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Transition-Metal-Catalyzed Decomposition of Diazo(trialkylsilyl)-acetates: Intermolecular Formation and Trapping of Carbonyl Ylides

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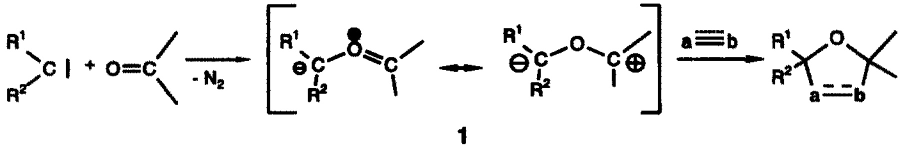
Abstract: Transition-metal-catalyzed decomposition of diazoesters **2** in the presence of benzaldehyde, crotonaldehyde, or acetaldehyde generates carbonyl ylides which can be trapped with dimethyl fumarate, dimethyl maleate, and dimethyl acetylenedicarboxylate to give tetrahydrofurans **4**,**6**,**7**, and **8** and dihydrofuran **10**, respectively. Decomposition of **2a** in the presence of benzaldehyde and methyl cyanoformate affords no products derived from a carbonyl ylide, but rather the oxazole **12**. X-ray crystal structures of **4a** and **6** are provided.

The combination of a carbene or carbenoid with an aldehyde or a ketone provides a straightforward access to carbonyl ylides.[1] These dipolar species are in general reactive intermediates which can undergo rapid isomerization reactions such as cyclization or 1,4-proton shift, but they can also be trapped by intra- or intermolecular [3+2]-cycloaddition reactions. The carbonyl ylide / cycloaddition sequence could be synthetically valuable, since it offers a fast access to highly functionalized oxygen-containing five-membered rings (Scheme 1). Thus, the carbonyl ylides **1** generated from electrophilic carbenes can be intercepted with electron-poor olefinic and acetylenic dipolarophiles to give tetrahydrofuran or dihydrofuran derivatives, respectively. Furthermore, the carbonyl compound which becomes a constituent of **1** may also play the part of the dipolarophile, thus giving rise to the formation of dioxolanes.



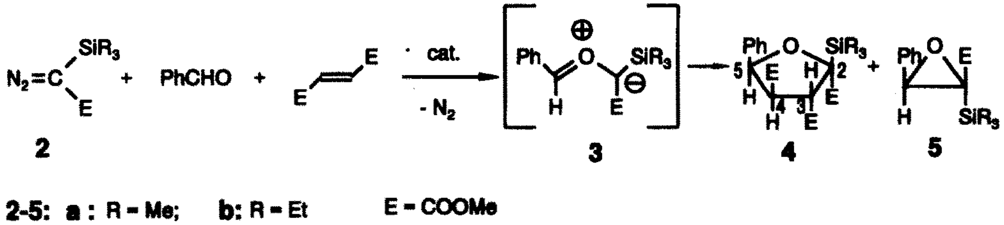
Scheme 1

Recently, the reaction sequence that involves intramolecular generation of carbonyl ylides by dediazoniation of appropriate diazocarbonyl compounds, followed by intra- or intermolecular [3+2]-cycloaddition reaction, has been used extensively for the construction of oxygen-containing polycycles.[1-4] In contrast, the purely *inter*molecular three-component reaction has found less attention as a synthetic method, although its viability has been demonstrated for a variety of electrophilic carbenes, generated in situ from a suitable precursor.[1,5] Of particular interest in this respect is the carbonyl ylide chemistry of acylcarbenes, since the latter can be conveniently generated from readily available α-diazocarbonyl compounds and provide a useful functionality in the final product. Carbonyl ylides have been generated starting from α-diazoacetic esters,[6-10] dimethyl diazomalonate,[11,12] α-diazoacetoacetic esters,[13,14] and α-diazoketones.[15] For the three-component reaction between an α-diazocarbonyl compound, an aldehyde, and an olefinic or acetylenic dipolarophile, it is important to note that the dipolarophile may not only intercept the carbonyl ylide (Scheme 1), but may also react with the intact diazocompound in a 1,3-dipolar cycloaddition reaction; as a consequence, the effectiveness of the carbonyl ylide pathway will be limited. This complication has in fact been observed for the copper-catalyzed decomposition of methyl diazoacetate in the presence of benzaldehyde and dimethyl fumarate, where the expected 1:1:1 adduct was obtained in only 14 % yield; in contrast, dimethyl diazomalonate did not react with the same dipolarophile, and the carbonyl ylide / cyloaddition sequence proceeded cleanly.[11b]

We reasoned that α-diazo(trialkylsilyl)acetic esters, due to the π-acceptor character of the silyl group, should be comparable in reactivity to diazomalonic esters. In fact, it is known that ethyl diazo(trimethylsilyl)acetate undergoes [3+2]-cycloaddition to acrylic and acetylenic esters only under forcing conditions.[16] Thus, by decomposition of these diazoesters under mild conditions the carbonyl ylide / cycloaddition sequence should take place effectively, and novel 2-silyl-tetrahydrofuran and dihydrofuran derivatives should become available.

