Intramolekulare konzertierte Insertion von Vinylkationen in C–H-Bindungen: Cyclisierende Hydroalkylierung von Alkinen mit Chlorameisensäurealkylestern zu Cyclopentanen**

Ursula Biermann, Rainer Koch und Jürgen O. Metzger*

Supporting Information.

Experimental Section

All reactions were performed under nitrogen. Solvents were dried and distilled according to standard procedures. 4-Octyne (**2a)**, 5-decyne (**2b)**, 3-hexyne (**2c)**, and 1-octyne (**2d)** were obtained from Aldrich and used as received. $Et_3Al_2Cl_3$ was purchased from Crompton GmbH and isopropyl (**1a)** and 2-butyl chloroformate (**1b)** were obtained from BASF and Laxness, respectively. Analytical GC was performed on a Carlo Erba GC series 4160 with a FID detector and fused silica capillary column DB1, 29m. Tetradecane (Aldrich) was used as internal standard for quantitative GC-analyses of cyclopentanes **9** and **10.** ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or Bruker AM 500 spectrometer at 20°C using TMS (^{1}H NMR) and $CDCl_3$ (δ = 77.0 ppm, ^{13}C NMR) as internal standard. Mass spectra were recorded on a Finnigan MAT 95. Unsaturated hydroalkylation products **4** were identified and separated by addition of bromine.

Reaction of 4-octyne (2a) and isopropyl chloroformate (**1a**):

A mixture of 4-octyne (**2a**, 1.1g, 10mmol) and of isopropyl chloroformate (**1a**, 1.2g, 10mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (1.16g, 10mmol) and $Et_3Al_2Cl_3$ (2.48 g, 10mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 1h. Diethyl ether

(100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue filtrated over silica gel 60 with pentane (150 mL) to remove triethylsilyl derivatives. Purification of the crude product by Kugelrohr distillation (16mbar, 100°C) gave 1.21g (79%) of 1-isopropyl-2-propylcyclopentane (**5a**) as a mixture of two diastereomers (ratio: 4.6 : 1).- ^{13}C NMR (125.8 MHz), main product: δ = 14.46 (*prim.*), 18.73 (*prim.*), 21.71 (*sec.*), 23.0 (*prim.*), 24.73 (*sec.*), 28.42 (*sec.*), 30.84 (*tert.*), 33.05 (*sec.*), 38.83 (*sec.*), 42.31 (*tert.*), 52.42 (*tert.*); minor product: δ = 14.46 (*prim.*), 18.73 (*prim.*), 21.29 (*sec.*), 22.33 (*prim.*), 28.16 (*sec.*), 28.99 (*sec.*), 29.18 (*tert.*), 30.0 (*sec.*), 38.67 (*sec.*), 40.23 (*tert.*), 52.68 (*tert.*).- GC/MS (EI), main product: m/z (%) 154 (7) [M^+], 139 (3), 126 (2), 112 (5), 111 (66), 110 (35), 84 (4), 83 (6), 70 (11), 69 (100), 55 (40), 41 (32); minor product: m/z (%) 154 (6) [M^+], 139 (2), 126 (3), 112 (7), 111 (73), 110 (31), 84 (7), 83 (10), 70 (15), 69 (100), 55 (41), 41 (32)..- HR-MS (EI) $C_{11}H_{22}$ calcd. 154.1722; found 154.1722.

Comparison of the mass spectra with mass spectra of 1,2-dipropylcyclopentane[1] give evidence that the major product should be *trans*-**5a** and the minor product *cis*-**5a.**

Reaction of 5-decyne (2b) and isopropyl chloroformate (**1a**):

A mixture of 5-decyne (**2b**, 1.38g, 10mmol) and of isopropyl chloroformate (**1a**, 1.2g, 10mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (1.16g, 10mmol) and $Et_3Al_2Cl_3$ (2.48 g, 10mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 1h. Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue was dissolved in pentane and filtrated over silica gel 60 to remove triethylsilyl derivatives.

