Selective Dimerisation and Addition of Carboxylic Acids to Terminal Alkynes, Catalysed by Thermolysed Grubbs' Catalyst: A Novel Synthesis of Enynes and Vinyl Esters

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Keywords: Alkynes / Dimerisation / Homogeneous catalysis / Markovnikov addition / Ruthenium

The transformation of triple bonds of terminal alkynes was carried out at 110 °C in the presence of the thermolysed Ru^{II}-alkylidene $[Cl_2(PCy_3)_2Ru{=}CHPh]$. The transformation of phenylacetylene is strongly pK_a-dependent, the preference switching from vinylation to dimerisation at increasing pK_a values. Aliphatic alkynes only give rise to vinylation adducts, with a regioselectivity for Markovnikov addition.

Introduction

Since the first preparation of a vinyl ester (vinyl acetate in 1912), vinylation has emerged as a powerful tool for organic synthesis.[1] Carboxylic acids have been added to the internal C-2 carbon atoms of terminal alkynes by use of metal catalysts based on zinc, mercury, palladium and rhodium.[2−5] The best catalytic systems, however, appear to be based on ruthenium. The regioselectivity towards Markovnikov addition has been significantly increased by the use of a variety of Ru precursors such as $Ru_3(CO)_{12}$,[6−7] (arene)$RuCl_2(PR_3)$[8−10] and bis (η^5-cyclooctadienyl)ruthenium/PR_3, with and without addition of maleic anhydride.[11−14] The first *anti*-Markovnikov *trans*-addition in the presence of the Ru(dppb)(η^3-$CH_2C(Me){=}CH_2$)$_2$ catalyst was reported by Dixneuf et al.[15] A diphosphane ligand bearing a longer chain, such as dppb ($Ph_2P(CH_2)_nPPh_2$), affords better chemoselectivity. Steric factors rather than electronic factors are responsible for the regioselective attack of carboxylic acids at the C-1 position of 1-alkynes. Another type of Ru-catalysed C−C bond formation is the olefin metathesis reaction, in which alkenes are converted into new alkene products through the rupture and reformation of the double bond. The use and applications of olefin metathesis have increased immensely with the discovery of the stable Ru-alkylidene complexes $[Cl_2(PR_3)_2Ru{=}CHPh]$.[16−19] The widespread use of the Ru-alkylidene complexes is due to their activity, stability and functional group tolerance. Despite the major accomplishments represented by Grubbs' ′first generation′ catalyst, thermolytic decomposition occurs at elevated temperature,[20] which limits the use of the Ru-alkylidene under more challenging organic reactions. Recent research in our group revealed the unexpected capacity of Grubbs' catalyst to catalyse the dimerisation of terminal alkynes. At elevated temperature and in the presence of phenylacetylene, the Ru-alkylidene transforms into a Ru-vinylidene, which selectively catalyses tail-to-tail addition. The nucleophilic addition of carboxylic acids to 1-alkynes is thought to proceed by the same fundamental mechanism. Both alkyne transformations are initiated by a transition metal vinylidene species (Scheme 1).

This tempted us to explore the catalytic activity of Grubbs' ′first generation′ catalyst towards the vinylation or nucleophilic attack of carboxylic acids on terminal alkynes.

Results and Discussion

After thermal treatment of Grubbs' catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ at 110 °C for 1 h, 96 equiv. of phenylacetylene and 112 equiv. of carboxylic acid were added (Table 1). The yield (%) was low when no carboxylic acid (21%) or formic acid (35%) is added to phenylacetylene (entries 1−2). When acetic acid and trichloroacetic acid were used as carboxylic acid sources, nearly full conversion of the triple bond was achieved (entry 3−4). As expected, the reaction exclusively yielded dimeric products when no acid was added (entry 1). At 110 °C, formic acid is mainly present in the vapour phase, which is illustrated in the low regioselectivity (63:37 dimerisation/vinylation) (entry 2). Surprisingly, the addition of acetic acid only produced enynes and no enol ester derivatives (entry 3), while trichloroacetic acid gave nearly 100% vinylation adducts (entry 4). The acidity of the carboxylic acid plays a key role in the preference of terminal alkynes towards dimerisation or to-

