Cycloadditions, 34[1]

Donor-Substituted Allenes in Diels-Alder Reactions with Inverse Electron Demand

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Several cycloaddition reactions of 1-alkoxy-1,2-propadienes **1** with 1-oxa-1,3-dienes **2**, catalyzed by acid-free silica gel, are described. The resulting 3,4-dihydro-3-methylene-2*H*-pyrans **3** are transformed into synthetically interesting glutaraldehyde derivatives **10**–**13**.

The inverse Diels-Alder reaction[3] of 1-oxa-1,3-butadienes with enol ethers[4] or allenic dienophiles[5,6,7] often suffers from low conversions, which can be improved by the use of electron-poor dienes[8], by Lewis acid catalysis, by high-pressure techniques[9] or by the use of (*c*, *d*) olefins[10] as dienophiles[11].

In the course of our investigations concerning the activation of dienophiles in $LUMO_{diene}$-controlled Diels-Alder reactions[11] we have studied some reactions of allenic compounds with various 1-oxa-1,3-dienes. The reaction of 1-ethoxy-1,2-propadiene (**1a**) with 2-propenal (**2a**) or 3-methyl-2-propenal (**2d**) at 150°C leads to the desired dihydropyrans **3a/d**[6a,12], in moderate yields. Using Lewis-acid catalysts [e. g. ZnI_2, F_3B-OEt_2, $EtAlCl_2$, Cu(II) acetate] we have found a decrease in selectivity. In addition, allenol ethers have been found to undergo a 1,3-intermolecular rearrangement under the catalytic influence of F_3B-OEt_2[13]. Soluble lanthanide complexes, which allow the presence of acid-sensitive functionalities, have proved to be efficient catalysts for hetero Diels-Alder reactions[14]. So we tried to use $Yb(fod)_3$ in the reactions of **1a** with **2a**–**c**. This catalyst accelerates the rate of the cycloadditions, but its use is limited by its price. In this paper we present a new method for performing such reactions with higher yields and selectivities.

There are some examples which show that silica gel can control the regioselectivity and the rate of photochemical reactions if the starting materials are adsorbed on the SiO_2 surface[15]. Other research groups have demonstrated that silica gel can serve as a catalyst in reactions which need Lewis-acid catalysis[16]. This and some work on Diels-Alder reactions under *dry-state adsorption conditions* (DSAC)[17] prompted us to investigate the influence of silica gel on hetero Diels-Alder reactions of allenes. A crucial problem arises from the high surface acidity of pure silica which often leads to decomposition and polymerization of the cycloaddition products. One way for avoiding these acid-catalyzed reactions is the use of the more basic Florisil ($MgO \cdot SiO_2$) as support for hetero Diels-Alder reactions[17], but this leads to a decrease in the rate of reaction. We have found a simple way to avoid side reactions by deactivating the dried SiO_2 with NEt_3 (0.2–0.5%). Alumina shows no catalytic activity in these inverse Diels-Alder reactions, while there is an influence on the rate and selectivity of alumina-supported normal Diels-Alder reactions[18].

Cycloadditions with 1-Oxa-1,3-dienes

Under DSAC the reactions of 1-ethoxy-1,2-propadiene (**1a**)[19] with acrolein (**2a**), 3-buten-2-one (**2b**), and 2-methyl-2-propenal (**2c**) are accelerated (Table 1). The reaction of **1a** with 2-butenal (**2d**) at 70°C yields only traces of products even after 2 weeks. This may be explained by the steric hindrance by the methyl group if the enone is adsorbed with the less hindered side to the silica gel[20].

In all reactions we have found traces of products formed from a dimerization product of the enone and **1**. Another byproduct of the [4 + 2] cycloadditions are the [2 + 2] cycloadducts **4**. Whereas the reactions of **2a** and **2b** show high selectivities for the Diels-Alder products, the cyclobutane **4b** is formed as a main product in the reaction of **2c**. Under DSAC the Diels-Alder selectivity is strongly enhanced.

