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Kinetic Isotope Effects in the Thermal C^2-C^6 Cyclization of Enyne-allenes: Experimental Evidence Supports a Stepwise Mechanism

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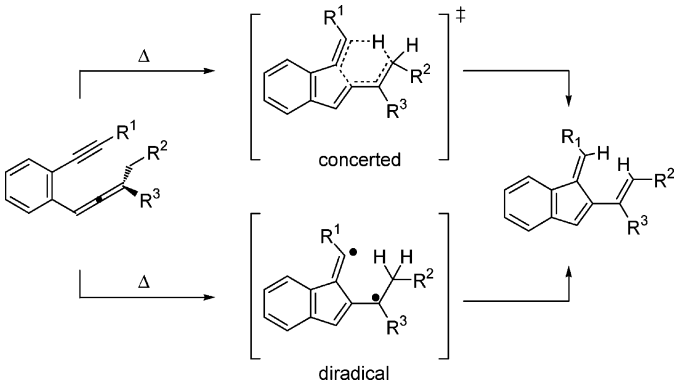

Kinetic isotope effects suggest that the thermal C^2-C^6 cyclization of enyne-allenes proceeds through a stepwise diradical mechanism. This is even true if steric bulk at the alkyne terminus is large, contrary to theoretical predictions by Engels.

Thermal cycloaromatizations of enediynes (Bergman)[1] and enyne-allenes (Myers−Saito, C^2-C^7)[2] have elicited extensive attention over the past decade,[3] as the resultant diradicals represent key intermediates in the mode of action of natural enediyne antitumor antibiotics.[4] In 1995, a competing thermal reaction mode of enyne-allenes (see Scheme 1) was disclosed.[5,6] Since then, the so-called C^2-C^6 cyclization has been extensively studied mechanistically[7] and theoretically,[8] in particular due to its use in the synthesis of complex carbocycles,[9] for DNA cleavage,[10] and recently in photochemical[11] applications. The kinetic competition between the C^2-C^6 and C^2-C^7 cyclization can be most conveniently steered through the proper choice of substituents at the alkyne terminus: with radical stabilizing groups or bulky groups at C7 the C^2-C^6 cyclization is preferred, whereas with hydrogen or *n*-alkyl substituents the C^2-C^7 reaction mode is observed. Moreover, it has been emphasized that benzannulation[12] and oxyanion substitution at the allene[13] provide a kinetic advantage for the C^2-C^6 cyclization.

Mechanistic and theoretical evidence is clearly in favor of the intermediacy of a fulvenyl diradical in the course of the C^2-C^6 cyclization, although most examples in the literature could also be reconciled with a concerted ene or Diels−Alder reaction.[7,10] Certainly, the reaction does not involve a polar transition state or polar intermediates.[14] To date, the most convincing evidence for a stepwise mechanism comes from direct trapping of the fulvenyl diradical through hydrogen transfer,[7e] a kinetic indifference in stepwise Diels−Alder processes,[7b] and from computational studies.[7e,8] Due to the wide variation of substituents tolerated in the C^2-C^6 cyclization, however, there may be a changeover from the stepwise to the concerted pathway.[15] In this context, Engels[16] has computationally investigated the C^2-C^6 cyclization lead-