RESULTS

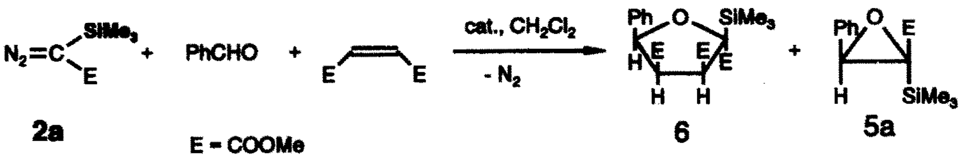
Diazoesters **2a** and **2b** were chosen for the present study. Since transition-metal-catalyzed decomposition of diazoesters has been shown to the beneficial for the yields of products derived from carbonyl ylides, we chose the same methodology for dediazoniation of **2a** and **2b**. In earlier studies, we have identified rhodium(II) perfluorobutyrate [$Rh_2(pfb)_4$] and copper(I) triflate as catalysts which smoothly decompose **2a,b** already at room temperature,[17] whereas the ruthenium(I) complex [$Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ requires elevated temperatures.[18] These three catalysts proved also appropriate for the carbonyl ylide reactions, but copper(I) triflate had to be applied in unusually high concentration in order to guarantee complete decomposition of **2a** and **2b**. The results obtained with benzaldehyde as carbonyl component and dimethyl fumarate or maleate as dipolarophiles are shown in Schemes 2, 3 and Tables 1, 2.



Scheme 2

Table 1. Conditions, products, and yields for the reactions shown in Scheme 2.

Diazoester	Catalyst (mol-%)	Temp. [°C]	Solvent	Yield [%] of **4**	Yield [%] of **5**
2a	$Rh_2(pfb)_4$ (3.2)	22	CH_2Cl_2	41	/
	$[Ru_2(CO)_4(OAc)_2]_n$ (4.4)	80	benzene	54	/
	$Cu(O_3SCF_3)$ (13.5)	22	CH_2Cl_2	11.5	38
2b	$Rh_2(pfb)_4$ (2.0)	22	CH_2Cl_2	46	/



Scheme 3

Table 2. Conditions, products, and yields for the reactions shown in Scheme 3.

Catalyst (mol-%)	Yield of **6** [%]	Yield of **5a** [%]
$Rh_2(pfb)_4$ (4.4)	49	/
$Cu(O_3SCF_3)$ (7.9)	16	38

Decomposition of **2a** with $Rh_2(pfb)_4$ or $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ in the presence of an excess of benzaldehyde and dimethyl fumarate afforded only one product which was identified as the *(2α ,3β,4α ,5α)*-tetrahydrofuran derivative **4a** by an X-ray crystal structure analysis (see below). Analogously, **4b** was obtained from **2b**. In contrast, CuOTf-catalyzed decomposition of **2a** under the same conditions as before yielded oxirane **5a** as the major product at the expense of tetrahydrofuran **4**. The oxirane is likely to result from carbonyl ylide **3a** by a conrotatory 4π-electrocyclization, and therefore, the *(2α ,3β)* configuration must be assumed.

The formation of **5a** as the major product in the CuOTf-catalyzed reaction is somewhat surprising, especially so since this was not observed for the analogous reaction of dimethyl diazomalonate.[11a] As the combined yield of **4a** and **5a** in the CuOTf-catalyzed reaction is comparable to the yield of **4a** in the Rh- or Ru-catalyzed reactions, it may be concluded that the effectiveness of carbonyl ylide formation is similar in all three cases; however, the presence of copper triflate seems to reduce the rate of the 1,3-dipolar cycloaddition reaction so that the cyclization **3a** → **5a** becomes dominating.

When **2a** was decomposed in the presence of benzaldehyde and dimethyl maleate, the tetrahydrofuran **6** was obtained as a single stereoisomer, the structure of which was determined by an X-ray diffraction analysis. Like in the presence of dimethyl fumarate as dipolarophile, **6** was the only isolated product with $Rh_2(pfb)_4$ as catalyst, while catalysis by CuOTf produced mainly oxirane **5a** besides some **6**.

The stereochemistry of **4a** and **6** could not be firmly established from the NMR data. The ^{1}H-NMR spectra gave clear evidence only for the *cis*-relationship between the phenyl ring and the 4-COOMe group in both compounds because of the large diamagnetic shift of one of the three methoxy signals ($\delta = 3.11$ and 3.16 ppm, respectively). Since 1,3-dipolar cycloaddition reactions in general occur stereospecifically,[19] it was to be expected that the configuration of the dipolarophile would be retained in the products. The X-ray crystal structure analyses (Figures 1 and 2) showed that **4a** and **6** are epimers with different configuration at the ring atom C-3 (C2 in the numbering scheme of the molecule plots). With this information at hand, the NMR spectra could be checked again for diagnostic differences. The ^{13}C chemical shifts of the two epimers are identical within 0.8 ppm except for the *C*=O signal at lowest field which appears at $\delta = 173.2$ ppm in **4a** and at $\delta = 175.8$ ppm in **6**. It appears reasonable to assign these low-field signals to the ester carbonyl at C-2; then, the upfield shift in **4a**, where the neighboring ester groups at C-2 and C-3 are in a *cis*-relationship, is in line with the well-known γ-effect.

In the ^{1}H-NMR spectra, the ABX system formed by protons 3-H, 4-H, and 5-H were analyzed and simulated. The different torsion angles found in the crystal structures are reflected in the magnitude of the vicinal coupling constants according to the Karplus-Conroy relationship (Table 3). For $J_{3,4}$, the relationship $^{3}J_{cis} > {}^{3}J_{trans}$ is found in agreement with other tetrahydrofurans that do not deviate much from planarity.[20] Interestingly, a longe-range coupling constant between 3-H and 5-H was found in **4a** ($^{4}J = -1.1$ Hz) but not in **6**. Since **4b** does not exhibit such a ^{4}J coupling, although the same relative configuration as in **4a** must be assumed, we do not consider the ^{4}J(3-H, 5-H) coupling as a diagnostic tool to elucidate the stereochemical relationship between these two protons.