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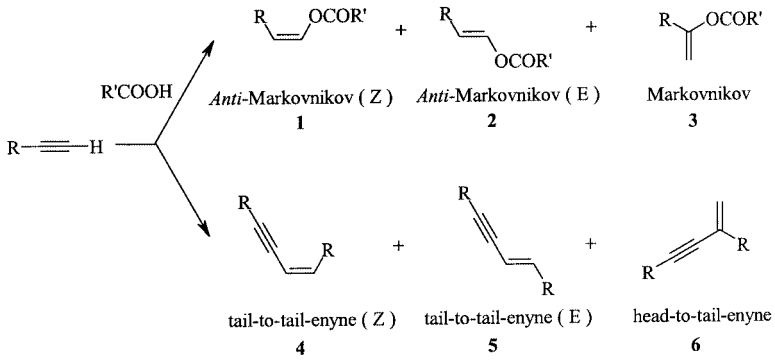


Scheme 1

Table 1. Influence of the acidity on the triple bond transformation of phenylacetylene initiated by $[Cl_2(PCy_3)_2Ru{=}CHPh]$

Entry	pK_a	Acid[a]	Time (h)[b]	Yield (%)	Vinylation (%)[c]	Product ratio **1**:**2**:**3**[c]	Dimerisation (%)[c]	Product ratio **4**:**5**:**6**[c]
1	/	no	5	21	0	/	100	5:87:8
2	3.80	HCOOH	6	35	37	35:65	63	12:84:4
3	4.76	CH_3COOH	4	92	0	/	100	70:10:20
4	0.65	CCl_3COOH	7	99	94	8:2:90	6	18:29:53

[a] Reaction conditions: catalyst/phenylacetylene/carboxylic acid, 1:96:112, temperature 110 °C. [b] Time represents the time period at which the conversion reaches a plateau or is complete. [c] Yield and selectivity as determined by ^{1}H NMR and GC-MS.

wards vinylation of the triple bond. The selectivity is strongly pK_a-dependent: vinylation is preferred at low pK_a, but at increasing pK_a the selectivity changes towards the formation of dimeric products.

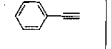
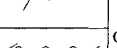
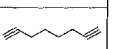
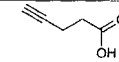
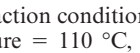
The catalyst preferentially produces tail-to-tail dimeric adducts, except for the reaction between phenylacetylene and trichloroacetic acid, in which proportional amounts of both tail-to-tail and head-to-tail adducts are formed. The reaction products show a stereoselectivity for the *E*-enynes when no acid or formic acid is added. The stereoselectivity is reversed for the addition of acetic acid, where 70% of the enynes consist of the *cis* isomer.

The regioselectivity upon addition of formic acid shows a 65:35 *anti*-Markovnikov/Markovnikov ratio. The nucleophilic addition of trichloroacetic acid proceeds regioselectively with 90% Markovnikov addition. With increasing acidity, the regioselectivity for Markovnikov addition is preferred.

The influence of the 1-alkyne on the catalytic activity and selectivity was tested (Table 2). After thermal treatment of Grubbs' catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ at 110 °C for 1 h, 96 equiv. of the terminal alkyne and 112 equiv. of acetic acid were added. Phenylacetylene, 3,3-dimethyl-1-butyne and 4-pentynoic acid reached nearly total triple bond conversion (entries 5, 6 and 9), while with 1-octyne and 1,7-octadiyne the reaction yields were only 33% and 49%, respectively (entries 7−8).

Only phenylacetylene shows a 100% preference for dimerisation. As described before, its dimerisation selectively produces *Z*-enynes. The other terminal alkynes − i.e., 3,3-dimethyl-1-butyne, 1-octyne, 1,7-octadiyne and 4-pentynoic acid − prefer nucleophilic addition of the carboxylic acid

Table 2. Influence of the nature of the terminal alkyne on the catalytic activity of $[Cl_2(PCy_3)_2Ru{=}CHPh]$

Entry	Alkyne[a]	Acid	Yield (%)[b]	Vinylation (%)[b]	product ratio 1:2:3[b]	Dimerisation (%)[b]	product ratio 4:5:6[b]
5		CH_3COOH	92	0	/	100	70:10:20
6			86	100	20:0:80	0	/
7			33	100	12:3:85	0	/
8a[c]			49	68	9:2:89	1	/
8b[c]				99 31	18:7:75		
9[d]			100	100	100:0	0	/

