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THE CONVERSION OF α,α-DIBROMOBENZYLSILANES INTO ACYLSILANES ON SILICA GEL

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Summary: Acylsilanes may be prepared in high yield by treating α,α-dibromobenzylsilanes with silica gel.

Whilst attempting to develop new and to improve existing routes to acylsilanes, we found that α,α-dibromobenzylsilanes can be converted cleanly and in high yield into the corresponding acylsilanes simply by treatment with silica gel. The reaction is convenient and much cheaper than the existing procedure which uses large quantities of expensive silver acetate.[1)]

In a typical reaction, α,α-dibromobenzyl(trimethyl)silane (1 g) and silica gel (Merck 60, 60-230 mesh ASTM, Art 7734) were intimately mixed and thermostatted at 50°. Samples were withdrawn at intervals and progress of the conversion, which was followed by g.l.c. (1.5% OV1 2 m column operating at 100°), was judged to be complete after 90 min. The bulk of the reaction mixture was then extracted with diethyl ether and removal of solvent by evaporation left benzoyl(trimethyl)silane (0.52 g, 95%) whose physical and spectral characteristics were identical to those of an authentic specimen.

Other examples of the transformation are given in the Table. Rates of reaction appear to be quite unaffected by passage of air through the mixture, whereas the relative quantities of substrate and silica are important, as is the degree of hydration of the silica gel. Best results are obtained with a 20:1 w:w gel-to-substrate ratio; the rate of product formation decreases markedly if the silica gel is preheated at 200° for 48 h prior to use (cf. Table, entry 2). Experiments carried out under the same conditions but using Alumina (Merck 90-std, Art 1097) still gave acylsilanes, but the conversion rate was markedly lower (eg. $PhCOSiMe_3$ was obtained in 80% yield after 5 h). Electron-supplying groups (eg. p-OMe) on the acyl moiety appear to enhance the reaction rate (Entry 1), whereas electron-withdrawing substituents and replacement of methyl by aryl groups on silicon (Entries 4-9) retard the rate. The latter effect

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is probably of steric origin.

A further advantage of the method is that crude α,α-dibromobenzyl(trimethyl)silane can be used. Any $PhCHBrSiMe_3$ present as a result of incomplete dibromination of $PhCH_2SiMe_3$,[1] is unaffected by the silica gel, can be separated easily in the chromatographic work up and recycled.

These conversions are yet further examples of sensitive reactions which can usefully be carried out on silica gel.[4]

Table. Conversion of $XC_6H_4CBr_2SiR_2R'$ into $XC_6H_4COSiR_2R'$ compounds on silica gel[a]

Entry	X	R	R'	Reaction time (h)	Conversion[b] (%)	Ref[c]
1	p-OMe	Me	Me	0.2	98	2
2	H	Me	Me	1.5	95	1
3	H	Me	Me	5.0	65	1
4	H	Me	Ph	20	96	3
5	H	Ph	Ph	450	15	1
6	p-Cl	Me	Me	8.0	95	2
7	m-Cl	Me	Me	50	98	2
8	m-Cl	Me	Ph	110	90	
9	m-Cl	Me	$m-ClC_6H_4$	144	15	

[a] All experiments were conducted using a 20:1 w:w gel-to-substrate ratio.

[b] For dibromo compounds requiring longer reaction times (Entries 5,8 and 9), the ether extract was concentrated and chromatographed on silica using 8:1 light petroleum (40-70° fraction) - ether as eluent in order to remove traces of unreacted starting material. Small amounts of aldehyde, ArCHO, were formed, probably as a result of desilylation of the product during this work up procedure.

[c] Satisfactory elemental analyses were obtained for new compounds.

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