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ACETYLDI-t-BUTYLSILANE AND ACETYLDI-t-BUTYLFLUOROSILANE: SYNTHESIS OF FUNCTIONALIZED ACYLSILANES

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Summary

The preparation of acetyldi-t-butylsilane and acetyldi-t-butylfluorosilane, the first stable acylsilanes containing functional groups on silicon, is described. The new preparative procedure involves treatment of α-ethoxyvinyllithium with a halosilane to give an α-silyl enol ether, which is hydrolyzed under mild conditions to give the corresponding acetylsilane. Bulky t-butyl groups on silicon can be used to protect a reactive fluorine substituent during the hydrolysis step.

Introduction

Acylsilanes are of interest because they are simple organosilicon compounds which are colored, ranging from yellow to red-violet, whereas the analogous, all-carbon ketones are colorless. Numerous explanations of the cause of such absorption in the visible region of the spectrum have been put forth [1,2], but none has gained universal acceptance. The controversy surrounding these compounds and the need for many model structures has led to the development of several different routes to their synthesis. Principal among these have been the hydrolysis of geminal dihalides and dithianes and the oxidation of benzyl- or α-hydroxyalkylsilanes [1,3]. Other recent procedures include the addition of triphenylsilyllithium to pivaloyl chloride [4], and the reaction of the system $Me_3SiCl/Mg/$ HMPT (hexamethylphosphoric triamide) with *N*-acylimidazoles [5], with *N*-phenylpivalimidoyl chloride [6], and with α-ethylenic acid chlorides [7]. The latter routes are particularly limited in the structural variations permitted for both the acyl and silyl portions of the molecule.

One defect shared by all the above methods is that they are inappropriate

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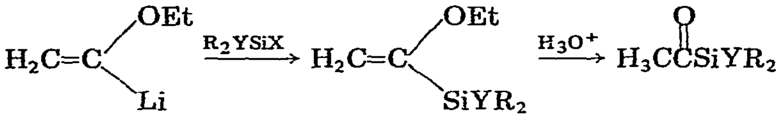
for the synthesis of acylsilanes with substituents on silicon other than alkyl, alkenyl, or aryl groups. The only heteroatom-substituted acylsilanes reported, $Ph_2XSiCOPh$, where X = OH, OMe, were prepared by hydrolysis of the corresponding *α,α-dibromobenzylsilanes* and were too unstable to allow complete characterization [8]. Acylhydrosilanes, compounds formally capable of keto-enol tautomerism (eq. 1), were felt to present a major preparative challenge

$$R_2C{=}\overset{OH}{\overset{|}{C}}{-}SiHR'_2 \rightleftharpoons R_2HC\overset{O}{\overset{\|}{C}}SiHR'_2 \rightleftharpoons R_2HC\overset{OH}{\overset{|}{C}}{=}SiR'_2 \qquad (1)$$

because the oxidizing nature of the carbonyl and the reducing nature of the hydrosilyl functions limited considerably the approaches which could be taken.

Recent reports on the utility of α-methoxyvinyl anion as an acyl anion equivalent [9a,b], together with information that the anion may be successfully silylated [10], encouraged us to attempt the preparation of acylsilanes via their enol ethers (eq. 2).



(2)

X = Cl, F (I) (II)

a: Y = CH_3, R = CH_3; b: Y = H, R = CH_3; c: Y = F, R = t-Bu; d: Y = H, R = t-Bu

Results and discussion

In order to test the synthesis route of eq. 2, trimethylchlorosilane was added to a chilled (−50°C) tetrahydrofuran (THF) solution of α-ethoxyvinyllithium, generated by lithiation of ethyl vinyl ether with t-butyllithium [9b]. Upon pouring the reaction mixture into water buffered with NH_4Cl and distilling the organic portion, acetyltrimethylsilane (IIa) was obtained directly in 31% yield. The spontaneous hydrolysis of the intermediate (Ia) may have been caused either by the pH of the NH_4Cl solution or by extra acidity arising from HCl liberated by hydrolysis of excess trimethylchlorosilane.

The seemingly facile hydrolysis of Ia suggested that repetition of the synthesis with dimethylchlorosilane should yield the acylhydrosilane (IIb). Although 2-ethoxy-3-methyl-3-sila-1-butene (Ib) was readily prepared in 44% yield following an anhydrous work-up of the reaction mixture, all attempts to form IIb by hydrolysis of Ib with dilute NH_4Cl or HCl were unsuccessful. Hydrogen evolution was observed in all such experiments. It appears that any acylsilanes formed containing either hydrogen or hydroxy substituents on silicon decomposed under the conditions of hydrolysis or else they never formed because of a more facile side reaction of Ib.

