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THE REACTION OF ORGANOSILICON HYDRIDES WITH CARBOMETHOXYCARBENE GENERATED FROM METHYL DIAZOACETATE

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Summary

The reaction of various organosilicon hydrides including hydropolysilanes with methyl diazoacetate in the presence of copper catalyst gave α-silyl- and polysilyl- esters in 44 - 90% yields. The relative reactivities of a series of *m*- and *p*-substituted phenyldimethylsilanes towards the active species generated from the diazoacetate correlate well with the Hammett σ constants for the ring substituents, with a ρ value of -0.26 and a correlation coefficient of 0.984. Based on the consideration of the observed ρ value, it is concluded that the reaction involves the insertion of the free carbomethoxycarbene into the silicon—hydrogen bond via an only slightly ionic transition state.

Introduction

The insertion of carbene species into the Si—H bond was first reported by Kramer and Wright who studied the reaction of diazoalkanes with organosilicon hydrides [1]. Several years later, Seyferth et al. measured the relative rate constants for reactions of aryldimethylsilanes with dihalomethylenes obtained from phenyl(trihalomethyl)mercury compounds [2]. More recently we have shown that the photolysis of benzoyltrimethylsilane in various hydrosilanes give compounds of the type $R_3SiCH(Ph)OSiMe_3$ rather than $PhCH(SiMe_3)OSiR_3$; these products were accounted for by the insertion reaction of siloxycarbene species (derived by photoisomerization of the acylsilane) into the silicon—hydrogen bond [3, 4]. Since these insertion reactions proceed readily to give workable yields of product, we have undertaken a detailed investigation of the features of the insertion reactions into the Si—H bond using a variety of carbene precursors.

The present study concerns the reaction of various hydrosilanes with carbomethoxycarbene generated from methyl diazoacetate, yielding α-silyl esters.

Various methods have been devised for the synthesis of α-silylesters, the subject of recent attention [5 - 11]. For example, Rijkens et al. [11] have reported the preparation of ethyl trimethylsilylacetate by the same type of reaction as that of our present study.

Results and discussion

Decomposition of methyl diazoacetate (II) in various organosilicon hydrides (I) in the presence of copper powder as catalyst was effected very readily to give α-silyl esters (III) in moderate to excellent yields. All the products thus obtained were characterized on the basis of their analyses and spectra. The reaction conditions and product yields are summarized in Table 1.

$$\underset{\text{(I)}}{R^1R^2R^3Si{-}H} + \underset{\text{(II)}}{N_2CHCO_2Me} \xrightarrow{Cu} \underset{\text{(III)}}{R^1R^2R^3SiCH_2CO_2Me}$$

(a) $R^1 = R^2 = R^3 = Et$
(b) $R^1 = H, R^2 = Me, R^3 = Ph$
(c) $R^1 = R^2 = Me_3Si, R^3 = Me$
(d) $R^1 = R^2 = R^3 = Me_3Si$
(e) $R^1 = R^2 = Me, R^3 = Ph$
(f) $R^1 = R^2 = Me, R^3 = p\text{-}MeOC_6H_4$
(g) $R^1 = R^2 = Me, R^3 = p\text{-}MeC_6H_4$
(h) $R^1 = R^2 = Me, R^3 = p\text{-}ClC_6H_4$
(i) $R^1 = R^2 = Me, R^3 = m\text{-}ClC_6H_4$

Reaction of dihydrosilanes gave the corresponding α-silyl mono-esters but not diesters: e.g., phenylmethylsilane (Ib) gave methyl phenylmethylsilylacetate (IIIb, 74%). Hydropolysilanes such as *sym*-heptamethyltrisilane and tris(trimethylsilyl)silane were found to behave normally, giving methyl α-polysilylacetates in reasonable yields. This reaction thus provides an excellent method of preparing α-polysilylacetates.

In the reactions of substituted phenyldimethylsilanes, the respective product yields were not determined, but they are presumed to be around 90% based on the yield of the reaction of phenyldimethylsilane itself and the relative rate data for the aryldimethylsilanes (see below and Table 2).

Study by competition experiments of the relative reactivity of substituted phenyldimethylsilanes towards methyl diazoacetate was also carried out. Phenyldimethylsilanes, $XC_6H_4SiMe_2H$, where X = H, *p*-MeO, *p*-Me, *p*-Cl, and *m*-Cl, were

TABLE 1

THE REACTION OF HYDROSILANES WITH METHYL DIAZOACETATE IN THE PRESENCE OF COPPER

Reactants Hydrosilane	(mmol)	II(mmol)	Cu (mg)	Temp. (°C)	Time (min)	Product	Yield (%)[a], [b]
Ia	15.01	5.20	18	89	8	IIIa	57
Ib	26.88	11.12	35	94	6	IIIb	74
Ic	8.31	4.17	35	91	8	IIIc	63
Id	6.01	2.56	35	94	4	IIId	44
Ie	15.13	5.29	18	90	7	IIIe	90

[a] Based on methyl diazoacetate. [b] GLPC yield: thermal conductivity correction with an internal standard was made.

