Catalytic reaction of methyl diazoacetate with silylated enynes

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Factors affecting the regioselectivity of the catalytic reaction of methyl diatoacetate with 1-trimethylsilylalkene-1-ynes have been revealed. Conditions for selective cyclopropanation of the double bond in 1-trimethylsilylbut-3-ene-1-yne and 1-trimethylsilyl-3-methylbut-3-ene-1-yne in the presence of $Rh_2(OAc)_4$ have been found.

Key words: diazoacetate, enynes, catalysis, cyclopropanecarboxylic acids, cyclopropene-3-carboxylic acids.

It has been shown previosly[1] that the reaction of methyldiazoacetate (MDA) with vinylacetylene in the presence of $Rh_2(OAc)_4$ proceeds selectively at the vinyl-acetylene triple bond to give dimethyl *anti*-1,2-divinyltricyclo[3.1.0.0^{2,4}]hexane-3,6-dicarboxylate, which is a [2+2]-cyclodimer of methyl 1-vinylcyclopropene-3-carboxylic acid. On the other hand, the reaction of MDA with 1-trimethylsilyl-3-methylbut-3-ene-1-yne (**1b**) catalyzed by $CuSO_4$ gives methyl 2-methyl-2-(trimethylsilylethynyl)cyclopropanecarboxylate (**2b**) — a product of the cycloaddition at the double bond.[2] In order to reveal the synthetic possibilities and characteristic features of the reaction of MDA with silylated enynes we have studied this process in detail using silylated enynes with both conjugated (**1a—c**) and unconjugated (**1d**) multiple bonds and $Cu(acac)_2$, $CuSO_4$ or $Rh_2(OAc)_4$ as the catalyst.

Enynes **1a—c** were obtained by silylation of the corresponding enynes **3a—c** in 75—85 % yield. The initial compound **3c** was prepared by reductive dehydrochlorination of 1,1-dichloro-4-methyl-1,3-pentadiene with Na dispersed in nonane at 50°C in 68% yield.

$$Cl_2C{=}CHCH{=}CMe_2 \xrightarrow[C_9H_{20}]{Na,\ 50^\circ C} HC{\equiv}CCH{=}CMe_2$$
3c

Synthesis of **1d** (yield 86%) was performed by condensation of trimethylsilylacetylene with allyl bromide in THF in the presence of CuBr at 50°C.

$$Me_3SiC{\equiv}CH \xrightarrow[2.\ BrCH_2CH{=}CH_2,\ CuBr,\ 50^\circ C,\ THF]{1.\ EtMgBr,\ THF} Me_3SiC{\equiv}CCH_2{}^{d}C{=}C\begin{matrix}H^b\\ \diagup\\ \\ \diagdown\\ H^c\end{matrix}$$
1d H^a

It was found that catalytic interaction between MDA and a threefold excess of **1a—d** proceeds with the participation of both the double and the triple bonds to give methyl esters **2** together with methyl 1-(trimethylsilyl)-2-alkenylcyclopropene-3-carboxylates (**4**) and dimethyl esters of maleic and fumaric acids (**5**) (the total of esters **5** reach 15%) (Table 1).

Table 1. Conditions, yields and ratios of the reaction products (mole ratio 1:MDA = 3:1, rate of addition of MDA 8-10 mmol/h)

Initial enyne	Catalyst[a] and temperature of the reaction	Total yield[b] **2+4** (%)	Ratio of the products (%) [c] **2:4**	*E*-**2**/*Z*-**2**
1a	$CuSO_4$, 110°C	40	86:14	1.4[d]
	$Cu(acac)_2$, 40°C	24	90:10	2.8[d]
	$Rh_2(OAc)_4$, 20°C	79	97:3	1.2[d]
1b	$CuSO_4$, 110°C	54	98:2	1.1
	$Cu(acac)_2$, 40°C	43	99:1	1.2
	$Rh_2(OAc)_4$, 20°C	69	100:0	1.0
1c	$CuSO_4$, 110°C	35	25:75	3.8
	$Cu(acac)_2$, 40°C	30	28:72	5.8
	$Rh_2(OAc)_4$, 20°C	44	42:58	1.9[d]
1d	$CuSO_4$, 110°C	44	70:30	3.3
	$Cu(acac)_2$, 40°C	32	79:21	4.1
	$Rh_2(OAc)_4$, 20°C	65	87:13	1.3

[a] $CuSO_4$ and $Cu(acac)_2$ 2 % mol; $Rh_2(OAc)_4$ 0.2 % mol. [b] For the separated mixture of the products without **5**. [c] GLC-MS data. [d] ^1H NMR data.

