chloride for reduction. The reducing agent tributyltin hydride is readily prepared from the very cheap polymethylhydrogensiloxan and bis(tributyltin) oxide; tributyltin chloride which is produced in the reduction process may be converted back to bis(tributyltin) oxide by simple treatment with sodium hydroxide; as a result, the present method may be seen as a rather inexpensive way of synthetizing aldehyde, provided that the catalyst is recovered.

Experimental Section

General Methods. Melting points were taken on a Kofler hot bench. Infrared spectra were obtained on a Perkin-Elmer Model 157 or on a Perkin-Elmer Model 577. ^{1}H NMR spectra were obtained on a Varian Associates Model T-60 or on a Brucker WH 90 spectrometer. They are reported in δ units, Me_4Si being used as the internal standard. ^{13}C NMR spectra were recorded at 22.63 MHz on the Brucker WH 90 spectrometer. GLC analysis were performed on a Girdel Model 75-FS-2 equipped with a 0.25 in. × 12 ft column packed with 20% Carbowax 20M on Chromosorb W or a 0.25 in. × 6 ft column packed with 15% Silicon SE-30 on Chromosorb W HMDS. Peak areas were measured by the cut and weigh method.

Materials. All solvents were freshly distilled, and in all the experiments involving palladium complexes they were degassed and saturated with argon just before use. THF and diethyl ether were distilled over lithium aluminum hydride. Benzene and toluene were distilled over sodium wires.

Most of the acyl chlorides used here were either commercial products or they were synthetized by reacting the corresponding carboxylic acids with thionyl chloride according to literature procedures. 3-Pyridine carbonyl chloride was prepared from the sodium salt of 3-pyridine carboxylic acid and thionyl chloride.[36] 3,7-Dimethyl-6-octenoic acid (citronellic acid) and 5-methyl 4-hexenoic acid were obtained by oxidation of citronellal and 5-methyl-4-hexenal[37] with silver oxide.[38] These two acids were converted to the corresponding acyl chlorides with thionyl chloride in the presence of pyridine.[39]

Triphenylacetyl chloride was prepared from triphenylacetic acid[40] according to the literature procedure;[41] however, instead of refluxing the mixture of thionyl chloride and triphenylacetic acid for 2 h as described, the reaction was run at 50 °C, monitored by infrared spectroscopy and stopped as soon as the ν(CO) absorption of the starting acid had disappeared; in our hands, overheating or prolonging unduly the reaction time resulted in substantial decarbonylation of triphenylacetyl chloride to trityl chloride.

Tri-*n*-butyltin hydride was prepared from polymethylhydrogensiloxane (Fluka) and bis(tri-*n*-butyltin) oxide.

Benzylchlorobis(triphenylphosphine)palladium(II),[43] benzoylchlorobis(triphenylphosphine)palladium(II),[44] and dichlorobis(triphenylphosphine)palladium(II)[45] were prepared according to published procedures.

Tetrakis(triphenylphosphine)palladium(0). This compound was prepared by reducing disodium tetrachloropalladate with sodium borohydride in the presence of triphenylphosphine.[46] For Na_2PdCl_4, 0.9 g (5.08 mmol) of $PdCl_2$ and 0.595 g (10.16 mmol) of NaCl were stirred overnight at room temperature in 25 mL of methanol. The resulting dark red solution was filtered through a cotton plug, and most of the methanol was removed on a rotary evaporator. The residue was rediluted in 20 mL of water. For $Pd(PPh_3)_4$, the reaction was carried out with thoroughly degassed solutions or solvents. A 250-mL Schlenck tube fitted with a magnetic stir bar and connected to a gas outlet was weighed with

(34) R. C. Larock, K. Oertle, and G. F. Potter, *J. Am. Chem. Soc.*, **102**, 190 (1980).
(35) R. E. Campbell, Jr., C. F. Lochow, K. P. Vora, and R. G. Miller, *J. Am. Chem. Soc.*, **102**, 5824 (1980).
(36) M. C. Ford and D. Mackay, *J. Chem. Soc.*, 1294 (1958).
(37) R. Marbet and G. Saucy, *Helv. Chim. Acta*, **50**, 2095 (1967).
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(39) The procedure used for the synthesis of 2,4-dimethylthiazole-5-carbonyl chloride was followed: W. R. Boon, *J. Chem. Soc.*, 601 (1945).
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(43) P. Fitton, J. E. McKeon, and B. C. Ream, *Chem. Commun.*, 370 (1969).
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(46) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc. A*, 164 (1968).

