Unexpected High Temperature Behaviour of 2,2'-Diethynylbiphenyl in the Gas Phase – A Precursor for Acephenanthrylene Instead of Pyrene

Martin Sarobe, Rieko van Heerbeek, Leonardus W. Jenneskens*, and Jan W. Zwikker

Debye Institute, Department of Physical Organic Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands Fax: (internat.) +31-30/253-4533 E-mail: jennesk@chem.ruu.nl

Received July 1, 1997

Keywords: Polycyclic aromatic hydrocarbons / Flash vacuum thermolysis / Rearrangements / Intramolecular cyclization

Flash Vacuum Thermolysis (FVT) of 2,2'-diethynylbiphenyl (6) gave, instead of pyrene (5), acephenanthrylene (10) and fluoranthene (11) as major products. The unequivocal identification of 9-ethynylphenanthrene (12) at $T \leq 800$ °C suggests that 12 is the initial stable product derived from 6. It is documented that under high-temperature conditions in the gas phase compound 12 is efficiently converted into 10,

Introduction

The recognition that polycyclic aromatic hydrocarbons (PAH) are invariably generated during combustion^[1] in combination with their potentially genotoxic properties^[2] has made the elucidation of their build up mechanism under high-temperature conditions in the gas phase a topical issue.^[3] Important processes proposed to be operational are either C_2 or ethyne (C_2H_2) addition to PAH^[4] as well as PAH isomerizations and interconversions ("annealing").^{[3][5]} Remarkably, only a distinct set of ubiquitous (non-)alternant PAH is found in combustion samples.^[1] Examples are naphthalene ($C_{10}H_8$), phenanthrene (1; $C_{14}H_{10}$), anthracene ($C_{14}H_{10}$) and pyrene (5, $C_{16}H_{10}$), and the cyclopenta-fused PAH (CP-PAH) acenaphthylene (C12H8), acephenanthrylene (10, $C_{16}H_{10}$), fluoranthene (11, $C_{16}H_{10}$), cyclopenta[cd]pyrene (C18H10) and benzo[ghi]fluoranthene $(C_{18}H_{10}).$

With regard to PAH build-up under high-temperature conditions in the gas phase a seminal result has been reported by Brown et al. for phenanthrene (1; $C_{14}H_{10}$).^[6] They have shown that Flash Vacuum Thermolysis (FVT, $p = 3 \times 10^{-2}$ Torr) of 2-ethynylbiphenyl (2) gave 1 and benzazulene (3; ratio of 2/1/3 at T = 560 °C 94:3:3 and at T = 700 °C 0:72:28). The formation of 1 and 3 upon FVT of 2 was interpreted as evidence for the occurrence of ethynyl-ethylidene carbene equilibration ($2 \rightarrow 4$) followed by carbene C-H insertion ($4 \rightarrow 1$) and carbene addition, respectively ($4 \rightarrow 3$; Scheme 1).^{[3][6]}

Surprisingly, the thermal build up of the abundant PAH effluent pyrene (5), is still unresolved. This is unfortunate since 5 has also been proposed as the PAH precursor for 1-ethynylpyrene, which under high-temperature conditions is converted into the genotoxic PAH cyclopenta[cd]pyrene.^[7]

which subsequently rearranges to **11**. The formation of **12** from **6** is rationalized by invoking the transient formation of cyclobuta[*l*]phenanthrene (**13**) by intramolecular cyclization of the ethynyl moieties of **6** followed by a *retro*-carbene C-H insertion and a 1,2-H shift. This interpretation is supported by the results of independent FVT of 2,2'-bis(1-chloroethe-nyl)biphenyl (**15**).





Despite the lack of experimental data, in analogy to the formation of phenanthrene (1) from 2-ethynylbiphenyl (2),^[6] 2,2'-diethynylbiphenyl (6)^[8] is frequently put forward as the pivotal precursor for 5, i.e. compound 6 is converted into 5 by twofold consecutive ethyne-ethylidene carbene equilibration followed by carbene C-H insertion (Scheme 2),^[9]

Here we report some unexpected results obtained upon FVT of 6. In contrast to expectation, the alternant PAH 5 is only a minor product! Instead of 5, the non-alternant cyclopenta-PAH (CP-PAH) acephenanthrylene (10) and fluoranthene (11) are the major products. Product analysis of the pyrolysates obtained at $T \leq 800$ °C reveals that 9-ethynylphenanthrene (12) is the initial stable C₁₆H₁₀ product. This suggests that 12 is presumably derived from the transient intermediate cyclobuta[*I*]phenanthrene (13) obtained by intramolecular cyclization of the ethynyl functionalities of 6 (vide infra).

