

Reaction of dihydrosilanes with ethyl diazoacetate: synthesis of 3,3-disubstituted 3-silaglutarates

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Abstract

Although polyhydrosilanes themselves react in the presence of rhodium(II) acetate dimer hydrate, it is possible to synthesize 3-silaglutarates by addition at 20°C of ethyl diazoacetate to a mixture of this catalyst and a dihydrosilane in methylene chloride. The yields of the silaglutarates are addition time dependent with an optimum value. This type of insertion of a carbenoid into an Si–H bond was also used to prepare a silatriester from a trihydrosilane.

Keywords: Si; 3-Silaglutarates; Ethyl diazoacetate; Synthesis; Rhodium catalysis; Silicon hydrides

1. Introduction

Recently, the preparation of 3-silaglutarates by reaction of dichlorosilanes with the lithium enolates of alkyl acetates in THF at –94°C was described [1]. When an aryl substituent was not linked to the silicon atom, HMPA was used as co-solvent to decrease the amount of alkylsilylketene acetals resulting from a competitive O-silylation.

Another approach to 3-silaglutarates was attempted by insertion of carbenes or carbenoid species into Si–H bonds of dihydrosilanes, to avoid the use of low temperature and the carcinogenic HMPA.

The insertion of carbenes or carbenoids into an Si–H bond seems to be a common reaction [2]. Various types of methylenic derivative have been trapped with hydrosilanes [2–17], and this reaction appears frequently in the literature as a tool to prove the existence of carbenic species.

This reaction with dihydro- and trihydrosilanes generally gave compounds resulting from monoinsertion, but the silanes were frequently used in large excess with regard to the carbenic species [3a,4d,6a,8b,10a,14b,14c]. When the ratio of the carbenic precursor to the silane was appropriate, compounds resulting from di- or triin-

sertion of CH₂ [3b], CCl₂ [4a], CF₂ [6b] and CHBr [6,11] have been isolated. The preparation of alkyl α-silylacetate by reaction of alkyl diazoacetate with hydrosilanes in the presence of copper powder [10a,18] or under irradiation [10a] was also reported. These reactions were interpreted by the insertion of the true carbene CHCO₂R into the Si–H bond, the copper powder probably catalyses only the extrusion of nitrogen from the diazoacetate [18b]. With the monophenyl- [10a], diphenyl- [10a] and methylphenylsilane [18b] in excess, the α-(hydrosilyl)acetates (RR'SiH–CH₂CO₂R'') resulting from a monoinsertion were isolated. Cuprous chloride was also used to catalyse such a reaction [19] and more recently it was shown [20] that rhodium(II) acetate allowed these insertions at room temperature with very good yields using a ratio of silane to diazoester close to the stoichiometry. With the rhodium acetate the reaction probably occurred via a metal carbene complex [21], which also reacts with chloromonohydrosilanes to give α-(chlorosilyl)acetates [22]. In these reactions, no products resulting from the known insertion of carbenes or diazoalkanes into the Si–Cl bond were noticed.

2. Results and discussion

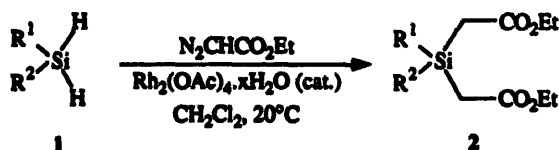
Slow addition at room temperature of a slight excess of ethyl diazoacetate (2.5 molar equivalents) to a solu-

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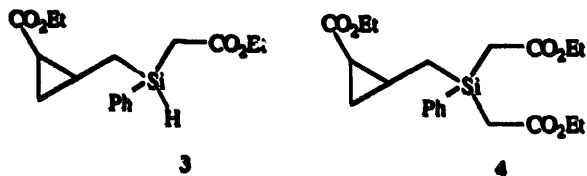
Table 1
Yield of diethyl 3-silagutarate **2** isolated from the rhodium-catalyzed reaction of dihydrosilane $[R^1R^2SiH_2]$ **1** with ethyl diazoacetate

	R ¹	R ²	Reaction addition time (h)	Yield (%)
a	Phenyl	Methyl	2	64
b	Phenyl	tert-Butyl	3	64
c	Phenyl	Allyl	6	24
d	Phenyl	Vinyl	3	55
e	Methyl	Octyl	6	64
f	Methyl	2-(4-Methylphenyl)ethyl	2	62

tion of dihydrosilane (**1**) in CH_2Cl_2 containing a catalytic amount of rhodium(II) acetate dimer hydrate [23] gave mainly 3-silagutarate (**2**)

