Rearrangements of 2-Furfurylidenes − Synthesis of Acylsilanes and Acylstannanes

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Dedicated to Professor Henning Hopf on the occasion of his 60th birthday

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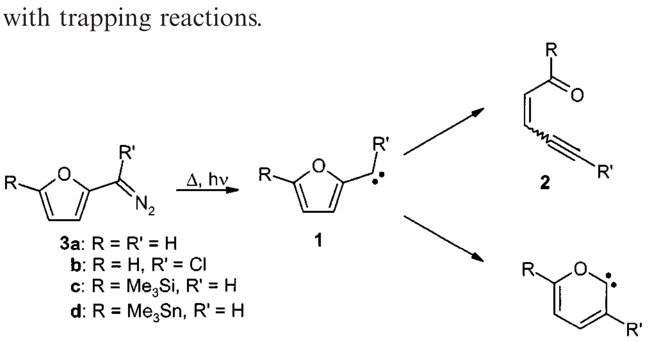
The 2-furfuryldiazomethanes **3c** and **3d**, with trimethylsilyl and trimethylstannyl groups, respectively, in the 5-position, were generated from the sodium salts of the corresponding tosylhydrazones and matrix-isolated in argon at 10 K. Photolysis of the diazo compounds **3** resulted in the formation of the highly unsaturated acylsilanes and acylstannanes **2** in clean reactions. Comparison of the experimentally obtained IR spectra with those obtained from DFT calculations revealed that compounds **2** were formed in their thermodynamically less favorable (*Z*) conformations.

Introduction

Arylcarbenes are easily generated from the corresponding diazo compounds or diazirines and have been extensively studied by trapping experiments, by matrix isolation, and by time-resolved spectroscopy.[1−7] Thus, photolysis of phenyldiazomethane in solid argon at 10 K produces phenylcarbene, which under these conditions is a completely stable compound.[8] In contrast, photolysis of matrix-isolated furfuryldiazomethanes (**3**, R′ = H) does not result in furfurylidenes **1**, but rather in rearranged products.[9,10]

The ring-opening reactions of furfurylidenes **1** were investigated by Hoffman and Shechter almost 30 years ago.[11−13] The thermal decomposition of diazo compounds **3**, generated in situ, resulted in the formation of (*E*)/(*Z*) mixtures of the acetylenic aldehydes or ketones **2** (Scheme 1). In some cases, carbenes **1** could be trapped in low yield, while α-pyranylidenes, the products of the ring expansion of **1** by a [1,2]-shift, were not observed. Obviously, the thermal ring opening of **1** can compete efficiently with trapping reactions.



Scheme 1

Photolysis of 2-furfuryldiazo compound **3a** (R = R′ = H) in argon at 10 K exclusively produced **2a**, in its (*Z*) configuration; carbene **1a** was not found.[9] Irradiation of 2-furylchlorodiazirine, on the other hand, resulted in chloro(2-furyl)carbene **1** (R = H, R′ = Cl), which, on subsequent visible irradiation, rearranged to the corresponding alkyne **2**.[14] The ring opening of furfurylidenes has been described by Herges as a "coarctate reaction", in which simultaneous bond breaking and bond formation take place at one atom.[15] This concerted process proceeds over a low activation barrier, as long as the carbene is not stabilized by substituents such as chlorine atoms. Recently, the transition states for the rearrangements of a series of 2-furfurylidenes **1** (R = H, R′ = H, SiH_3, OH, Cl, etc.) were investigated by ab initio theory.[16] In agreement with the experimental findings and Herges' qualitative theory, very low activation barriers were found with R′ = H and SiH_3, while electronegative substituents with lone pairs (OH, NH_2, halogen atoms) resulted in substantial barriers. This was rationalized by the substantial stabilizing of carbenes by the latter substituents, with the transition state much less affected.