Whereas dihydropyrans can be formed in a concerted [4 + 2] cycloaddition via a less polar transition state, cyclobutanes have to be generated by a dipolar intermediate mechanism, as has been shown mainly by solvent effects on the reaction rates[21]. In the case of other electron-rich dienophiles (e. g. enamines, ynamines, ketene acetals) it has been shown that the reaction of the zwitterionic intermediate leads to [2 + 2] and [4 + 2] products[4b,22], and the resulting cyclobutanes isomerize on heating to the thermodynamically more stable dihydropyrans. For the reactions studied in this work, a similar mechanism may be possible, but a

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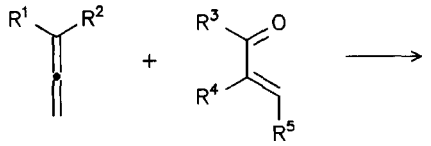
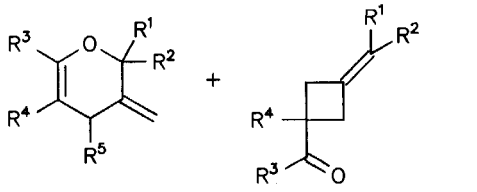
rearrangement of **4b** to **3c** has not been observed, even at 130°C.



1a–c **2a–d**



3a–i **4a–f**

	R^1	R^2	R^3	R^4	R^5
1a	EtO	H			
1b	MeO	Me_3Si			
1c	MeO	H			
2a			H	H	H
2b			Me	H	H
2c			H	Me	H
2d			H	H	Me
3a	EtO	H	H	H	H
3b	EtO	H	Me	H	H
3c	EtO	H	H	Me	H
3d	EtO	H	H	H	Me

	R^1	R^2	R^3	R^4	R^5
3e	MeO	Me_3Si	H	H	H
3f	MeO	Me_3Si	Me	H	H
3g	MeO	Me_3Si	H	Me	H
3h	MeO	H	H	H	H
3i	MeO	H	Me	H	H
4a	EtO	H	Me	H	H
4b	EtO	H	H	Me	H
4c	MeO	Me_3Si	H	H	H
4d	MeO	Me_3Si	Me	H	H
4e	MeO	Me_3Si	H	Me	H
4f	MeO	H	H	Me	H

Table 1. Diels-Alder reactions of 1-ethoxy-1,2-propadiene (**1a**)

Diene	Reaction conditions	Yield[a]	Selectivity[b]
2a	150 °C, 2h	41%[6a]	
	70 °C, 20h	66%	
	25 °C, 20h	15%[c]	
	70 °C, 10h, SiO_2	71%	
	25 °C, 20h, $Yb(fod)_3$[d]	72%[c]	
2b	70 °C, 20h	35%[c]	90%
	50 °C, 48h	62%	85%
	25 °C, 20h	5%[c]	
	50 °C, 10h, SiO_2	68%	91%
	25 °C, 20h, $Yb(fod)_3$[d]	40%[c]	87%
2c	70 °C, 24h	54%	60%
	70 °C, 15h, SiO_2	58%	>90%
	25 °C, 20h, $Yb(fod)_3$[d]	only dimers	
2d	150 °C, 3h	19%[6a]	
	70 °C, 14d, SiO_2	< 5%	

[a] Yield of 1:1 products. — [b] Diels-Alder products **3**. — [c] From GC. — [d] 5 mol-%.

The regioselectivity of this [2 + 2] cycloaddition is remarkable, because the allene forms only the head-to-tail product of the terminal double bond[23]. In contrast, photocycloaddition reactions of 1,2-propadiene with enones preferably result in the formation of the head-to-head products[24]. One reason for the high head-to-tail selectivity may be the methylenecyclobutane rearrangement which leads to the most stable cyclobutane[25]. Furthermore, the head-to-head products (2-alkoxy-3-methylenecyclobutanecarbaldehydes) should quickly rearrange to afford dihydropyrans as has been shown for 2,2-dialkoxycyclobutanecarbaldehydes[26].

In order to test the scope and limitations of silica gel catalysis we have studied the reactions of some substituted allenes with enone **2a**. 1,2-Cyclononadiene[27] reacts with **2a** at 70°C (4 days) to give four 1:1 adducts, which cannot be separated. Silica gel has nearly no influence on the selectivity and rate of this addition. 1,2-heptadiene[27] does not react either under DSAC (70–120°C, 2 weeks) or under Lewis-acid catalysis conditions [$EtAlCl_2$, $Yb(fod)_3$]. The thermal reaction of 2,4-dimethylpenta-2,3-diene (TMA) with **2a** yields 4-isopropenyl-5-methyl-4-hexenal[1b], the product of the ene reaction, which is often found as side reaction in cycloadditions of TMA with electron-deficient olefins[28].

1-Methoxy-1-(trimethylsilyl)-1,2-propadiene (**1b**) as dienophile displays a lower Diels-Alder selectivity in reactions with **2a–c**. The additional substituents at the allene moiety lead to a decrease in the selectivity and rate of reaction. Steric reasons limit the influence of silica-gel catalysis in this case.

