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THE ONE-POT CONVERSION OF CARBOXYLIC ACIDS TO ALDEHYDES VIA ACTIVATED SILYL CARBOXYLATES.

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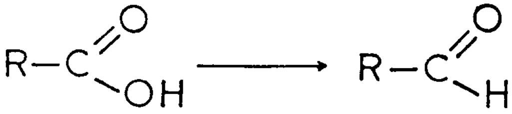
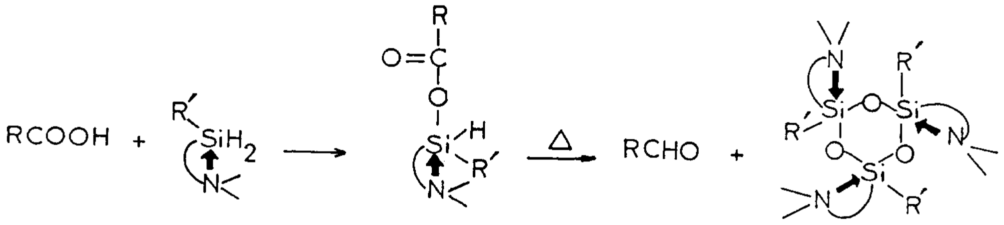
The transformation of acids into aldehydes in a one-pot process is performed through the thermal decomposition of pentacoordinated silicon species.

The direct reduction of free carboxylic acids to aldehydes is usually not accomplished easily.[1]



Some reagents used for this purpose are lithium in dimethylamine,[2] thexylborane,[3] 2-thiazoline-2-thiol,[4] isobutyl magnesien bromide/dichloro bis (Π cyclopentadienyl) titanium,[5] or bis(4-methylpiperazinyl)-aluminium hydride.[6] The reduction of a carboxylic acid with borane /dimethylsulfide followed by oxidation of the resultant trialkoxyboroxine (without isolation) with pyridinium chloroformate in refluxing dichloromethane is perhaps of wider applicability.[7]

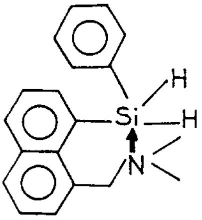
We report here a very simple method involving the one-pot transformation of a carboxylic acid into the corresponding aldehyde via an activated pentacoordinated silyl carboxylate (Scheme)



In a previous communication, we have described the enhancement of Si-H bond reactivity towards nucleophiles in pentacoordinated structures.[8] For instance, carboxylic acids react, without any catalyst, with evolution of hydrogen to form silyl carboxylates.

We have now found that simple heating of these silyl esters at relatively low temperature (110-160°C) affords the aldehydes in 50-95% yields (Table). The overall reduction can be performed without isolation of the silyl esters. The aldehydes are extracted from the crude (using the Kugelrohr technique) or separated by chromatography. They have been characterized by NMR and/or by their 2,4-dinitrophenylhydrazones. The residual silicon moiety is identified as cyclosiloxane, D'_3.

The reaction is selective, since fluoro, nitro, cyano, methoxy and heteroaryl substituents do not react with the silane. The aliphatic acids can be successfully reduced in fair to good yields. The present method also permits the desirable reduction of α,β unsaturated acids. The six-membered cyclic coordinated compound 1 is more efficient than the five-membered ring derivatives 2,3. Generally, better yields are obtained when the silylcarboxylates are solid compounds.



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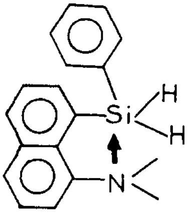

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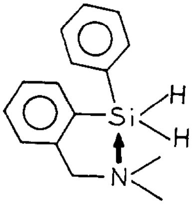

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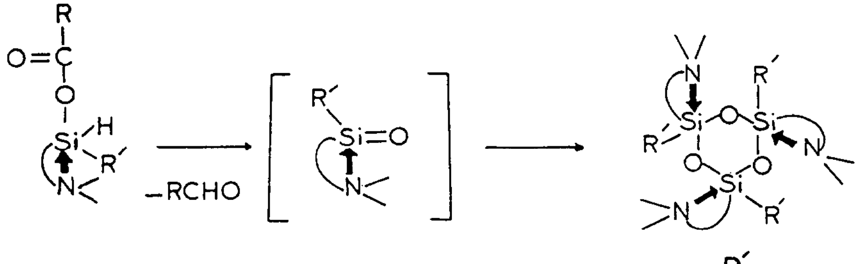
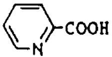
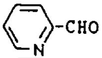
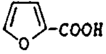
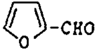
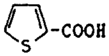
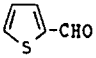
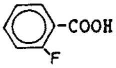
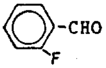
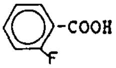
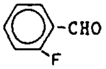
The parent silyl ester PhαNpHSiOCOPh is inactive in similar conditions : less than 3% of benzaldehyde is detected after 48 h at 200°C in an autoclave. Obviously, the enhanced reactivity of the Si-H bond through intramolecular coordination is essential for the reaction.

A possible mechanism we propose for the thermal decomposition corresponds to an elimination of the aldehyde with formation of the unstable silanone which then gives the D'_3 trimer.



D'_3

Table : Synthesis of aldehydes from carboxylic acids

Silanes	Acids	Conditions[a]	Aldehydes	Yields %
1	CH_3CH_2COOH	B	CH_3CH_2CHO	85
	$CH_3(CH_2)_6COOH$	A	$CH_3(CH_2)_6CHO$	50
	$C_6H_{11}COOH$	A	$C_6H_{11}CHO$	68
	$(CH_3)_3CCOOH$	D	$(CH_3)_3CCHO$	50
	Ph-CH=CH-COOH	B	Ph-CH=CH-CHO	71
	$(CH_3)_2CH=CHCOOH$	D	$(CH_3)_2CH=CHCHO$	-[b]
	PhCOOH	C	PhCHO	83
	pF C_6H_4COOH	A	pF C_6H_4CHO	94
	oF C_6H_4COOH	B	oF C_6H_4CHO	96
	pMeO C_6H_4COOH	B	pMeO C_6H_4CHO	76
	pNO_2 C_6H_4COOH	A	pNO_2 C_6H_4CHO	60
	mNO_2 C_6H_4COOH	A	mNO_2 C_6H_4CHO	60
	oNO_2 C_6H_4COOH	A	oNO_2 C_6H_4CHO	50
	mNC C_6H_4COOH	A	mNC C_6H_4CHO	60
		A		90
		B		76
		B		88
2	Ph-CH=CH-COOH	C	Ph-CH=CH-CHO	50
		B		72
3	Ph-CH=CH-COOH	B	Ph-CH=CH-CHO	65
		C		60

[a] Experimental conditions : A - decomposition performed under vacuum with Kugelrohr at 110-140°C ; B - identical, but at 150-170°C ; C - identical, but at temperature above 180°C ; D - decomposition at 180°C performed at atmospheric pressure.

[b] Yield not determined.

The existence of a free silicon-oxygen double bond is still debated. No silanone has yet been reported either in pure form or in solution because of their very high reactivity.[9] The only direct observations have been performed with the matrix isolation technique.[10] However, a transient silanone can be reasonably considered in the present case, since the expected trimer is the only silyl product quantitatively isolated from the crude, when the reaction is performed in the strict absence of oxygen or water, using a vacuum line technique with degassed solvents under argon.

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