In order to minimize such possible side reactions during hydrolysis, it was decided to inhibit reaction at silicon sterically. The t-butyl group was selected as a substituent because of its great steric requirement and demonstrated ability to inhibit hydrolysis at silicon [11,12,13]. Addition of di-t-butyldifluorosilane to α-ethoxyvinyllithium resulted in a 50% yield of the α-ethoxyvinylsilane, 2-ethoxy-3-t-butyl-3-fluoro-4,4-dimethyl-3-sila-1-pentene (Ic). Subsequent hydrolysis of Ic with a homogeneous solution of aqueous HCl in THF gave acetyldi-t-butylfluorosilane (IIc) in 78% yield.

Treatment of Ic with $LiAlH_4$ in refluxing THF quantitatively reduced the fluorosilane to its corresponding hydrosilane (Id). This compound could then be hydrolyzed in good yield (81%) to form acetyldi-t-butylsilane (IId). The acylsilanes IIc and IId are stable, pale-yellow liquids. No decomposition has been observed after storage for 50 days at 25°C. They exhibit IR, UV and ^{13}C NMR spectral properties characteristic of their class (Table 1). Thus any inductive effect felt by the carbonyl group due to the presence of a hydrogen or fluorine atom on silicon does not manifest itself in a significant shift of the carbonyl absorption in the IR, UV, or ^{13}C NMR spectrum. A detailed discussion of the spectra of acylsilanes will be presented in a later paper.

The enol ether hydrolysis method described above will permit generation of a wide variety of acylsilane systems. Yields of acylsilanes from hydrolysis are high and although the enol ethers are only formed in moderate yield, optimization of conditions could significantly increase that yield. Even without optimization, the conversion of di-t-butyldifluorosilane to IId through a three-step reaction sequence occurred in 40% overall yield.

Finally, the importance of the sterically demanding t-butyl groups to the stability of these compounds towards hydrolysis must be emphasized. As can be seen from the above hydrolyses, a large increase in the stability of substituents on silicon is observed in changing from two methyl to two t-butyl groups. The inhibiting effect of the t-butyl groups may well bring success to other attempts to prepare organosilanes which have failed with methyl or phenyl substituents due to side reactions of a functional group at silicon.

Experimental

The IR spectra of all compounds reported were recorded on a Perkin—Elmer 21 spectrometer as neat films using polystyrene as a standard. Precise determination of the carbonyl stretching frequencies was made with a Perkin—Elmer 521 spectrometer operating at a 10:1 scale expansion. UV absorptions were measured with a Cary 14A spectrometer. Proton NMR (PMR) spectra were determined using 10% solutions in CCl_4 with a Varian Associates A-60A spectrometer and ^{13}C NMR spectra were determined using 0.5 M solutions in $CDCl_3$ with a Varian Associates XL-100-15 spectrometer operating in the FT mode. Gas chromatography (GLC) was performed with a Series 1700 Varian Aerograph, using a 0.25 in × 10 ft copper column packed with 5% QF-1 on 60/80 mesh Chromsorb W. The yields of Id, IIc and IId were determined by GLC analysis.

Acetyltrimethylsilane (IIa)

The method of Baldwin et al. [9] was used to prepare α-ethoxyvinyllithium from 11.5 g (0.16 mole) of ethyl vinyl ether, 50 ml of THF, and 0.10 mole of t-butyllithium in 56 ml of pentane. The temperature of the solution was maintained below —50°C while 16.2 g (0.15 mol) of trimethylchlorosilane was added dropwise. After addition was complete the temperature was allowed to rise slowly to 25°C. Hydrolysis of the reaction mixture with dilute aqueous NH_4Cl

TABLE 1

CARBONYL SPECTRAL DATA FOR $H_3C\overset{\overset{O}{\|}}{C}SiYR_2$ (II)

Compound	IR (cm^{-1})	UV: λ_{max} (nm) [a]	^{13}C NMR: δ (ppm) [b]
IIa	1645	388 (ϵ 93) 372 (ϵ 126) 358 (ϵ 100)	254.1
IIc	1650	388.0 (ϵ 160) 373.7 (ϵ 210) 360.5 (ϵ 149)	252.4
IId	1645	390.0 (ϵ 123) 374.3 (ϵ 169) 360.5 (ϵ 131)	251.5

[a] In cyclohexane. [b] Downfield from internal TMS.

was followed by phase separation and distillation of the organic layer to give 3.6 g (31% yield) of IIa, identified by comparison of its IR, UV and PMR spectra with published values [1,14].