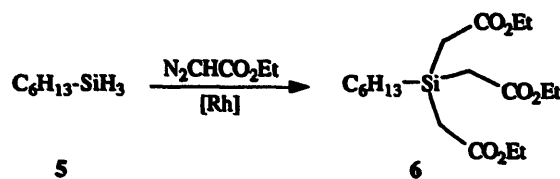


The yields were optimized by varying the addition reaction time from 2 to 6 h. The best yields of isolated pure silagutarates **2** are collected in Table 1. Except for the case of the allylphenylsilane **1c** the yields were generally satisfactory (the average yield of each insertion being between 74 and 80%). The reaction has been run with the dialkylsilanes **1e** and **1f** and with various phenylsilanes, **1a–d**. Interestingly, the yield of the silagutarate **2b** was not affected by the presence of the bulky tertibutyl substituent on the silicon atom. From the vinylsilane **1d** no cyclopropanecarboxylate was detected as expected from the low reaction rate of carbenic species additions to such a $C=C$ double bond compared with the rate of $Si-H$ bond insertion [24]. The reaction rate of addition of carbenic species to the $C=C$ double bond of allylsilanes was generally similar to that of $Si-H$ bond insertion [24] and, in the case of allylsilane **1c**, cyclopropanated compounds **3** (15%) and **4** (4%) were formed in competition to the expected silagutarate **2c**.



Moreover, it has been possible to synthesize the triester **6** with 56% yield by treatment of the hexyltrihydrosilane **5** with 3.6 molar equivalents of ethyl diazoac-

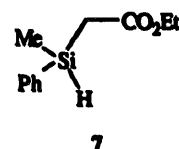
etate in the presence of rhodium acetate [25].



As reported [20] the slow addition of ethyl diazoacetate to the reaction mixture containing a dihydrosilane minimized the carbene dimer formation (ethyl fumarate and maleate were always detected and isolated after the end of the reaction), and the yield of the silagutarate was generally improved when the reaction time was increased. For example, with the methylphenylsilane **1a**, the silagutarate yield was increased from 50 to 66% by increasing the addition time from 1 to 2 h. When the addition time was further increased to 6 h, the yield of the silagutarate **2a** (64%) was similar to the best yield previously obtained, but a significantly lower yield (51%) was obtained when the addition was run over 9 h.

In a separate experiment the dihydrosilane **1a** was mixed with the rhodium acetate catalyst in CH_2Cl_2 at room temperature and a slow gas evolution was noticed (probably hydrogen). After 6 h a 1H NMR spectrum of the reaction mixture showed the quasi-complete consumption of the starting material (a decrease of the signal at 4.35 ppm being attributed to the protons of **1a** linked to the silicon atom) and the formation of unidentified products (various singlets in the 0 to 0.5 ppm region were noticed). In fact, the best yield of a silagutarate results from a compromise between the insertion of the carbenoid into the $Si-H$ bond, the formation of the carbenic dimers and the destruction of the starting material.

The methylphenylsilane **1a** was completely recovered after 14 h in the presence of copper powder, but no conditions were found with this catalyst to prepare the silagutarate **2a** with good yield and generally the ethyl α -(methylphenylsilyl)acetate **7** was, as reported [18b], the major or exclusive product resulting from an $Si-H$ bond insertion of ethyl diazoacetate. With the cuprous triflate (Cu^+OTf) catalyst, a rapid gas evolution occurred even at $0^\circ C$, and in the presence of ethyl diazoacetate small amounts of the silagutarate **2a** and of the α -silylated monoester **7** were formed in competition with various unidentified silanes.



Treatment of the silane **1a** with one molar equivalent of ethyl diazoacetate in the presence of rhodium acetate has shown that the rates of the first and second insertion into an Si–H bond were not sufficiently different to allow a selective synthesis of the ethyl α -(methylphenylsilyl)acetate **7**. Using a 9 h addition time, a mixture of the silaglutarate **2a** and the α -silylacetate **7** in the ratio 52/48 was obtained.

This work shows that synthesis of 3-silaglutarates is possible by reaction of a dihydrosilane with ethyl diazoacetate in the presence of rhodium(II) acetate at room temperature. This method appears to be generally more easily accomplished than the synthesis from a dichlorosilane and the lithium enolate of an alkyl acetate. Nevertheless, the two methods are complementary because carbene insertion into Si–H bonds is sometimes competitive with the formation of cyclopropanic compounds in the case of alkenylsilanes.