8 g (30.6 mmol) of finely powdered triphenylphosphine and filled with argon. Ethanol (100 mL) was introduced, via syringe, and the heterogenous mixture was stirred for a few minutes. The aqueous solution of Na_2PdCl_4 was added, upon which a heavy precipitate formed. Dropwise addition of an aqueous solution (10 mL) of 0.59 g (15.3 mmol) of $NaBH_4$ was then carried out, and the reaction mixture was stirred and occassionally shaken for 20 min. After the addition of 50 mL of water, the solid compound was collected by filtration under a stream of argon and washed rapidly and successively with water, ethanol, a small volume of ether, and pentane. $Pd(PPh_3)_4$ was finally vacuum dried and stored in an argon atmosphere.

Chloro(4-pentenoyl)bis(triphenylphosphine)palladium-(II). To a suspension of 0.9 g (0.78 mmol) of tetrakis(triphenylphosphine)palladium(0) in 7 mL of degassed anhydrous benzene was added 0.110 g (0.935 mmol) of freshly distilled 4-pentenoyl chloride. The heterogeneous mixture was stirred for 10 min under argon and filtered to give 170 mg of dichlorobis-(triphenylphosphine)palladium(II) which was identified by its infrared spectrum (ν(PdCl) 357 cm^{-1}). The filtrate was concentrated on a rotary evaporator, and the oily residue was triturated in 6 mL of hexane until a solid product was obtained. Hexane was removed, and the solid was dissolved in a small volume of benzene and reprecipitated with hexane. The mixture was cooled at 0 °C, and the palladium(II) complex (396 mg) was collected by filtration. Purification by dissolution–reprecipitation was repeated once to give filnally 250 mg (42%) of lemon-yellow chloro(4-pentenoyl)bis(triphenylphosphine)palladium(II): IR (Nujol) 1672 (C=O), 330 (PdCl) cm^{-1}; NMR ($CDCl_3$, at −30 °C for better resolution) δ 0.97 (br dt, 2 H, CH_2C=C) 2.0 (br t, 2 H, CH_2CO), 4.22–5.42 (m, 3 H, CH_2=CH) 7.4–8 (m). Assignments were confirmed by decoupling experiments.

General Procedure for the Reduction of Acyl Chlorides to Aldehydes on an Analytical Scale. Reactions were performed under an argon atmosphere and in degassed solvents by using Schlenck tubes equipped with a magnetic stir bar and a rubber septum cap. With some exceptions which are described later, the following procedure was used. To the acyl chloride (generally 1 or 2 mmol), approximately 0.5 M in solution (benzene, toluene, THF, or diethyl ether), were added the catalyst (generally 10^{-2} equiv) in a stream of argon and then, with a syringe, tributyltin hydride (1.1–1.2 equiv) over a period of 0.5–3 min. The reactions were generally moderately exothermic and could be easily monitored by infrared spectroscopy. In many cases the end of the reaction could be visualized through a sudden and typical darkening of the reaction mixture, from a lemon-yellow to a brownish yellow; gas evolution resulting from the decomposition of tributyltin hydride in excess was also often observed. After completion of the reaction (usually 10 min or less), the solvent was evaporated, and the reaction mixture was analyzed by infrared and NMR spectroscopy. In the case of volatile compounds, spectra were recorded directly on the bulk after suitable dilution. Yields of aldehydes were obtained from the integration of the NMR aldehydic proton peaks by using anisole, dimethyloxalate, or another aldehydic compound as the reference. When necessary, GLC analysis or thin-layer chromatography were also performed, either to fully characterize the aldehyde formed or to search for other possible reduction products.