Table 3. ^{1}H-NMR Chemical Shifts, Coupling Constants, and Torsion Angles for Ring Protons in **4a**, **4b**, and **6**.

	δ [ppm]			Coupling Constants [Hz]			Torsion Angles [°]	
	3-H	4-H	5-H	$J_{3,4}$	$J_{4,5}$	$J_{3,5}$	3-H / 4-H[a]	4-H / 5-H[b]
4a	3.96	3.93	5.57	8.1	10.4	-1.1	-132.5	-16.9
4b	3.89	3.78	5.40	7.8	9.6			
6	3.99	3.71	5.27	9.2	7.8		-18.6	34.6

[a] Torsion angle H2-C2-C3-H3 in Figures 1 and 2.

[b] Torsion angle H3-C3-C4-H4 in Figures 1 and 2.

It is remarkable that tetrahydrofurans **4** and **6** have been obtained as single diastereomers. Although the isolated yields were only 41-54 %, the ^{1}H-NMR spectra of the reaction mixtures before distillative workup did not indicate the presence of another diastereomer. For the intermediate carbonyl ylide **3**, a W-shaped planar geometry[22] with the bulkier groups at both termini in *exo*-position is to be assumed. As the molecule plots of **4a** and **6** (Figures 1 and 2) show, this carbonyl ylide configuration has been intercepted by dimethyl fumarate and maleate diasterospecifically and with retention of the configuration of the dipolarophile. In this manner, a unique relative configuration of four contiguous stereogenic centers has been achieved. The diastereoselectivity of the 1,3-dipolar cycloaddition between **3a** and dimethyl maleate is especially notable. It appears that π-attractive interactions between the phenyl ring and an ester carbonyl function in the transition state have dominated over the repulsive steric interaction between the $SiMe_3$ and the other COOMe group of the dipolarophile. A similar observation has already been made.[11b]

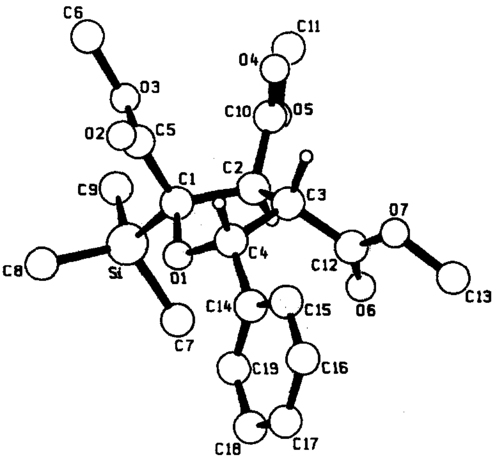


Fig. 1. SCHAKAL[21] plot of **4a**

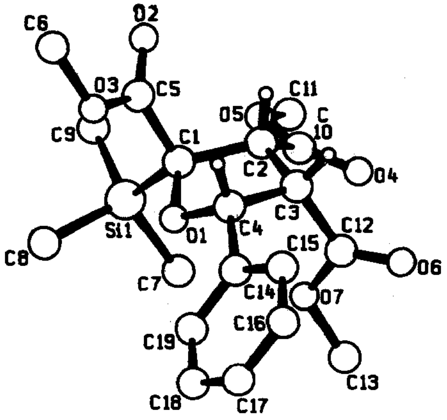
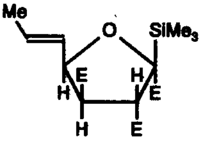


Fig. 2. SCHAKAL[21] plot of **6**

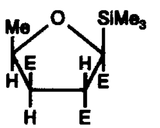
Rhodium(II)-catalyzed decomposition of **2a** in the presence of crotonaldehyde and acetaldehyde, respectively, was investigated next. In both cases, the carbonyl ylide intermediate could be trapped with dimethyl fumarate, and the tetrahydrofuran derivatives **7** (44 % yield) and **8** (43 %) were isolated. The (2α,3β,4α,5α) configuration was tentatively assigned based on the assumption that the carbonyl ylide was intercepted in its energetically most favorable configuration (i.e. with the bulkier groups in *exo*-position). Furthermore, the stereochemical relationship between the vicinal COOMe groups at C-2 and C-3 should be *cis* as in **4a**, since the δ(*C*=O) values in the ^{13}C-NMR spectrum agree well with those of **4a**, but not with those of **6**.

No three-component adduct was found when **2a** was decomposed in the presence of cyclohexanone and dimethyl fumarate. Rather, enolether **9**, contaminated with an unknown compound, was isolated in low yield. A 1,4-proton shift in the intermediate carbonyl ylide is likely to account for the formation of **9**; the Cu-catalyzed reaction of ethyl diazoacetate with aliphatic ketones proceeds analogously.[8]



7

E = COOMe



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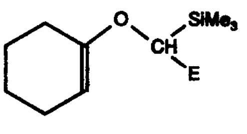
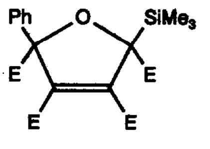


9

Similar to the carbonyl ylide generated from bis(methoxycarbonyl)carbene and benzaldehyde,[11b] the intermediate **3** could also be intercepted with dimethyl acetylenedicarboxylate as dipolarophile, and the dihydrofuran **10** was obtained. Trapping of **3** with 1-phenylsulfonyl-1-propyne was not successful, however. Rhodium-catalyzed decomposition of **2a** in the presence of benzaldehyde and of this alkyne furnished only the two diastereomeric 1,3-dioxolanes **11a,b** in a 2.3:1 ratio, albeit in low yield. These products obviously result from the cycloaddition of carbonyl ylide **3** to excess aldehyde. Notably, only **11a** was obtained when [$Ru_2(CO)_4(\mu$-$OAc)_2]_n$ was used as catalyst. Based on the ^{1}H-NMR spectrum, it was concluded that the two isomers have the same relative configuration at C-4 and C-5. The OMe signal appears at rather high field in both isomers (δ = 3.26 and 3.23 ppm), which is readily explained by the magnetic anisotropy of the phenyl ring at C-5, oriented perpendicular to the dioxolane ring. By the same token, the *cis*-2-H in **11a** is considerably deshielded with respect to the *trans*-2-H in **11b**. De March and Huisgen[11a] have made a similar observation.