[a] Reaction conditions: catalyst/1-alkyne/acetic acid: 1:96:112, temperature = 110 °C, time = 4 h. [b] Yield and selectivity as determined by ^{1}H NMR and GC-MS. [c] **8a** represents the monosubstituted enol ester, **8b** the disubstituted enol ester. [d] Reaction conditions: catalyst/substrate: 1:100, temperature = 110 °C, time = 4h

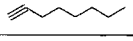
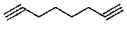
at the triple bond of the alkyne or vinylation. The major product formed from the reaction between the dialkyne 1,7-octadiyne and acetic acid is the monosubstituted alkyne (entry 8a), the yield of reaction product possessing two enol ester end groups being only 31% (entry 8b). The intramolecular addition gives unsaturated lactones, with a high regioselectivity for *anti*-Markovnikov addition (entry 9).

The preference for dimerisation or vinylation is strongly dependent on the nature of the terminal alkyne. Aliphatic alkynes produce only vinylation products, with a high regioselectivity for Markovnikov addition. Increasing the steric hindrance of the alkyl group from a linear C-chain to

a steric *tert*-butyl group results in higher degrees of conversion of the triple bond. Dimerisation only takes place with a conjugated arylacetylene.

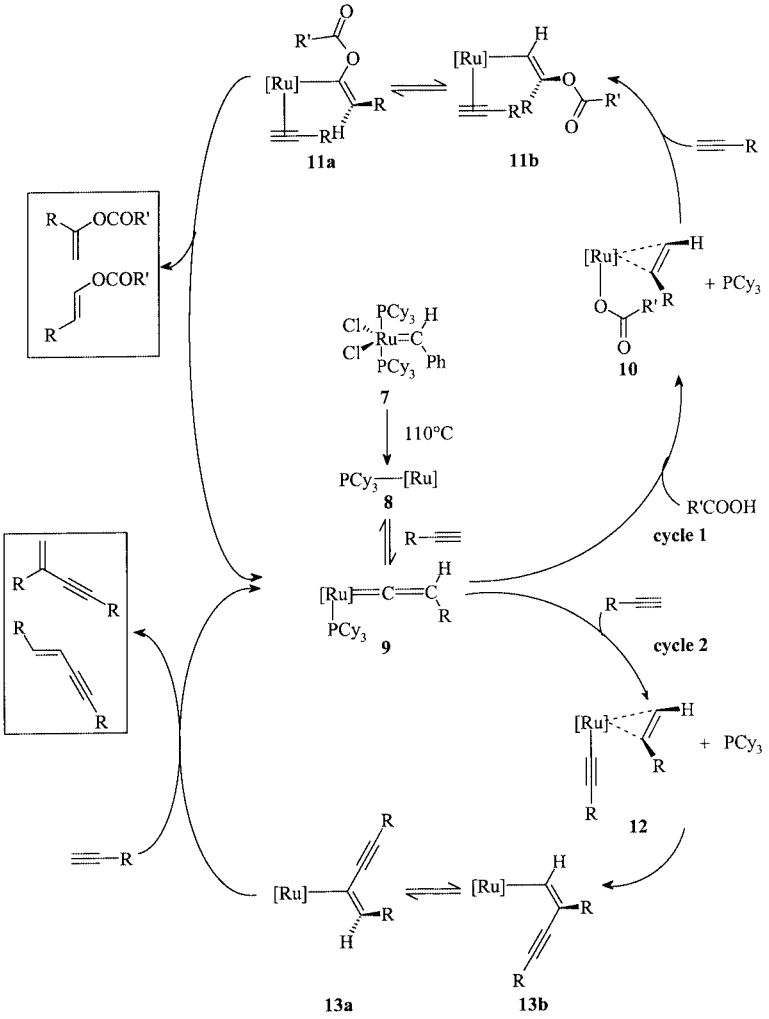
Another catalysed carbon−carbon bond-formation reaction in which acetylene compounds are involved is the dimerisation of 1-alkynes. A solution of Grubbs' catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (0.032 mmol) in toluene (3 mL) was heated at 110 °C for 1 h. 1-Alkyne (3.20 mmol, 100 equiv.) was added to this solution, and the reaction mixture was stirred at 110 °C for 5 h (Table 3). The yield is low for all terminal alkynes. Only phenylacetylene shows selectivity for the formation of *E*-enynes (entry 10). The aliphatic monoalkynes 3,3-dimethyl-1-butyne and 1-octyne show no selectivity at all (entry 11−12), while the reaction with the dialkyne 1,7-octadiyne gives rise only to polymerisation products.