Reduction of 3-Pyridinecarboxylc Acid to 3-Pyridinecarboxaldehyde via 3-Pyridinecarbonyl Chloride Hydrochloride. In a 20-mL Schlenck tube equipped with a magnetic stir bar was refluxed 0.487 g (3.96 mmol) of 3-pyridinecarboxylic acid in 1.73 mL (23.7 mmol) of thionyl chloride for 5 h. After the mixture cooled at room temperature, excess $SOCl_2$ was removed by evaporation under vacuum (1 mmHg), leaving 3-pyridinecarbonyl chloride as a white solid. The Schlenck tube was filled with argon, and 8 mL of freshly distilled deoxygenated THF was added. The heterogeneous mixture was magnetically stirred, and 1.4 g (4.8 mmol) of tributyltin hyride was added in three portions at intervals of 10 min; gas evolution was observed while the acyl chloride gradually dissolved in the medium. When the reaction mixture was almost totally homogeneous, 0.0456 g of tetrakis(triphenylphosphine)palladium(0) (0.04 mmol) was added, followed by 1.25 g (4.3 mmol) of tributyltin hydride dropwise over a period of 15 min. The reaction gave 3-pyridinecarboxaldehyde in 75–80% yield as determined by NMR spectroscopy with isobutyraldehyde as the internal reference.

Reduction of 4-Pentenoyl Chloride. To a mixture of 2.220 g (1.856 mmol) of 4-pentenoyl chloride and 0.107 g (9.3×10^{-2} mmol) of tetrakis(triphenylphosphine)palladium(0) in 4 mL of benzene cooled at 5 °C was added over a period of 15 min 0.650 g (2.08 mmol) of tributyltin hydride. A blackening of the solution occurred as soon as the addition was started, and some gas evolution was observed. 4-Pentenal (analytical yield 71%) was characterized by infrared, NMR, and GLC (column, Carbowax) analyses and by comparison with an authentic sample; no cyclopentanone could be detected.

Reduction of Triphenylacetyl Chloride. To a stirred solution of 240 mg (0.79 mmol) of triphenylacetyl chloride and 45 mg (0.040 mmol) of tetrakis(triphenylphosphine)palladium(0) in 3 mL of benzene at 60 °C was added slowly over a period of 60 min. 0.350 g (1.2 mmol) of tributyltin hydride in 4 mL of benzene. The reaction gave 0.15 mmol (19%) of triphenylmethane and 0.56 mmol (71%) of triphenylacetaldehyde as determined by NMR spectroscopy. Pure samples of triphenylacetaldehyde were obtained by thin-layer chromatography on silica gel: IR (CCl_4) 3050, 2750, (H–CO), 1950, 1885, 1810, 1730 (CO), 1600 cm^{-1}; NMR ($CDCl_3$) δ 7–7.6 (m, 15 H), 10.3 (s, 1 H).

Reduction of Pinaloyl Chloride. See Table I, entries 22a and 22b. The same procedure as for triphenylacetyl chloride was used. The reactions were run at room temperature (entry 22a) or at 60 °C (entry 22b).

Reduction of Succinyl Dichloride. Succinyl dichloride (339 mg, 2.19 mmole) and 1.4 g (4.8 mmol) of tributyltin hydride were mixed in 8 mL of THF. The flask was immersed in a cold water bath, and the catalyst was added. The solution immediately took on a deep violet color (the same color was observed in the absence of tributyltin hydride). The reaction mixture was stirred for 30 min and analyzed in the usual way. All the starting acid chloride had been consumed, and 4-chloro-4-butyrolactone, identified by comparison with an authentic sample,[47] was found as the only product of reduction: NMR ($CDCl_3$) δ 2.7 (m, 4 H) 6.5 (m, 1 H); IR (neat) 1810 (CO) cm^{-1}.

Tri-*n*-butyltin Hydride Reductions of Acyl Chlorides to Aldehydes on a Preparative Scale. (A) Reduction of Benzoyl Chloride. To a mixture of 2.81 g (20 mmol) of benzoyl chloride and 0.230 g (0.2 mmol) of tetrakis(triphenylphosphine)palladium(0) in 10 mL of benzene was added dropwise over a period of 10 min 6.4 g (2.2 mmol) of tributyltin hydride. The temperature of the reaction mixture rose to about 30–40 °C, and the solution darkened almost as soon as all the hydride had been added. Stirring was continued for 1 h; the solvent was removed by evaporation at room temperature, pentane was added, and the precipitated palladium compounds were filtered off. Pentane was evaporated from the filtrate, and benzaldehyde was distilled under reduced pressure from the high-boiling tin compounds; yield 1.72 g (81%).