By varying the substituents R and R′ in **3**, the highly unsaturated carbonyl compounds **2**, with substituent R at the carbonyl group and R′ at the alkyne functionality, are preparatively accessible. Since metalated acyl compounds are generally difficult to synthesize, we became interested in using the Hoffman−Shechter rearrangement for the synthesis of acylsilanes and acylstannanes. 2-(Diazomethyl)furans with silyl or stannyl groups in the 5-position are readily synthesized and thus provide a novel route to highly unsaturated metalated acyl compounds of type **2c** and **d** (Scheme 2).

Results and Discussion

1-(Trimethylsilyl)pent-2-en-4-yn-1-one (2c)

2-Diazomethyl-5-(trimethylsilyl)furan (**3c**) was synthesized by vacuum thermolysis (115 °C, 10^{-6} mbar) of the sodium salt of the corresponding tosyl hydrazone and directly trapped with a large excess of argon on top of a spec-

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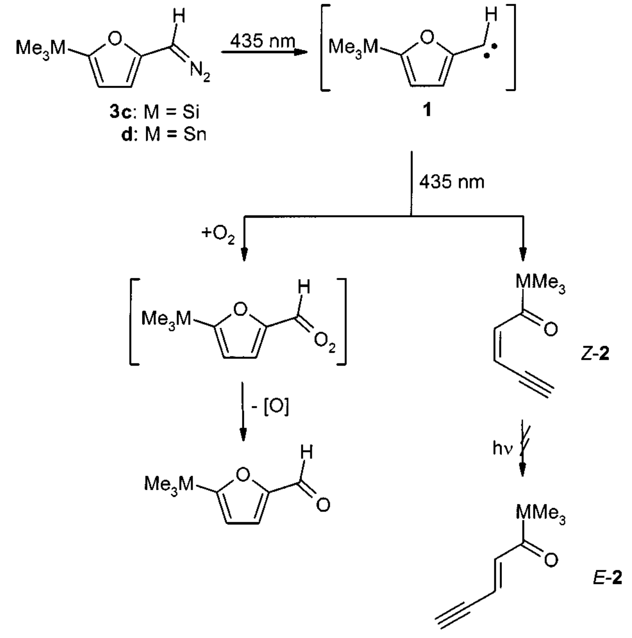

Scheme 2

troscopic window kept at 30 K. The formation of a diazo compound is easily detected by IR spectroscopy, and the most characteristic absorption in the IR spectrum of **3c** is the strong C=N=N stretching vibration at 2071 cm^{-1}. Other strong absorptions at 1252 and 840 cm^{-1} may be assigned to a CH_3 deformation and the Si−C stretching vibration, respectively. This last vibration is by far the strongest absorption in the spectrum.

As expected, **3c** is photolabile, and irradiation with visible light ($\lambda > 435$ nm, argon, 10 K) rapidly resulted in the decrease of all IR absorptions assigned to **3c** (Scheme 2, Figure 1, Table 1). The newly formed compound exhibited a sharp and strong absorption at 3329 cm^{-1}, highly characteristic of terminal acetylene groups (H−C≡ stretching vibration).[17] A strong absorption at 1639 cm^{-1} was assigned to the C=O stretching vibration of an acylsilane. The unusually low frequency is characteristic for acylsilanes; phenyl trimethylsilyl ketone, for example, exhibits a C=O stretching vibration at 1628 cm^{-1}.[18] Intense absorptions at 1252 and 839 cm^{-1} were close to the corresponding absorptions in **3c**, and indicated the presence of a trimethylsilyl group. With these characteristic vibrations, it is tempting to assign the structure of **2c** to the novel compound (Scheme 2). Comparison with **2a** showed the similarity of the IR spectra of **2a** and **c** (Table 2, Figure 2). The terminal H−C≡ stretching vibration of **2a** is found at 3327 cm^{-1}, in good agreement with that observed in **2c**. The C=O (1639 cm^{-1}) and the C=C (1555 cm^{-1}) stretching vibrations of **2c** correspond to analogous vibrations of **2a** at 1700 and 1593 cm^{-1}.

