JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

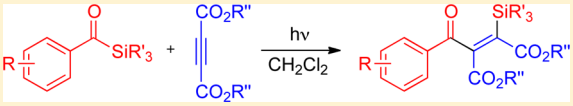
Photochemical Intermolecular Silylacylations of Electron-Deficient Internal Alkynes

Peter Becker, Daniel L. Priebbenow, Hui-Jun Zhang,† Ramona Pirwerdjan, and Carsten Bolm*

Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074 Aachen, Germany

Supporting Information

ABSTRACT: Light-induced Brook rearrangements of acylsilanes facilitate silylacylation reactions of electron-deficient internal alkynes. A wide range of aromatic substituents on the acylsilane aryl group are tolerated, affording a series of functionalized enonyl silanes. The presence of electron-withdrawing substituents on the alkyne is crucial for the success of the addition process.

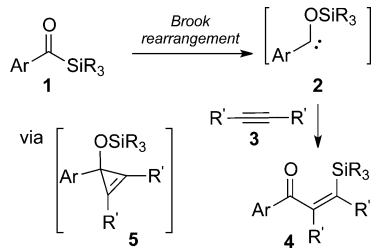


Over the past 40 years, the hydroacylation reactions of alkenes and alkynes with aldehydes have been developed as efficient tools for C−C bond formation in organic chemistry.[1] Various transition metals have been applied as catalysts in the aforementioned process to form the corresponding adducts in a highly atom-economic manner. Interestingly, the analogous silylacylation reactions utilizing acylsilanes instead of aldehydes to afford useful silylated products have attracted very little interest.[2] In this context, Narasaka and co-workers reported the rhodium-catalyzed cyclization of alkynyl-substituted acylsilanes to form cyclic ketones. However, the silyl group was not incorporated into the final product during this transformation.[3]

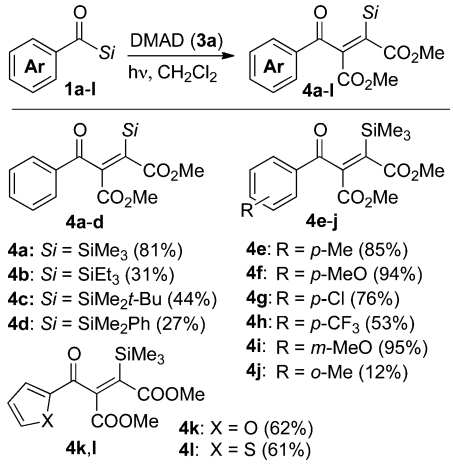
In his early reports, Brook described his thorough investigations into the thermally or photochemically induced silicon-to-oxygen shift of acylsilanes (now known as the Brook rearrangement).[4] Despite this work, only a few reports describing synthetically useful transformations based on this unique process exist.[4g−i,j] Encouraged by Brook's seminal reports, our group recently investigated silylacylation reactions of acylsilanes with *ortho*-tethered alkynes. During this process, a siloxycarbene generated in situ by light irradiation reacted with the proximal alkyne, and this was followed by a retro-Brook rearrangement step to afford highly fuctionalized chromone derivatives containing a vinylic silane moiety.[5] To further explore this chemistry, we next focused our attention on the previously unknown intermolecular silylacylation of alkynes (Scheme 1).[6]

Assuming an analogous reaction pathway[7] as in the previously reported intramolecular process,[5] we started our investigation by applying a range of aroylsilanes with various silyl moieties under conditions that involved light irradiation of the acylsilane in the presence of 2.0 equiv of dimethyl acetylenedicarboxylate (DMAD, **3a**) in CH_2Cl_2 (Scheme 2). Compared with the trimethylsilyl-containing aroylsilane **1a**, which gave an 81% yield of the corresponding product **4a**, the reactions of triethylsilyl (**1b**), *tert*-butyldimethylsilyl (**1c**), and dimethylphenylsilyl (**1d**) aroylsilanes with DMAD resulted in lower yields of the respective enonyl silanes (**4b**, 31%; **4c**, 44%; **4d**, 27%), presumably as a result of steric factors associated with the bulkier groups attached to silicon. Whether or not that effect was related to the formation of the suggested intermediates **5** or their rearrangements to the corresponding products **4** (Scheme 1) remained unanswered.