Results and Discussion

High-Temperature Behaviour of 2,2'-Diethynylbiphenyl (6): FVT of 6 in the temperature range 600-1100 °C gave

FULL PAPER

Scheme 2. Proposed formation of pyrene (5) from 2,2'-diethynylbiphenyl (6) under high-temperature conditions in the gas phase



pyrolysates with reasonable to good mass recoveries. Instead of pyrene (5), which is a minor product at all temperatures, phenanthrene (1), acephenanthrylene (10), fluoranthene (11) and 9-ethynylphenanthrene (12) were unambiguously identified. With the exception of $1 (C_{14}H_{10})$ all products belong to the $C_{16}H_{10}$ potential energy surface. Whereas with increasing temperature the amount of 5 does not vary substantially (yield ca. 2-7%), considerable changes in the product ratio of the compounds 10, 11 and 12 are discernible (Table 1). According to the temperatureconversion data, compound 10 is the major product at $700^{\circ}C \leq T \leq 1000^{\circ}C$ and appears to be formed at the expense of 12, which is only present in the 600 °C $\leq T \leq$ 800°C pyrolysates. This is in line with the results of independent FVT of 12. Compound 12 is efficiently converted into 10, which concomitant with increasing temperature rearranges into 11.^[5b]

Table 1. Product composition of the pyrolysates obtained uponFVT of 2,2'-diethynylbiphenyl (6)

Com- pound	Tempe- rature [°C]	1 [%]	5 [%]	6 [%]	10 [%]	11 [%]	12 [%]	Mass re- covery [%]
6	600	5	2	13	29	5	46	98
·	700	5	$\overline{2}$	-	63	5	25	98
	800	8	4	_	77	9	2	80
	900	13	7	_	50	30		70
	1000	10	5		50	35	—	61
	1100	11	5		34	50	-	37

These observations suggest that two different thermal pathways are operational, viz. a minor pathway leading to 5 presumably by consecutive ethyne-ethylidene carbene equilibration followed by carbene C–H insertion, and a major pathway leading to 12. The latter is subsequently converted consecutively into 10 and 11.^[5b] It is noteworthy that independent FVT of 5 under similar conditions gave pyrolysates containing only starting material; neither 10, 11 nor 12, could be identified.

A rationalization for the different course of reaction is suggested by available literature data for 2,2'-diethynyl-substituted biphenyl derivatives. For example, both in solution and in the melt, 2,2'-distyrylbiphenyl^[10] undergoes photoinduced as well as thermally induced intramolecular cyclization; either the kinetically controlled product 1,2,2a,10btetrahydro-1,2-diphenylcyclobuta[/]phenanthrene or the thermodynamically controlled product 4,5,9,10-tetrahydro-4,9-diphenylpyrene are obtained. For 2,2'-bis(phenylethynyl)biphenyl the cyclization product, viz. 1,2-diphenylcyclobuta[/]phenanthrene^[11], can only be observed after stabilization as its transition-metal complex. In the absence of transition-metal stabilization, rearrangements occur leading ultimately to 4-phenylbenzo[*b*]triphenylene.^[12]

Apparently, under unimolecular FVT conditions at $T \leq$ 600°C, 6 undergoes a similar intramolecular cyclization (Scheme 3). It is expected that the highly strained and kinetically unstable cvclobuta[/lphenanthrene (13) will be generated as a transient intermediate, which immediately will undergo four-membered ring opening giving the ethylidene carbene 14. This process can be envisaged as a retro-carbene C-H insertion, i.e. the opposite route of the usual process occurring with ethynyl-PAH under high-temperature conditions in the gas phase (Scheme 3).^{[3][6]} Intermediate 14 can either give 9-ethynylphenanthrene (12) by a 1,2-H shift in the lower temperature range or furnish acephenanthrylene (10) upon carbene C-H insertion. As expected, compound 12 will also be converted into 10 and the latter will ultimately rearrange into 11 under FVT conditions (Table 2).^[5b] Furthermore, since neither 10 nor 12 are converted into 1 under FVT conditions,^[5b] we expect that the proposed transient intermediate 13 is also the precursor for 1, i.e. 1 is presumably obtained by C_2 extrusion^{[3][13]} from 13. The small amount of 1 found in the whole temperature range indicates that retro-carbene C-H insertion is preferred over C₂ extrusion.