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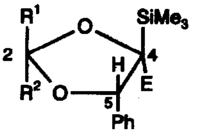
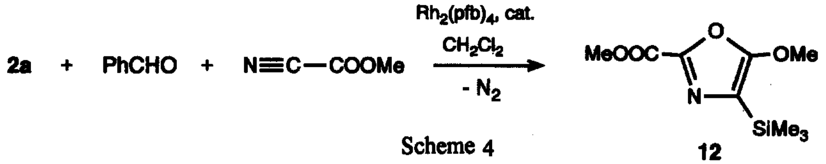


11a : R¹ = Ph, R² = H
11b : R¹ = H, R² = Ph

$Rh_2(pfb)_4$-catalyzed decomposition of **2a** in the presence of benzaldehyde and methyl cyanoformate did not furnish a product derived from a carbonyl ylide. Rather, oxazole **12** was the only isolated product (51 % yield). Formation of oxazoles upon Rh(II)-catalyzed decomposition of α-diazocarbonyl compounds in the presence of nitriles is well precedented[23,24] and has been explained by cycloaddition of the ketocarbenoid intermediate to the nitrile[23] or by 1,5-cyclization of an acyl-substituted nitrile ylide intermediate.[24] The latter mode of formation has recently been corroborated by trapping of the nitrile ylide in a [3+2]-cycloaddition reaction.[24]



Scheme 4 **12**

In summary, we have shown that the Rh(II)-catalyzed reaction between diazo(trialkylsilyl)acetic esters, aldehydes, and sufficiently electron-poor olefinic (acetylenic) dipolarophiles yields tetrahydrofurans (2,5-dihydrofurans) with a remarkable diastereoselectivity. The presence of a trialkylsilyl group at C-2 should be useful for further synthetic transformations of these heterocycles.

EXPERIMENTAL

General Information

NMR spectra: Bruker WP 200 (^{1}H: 200 MHz) and Bruker AM 400 (^{1}H: 400 MHz; ^{13}C-NMR: 100.6 MHz). All spectra were recorded in $CDCl_3$ with CH_2Cl_2 (^{1}H: δ = 5.32) or $CDCl_3$ (^{13}C: δ = 77.0) as internal standard. IR spectra: Perkin-Elmer IR 397; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin-Elmer EA 2400. Diazoacetic esters **2a**[25] and **2b**[25], $Rh_2(C_3F_7COO)_4$[26], $Cu(O_3SCF_3) \cdot ½\, C_6H_6$[27] and $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$[28] were prepared by literature methods. All reactions were carried out in dried solvents and under an argon atmosphere.

Decomposition of Methyl Diazo(trialkylsilyl)acetates 2 in the Presence of Carbonyl Compounds; General Procedure

Carbonyl compounds were generally purified by distillation prior to use. A solution of **2a** or **2b** (2-3 mmol) and carbonyl compound (1 equiv. with respect to the diazo compound) in dichloromethane (15-20 ml) was added over 1.5-2 h at a controlled rate to a stirred solution of catalyst, carbonyl compound (1 equiv.) and dipolarophile (4 equiv.). Stirring was continued until evolution of N_2 had ceased (6-8 h). The solvent was removed at 20 °C / 0.01 mbar, excess carbonyl compound and dipolarophile were distilled off at 40 °C / 0.005 mbar, and the residue was worked up as described below. - Dimethyl fumarate as dipolarophile: At the end of the reaction, the solvent was evaporated, the residue was extracted with pentane (10ml), and the extract was subjected to distillative workup as described.

1. Decomposition of 2a in the presence of benzaldehyde and dimethyl fumarate: 1.1. From **2a** (0.52 g, 3 mmol) and $Rh_2(C_3F_7COO)_4$ (0.10 g, 0.095 mmol, 3.2 mol-%) as catalyst, a crude reaction product was obtained which was subjected to Kugelrohr distillation. At 180 °C / 0.01 mbar a colorless oil was isolated which crystallizes from methanol at 4 °C yielding 0.49 g (41 %) of (2α,3β,4α,5α)-*tetrahydro-5-phenyl-2-trimethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**4a**), mp. 75 °C - ^{1}H-NMR (200 MHz): δ = 0.32 (s, 9 H, $SiMe_3$), 3.11 (s, 3 H, 4-COOMe), 3.75 (s, 6 H, 3- and 2-COOMe); 3.93, 3.96 and 5.57 (ABX system, 4-H, 3-H, 5-H; *J*(3-H, 4-H) = 8.1 Hz, *J*(3-H, 5-H) = -1.1 Hz, *J*(4-H, 5-H) = 10.4 Hz); 7.30 (m, 5 H, Ph). - ^{13}C-NMR: δ = -3.36 ($SiMe_3$), 51.39, 51.79, 51.98 (OMe), 53.35, 53.70 (C-3, C-4), 82.74 (d, C-5), 83.54 (s, C-2), 126.81 (d, 2 C), 127.78 d, 2 C), 128.04 (d), 137.53 (s), 170.50, 171.16, 173.20 (C=O). - IR (KBr): 1715 (C=O). - Anal. calcd. for $C_{19}H_{26}O_7Si$ (394.5): C, 57.84; H, 6.64. Found: C, 57.5; H, 6.6.