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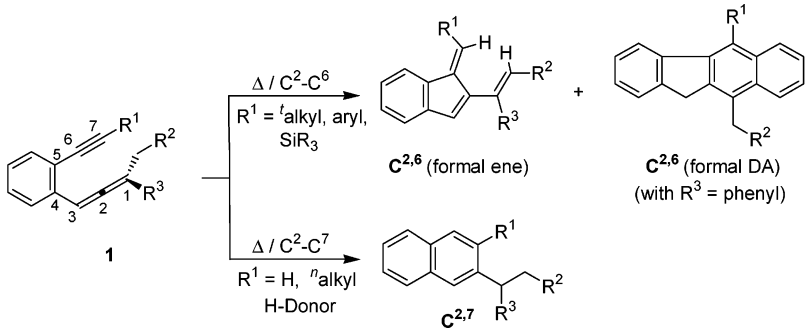
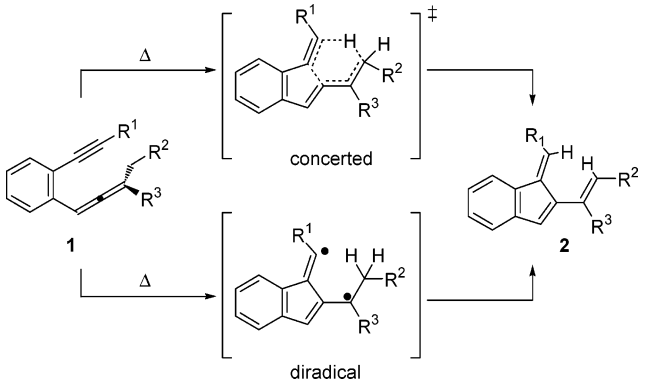
SCHEME 1. Thermal C^2-C^7 (Myers–Saito) and C^2-C^6 Cyclization of Enyne-allenes[a]



[a] The latter reaction leads to a formal ene or formal Diels–Alder (DA) products.

ing to ene products. On the basis of calculations, he inferred that there is a transition from the stepwise to concerted pathway with a *tert*-butyl group at the alkyne terminus. This prediction seems to be in accordance with the experimental finding that C^2-C^6 ene reactions indeed proceed much cleaner with bulky groups than with aryl groups at the alkyne terminus.[17] For the concerted ene reaction, the kinetic isotope effect k_H/k_D was calculated to be 2–2.3,[16] whereas for the diradical mechanism k_H/k_D should be close to unity. Herein, we describe an experimental study of the kinetic isotope effect that demonstrates that, even with sterically extremely bulky groups, the observed ene reaction proceeds in a stepwise manner, lending further support to a diradical mechanism of the C^2-C^6 cyclization.

SCHEME 2. Mechanistic Options for the Thermal Ene Reaction of Enyne-allenes



Results and Discussion

To evaluate the kinetic isotope effect, we have chosen the benzannulated enyne-allene **1a** and its deuterium analogue **1b** that are both characterized by a very bulky substituent at the alkyne terminus and an alkyl group at the allene terminus for hydrogen transfer. Prior screening of a wide variety of substituents R^1-R^3 had indicated that other enyne-allenes **1** were less suited due to yields for the ene reaction of less than 85%.

Preparation of **1a**,**b** started out with a Sonogashira cross coupling of *o*-bromobenzaldehyde (**3**) with triisopropylsilyl acetylene to afford **4** in 83% yield (Scheme 3).[18] Addition of BrMgC≡C–R (R = *n*-Bu, $-CD_2CH_2CH_2CH_3$; cf. Scheme 4) provided the propargyl alcohols **5a**,**b**.[19] Reaction of **5a**,**b** with acetic anhydride at room temperature in the presence of 4-*N*,*N*-(dimethylamino)-pyridine (DMAP) afforded the corresponding propargyl acetates[20] **6a**,**b**. Enyne-allenes **1a**,**b** were finally received through a Pd-promoted reaction of *p*-AnZnCl[21] with **6a**,**b** at −60 °C. ^{1}H and ^{13}C NMR, IR, and HRMS convincingly supported the structural assignment of **1a**,**b**.

Thermolysis of enyne-allene **1a** in toluene furnished the cyclization product **2a** in high yield (91% after isolation). It was completely characterized using ^{1}H and ^{13}C NMR, IR, and HRMS. Importantly, in the ^{1}H NMR, the methoxy group of **2a** at δ 3.78 ppm was well separated from the methoxy group signal of **1a** at δ 3.81 ppm.