Table 3. Dimerisation of terminal alkynes in the presence of $[Cl_2(PCy_3)_2Ru{=}CHPh]$

Entry	Alkyne[a]	Yield[b]	Product ratio 4:5:6
10		21	5:87:8
11		3	/[c]
12		18	32:27:41
13		11	polymerisation

[a] Reaction conditions: catalyst/alkyne: 1:100, temperature = 110 °C, time = 5 h. [b] Yield and selectivity as determined by ^1H NMR and GC-MS. [c] Because of the low yield, no unequivocal distinction between the three possible dimeric products is possible.

In order to explain the catalytic activity of a Ru-alkylidene, two reactions were monitored by NMR. In the first, thermal treatment of Grubbs' catalyst was examined. A solution of $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (0.012 mmol) in 0.8 mL $[D_8]$toluene was stirred at 110 °C for 1 h. The Ru=CH bond disappeared, which is in agreement with the results described by Grubbs et al.,[20] who performed similar reactions at 55 °C and established that the decomposition proceeds by a second order reaction pathway requiring phosphane dissociation. The organic product was identified as stilbene, but the inorganic compound remained unclear. Our attempts to monitor the thermal decomposition products gave the same experimental data. The isolation and



Scheme 2

crystallisation of the inorganic compound was unsuccessful, so the nature of the inorganic complex still remains undetermined.

In the second reaction, a solution of $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (0.012 mmol), 3,3-dimethyl-1-butyne (0.12 mmol) and CH_3COOD (0.12 mmol) in 0.8 mL $[D_8]$toluene was stirred at 110 °C for 4 h. A colour change from purple to orange occurred. $^{31}P\{H\}$ NMR revealed a new type of coordinated PCy_3 (δ = 54 ppm) and free phosphane. A Ru-vinylidene complex had been formed, $^{13}C\{H\}$ NMR showing the C_α and C_β of the Ru-vinylidene formed at δ = 338.2 and δ = 109.7 ppm, respectively. After 4 h reaction time, 80% of the 3,3-dimethyl-1-butyne had been converted into the enol esters *t*Bu($OCOCH_3$)C=CHD and *t*Bu-CH=CD−$OCOCH_3$, and a signal due to CH_3COOH at δ = 12.4 ppm had appeared. This was confirmed by GC-MS analysis, which shows a defragmentation pattern characteristic of *t*Bu($OCOCH_3$)C=CHD and *t*Bu-CH=CD−$OCOCH_3$.

Although the detailed mechanism of the catalytic reaction and the nature of the inorganic species after thermal treatment of $[Cl_2(PCy_3)_2Ru{=}CHPh]$ have not been elucidated, the outcomes of the two NMR reactions and the catalytic performance of the Grubbs catalyst suggest some mechanistic insights (Scheme 2). Decoordination of a PCy_3 ligand takes place on the metal centre. This creates a vacant site for the incoming carboxylic acid (cycle 1) or 1-alkyne (cycle 2).

Nucleophilic addition of the carboxylic acid onto the alkyne or vinylation (cycle 1) is preferred for the aliphatic alkynes. The Ru-vinylidene catalyses the regioselective intermolecular attack of the acid at the internal C-2 carbon atom of the terminal alkyne, and thus production of Markovnikov adducts (**11b**). Generally, Ru-based systems afford enol esters bearing *exo*-olefins. The ring-closure of the intramolecular addition proceeds by attack on the C-1 carbon atom of the triple bond and formation of the *anti*-Markovnikov 6-*endo* compound (**11a**).