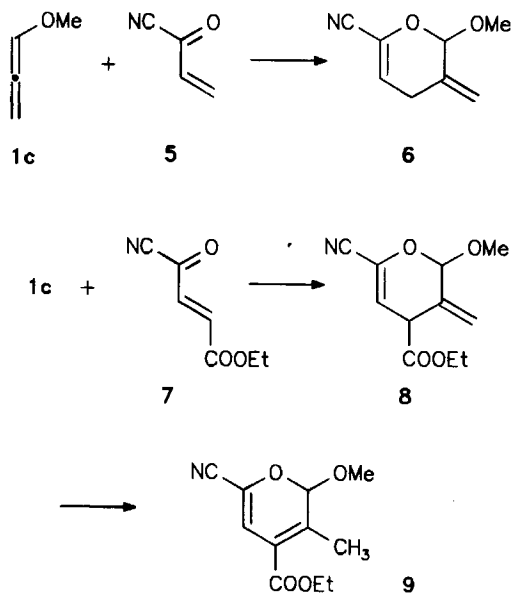
Table 2. Diels-Alder reactions of 1-methoxy-1-(trimethylsilyl)-1,2-propadiene (**1b**)

Diene	Reaction conditions	Yield[a]	Selectivity[b]
2a	70 °C, 24h	78%	64%
	100 °C, 8h	65%	74%
	70 °C, 72h, SiO_2[c]		54%
	70 °C, 120h, SiO_2		84%
2b	70 °C, 72h	47%	64%
	70 °C, 24h		53%
	70 °C, 24h, SiO_2		34%
2c	70 °C, 64h	60%	15%
	70 °C, 24h, SiO_2	70%	55%

[a] Yield of 1:1 products. — [b] Diels-Alder products **3**. — [c] Without NEt_3.

Hetero Diels-Alder Reactions with Activated Enones

The α,β-unsaturated acyl cyanides, described by Wyler[29], exhibit excellent thermal reactivity towards ethyl vinyl ether cleanly providing the [4 + 2] cycloadducts. Accordingly, we have tested the reactions of 1-methoxy-1,2-propadiene (**1c**) with the acyl cyanides **5** and **7**. Both additions are complete within one hour at room temperature and afford the expected six-membered rings in good yields. The dihydropyran **8** rearranges at room temperature to give the pyran derivative **9**.



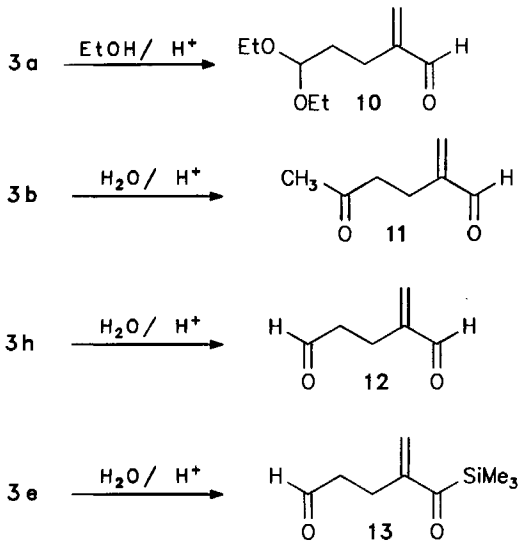
1c 5 6

1c + 7 8

9

Transformations of the Dihydropyrans

The formerly prepared 2-alkoxy-3,4-dihydro-3-methylene-2*H*-pyrans are hydrolyzed by treatment with an acidic ion-exchange resin (Lewatit SC 108) in aqueous methanol or ethanol to give the corresponding carbonyl compounds. In this manner we have prepared glutaraldehyde derivatives, which can serve as useful anellating reagents for the construction of heterocycles[30]. Hydrolysis of the trimethylsilyl-substituted dihydropyrans leads to acyl silanes[31].



In summary, we have been able to show, that alkoxyallenes are suitabel dienophiles in inverse Diels-Alder reactions with 1-oxa-1,3-dienes. Catalysis of these reactions by silica gel under dry-state adsorption conditions may influence selectivity and rate of reaction. The hetero Diels-Alder reaction of alkoxyallenes offers a route to some synthetically interesting compounds.

Studies of the full scope of the [4 + 2] cycloaddition reactions of electron-rich allenes and the synthetic use of the obtained products are in progress. The presence of a six-membered oxygen heterocyclic ring in a range of naturally occuring compounds[32] provides the stimulus for further work on this subject.