Kinetic isotope effect (KIE) measurements are a powerful diagnostic tool for the distinction between stepwise and concerted mechanisms.[22] The observation of a large KIE ($k_H/k_D > 2$) should be indicative of a hydrogen transfer in the rate-limiting step and has often been taken as evidence for a concerted mechanism,[23] while absence of a substantial deuterium KIE was considered to be the signature of a stepwise mechanism.[24]

Thermolysis of **1a**,**b** was carried out in closed vessels at 100.0 ± 0.1 °C in toluene after a first evaluation of the thermal reactivity had been made by differential scanning calorimetry. A kinetic isotope effect k_H/k_D = 1.174 ± 0.039 (at 100.0 ± 0.1 °C) was determined from six rate constants for thermal cyclization of enyne-allene **1a** and its deuterated analogue **1b** (Table 1).

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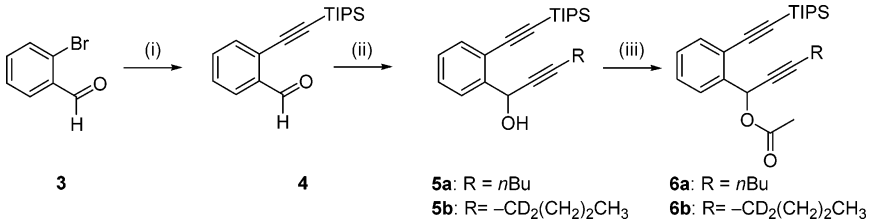
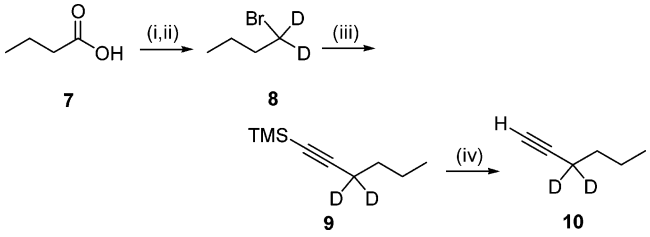
SCHEME 3[a]



[a] Reaction conditions: (i) TIPS−C≡C−H, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 90 °C, 78 h, 83%. (ii) EtMgBr, H−C≡C−*n*Bu, THF, rt, 14 h, **5a**: 96%; or EtMgBr, H−C≡C−$CD_2(CH_2)_2CH_3$, THF, rt, 14 h, **5b**: 66%. (iii) Ac_2O, DMAP, Et_3N, CH_2Cl_2, rt, 12 h, **6a**: 92%; **6b**: 84%.

SCHEME 4[a]



[a] Reaction conditions: (i) $LiAlD_4$, Et_2O, 0 °C to rt. (ii) 48% HBr, H_2SO_4, 3 h, 62%. (iii) *n*-BuLi, HMPA, TMS−C≡C−H, THF, −78 °C to rt, 12 h, 63%. (iv) KOH, *t*-BuOH, H_2O, 4 h, rt, 45%.

TABLE 1. Rate Constant for the Cyclization of Enyne-allene in Toluene at 100.0 ± 0.1 °C

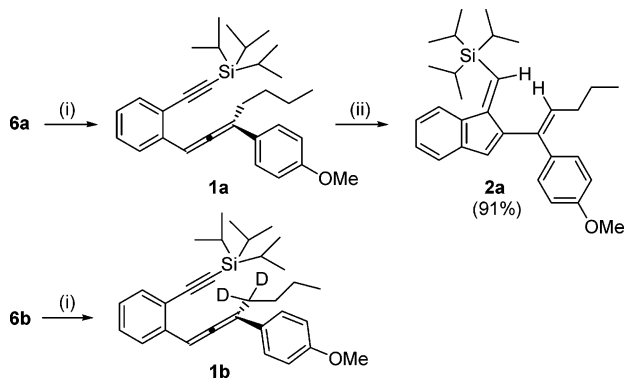
entry	compd	no. of points	R	k_{obsd}[a] (10^{-4} s^{-1})	k_{obsd}[b] (10^{-4} s^{-1})
1	**1a** (d_0)	8	0.9977	2.16	
2	**1a** (d_0)	8	0.9975	2.28	2.22 ± 0.06
3	**1a** (d_0)	8	0.9979	2.23	
4	**1b** (d_2)	8	0.9993	1.88	
5	**1b** (d_2)	8	0.9986	1.95	1.89 ± 0.04
6	**1b** (d_2)	8	0.9972	1.85	

[a] First-order rate constant. [b] Average rate constant from three runs.