TABLE 2

RELATIVE RATE CONSTANTS FOR THE REACTION OF SUBSTITUTED PHENYLDIMETHYLSILANES ($XC_6H_4SiMe_2H$)

X	σ	k_a/k_b
p-MeO	−0.268	1.25
p-Me	−0.170	1.14
H	0.00	1.00
p-Cl	0.227	0.89
m-Cl	0.373	0.85

prepared and allowed to compete for a deficiency of the diazoacetate. A stirred and heated mixture of two aryldimethylsilanes and methyl diazoacetate in ca. 5/5/1 molar ratio was allowed to react. The relative rates of reaction were calculated using the Doering equation [12] where P_a and P_b represent the product concentrations derived from different hydrosilanes (a and b), S_a and S_b the initial concentrations of the two hydrosilanes and k_a/k_b the ratio of rate constants for attack by the active species derived from the diazoacetate (eqn. 1).

$$k_{rel} = k_a/k_b = (P_a/S_a)/(P_b/S_b) \quad (1)$$

The relative rate constants for the reactions of various substituted phenyldimethylsilanes with methyl diazoacetate are listed in Table 2, based on k_{PhSiMe_2H} as unity. Table 2 shows clearly that an electron-donating substituent increases the relative rate constant of the insertion reaction, but with this range of substituents the rate constants differ only by a factor of 1.5. In Fig. 1, log k_{rel} values are plotted against the Hammett σ values for the ring substituents, resulting in a satisfactory correlation. The slope of the line was found to be — 0.26, by the method of least squares, with a correlation coefficient of 0.984. The sign of ρ indicates that electrophilic attack by carbomethoxycarbene on the Si—H bond is involved; the value of ρ is very small and suggests that charge separation in the transition state of the reaction is very small.

Values of ρ previously obtained for reactions of aryldimethylsilanes with various carbene reagents may be profitably compared with these values and are

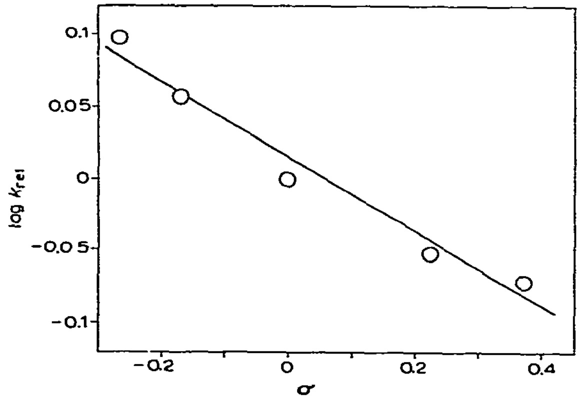


Fig. 1. Plot of log k_{rel} against σ.

TABLE 3

COMPARISON OF ρ VALUES FOR THE INSERTION REACTIONS OF CXY INTO THE Si—H BOND OF SUBSTITUTED PHENYLDIMETHYLSILANES

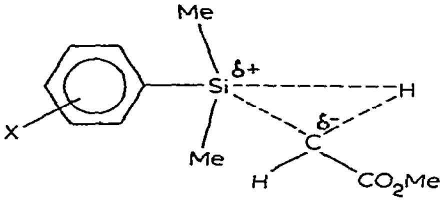
Precursor	Solvent	Temp (°C)	ρ	$\Sigma\sigma^{*a}$	ref.
N_2CHCO_2Me	none	90	−0.26	2.49	this work
$PhHgCCl_2Br$	PhH	79	−0.63	5.88	2
$Hg(CH_2Br)$	PhH	80	−1.31	0.98	13
$XZnCH_2I$	Et_2O	24	−1.11	0.98	14

^{a}Sum of Taft σ^* for X and Y in CXY

listed in Table 3. Also included are the sum of the Taft σ^* values for X and Y in CXY, where CXY represents the bivalent species to be inserted formally into the Si—H bond. This value reflects the polar character (i.e., electrophilicity) of the free CXY species and serves as a convenient tool for the elucidation of the reaction mechanism.