Purification of the crude product by Kugelrohr distillation (16mbar, 85°C) gave 1.35g (74%) of 2-butyl-1-isopropyl-3-methylcyclopentane (**5b**) as a mixture of four diastereomers (ratio: a) : b) : c) : d) = 11 : 1: 6: 1).- ^{13}C NMR (125.8 MHz), main diastereomer: δ = 14.16, 18.52, 22.26, 23.14, 23.66, 26.37, 30.08, 31.12 (*tert.*), 33.84 (*sec.*), 34.94 (*sec.*), 40.11 (*tert.*), 50.12 (*tert.*), 52.41 (*tert*).- GC/MS (EI), main diastereomer a): m/z (%) 182 (6)[M^+], 140 (6), 139 (39), 138 (47), 126 (5), 125 (7),112 (6), 111 (5), 98 (8), 97 (46), 96 (8), 84 (14), 83 (100), 70 (17), 69 (73), 56 (24), 55 (56), 41 (35); diastereomer b): m/z (%) 182 (4)[M^+], 140 (7), 139 (31), 138 (28), 126 (8), 125 (28), 112 (6), 111 (5), 98 (9), 97 (39), 96 (5), 84 (19), 83 (98), 70 (26), 69 (100), 56 (37), 55 (52), 41 (32); diastereomer c): m/z (%) 182 (12) [M^+], 140 (6), 139 (32), 138 (30), 126 (10), 125 (18), 112 (14), 111 (6), 98 (10), 97 (48), 96 (8), 84 (20), 83 (100), 70 (23), 69 (92), 56 (42), 55 (64), 41 (42); diastereomer d): m/z (%) 182 (9)[M^+], 140 (8), 139 (38), 138 (25), 126 (10), 125 (9), 112 (16), 111 (6), 98 (11), 97 (49), 96 (7), 84 (28), 83 (100), 70 (35), 69 (97), 56 (69), 55 (82), 41 (63)..- HR-MS (EI) $C_{13}H_{26}$ calcd. 182.2035; found 182.2023.

Comparison of the mass spectra of the diastereomers of **5b** with the mass spectra of authentic diastereomers of 1-ethyl-2,3-dimethylcyclopentane and 2-ethyl-1,3-dimethylcyclopentane[2] give evidence that the major diastereomer should be *trans, trans*-**5b**.

Reaction of 3-hexyne (2c) and isopropyl chloroformate (**1a**):

A mixture of 3-hexyne (**2c**, 0.82g, 10mmol) and of isopropyl chloroformate (**1a**, 1.2g, 10mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (1.16g, 10mmol) and $Et_3Al_2Cl_3$ (2.48 g, 10mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 30min. with occasionally cooling (-10°C). Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue was dissolved in pentane and filtrated over silica gel 60 to remove triethylsilyl derivatives. Purification of the crude product by Kugelrohr distillation (17mbar, 65°C) gave 0.61g (38%) of 3-chloro-4-isopropyl-3-hexene (**6c**) as a mixture of the [*E*]- and [*Z*]-stereoisomer (3 : 1).- HR-MS (EI) $C_9H_{17}Cl$ calcd. 160.1019; found 160.1020.

Reaction of 1-octyne (2d) and isopropyl chloroformate (**1a**):

A mixture of 1-octyne (**2d**, 0.55g, 5mmol) and of isopropyl chloroformate (**1a**, 0.61g, 5mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then $Et_3Al_2Cl_3$ (1.86g, 7.5mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 30min with occasionally cooling (-5°C). Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue was dissolved in pentane and filtrated over silica gel 60 to remove triethylsilyl derivatives. Purification of the crude product by Kugelrohr distillation (4mbar, 85°C) gave 0.33g (35%) of 4-chloro-2-methyl-3-decene (**6d**) as a mixture of the [*E*]- and [*Z*]-stereoisomer (1 : 1).- HR-MS (EI) $C_{11}H_{21}Cl$ calcd. 188.1332; found 188.1332.

Reaction of 4-octyne (2a) and 2-butyl chloroformate (**1b**):