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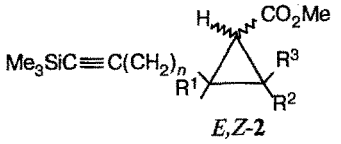
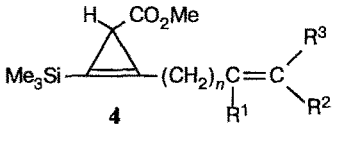
Table 2. ^{1}H NMR spectra of methyl 2-(trimethylsilylalkynyl)cyclopropanecarboxylates (**2**) and methyl 1-trimethylsilyl-2-alkenylcyclopropene-3-carboxylates (**4**) ($CDCl_3$, TMS as internal standard).



E,Z-**2**



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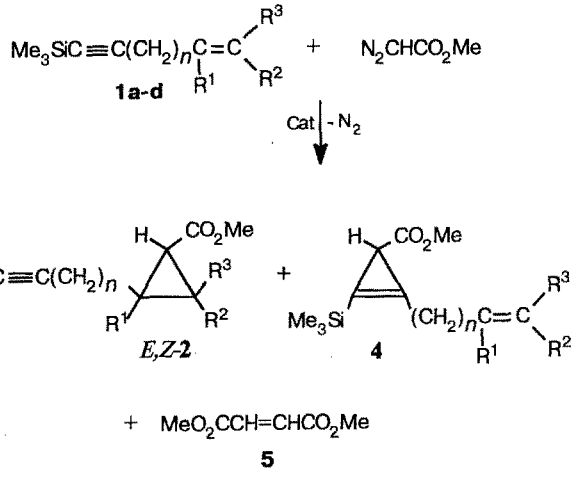
$R^1 = R^2 = R^3 = H$, $n = 0$ (**a**); $R^1 = Me$, $R^2 = R^3 = H$, $n = 0$ (**b**); $R^1 = H$, $R^2 = R^3 = Me$, $n = 0$ (**c**); $R^1 = R^2 = R^3 = H$, $n = 1$ (**d**)

Compound	δ							*J*/Hz							
	Me_3Si	OMe	CH_2	R^1	R^2	R^3	H	$J_{R^1R^2}$	$J_{R^1R^3}$	J_{R^1H}	$J_{R^2R^3}$	J_{R^2H}	J_{R^3H}	$^2J_{CH_2}$	$^3J_{R^1CH_2}$
E-**2a**	0.13 s	3.70 s	—	1.92 m	1.18 m	1.35 m	1.83 m	8.0	5.5	4.0	4.0	6.4	8.8	—	—
Z-**2a**	0.13 s	3.67 c	—	1.95 m	1.16 m	1.42 m	1.80 m	7.5	5.9	8.5	4.5	8.5	6.5	—	—
E-**2b**	0.13 s	3.70 s	—	1.39 s	1.28 q	1.38 q	2.07 q	—	—	—	4.6	6.4	8.5	—	—
Z-**2b**	0.13 s	3.71 s	—	1.37 s	1.04 q	1.63 q	1.76 q	—	—	—	4.6	7.8	6.5	—	—
E-**2c**	0.14 s	3.68 s	—	1.70 d	1.30 s	1.23 s	1.96 d	—	—	5.3	—	—	—	—	—
Z-**2c**	0.16 s	3.63 s	—	1.71 d	1.37 s	1.17 s	1.73 d	—	—	8.8	—	—	—	—	—
E-**2d**	0.14 s	3.67 s	2.53 m 2.48 m	1.58 m	0.97 m	1.18 m	1.62 m	6.3	4.8	4.0	-4.3	8.4	9.0	-17.5	4.8 5.2
Z-**2d**	0.14 s	3.69 s	2.57 m 2.40 m	1.52 m	1.11 m	1.02 m	1.78 m	7.0	8.4	8.8	-4.8	8.0	5.6	-17.5	6.7 7.9
4a	0.19 s	3.61 s	—	6.63 q	5.69 dm	5.55 dm	2.15 s	10.0	17.0	—	2.0	—	—	—	—
4c	0.21 s	3.66 s	—	6.05 m	1.90 br.s	1.94 br.s	2.22 s	1.5	1.3	—	—	—	—	—	—
4d	0.19 s	3.64 s	3.28 dm	5.92 m	5.12 dm	5.17 dm	2.05 s	10.0	17.0	—	2.0	—	—	—	6.5