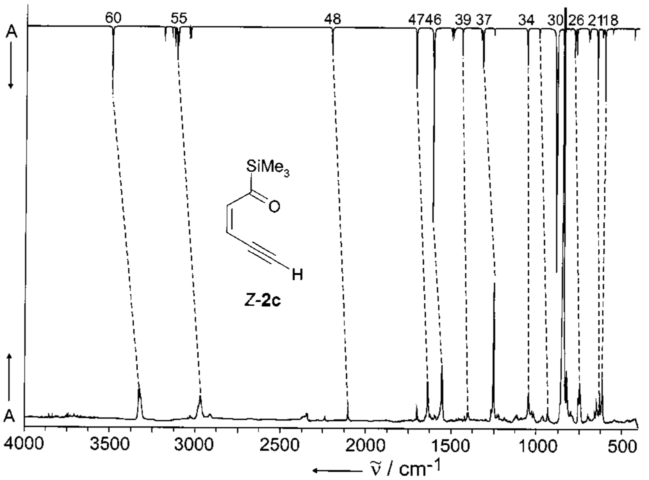

Figure 1. IR spectrum of (*Z*)-1-(trimethylsilyl)pent-2-en-4-yn-1-one [(*Z*)-**2c**]; bottom: experimental spectrum of **2c**, matrix-isolated in argon at 10 K; top: spectrum calculated at the B3LYP/6−31G(d,p) level of theory

Table 1. Experimental (argon, 10 K) and calculated [B3LYP/6−31G(d)] IR data for (*Z*)-1-(trimethylsilyl)pent-2-en-4-yn-1-one (**2c**)

B3LYP/6-31G(d)				Argon, 10 K		
No.	Sym.	ν̃ [cm^{-1}]	*I* [km/mol]	ν̃ [cm^{-1}]	I_{rel}[a]	Assignment
60	A′	3495.2	27	3329.6	4	ν(C≡)C−H
55	A′	3119.2	7	2971.8	3	νC−H
48	A′	2209.7	10	2104.5	2	νC≡C
				1700.3	2	
47	A′	1718.8	27	1639.1	5	νC=O
46	A′	1618.9	72	1555.3	8	νC=C
39	A′	1446.2	9	1407.8	1	δC−H (sym.)
37	A′	1328.0	15	1253.0	19	δ(Si)C−H (sym.)
34	A′	1058.0	12	1048.0	4	νC−C
32	A′	991.4	3	934.5	2	δC−C
29	A′	884.0	100	841.0	100	δ(Si)C−H (asym.)
26	A″	783.9	13	749.7	6	γC−H
25	A′	779.0	12	744.0	2	δ(Si)C−H
22	A″	692.2	4	649.9	2	δ(Si)C−H
21	A″	648.3	20	631.6	2	γ(C≡)C−H
18	A′	604.9	29	617.0	6	δ(C≡)C−H

[a] Relative intensities based on the strongest absorption.

Table 2. Some characteristic IR absorptions of compounds **2a**, **2c**, and **2d**, matrix-isolated in argon at 10 K

2a ν̃ [cm^{-1}]	I_{rel}[a]	**2c** ν̃ [cm^{-1}]	I_{rel}[a]	**2d** ν̃ [cm^{-1}]	I_{rel}[a]	Assignment
3327.3	19	3329.6	4	3309.9	67	ν(C≡)C−H
2109.3	3	2104.5	2	2136.6	35	νC≡C
1700.0	100	1639.1	5	1631.1	100	νC=O
1592.5	5	1555.3	8	1557.7	60	νC=C
643.6	11	631.6	2	648.5	36	γ(C≡)C−H
637.5	15	617.0	6	633.5	27	δ(C≡)C−H

[a] Relative intensities based on the strongest absorption.