A mixture of 4-octyne (**2a**, 1.1g, 10mmol) and of 2-butyl chloroformate (**1b**, 1.36g, 10mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (1.16g, 10mmol) and $Et_3Al_2Cl_3$ (2.48 g, 10mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 1h. Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue filtrated over silica gel 60 with pentane (150 mL) to remove triethylsilyl derivatives. Purification of the crude product by Kugelrohr distillation (16mbar, 100°C) gave 0.88g (52 %) of a mixture of 1-methyl-2,3-dipropylcyclopentane (**9a**) and 1-*sec*.butyl-2-propylcyclopentane (**10a**) in a ratio of 1 : 3. **9a** and **10a**, respectively, was formed as a mixture of 4 diastereomers. GC/MS (EI), main diastereomer of **9a**: m/z (%)168 (23)[M^+], 126 (32), 125 (54), 112 (15), 111 (16), 98 (18), 97 (15), 84 (57), 83 (57), 70 (40), 69 (100), 56 (57), 55 (65), 41 (34); main diastereomer of **10a**: m/z (%)168 (4) [M^+], 126 (0.5), 125 (4); 139 (24), 111 (58), 110 (38), 98 (3), 97 (17), 84 (6), 83 (46), 70 (25), 69 (100), 56 (15), 55 (52), 41 (30).

Reaction of 3-hexyne (2c) and 2-butyl chloroformate (**1b**):

A mixture of 3-hexyne (**2c**, 0.41g, 5mmol), tetradecane (0.4g, 2mmol) and 2-butyl chloroformate (**1b**, 0.68g, 5mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (0.58g, 5mmol) and $Et_3Al_2Cl_3$ (1.24g, 5mmol) was added dropwise over 1h at –15°C and the solution was stirred at room temperature for a further 1h with occasionally cooling (-5°C). Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue was dissolved in pentane and filtrated over silica gel 60 to remove triethylsilyl derivatives. Quantitative analysis was performed by GC, based on tetradecane as internal standard, giving as main product 1,2-diethyl-3-methylcyclopentane (**9c**) as a mixture of four diastereomers (ratio: 3.8:1.9:1.4:1) in a yield of 0.18g (26 %).- GC/MS (EI), main diastereomer a): m/z (%) 140 (15) [M^+], 112 (10), 111 (75), 98 (22), 84 (33), 70 (50), 69 (100), 56 (32), 55 (71), 41 (46); diastereomer b): m/z (%) 140 (6) [M^+], 112 (5), 111 (41), 98 (25), 84 (22), 70 (65), 69 (100), 56 (40), 55 (89), 41 (73); diastereomer c): m/z (%) 140 (12) [M^+], 112 (9), 111 (66), 98 (25), 84 (56), 70 (43), 69 (100), 56 (54), 55 (73), 41 (46); diastereomer d): m/z (%) 140 (7) [M^+], 112 (6), 111 (25), 98 (35), 84 (52), 70 (69), 69 (98), 56 (86), 55 (100), 41 (89).

Comparison of the mass spectra of the diastereomers of **9c** with the mass spectra of authentic diastereomers of 1-ethyl-2,3-dimethylcyclopentane and 2-ethyl-1,3-dimethylcyclopentane[2] give evidence that the major diastereomer should be *trans, trans*-**9c** and the less diastereomer *cis, cis*-**9c.**

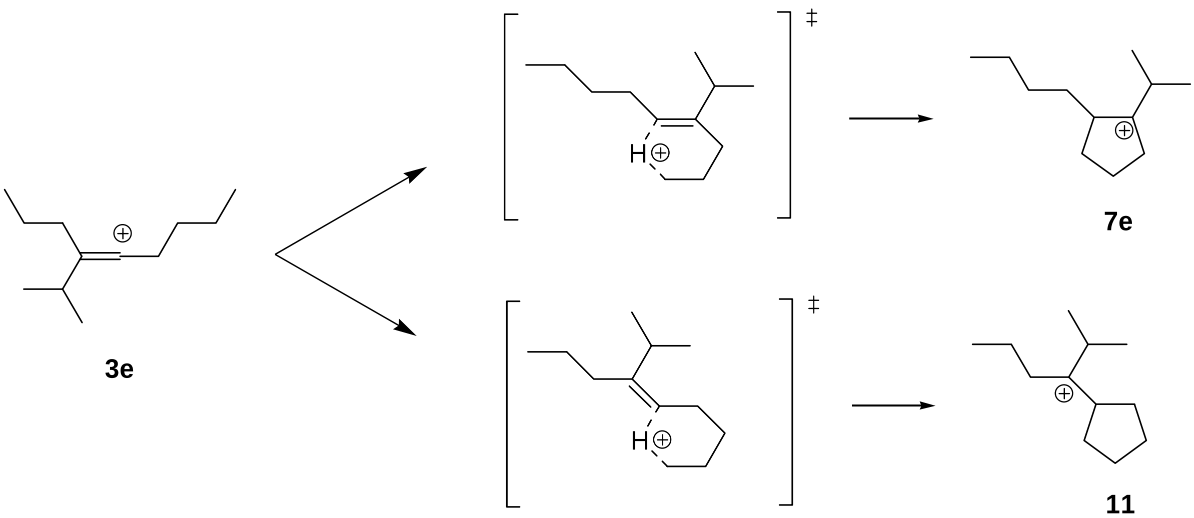
Reaction of 1-octyne (2d) and 2-butyl chloroformate (1b):