The structures of the reactions products were established on the basis of spectral data (Tables 2—4).

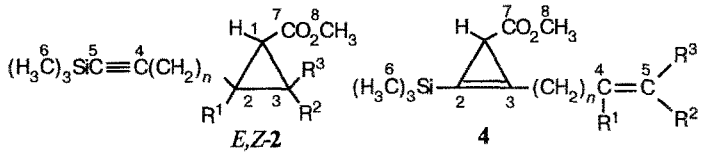
For NMR analysis the isomers *E*-**2a**, *E*-**2b**, *Z*-**2c** and *Z*-**2d** were separated in the individual form. In the high resolution (300 MHz) ^{1}H NMR spectrum of *E*-**2a** the signals of the protons of the cyclopropane ring appear as an ABCD system. Analysis of this spin system was carried out using a heteronuclear double resonance procedure in the ^{13}C NMR spectrum. The assignment of the cyclopropane ring methyne protons was made by observing the polarization transfer effects for the carbon atoms of the carbonyl and acetylenic groups in the ^{13}C NMR spectrum. The relatively low value of the coupling constant between the methyne protons of the cyclopropane cycle (^3J = 4.0 Hz) corresponds to the assumed *trans*-arrangement of the carbonyl and acetylenic groups.

Analysis of the spectra of the other separated compounds was performed similarly. The spectra of the other isomers were obtained by substraction of the established spectra from the spectra of the reaction mixtures. In the spectra of the isomers **2d**, the protons form a complex 6-spin system. In this case the values of the coupling constants were determined by calculation using the program CALM. *

Regular differences in the chemical shifts for the C(1) and C(2) carbon atoms of the cyclopropane ring and the C(4) and C(5) carbon atoms of the triple bond in the *Z*- and *E*-isomers of compounds **2a—c** draw attention. The carbon atoms C(1) adjacent to the carbonyl group are shifted up-field (10—12 ppm) relative to the C(2) carbon atoms adjacent to the triple bond. On the other hand, the triple bond carbon atoms C(4) bonded with the cyclopropyl ring have smaller chemical

* The authors express their gratitude to Dr. Yu. A. Strelenko for performing this calculation.

Table 3. ^{13}C NMR spectra of methyl 2-(trimethylsilylalkynyl)cyclopropanecarboxylates (**2**) and methyl 1-trimethylsilyl-2-alkenylcyclopropene-3-carboxylates (**4**)



E,Z-**2** **4**

$R^1 = R^2 = R^3 = H$, $n = 0$ (**a**); $R^1 = Me$, $R^2 = R^3 = H$, $n = 0$ (**b**); $R^1 = H$, $R^2 = R^3 = Me$, $n = 0$ (**c**); $R^1 = R^2 = R^3 = H$, $n = 1$ (**d**)