2-Ethoxy-3-methyl-3-sila-1-butene (Ib)

α-Ethoxyvinyllithium, prepared from 23.0 g (0.32 mol) of ethyl vinyl ether, 150 ml of THF, and 0.20 mol of t-butyllithium in 50 ml of pentane, was treated with 28.4 g (0.30 mol) of dimethylchlorosilane at −70°C. After it had been warmed slowly to 25°C, the reaction mixture was filtered and distilled to give 14.7 g (44% yield) of Ib, b.p. 107°C. IR (cm^{-1}): 3067w, 2956s, 2890m, 2128s, 1585s, 1247m, 1218s, 1054s, 969m, 880s; PMR: δ (ppm) 4.42 (AB pattern, 9 Hz, $=CH_2$), 4.03 (sept., 4 Hz, SiH), 3.67 (q, 7 Hz, OCH_2), 1.28 (t, 7 Hz, $OCH_2C\underline{H}_3$), and 0.17 (d, 4 Hz, $(CH_3)_2Si$). (Found: C, 55.39; H, 10.88. $C_6H_{14}OSi$ calcd.: C, 55.32; H, 10.83%).

2-Ethoxy-3-t-butyl-3-fluoro-4,4-dimethyl-3-sila-1-pentene (Ic)

The above procedure was repeated using 0.1 mol of α-ethoxyvinyllithium and 18.0 g (0.10 mole) of di-t-butyldifluorosilane [11]. Distillation gave 11.5 g (50% yield) of Ic, b.p. 110°C/30 mmHg; IR (cm^{-1}): 2915s, 2849s, 1587m, 1468m, 1387w, 1381w, 1364w, 1222s, 1054s, 972m, 840s, 728m; PMR: δ (ppm) 4.60 (AB pattern, 6 Hz, $=CH_2$), 3.74 (q, 7 Hz, OCH_2), 1.30 (t, 7 Hz, $OCH_2C\underline{H}_3$), and 1.06 (d, 1 Hz, $(CH_3)_3C$). (Found: C, 62.14; H, 10.89. $C_{12}H_{25}FOSi$ calcd.: C, 62.01; H, 10.84%).

2-Ethoxy-3-t-butyl-4,4-dimethyl-3-sila-1-pentene (Id)

A solution of 4.6 g (0.02 mol) of Ic and 1.1 g (0.03 mol) of $LiAlH_4$ in 50 ml of ether was stirred for 18 h at 25°C. Ether was removed under vacuum, the product diluted with pentane, filtered and distilled to give 4.2 g (100% yield by GLC) of Id; IR (cm^{-1}): 2933s, 2865s, 2114s (Si—H), 1587m, 1468s, 1381w, 1364w, 1217s, 1060s, 1015w, 973m, 942w, 824s, 806s; PMR: δ (ppm) 4.49 (AB pattern, 9 Hz, $=CH_2$), 3.72 (q, 7 Hz, OCH_2), 3.46 (s, SiH), 1.29 (t, 7 Hz, $OCH_2C\underline{H}_3$), and 1.06 (s, $(CH_3)_3C$). (Found: C, 67.01; H, 12.08. $C_{12}H_{26}OSi$ calcd.: C, 67.21; H, 12.22%).

Acetyldi-t-butylfluorosilane (IIc)

Compound Ic (2.3 g, 0.01 mol) was dissolved in 25 ml of THF and 1.5 ml of 6 *N* HCl was added. The homogeneous solution was stirred for 15 min, at which time GLC analysis of an aliquot showed complete hydrolysis. Evaporation of all volatile materials left 1.6 g (78% yield by GLC) of IIc; IR (cm^{-1}): 2933s, 2857s, 1650s (C=O), 1472s, 1410w, 1395w, 1368m, 1342m, 1147m, 1015w, 1008w, 953w, 939w, 844s, 827s, 814m; PMR: δ (ppm) 2.28 (d, 1 Hz, $COCH_3$) and 1.03 (d, 1 Hz, $(CH_3)_3C$). (Found: C, 58.78; H, 10.41. $C_{10}H_{21}FOSi$ calcd.: C, 58.77; H, 10.36%).

Acetyldi-t-butylsilane (IId)

The above procedure was repeated using 2.1 g (0.01 mol) of Id, 1.8 ml of 6 *N* HCl, and 30 ml of THF. Hydrolysis was complete within 20 min to give 1.5 g (81% yield by GLC) of IId; IR (cm^{-1}): 2994s, 2857s, 2110s (Si—H), 1645s (C=O), 1479s, 1389w, 1366m, 1348m, 1135m, 1015m, 940w, 824s, 807s, 763s; PMR: δ (ppm) 3.75 (s, SiH), 2.26 (s, $COCH_3$), and 1.03 (s, $(CH_3)_3C$). (Found: C, 64.53; H, 11.90. $C_{10}H_{22}OSi$ calcd.: C, 64.44; H, 11.90%).

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