Remarkably, the extent of conversion under FVT conditions of 6 into 12, 10 and finally 11 is considerably more efficient than the direct conversion of 12 (cf. Tables 1 and 2^[5b]). This is rationalized by the results of semiempirical AM1 calculations.^[14] Whereas the AM1 heats of formation $(\Delta H_{\rm f}^{\rm o})$ for 6 and 13 are 673.7 kJ mol⁻¹ and 666.6 kJ mol⁻¹, respectively, the $\Delta H_{\rm f}^{\rm o}$ values for 12, 10, and 11 are 474.0 kJ mol⁻¹, 401.2 kJ mol⁻¹ and 367.8 kJ mol⁻¹, respectively. Hence, the overall conversion $6 \rightarrow 11$ ($\Delta H_r = -305.9$ kJ mol^{-1}) is predicted to be considerably more exothermic than that of $12 \rightarrow 11 \ (\Delta H_r = -106.2 \text{ kJ mol}^{-1}).^{[15]}$ We expect that, due to the exothermicity of the conversion of 6 to 12 via 13, intermediate 12 is obtained in a highly thermally excited state (Scheme 3). Consequently, the subsequent conversion of 12 into 10 and finally the rearrangement of 10 into 11 will occur more readily than during independent FVT of 12.[5b]

High-Temperature Behaviour of 2,2'-Bis(1-chloroethenyl)biphenyl (15): Further support for the formation of 13 as transient intermediate was obtained by FVT of 2,2'-bis(1chloroethenyl)biphenyl (15).^[8] We anticipated that upon FVT of 15, besides facile twofold HCl elimination leading to 6, also intramolecular cyclization could take place giving 1,2,2a,10b-tetrahydro-2a,10b-dichlorocyclobuta[*l*]phenanthrene (16; Scheme 4).

FULL PAPER

Scheme 3. Conversion of 2,2'-diethynylbiphenyl (6) under FVT conditions



Table 2. Product composition of the pyrolysates obtained uponFVT of 9-ethynylphenanthrene (12)

Compound	Temperature [°C]	10 [%]	11 [%]	12 [%]	Mass reco- very [%]
12	700 800	20 55	_	80 45	98 96
	900	98	2	-	97 04
	1100	97 86	3 14		94 82

Compound 15 was subjected to FVT in the temperature range 600-1000°C; reasonable to good mass recoveries were found (Table 3). At T = 600 °C compound 16, 9,10dichlorophenanthrene (17),^[16] 9-chloro-10-ethenvlphenanthrene (19) and a minor amount of pyrene (5) were unequivocally identified in the pyrolysate. Apparently, compound 16 either undergoes fragmentation into 17 or HCl elimination giving transient 2,2a-dihydro-2a-chlorocyclobuta[/]phenanthrene (20). The latter will either give 19 by a ring opening process^[17] or transient 13 after elimination of a second equiv. of HCl. At T = 600 °C the first process appears to be more favourable, whereas at $T \ge 700$ °C the identification of compounds 10, 11 and 12 points to the transient formation of 13 (vide supra). Nonetheless in the temperature range 600-800°C compounds 17 and 19 are the major products identified in the pyrolysates (Table 3). However, since the amount of 19 decreases above 700°C, our results indicate that concomitant with increasing temperature the conversion of transient 20 into 12 via 13 becomes more favourable. As expected, ^[5b] increasing amounts of 11 are then found with increasing temperature $(T \ge T)$ 800°C).

Furthermore, it is noteworthy that 10 and 11 are generated less effectively by FVT of 15 compared to 6. As reflected by the presence of 17 ($600^{\circ}C \le T \le 1000^{\circ}C$) and 9-chlorophenanthrene (21; $T \ge 800^{\circ}C$), the temperatureconversion data reveals that considerable fragmentation of 16 and transient 20, respectively, takes place. Thus, upon FVT of 15 the access to 12 via 13, and its consecutive rearrangement products 10 and 11, is less effective (Scheme 4 and Table 3).