The observed ρ value for the $ArMe_2SiH—N_2CHCOOMe$ reactions in the presence of copper is approximately 0.4 times as large as that found for the $ArMe_2SiH—PhHgCCl_2Br$ reactions [2]. This trend is reasonable since CHCOOMe is likely to be less electrophilic than CCl_2, as is implied by the $\Sigma\sigma^*$ values shown in the fifth column of Table 3 where $\Sigma\sigma^* = 2.49$ for CHCOOMe and 5.88 for CCl_2. (The more positive the $\Sigma\sigma^*$ value, the more electrophilic is the bivalent carbon species.) Interestingly, the ratio of the ρ values for the above two reactions was found to be nearly identical with the ratio of the $\Sigma\sigma^*$ values for CXY. According to this criterion, it is expected that the ρ values for the reactions of $Hg(CH_2Br)_2$ [13] and $Zn(C_2H_5)_2—CH_2I_2$ [14] with aryldimethylsilanes should be smaller than those for the $ArMe_2SiH—PhHgCCl_2Br$ and $ArMe_2SiH—N_2CHCOOMe$ reactions, if such reagents as $Hg(CH_2Br)_2$ and $Zn(C_2H_5)_2—CH_2I_2$ act to generate free CH_2 species inserting into the Si—H bond. This view may be advanced from the consideration that the $\Sigma\sigma^*$ value for CH_2 is much smaller (0.98). However, the facts contradict this prediction: i.e., the ρ values for the former two reactions are much larger (−1.31 and −1.11), in an absolute sense, than those for the latter two reactions, and the trend of the ρ values indicates that the $Hg(CH_2Br)_2$ and $Zn(C_2H_5)_2—CH_2I_2$ reactions involve species which are more electrophilic than those involved in the diazoacetate and $PhHgCCl_2Br$ reactions. An explanation for this trend can be advanced by taking into account the differences in the attacking species involved. Thus, comparing of ρ values for the $Hg(CH_2Br)_2$ and $Zn(C_2H_5)_2$ $—CH_2I_2$ reactions with those for the $PhHgCCl_2Br$ and N_2 CHCOOMe reactions suggests to us that a carbenoid mechanism, not a free carbene mechanism, was operative in reactions of the former types.

From the results of the Hammett treatment [15] of the present reaction between a hydrosilane and the diazoacetate, it seemed likely that electrophilic attack of the free carbene CHCOOMe (derived from diazoacetate) on the Si—H bond was occurring to form the insertion products. The copper powder is perhaps serving simply as a catalyst which accelerates decomposition of the diazoacetate [16]. The proposed mechanism, wherein the generation of the free carbene from methyl diazoacetate under the conditions used is postulated, is consistent with the fact that dimethyl fumarate was detected in some cases. Seyferth et al. [2] suggested three possible mechanisms for the dichlorocarbene insertion reaction into the Si—H bond: (a) insertion of CCl_2 into the Si—H bond via a three-centered transition state; (b) hydride abstraction by CCl_2, followed by collapse of the resulting tight ion pair to give the product; (c) radical abstraction of a hydrogen atom followed by a rapid radical coupling step within the solvent cage. They pointed out that differences between the three mechanisms are rather slight if tight binding of the ion pair and radical pair is assumed, and they preferred the three-centered transition state because of its simplicity. Similarly, in the present reaction, insertion of the carbene species generated from diazoacetate into the Si—H bond via a very slightly polar transition state (IV) is likely and at the present time no evidence against it seems to be available.



(IV)

Experimental

All the reactions were carried out under an atmosphere of dry nitrogen. IR spectra were recorded with neat liquid films using a Hitachi EPI-G3 spectrometer, and NMR spectra of CCl_4 solutions were measured using a Varian A-60D spectrometer. MS spectra were obtained with a Hitachi RMU-6L spectrometer. GLC analyses were made using Ohkura Model 802 and 1700 Gas chromatographs.

Materials

Methyl diazoacetate (b.p. 59.5 - 61°, n_D^{25} 1.4863) was prepared from methyl glycinate hydrochloride by the method described in the literature [17]. Triethylsilane, phenylmethylsilane, and substituted phenyldimethylsilanes were made as described previously [3, 4]. 1,1,1,2,3,3,3-Heptamethyltrisilane was made by the reduction of the corresponding chlorosilane, which was obtained by the method of Kumada and co-workers [18]. Tris(trimethylsilyl)silane was prepared from tetrakis(trimethylsilyl)silane [19a] by metalation with methyllithium followed by acid hydrolysis [19b]. Physical constants and GLC analyses confirmed the purity of the materials.