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Experimental

All cycloaddition reactions were carried out under argon in sealed tubes or glass autoclaves. 2-Propenal (**2a**), 3-buten-2-one (**2b**), 2-methyl-2-propenal (**2c**), and 2-butenal (**2d**) were purchased from Aldrich, distilled before use, and stabilized with 2,6-di-*tert*-butylphenol. All reagents were of commercial quality from freshly opened containers. Merck silica gel 60 (0.063–0.2 mm) and Florisil (Fluka) were dried at 150°C in vacuo for 6 h. Diethyl ether was dried with potassium hydroxide and distilled over $LiAlH_4$. Dichloromethane was distilled over calcium hydride. The other solvents were purified by distillation. – ^1H and ^{13}C NMR: Varian VXR 300 (300/75 MHz) or Bruker WM 300 (300/75 MHz), TMS internal standard, all ^{13}C NMR with proton-noise decoupling. – IR: Perkin-Elmer 257 or Perkin-Elmer 1750. – MS: Varian Mat 212. – Melting points: Büchi 510, uncorrected. – Microanalyses: Mikroanalytisches Laboratorium der Technischen Hochschule Aachen and Analytisches Laboratorium des Organisch-Chemischen Instituts der Universität Münster. – GC analyses: Siemens Sichromat 3 with 25 m HP Ultra 2. – Silica gel 60 (230–400 mesh): Macherey & Nagel. – Analytical TLC plates: Merck. – HPLC: Kontron HPLC-Pumpe 420, Kontron UV-Detektor 432, RI-Detektor 8110 (Fa. Bischoff), a column LiChrosorb Si 60-5 (2 × 25 cm) (Chromatographie-Service).

General Procedure for the Hetero Diels-Alder Reactions: A mixture of 1 equivalent of the hetero diene and 1 equivalent of the allene was prepared at 0°C. For reactions under DSAC silica gel (2.5–3 weight equivalents) and 0.2–0.5% of NEt_3 were added, and the reaction vessel was shaken vigorously. The mixture was allowed to stand at the temperature and time indicated for each compound. Usual product isolation was effected by extraction of the silica gel with ether, solvent removal, and distillation of the residue.

3,4-Dihydro-2-methoxy-3-methylene-2-(trimethylsilyl)-2H-pyran (**3e**): From 18.0 g (0.32 mol) of **2a** and 20.0 g (0.14 mol) of **1b**[27] after 24 h at 70°C. In order to remove polymers, the crude mixture was filtered (silica gel, ether) and then fractionated through a 20-cm Vigreux column (b.p. 65°C/16 mbar). Yield 12.9 g (47%) of **3e**. A second fraction (b.p. 80°C/16 mbar) contained the [2 + 2] cycloaddition product **4c**; yield 7.2 g (26%) of **4c**. – IR (film): $\tilde{\nu}$ = 3060, 2955, 2900, 2820 cm^{-1} (CH), 1660 (C=C), 1250 (C–Si). – ^1H NMR ($CDCl_3$): δ = 0 (s, 9H, $SiMe_3$), 2.71 (d/d/d, *J* = 20/5/1 Hz, 1H, 4-H), 2.85 (d/m, *J* = 20 Hz, 1H, 4-H), 3.20 (s, 3H, CH_3O), 4.61 (d/d/d, *J* = 6/5/2.5 Hz, 1H, 5-H), 4.92 (d/d, *J* = 2.3/1.7 Hz, 1H, =CH), 5.08 (d/d, *J* = 2.7/2.3 Hz, 1H, =CH), 6.45 (d/d/d, *J* = 6/2.7/1 Hz, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = –2.99 ($SiMe_3$), 28.77 (C-4), 50.05 (CH_3O), 98.98 (C-5), 106.34 (C-3), 111.78 (=CH_2), 139.75 (C-2), 144.54 (C-6). – MS (70 eV): *m/z* (%) = 199 (3.31), 198 (19.25) [M^+], 73 (100).

3-[Methoxy(trimethylsilyl)methylene]cyclobutanecarbaldehyde (**4c**): For preparation see **3e**. – IR (film): $\tilde{\nu}$ = 2960, 2910, 2820, 2705 cm^{-1} (CH), 1720 (C=O), 1640 (C=C), 1250 (C–Si). – ^1H NMR ($CDCl_3$): δ = 0.07 (s, 9H, $SiMe_3$), 2.93–2.96 (m, 2H, 2-H_{trans}/4-H_{trans}), 3.06–3.18 (m, 3H, 1-H/2H_{cis}/4-H_{cis}), 3.52 (s, 3H, CH_3O),

9.74 (d, J = 0.9 Hz, CHO). – ^{13}C NMR ($CDCl_3$): δ = −1.74 (CH_3Si), 29.41/30.83 (CH_2), 40.85 (C-1), 57.64 (CH_3O), 124.47 (C-2), 154.94 (=$CSiMe_3$), 200.61 (CHO). – MS (70 eV): m/z (%) = 198 (11.1) [M^+], 73 (100).