Scheme 4. Conversion of 2,2'-bis(1-chloroethenyl)biphenyl (15) under FVT conditions



Conclusions

FVT of 2,2'-diethynylbiphenyl (6) in the temperature range 600–1100°C shows that the initially anticipated product pyrene (5) is only a minor product. Instead of 5, the $C_{16}H_{10}$ (CP-)PAH 9-ethynylphenanthrene (12), acephenanthrylene (10) and fluoranthene (11) are the major products. The formation of 10 and 11 is rationalized by invoking an intramolecular cyclization of 6 involving both ethynyl moieties giving cyclobuta[/]phenanthrene (13) as transient intermediate, which is immediately converted into ethylidene carbene 14 presumably by a retro-carbene C-H

Compound	Temperature [°C]	1 [%]	5 [%]	10 [%]	11 [%]	12 [%]	16 [%]	17 [%]	19 [%]	21 [%]	Mass reco- very [%]
15	600 700 800 900		3 5 5 9	 1 9 28	2 8	$\frac{-}{2}$ 1 1	17 	38 38 44 44	42 54 38 8	- 1 2	98 85 82 78
	1000	4	5	36	22	1	_	25	-	7	70

Table 3. Product composition of the pyrolysates obtained upon FVT of 2,2'-bis(1-chloroethenyl)biphenyl (15)

insertion. The latter is converted either into 12 by a 1,2-H shift or into 10 (carbene C-H insertion), which subsequently rearranges into fluoranthene (11) under FVT conditions.^[5b]

Hence, further investigations are required to disclose the thermal pathways towards **5** under high-temperature conditions in the gas phase. Based on the results presented, 4-ethynylphenanthrene (**8**; see Scheme 2) is envisaged to be the penultimate precursor for **5**; experiments to substantiate this conjecture are in progress.

Financial support from the *Basque Government [Beca para Formacion de Investigadores (M. S.)]* and experimental contributions by Mrs. L. van Pieterson are gratefully acknowledged.

Experimental Section

All reactions were carried out under N₂. All solvents were purified and dried by standard procedures. Commercially available reagents were used without purification. – Column chromatography was performed on Merck kiesegel 60 silica gel (230–400 ASTM). – Melting points are uncorrected. – ¹H- (300.13 MHz) and ¹³C-NMR (75.47 MHz) spectra were obtained with a Bruker AC 300 spectrometer. Samples were dissolved in deuterated chloroform. *J* values are given in Hz. – GC-MS spectra were measured with an ATI Unicam Automass System 2 quadrupole mass spectrometer (column: JW Scientific DB-17, length 30 m, ID 0.32 mm and film thickness 0.25 µm; injector temperature 300°C, temperature program 2 min 200°C – (10°C min⁻¹) \rightarrow 280°C; carrier gas He). *Caution:* Many polycyclic aromatic hydrocarbons and their derivatives are potential genotoxic compounds.

Phenanthrene (1): All analytical data were in agreement with those of commercially available 1.

Pyrene (5): All analytical data were in agreement with those of commercially available 5.

2.2'-Diethynylbiphenyl (6)^[8]: To a suspension (cooled at -40° C) of sodium (0.67 g, 29 mmol) in liquid ammonia (45 ml), **15** (0.74 g, 2.7 mmol) in diethyl ether (10 ml) was slowly added. The reaction mixture was stirred for 2 h at -40° C after which the temperature was slowly raised to room temperature. After all ammonia had evaporated, 1 M sulphuric acid (100 ml) was added. The reaction mixture was extracted with diethyl ether (3 × 50 ml), the combined organic fractions dried with MgSO₄, filtered and concentrated in vacuo yielding 0.51 g (2.5 mmol, 93%) of pure **6** as a white solid, m.p. 49–50°C (ref^[8] m.p. 49°C). – ¹H NMR: δ = 7.64 (2 H, d, J = 7.2), 7.44–7.32 (6 H, m), 2.98 (2 H, s). – ¹³C NMR: δ = 143.3, 133.1, 130.1, 128.3, 127.5, 121.6, 82.6, 80.3. – GC-MS; *mlz*: 202 [M⁺].