3. Experimental

NMR spectra were recorded on Bruker AM 200 or AM 250 spectrometers. Mass spectra were generally determined at an ionizing voltage of 70 eV. Column chromatography was performed with silica gel (70–230 mesh). TLC was performed on 0.25 mm silica gel (Merck 60 F₂₅₄). Dry solvents were obtained as follows: dichloromethane was distilled over P₂O₅, diethylether was distilled over LiAlH₄, tert-Butylphenylsilane **1b**, phenylvinylsilane **1d** and methyl(*p*-methylphenethyl)silane **1f** were prepared by reduction of the corresponding dichlorosilanes using LiAlH₄ in diethyl ether [26]. Ethyl diazoacetate was purchased from Fluka and Rh₂(OAc)₄ from ACROS Janssen. The dihydrosilanes **1a**, **1c**, and **1e**, the hexylsilane **5**, the tert-butyl-dichlorophenylsilane, the dichlorophenylvinylsilane and the dichloromethyl(*p*-methylphenethyl)silane were purchased from Hüls America Inc. and were distilled before use.

3.1. General procedure for the alkylation of dihydrosilanes with ethyl diazoacetate

To a suspension of Rh₂(OAc)₄ · xH₂O (7 mg, 0.015 mmol) in a mixture of dihydrosilane (2 mmol) and CH₂Cl₂ (2 ml) was added slowly under argon atmosphere at room temperature a solution of ethyl diazoacetate (570 mg, 552 μ l, 5 mmol) in CH₂Cl₂ (1.5 ml) using a syringe pump (see Table 1 for the addition time). At the end of the addition, the reaction mixture was filtered through a pad of Florisil®, the solvent was evaporated under reduced pressure and the product was purified by silica gel column chromatography (pentane/diethyl ether: 80/20).

3.1.1. Diethyl 3-methyl-3-phenyl-3-silaglutarate (**2a**)

Analytical and spectroscopic properties were as reported in Ref. [1].

3.1.2. Diethyl 3-(1,1-dimethylethyl)-3-phenyl-3-silaglutarate (**2b**)

$R_f = 0.5$ (pentane/Et₂O: 4/1). IR (neat) (cm⁻¹): 3080; 2960; 1730 ($\nu_{C=O}$); 1470; 1440; 1260 (δ_{Si-C}); 1160; 1120; 1040; 870; 830; 810. ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.70–7.55 (m, 2H); 7.42–7.30 (m, 3H); 4.05 (q, $J = 7$ Hz, 4H); 2.39 (s, 4H); 1.15 (t, $J = 7$ Hz, 6H); 0.97 (s, 9H). ¹³C NMR (CDCl₃, 50.3 MHz) δ (ppm): 172.03 (C=O); 134.75; 131.74; 129.61; 127.42; 60.07 (CH₂–O–C=O); 26.24 (C(CH₃)₃); 20.28 (Si–CH₂–C=O); 18.88 (C(CH₃)₃); 13.88 (CH₂–CH₃). MS ($M = 336$) m/z (%): 279(0.22, M⁺ – 57); 249(11, M⁺ – 87); 237(38); 196(17); 195(100); 139(11); 103(8). Anal. Found: C, 64.32; H, 8.45%. C₁₈H₂₈O₄Si Calc.: C, 64.28; H, 8.33%.

3.1.3. Diethyl 3-phenyl-3-(2-propenyl)-3-silaglutarate (**2c**)

Analytical and spectroscopic properties were as reported in Ref. [1].

After elution of the silaglutarate **2c** two fractions were isolated. The first one contained mainly a 50/50 mixture of silaglutarate **2c** and **3**. The ¹H NMR spectrum exhibits characteristic cyclopropanic multiplets at 0.98–0.85 ppm and 0.80–0.66 ppm and a multiplet at 4.55 ppm attributed to the proton linked to the silicon atom. The IR spectrum shows the characteristic Si–H bond absorption at 2150 cm⁻¹ and one product detected by GC-MS analysis gave a mass spectrum with the base peak at $m/z = 151$ and with three peaks at $m/z = 291$ (12%), 233 (12%) and 193 (74%) which can be attributed to fragments of **3** ($M = 320$) obtained respectively by cleavage of C₂H₅ (M⁺ – 29), CH₂–CO₂Et (M⁺ – 87) and CH₂–C₃H₄–CO₂Et (M⁺ – 127).