This assignment was confirmed by calculations at the B3LYP/6−31G(d) level of theory, which nicely reproduced the experimental spectrum (Table 1, Figure 1). The calculations also revealed that **2c** had been formed in its (*Z*) configuration, in conformity with (*Z*)-**2a**, which is the primary photoproduct of the photolysis of **3a**.[13] However, while UV irradiation of (*Z*)-**2a** rapidly led to (*E*)/(*Z*) isomerization, (*Z*)-**2c** was remarkably stable, even towards prolonged UV irradiation. At the B3LYP/6−31G(d) level of theory, the (*E*) isomer was predicted to be more stable than

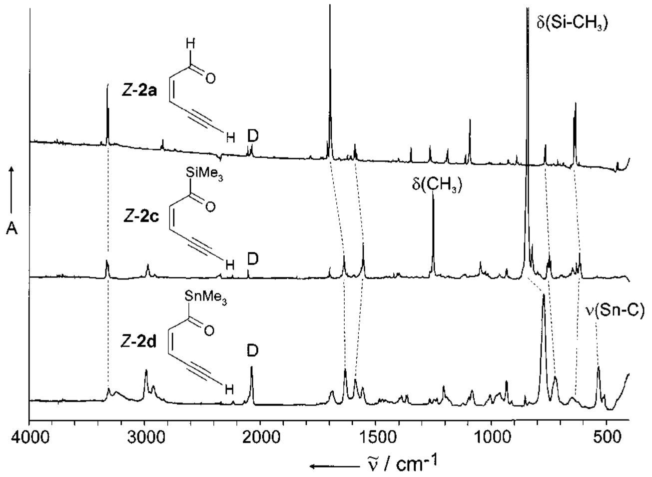

Figure 2. Comparison of the IR spectra of the matrix-isolated (argon, 10 K) alkynes (*Z*)-**2a**, (*Z*)-**2c**, and (*Z*)-**2d**

the (*Z*) isomer by 3.4 kcal/mol. Thus, the preferential formation of the less stable stereoisomer (*Z*)-**2c** clearly indicated the absence of a thermal equilibration during ring opening.

The IR spectrum of the product of the photolysis of **3c** did not show any evidence for the presence of carbene **1c**. It is plausible to assume that carbene **1c** is the precursor of **2c**; however, our experiments did not allow us, during irradiation of diazomethane **3c**, to distinguish between thermal ring opening with a very low activation barrier and a secondary photochemical reaction. During irradiation of **3c**, the carbene **1c** is initially formed in its singlet state S-**1c**, which might either rearrange to **2c** or produce the triplet ground state carbene T-**1c** by intersystem crossing. The singlet − triplet splitting ΔE_{ST} of **1c** is calculated as −2.8 kcal/mol [B3LYP/6−31G(d)].

Indirect evidence for the formation of carbene **1c** as an intermediate comes from oxygen trapping studies. If **3c** was irradiated in a 5% O_2-doped argon matrix at 10 K with $\lambda > 305$ nm, a mixture of oxidized products was formed. By comparison with the IR spectrum of independently synthesized and matrix-isolated **4c**, this aldehyde was identified as one of the products. A plausible route to **4c** is trapping of **1c** with O_2 to produce the labile carbonyl oxide **5c**, followed by loss of an oxygen atom.[19] Usually, carbonyl oxides are synthesized by the thermal reaction of carbenes with molecular oxygen (e.g., by annealing of 0.5−1% O_2-doped argon matrices at 35−40 K).[6,7,20−22] Since **1c** is short-lived even under the conditions of matrix isolation, much higher concentrations (5%) of O_2 are required to trap the carbene. At these high O_2 concentrations, the diazo precursor is in contact with O_2 molecules in the same matrix cage, and thus diffusion of O_2 is not required to give products. An alternative route to **4c** might be the direct photooxidation of **3c**, and therefore the formation of oxidation products does not necessarily indicate the formation of carbene **3c** as an intermediate.