Scheme 1. Photochemically Induced Intermolecular Silylacylation of Alkynes



Scheme 2. Scope of Aroylsilanes in the Intramolecular Silylacylation Reaction



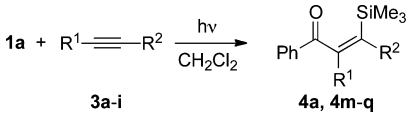
Received: November 5, 2013
Published: December 18, 2013

   dx.doi.org/10.1021/jo402457x | J. Org. Chem. 2014, 79, 814−817

Subsequently, other aroylsilanes (**1e**–**l**) with different aryl groups were investigated. The presence of an electron-neutral methyl group at the *para* position of the aryl ring (as in **1e**) did not significantly affect the product yield (85%) compared with the unsubstituted aroylsilane. A substitution with an electron-withdrawing group at the *para* position of the aromatic ring, such as Cl (as in **1g**) or CF_3 (as in **1h**), led to a decrease in the yield (**4g**, 76%; **4h**, 53%). An electron-donating methoxy group attached to the *para* or *meta* position of the aroylsilane (as in **4f** and **4i**, respectively) afforded the corresponding enonyl silanes in excellent yields (**4f**, 94%; **4i**, 95%). Dramatically, substitution at the *ortho* position of the arene (as in **1j**) led to a very poor yield in this reaction process (**4j**, 12%). The replacement of the aryl group with a furanyl moiety (as in **1k**) or a thiophenyl moiety (as in **1l**) afforded the desired adducts in moderate yields (**4k**, 62%; **4l**, 61%).

Next, the application of alkynes other than DMAD (**3a**) in this reaction process was explored. With diethyl acetylenedicarboxylate (**3b**), the yield of the corresponding product (**4m**, 67%) decreased only slightly, whereas more bulky ester groups such as isopropyl (as in **3c**) or *tert*-butyl (as in **3d**) significantly lowered the yields of the resulting products (**4n**, 40%; **4o**, 53%), proposedly as a result of steric effects (Table 1, entries 2–4).

Table 1. Investigations into the Different Types of Alkynes Applicable to This Reaction Process[a]



3a-i 4a, 4m-q

entry	alkyne	R^1	R^2	product	yield (%)
1	**3a**	CO_2Me	CO_2Me	**4a**	81
2	**3b**	CO_2Et	CO_2Et	**4m**	67
3	**3c**	CO_2i-Pr	CO_2i-Pr	**4n**	40
4	**3d**	CO_2t-Bu	CO_2t-Bu	**4o**	53
5	**3e**	CO_2Me	CO_2Ph	**4p**	50[c]
6[b]	**3f**	CO_2Me	CO-morpholinyl	**4q**	28
7	**3g**	Et	Et	**4r**	–
8	**3h**	Ph	Ph	**4s**	–
9	**3i**	CO_2Me	H	**4t**	–

[a]Reaction conditions: acylsilane **1a** (1.0 equiv), alkyne **3** (2.0 equiv), CH_2Cl_2, light irradiation, 3 days. [b]Reaction time of 6 days. [c]*E*/*Z* ratio = 11/1.

In order to investigate the regioselectivity of the siloxycarbene addition, the mixed diester methyl phenyl acetylenedicarboxylate (**3e**) was applied (Table 1, entry 5). The reaction resulted in the formation of a single isomer (**4p**, 50%), with the silyl group next to the phenyl ester moiety. Interestingly, an *E*/*Z* isomer mixture in a ratio of 11:1 was observed in this case. Finally, the use of alkyne **3f** containing both an ester and an amide functionality was explored. Suitable amounts of the corresponding product **4q** could be obtained only after 6 days of reaction time, and even under those optimized conditions, **4q** was formed in only 28% yield (Table 1, entry 6). We hypothesize that the decrease in reactivity of **3f** is due to the reduced electron-withdrawing capability of the amide group.

Electron-neutral internal alkynes such as 3-hexyne (**3g**) and 1,2-diphenylethyne (**3h**) did not afford the corresponding products, and the starting materials were recovered (Table 1, entries 7 and 8). When the terminal alkyne methyl propiolate (**3i**) was applied, none of the expected addition product was obtained (Table 1, entry 9).