3,4-Dihydro-2-methoxy-6-methyl-3-methylene-2-(trimethylsilyl)-2H-pyran (**3f**): From 10.5 g (0.15 mol) of **2b** and 20.0 g (0.14 mol) of **1b** at 70°C after 72 h. Distillation gave 14.0 g (47%) of **3f**, b.p. 110°C/14 mbar. – IR (film): $\tilde{\nu}$ = 3060, 2960, 2812 cm^{-1} (CH), 1690 (C=C), 1250 (C–Si). – ^{1}H NMR ($CDCl_3$): δ = 0.04 (s, 9H, $SiMe_3$), 1.78 (m, 3H, CH_3), 2.68 (d/d/m, J = 19.1/5 Hz, 1H, 4-H), 2.82 (d/m, J = 19.1 Hz, 1H, 4-H), 3.2 (s, 3H, CH_3O), 4.41 (m, 1H, 5-H), 4.90 (m, 1H, =CH), 5.04 (d/m, J = 5 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = −4.08 ($SiMe_3$), 19.57 (CH_3), 28.36 (C-4), 48.7 (CH_3O), 93.2 (C-5), 105.13 (C-2), 109.53 (=CH_2), 138.79 (C-6), 150.38 (C-3).

$C_{11}H_{20}O_2Si$ (212.3) Calcd. C 62.21 H 9.49
Found C 62.34 H 9.70

3,4-Dihydro-2-methoxy-5-methyl-3-methylene-2-(trimethylsilyl)-2H-pyran (**3g**): From 0.70 g (10 mmol) of **2c**, 1.4 g (10 mmol) of **1b**, and 5.0 g of silica gel at 70°C after 20 h. Distillation gave 0.80 g (38%) of **3g**, b.p. 105°C/14 mbar. – IR (film): $\tilde{\nu}$ = 2975, 2935, 2870 cm^{-1} (CH), 1635 (C=C), 1250 (C–Si). – ^{1}H NMR ($CDCl_3$): δ = 0.06 (s, 9H, $SiMe_3$), 1.54 (s, 3H, CH_3), 2.58 (d, J = 19 Hz, 1H, 4-H), 2.80 (d/d/d, J = 19/2/1 Hz, 1H, 4-H), 3.18 (s, 3H, CH_3O), 4.91 (t, J = 2 Hz, 1H, =CH), 5.06 (t, J = 1 Hz, 1H, =CH), 6.26 (s, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = −3.06 ($SiMe_3$), 18.41 (CH_3), 34.36 (C-4), 49.90 (CH_3O), 105.19/108.34 (C-3/C-5), 111.36 (=CH_2), 139.13 (C-6), 140.30 (C-2), 140.3 (C-3). – MS (70 eV): m/z (%) = 212 (7.6) [M^+], 73 (100).

$C_{11}H_{20}O_2Si$ (212.3) Calcd. C 62.21 H 9.49
Found C 62.70 H 9.66

3,4-Dihydro-2-methoxy-3-methylene-2H-pyran (**3h**): From 20.4 g (0.36 mol) of **2a** and 21.0 g (0.3 mol) of **1c**[27] after 18 h at 60°C. Yield 11.7 g (47%) of **3h** after distillation (b.p. 60°C/37 mbar). – IR (film): $\tilde{\nu}$ = 3080, 3065, 2990, 2930, 2837 cm^{-1} (CH), 1725, 1690, 1655 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 2.57 (d/d/t, J = 19/5/1 Hz, 1H, 4-H), 2.91 (d/quint, J = 19/3 Hz, 1H, 4-H), 3.44 (s, 3H, OCH_3), 4.76 (m, 1H, 5-H), 4.98 (m, 1H, =CH), 5.0 (s, 1H, 2-H), 5.04 (m, 1H, =CH), 6.19 (m, 1H, 6-H). – ^{13}C NMR ($CDCl_3$): δ = 25.53 (C-4), 55.22 (OCH_3), 97.51 (C-2), 100.68 (C-5), 111.93 (=CH_2), 139.68 (C-3), 139.8 (C-6). – MS (70 eV): m/z (%) = 126 (17.4) [M^+], 41 (100).