1-(Trimethylstannyl)pent-2-en-4-yn-1-one (2d)

2-Diazomethyl-5-(trimethylstannyl)furan (**3d**) was synthesized − wholly in analogy to the synthesis of **3c** − by vacuum thermolysis (70 °C, 10^{-6} mbar) of the sodium salt of the corresponding tosyl hydrazone, with subsequent trapping of the volatile product in a large excess of argon at 30 K. The most intense absorption in the IR spectrum of diazo compound **3d** is the C=N=N stretching vibration at 2069 cm^{-1}. A strong absorption at 774 cm^{-1} can be assigned to a CH_3 deformation vibration. The symmetric and asymmetric Sn−C vibrations are found at 537 and 517 cm^{-1}, respectively.

Visible light irradiation ($\lambda > 420$ nm, argon, 10 K) of diazo compound **3d** rapidly results in the decrease of all IR absorptions of **3d** and the appearance of new and characteristic absorptions at 3310 and 1631 cm^{-1} (Table 3, Figure 3). The 3310 cm^{-1} absorption is indicative of a terminal acetylene group (C−H stretching vibration), while the 1631 cm^{-1} vibration suggests the formation of a carbonyl group. A similar low frequency C=O stretching vibration was found in acylstannanes, [23,24] and thus the newly formed compound can be assigned the structure of acylstannane **2d** (Scheme 2). Weak absorptions at 531 and 510 cm^{-1} can be attributed to Sn−C vibrations of the trimethylstannyl group.

The assignment of the experimental IR spectrum of **2d** was verified by calculations at the B3LYP/6−31G(d) level of theory, using the pseudopotential approximation for the tin atom.[25] The calculated vibrational data are in good agreement with the experimental IR spectrum and clearly show that **2d** is formed in its (*Z*) configuration (Table 3, Figure 3). As with **2c**, prolonged UV irradiation of (*Z*)-**2d** does not lead to the formation of the (*E*) isomer. Figure 2 compares the IR spectra of **2a**, **2c**, and **2d** and clearly shows

Table 3. Experimental (argon, 10 K) and calculated [B3LYP/6−31G(d)] IR data for (*Z*)-1-(trimethylstannyl)pent-2-en-4-yn-1-one (**2d**)

B3LYP/6-31G(d)			Argon, 10 K		
No.	ṽ [cm^{-1}]	*I* [km/mol]	ṽ [cm^{-1}]	I_{rel}[a]	Assignment
60	3496.4	27	3309.9	67	ν(C≡)C−H
55	3137.9	8	2985.6	71	νC−H
50	3056.6	8	2920.0	57	νC−H
48	2209.2	11	2136.6	35	νC≡C
			1687.7	55	
47	1720.3	53	1631.1	100	νC=O
46	1617.7	65	1557.7	60	νC=C
44	1502.5	1	1266.9	30	δ(Sn)C−H
39	1438.0	9	1206.1	40	δC−H (sym.)
35	1254.9	5	1082.6	35	δC−H (asym.)
34	1034.6	16	968.6	34	νC−C
32	954.3	59	934.5	69	δC−C
29	804.4	100	774.3	99	δ(Sn)C−H
26	745.0	8	723.8	46	δ(Sn)C−H
25	726.4	9	712.2	44	δ(Sn)C−H
23	650.5	17	648.5	36	γ(C≡)C−H
22	608.3	25	633.5	27	δ(C≡)C−H
18	499.8	10	531.3	66	νSn−C (asym.)
17	476.4	8	509.6	40	νSn−C (sym.)

[a] Relative intensities based on the strongest absorption.