Compound	δ ($CDCl_3$)								
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	Other carbon atoms
E-**2a**	10.74	22.49	16.59	105.70	81.81	-0.37	171.96	51.53	—
Z-**2a**	9.65	21.41	14.04	103.48	83.44	-0.37	169.63	51.15	—
E-**2b**	28.34	17.37	22.64	111.32	81.03	0.06	171.03	51.82	17.69 (CH_3)
Z-**2b**	29.97	17.69	22.19	107.51	83.67	0.06	171.87	52.02	24.99 (CH_3)
E-**2c**	23.14	35.33	28.67	104.46	84.63	0.07	170.98	51.64	22.76 и 19.08 ($2CH_3$)
Z-**2c**	22.76	32.03	26.50	102.18	87.12	0.07	169.14	51.15	27.26 и 15.94 ($2CH_3$)
E-**2d**	18.38	19.30	13.50	102.62	86.20	-0.10	174.07	51.37	21.68 (CH_2)
Z-**2d**	17.73	20.27	13.72	105.54	84.31	-0.10	172.61	51.37	18.21 (CH_2)
4a	19.03	109.6	122.33	122.88	125.37	-1.99	175.53	50.83	—
4c	21.03	102.72	119.95	111.72	146.34	-1.61	176.73	51.04	26.01 и 19.03 ($2CH_3$)
4d	20.60	124.88	104.78	132.63	117.03	-1.67	176.78	50.93	30.62 (CH_2)

Table 4. IR- and mass-spectra of methyl 2-(trimethylsilylalkynyl)cyclopropanecarboxylates (**2**) and methyl 1-trimethylsilyl-2-alkenylcyclopropene-3-carboxylates (**4**)

Compound	IR spectrum, ν/cm^{-1}			Mass spectrum (EI, 70 eV), *m/z* (I_{rel} (%))				
	C=O	C=C	Other bonds	$[M]^+$	$[M-Me]^+$	$[M-CO_2Me]^+$	$[M-SiMe_3]^+$	Other peaks
E-**2a**	1751	2175	—	196(24)	181(52)	—	123(15)	151(62), 91(43), 89(57), 75 (54)
Z-**2a**	1751	2175	—	196(24)	181(52)	—	123(15)	151(62), 91(43), 89(57), 75 (54)
E-**2b**	1751	2160	—	210(13)	195(51)	—	137(23)	165(17), 109(25), 106(93), 89(57)
Z-**2b**	1759	2168	—	210(10)	195(35)	—	137(17)	165(14), 109(21), 106(69), 89(49)
E-**2c**	1751	2160	—	224(1)	209(14)	165(12)	—	137(8), 105(11), 89(46), 73(100)
Z-**2c**	1759	2168	—	224(1)	209(16)	165(14)	—	137(9), 105(11), 89(43), 73(100)
E-**2d**	1751	2175	—	210(1)	195(35)	—	137(8)	165(20), 109(37), 91(40), 89(93)
Z-**2d**	1751	2175	—	209(2)*	195(28)	—	137(10)	165(10), 135(31), 105(19), 89(80)
4a	1743	—	1805 (*cyclo*-C=C)	196(5)	181(2)	137(11)	—	92(100), 89(17), 83(6),73(80)
4b	—	—	—	210(6)	195(4)	151(11)	—	107(8), 106(100), 78(47)
4c	1743	—	1635 (C=C), 1790 (*cyclo*-C=C)	224(9)	209(2)	165(10)	—	120(100), 92(37), 91(93), 73(89)
4d	1743	—	1651 (C=C), 1828 (*cyclo*-C=C)	210(6)	195(3)	151(17)	-	106(53), 89(24), 78(66), 73(100)

*There is a $[M-1]^+$ peak in the spectrum.

shifts ($\Delta\delta \approx 2$—4 ppm) in the *Z*-isomers than in the *E*-isomers. For the carbon atoms C(5) adjacent to the trimethylsilyl group the reverse dependence is observed. These empirical rules can serve as an additional analytical feature for the correct assignment of the signals of the *Z*- and *E*-isomers for the alkynylcyclopropanecarboxylic acid esters.

In the ^{1}H NMR spectra of the cyclopropenes **4a,c,d** a cyclic proton appears as a characteristic singlet in the narrow area δ 2.05—2.20 ppm. Due to the influence of the cyclopropene ring the signal of the Me_3Si group protons undergoes a down-field shift (δ 0.19—0.21 ppm).