For arylacetylene derivatives, vinylation (cycle 1) is preferred when strong acids are used or at low pK_a values (trichloroacetic acid), while dimerisation (cycle 2) is favoured when weak acids are added or at high pK_a values (acetic acid). The vinylation of arylacetylene compounds proceeds preferentially by attack of the acid on the internal C-2 atom of the 1-alkyne (**11b**) and formation of Markovnikov products. With acetic acid, the dimeric products are formed by an intermolecular attack of the incoming alkyne on the terminal C-1 atom of the coordinated alkyne (**13a**).

In the absence of carboxylic acids, only dimerisation (cycle 2) occurs for all terminal alkynes. For arylacetylene derivatives, the intermolecular attack proceeds preferentially on the internal C-2 of the terminal alkyne, with a supplementary stereoselectivity for *trans* addition (**13a**).

Conclusion

The transformation of phenylacetylene initiated by thermolysed Grubbs' Ru-alkylidene is pH-dependent. At low pK_a values, vinylation is preferred. Increasing the pK_a of the carboxylic acid results in a change of preference towards dimerisation of the 1-alkynes. Terminal alkynes other than arylacetylenes only undergo nucleophilic addition of the carboxylic acid at the triple bond or vinylation. Like most Ru complexes, $[Cl_2(PCy_3)_2Ru{=}CHPh]$ exhibits a regioselectivity for Markovnikov addition. The activity and selectivity for the dimerisation of terminal alkynes is low.

Experimental Section

General Remarks: All reactions were performed under inert atmosphere by use of Schlenk techniques. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer. GC-MS analysis was performed on a GC (column SPB™-5: 30 m × 0.25 mm × 0.25 μm film thickness, carrier gas: He, 100 kPa, detector: FID, gas chromatograph: Varian 4600) and MS (Finnigan MAT ITD) setup. $[D_8]$toluene (obtained from Acros) and toluene were dried over Na. $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (obtained from Strem Chemicals), alkynes and carboxylic acids (obtained from Acros) were used without further purification.

General Procedure for Vinylation Catalysed by $[Cl_2(PCy_3)_2Ru{=}CHPh]$: A solution of Grubbs' catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (0.032 mmol) in toluene (3 mL) was heated at 110 °C for 1 h. 1-Alkyne (3.072 mmol, 96 equiv.) and carboxylic acid (3.584 mmol, 112 equiv.) were added, and the reaction mixture was stirred at 110 °C. The reaction was monitored by ^1H NMR and GC-MS.

General Procedure for Dimerisation Catalysed by $[Cl_2(PCy_3)_2Ru{=}CHPh]$: A solution of Grubbs' catalyst $[Cl_2(PCy_3)_2Ru{=}CHPh]$ (0.032 mmol) in toluene (3 mL) was heated at 110 °C for 1 h. 1-Alkyne (3.20 mmol, 100 equiv.) was added, and the reaction mixture was stirred at 110 °C. The reaction was monitored by ^1H NMR and GC-MS.

1. Phenylacetylene and Acetic Acid

***anti*-Markovnikov *cis*-Ph-CH=CH−$OCOCH_3$:** ^1H NMR ($[D_8]$toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 6.54 (d, J = 11.3 Hz, =C*H*$OCOCH_3$), 5.78 (d, J = 11.3 Hz, Ph-C*H*=CH), 2.05 (s, OCH_3) ppm. GC-MS: m/z = 162 [M^+].

***anti*-Markovnikov *trans*-Ph-CH=CH−$OCOCH_3$:** ^1H NMR ($[D_8]$toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 6.91 (d, J = 16.2 Hz, =C*H*$OCOCH_3$), 6.25 (d, J = 16.2 Hz, Ph-C*H*=CH), 2.05 (s, OCH_3) ppm. GC-MS: m/z = 162 [M^+].

Markovnikov (Ph)($OCOCH_3$)C=CH_2: ^1H NMR ($[D_8]$toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 5.31 (s, =CH_2), 4.87 (s, =CH_2), 2.05 (s, OCH_3) ppm. GC-MS: m/z = 162 [M^+].

2. Phenylacetylene and Formic Acid

***anti*-Markovnikov *cis*-Ph-CH=CH−OCOH:** ^1H NMR ($[D_8]$toluene, 300 MHz, 25 °C): δ = 9.45 (br. s, O*H*), 8.05−7.05 (m, Ph), 6.65 (d, J = 16.6 Hz, =C*H*OCOH), 5.67 (d, J = 16.6 Hz, Ph-C*H*=CH) ppm. GC-MS: m/z = 148 [M^+].