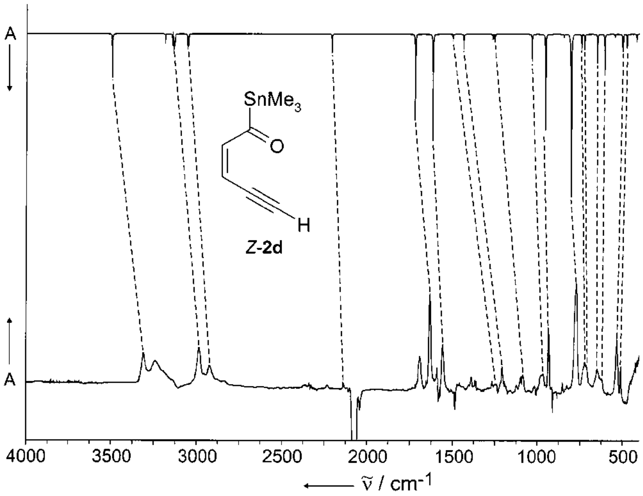

Figure 3. IR spectrum of (*Z*)-1-(trimethylstannyl)pent-2-en-4-yn-1-one [(*Z*)-**2d**]; bottom: experimental spectrum of **2d**, matrix-isolated in argon at 10 K; top: spectrum calculated at the B3LYP/6−31G(d,p) level of theory

the expected similarity of absorptions associated with vibrations of the carbon framework and the C−H bonds.

Again, no carbene (**1d**) was detected as a product of the **3d** photolysis. In this case, irradiation of **3d** in 5% O_2-doped argon at 10 K with $\lambda > 305$ nm did not result in oxidized products. In particular, formation of aldehyde **4d** could be ruled out, by comparison of the IR spectrum of the photolysis product of **3d** in O_2-doped argon with that of independently synthesized and matrix-isolated **4d**.

In conclusion, our results demonstrate that metalated 2-furyldiazomethanes **3c** and **3d** are viable precursors of highly unsaturated acylsilanes and acylstannanes, respectively. Carbenes **1c** and **1d** are unstable even under matrix-isolation conditions, and thus could not be characterized by direct spectroscopic methods.

Experimental Section

General Methods and Materials: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as internal standard with Bruker AC-200 and AM-400 instruments. − IR spectra were obtained with Bruker IFS66 or Equinox 55 FTIR spectrometers.

Synthesis of Diazo Precursors: 5-Trimethylsilyl- and 5-trimethylstannylfuran-2-carbaldehyde **4c** and **4d** and their corresponding tosyl hydrazones were synthesized according to a literature procedure.[26] Sodium hydride (80% suspension in methanol, 1.1 equiv.) was added to a solution of the tosylhydrazones in THF or CH_2Cl_2 at 0 °C. The solution was stirred for 0.5 h at 0 °C. The solvent was evaporated and the remaining solid washed several times with dry pentane. After removing the remaining solvent in vacuo, the solid was used directly for generating the diazomethanes **3c** and **3d**.

Sodium Salt of the Tosyl Hydrazone of 5-Trimethylstannylfuran-2-carbaldehyde: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.1 (s, 2 H), 7.1 (s, 2 H), 6.7 (s, 1 H), 6.4 (s, 1 H), 2.6 (s, 3 H), 0.7 (s, 3 H) ppm. − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 151.3, 139.6, 128.7, 126.5, 122.7 110.8, 21.2, −9.0.

Matrix Spectroscopy: Matrix-isolation experiments were performed using standard techniques, with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde 99.9999%) at 30 K on top of a CsI (IR) or sapphire (UV/Vis) window at a rate of approximately 0.15 mmol min^{-1}. Irradiation was carried out with Osram HBO 500-W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water and by a Schott KG1 filter. For broad-band irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors and cut-off filters were used. Infrared spectra were measured with a Bruker IFS66 FTIR or an Equinox 55 FTIR spectrometer, with a standard resolution of 0.5 cm^{-1} in the range 400−4000 cm^{-1}. UV/Vis spectra were recorded with a Hewlett Packard 8452A diode array spectrophotometer, with a resolution of 2 nm.

Calculations: The DFT calculations were performed employing Becke's three parameter functional B3LYP[27] and Pople's 6−31G(d,p) basis set.[28] All calculations were performed using the GAUSSIAN 98[29] set of programs.

Acknowledgments

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