A mixture of 1-octyne (**2d**, 1.1g, 10mmol), tetradecane (0.99g, 5mmol) and 2-butyl chloroformate (**1b**, 1.36g, 10mmol) in CH_2Cl_2 (10 mL) was stirred in a N_2 atmosphere (1 bar) for 5 min at –15°C. Then a mixture of triethylsilane (1.16g, 10mmol) and $Et_3Al_2Cl_3$ (2.48 g, 10mmol) was added dropwise over 1h at –15°C and the solution was stirred at +10°C for a further 1h. Diethyl ether (100 mL), H_2O (40 mL), and 10% HCl to dissolve precipitated aluminum salts were then added. The organic phase was separated and washed with H_2O (3 x 30 mL). The combined extracts were dried over Na_2SO_4, the solvent was removed in vacuo and the residue was dissolved in pentane and filtrated over silica gel 60 to remove triethylsilyl derivatives. Quantitative analysis was performed by GC, based on tetradecane as internal standard, giving as main product 1-hexyl-3-methylcyclopentane (**9d**) in a yield of 0.22g (13%). **9d** was obtained as a mixture of two diastereomers which could not be separated by GC.- GC/MS (EI), m/z (%) 168 (12)[M^+], 140 (22), 139 (10), 112 (9), 111 (11), 98 (10), 97 (38), 83 (100), 82 (49), 70 (37), 69 (31), 56 (37), 55 (69), 41 (30).

Mass spectra give evidence of the formation of **9d** by comparison with literature data. However, the mass spectra of *cis*- and *trans*-isomers are most similar and could not be differentiated.[1]

Table S1: **Energies of calculated structures.**

	MP2/6-31G(d)	MP2/6-311+G(d,p) SP	MP2/6-31G(d)		MP2 SP + ZVPE
	Absolute energies		ZPVE	ZPVE scaled	Rel. energies
	a.u.		kcal/mol		kJ/mol
2-Propylcation	-117.74125	-117.82872	56.767	54.894	
4-Octyne **2a**	-312.07913	-312.30152	127.683	123.469	
Reactants	-429.82038	-430.13024	184.450	178.363	0.0
Vinyl cation **3a**	-429.90154	-430.21282	189.250	183.005	-197.4
TS	-429.89486	-430.21003	189.496	183.243	-189.1
Cyclopentyl cation **7a**	-429.95383	-430.26418	190.953	184.652	-325.4
Vinyl cation **3e**	-469.06816	-469.40914	207.612	200.761	0.0
TS endo	-469.06152	-469.40683	207.830	200.972	7.0
TS exo	-469.05288	-469.39843	207.300	200.459	26.9
Cyclopentyl cation **7e**	-469.12010	-469.46032	209.291	202.384	-127.6
Cyclopentyl cation **11**	-469.12208	-469.46337	210.850	203.892	-129.3



Scheme S1: Model reaction of vinyl cation **3e** via the endo- (top) and exocyclic (bottom) pathways to give cyclopentyl cation **7e** and **11,** respectively.