The $k_H/k_D = 1.17$ has to be compared with KIEs from Engels' calculations and from experimental ene reactions. Engels[16] calculated a $k_H/k_D = 1.97$ for the concerted thermal ene reaction of **1** (R^1 = *t*-Bu, $R^2 = R^3 = H$), while experimental k_H/k_D for concerted ene reactions range from 2.3 to 3.2.[23e,25] As such, the observed $k_H/k_D = 1.17$ clearly suggests a stepwise mechanism. While, it is too small to represent a primary kinetic isotope effect, the observed KIE is notably higher than $k_H/k_D = 1.00-1.04$ as found by Singleton and Hang[26] for a stepwise ene reaction. Also, hyperconjugation cannot explain a $k_H/k_D = 1.17$, though it is generally accepted as the major contributor to β-deuterium secondary kinetic isotope effects for reactions with radicaloid transition states and for equilibrium isotope effects involving radicals.[15b,27] To understand this discrepancy, we have analyzed the bona fide diradical C^2-C^6 cyclization of **1** (R^1 = Ph, $R^2 = R^3 = H$) as described in a computational study by Engels.[16] C^2-C^6 diradical cyclizations are special insofar as there exist two competing pathways, one leading to an s-cis and the other to an s-trans diradical (Scheme 6).

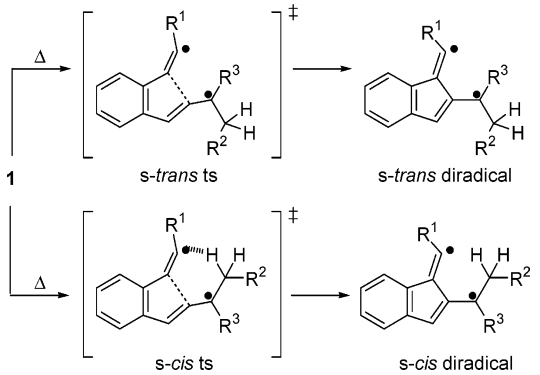
This is a consequence of the rotation of the terminal allene carbon in order to maximize overlap of the incipient radical center with the fulvene unit. In a first

SCHEME 5[a]



[a] Reaction conditions: (i) *p*-AnMgBr, $ZnCl_2$ (1 M in diethyl ether), $Pd(PPh_3)_4$, −60 °C to rt, 16 h, **1a**: 93%, **1b**: 75%. (ii) toluene, reflux, 14 h, 91%.

SCHEME 6. Visualization of the Two Competing Transition States in the Diradical Cyclization of 1 that Arise from the Rotation about the Terminal Allene Terminus



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approximation, both pathways should exhibit the same C(HR²)−H elongation due to equal hyperconjugation effects in the transition state. However, the calculations reveal that for the s-cis diradical transition state, there is a notable C(HR²)−H elongation to 1.108 Å that is less pronounced in the s-trans transition state (1.099 Å) of **1** (R^1 = Ph, R^2 = R^3 = H). Although this difference (ca. 0.01 Å) seems to be small, one has to keep in mind that the transition state for the concerted ene reaction of **1** (R^1 = *t*-Bu, R^2 = R^3 = H) is characterized by only a slightly increased C(HR²)−H bond (l = 1.190 Å), resulting in a calculated k_H/k_D = 1.97. How can one, however, understand the difference in the C(HR²)−H elongation of the s-cis and s-trans transition state structures? We suggest that in the bona fide diradical cyclization of **1** (R^1 = Ph, R^2 = R^3 = H), a slight C(HR²)−H elongation results in the s-cis transition state due to a weakly bonding C7·····H interaction that is not possible in the s-trans pathway. Therefore, the experimental k_H/k_D = 1.17 for **1a**,**b** is slightly increased due to a C(HR²)−H stretching that is only observable in the s-cis transition state. Further investigation, however, will have to await high-level calculations on the cyclization of **1a**,**b** that are beyond the scope of this paper.