1.2. Diazoester **2a** (0.46 g, 2.67 mmol) was decomposed with $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ (51 mg, 0.12 mmol, 4.4 mol-%) in benzene at 80 °C. Workup as described under 1.1 afforded 0.57 g (54%) of **4a**.

1.3. Diazoester **2a** (0.30 g, 1.74 mmol) was decomposed with $CuO_3SCF_3 \cdot ½\, C_6H_6$ (40 mg, 13.5 mol-%). Kugelrohr distillation of the crude product yielded *(2α ,3β)-2-methoxycarbonyl-3-phenyl-2-trimethylsilyl-oxirane* (**5a**) as a colorless oil at 70 °C / 0.01 mbar and tetrahydrofuran **4a** (79 mg, 11.5 %) at 180 °C / 0.01 mbar. - Spectroscopic and analytical data of **5a**: ^{1}H-NMR (400 MHz): δ = -0.05 (s, 9 H, $SiMe_3$), 4.25 (s, 1 H, 3-H), 4.75 (s, 3 H, COOMe), 7.36 (m, Ph). - ^{13}C-NMR: δ = -1.29 ($SiMe_3$), 51.53 (COOMe), 57.44 (C-2), 61.7

(C-3, d, $^1J_{C,H}$ = 176 Hz), 126.63 (d, 2 C), 128.08 (d, 2 C), 128.32 (d), 135.8 (s), 172.71 (C=O). - IR (neat): 1745, 1715 (C=O). - Anal. calcd. for $C_{13}H_{18}O_3Si$ (250.4): C, 62.36; H, 7.25. Found: C, 61.1; H, 7.3.

*2. Decomposition of **2b** in the presence of benzaldehyde and dimethyl fumarate:* From **2b** (0.41 g, 1.9 mmol) and $Rh_2(C_3F_7COO)_4$ as catalyst (41 mg, 0.039 mmol, 2 mol-%), a crude product was obtained which was subjected to Kugelrohr distillation. At 230 °C / 0.1 mbar, *(2α,3β,4α,5α)-tetrahydro-5-phenyl-2-triethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**4b**) was obtained as a colorless oil which crystallized from methanol at 4 °C; yield: 0.37 g (46 %); mp. 47 °C. - ^{1}H-NMR (400 MHz): δ = 0.78 - 0.86 (m, 6 H, $SiCH_2$), 0.99 (t, 9 H, $SiCH_2$-CH_3), 2.99 (s, 3 H, 4-COOMe), 3.63, 3.66 (each s, 3 H, COOMe), 3.78 (dd, *J* = 9.6, 7.8 Hz, 4-H), 3.89 (d, *J* = 7.8 Hz, 3-H), 5.40 (d, *J* = 9.6 Hz, 5-H), 7.30 (m, 5 H, Ph). - ^{13}C-NMR: δ = 2.11 (Si-CH_2-), 7.35 (Si-CH_2-CH_3), 51.42, 51.74, 52.04 (OMe), 52.49, 53.53 (C-3, C-4), 82.79 (C-5), 83.92 (C-2), 127.80 (d, 2 C), 127.82 (d, 2 C), 128.98 (d), 137.45 (s), 170.64, 171.46, 173.42 (C=O). - IR (neat): 1720 (C=O). - Anal. Calcd. for $C_{22}H_{32}O_7Si$ (436.6): C, 60.53; H, 7.39. Found: C, 60.4; H, 7.4.

*3. Diazoester **2a**, benzaldehyde, and dimethyl maleate: 3.1.* From **2a** (0.44 g, 2.55 mmol) and $Rh_2(C_3F_7COO)_4$ as catalyst (0.12 g, 0.11 mmol, 4.4 mol-%), a crude product was obtained which was subjected to Kugelrohr distillation. At 180 °C / 0.1 mbar *(2α,3α,4α,5α)-tetrahydro-5-phenyl-2-trimethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**6**) was obtained as a colorless oil which crystallized from methanol at 4 °C; yield: 0.49 g (49 %); mp. 73 °C. - ^{1}H-NMR (400 MHz): δ = 0.31 (s, 9 H, $SiMe_3$), 3.16 (s, 3 H, 4-COOMe), 3.69 (s, 3 H, COOMe), 3.79 (s, 3 H, COOMe), 3.71 (dd, *J* = 9.2, 7.8 Hz, 4-H), 3.99 (d, *J* = 9.2 Hz, 3-H), 5.27 (d, *J* = 7.8 Hz, 5-H), 7.25-7.42 (m, 5 H, Ph). - ^{13}C-NMR: δ = -3.32 ($SiMe_3$), 51.15, 51.86, 52.01 (OMe), 53.52, 53.86 (C-3, C-4), 82.31 (d, C-5), 84.40 (s, C-2), 126.76 (d, 2 C), 127.73 (d, 2 C), 127.78 (d), 136.76 (s), 169.70, 171.05, 175.81 (C=O). - IR (KBr): 1695 - 1740 (broad, C=O). - Anal. calcd. for $C_{19}H_{26}O_7Si$ (394.5): C, 57.84; H, 6.64. Found: C, 57.5; H, 6.4.