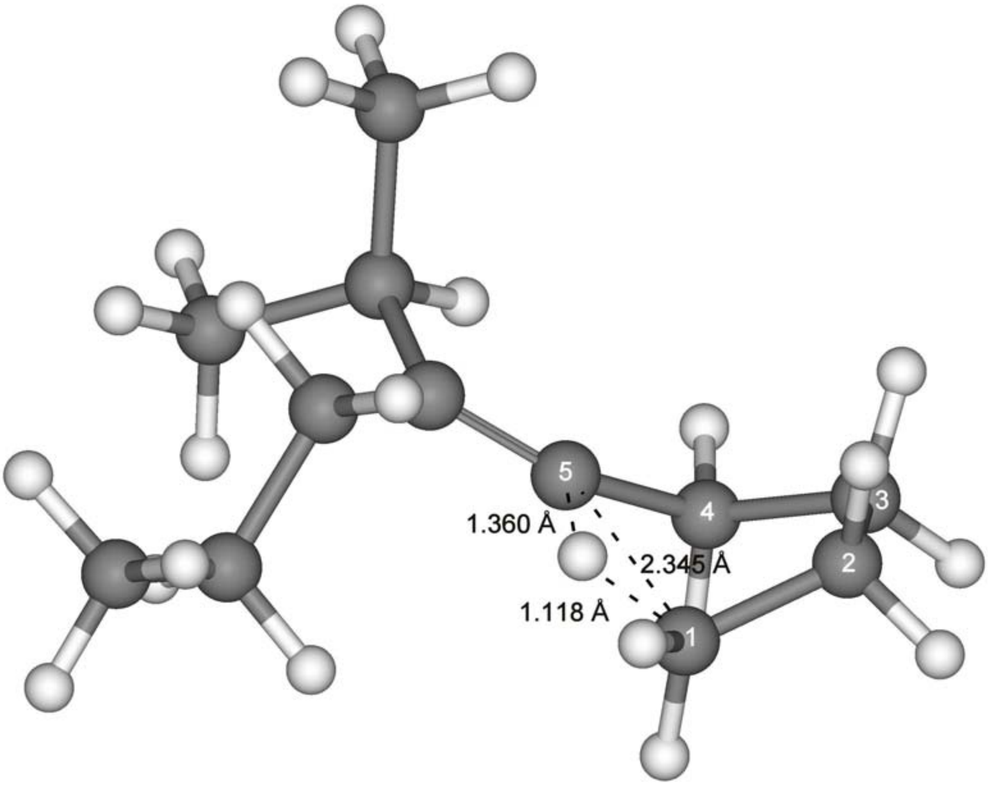


Figure S1: Model transition structure for the formation of the exocyclic cyclopentyl cation **11**. Carbon atoms 2 and 3 are situated above the plane formed by carbon atoms 1, 4, 5 and the transferred hydrogen atom. The angle between C – 1, H, C – 5 is 134°.

Cartesian coordinates of MP2/6-31G(d)-optimized structures

Vinyl cation **3a**

C 0.4810216921 0.0225548844 -0.2216284441
C -0.7226762475 0.3580069675 -0.0972587986
C -1.7300002666 1.4244891712 0.1561448063
C 1.846927987 -0.4385461515 -0.3565570025
C -1.2444677788 2.7931214991 -0.3393353685
C 0.0350221506 3.2656084916 0.3396296868
C 2.3234336251 -1.3851332482 0.759643785
C 3.8038195899 -1.7155070869 0.5929128224
C -1.9134039419 -1.6114636393 0.9530768197
C -1.1502081875 -1.2363025439 -0.312352103
C -1.930415272 -1.3011609118 -1.6179814856
H -1.9197295827 1.4535953616 1.2363157066
H -2.6699705946 1.1470418937 -0.3296816937
H 2.4407489883 0.4913029659 -0.3377176834
H 1.9993293502 -0.8680059427 -1.3554906199
H -2.0532428616 3.5047271325 -0.1425130143
H -1.1145529065 2.7568271925 -1.4258839241
H 0.3000175938 4.269227772 -0.000785724
H 0.8843512975 2.6138411946 0.1064209475
H -0.081977395 3.2990937114 1.4267649214
H 1.7296491337 -2.3055697648 0.7308153612
H 2.142079567 -0.9119404184 1.7296758173
H 4.1284051033 -2.4001242498 1.3793036948
H 4.4183093913 -0.8135414369 0.6578335133
H 3.9966532547 -2.194930441 -0.3706501236
H -2.8132188241 -1.0036864389 1.0686452897
H -1.2901100837 -1.5072798047 1.8441293182
H -2.2175866739 -2.6592656996 0.8660695686
H -0.2861357968 -1.909761046 -0.3948725234
H -2.8310880049 -0.6853408094 -1.5812159487
H -2.2379303499 -2.3395013484 -1.7772014328
H -1.3183207084 -0.9907144162 -2.4677297583

TS concerted of the formation of cyclopentyl cation **7a** (see Figure 1 of the main text)