IR spectra of compounds **2a—d** and **4a,c,d** were measured using an IR spectrometer combined with a chromatograph; mass spectra of all of the cyclopropanes **2** and cyclopropenes **4** were obtained by a GLC-MS instrument. The characteristic bands of the disubstituted triple bonds at 2160—2175 cm^{-1} are present in the IR spectra of cyclopropanes **2**. In the spectra of the cyclopropenes **4a,c** the bands of the endocyclic conjugated double bonds at 1790 and 1805 cm^{-1} have a significant bathochromic shift compared to the unconjugated double bond in compound **4d** (1828 cm^{-1}). In the mass-spectra of all the cyclopropanes **2** (excluding *Z*-**2d**) and cyclopropenes **4** the molecular ion peaks are present; in the spectrum of *Z*-**2d** there is a $[M-1]^+$ ion peak.

The regioselectivity and yields of the reaction products are dependent on the structure of the initial enyne and on the catalyst used. As can be seen from the data given in Table 1, the reaction of MDA with enynes **1** in the presence of $Rh_2(OAc)_4$ proceeds at 20 °C and gives compounds **2** and **4** with a greater total yield than can be obtained using Cu-catalysts. The main side products are dimers **5** and resinification is insignificant. Moreover, Cu-catalysts enable the triple bond to participate in the reaction with MDA, which increases the yield of the cyclopropenes **4** and decreases the regioselectivity of the process. Also, trans-isomers **2** are mostly obtained when $Cu(acac)_2$ is used.

The regioselectivity of the reaction of MDA with conjugated enynes **1a—c** is mostly affected by the character of the double bond substitution. Thus, enynes **1a** and **1b** with terminal double bonds react with MDA preferentially at this double bond. The use of $Rh_2(OAc)_4$ in these reactions makes it possible to get the corresponding cyclopropanes **2a,b** with selectivity higher than 97 % and in 70—80 % yield. The introduction of methyl substituents to the terminal position dramatically decreases the reactivity of the double bond. This effect can be distinctly seen for enyne **1c**. As a result, in the latter case cyclopropene **4c** becomes the main product of the reaction; the fraction of **4c** in the reaction mixture can reach 72—75 % if MDA is dediazotated under the treatment with copper compounds.

The regioselectivity of the reaction of MDA with enynes is also strongly affected by conjugation. In the unconjugated enyne **1d** the reactivity of the triple bond is somewhat higher than in the conjugated enyne of similar structure, **1a**. The total yields of compounds **2d** + **4d** and **2a** + **4a** are comparable, however the fraction of cyclopropene **4d** in the reaction products is 2—5 times higher (depending on the catalyst) than the yield of the corresponding analog **4a**. These results are in good agreement with the data on the similar reactivity of isolated triple and double bonds in reactions with alkyl diazoacetates.[3]

Thus, the reaction of MDA with silylated enynes catalyzed by $Rh_2(OAc)_4$ can be used for the selective cyclopropanation of conjugated enynes. Since the silyl group can be easily removed from cyclopropanes **2** by hydrolytic cleavage with an alcohol solution of a strong base,[2] this reaction can be used for the directed synthesis of ethynyl- and (2-propenyl)cyclopropanecarboxylic acids from the corresponding terminal enynes.

Experimental

GLC-MS data were obtained on a «Finnigan MAT INCOS-50» instrument with a 30 m cappilary column RSL-200. A temperature change program was used in the temperature interval 50—250 °C, evaporator temperature 250°C, carrying gas — helium. ^{1}H and ^{13}C NMR spectra were recorded on «Bruker WM-250» (250 MHz), «Bruker AM-300» (300 MHz) and «Jeol FX-90Q» (90 MHz) instruments. $CDCl_3$ solutions and TMS as the internal standard were used. IR spectra were obtained using a «Bruker IFS-113V» instrument.* Reaction products were separated by column chromatography on silica gel L 40/100, eluent hexane—ether, 5:1.