Acephenanthrylene (10): All analytical data were in agreement with those previously reported.^[5b]

Fluoranthene (11): All analytical data were in agreement with those of commercially available 11.

9-Ethynylphenanthrene (12): All analytical data were in agreement with those previously reported.^[5b]

2,2'-Bis(1-chloroethenyl)biphenyl (15)^[8]: A mixture of 2,2'-diacetylbiphenyl (22, 2.34 g, 9.8 mmol), PCl₅ (8.15 g, 39.1 mmol) and PCl₃ (19.5 ml) was heated overnight at 40°C. After cooling to room temperature, water (25 ml) was added to the reaction mixture, which subsequently was extracted with CH₂Cl₂ (3 × 25 ml). The combined organic fractions were dried with MgSO₄, filtered and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, eluent benzene) yielding 0.64 g (2.3 mmol, 23%) of pure 15 as a colourless oil. – ¹H NMR: δ = 7.57–7.53 (2 H, m), 7.40–7.30 (6 H, m), 5.44 (2 H, d, *J* = 1.4), 5.18 (2 H, d, *J* = 1.4). – ¹³C NMR: δ = 139.2, 138.7, 137.3, 130.8, 129.5, 129.1, 127.5, 118.0. – GC-MS; *m/z*: 274, 276 and 278 [M⁺, M + 2⁺ and M + 4⁺ with isotope pattern]. – All analytical data were in agreement with those previously reported.^[8]

2*a*,10*b*-Dichloro-1,2,2*a*,10*b*-tetrahydroclobuta[1]phenanthrene (**16**): Compound **16** was isolated from a 600°C pyrolysate (100 mg, cf. Table 3) by column chromatography (silica gel, eluent *n*-hexane) as a slightly yellow waxy solid. Isolated yield of **16** 10 mg (0.04 mmol). - ¹H NMR: $\delta = 8.73$ [H(6) and H(7), m], 8.46 [H(3), m], 8.12 [H(10), m], 7.70 [H(4), H(5), H(8) and H(9), m], 3.84 (4 H, cyclobuta-, m). - ¹³C NMR: $\delta = 130.9, 130.8, 130.0, 128.8, 127.7, 127.6, 127.4, 126.8, 125.8, 124.3, 123.4, 122.6, 68.2, 60.7, 41.9, 33.9. - GC-MS;$ *m/z*: 274, 276 and 278 [M⁺, M + 2⁺ and M + 4⁺ with isotope pattern]. - Due to its susceptibility to decomposition, i.e. presumably by HCl elimination, compound**16**has to be stored at -20°C.

9,10-Dichlorophenanthrene (17): Compound 17 was isolated from a 700 °C pyrolysate (35 mg, cf. Table 3) by column chromatography [silica gel, eluent petroleum ether (40-60 °C)], and recrystallized from petroleum ether (40-60 °C) giving 17 (10 mg, 0.04 mmol) as white needles; m.p. 158–159 °C (ref.^[16] 157.5–159 °C). All analytical data were in agreement with those previously reported.^[16]

9-Chloro-10-ethenylphenanthrene (19): Compound 19 was isolated from the 600 °C pyrolysate (100 mg, cf. Table 3) by column chromatography (silica gel, eluent *n*-hexane) as a yellow waxy solid. Isolated yield of 19 15 mg (0.06 mmol). - ¹H NMR: $\delta = 8.68$ [H(4) and H(5), m], 8.48 [H(1), m], 8.25 [H(8), dd, J = 1,2, 7.9], 7.68 [H(2), H(3), H(6) and H(7), m], 7.11 [H(9) ethenyl, dd, J =11.5, 18.0), 5.92 [H(10) ethenyl, dd, J = 1.7, 11.5], 5.62 [H(11) ethenyl, dd, J = 1.7, 18.0]. The assignment of the ¹H-NMR resonances was further supported by APT experiments. - ¹³C NMR: $\delta = 133.3$ (two isochronous quaternary carbon atoms), 133.2, 130.9, 130.6, 129.5, 129.4, 127.4, 127.2, 127.0, 126.7, 126.6, 125.6, 122.9, 122.6 (two isochronous carbon atoms). - GC-MS; *m/z*: 238 and 240 [M⁺ and M + 2⁺ with isotope pattern].