Conclusion. The present study supports the view that the C²−C⁶ cyclization proceeds through a stepwise diradical mechanism. This is even true if steric bulk at the alkyne terminus is large, contrary to theoretical predictions by Engels.[16] One must state that these conclusions were drawn on the basis of the classical interpretation of KIEs, as the role of nonstatistical effects has not been taken into consideration. Hence, further insight may become possible through molecular dynamics simulations.[22f]

Experimental Section

Triisopropyl-{2-[3-(4-methoxyphenyl)-hepta-1,2-dienyl]-phenylethynyl}-silane (1a). *p*-Anisole magnesium bromide solution [prepared from 59.0 mg (2.43 mmol) of Mg and 450 mg (2.43 mmol) of *p*-bromoanisole in dry THF (10 mL)] was added dropwise to a 1 M solution of $ZnCl_2$ (323 mg in 2.35 mL of dry diethyl ether) at room temperature under a nitrogen atmosphere. The reaction mixture was stirred for 30 min at room temperature. Then, it was cooled to −60 °C, and $Pd(PPh_3)_4$ (0.35 g, 0.30 mmol) in dry THF (3 mL) was added dropwise. After the reaction mixture was stirred for 15 min at the same temperature, propargyl acetate **6a** (0.25 g, 0.61 mmol) in dry THF (5 mL) was added dropwise. After stirring for 16 h at room temperature, the reaction mixture was quenched with saturated ammonium chloride solution. The aqueous layer was extracted with diethyl ether (2 × 25 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. After purification by column chromatography (silica gel, *n*-pentane/diethyl ether = 19:1), compound **1a** was isolated as colorless oil (0.26 g, 93%): IR (KBr) 3059, 2943, 2864, 2151, 1929, 1607, 1510, 1444, 1388, 1297, 1073, 883, 835 cm⁻¹; ¹H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, J = 7.3 Hz, 3H), 1.10 (bs, 21H), 1.43 (sextet, J = 7.1 Hz, 2H), 1.54−1.66 (m, 2H), 2.48−2.61 (m, 2H), 3.81 (s, 3H), 6.87 (d, J = 8.8 Hz, 2H), 7.13 (td, J = 7.8, 1.5 Hz, 1H), 7.14 (t, J = 1.8 Hz, 1H), 7.22 (td, J = 7.8, 1.5 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.45 (dd, J = 7.8, 1.3 Hz, 1H), 7.48 (dd, J = 7.8, 1.3 Hz, 1H); ¹³C NMR (100 MHz, $CDCl_3$) δ 11.3, 13.9, 18.7, 22.6, 29.9, 30.1, 55.2, 95.6, 95.9 105.1, 109.3, 113.9, 121.3, 126.1, 126.4, 127.2, 128.1, 128.5, 133.0, 136.8, 158.8, 207.0; MS-EI (70 eV) *m/z* 458.3 [M⁺]; HRMS calcd for $C_{31}H_{42}OSi$ 458.300, found 458.301.