In summary, we investigated light-induced additions of aroylsilanes to alkynes and obtained enonyl silanes in good to excellent yields. The process is highly regio- and chemoselective and proceeds with complete atom economy. Presumably, the aroylsilanes undergo Brook rearrangements to provide siloxycarbenes as intermediates, which add to electron-deficient alkynes leading to cyclopropene derivatives that rearrange to form the observed products.

EXPERIMENTAL SECTION

General Experimental. Unless otherwise stated, the reactions were carried out in oven-dried reaction vessels under an argon atmosphere. The CH_2Cl_2 used for the experiments was dried by distillation over CaH_2. All of the product mixtures were analyzed by thin-layer chromatography using TLC silica gel plates with fluorescent indicator (λ = 254 nm). NMR spectra were recorded in deuterated chloroform at 25 °C. Chemical shifts (δ) are reported in parts per million, and spin–spin coupling constants (J) are quoted in hertz. The multiplicities in NMR are given by the standard abbreviations: br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Mass spectrometry was performed on a hybrid ion trap–Orbitrap mass spectrometer. IR spectra were recorded on an FT-IR spectrometer, and the wavenumbers of the absorption peaks are reported in cm^{-1}. All of the acylsilanes used in the following experiments were prepared in accordance with previously published synthetic strategies.[8]

General Procedure for the Intermolecular Silylacylation. The acylsilane (0.3 mmol, 1 equiv) was added to a solution of the electron-deficient alkyne (0.6 mmol, 2 equiv) in dry DCM (1 mL) in a common 4 mL screw-capped vial under an argon atmosphere. The resulting solution was stirred for 2–4 days under light irradiation[9] with a Philips Genie Long Life 23 W fluorescent lamp. Then the solvent was removed under reduced pressure, and the product was purified by column chromatography (EtOAc/pentane, 1:9).

*Dimethyl 2-Benzoyl-3-(trimethylsilyl)maleate (**4a**).* Following the general procedure, the product was obtained as colorless crystals in 81% yield (78 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 2H), 7.62–7.55 (m, 1H), 7.50–7.43 (m, 2H), 3.84 (s, 3H), 3.61 (s, 3H), 0.04 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.4, 170.8, 163.1, 154.5, 141.0, 136.6, 134.1, 129.4, 128.9, 52.8, 52.2, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{16}H_{20}O_5Si + Na]^+$, 343.0978; found, 343.0972. IR ν (cm^{-1}): 2956, 1727, 1678, 1595, 1440, 1238, 1238, 1117, 938, 850. Mp: 72 °C.

*Dimethyl 2-Benzoyl-3-(triethylsilyl)maleate (**4b**).* Following the general procedure, the product was obtained as colorless crystals in 31% yield (34 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.88 (m, 2H), 7.63–7.57 (m, 1H), 7.51–7.45 (m, 2H), 3.86 (s, 3H), 3.63 (s, 3H), 0.85 (t, J = 7.9 Hz, 9H), 0.55 (q, J = 7.6 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.3, 171.0, 163.3, 153.5, 142.0, 136.6, 134.0, 129.4, 128.9, 52.8, 52.2, 7.1, 3.2 ppm. HRMS (ESI-MS): calcd for $[C_{19}H_{26}O_5Si + Na]^+$, 385.1447; found, 385.1442. IR ν (cm^{-1}): 2955, 1727, 1593, 1447, 1233, 1114, 1020, 724. Mp: 54 °C.

*Dimethyl 2-Benzoyl-3-(tert-butyldimethylsilyl)maleate (**4c**).* Following the general procedure, the product was obtained as colorless crystals in 44% yield (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.89 (m, 2H), 7.62–7.55 (m, 1H), 7.51–7.44 (m, 2H), 3.83 (s, 3H), 3.61 (s, 3H), 0.91 (s, 9H), −0.05 (s, J = 0.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.2, 171.1, 163.4, 152.2, 142.8, 136.8, 134.0, 129.3, 128.9, 52.9, 52.2, 27.2, −4.54 ppm. HRMS (ESI-MS): calcd for $[C_{19}H_{26}O_5Si + Na]^+$, 385.1447; found, 385.1442. IR ν (cm^{-1}): 2948, 1726, 1592, 1447, 1234, 1113, 1019, 816. Mp: 45 °C.