9-Chlorophenanthrene (21): In the 1000°C pyrolysate compound 21 was readily identified on the basis of its characteristic ¹H-NMR and MS data, which were in agreement with those determined for an authentic, commercially available sample of 21.

2,2'-Diacetylbiphenyl (22)^[18]: To 9,10-dihydro-9,10-dihydroxy-9,10-dimethylphenanthrene (23; 2.66 g, 11.1 mmol), dissolved in acetic acid (25 ml) and heated to 70°C (oil bath), a solution of chromium oxide (1.66 g, 16.6 mmol) in water (16 ml) was added within ca. 12 min. The reaction mixture was subsequently stirred for an additional 12 min at 70°C and then cooled to room temperature. After addition of water (100 ml), the reaction mixture was extracted with diethyl ether (4 \times 50 ml). The combined organic fractions were dried with MgSO4, filtered and concentrated in vacuo to yield 2.38 g (10.0 mmol, 90%) of pure 22 as a white crystalline solid; m.p. 90-91°C (ref.^[18] 93-94°C). - ¹H NMR: $\delta =$ 7.75-7.22 (2 H, m), 7.49-7.44 (4 H, m), 7.19-7.16 (2 H, m), 2.27 $(6 \text{ H}, \text{s}). - {}^{13}\text{C} \text{ NMR}; \delta = 201.6, 140.6, 138.7, 131.0, 130.7, 128.6,$ 127.6, 29.3. - GC-MS; m/z: 238 [M⁺].

9,10-Dihydro-9,10-dihydroxy-9,10-dimethylphenanthrene (23)^[18]: To a suspension of magnesium (2.69 g, 110 mmol) in diethyl ether (25 ml), a mixture of 1,2-dibromoethane (2.25 g, 12 mmol) and methyl iodide (14.19 g, 100 mmol) in diethyl ether (200 ml) was slowly added. The reaction mixture was heated at reflux temperature for 1 h and, after cooling to room temperature, phenanthrenequinone (5.41 g, 26 mmol) was added in portions, after which stirring was continued overnight. The reaction mixture was poured into ice/water and 2 M sulphuric acid (200 ml) was added until no colour change could be observed. After a standard workup procedure, the crude product was purified by recrystallization from benzene. Yield 2.76 g (12 mol, 44%) of pure 23 as colourless crystals, m.p. 164–166°C (ref.^[18] 163–164°C). – ¹H NMR: δ = 7.73-7.69 (4 H, m), 7.39-7.34 (4 H, m), 2.28 (2 H, s), 1.33 (6 H, s). $- {}^{13}$ C NMR: $\delta = 142.3$, 131.7, 128.4, 127.7, 123.6 (two isochronous resonances), 77.4, 24.5. - GC-MS; m/z: 240 [M⁺].

General Flash Vacuum Thermolysis Procedure: A commercial Thermolyne 21100 tube furnace containing an unpacked quartz tube (length 40 cm and diameter 2.5 cm) was used for all FVT experiments. Temperature-conversion tables were determined by evaporating 50 mg aliquots of the different precursors into the quartz tube (evaporation temperature 90°C) at $p = 10^{-2}$ Torr.

Semiempirical AM1 Calculations: Calculations were performed with AM1 as implemented in MOPAC 6.0.[14] Geometry optimization was executed without imposing any symmetry constrains until GNORM ≤ 0.5 . Transition states were located using an appropriate reaction coordinate and, subsequently, refined using the Eigenvector Following routine (keyword TS) until GNORM ≤ 0.5 . All minima and transition states were characterised by a Hessian calculation (keywords FORCE and LARGE); either none or one imaginary vibration, respectively, was found. Data concerning the geometry optimization, optimized geometries and the Hessian calculations are available upon request from one of the authors (L. W. J.).