The second fraction contained mainly a 2/1 mixture of *cis* and *trans* isomers **4** [27] (the stereochemistry of these isomers was not attributed). IR (neat) (cm⁻¹): 1730 ($\nu_{C=O}$). ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.62–7.48 (m, 2H); 7.46–7.30 (m, 3H); 4.17–3.95 (various quadruplets, $J = 7$ Hz, 6H); 2.35 (s) and 2.34 (s) (4H); 1.71–1.62 (m, 0.33H, minor isomer); 1.45–1.07 (m and various triplets, $J = 7$ Hz, 12.66H); 1.06–0.83 (m, 1.33H); 0.82–0.71 (m, 0.66H, major isomer). MS (CI, NH₃) ($M = 406$) m/z (%): 424(6, M⁺ + 18); 407(29, M⁺ + 1); 406(6, M⁺); 321(8); 320(100).

3.1.4. Diethyl 3-phenyl-3-vinyl-3-silaglutarate (**2d**)

$R_f = 0.60$ (pentane/Et₂O: 4/1). IR (neat) (cm⁻¹): 3060; 2990; 1730 ($\nu_{C=O}$); 1440; 1410; 1250 (δ_{Si-C}); 1160; 1100; 1060; 840; 810. ¹H NMR (CDCl₃, 200 MHz) δ (ppm): 7.70–7.50 (m, 2H); 7.48–7.30 (m, 3H);

6.38–6.20 (m, 2H); 6.15–5.85 (m, 1H); 4.04 (q, $J = 7$ Hz, 4H); 2.38 (s, 4H); 1.13 (t, $J = 7$ Hz, 6H). ^{13}C NMR (CDCl_3 , 50.3 MHz) δ (ppm): 171.33 (C=O); 136.7; 134.3 (vinyl); 133.93; 131.90; 130.05; 127.81; 60.13 ($\text{CH}_2\text{-O-C=O}$); 23.12 (Si- $\text{CH}_2\text{-C=O}$); 14.01 ($\text{CH}_2\text{-CH}_3$). MS ($M = 306$) m/z (%): 279(4, $M^+ - 27$); 219(72, $M^+ - 77$); 177(100); 149(27); 145(46); 133(47); 123(56); 105(37); 91(16); 45(57). Anal. Found: C, 62.87; H, 7.33%. $\text{C}_{16}\text{H}_{22}\text{O}_4\text{Si}$ Calc.: C, 62.74; H, 7.19%.

3.1.5. Diethyl 3-methyl-3-octyl-3-silaglutarate (2e)

Analytical and spectroscopic properties were as reported in Ref. [1].

3.1.6. Diethyl 3-methyl-3-[2-(4-methylphenyl)ethyl]-3-silaglutarate (2f)

Analytical and spectroscopic properties were as reported in Ref. [1].

3.2. Preparation of diethyl 3-ethoxycarbonylmethyl-3-hexyl-3-silaglutarate (6)

Hexylsilane **5** (232 mg, 2 mmol) was treated with ethyl diazoacetate (820 mg, 7.2 mmol) in the presence of $\text{Rh}_2(\text{OAc})_4 \cdot x\text{H}_2\text{O}$ (7 mg, 0.015 mmol) using the same conditions as above (6 h addition time) and the triester **6** (411 mg, yield 56%) was isolated and purified by two bulb-to-bulb distillations (240°C/0.1 mmHg).

IR (neat) (cm^{-1}): 3000; 2950; 1735 ($\nu_{\text{C=O}}$); 1470; 1410; 1260 ($\delta_{\text{Si-C}}$); 1155; 1100; 1060; 875; 815. ^1H NMR (CDCl_3 , 200 MHz) δ (ppm): 4.10 (q, $J = 7$ Hz, 6H); 2.10 (s, 6H); 1.48–1.08 (m, 17H); 0.98–0.71 (m, 5H). ^{13}C NMR ($\text{CDCl}_3/\text{C}_6\text{D}_6$; 1/1, 50.3 MHz) δ (ppm): 171.48 (C=O); 60.53 ($\text{CH}_2\text{-O-C-C=O}$); 33.32; 31.62; 22.95; 22.78; 22.68 (Si- $\text{CH}_2\text{-C=O}$); 14.42 ($\text{OCH}_2\text{-CH}_3$); 14.26 ($\text{CH}_2\text{-CH}_2\text{-CH}_3$); 12.93 (Si- $\text{CH}_2\text{-CH}_2$). MS ($M = 374$) m/z (%): 287(1.33, $M^+ - 87$); 205(100); 203(28, $M^+ - 99$); 163(29); 119(17); 103(6). Anal. Found: C, 57.50; H, 9.22%. $\text{C}_{18}\text{H}_{34}\text{O}_6\text{Si}$ Calc.: C, 57.75; H, 9.09%.

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