3.2. Diazoester **2a** (0.52 g, 3.02 mmol) was decomposed with $CuO_3SCF_3 \cdot \frac{1}{2} C_6H_6$ (60 mg, 7.9 mol-%) according to the general procedure. Kugelrohr distillation of the crude product yielded *(2α,3β)-2-methoxycarbonyl-3-phenyl-2-trimethylsilyl-oxirane* (**5a**) as a colorless oil at 70 °C / 0.01 mbar and tetrahydrofuran **6** (0.18 g, 15.5 %) at 180 °C / 0.01 mbar.

*4. Diazoester **2a**, crotonaldehyde, and dimethyl fumarate.* Diazoester **2a** (0.36 g, 2.08 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (50 mg, 0.047 mmol, 2.3 mol-%) according to the general procedure. Kugelrohr distillation at 130 °C / 0.1 mbar yielded 0.32 g (44 %) of *tetrahydro-5-(1-propenyl)-2-trimethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**7**). The *(2α,3β,4α,5α)*-configuration was tentatively assigned. - ^{1}H-NMR (200 MHz): δ = 0.14 (s, 9 H, $SiMe_3$), 1.61 (d, 3 H, Me), 3.57, 3.62, 3.65 (3 x s, each 3 H, 2-, 3- and 4-COOMe), 3.55-3.69, (m, 3-H, 4-H); 4.83 (m_c, 5-H); 5.20 (m, Me-CH=C*H*), 5.72 (ddq, *J* = 15.1, 6.6, 0.7 Hz Me-C*H*=). - ^{13}C-NMR: δ = -3.49 ($SiMe_3$), 17.56 (Me), 52.22, (OMe, C-3, C-4), 81.03 (d, C-5), 82.92 (s, C-2), 127.14 (d), 130.65 (d), 170.03, 171.01, 173.46 (C=O). - IR (neat): 1735, 1728, 1715 (C=O). - Anal. calcd. for $C_{16}H_{26}O_7Si$ (358.5): C, 53.61; H, 7.31. Found: C, 53.4; H, 7.2.

*5. Diazoester **2a**, acetaldehyde, and dimethyl fumarate.* Diazoester **2a** (0.47 g, 2.73 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (64 mg, 0.06 mmol, 2.2 mol-%) according to the general procedure. Kugelrohr distillation at 70 °C / 0.01 mbar yielded 0.39 g (43 %) of *tetrahydro-5-methyl-2-trimethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**8**). The *(2α,3β,4α,5α)*-configuration was tentatively assigned. - ^{1}H-NMR (400 MHz): δ = 0.14 (s, 9 H, $SiMe_3$), 1.25 (d, *J* = 6.4 Hz 3 H, Me), 3.64, 3.66, 3.67 (s, 3 H, 2-, 3- and 4-COOMe); 3.70-3.80 (m, 3-H, 4-H), 4.73 (m, 5-H). - ^{13}C-NMR: δ = -3.58 ($SiMe_3$), 17.57 (Me), 50.93, 51.40, 51.71 (OMe), 51.55 (C-3, C-4), 75.85 (d, C-5), 82.69 (s, C-2), 170.15, 171.32, 173.38 (3 x C=O). - IR (neat): 1710 (broad, C=O). - The product did not give a satisfactory elemental analysis. (^{1}H-NMR: Impurities in the aliphatic region.)

6. *Diazoester 2a, cyclohexanone, and dimethyl fumarate.* Diazoester **2a** (0.45 g, 2.61 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (42 mg, 0.039 mmol, 1.5 mol-%) according to the general procedure. Kugelrohr distillation at 70 °C / 0.005 mbar afforded a colorless oil which was purified further by column chromatography (Merck Lobar column, silica gel, eluant ether / petroleum ether (3:7)). A fraction (0.15 g) was obtained which consisted mainly of *methyl (1-cyclohexenyloxy)trimethylsilylacetate* (**9**) but contained also 20-25 % of an unknown ester. ^{1}H-NMR (200 MHz): δ = 0.78 (s, 9 H, $SiMe_3$), ca. 1.4-2.2 (m, CH_2, cyclohexenyl), 3.65 (s, 3 H, COOMe), 4.12 (s, *CH*-Si), 4.45 (m, *CH*=). - ^{13}C-NMR: δ = -3.57 ($SiMe_3$), 22.56, 22.78, 23.36, 27.53 (CH_2, cyclohexenyl), 51.06 (OMe), 70.62 (O-CH), 94.23 (CH=), 155.60 (=C-O), 172.85 (C=O). -

7. *Diazoester 2a, benzaldehyde, and dimethyl acetylenedicarboxylate.* Diazoester **2a** (0.36 g, 2.08 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (48 mg, 0.045 mmol, 2.2 mol-%) according to the general procedure. After removal of excess aldehyde and alkyne by distillation at 50 °C / 0.05 mbar, the residue was recrystallized from pentane, yielding 0.50 g (62 %) *(2α,5α)-2,5-dihydro-5-phenyl-2-trimethylsilyl-2,3,4-furantricarboxylic acid trimethyl ester* (**10**); mp. 103 °C.- ^{1}H-NMR (400 MHz): δ = 0.22 (s, $SiMe_3$), 3.60, 3.78, 3.86 (each s, 2-, 3-, and 4- COOMe); 6.23 (s, 5-H); 7.35 (m, 5 H, Ph). - ^{13}C-NMR: δ = -3.18 ($SiMe_3$), 51.96, 52.12, 52.36 (OMe), 88.48 (C-5), 91.43 (C-2), 127.70 (d, 2 C); 128.29 (d, 2 C); 128.69 (d, 1 C); 137.77 (s); 141.28 (C-4); 162.56, 163.41, 171.37 (3 x C=O). - IR (KBr): 1735 - 1705 (broad, C=O), 1695 (sh), 1645 (m, C=C). - Anal. calcd. for $C_{19}H_{24}O_7Si$ (392.5): C, 58.14; H, 6.16. Found: C, 56.7; H, 5.9.