(B) Reduction of 10-Undecenoyl Chloride. The same conditions as with benzoyl chloride were used with 6.1 g (30.1 mmol) of 10-undecenoyl chloride, 0.353 g of tetrakis(triphenylphosphine)palladium(0), 15 mL of benzene, and 9.9 g (34 mmol) of tributyltin hydride. After removal of the solvent, precipitation with pentane gave 0.146 g (42% of the starting amount) of tetrakis(triphenylphosphine)palladium(0) identified by infrared spectroscopy. Pentane was evaporated from the filtrate, and distillation under reduced pressure gave 4.48 g (86%) of 10-undecenal: bp 42 °C (0.05 mmHg); n_D 1.4432; IR (CCl_4) 2700 (H–CO), 1727 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.3–1.85 (m, 10 H), 1.85–2.26 (m, 3 H), 2.40 (dt, $J \approx 1.5$, 6 Hz, 3 H), 4.8–5.26 (m, 2 H, $=CH_2$), 5.53–6.23 (m, 1 H, HC=), 9.73 (t, $J = 1.5$ Hz, H–CO); the absorption pattern for vinylic protons was in all respects identical with the one of the starting acyl chloride; ^{13}C NMR ($CDCl_3$) δ 21.8, 28.7, 28.9, 29.1, 33.5, 43.6, 113.9 ($=CH_2$, 138.8 (HC=), 202.3 (C=O).

(C) Reduction of 4-Nitrobenzoyl Chloride. The same experimental procedure was used with 5.57 g (30 mmol) of 4-nitrobenzoyl chloride, 0.350 g (0.305 mmol) of tetrakis(triphenylphosphine)palladium(0), 40 mL of benzene, and 9.75 g (3.35 mmol) of tributyltin hydride. Upon evaporation of the benzene,

(47) H. G. Kuivila, *J. Org. Chem.*, **25**, 284 (1960).

a solid product formed. Hexane was added, and the precipitate was collected by filtration. The filtrate was cooled to −20 °C for 1 h, and more precipitate was collected by a second filtration. Infrared analysis revealed that there were no aldehyde products left in the final filtrate. Both precipitates were combined and purified by chromatography on a short column (Florisil, benzene as the eluant); 3.3 g (73%) of 4-nitrobenzaldehyde was collected; mp 106 °C (lit.[48] mp 106 °C).

(D) Reduction of 4-Bromobenzoyl Chloride. The same experimental conditions were used with 1.095 g (5 mmol) of 4-bromobenzoyl chloride, 0.057 g (0.05 mmol) of tetrakis(triphenylphosphine)palladium(0), 8 mL of THF, and 1.53 g (5.25 mmol) of tributyltin hydride. After completion of the reaction, THF was removed on a rotary evaporator. To the residue were then added 25 mL of diethyl ether and 25 mL of an aqueous solution containing 2.3 g of KF. The two-phase system was vigorously shaken for 5 min. The white precipitate of Bu_3SnF was filtered off and washed several times with diethyl ether. The aqueous layer of the filtrate was decanted and extracted with diethyl ether. The ethereal solutions were combined, washed with aqueous sodium hydrogen carbonate, and dried over $MgSO_4$, and the solvent was evaporated. Crystalline 4-bromobenzaldehyde was obtained with a small amount of tin compound, probably hexabutyldistannane as no SnCl absorption (322 cm^{-1}) was visible on the infrared spectrum. The crude 4-bromobenzaldehyde was further purified on a short column (Kieselgel 60, Merck). Tin impurities were first eluted with hexane, and 4-bromobenzaldehyde was collected upon elution with 1:1 hexane–benzene: mp 56.5–57 °C (lit.[48] mp 57 °C); yield 0.72 g (78%).