*Dimethyl 2-Benzoyl-3-(dimethyl(phenyl)silyl)maleate (**4d**).* Following the general procedure, the product was obtained as colorless crystals in 27% yield (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, J = 8.3, 1.3 Hz, 2H), 7.51–7.45 (m, 1H), 7.36–7.27 (m, 4H),

dx.doi.org/10.1021/jo402457x | J. Org. Chem. 2014, 79, 814–817

7.18−7.08 (m, 3H), 3.74 (s, 3H), 3.60 (s, 3H), 0.40 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 192.9, 170.7, 163.2, 153.3, 142.0, 136.2, 134.6, 133.7, 133.5, 129.9, 129.3, 128.5, 127.6, 52.8, 52.2, −2.6 ppm. HRMS (ESI-MS): calcd for $[C_{21}H_{22}O_5Si + Na]^+$, 405.1129; found, 405.1139. IR ν (cm^{-1}): 2954, 1728, 1676, 1595, 1433, 1236, 1116, 938, 843, 817, 787, 735, 697. Mp: 72 °C.

Dimethyl 2-(4-Methylbenzoyl)-3-(trimethylsilyl)maleate (**4e**). Following the general procedure, the product was obtained as white crystals in 85% yield (85 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.83−7.76 (m, 2H), 7.30−7.24 (m, 2H), 3.85 (s, 3H), 3.63 (s, 3H), 2.42 (s, 3H), 0.05 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.0, 171.0, 163.3, 154.1, 145.3, 141.2, 134.3, 129.7, 129.6, 52.8, 52.2, 22.0, −1.2 ppm. HRMS (ESI-MS): calcd for $[C_{17}H_{22}O_5Si + Na]^+$, 357.1129; found, 357.1128. IR ν (cm^{-1}): 2955, 1726, 1674, 1605, 1435, 1238, 1116, 848. Mp: 79 °C.

Dimethyl 2-(4-Methoxybenzoyl)-3-(trimethylsilyl)maleate (**4f**). Following the general procedure, the product was obtained as yellow crystals in 94% yield (99 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90−7.83 (m, 2H), 6.97−6.89 (m, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.62 (s, 3H), 0.03 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.8, 171.0, 164.4, 163.3, 153.6, 141.3, 131.9, 129.8, 114.1, 55.6, 52.8, 52.1, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{17}H_{22}O_6Si + Na]^+$, 373.1078; found, 373.1076. IR ν (cm^{-1}): 2438, 2953, 1725, 1667, 1596, 1436, 1245, 1174, 1115, 849. Mp: 62 °C.

Dimethyl 2-(4-Chlorobenzoyl)-3-(trimethylsilyl)maleate (**4g**). Following the general procedure, the product was obtained as white crystals in 76% yield (81 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86−7.80 (m, 2H), 7.48−7.42 (m, 2H), 3.85 (s, 3H), 3.62 (s, 3H), 0.05 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.3, 170.7, 162.9, 155.2, 140.7, 140.5, 135.1, 130.7, 129.3, 52.9, 52.3, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{16}H_{19}ClO_5Si + Na]^+$, 377.0583; found, 377.0579. IR ν (cm^{-1}): 2956, 1715, 1676, 1585, 1430, 1230, 1116, 1093, 841. Mp: 74 °C.

Dimethyl 2-[4-(Trifluoromethyl)benzoyl]-3-(trimethylsilyl)-maleate (**4h**). Following the general procedure, the product was obtained as a colorless oil in 53% yield (62 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 3.63 (s, 3H), 0.07 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.6, 170.6, 162.8, 156.2, 140.2, 139.3, 135.9, 135.4, 135.0, 134.6, 129.6, 126.1, 121.8, 53.0, 52.3, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{17}H_{19}O_5F_3Si + Na]^+$, 411.0852; found, 411.0846. IR ν (cm^{-1}): 2958, 1729, 1688, 1435, 1323, 1240, 1173, 1129, 851.