$C_7H_{10}O_2$ (126.1) Calcd. C 66.95 H 7.99
Found C 66.29 H 8.05

3,4-Dihydro-2-methoxy-6-methyl-3-methylene-2H-pyran (**3i**): From 14.0 g (0.20 mol) of **2b** and 14.0 g (0.20 mol) of **1c** after 24 h at 80°C. Yield 18.3 g (65%) of **3i** after distillation (b.p. 48°C/14 mbar). An additional fraction (6.3 g) was contaminated with another product, which could not be isolated. – IR (film): $\tilde{\nu}$ = 2985, 2940, 2835 cm^{-1} (CH), 1690 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.73 (m, 3H, CH_3C=C), 2.56 (d/d/t, J = 19/5/1 Hz, 1H, 4-H), 2.88 (d/sept, J = 19/2.5 Hz, 1H, 4-H), 3.45 (s, 3H, OCH_3), 4.55 (br s, 1H, 5-H), 4.99 (d/t, J = 3/1.5 Hz, 1H, =CH), 5.02 (s, 1H, 2-H), 5.04 (br t, J = 1.5 Hz, 1H, =CH). – ^{13}C NMR ($CDCl_3$): δ = 18.67 (CH_3), 25.36 (C-4), 54.13 (OCH_3), 95.04 (C-2), 100.12 (C-5), 110.39 (=CH_2), 139.32 (C-3), 146.13 (C-6).

$C_8H_{12}O_2$ (140.1) Calcd. C 68.55 H 8.63
Found C 67.72 H 8.75

3-[Methoxy(trimethylsilyl)methylen]-1-methylcyclobutanecarbaldehyde (**4e**): From 0.70 g (10 mmol) of **2c** and 1.4 g (10 mmol) of **1b** after 64 h at 70°C. Distillation yielded 0.90 g (43%) of **4e**, b.p. 100°C/14 mbar. – IR (film): $\tilde{\nu}$ = 2960, 2900, 2815, 2705 cm^{-1} (CH), 1725 (C=O), 1644 (C=C), 1250 (C–Si). – ^{1}H NMR ($CDCl_3$): δ = 0 (s, 9H, $SiMe_3$), 1.22 (s, 3H, CH_3), 2.39 (d/d, J = 15.2/3.0 Hz, 1H, 4-H_{trans}), 2.60 (d/d, J = 15.8/3 Hz, 1H, 2-H_{trans}), 2.97 (d/d, J = 15.2/3.2 Hz, 1H, 4-H_{cis}), 3.15 (d/d, J = 15.8/3.2 Hz, 1H, 2-H_{cis}), 3.45 (s, 3H, CH_3O), 9.55 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = −1.18 ($SiMe_3$), 20.32 (CH_3), 36.79/38.05 (C-2/C-4), 44.87 (C-1), 58.33 (CH_3O), 122.82 (C-3), 156.47 (=CSi), 202.77 (CHO).

$C_{11}H_{20}O_2Si$ (212.3) Calcd. C 62.21 H 9.49
Found C 62.32 H 9.52

3-(Methoxymethylene)-1-methylcyclobutanecarbaldehyde (**4f**): 6.2 g (88 mmol) of **2c** was treated with 6.5 g (93 mmol) of **1c** at 70°C for 24 h. Workup gave 10.2 g (82%) of a 1:1 mixture of the [4 + 2] and [2 + 2] product (determined by GC), which could not be fractionated completely by distillation with a 40-cm Vigreux column. One fraction (b.p. 60°C/12 mbar) contained the enriched [2 + 2] adduct **4f** (70%). – IR (film): $\tilde{\nu}$ = 3030, 2846, 2770 (CH) cm^{-1}, 1722 (C=O), 1620 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 3H, CH_3), 2.38 (d/d/d, J = 15/3/2 Hz, 1H, 4-H), 2.49 (d/t, J = 15/3 Hz, 1H, 2-H), 2.96 (d/d/d, J = 15/3/2 Hz, 1H, 4-H), 3.02 (d/t, J = 15/3 Hz, 1H, 2-H), 5.98 (quint, J = 2 Hz, 1H, =CH), 9.66 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 20.19 (C-5), 34.01/34.50 (C-4/C-2, 2 × CH_2), 45.32 (C-1), 52.19 (CH_3O), 107.62 (C-3), 141.47 (=CH), 202.93 (CHO).