C 0 -0.4752185301 0.2648820965 -0.710489088
C 0 0.7541173519 0.11145674 -0.2398003294
C 0 1.4739008157 1.3212206006 0.3119621566
C 0 -1.6581666582 -0.4535934367 -1.2353963852
C 0 0.4126946579 2.2446562198 0.9190127269
C 0 -0.7541353098 2.3786270759 -0.0232682707
C 0 1.6119239177 -1.7833777107 1.1497067025
C 0 1.4341499413 -1.2463022747 -0.2752675097
C 0 2.7679147946 -1.1425892255 -1.0216398008
C 0 -2.8796430503 -0.4332489621 -0.3039531091
C 0 -2.5874724759 -0.9891717064 1.0847672663
H 0 2.0362648353 1.8094111198 -0.4950625752
H 0 2.2008628434 1.029849418 1.0733625669
H 0 -1.9150762347 -0.0870981858 -2.2363502972
H 0 -1.3052307471 -1.4882095335 -1.3597808946
H 0 0.8289801898 3.2402361267 1.1120700185
H 0 0.0749263623 1.824082715 1.869182085
H 0 -0.6616699078 3.1609238971 -0.7870245436
H 0 -1.7574753909 2.3383106574 0.3983070771
H 0 0.655656501 -1.8509684551 1.6755904514
H 0 2.2907009523 -1.1557877111 1.7337940702
H 0 2.0466256728 -2.7859419573 1.1028411229
H 0 0.7890585149 -1.9416578806 -0.8240708981
H 0 3.4734506973 -0.4992991021 -0.4881243839
H 0 2.6332451105 -0.7533288766 -2.0346176663
H 0 3.2164280105 -2.1368730438 -1.097500963
H 0 -3.2716535803 0.5885059902 -0.2380124618
H 0 -3.6631827212 -1.0236848331 -0.7895212807
H 0 -1.839899314 -0.3897917148 1.6134494285
H 0 -2.2156998764 -2.0166242314 1.0237561669
H 0 -3.4953324527 -1.0004288483 1.692100195
H 0 -0.7213721934 1.5030179478 -0.8781933747

Cyclopentyl cation **7a**

C 0.4038130394 -0.5177630911 0.0441144826
C 0.2435301715 0.9428617088 0.1324935232
C 1.3076728689 1.5154353485 0.9629985621
C -0.8583552452 -1.378742375 -0.0712991567
C 2.3191678065 0.3865072987 1.1926679075
C 1.4317733846 -0.8594264523 1.1448604661
C -0.2135385129 1.8780602267 -2.0005429048
C -0.7856372703 1.7219906089 -0.5426707148
C -1.0883344083 3.0895857378 0.068666405
C -0.5380867752 -2.8666573041 -0.220389747
C -1.8039687988 -3.6975619141 -0.4122180525
H 0.9639167893 -0.5865322177 -0.9209791561
H 0.7539340329 1.7151828872 1.9088920726
H 1.6743460136 2.4948160553 0.6370029386
H -1.4741944667 -1.2214058534 0.8236342109
H -1.4538826707 -1.0543674858 -0.932925438
H 2.8643082712 0.5002752325 2.1315951771
H 3.0521642207 0.3727781343 0.3788271619
H 1.9825360849 -1.7746467153 0.9215868896
H 0.9072554965 -1.0057912507 2.0972664794
H -0.1216291914 0.9161706778 -2.5081347774
H 0.7528127411 2.3882548513 -1.9948278968
H -0.930000035 2.4972522906 -2.545425174
H -1.6981876355 1.1233456918 -0.6312933928
H -0.2195663773 3.7513752005 0.0336486464
H -1.4243963802 3.0000176767 1.1051196724
H -1.8907108471 3.5615928024 -0.5029491155
H 0.1339955999 -3.0079106995 -1.0763281255
H 0.0002425264 -3.2189477448 0.6659883353
H -2.3414497702 -3.3940044589 -1.3151602328
H -2.4798660097 -3.5852040179 0.4403283614
H -1.5598459541 -4.7579898129 -0.5079512608