Dimethyl 2-(3-Methoxybenzoyl)-3-(trimethylsilyl)maleate (**4i**). Following the general procedure, the product was obtained as a colorless oil in 95% yield (100 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47−7.40 (m, 2H), 7.38−7.32 (m, 1H), 7.15−7.10 (m, 1H), 3.84 (s, 6H), 3.61 (s, 3H), 0.05 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.2, 170.8, 163.1, 160.1, 154.4, 140.9, 137.9, 129.9, 122.7, 120.9, 112.5, 55.5, 52.8, 52.2, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{17}H_{22}O_6Si + Na]^+$, 373.1078; found, 373.1074. IR ν (cm^{-1}): 2955, 1726, 1678, 1593, 1437, 1240, 1110, 1040, 853.

Dimethyl 2-(2-Methylbenzoyl)-3-(trimethylsilyl)maleate (**4j**). Following the general procedure, the product was obtained as a colorless oil in 12% yield (12 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, J = 7.8, 1.3 Hz, 1H), 7.43 (td, J = 7.5, 1.4 Hz, 1H), 7.31−7.23 (m, 2H), 3.85 (s, 3H), 3.59 (s, 3H), 2.63 (s, 3H), 0.11 (s, 9H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 195.1, 171.1, 163.5, 154.0, 142.4, 140.4, 135.6, 132.9, 132.5, 131.9, 125.9, 52.8, 52.2, 21.9, −1.2 ppm. HRMS (ESI-MS): calcd for $[C_{17}H_{22}O_5Si + Na]^+$, 357.1129; found, 357.1136. IR ν (cm^{-1}): 2955, 1727, 1677, 1600, 1438, 1236, 1102, 849.

Dimethyl 2-(Furan-2-carbonyl)-3-(trimethylsilyl)maleate (**4k**). Following the general procedure, the product was obtained as a colorless oil in 62% yield (58 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65−7.63 (m, 1H), 7.24−7.20 (m, 1H), 6.59−6.56 (m, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 0.10 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 180.8, 170.7, 163.0, 155.4, 152.6, 147.8, 139.8, 129.9, 120.0, 112.8, 52.9, 52.2, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{14}H_{18}O_6Si + Na]^+$, 333.0770; found, 333.0763. IR ν (cm^{-1}): 2955, 1726, 1678, 1593, 1437, 1240, 1110, 1040, 853.

Dimethyl 2-(Thiophene-2-carbonyl)-3-(trimethylsilyl)maleate (**4l**). Following the general procedure, the product was obtained as colorless crystals in 61% yield (60 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (dd, J = 4.9, 0.8 Hz, 1H), 7.62 (dd, J = 3.7, 0.9 Hz, 1H), 7.14 (dd, J = 4.8, 3.9 Hz, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 0.09 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 185.5, 170.7, 163.1, 154.4, 144.2, 140.4, 135.8, 135.2, 128.5, 52.9, 52.2, −1.3 ppm. HRMS (ESI-MS): calcd for $[C_{14}H_{18}O_5SSi + Na]^+$, 349.0536; found, 349.0544. IR ν (cm^{-1}): 2954, 1723, 1647, 1409, 1218, 1110, 1018, 845. Mp: 54 °C.

Diethyl 2-Benzoyl-3-(trimethylsilyl)maleate (**4m**). Following the general procedure, the product was obtained as a colorless oil in 67% yield (70 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91−7.87 (m, 2H), 7.60−7.56 (m, 1H), 7.48−7.45 (m, 2H), 4.32 (q, J = 7.2 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H), 0.07 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.7, 170.4, 162.7, 154.2, 141.3, 136.9, 133.9, 129.3, 128.8, 61.8, 61.2, 14.3, 13.8, −1.1 ppm. HRMS (ESI-MS): calcd for $[C_{18}H_{24}O_5Si + Na]^+$, 371.1285; found, 371.1281. IR ν (cm^{-1}): 2981, 1724, 1678, 1450, 1367, 1230, 1111, 1033, 850.