Preparation of methyl α-silylacetates

These compounds were prepared by the $R^1R^2R^3SiH—N_2CHCOOMe$ reactions and the method for methyl phenyldimethylsilylacetate is representative. Phenyldimethylsilane (2.062 g, 15.13 mmol), methyl diazoacetate (0.530 g, 5.29 mmol), and commercial copper powder (15 - 20 mg) were placed in a dry, small round-bottomed flask fitted with a reflux condenser which was flushed with dry nitrogen. The mixture was immersed in an oil bath maintained at 90°. After stirring (magnetic stirrer) for a few minutes vigorous gas evolution occurred. The flask was intermittently removed from the bath in order to maintain a gentle reaction

TABLE 4

PHYSICAL PROPERTIES OF METHYL α-SILYLACETATES

Compound	n_D^{20}	Analysis found (calcd.) (%)		Mol. wt.[a]
		C	H	Found(calcd.)
IIIa	1.4407	57.67 (57.39)	10.88 (10.70)	
IIIb	1.5087	61.61 (61.81)	7.45 (7.26)	
IIIc	1.4769	46.02 (45.74)	9.57 (9.98)	
IIId		44.67 (44.94)	9.84 (10.06)	
IIIe	1.5032	63.17 (63.42)	7.49 (7.74)	
IIIf	1.5128	60.46 (60.47)	7.60 (7.61)	238 (238.4)
IIIg	1.5029	64.51 (64.82)	8.18 (8.16)	222 (222.5)
IIIh	1.5164	54.30 (54.42)	6.30 (6.23)	242 (242.8)
IIIi	1.5154	54.38 (54.42)	6.26 (6.23)	242 (242.8)

[a] By mass spectrometry.

TABLE 5

NMR CHEMICAL SHIFTS OF METHYL α-SILYLACETATES[a]

Compound	ArH	OCH_3^b	SiH	$SiCH_3$	CH_2^c	SiC_2H_5
IIIa		3.53(s)			1.78(s)	0.74(m, 15H)
IIIb	7.42(m, 5H)	3.53(s)	4.50(q, 1H)	0.45(d, 3H)	2.09(d)	
IIIc		3.62(s)		0.22(s) 0.11(s) } (21 H)	1.92(s)	
IIId		3.64(s)		0.23(s, 27H)	1.95(s)	
IIIe	7.38(m, 5H)	3.50(s)		0.35(s)[d]	2.01(s)	
IIIf	7.09(q, 4H)	3.51(s) 3.77(s)[e]		0.33(s)[d]	1.99(s)	
IIIg	7.22(q, 4H)	3.51(s) 2.33(s)[f]		0.34(s)[d]	1.99(s)	
IIIh	7.36(q, 4H)	3.52(s)		0.36(s)[d]	2.05(s)	
IIIi	7.33(m, 4H)	3.56(s)		0.38(s)[d]	2.03(s)	

[a] Values (δ, ppm) are reported downfield from TMS (s singlet, t triplet, q quartet, m multiplet) in CCl_4 solution. [b] 3H. [c] 2H. [d] 6H. [e] Benzene ring methoxy protons. [f] Benzene ring methyl protons.

TABLE 6

CHARACTERISTIC INFRARED ABSORPTION PEAKS OF α-SILYLACETATES^a

Compound	ν(C=O)	ν(Si—H)	(Si—Me)	(Si—Ph)
IIIa	1735 1725		1255	
IIIb	1755 1740	2130	1253	1430 1125
IIIc	1725		1250 840	
IIId	1727		1250 840	
IIIe	1728		1251 840	1440 1430 1120
IIIf	1724		1244 835 817	1430
IIIg	1730		1250 840 800	1435
IIIh	1720		1245 830 800	1427
IIIi	1726		1250 830	1430

^{a}cm^{-1}; neat liquid film (sandwich method).

and again heated for several minutes; to complete the reaction 4 - 15 min. was required. After cooling, the resulting mixture was subjected to GLC analysis (polydiethyleneglycol succinate). The major product was isolated by preparative GLC. From the elemental analysis, IR spectrum, and the mol. wt. (from mass spectrum), this product was identified as methyl dimethylphenylsilylacetate. The yield by GLC was 90% (Based on II). Pertinent physical, spectral and analytical data for all the compound thus prepared are given in Tables 4—6.

Procedure for competitive reactions

Methyl diazoacetate was mixed with two different aryldimethylsilanes in the molar ratio 1/5/5. To this was added ca. 5 mol% (based on the amount of methyl diazoacetate used) copper powder and the resulting mixture was heated to 90° (constant temperature bath) with stirring until gas evolution ceased (14 min.). The reaction mixture was subjected to GLC analysis using a silicone column (SE-52). Corrections were made for the differing thermal conductivities of the various components by means of an internal standard. The relative rates for the two hydrosilanes were calculated from eqn. 1, and the relative reactivities are expressed by taking that for phenyldimethylsilane as the standard (Table 2).

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