Triisopropyl-{2-[3-(4-methoxyphenyl)-[4,4-²H₂]-hepta-1,2-dienyl]-phenylethynyl}-silane (1b). Procedure as described for the synthesis of **1a**, yield 75%: IR (KBr) 3061, 2942, 2864, 2151, 1929, 1606, 1510, 1444, 1383, 1297, 1089, 883, 835 cm⁻¹; ¹H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H), 1.11 (bs, 21H), 1.43 (sextet, J = 7.1 Hz, 2H), 1.53−1.65 (m, 2H), 3.81 (s, 3H), 6.88 (d, J = 8.8 Hz, 2H), 7.13 (td, J = 7.8, 1.3 Hz, 1H), 7.15 (s, 1H), 7.23 (td, J = 7.8, 1.3 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 7.45 (dd, J = 7.8, 1.3 Hz, 1H), 7.49 (dd, J = 7.8, 1.3 Hz, 1H); ¹³C NMR (100 MHz, $CDCl_3$) δ 11.3, 13.9, 18.7, 22.6, 29.2 (CD_2), 29.8, 55.2, 95.6, 95.9, 105.1, 109.2, 113.9, 121.3, 126.0, 126.4, 127.2, 128.1, 128.5, 133.0, 136.8, 158.7, 207.0; MS-EI (70 eV) *m/z* 460.3 [M⁺]; HRMS calcd for $C_{31}H_{40}D_2OSi$ 460.313, found 460.313.

Triisopropyl-{2-[1-(4-methoxyphenyl)-pent-1-enyl]-inden-1-ylidenemethyl}-silane (2a). Enyne-allene **1a** (35 mg, 76 μmol) was dissolved in dry toluene (30 mL), and after degassing the resulting solution was refluxed for 14 h. After removal of toluene under reduced pressure and purification by chromatography (preparative TLC, silica gel 60 F_{254}, *n*-pentane), compound **2a** was isolated as a yellow oil (32 mg, 91%): IR (KBr) 3053, 2960, 2942, 2865, 1606, 1558, 1509, 1246, 1037, 881 cm⁻¹; ¹H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.03 (d, J = 7.5 Hz, 18H), 1.39 (septet, J = 7.5 Hz, 3H), 1.44 (sextet, J = 7.3 Hz, 2H), 2.15 (q, J = 7.3 Hz, 2H), 3.78 (s, 3H), 6.23 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 0.8 Hz, 1H), 6.71 (s, 1H), 6.81 (d, J = 8.8 Hz, 2H), 7.14−7.18 (m, 1H), 7.28 (t, J = 3.4 Hz, 1H), 7.29 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 3.4 Hz, 1H), 7.72 (dd, J = 7.3, 0.8 Hz, 1H); ¹³C NMR (100 MHz, $CDCl_3$) δ 12.8, 13.8, 19.0, 23.0, 32.2, 55.2, 113.4, 120.4, 122.0, 124.5, 127.3, 128.0, 130.2, 130.8, 132.3, 134.9, 135.3, 135.9, 143.6, 144.2, 155.5, 158.5; MS-EI (70 eV) *m/z* 458.3 [M⁺]; HRMS calcd for $C_{31}H_{42}OSi$ 458.300, found 458.298.

Kinetics. The temperature of the bath was maintained at 100.0 ± 0.1 °C. For the determination of the rate constant, an enyne-allene solution was prepared in a 10 mL volumetric flask. A portion of this standard solution (0.5 mL) was then pipetted into the glass ampules, degassed, sealed under a vacuum, and heated. Samples were removed at known intervals and quenched by cooling to −40 °C. Then, 0.5 mL of a *m*-nitroacetophenone solution in toluene was added to the reaction ampule. After the removal of the solvent, the ¹H NMR integration of selected hydrogen resonances [methoxy group (δ 3.81 ppm) in enyne-allene to methyl group in *m*-nitroacetophenone (δ 2.21 ppm)] was determined on a 400 MHz ¹H NMR apparatus. In general, eight aliquots were collected. All samples for a given kinetic run were analyzed under identical conditions. The kinetic results from three such reaction sets with enyne-allene **1a** and **1b** are displayed in Table 1.

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Supporting Information Available: Experimental procedures, characterization data for compounds **4**, **5a-b**, **6a-b**, **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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