8. *Diazoester 2a, benzaldehyde and 1-phenylsulfonyl-1-propyne. 8.1.* Diazoester **2a** (0.46 g, 2.67 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (74 mg, 0.07 mmol, 2.6 mol-%) according to the general procedure. Kugelrohr distillation of the crude product at 250 °C / 0.1 mbar afforded a colorless oil which was purified further by a column chromatography (Merck Lobar column, silica gel, eluant diethyl ether / petroleum ether (2:8)) to give 0.21 g (22 %) of *2,5-diphenyl-4-methoxycarbonyl-4-trimethylsilyl-1,3-dioxolane* [diastereomeric mixture of *(2α,4α,5β)* (**11a**) and *(2α,4β,5α)* (**11b**) in the ratio 2.3:1]. - Spectral data of **11a**: ^{1}H-NMR (400 MHz): δ = 0.26 (s, 9 H, $SiMe_3$), 3.26 (s, 3 H, COOMe), 5.37 (s, 5-H), 6.63 (s, 2-H). - ^{13}C-NMR: δ = -3.12 ($SiMe_3$), 50.84 (OMe), 82.87 (C-5), 84.46 (C-4), 105.11 (C-2), 126.64-129.77 (Ph), 137.54 (s), 137.98 (s), 172.48 (C=O). - Spectral data of **11b**: ^{1}H-NMR (400 MHz): δ = 0.29 (s, 9 H, $SiMe_3$), 3.23 (s, 3 H, COOMe), 5.35 (s, 5-H), 5.92 (s, 2-H). - ^{13}C-NMR: δ = -2.91 ($SiMe_3$), 50.84 (OMe), 83.29 (C-5), 84.35 (C-4), 105.11 (C-2), 126.64-129.77 (Ph), 135.67 (s), 137.66 (s), 172.68 (C=O). - IR (neat): 1712 (C=O). - Anal. calcd. for $C_{20}H_{24}O_4Si$ (356.5): C, 67.38; H, 6.79. Found: C, 66.9; H, 6.8.

From **2a** (0.50 g, 2.9 mmol) and $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ (0.12 g, 0.28 mmol, 9.6 mol-%) as catalyst, a crude reaction product was obtained which was subjected to Kugelrohr distillation. At 180 °C / 0.01 mbar a colorless oil was obtained which was further purified by a column chromatography (Merck Lobar column, silica gel, eluant ether / pertroleum ether (3:7)), yielding 0.24 g (23 %) of **11a**.

9. *Diazoester 2a, benzaldehyde, and methyl cyanoformate.* Diazoester **2a** (0.43 g, 2.5 mmol) was decomposed with $Rh_2(C_3F_7COO)_4$ (70 mg, 0.07 mmol, 2.7 mol-%). Kugelrohr distillation of the crude product at 150 °C / 0.004 mbar yielded a colorless oil which was purified further by column chromatography (Merck Lobar column, silica gel, eluant diethyl ether / petroleum ether (1:1)) to afford 0.29 g (51 %) of *5-methoxy-2-methoxycarbonyl-4-trimethylsilyl-1,3-oxazole* (**12**). - ^{1}H-NMR (400 MHz): δ = 0.19 (s, 9 H, $SiMe_3$), 3.88 (s, 3 H), 4.00 (s, 3 H). - ^{13}C-NMR: δ = -1.71 ($SiMe_3$), 52.61 (OMe), 58.83 (OMe), 115.11 (C-4), 144.38 (C-2), 155.70 (C-5), 165.50 (C=O). - IR (neat): 1740 (s), 1720 (sh), 1687 (s). Anal. calcd. for $C_9H_{15}NO_4Si$ (229.4): C, 47.12; H, 6.59; N, 6.11. Found: C, 47.1; H, 6.5; N, 6.0.

X-Ray Crystal Structure Analysis of 4a[29]

Crystal Data: $C_{19}H_{26}O_7Si$, f.w. = 394.5; orthorhombic, space group Pbca; a = 16.188(3), b = 15.064(3), c = 17.418(4) Å; $\alpha = \beta = \gamma = 90°$; V = 4247.5 Å^3; Z = 8, D_x = 1.24 g·cm^{-3}; crystal size 0.6 x 0.55 x 0.5 mm. - *Data collection*: T = 295 K; diffractometer Enraf-Nonius CAD4, monochromatized Mo-K_α radiation; $\omega/2\theta$-

scan, scan width (0.85 + 0.35 tan θ) °; 3312 unique reflections with $2.0 \leq \theta \leq 24.0$ °; no absorption correction ($\mu = 1.4$ cm^{-1}) - ***Structure solution and refinement***: Structure solution by *SHELXS-86*, full-matrix least-squares refinement by *SHELX-76*, hydrogen atoms were in calculated positions and only H3, H4, H16, H18, H19 were refined; unit weights, 2129 observed reflections [$I > 3\ \sigma(I)$], 287 variables, $R = 0.074$, $R_w = 0.074$; residual electron density 0.33 e·Å^{-3}.