TS formation of endocyclic cyclopentyl cation **7e**

C -0.1303139193 0.3624879925 -0.8746264063
C 1.0978595679 0.2484274602 -0.3904338554
C 1.7496002222 1.4661903858 0.2244890637
C -1.2698776988 -0.3887803487 -1.4467538878
C 0.6352672141 2.3096020234 0.8524075156
C -0.5225867645 2.4282883081 -0.1029905256
C 2.0066244765 -1.6635804554 0.9390403721
C 1.8405891485 -1.0743291862 -0.4666116928
C 3.1860148856 -0.8793602778 -1.1724196311
C -2.5161578297 -0.4309579011 -0.5498975475
C -2.2491674183 -0.9813326546 0.8479905668
C -3.5257135996 -1.0896634162 1.6780018283
H 2.299610875 2.0158913569 -0.5508812006
H 2.4783208511 1.1771285396 0.9851337166
H -1.5118138418 -0.0134746796 -2.4483777936
H -0.874583859 -1.4070762969 -1.578159157
H 0.9990783724 3.3146698277 1.0958705733
H 0.3039915125 1.8311635339 1.7771677007
H -0.457620246 3.247467717 -0.8300330737
H -1.5286818701 2.3202018362 0.2996631875
H -0.4351384402 1.5938304347 -0.9941113901
H 1.0407959161 -1.7968870216 1.4341968149
H 2.6395235842 -1.0309375523 1.5675881821
H 2.4889928412 -2.6422874506 0.8628886772
H 1.2416345682 -1.7732595888 -1.0612385352
H 3.8486031452 -0.2295372382 -0.5936693032
H 3.0585540594 -0.452378654 -2.1710342094
H 3.680787347 -1.8485800566 -1.2789566206
H -2.9587845286 0.571505995 -0.4863516879
H -3.2601450068 -1.0540484908 -1.0589249144
H -1.7802936281 -1.9699141214 0.760580022
H -1.5246107261 -0.3411644951 1.3680813903
H -4.2444769865 -1.7616846822 1.2014997853
H -4.0042770828 -0.1126772772 1.7939645792
H -3.312296564 -1.479903216 2.6759284565

TS formation of exocyclic cyclopentyl cation **11**

C 0.8070084267 -0.3365242079 0.2516018651
C 2.0197181633 -1.0074963915 0.7287063424
C 3.208333056 -0.7797151636 -0.2213229028
C -0.4746985918 -0.3769398993 -0.0413150967
C 3.2247515468 0.6771262074 -0.7579480653
C 2.1721636923 1.5353473113 -0.1097840088
C -1.2821365364 0.7982358469 -0.5425731545
C -1.5966295362 1.816536527 0.5641092284
C -2.4581359891 2.9610321723 0.0379899266
C -1.1588008843 -1.7371068282 0.1847643816
C -2.342294743 -1.5810871452 1.1417873255
C -1.5726472352 -2.3276343844 -1.166134918
H 1.1459378215 0.9365560086 -0.0859603572
H 2.2525845004 -0.681597671 1.7494294261
H 1.7776047443 -2.0774784645 0.7779677744
H 3.1378856181 -1.472176691 -1.0634497308
H 4.1299428753 -1.0172047295 0.314529879
H 3.0802998965 0.6843408888 -1.84055105
H 4.1962848536 1.1431511309 -0.5610833241
H 1.8377908541 2.4035015285 -0.6857997819
H 2.3395553204 1.7857521521 0.9395249799
H -0.7367611815 1.2922746181 -1.3570946995
H -2.2131166265 0.4262590398 -0.9783675732
H -2.1065810011 1.3113231132 1.3901781994
H -0.6582743736 2.2114254544 0.9741066117
H -3.4157900882 2.5889845683 -0.3363865282
H -1.9583635028 3.4907337659 -0.7784051939
H -2.6663898539 3.6833344883 0.8308180135
H -0.4377258631 -2.4191452358 0.6489120851
H -3.120672865 -0.9419430526 0.7166653462
H -2.0308915602 -1.1673092054 2.1044589468
H -2.7834372093 -2.5656899012 1.3226604716
H -0.7147873999 -2.4391787617 -1.8347765342
H -2.3248689238 -1.7093600515 -1.6627726499
H -2.0100142502 -3.3171972618 -1.0038898509