4-Methylpent-3-ene-1-yne (3c). To a suspension (50°C) of 27.4 g (1.19 mol) of dispersed Na in 150 ml of nonane were added 46.8 g (0.31 mol) of 1,1-dichloro-4-methyl-1,3-pentadiene over 4—5 h; the temperature was maintained in the interval 50—60 °C. Then the reaction mixture was cooled to 20 °C and treated carefully with 200 ml of water. The fraction with boiling point 50—95 °C was distilled at atmospheric pressure from the organic layer. The fraction obtained was dried over anhydrous Na_2SO_4 and once more distilled. In this way 16.9 g (68 %) of **3c** were obtained, b.p. 80—82 °C (b.p. 73—75 °C)[4], n_D^{20} 1.4475. IR spectrum (neat, ν/cm^{-1}): 3325 (≡C—H); 2098 (C≡C); 1635 (C=C). ^{1}H NMR (250 MHz, δ, (*J*, Hz)): 5.26 (m, =CH, 1H, $^4J_{trans}$ = 1.0, $^4J_{cis}$ = 1.5); 2.99 (br.s, ≡CH, 1H, ^4J = 2.5); 1.92 (s, *cis*-Me, 3H); 1.82 (s, *trans*-Me, 3H). ^{13}C NMR (22.5 MHz, δ): 150.33 (C); 104.56 (HC=); 81.80 (≡C—), 79.20 (HC≡), 24.70 (*trans*-Me); 20.86 (*cis*-Me). Mass-spectrum (EI, 70 *e*V), *m/z* (I_{rel} (%)): 80 $[M]^+$ (72), 79 $[M-1]^+$ (68), 65 $[M-Me]^+$ (33).

1-Trimethylsilyl-4-methylpent-3-ene-1-yne (1c). 17.35 g (0.217 mol) of enyne **3c** were added to a solution of EtMgBr, made from 0.26 mol of EtBr and 0.39 mol of Mg, in 100 ml of THF over 30 min. The reaction mixture was stirred for 2 h at 25 °C. Then 28.21 g (0.260 mol) of trimethylchlorosilane were added, the mixture was heated at 70 °C for 2 h, then cooled to 20 °C and treated with 150 ml of saturated NH_4Cl solution.

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The water layer was extracted with ether (2 × 50 ml), 4/5 of the volume of the organic layer was evaporated at atmospheric pressure, the residue was diluted with 100 ml of ether, and mixed with the ether extract. The ether solution obtained was washed with a saturated NH_4Cl solution (4 × 100 ml), dried over anhydrous Na_2SO_4, and the solvent was evaporated. The residue was distilled in a vacuum to give 22.20 g (67 %) of enyne **1c**, b.p. 66—70 °C (40 Torr), n_D^{20} 1.4629. IR spectrum (neat, ν/cm^{-1}): 2152 (C≡C); 1635 (C=C). ^{1}H NMR (90 MHz, δ, (*J*, Hz)): 5.21 (m, =CH, 1H, $^4J_{trans}$ = 1.4, $^4J_{cis}$ = 1.6); 1.84 (br.s, *trans*-Me, 3H); 0.11 (s, Me_3Si, 9H). ^{13}C NMR (75 MHz, δ): 150.10 (C); 105.60 (=CH); 103.55 (—C≡); 95.98 (≡CSi); 24.74 (*trans*-Me); 21.04 (*cis*-Me); 0.14 ($SiMe_3$). Mass-spectrum (EI, 70 *e*V), *m*/*z* (I_{rel} (%)): 153 $[M+1]^+$ (3); 152 $[M]^+$ (20); 137 $[M-Me]^+$ (100); 109 (10); 97 (10); 83 (20); 69 (19).