- ^[1] J. B. Howard, J. P. Longwell, J. A. Marr, C. J. Pope, W. F. Busby, A. L. Lafleur, K. Taghizadeh, Combust. Flame 1995, 101, 262-270.
- ^[2] J. Jacob, Pure Appl. Chem. 1996, 68, 301-308 and references cited therein.
- [3] L W. Jenneskens, M. Sarobe, J. W. Zwikker, Pure Appl. Chem. 1996, 68, 219-224 and references cited therein; L. T. Scott, Pure Appl. Chem. 1996, 68, 291-300 and references cited ther-
- [4] H. Bockborn, F. Fetting, H. Wenz, Ber. Bunsenges. Phys. Chem. **1983**, 87, 1067–1073. ^[5] [^{5a]} L. T. Scott, N. H. Roelofs, J. Am. Chem. Soc. **1987**, 109,
- 5461-5465. ^[5b] M. Sarobe, L. W. Jenneskens, J. Wesseling, J. D. Snoeijer, J. W. Zwikker, U. E. Wiersum, *Liebigs Ann.* 1997, 1207-1213. - ^[5c] M. Sarobe, J. D. Snoeier, L. W. Jenneskens, J. W. Zwikker, J. Wesseling, *Tetrahedron Lett.* 1995, 36, 9565–9566. – ^[5d] M. Sarobe, L.W. Jenneskens, J. Wesseling, U.E. Wiersum, J. Chem. Soc., Perkin Trans. 2 1997, 703-708.
- [6] R.F.C. Brown, F.W. Eastwood, K.J. Harrington, G.L. McMullen, Aust. J. Chem. 1974, 27, 2393-2402.
- M. Sarobe, J. W. Zwikker, J. D. Snoeijer, U. E. Wiersum, L. W. Jenneskens, J. Chem. Soc., Chem. Commun. 1994, 89-90 and references cited therein.
- [8] W. Ried, V. B. Saxena, Angew. Chem. 1968, 80, 366.
- See for example: J. Hofmann, G. Zimmermann, K. Guthier, P. Hebgen, K.-H. Homann, Liebigs Ann. 1995, 631-636.
- ^[10] P. H. G. op het Veld, W. H. Laarhoven, J. Chem. Soc., Perkin Trans. 2 1977, 268–273.
- [11] G. M. Reisner, I. Bernal, M. D. Rausch, S. A. Gardner, A. Clearfield, J. Organomet. Chem. 1980, 184, 237-254.
 [12] E. Müller, J. Heiss, M. Sauerbier, D. Streichfuss, R. Thomas, The Mathematical Content of the second second
- Tetrahedron Lett. 1968, 1195-1200. Cf. also: W. Baidossi, H. Schumann, J. Blum, *Tetrahedron* **1996**, *52*, 8349–8364. ^[13] R. F. C. Brown, K. J. Coulston, F. W. Eastwood, *Tetrahedron*
- Lett. 1996, 37, 6819-6820.
- ^[14] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, J Am. Chem. Soc. 1985, 107, 3902-3909; MOPAC 6.0: J. J. P. Stewart, Quant. Chem. Prog. Exchange; QCPE 504; Bloomington, IN, USA, 1990.
- ^[15] Furthermore, the AM1 activation enthalpies (ΔH^{+}) for the retro-carbene insertion [AM1: $\Delta H^{\pm}(13 \rightarrow \hat{1}4) = 272.4 \text{ kJ mol}^{-1}$] is predicted to be considerably lower than those for the conversion of 14 to 10 [AM1: $\Delta H^+(14 \rightarrow 10) = 328.9 \text{ kJ mol}^{-1}$] and the consecutive 1,2-H/1,2-C shift in going from 10 to 11 [AM1: $\Delta H^+(1,2-H \text{ shift}) = 368.7 \text{ kJ mol}^{-1}$ and subsequent $\Delta H^+(1,2-C \text{ shift}) = 123.9 \text{ kJ mol}^{-1}$; Scheme 3].^[5b]
- ^[16] A. R. Oyler, R. J. Llukkonen, M. K. Lukasewycz, K. E. Heikklla, D. A. Cox, R. M. Carlson, Environ. Sci. Technol. 1983, 17, 334-342
- ^[17] T. L. Gilchrist, R. C. Storr, Organic Reactions and Orbital Symmetry, 2nd ed., Cambridge University Press, Cambridge, 1979.
- ^[18] D. M. Hall, J. E. Ladbury, M. S. Lesslie, E. E. Turner, J. Chem. Soc. 1956, 3475-3482. [97193]