3,4-Dihydro-2-methoxy-3-methylene-2H-pyran-6-carbonitrile (**6**)

a) *2-Oxobutenenitril* (**5**)[29]: 3.6 g (40 mmol) of CuCN and 11.5 g (75 mmol) of NaI were stirred in 100 ml of dry CH_3CN until complete dissolution of the salts. Then 3.62 g (40 mmol) of acryloyl chloride was added and stirring continued for 30 min. The flask was then connected by a bridge to a second flask and cooled with liquid N_2. This system was evacuated to 0.03 mbar, and by cooling the second flask and heating the reaction mixture to room temp. the solvent and **5** were distilled.

b) **6**: The frozen distillate was treated with 11 g (157 mmol) of **1c** and allowed to warm to room temp. The excess of liquid was removed in vacuo and the residue distilled; b.p. 45–50°C/0.08 mbar; yield 2.14 g (35%) of **6**. – IR (film): $\tilde{\nu}$ = 3075, 2990, 2935, 2835 cm^{-1} (CH), 2230 (CN), 1640 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 2.78 (d/d, J = 21/5 Hz, 1H, 4-H), 3.09 (d/d, J = 21/3 Hz, 1H, 4-H), 3.53 (s, 3H, CH_3O), 5.11 (d, J = 3 Hz, 1H, =CH), 5.16 (s, 1H, 2-H), 5.17 (d, J = 3 Hz, 1H, =CH), 5.76 (m, J = 3/5 Hz, 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 25.89 (C-4), 55.03 (CH_3O), 100.89 (C-2), 113.41 (=CH_2), 113.84 (C-3), 116.88 (C-5), 125.0 (CN), 135.70 (C-6). – MS (70 eV): m/z (%) = 152 (5.5), 151 (57.5) [M^+], 97 (100).

Ethyl 6-Cyano-2-methoxy-3-methyl-2H-pyran-4-carboxylate (**9**): 5.0 g (32 mmol) of ethyl 4-cyano-4-oxo-2-butenoate (**7**)[29] and 6.7 g (96 mmol) of **1c** were mixed at 0°C. The reaction was complete after 15 min (GC), and an excess of **1c** was removed by evaporation. The residual oil was bulb-to-bulb distilled (bath temp. 140°C/0.03 mbar) to give 5.7 g (74%) of a yellow oil, which slowly solified; m.p. 40°C. The crude product contained a small amount of ethyl 6-cyano-3,4-dihydro-2-methoxy-3-methylene-2*H*-pyran-4-carboxylate (**8**), which isomerized at room temp. during a week. A sample of the crude product (1 g) was purified by HPLC (Si60, ethyl acetate/cyclohexane 30:70, 10 ml/min) to furnish pure **9** (0.9 g). – IR ($CDCl_3$): $\tilde{\nu}$ = 3085, 2980, 2935, 2838 cm^{-1} (CH), 2228 (CN), 1722 (C=O), 1640 (C=C). – ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, J = 7 Hz, 3H, CH_3CH_2), 2.24 (s, 3H, CH_3), 3.49 (s, 3H, CH_3O), 4.24 (q, J = 7 Hz, 2H, CH_2O), 5.23 (s, 1H, 2-H), 6.64 (s, 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 13.51 (CH_3CH_2), 17.17 (CH_3), 55.89 (CH_3O), 60.78 (CH_2O), 100.54 (C-2), 113.67 (C-5), 120.84/123.09 (CN/C-4), 138.52 (C-6), 163.08 (C=O). – MS (70 eV): m/z (%) = 224 (4.8), 223 (39) [M^+], 193 (100).

$C_{11}H_{13}NO_4$ (223.2) Calcd. C 59.19 H 5.87 N 6.28
Found C 59.11 H 5.86 N 5.98

5,5-Diethoxy-2-methylenepentanal (**10**): A solution of 1.0 g (7.0 mmol) of **3a** in 20 g of ethanol was treated with acidic ion-exchange resin (Lewatit SC 108, 3 × 1 g) at room temp. for 72 h. Distillation gave 1.1 g (85%) of **10**; b.p. 54°C/0.07 mbar. – IR (film): $\tilde{\nu}$ = 3080, 2980, 2935, 2900, 2880 cm^{-1} (CH), 1695 (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$): δ = 1.2 (t, *J* = 7 Hz, 6H, 2 × CH_3), 1.77 (t/d, *J* = 8/6 Hz, 2H, 4-H), 2.33 (t/m, *J* = 8/1 Hz, 2H, 3-H), 3.5/3.65 (2 × d/q, *J* = 9.4/7 Hz, each 2H, 2 × CH_2O), 4.49 (t, *J* = 6 Hz, 1H, 5-H), 6.02/6.28 (2 × s, each **1H**, =CH), 9.55 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 15.34 (CH_3), 23.4 (C-3), 31.66 (C-4), 61.16 (CH_2O), 102.36 (C-5), 133.95 (=CH_2), 149.78 (C-2), 194.37 (CHO).