***anti*-Markovnikov *trans*-Ph-CH=CH−OCOH:** ^1H NMR ($[D_8]$toluene, 300 MHz, 25 °C): δ = 9.45 (br. s, O*H*), 8.05−7.05 (m, Ph), 7.87 (d, J = 12.2 Hz, =C*H*OCOH), 6.32 (d, J = 12.2 Hz, Ph-C*H*=CH) ppm. GC-MS: m/z = 148 [M^+].

Markovnikov (Ph)(OCOH)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 9.45 (br. s, O*H*), 8.05−7.05 (m, Ph), 5.15 (s, =CH_2), 4.73 (s, =CH_2) ppm. GC-MS: *m*/*z* = 148 [M$^+$].

3. Phenylacetylene and Isovaleric Acid

***anti*-Markovnikov *cis*-Ph-CH=CH−OCOCH$_2$−CH−(CH$_3$)$_2$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph, 6.50 [d, *J* = 19.9 Hz, = C*H*OCOCH$_2$−CH−(CH$_3$)$_2$], 5.66 (d, *J* = 19.9 Hz, Ph-C*H*=CH), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH_3) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

***anti*-Markovnikov *trans*-Ph−CH=CH−OCOCH$_2$−CH−(CH$_3$)$_2$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 8.07 [d, *J* = 13.2 Hz, =C*H*OCOCH$_2$−CH−(CH$_3$)$_2$], 6.36 (d, *J* = 13.2 Hz, Ph-C*H*=CH), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH_3) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

Markovnikov (Ph)(OCOCH$_2$−CH−(CH$_3$)$_2$]C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 5.32 (s, =CH_2), 5.03 (s, =CH_2), 2.38 (d, OCH_2), 1.51 (m, C*H*), 1.20 (s, CH$_3$) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

4. Phenylacetylene and Trichloroacetic Acid

***anti*-Markovnikov *cis*-Ph-CH=CH−OCOCCl$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 6.46 (d, *J* = 11.7 Hz, = C*H*OCOCCl$_3$), 6.11 (d, *J* = 11.7 Hz, Ph-C*H*=CH), ppm. GC-MS: *m*/*z* = 277 [M$^+$].

***anti*-Markovnikov *trans*-Ph-CH=CHOCOCCl$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 7.00 (d, *J* = 8.2 Hz, =C*H*OCOCCl$_3$), 6.58 (d, *J* = 8.2 Hz, Ph-C*H*=CH) ppm. GC-MS: *m*/*z* = 277 [M$^+$].

Markovnikov (Ph)(OCOCCl$_3$)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.05−7.05 (m, Ph), 5.67 (s, =CH$_2$), 5.55 (s, =CH$_2$) ppm. GC-MS:*m*/*z* = 277 [M$^+$].

5. 1-Octyne and Acetic Acid

***anti*-Markovnikov *cis*-CH$_3$−(CH$_2$)$_5$−CH=CH−OCOCH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.37 (d, *J* = 11.5 Hz, = C*H*OCOCH$_3$), 5.24 [d, *J* = 11.5 Hz, CH$_3$−(CH$_2$)$_5$C*H*=CH], 2.12 (s, OCH_3), 1.31−1.20 (m, CH_2), 0.87 (t, CH_3) ppm. GC-MS:*m*/*z* = 170 [M$^+$].

***anti*-Markovnikov *trans*-CH$_3$−(CH$_2$)$_5$−CH=CH−OCOCH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.86 (d, *J* = 8.2 Hz, = C*H*OCOCH$_3$), 5.80 [d, *J* = 8.2 Hz, CH$_3$−(CH$_2$)$_5$C*H*=CH], 2.12 (s, OCH_3), 1.31−1.20 (m, CH_2), 0.87 (t, CH_3) ppm. GC-MS:*m*/*z* = 170 [M$^+$].

Markovnikov [CH$_3$−(CH$_2$)$_5$](OCOCH$_3$)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 4.78 (s, =CH_2), 4.63 (s, =CH_2), 2.12 (s, OCH_3), 1.31−1.20 (m, CH_2), 0.87 (t, CH_3) ppm. GC-MS:*m*/*z* = 170 [M$^+$].