X-Ray Crystal Structure Analysis of ***6***[29,30]

Crystal Data: $C_{19}H_{26}O_7Si$, f.w. = 394.5; monoclinic, space group $P2_1/c$; a =12.167(3), b = 9.934(2), c = 17.504(3) Å; $\alpha = 90$, $\beta = 110.38(2)$, $\gamma = 90°$; V = 1983.1 A^3; $Z = 4$, $D_x = 1.32$ g·cm^{-3}; crystal size 0.65 x 0.6 x 0.4 mm. - *Data collection*: $T = 295$ K; diffractometer Enraf-Nonius CAD4, monochromatized Mo-$K\alpha$ radiation; ω/2θ-scan, scan width (1.00 + 0.35 tan θ) °; 4417 reflections measured, 4137 unique reflections with $2.0 \leq \theta \leq 26.0$ °; no absorption correction ($\mu = 1.49$ cm^{-1}) - ***Structure solution and refinement***: Structure solution by *SIR*, full-matrix least-squares refinement. Refinement converged at $R = 0.0483$, $R_w = [\sum w\Delta^2 F / \sum wF_o^2]^{1/2} = 0.0497$ [3215 reflections with $I > 2\ \sigma(I)$, 348 variables, $w = 4\ F_{obs}^2 / \sigma^2(F_{obs}^2)$]. The residual electron density was 0.50 e·Å^{-3}.

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REFERENCES AND NOTES

1. Padwa, A.; Hornbuckle, S. *Chem. Rev.* **1991**, *91*, 263-309.
2. Padwa, A. *Acc. Chem. Res.* **1991**, *24*, 22-28.
3. Ibata, T.; Nakano, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1362-1370; and references cited therein.
4. Padwa, A.; Chinn, R.L.; Hornbuckle, S.F.; Zhang, Z.J. *J. Org. Chem.* **1991**, *56*, 3271-3278. Rodgers, J.D.; Caldwell, G.W.; Gauthier, A.D. *Tetrahedron Lett.* **1992**, *33*, 3273-3276. Cox, G.G.; Moody, C.J.; Austin, D.J.; Padwa, A. *Tetrahedron* **1993**, *49*, 5109-5126. Padwa, A.; Dean, D.C.; Fairfax, D.J.; Xu, S.L. *J. Org. Chem.* **1993**, *58*, 4646-4655.
5. Regitz, M. (Ed.): *Methoden der organischen Chemie (Houben-Weyl)*; Vol. E19b; Thieme: Stuttgart, 1989.
6. Dieckmann, W. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1024-1031.
7. Kharash, M.S.; Rudy, T.; Nudenberg, W.; Büchi, G. *J. Org. Chem.* **1953**, *18*, 1030-1044.
8. Landgrebe, J.A.; Iranmanesh, H. *J. Org. Chem.* **1978**, *43*, 1244. Lottes, A.C.; Landgebe, J.A.; Larsen, K. *Tetrahedron Lett.* **1989**, *30*, 4089-4092 and 4093-4096.
9. Joshi, G.S.; Kulkarni, G.H.; Shapiro, E.A. *Chem. Ind.* **1988**, 631-632.
10. Saltykova, L.E.; Vasil'vitskii, A.E.; Shostakovskii, V.M.; Nefedov, O.M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 842-847.
11. (a) De March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4952. (b) Huisgen, R.; de March, P. *ibid.*, 4953-4954.
12. L'Esperance, R.P.; Ford, T.M.; Jones jr., M. *J. Am. Chem. Soc.* **1988**, *110*, 209.
13. Dworschak, H.; Weygand, F. *Chem. Ber.* **1968**, *101*, 289-301.
14. Alonso, M. E.; del Carmen Garcia, M. *J. Org. Chem.* **1985**, *50*, 3445-3449.
15. Takebayashi, M.; Ibata, T.; Ueda, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1500-1505.
16. Kaufmann, K.-D.; Rühlmann, K. Z. Chem. **1968**, *8*, 263-265.
17. Maas, G.; Gimmy, M.; Alt, M. *Organometallics* **1992**, *11*, 3813-3820.
18. Maas, G.; Werle, T.; Alt, M.; Mayer, D. *Tetrahedron* **1993**, *49*, 881 - 888.

19. Huisgen, R. in *1,3-Dipolar Cycloaddition Chemistry;* Padwa, A. Ed.; John Wiley and Sons, Inc.: New York, 1984; Vol. 1, pp. 1 - 176.
20. Gill, H.S.; Landgrebe, J.A. *J. Org. Chem.* **1983**, *48*, 1051 - 1055.
21. Keller, E. SCHAKAL: A Fortran Program for the Graphic Representation of Molecular and Crystallographic Models; Version 88B / V16; Freiburg (Germany) 1990.
22. Houk, K.N.; Rondan, N.G.; Santiago, C.; Gallo, C.J.; Wells Gandour, R.; Griffin, G.W. *J. Am. Chem. Soc.* **1980**, *102*, 1504-1512.
23. Huisgen, R.; König, H.; Binsch, G.; Sturm, H.J. *Angew. Chem.* **1961**, *73*, 368-371.
24. Ibata, T.; Fukushima, K.; *Chem. Lett.* **1992**, 2197 - 2200.
25. Allspach, T.; Gümbel, H.; Regitz, M. *J. Organomet. Chem.* **1985**, *290*, 33 - 39.
26. Drago, R.S.; Long, J.R.; Cosmano, R. *Inorg. Chem.* **1982**, *21*, 2196 - 2202.
27. Salomon, R.G.; Kochi, J.K.; *J. Am. Chem. Soc.* **1973**, *95*, 3300 - 3310.
28. Crooks, G.R.; Johnson, B.F.G.; Lewis, J.; Williams, I.G.; Gamlen, G. *J. Chem. Soc.(A)* **1969**, 2761 - 2766.
29. Tables of atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England. The data are available on request from the Director of CCDC by quoting the full literature citation of this paper.
30. Calculations were done with the *Structure Determination Package* (Enraf-Nonius, Delft, The Netherlands).

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