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ACYL SILANES AS SYNTHETIC INTERMEDIATES : FORMATION OF ACYL ANIONS AND UNUSUAL FLUORIDE-INITIATED SILICON TO CARBON ALKYL GROUP MIGRATION

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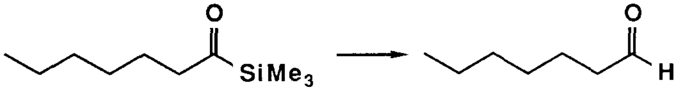
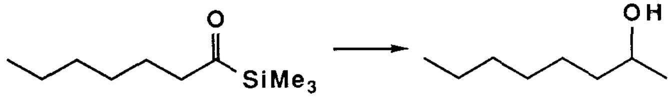
Summary: Acyl silanes react with fluoride ion in the presence of water to give products arising either from intermediates equivalent to acyl anions or from rearrangements involving alkyl group migration from silicon to carbon, depending upon the reaction conditions.

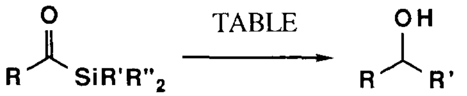
Walton and Heathcock have independently reported the use of phenyl acyl silanes as acyl anion equivalents by reaction with simple electrophiles in the presence of fluoride ion.[1,2] Following our interest in acyl silanes[3,4,5] we have re-examined this procedure. We find that while aryl acyl trimethylsilanes indeed undergo the reported reaction at all temperatures under neutral or acidic conditions, aryl acyl silanes bearing phenyl groups on the silicon atoms and simple alkyl acyl silanes require elevated temperatures and the presence of acid for this cleavage process to occur (e.g. equation 1).[8]



52% (Eq. 1)



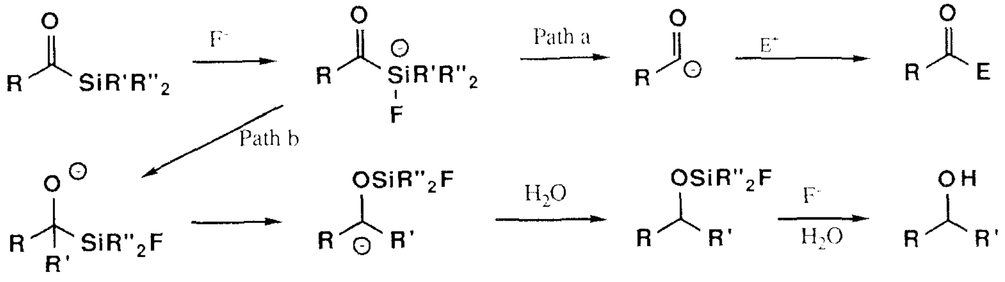
68% (Eq. 2)



Condition	R	R'	R"	Yield %
a	$CH_3(CH2)_5$	Me	Me	68
a	Ph	Ph	Me	52
a	Ph	Ph	Ph	54
a	$CH_3(CH2)_4$	Me	Me	62
b	$CH_3(CH2)_5$	Me	Me	57
c	$CH_3(CH2)_5$	Me	Me	67

a: $^nBu_4NF$ (3 eq.), thf, 25 C, 12h.
b: $^nBu_4NF$ (3 eq.), thf/H_2O, 60 C, 12h.
c: $^nBu_4NF$ (3 eq.), thf/H_2O, -10 C, 12h.

With the exception of aryl acyl trimethylsilanes simple acyl silanes in the absence of acid give products arising from alkyl or aryl group migration from the silicon atoms to the carbonyl carbon atoms in good yields (Table). For example, after treatment of heptyl acyl trimethylsilane with tetra-n-butyl ammonium fluoride containing ca. 5% water (3 equiv.) in thf solution at room temperature for twelve hours octan-2-ol could be isolated in good yield (equation 2). Similar treatment of acyl silanes containing triphenylsilyl or dimethyl phenyl silyl moieties results in exclusive migration of a phenyl group. These reactions are rare examples of the migration of simple alkyl groups from silicon to carbon and are similar to rearrangements suggested by Brook[6] to explain the complex product mixtures observed in the attack of acyl silanes by alkoxide ions.



Scheme 1

We believe the first step of these reactions to be nucleophilic attack by fluoride ion at the silicon atom to generate a pentacoordinate silicon anionic intermediate. This may be followed by cleavage to give an acyl anion which could react with any electrophile present, corresponding to one mechanism originally proposed by Brook for attack by ethoxide anion (Scheme 1, path a); indeed, pentacoordinate silicon species and acyl anions have both been detected in gas phase rections of acyl silanes with fluoride ion.[7] Alternatively a migration of one of the alkyl groups from silicon to carbon may occur to produce an alkoxide; subsequent Brook-type rearrangement and fluoride-induced desilylation could ultimately result in formation of a rearranged alcohol (Scheme 1, path b). One example of such a migration of a methyl group induced by ethoxide ion attack is quoted by Brook although the chemical yield is not given.

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8. Heathcock notes one instance of such a cleavage process occurring upon treatment of a β-hydroxy acyl silane with fluoride ion, water, and acetonitrile. No details are given. We find for simple alkyl acyl silanes that use of acetonitrile as solvent gives rearranged secondary alcohols as the major products over a range of temperatures.

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