Endocyclic cyclopentyl cation **7e**

C 0 0.0396376924 0.494918689 0.201929325
C 0 2.2752335779 1.3224893275 -0.1333350247
C 0 -1.0388834653 -0.4397396938 -0.3560706194
C 0 1.3691491022 2.5041777325 0.2315172993
C 0 -0.0137738709 1.9911784031 -0.176488884
C 0 -2.4525228083 0.0450244784 -0.0329409023
C 0 -3.5199592368 -0.9357685041 -0.5159674627
C 0 -4.9338015375 -0.4485949556 -0.2114772369
C 0 1.4503402212 0.1192892228 0.0148155032
C 0 1.9699229187 -1.2417091552 0.0243979336
C 0 3.3120706644 -1.4428446841 -0.6782850681
C 0 2.0910329637 -1.5651620981 1.5597128141
H 0 -0.0156413821 0.4656555815 1.3181557128
H 0 2.4575756791 1.3206226148 -1.2323947364
H 0 3.2708470145 1.2609499826 0.3193193743
H 0 -0.911945044 -0.5121266997 -1.4439660473
H 0 -0.905164103 -1.4488039338 0.051602569
H 0 1.6618530305 3.4255705292 -0.2755236109
H 0 1.4128750002 2.6867907831 1.3106685722
H 0 -0.8332527529 2.510928436 0.3226145386
H 0 -0.1648576103 2.0854559824 -1.259048106
H 0 -2.5510884973 0.1880097174 1.0519052285
H 0 -2.6264447343 1.0229181113 -0.4974160525
H 0 -3.3547627256 -1.9115193702 -0.0428655391
H 0 -3.4062356921 -1.08901794 -1.5960996227
H 0 -5.132583853 0.5087467898 -0.7018893436
H 0 -5.6789691318 -1.166121957 -0.5633085357
H 0 -5.0790931404 -0.3144865852 0.8644002959
H 0 1.2132556243 -1.9242394589 -0.3764338638
H 0 3.580149353 -2.5007726253 -0.6305521377
H 0 4.1114822909 -0.8738591977 -0.1974758113
H 0 3.2592811136 -1.1587085968 -1.7326505955
H 0 2.5217513317 -2.5668538795 1.6283729245
H 0 1.1181924724 -1.5652847963 2.054605864
H 0 2.7620984266 -0.8634060633 2.0611328599

Exocyclic cyclopentyl cation **11**

C 0 0.7394773785 -0.7851992667 -0.4348864857
C 0 3.080313541 -0.0117059896 -0.4413042513
C 0 -0.2752357291 0.0826053934 0.0959581146
C 0 -0.4100866555 2.1771428414 1.5394827991
C 0 2.9268833904 -1.0773581497 0.6385311744
C 0 1.4402784797 -1.0446303506 1.0166724854
C 0 -1.5535634065 -0.5215071569 0.5318692408
C 0 -2.4141966902 -0.9435632133 -0.6979711087
H 0 0.3382894611 -1.7471772953 -0.7615292858
H 0 3.0575304288 0.9869522445 0.0092113362
H 0 4.0219616213 -0.0964866936 -0.9900715043
H 0 3.5549048273 -0.9073578987 1.5179403025
H 0 3.168340929 -2.0653674979 0.2327206245
H 0 1.0384095755 -1.9690645518 1.4370404753
H 0 1.2526345216 -0.2394322033 1.7377066535
H 0 -1.3433348057 -1.4344985741 1.1040159751
H 0 -2.1293842362 0.1539066583 1.1668039697
H 0 -1.8568469487 -1.6642277048 -1.3037831792
H 0 -2.6132913248 -0.0738678035 -1.3291398027
C 0 -3.7296690498 -1.5580791654 -0.2264180966
H 0 -4.3117969288 -0.8440225094 0.3617830844
H 0 -4.3322710812 -1.8546745614 -1.0882118206
H 0 -3.5532736997 -2.4463460457 0.3859823901
C 0 1.8610192558 -0.2432093426 -1.3436988102
H 0 2.0832273304 -1.0185583981 -2.0828404496
H 0 1.5558633528 0.6451497192 -1.9040856848
C 0 -0.0615262765 1.5456242078 0.1857202768
C 0 -0.9382377389 2.1662881147 -0.9393557606
H 0 0.9825355049 1.7638379627 -0.0502827636
H 0 -0.1512032641 3.2384289257 1.4996838734
H 0 0.1553652631 1.7253179841 2.3590975308
H 0 -1.4756582554 2.1040839777 1.766096
H 0 -0.6778357701 3.2261107739 -1.0036658007
H 0 -1.9997676473 2.0879850024 -0.6956649695
H 0 -0.7571378483 1.710860954 -1.9164044226

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