6. 3,3-Dimethyl-1-butyne and Acetic Acid

***anti*-Markovnikov *cis*-*t*Bu-CH=CH−OCOCH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 6.96 (d, *J* = 6.8 Hz, =C*H*OCOCH$_3$), 4.52 (d, *J* = 6.8 Hz, *t*BuC*H*=CH), 1.84 (s, OCH_3), 1.09 (t, *t*Bu) ppm. GC-MS:*m*/*z* = 130 [M$^+$].

***anti*-Markovnikov *trans*-*t*Bu-CH=CH−OCOCH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 7.30 (d, *J* = 13.1 Hz, =C*H*OC-OCH$_3$), 5.49 (d, *J* = 13.1 Hz, *t*BuC*H*=CH), 1.84 (s, OCH_3), 1.09 (, *t*Bu) ppm. GC-MS: *m*/*z* = 130 [M$^+$].

Markovnikov (*t*Bu)(OCOCH$_3$)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 4.81 (s, =CH_2), 4.74 (s, =CH_2), 1.84 (s, OCH_3), 1.09 (t, *t*Bu) ppm. GC-MS: *m*/*z* = 130 [M$^+$].

7. 1,7-Octadiyne and Acetic Acid

Full and unequivocal analysis by NMR was impossible due to overlap of signals of the mono- and the disubstituted alkyne.

Monosubstituted Dialkyne:

***anti*-Markovnikov *cis*-CH≡C−(CH$_2$)$_4$−CH=CH−OCOCH$_3$:** GC-MS: *m*/*z* = 166 [M$^+$].

***anti*-Markovnikov *trans*-CH≡C−(CH$_2$)$_4$−CH=CH−OCOCH$_3$:** GC-MS: *m*/*z* = 166 [M$^+$].

Markovnikov [CH≡C−(CH$_2$)$_4$−](OCOCH$_3$)C=CH$_2$: GC-MS: *m*/*z* = 166 [M$^+$].

Disubstituted Dialkyne:

***anti*-Markovnikov *cis*-CH$_3$OCO−CH=CH−(CH$_2$)$_4$−CH=CH−OCOCH$_3$:** GC-MS: *m*/*z* = 226 [M$^+$].

***anti*-Markovnikov *trans*-CH$_3$OCO−CH=CH−(CH$_2$)$_4$−CH=CH−OCOCH$_3$:** GC-MS: *m*/*z* = 226 [M$^+$].

Markovnikov CH$_3$OCO−CH=CH−(CH$_2$)$_4$−CH=CH−OCOCH$_3$: GC-MS: *m*/*z* = 226 [M$^+$].

***anti*-Markovnikov-Markovnikov [CH$_3$OCO−CH=CH−(CH$_2$)$_4$−]-(OCOCH$_3$)C=CH$_2$:** GC-MS: *m*/*z* = 226 [M$^+$].

8. Pentynoic Acid

***anti*-Markovnikov:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.23 (d, *J* = 5.06 Hz, =C*H*OCO) 5.02 (d, *J* = 5.06 Hz, C*H*C= CHOCO), 2.32 (t, H_2CCOO), 1.61 (q, CH−CH_2−CH$_2$) ppm. GC-MS: *m*/*z* = 98 [M$^+$].

Markovnikov: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 4.63 (s, =C*H*OCO), 3.95 (t, *H*C=CHOCO), 2.49 (t, CH_2CCOO), 1.91 (q, CH$_2$=C−CH_2−CH$_2$) ppm. GC-MS: *m*/*z* = 98 [M$^+$].

Spectroscopic Data for Dimeric Products

1. Phenylacetylene

***cis*-Ph−CH=CH−C≡CPh:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.10−6.80 (m, Ph), 6.48 (d, *J* = 12.0 Hz, =C*H*Ph), 5.84 (d, *J* = 12.0 Hz, =C*H*C≡C) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

***trans*-Ph-CH=CH−C≡CPh:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.10−6.80 (m, Ph), 7.04 (d, *J* = 16.6 Hz, =C*H*Ph), 6.33 (d, *J* = 16.6 Hz, =C*H*C≡C) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

(Ph-C≡C−)(Ph)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 8.10−6.80 (m, Ph), 5.37 (s, =CH_2), 4.92 (s, =CH_2) ppm. GC-MS: *m*/*z* = 204 [M$^+$].