(E) Reduction of Crotonyl Chloride. Crotonyl chloride (5.67 g, 54.3 mmol) and 0.650 g (0.56 mmol) of tetrakis(triphenylphosphine)palladium(0) were mixed in 30 mL of diethyl ether. To the heterogenous mixture was added tributyltin hydride (16.4 g, 56.5 mmol) dropwise over a period of about 20 min. During the process the reaction mixture warmed to about 30 °C and became progressively homogeneous. The reaction mixture was further stirred for 30 min, and then most of the solvent was removed by distillation at atmosphere pressure through a Vigreux column. Distillation was carried out under reduced pressure, and the products were collected in a cold trap at −70 °C. A first fraction (4.98 g) was collected under 30 mmHg with a heating bath temperature up to 80 °C and a second fraction (0.45 g) was collected under 0.5 mmHg with a heating bath temperature up to 110 °C. The two fractions were combined and distilled at atmospheric pressure to give 2.34 g (62%) of pure crotonaldehyde: bp 103–104 °C (lit.[48] bp 104 °C); n_D 1.4380 (lit.[48] n_D 1.4373). The lower boiling fractions consisted of diethyl ether contaminated with small amounts of butanal (less than 2.5 mmol (5%) as estimated by GLC analysis with an internal reference).

(F) Reduction of Pivaloyl Chloride. To a stirred solution of 4.2 g (35 mmol) of pivaloyl chloride in 15 mL of toluene maintained at 65 °C were added 0.270 g (0.35 mmol) of chlorobenzylbis(triphenylphosphine)palladium(II) and then dropwise over a period of 60 min 14.35 g (49.5 mmol) of tributyltin hydride in 10 mL of toluene. Distillation of the reaction mixture at atmospheric pressure through a 3-in.-high helix-packed column gave (bp 75–109 °C) 6.31 g of a mixture of 2,2-dimethylpropanal (pivalinaldehyde), toluene, and a small amount of unreacted pivaloyl chloride. Redistillation gave (bp 75–76 °C) 2.12 g of 2,2-dimethylpropanal contaminated with about 3% of pivaloyl chloride and 6% of toluene (molar proportions, estimated by infrared and NMR spectroscopy). The yield (corrected for impurities) was 65%.

Catalytic Reduction of Cyclohexenone to Cyclohexanone. To a solution of 180 g (1.87 mmol) of cyclohexenone and 23 mg (0.02 mmol) of tetrakis(triphenylphosphine)palladium(0) in 2 mL of benzene containing 200 mg of mesitylene as an internal reference for GLC analysis was added 600 mg (2.05 mmol) of tributyltin hydride over a period of 5 min. Some gas evolution was perceptible throughout the addition process. Magnetic stirring was continued for 10 min more. A small sample of the solution was then withdrawn, acidified with a few drops of acetic acid, and analyzed on a gas chromatograph (column, SE-30, 85 °C). The whole process of adding 1.1 equiv of tributyltin hydride, stirring for 10 min, and analyzing acidified aliquot portions was repeated twice. GLC analysis gave the following results (equivalents of tin hydride added, percent cyclohexanone formed, percent unreacted cyclohexenone): none, 0, 100; 1.1, 39, 56; 2 × 1.1, 57.5, 25; 3 × 1.1, 68, 10.5.

Estimation of the Reaction Rate between Benzoyl Chloride and Tetrakis(triphenylphosphine)palladium(0). The experiment was conducted in a Y-tube equipped with a rubber septum and containing a magnetic stir bar and 96 mg (0.084 mmol) of tetrakis(triphenylphosphine)palladium(0) on one side and 2 mL of a THF solution 0.035 M in benzoyl chloride (0.07 mmol) and 0.03 M in acetophenone used as an internal reference for IR analysis on the other side. The tube was immersed in a cooling bath at −38 ± 1 °C; after temperature equilibration, the THF solution was transfered onto the palladium complex, and a vigorous magnetic stirring of the heterogeneous mixture was immediately started. After 4 and 12 min, respectively, two samples of about 0.8 mL were withdrawn via a syringe precooled at −80 °C and immediately injected into vials filled with 4 mL of pentane cooled at −70 °C, in order to ensure the complete precipitation of palladium compounds. After being allowed to stand at −70 °C for about 0.5 min, the pentane–THF mixtures were instantly filtered under water pump aspiration through a sintered-glass filter precooled at −80 °C. THF and pentane were then cautiously evaporated from the filtrate at room temperature, and the residue was analyzed by infrared spectroscopy after suitable dilution in carbon tetrachloride.

The amount of benzoyl chloride, relative to acetophenone, was then measured from the carbonyl absorptions by reference to standard mixtures of benzoyl chloride and acetophenone in carbon tetrachloride. The following results were obtained (time in minutes, percent benzoyl chloride consumed): 0, 0; 4, 28; 12, 66.

