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FACILE REDUCTION OF ACID CHLORIDES INTO ALDEHYDES USING HYPERVALENT SILICON HYDRIDES.

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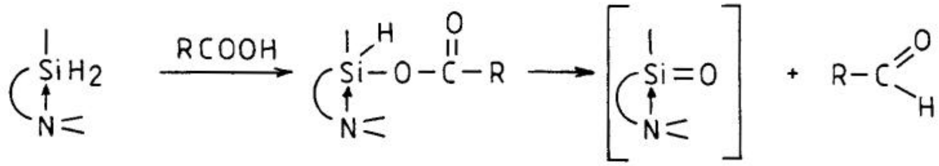
Acyl chlorides have been reduced to aldehydes by a simple exchange reaction with pentacoordinated silicon hydrides

Jenkins and Post have reported[1] the uncatalyzed reaction of aroyl chlorides with tribenzylsilane in refluxing ether giving low yields of aldehyde. With Pd/C as catalyst[2], the reaction proceeds at room temperature, but the yields are in the range 50-70% which is slightly less than that obtained with the Rosenmund reaction. Much better yields were obtained in the related reaction of tributyltin hydride with acyl chlorides[3]. We report here the usefulness of pentacoordinated hydrogenosilanes in the direct reduction of acyl chlorides into aldehydes.

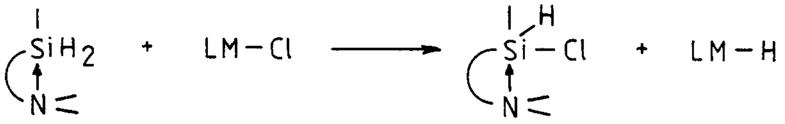
The reducing properties of silicon hydrides are enhanced by intramolecular pentacoordination[4]. We have previously reported the reduction of acids to aldehydes using the reactivity of these pentacoordinated hydrogenosilanes towards carboxylic acids and the thermal decomposition of the silyl esters (eq. 1)[5].

Eq. 1.



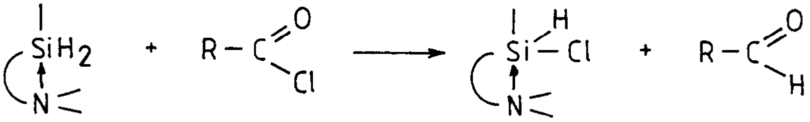
We have also observed the very easy hydrogen/chlorine exchange using chlorosilanes or PCl_5 (eq. 2).

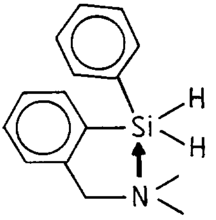
Eq. 2.



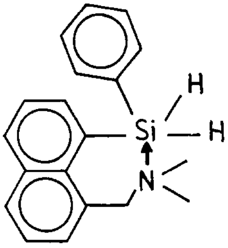
We report now the reactivity of these pentacoordinated hydrogenosilanes 1, 2, 3 towards acyl chlorides. The reactions are fast, exothermic and quantitative, with formation of aldehyde and chlorosilane (eq. 3).

Eq. 3.





1



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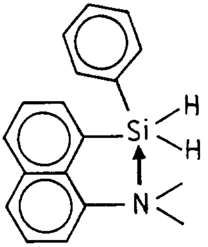


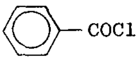
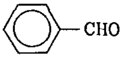
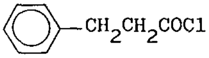
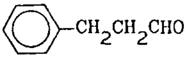
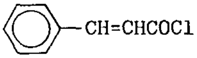
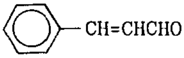
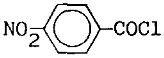
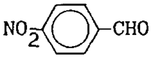
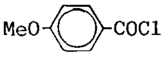
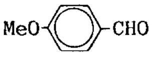
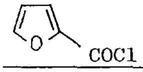
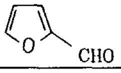
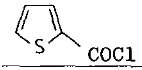
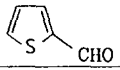
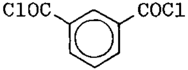
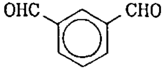
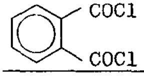
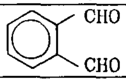
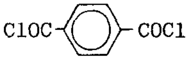
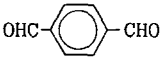
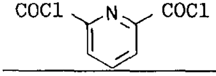
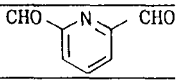
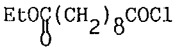
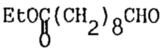
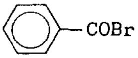
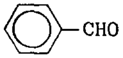
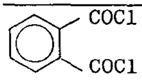
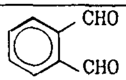
3

The aldehydes (Table) have been isolated by distillation after the silicon chloride was retained over wet silica (method A) or trapped in solution with CCl_4, on warming the crude material (method B). The selectivity of the method is demonstrated by several examples. Halogen, methoxy and nitroaryl substituents, heteroaryl groups and C=C double bonds remain unchanged. The method is also suitable for the conversion of dicarboxylic acid chlorides into dialdehydes.

The selectivity of silicon derivatives 1, 2, 3 has been checked. The best results are obtained with the silane 1, which is also the most readily and cheaply accessible reagent. In the case of poor reactants , like ethyl chlorothioformate, the yields are increased with the highly efficient silane 2. On the other hand, the conversion of benzoyl bromide into benzaldehyde is possible only when the less active silane 3 is used.

A modification of the Rosenmund reaction has been shown to improve yields [7], and more sophisticated reducing agents [8], including complex metal hydrides[9], $Na_2Fe(CO)_4$[10], $H\,Fe(CO)_4^-$[11], $(Ph_3P)_2CuBH_4$[12] have also been exploited successfully. Nevertheless, the present reaction represents a useful alternative method to convert acid chlorides into aldehydes directly.

Table

Silane	Acid chloride	Method	Aldehyde	Overall yield % *	
				Anal.	Isol.
1		A		>95	90
		A		>95	87
		A		>95	86
		A		>95	90
		A		>95	91
		A		>95	87
		A		>95	86
		A		>95	89
		A		15	-
		A		>95	85
		A		>95	–
	$\mathrm{Br(CH_2)_3COCl}$	A	$\mathrm{Br(CH_2)_3CHO}$	>95	90
	$\mathrm{Cl(CH_2)_3COCl}$	A	$\mathrm{Cl(CH_2)_3CHO}$	>95	82
	 $\mathrm{EtO\underset{\underset{O}{\|}}{C}(CH_2)_8COCl}$	A	 $\mathrm{EtO\underset{\underset{O}{\|}}{C}(CH_2)_8CHO}$	>95	80
	$\mathrm{ClCO(CH_2)_8COCl}$	A	$\mathrm{OHC(CH_2)_8CHO}$	>95	85
	$\mathrm{CH_3COCl}$	B	$\mathrm{CH_3CHO}$	>95	-
	$\mathrm{(CH_3)_3CCOCl}$	B	$\mathrm{(CH_3)_3CCHO}$	>95	-
2	EtSCOCl	B	EtSCHO	>95	-
3		A		45	-
		A		>95	89

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* The analytical yield was obtained by NMR integration.

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