Diisopropyl 2-Benzoyl-3-(trimethylsilyl)maleate (**4n**). Following the general procedure, the product was obtained as colorless crystals in 40% yield (45 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.90−7.86 (m, 2H), 7.59−7.55 (m, 1H), 7.47−7.43 (m, 2H), 5.21 (dt, J = 12.6, 6.3 Hz, 1H), 4.93 (dt, J = 12.5, 6.2 Hz, 1H), 1.33 (d, J = 6.3 Hz, 6H), 0.98 (d, J = 6.3 Hz, 6H), 0.08 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 194.0, 169.8, 162.1, 154.3, 141.6, 137.1, 133.7, 129.2, 128.7, 69.6, 68.9, 22.0, 21.4, −1.0 ppm. HRMS (ESI-MS): calcd for $[C_{20}H_{28}O_5Si + Na]^+$, 399.1598; found, 399.1604. IR ν (cm^{-1}): 2980, 1719, 1668, 1550, 1460, 1374, 1231, 1098, 1007, 915, 841, 767. Mp: 52 °C.

Di-tert-butyl 2-Benzoyl-3-(trimethylsilyl)maleate (**4o**). Following the general procedure, the product was obtained as colorless crystals in 53% yield (64 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.89−7.86 (m, 2H), 7.58−7.54 (m, 1H), 7.47−7.42 (m, 2H), 1.54 (s, 9H), 1.19 (s, 9H), 0.10 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 194.3, 169.2, 161.7, 153.5, 142.6, 137.4, 133.5, 129.0, 128.7, 82.6, 82.2, 28.3, 27.7, −0.8 ppm. HRMS (ESI-MS): calcd for $[C_{22}H_{32}O_5Si + Na]^+$, 427.1911; found, 427.1912. IR ν (cm^{-1}): 2978, 1719, 1667, 1595, 1452, 1368, 1244, 1154, 1116, 1001, 891, 842, 765. Mp: 115 °C.

1-Methyl 4-Phenyl 2-Benzoyl-3-(trimethylsilyl)maleate (**4p**). Following the general procedure, the product was obtained as white crystals in 50% yield (57 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98−7.96 (m, 2H), 7.65−7.61 (m, 1H), 7.53−7.50 (m, 2H), 7.46−7.42 (m, 2H), 7.34−7.31 (m, 2H), 7.29−7.25 (m, 1H), 3.70 (s, 3H), 0.18 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 193.4, 168.8, 163.1, 153.7, 150.6, 141.5, 136.6, 134.3, 129.7, 129.5, 129.0, 126.2, 121.8, 53.0, −1.0 ppm. HRMS (ESI-MS): calcd for $[C_{21}H_{22}O_5Si + Na]^+$, 405.1129; found, 405.1133. IR ν (cm^{-1}): 3062, 2960, 1725, 1671, 1590, 1487, 1448, 1314, 1235, 1181, 1115, 1023, 978, 841, 755, 730, 690, 662. Mp: 94 °C. Two isomers were observed in the NMR spectra in a ratio of 11:1.

Methyl (E)-2-Benzoyl-4-morpholino-4-oxo-3-(trimethylsilyl)but-2-enoate (**4q**). Following the general procedure, the product was obtained as yellow crystals in 28% yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91−7.88 (m, 1H), 7.61−7.58 (m, 1H), 7.49−7.46 (m, 2H), 3.89−3.85 (m, 1H), 3.81−3.74 (m, 2H), 3.64 (ddd, J = 15.4, 8.7, 4.9 Hz, 3H), 3.61 (s, 3H), 3.43 (ddd, J = 13.1, 7.4, 3.3 Hz, 1H), 3.37 (ddd, J = 13.1, 5.5, 3.3 Hz, 1H), 0.06 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$): δ = 194.0, 169.9, 163.4, 157.6, 140.1, 136.8, 134.2, 129.5, 129.0, 66.6, 66.3, 52.7, 46.5, 41.5, −0.8 ppm. HRMS (ESI-MS): calcd for $[C_{19}H_{25}NO_5Si + Na]^+$, 398.1394; found, 398.1390. IR ν (cm^{-1}): 2920, 2857, 1724, 1634, 1428, 1222, 1113, 1061, 991, 903, 847, 746, 699. Mp: 82 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/jo402457x | J. Org. Chem. 2014, 79, 814−817

AUTHOR INFORMATION

Corresponding Author

*E-mail: Carsten.bolm@oc.rwth-aachen.de.