It was independently checked that no loss of organic products occurred during treatment of the samples.

Acknowledgment. We are grateful to Professor L. S. Hegedus and to Dr. H. Riviere for very helpful discussions.

Registry No. PhCOCl, 98-88-4; 2-(COCl)Naph, 2243-83-6; 1-(COCl)Naph, 879-18-5; 2-MeC_6H_4COCl, 933-88-0; 4-$MeOC_6H_4COCl$, 100-07-2; 4-$NO_2C_6H_4COCl$, 122-04-3; 4-BrC_6H_4COCl, 586-75-4; 3-(COCl)Pyr, 10400-19-8; 3-(CO_2H)Pyr, 59-67-6; $H_2C{=}CH(CH_2)_8CO$-Cl, 38460-95-6; $(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2COCl$, 36392-06-0; $H_2C{=}CH(CH_2)_2COCl$, 39716-58-0; $(CH_3)_2C{=}CH(CH_2)_2COCl$, 65890-48-4; $PhCH{=}CHCOCl$, 102-92-1; $CH_3CH{=}CHCOCl$, 10487-71-5; n-$C_6H_{13}COCl$, 2528-61-2; n-$C_{15}H_{31}COCl$, 112-67-4; $(CH_3)_2CHC$-OCl, 79-30-1; c-$C_6H_{11}COCl$, 2719-27-9; $Ph_2CHCOCl$, 1871-76-7; $(C$-$H_3)_3CCOCl$, 3282-30-2; Ph_3CCOCl, 6068-70-8; 4-$ClCOC_6H_4COCl$, 100-20-9; $ClCO(CH_2)_4COCl$, 111-50-2; $ClCO(CH_2)_2COCl$, 543-20-4; $PhCH_2OCOCl$, 501-53-1; PhCHO, 100-52-7; 2-(CHO)Naph, 66-99-9; 1-(CHO)Naph, 66-77-3; 2-MeC_6H_4CHO, 529-20-4; 4-$MeOC_6H_4CHO$, 123-11-5; 4-$NO_2C_6H_4CHO$, 555-16-8; 4-BrC_6H_4CHO, 1122-91-4; 3-(CHO)Pyr, 500-22-1; $H_2C{=}CH(CH_2)_8CHO$, 112-45-8; $(CH_3)_2C{=}C$-$H(CH_2)_2CH(CH_3)CH_2CHO$, 106-23-0; $H_2C{=}CH(CH_2)_2CHO$, 2100-17-6; $(CH_3)_2C{=}CH(CH_2)_2CHO$, 764-32-9; $PhCH{=}CHCHO$, 104-55-2; $PhCH_2CH_2CHO$, 104-53-0; $CH_3CH{=}CHCHO$, 4170-30-3; CH_3C-H_2CH_2CHO, 123-72-8; n-$C_6H_{13}CHO$, 111-71-7; n-$C_{15}H_{31}CHO$, 629-80-1; $(CH_3)_2CHCHO$, 78-84-2; c-$C_6H_{11}CHO$, 2043-61-0; Ph_2CHCHO, 947-91-1; $(CH_3)_3CCHO$, 630-19-3; Ph_3CCHO, 42365-04-8; Ph_3CH, 519-73-3; 4-$HCOC_6H_4CHO$, 623-27-8; $HCO(CH_2)_4CHO$, 1072-21-5; 4-Cl-4-Btl, 36603-83-5; $HCOOCH_2Ph$, 104-57-4; $PhCH_3$, 108-88-3; $PhCH_2Cl$, 100-44-7; $PhCH_2OH$, 100-51-6; $PhCH_2OCOOCH_2Ph$, 3459-92-5; Bu_3SnH, 688-73-3; $Pd(PPh_3)_4$, 14221-01-3; $PhCH_2PdCl$-$(PPh_3)_2$, 22784-59-4; $PhCOPdCl(PPh_3)_2$, 29158-91-6; $PdCl_2(PPh_3)_2$, 13965-03-2; $PdCl_2$, 7647-10-1; chloro(4-pentenoyl)bis(triphenylphosphine)palladium(II), 78804-24-7; cyclohexenone, 25512-62-3; cyclohexanone, 108-94-1.

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