1-Trimethylsilylpent-4-ene-1-yne (1d). To a solution of EtMgBr, made from 0.24 mol of EtBr and 0.36 mol of Mg, in 150 ml of THF, 19.6 g (0.20 mol) of trimethylsilylacetylene were added at a temperature of about 35 °C. Then the reaction mixture was heated for 1 h at 50 °C and cooled to 20 °C. Then 0.32 g (2.2 mol) of CuBr were added at once and 36.3 g (0.30 mol) of allyl bromide were added over 1h, while the temperature was maintained at 50 °C. After 2 h at 50 °C the reaction mixture was cooled to 20 °C and hydrolyzed with 200 ml of saturated NH_4Cl solution, and the water layer was extracted with ether (2 × 100 ml). The main portion of THF was removed from the organic layer at atmospheric pressure. The residue was combined with the ether extracts, washed with water (3 × 150 ml) and saturated NH_4Cl solution (2 × 150 ml), dried over Na_2SO_4, and the solvents were removed. The residue was distilled in a vacuum to give 23.7 g (86 %) of enyne **1d**, b.p. 56—57 °C (40 Torr), n_D^{20} 1.4387 (compare to[5]). IR spectrum (neat, ν/cm^{-1}): 1643 (C=C); 2175 (C≡C). ^{1}H NMR (90 MHz, δ (*J*, Hz)): 5.83 (m, H_a, 1H, J_{ab} = 17.0, J_{ac} = 9.5, J_{ad} = 5.0); 5.31 (dm, H_b, 1H, J_{bd} = 2.0); 5.12 (dm, H_c, 1H, J_{cd} = 2.0); 3.01 (dm, H_d, 2H); 0.18 (s, $SiMe_3$, 9H). ^{13}C NMR (22.5 MHz, δ, ppm): 132.25 (CH_a); 116.21 (H_2C=); 103.48 (—C≡); 87.01 (≡CSi); 24.23 (CH_2); 0.18 ($SiMe_3$). Mass-spectrum (EI, 70 *e*V), *m*/*z* (I_{rel} (%)): 138 $[M]^+$ (5); 123 $[M-Me]^+$ (100); 96 (14); 83 (11); 73 (12); 65 $[M-SiMe_3]^+$(18).

General procedure for the reaction of MDA with enynes in the presence of $Rh_2(OAc)_4$. A solution of 21.7 mmol of MDA in 20 ml of CH_2Cl_2 was added to a solution of 65.0 mmol of enyne **1** and 0.045 mmol of $Rh_2(OAc)_4$ in a 20 ml of CH_2Cl_2 over 3 h at 20 °C. The reaction mixture was stirred for 30 min, its volume was reduced fivefold by evaporation, and the residual mixture was filtered through a layer (≈1 cm) of silica gel and the solvents were removed. The residue was analyzed by GLC-MS.

To separate the products the residue was distilled in a vacuum to give a mixture of the cyclopropanes *E,Z*-**2b**, b.p. 90—105 °C (30 Torr), and a mixture of compounds *E,Z*-**2c** and **4c**. Isomers *E*-**2b** (>95 % purity according to the ^{1}H NMR spectrum), and *Z*-**2c** with >80 % purity, not contaminated with *E*-**2c** and **4c** were separated from this mixture by column chromatography. Similarly compounds *Z*-**2a** (>95 % purity according to the ^{1}H NMR spectrum), n_D^{20} 1.4615 and *E*-**2a** (>95 % purity according to the ^{1}H NMR spectrum) were separated from the products of the reaction of MDA with the enynes **1d** and **1a**.

General procedure for the reaction of MDA with enynes in the presence of $CuSO_4$. A solution of 13.30 mmol of MDA in 12.10 mmol of enyne **1** was added to a suspension of 0.13 mmol of $CuSO_4$ in 28.23 mmol of enyne **1** heated to 100—110 °C over 1.5 h (the total amount of the enyne **1** was 40.33 mmol). The reaction mixture was heated for an additional 30 min, then cooled to 25 °C, filtred through a layer (≈1 cm) of silica gel, and the solvents were evaporated and the residue was analyzed by GLC-MS. To determine the total yield of the reaction products the residue was distilled in a vacuum.

General procedure for the reaction of MDA with enynes in the presence of $Cu(acac)_2$. 0.50 mmol of MDA were added at once (for the activation of the catalyst) to a suspension of 0.42 mmol of the catalyst in 5 ml of CH_2Cl_2 heated to 40 °C. After 1-2 minutes intense evolution of nitrogen was observed. A solution of 65.22 mmol of enyne **1** in 15 ml of CH_2Cl_2 was added to the catalytic solution thus prepared, and the temperature was maintained at 40 °C. Then a solution of 21.7 mmol of MDA in 20 ml of CH_2Cl_2 was added over 2—2.5 h. The reaction mixture was heated for additional 30 min at 40 °C, then treated and analyzed as described above.

To separate compound **4c**, after filtration through silica gel the reaction mixture was distilled in a vacuum to remove the initial enyne **1c**, and the residue was chromatographed to give cyclopropene **4c** with purity >95 % (^{1}H NMR data), n_D^{20} 1.4850.

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