Present Address

[†]H.-J.Z.: Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, P. R. China.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.L.P. and H.-J.Z. are grateful to the Alexander von Humboldt Foundation for postdoctoral fellowships.

REFERENCES

(1) (a) Fu, G. C. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: New York, 2005; pp 79−91. (b) Willis, M. C. *Chem. Rev.* **2010**, *110*, 725. (c) Biju, A. T.; Kuhl, N.; Glorius, F. *Acc. Chem. Res.* **2011**, *44*, 1182.

(2) For reviews of acylsilanes, see: (a) Zhang, H. J.; Priebbenow, D. L.; Bolm, C. *Chem. Soc. Rev.* **2013**, *42*, 8540. (b) Patrocínio, A. F.; Moran, P. J. S. *J. Braz. Chem. Soc.* **2001**, *12*, 7.

(3) Yamane, M.; Amemiya, T.; Narasaka, K. *Chem. Lett.* **2001**, 1210.

(4) For the formation of siloxycarbenes from acylsilanes, see: (a) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869. (b) Brook, A. G. *Adv. Organomet. Chem.* **1969**, *7*, 95. (c) Brown, R. S. *Can. J. Chem.* **1975**, *53*, 2446. (d) Bernardi, F.; Lunazzi, L.; Ricci, A.; Seconi, G.; Tonachini, G. *Tetrahedron* **1986**, *42*, 3607. (e) Perrin, H. M.; White, W. R.; Platz, M. S. *Tetrahedron Lett.* **1991**, *32*, 4443. (f) Trommer, M.; Sander, W. *Organometallics* **1996**, *15*, 189. (g) Bassindale, A. R.; Brook, A. G.; Harris, J. *J. Organomet. Chem.* **1975**, *90*, C6. (h) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (i) Shen, Z.; Dong, V. M. *Angew. Chem.* **2009**, *121*, 798; *Angew. Chem., Int. Ed.* **2009**, *48*, 784. (j) Becker, P.; Priebbenow, D. L.; Pirwerdjan, R.; Bolm, C. *Angew. Chem., Int. Ed.* **2013**, DOI: 10.1002/anie.201307446.

(5) Zhang, H.-J.; Becker, P.; Huang, H.; Pirwerdjan, R.; Pan, F.-F.; Bolm, C. *Adv. Synth. Catal.* **2012**, *354*, 2157.

(6) For a single example of an intermolecular addition of a photochemically generated silyoxycarbene to an internal alkyne that leads, however, to a different product type, see: Brook, A. G.; Kucera, H. W.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 1618.

(7) Additions of acylsilanes to alkenes have been suggested to proceed via short-lived 1,4-diradicals that rearrange and undergo ring closure to yield cyclopropane derivatives. See: Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699. Although we cannot exclude such a pathway here, we do not regard it as being relevant because (1) the presence of radical traps (TEMPO or 2,4,6-trimethylphenol) did not affect the product formation and (2) the addition of 2-propanol led to an acetal-like product, which is indicative of the involvement of a carbene-type intermediate.

(8) (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434. (c) Patrocínio, A. F.; Corrêa, I. R., Jr.; Moran, P. J. S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3133. (d) Patrocínio, A. F.; Moran, P. J. S. *J. Organomet. Chem.* **2000**, *603*, 220. (e) Wu, X.-F.; Neumann, H.; Beller, M. *Tetrahedron Lett.* **2012**, *53*, 582. (f) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653. (g) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G. *J. Org. Chem.* **1985**, *50*, 130. (h) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974. (i) Ito, K.; Tamashima, H.; Iwasawa, N.; Kusama, H. *J. Am. Chem. Soc.* **2011**, *133*, 3716.

(9) Under the assumption that visible light (410−440 nm, correlating to the maximal n−π^* absorption of the acylsilanes) promoted the reaction process, a low-cost household compact fluorescent lamp with a broad emission spectrum was used in this study. The yield was significantly lower when Pyrex glassware in combination with a high-pressure mercury lamp was applied. Utilizing a 420 nm LED as the light source for the reaction with aroylsilane **1a** shortened the reaction time.