2-Methylene-5-oxohexanal (**11**): 6.2 g (44 mmol) of **3b** was stirred with a mixture of 2 N HCl (15 ml) and water (30 ml) at room temp. for 4 h. The aqueous layer was extracted several times with CH_2Cl_2, and the combined organic extracts were washed with sat. $NaHCO_3$. After drying ($MgSO_4$) and evaporation of the solvent 4.1 g (75%) of pure **11** was obtained. – IR (film): $\tilde{\nu}$ = 3090, 3000, 2930, 2825 cm^{-1} (CH), 1712, 1688 (C=O). – ^1H NMR ($CDCl_3$): δ = 2.07 (s, 3H, CH_3), 2.45 (t, *J* = 7 Hz, 2H, 3-H), 2.56 (t, *J* = 7 Hz, 2H, 4-H), 5.97 (s, 1H, =CH), 6.24 (s, 1H, =CH), 9.46 (s, 1H, CHO).

$C_7H_{10}O_2$ (126.1) Calcd. C 66.65 H 7.99
Found C 63.88 H 7.92

2-Methylenepentanedial (**12**): 3.8 g (30 mmol) of **3h** was hydrolyzed as described. Yield 2.3 g (63%) of **12**. – IR (film): $\tilde{\nu}$ = 3090, 2930, 2837, 2735 cm^{-1} (CH), 1720, 1685 (C=O), 1630 (C=C). – ^1H NMR ($CDCl_3$): δ = 2.61 (t, *J* = 6 Hz, 2H, 3-H), 2.66 (t/d, *J* = 6/1.5 Hz, 2H, 4-H), 6.09 (s, 1H, =CH), 6.34 (s, 1H, =CH), 9.54 (s, 1H, 1-H), 9.77 (t, *J* = 1.5 Hz, 1H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 19.42 (C-3), 40.27 (C-5), 133.99 (=CH_2), 147.39 (C-2), 193.46 (C-1), 200.51 (C-5).

4-Methylene-5-oxo-5-(trimethylsilyl)pentanal (**13**): 2.0 g (10 mmol) of **3e** in methanol/water (3:1, 40 ml) was treated with 5 g of Lewatit SC 108 for 48 h. Distillation gave 1.1 g (63%) of **13**; b.p. 53–55°C/0.3 mbar. – IR (film): $\tilde{\nu}$ = 3085, 2960, 2900, 2822, 2720 cm^{-1} (CH), 1726 (C=O), 1600 (C=C), 1255 (C–Si). – ^1H NMR ($CDCl_3$): δ = 0.16 (s, 9H, $SiMe_3$), 2.45 (m, 4H, 2 × CH_2), 6.0 and 6.04 (2 × s, each 1H, =CH_2), 9.66 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ = –2.44 (Me_3Si), 21.18 (C-3), 41.32 (C-2), 127.96 (=CH_2), 151.1 (C-4), 200.1 (C-1), 225.16 (C-5). – MS (70 eV): *m/z* (%) = 184 (3.8) [M^+], 73 (100).

$C_9H_{16}O_2Si$ (184.3) Calcd. C 58.65 H 8.75
Found C 57.50 H 8.88

CAS Registry Numbers

1a: 13077-71-9 / **1b**: 77129-88-5 / **1c**: 13169-00-1 / **2a**: 107-02-8 / **2b**: 78-94-4 / **2c**: 78-85-3 / **2d**: 4170-30-3 / **3a**: 22082-47-9 / **3b**: 122722-51-4 / **3c**: 122722-49-0 / **3d**: 22082-48-0 / **3e**: 132803-18-0 / **3f**: 132803-19-1 / **3g**: 132803-20-4 / **3h**: 132803-21-5 / **3i**: 132803-22-6 / **4a**: 132803-23-7 / **4b**: 122722-50-3 / **4c**: 132803-24-8 / **4d**: 132803-25-9 / **4e**: 132803-26-0 / **4f**: 132803-27-1 / **5**: 60556-87-8 / **6**: 132803-28-2 / **7**: 111301-58-7 / **8**: 132803-34-0 / **9**: 132803-29-3 / **10**: 132803-30-6 / **11**: 132803-31-7 / **12**: 132803-32-8 / **13**: 132803-33-9 / CH_2=CHCOCl: 814-68-6

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