2. 3,3-Dimethylbutyne

***cis*-*t*Bu-CH=CH−C≡C*t*Bu:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.21 (d, *J* = 14.4 Hz, =C*H*t*Bu*), 4.97 (d, *J* = 14.4 Hz, = C*H*C≡C), 1.43 (s, *t*Bu) ppm. GC-MS: *m*/*z* = 140 [M$^+$].

***trans*-*t*Bu-CH=CH−C≡C*t*Bu:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.53 (d, *J* = 11.6 Hz, =C*H*t*Bu*), 5.65 (d, *J* = 11.6 Hz, =C*H*C≡C), 1.43 (s, *t*Bu) ppm. GC-MS: *m*/*z* = 140 [M$^+$].

(*t*Bu-C≡C−)(*t*Bu)C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.37 (s, =C*H*$_2$), 4.92 (s, =C*H*$_2$), 1.43 (s, *t*Bu) ppm. GC-MS: *m*/*z* = 140 [M$^+$].

3. 1-Octyne

***cis*-CH$_3$−(CH$_2$)$_5$−CH=CH−C≡C(CH$_2$)$_5$−CH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 4.52 (d, *J* = 18.7 Hz, = C*H*tBu), 4.42 (d, *J* = 18.7 Hz, =C*H*C≡C), 1.50−1.01 (m, C*H*$_2$), 0.88 (t, C*H*$_3$) ppm. GC-MS: *m*/*z* = 220 [M$^+$].

***trans*-CH$_3$−(CH$_2$)$_5$−CH=CH−C≡C(CH$_2$)$_5$−CH$_3$:** ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.18 (d, *J* = 14.0 Hz, = C*H*tBu), 4.95 (d, *J* = 14.0 Hz, =C*H*C≡C), 1.50−1.01 (m, C*H*$_2$), 0.88 (t, C*H*$_3$) ppm. GC-MS: *m*/*z* = 220 [M$^+$].

[CH$_3$-(CH$_2$)$_5$−C≡C−][(CH$_2$)$_5$−CH$_3$]C=CH$_2$: ^{1}H NMR ([D$_8$]toluene, 300 MHz, 25 °C): δ = 5.37 (s, =C*H*$_2$), 4.92 (s, =C*H*$_2$), 1.50−1.01 (m, C*H*$_2$), 0.88 (t, C*H*$_3$) ppm. GC-MS: *m*/*z* = 220 [M$^+$].

4. 1,7-Octadiyne

Full and unequivocal analysis by NMR was impossible due to the overlap of signals of the mono- and the disubstituted alkyne.

Monosubstituted Dialkyne:

***cis*-CH≡C−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡CH:** GC-MS: *m*/*z* = 212 [M$^+$].

***trans*-CH≡C−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡CH:** GC-MS: *m*/*z* = 212[M$^+$].

[CH≡C−(CH$_2$)$_4$][−C≡C−(CH$_2$)$_4$−C≡CH]−C=CH$_2$: GC-MS: *m*/*z* = 212 [M$^+$].

Disubstituted Dialkyne:

***cis*-HC≡C−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡CH:** GC-MS: *m*/*z* = 318 [M$^+$].

***trans*-HC≡C−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡C−CH=CH−(CH$_2$)$_4$−C≡CH:** GC-MS: *m*/*z* = 318 [M$^+$].

(CH$_2$=C)[−(CH$_2$)$_4$][−C≡C−(CH$_2$)$_4$−C≡CH](−C=CH$_2$)-[−C≡C−(CH$_2$)$_4$−C≡CH]: GC-MS: *m*/*z* = 318 [M$^+$].

Acknowledgments

K. M. and T. O. are indebted to the BOF (Bijzonder Onderzoeksfonds) of Ghent University for a research grant. F.V. is indebted to FWO (Fonds voor Wetenschappelijk Onderzoek-Vlaanderen) and the Research Funds of Ghent University for financial support.

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Received February 22, 2002
[O02098]